THE SYNTHESIS AND MECHANISM OF ACTION OF ORGANIC ACCELERATORS OF THE SULPHUR VULCANIZATION OF RUBBER

BY

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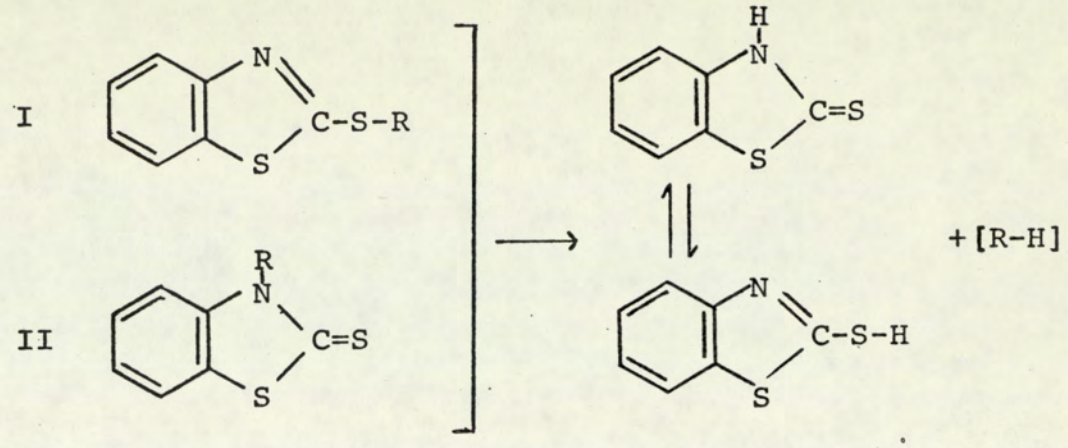
SUMMARY

The work was undertaken to lay the foundations for the development of a new class of delayed action accelerators for use in high temperature (above 200°C.) sulphur vulcanization of rubbers. Normal vulcanization temperatures are usually between 130° and 150°C.

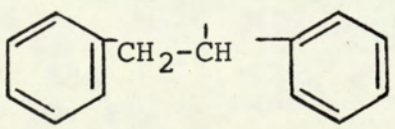
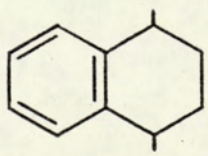
Initially 2-thiobenzothiazole derivatives were studied as 2-mercaptobenzothiazole is an accelerator. It has been shown that 2-(cyclohex-2'-enyl) thiobenzothiazole isomerised and partially decomposed on heating, to yield 2-mercaptobenzothiazole. It was hoped that the activation energy required to initiate the thermal decomposition at high temperatures would provide greater cure delay than is normally available with conventional accelerators. The synthesis and mechanism of the thermal rearrangement and decomposition of 2-thiobenzothiazoles and benzothiazoline-2-thione derivatives were studied with emphasis being placed on synthesis of the compounds of the general type I and II. The group R was introduced so that it would facilitate thermal decomposition of the type shown on the following page.



The R groups which facilitated complete thermal decomposition were mono-substituted 1,2 diphenylethanes and 1,4 bis substituted tetralins but other alkenyl and aralykl groups were investigated. The work was extended by changing the accelerating species while holding the R group constant. The accelerating species which replaced 2-thiobenzothiazole were dimethyldithiocarbamate, O-methyldithiocarbonate (methylxanthate), and 0,0 dimethl-phosphorodithioate, (see below).

$$X\text{-}SR \longrightarrow X\text{-}SH + [R\text{-}H]$$

$$X = (CH_3)_2\,N\text{-}\overset{|}{C}\text{=}S; \quad Ch_3\,O\text{-}\overset{|}{C}\text{=}S; \quad (CH_3O)_2\,\overset{|}{P}\text{=}S$$

$$R = \text{  } \quad ; \quad \text{  }$$

The above compounds were incorporated into a gum vulcanizate and the accelerator activity at 180°, 200°,

and 220°C. appraised. The evaluation indicated that the 2-thiobenzothiazole and dimethyldithiocarbamate derivatives possessed accelerator activity at 200°C., while the methyl xanthate and 0,0 dimethylphosphorodithioates derivatives were inactive.

The present work has demonstrated that new classes of delayed action accelerators could be developed using facile elimination processes to generate accelerating species.

This work was carried out between 1965 and 1968 at the University of Aston in Birmingham. It has been done independently and not submitted for any other degree.

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A. W. P. Jarvie

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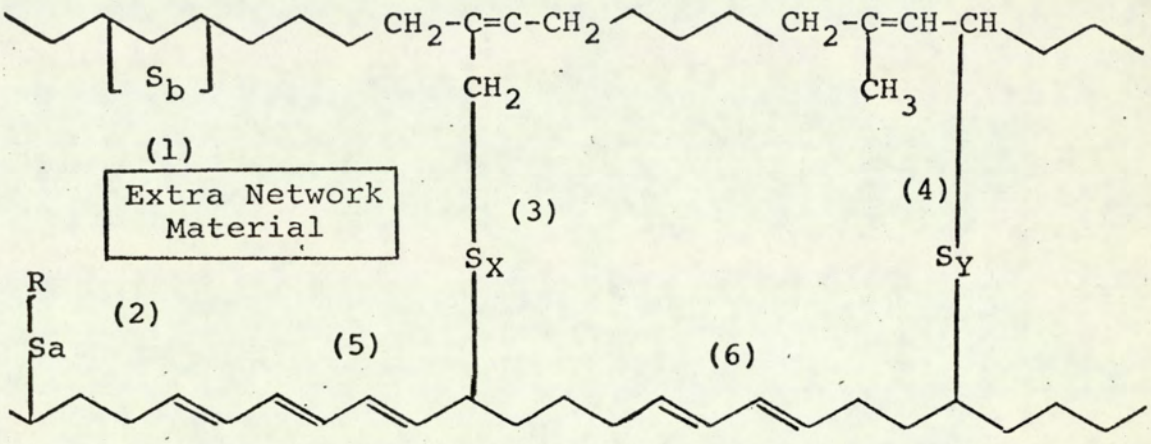
INTRODUCTION

Vulcanization

Sulphur vulcanization is a cross-linking process, the cross-linking occurring at points in the rubber molecule which are reactive to the vulcanization agents. The fullest potential of the sulphur vulcanization process is only realized when materials such as accelerators, which increase the rate of vulcanization, are used in conjunction with activators. The activators are often zinc oxide and a long chain fatty acid, e.g., stearic acid.[1]

The net result of the vulcanization process is to convent the rubber hydrocarbon chains, which form a weak, pliable rubber, into a highly elastic material of considerable strength. The changes brought about by sulphur vulcanization are manifested by large increases in such properties as tensile strength, modulus and elongation. Accelerators increase the rate of sulphur vulcanization and can reduce the cure time, which in the absence of an accelerator may take hours, to minutes; however, structural

modifications take place. Many of the structural features and modifications have been identified for accelerated vulcanization of natural rubber and are illustrated in the following diagram.



The accelerated vulcanizate as illustrated consists of:

(1) Cyclic mono or disulphides where b = 1 or 2.

(2) Pendant accelerator residues where a = 1.

(3) Cross-links attached via the allylic methyl group were x = 1, 2 or polysulphide.

(4) Cross-links via the α - allylic methylene where y = 1,2 or polysulphide.

(5) Conjugated trienes.

(6) Conjugated dienes.

In contrast unaccelerated sulphur vulcanization of natural rubber yields a structurally complex network[2]

with much of the sulphur being lost as regards cross-linking by being present as chain modifications. An overall measure of the complexity of the vulcanizate can be obtained by determining the cross-linking efficiency (E), which is defined as the number of sulphur atoms combined in the network per chemical cross-link present:

$$E = Sc/[2\ Mc,chem]^{-1}$$

where Sc= g. atoms of sulphur per g. atom of rubber hydrocarbon in the network and $2[Mc,chem]^{-1}$ is "moles" of chemical cross-links per gram of rubber hydrocarbon in the network. The large variations in cross-linking efficiency (E) for various vulcanizates are illustrated in Table I. The cross-linking efficiency (E) gives an overall value of the complexity of the vulcanizate but to obtain more detailed information regarding how the sulphur is distributed within the vulcanizate chemical probes are used. Chemical probes react quantitatively and specifically with particular sulphurated groups in the vulcanizate, for example, triphenylphosphine converts di and polysulphide linkages into monosulphide linkages. If the vulcanizate is treated with triphenylphosphine and the cross-linking efficiency is measured before treatment (E) and after treatment (E'), then a measure of the various main chain modifications is given by E'-1 and the amount of di and polysulphide sulphur is given by (E-E'). Other probes are

available and the methods by which the structural elucidation of vulcanizates is accomplished has been reviewed.[4]

TABLE 1

"E" VALUES FOR VARIOUS RUBBER NETWORKS

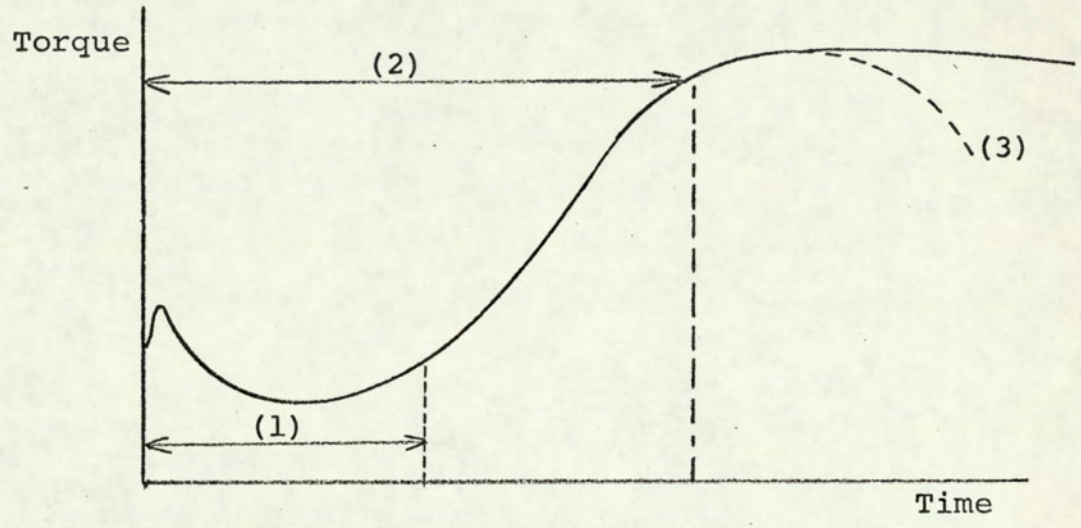
Vulcanizing System*	Cure Temperature °C.	E
N.R. 100, sulphur 6-10	140	40-55[3]
N.R. 100, sulphur 1.5, M.B.T. 1.5, zinc oxide 5.0, Lauric acid 1.0	140	15-21[4]
N.R. 100, sulphur 1.5, M.B.T. 1.5, zinc oxide 5.0, Lauric acid 10.0	140	6-4[5]
N.R. 100, sulphur 1.5, C.B.S. 2.4, zinc oxide 5.0, Lauric acid 1.0	140	8-4[6]

*Parts by weight of ingredients.

N.R. = natural rubber
C.B.S. = N-cyclohexylbenzothiazole-2-sulphenamide
M.B.T. = 2-mercaptobenzothiazole
E = g atoms of combined sulphur per g. of network
g molecules of chemical cross-links per g of network

When an accelerator is used with sulphur and an activating system to vulcanize natural rubber, utilization of the sulphur is more efficient in terms of cross-links produced and the cure time is usually shorter than vulcanization without an accelerator. A term which is commonly used when referring to accelerator activity is

scorch time and it is often referred to simply as scorch. The scorch is usually measured as the time taken from the beginning of the cure cycle to the time taken when cross-linking becomes appreciable.



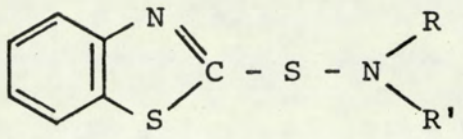
(1) Scorch Time
(2) Optimum Cure
(3) Reversion

The above diagram illustrates the important features of normal cure curve using a Monsanto Rheometer. Initially, the high torque of the compounded rubber drops to a minimum and then remains at this value for a short time and then a sharp increase in rheometer torque is observed. The sharp increase in rheometer torque coincides with the insertion of cross-links. It is common practice to express the induction period or scorch time as the time taken to a two unit rise above the minimum torque. The established

method of determining scorch time using the Mooney Viscometer is still used. In this case the time taken to a five unit rise above the minimum viscosity is commonly taken as a measure of the scorch time. Scorch time can be correlated with the processing safety that may be expected during the manufacture of a rubber product.

Amines[7,8,9,10] and derivatives[11,12] were one of the earliest classes of compounds discovered that accelerated vulcanization. After the First World War other accelerators were discovered, for example, dithiocarbamates, aldehyde ammonias, diarylthio ureas[13] and diaryl guanidines.[14,15] In an attempt to increase the scorch delay of dithiocarbamates, tetramethylthiuram disulphides[16,17] were developed, and these possessed longer scorch times than the corresponding dithiocarbamates. Considerable progress in the development of organic accelerators was made when it was discovered that 2-mercaptobenzothiazole and derivatives acted as accelerators.[18,19,20,21,22] Attempts to increase the scorch delay of 2-mercaptobenzothiazole lead to the development of dibenzothiazoyl disulphide.[23] The next major advance came with the discovery of sulphenamides, which had a longer scorch time than any of the previous accelerators. Currently used sulphenamides can give between ten and twenty minutes scorch time in natural rubber at 144°C.; whereas dithiocarbamates give scorch

times of two or three minutes at this temperature. Sulphenamides have the following general structure,

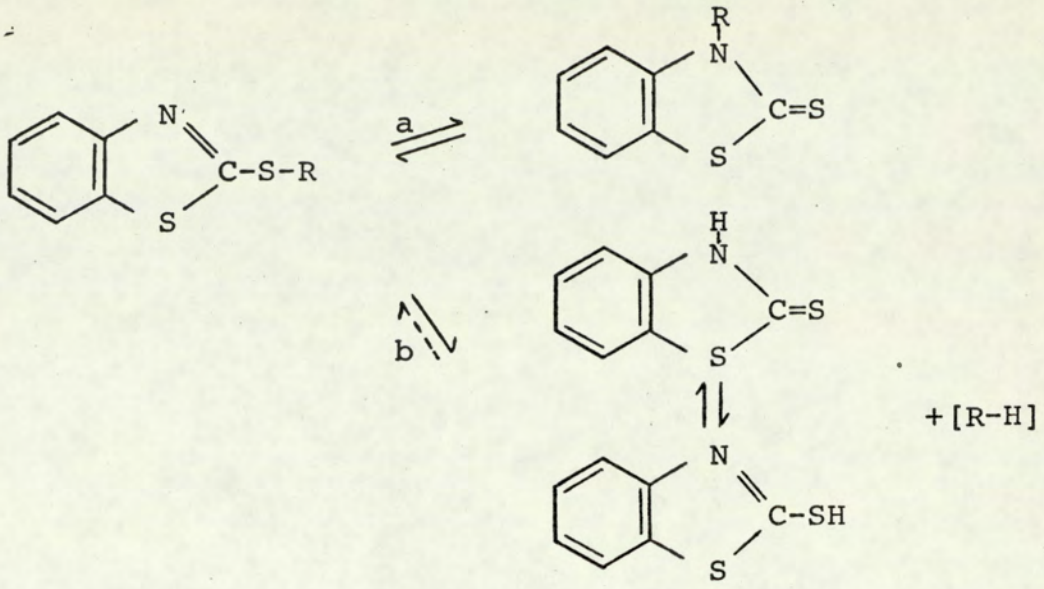


where the heterocyclic thiol is substituted with an amine R and R' may be hydrogen, alkyl, cycloalkyl or heterocyclic. Subsequent developments have concentrated on the extension of sulphenamides using a wide variety of amines and substituted amines. An insight into the significance of thiazoles derivatives can be gained by realizing that they account for approximately two-thirds of all accelerators produced.[26] More recently phosphorodithioates[27,28] have been claimed to act as accelerators but they have not found wide commercial acceptance.

When 2-substituted thiobenzothiazoles are heated two reactions are operative,[29]

(1) The reversible isomerisation of the 2-thiobenzothiazole to yield the corresponding 3-benzothiazoline-2-thione.

(2) Thermal decomposition to give 2-mercaptobenzothiazole and the hydrocarbon derived from the substituent R by the loss of hydrogen. The latter may subsequently degrade or polymerize.

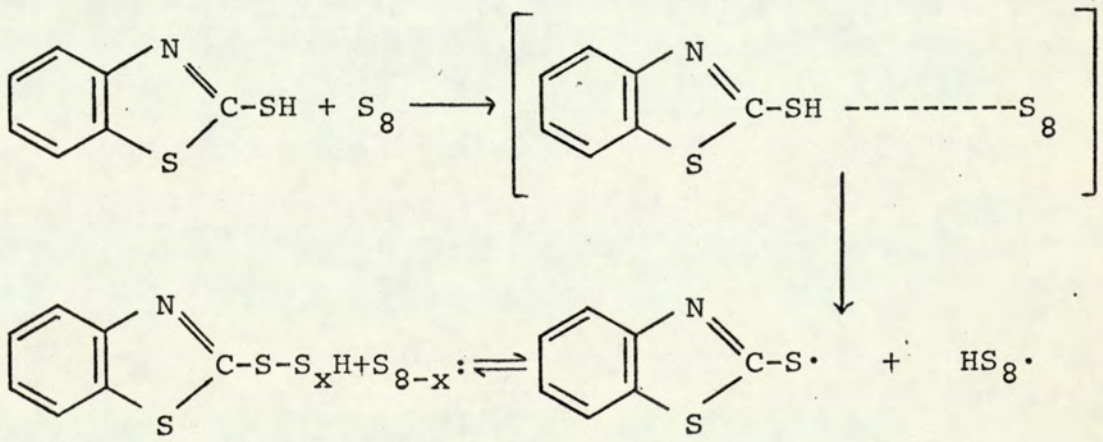


The investigations described in this thesis were carried out in order to find a substituent R group which would facilitate reaction b at the expense of reaction a. It was hoped that such an elimination would yield 2-mercaptobenzothiazole. The release of 2-mercaptobenzothiazole would be delayed due to the prior elimination step required and once released the 2-mercaptobenzothiazole would accelerate a sulphur vulcanization. When the most successful R groups were found other classes of accelerators could then be used in place of 2-mercaptobenzothiazole, for example, dimethyldithiocarbamate, o-methylxanthate and 0,0 dimethylphosphorodithioate.

In order to develop the above concept a knowledge of the theories concerned with vulcanization would be valuable

as any theory that attempts to describe a sulphur vulcanization process must first account for the effect of accelerators upon the rate of reaction. A second feature that must be explained is the structural properties conferred on the vulcanizate when an accelerator is used. The present theories, of which there are many, are mainly concerned with thiazole accelerators but the other classes of accelerators have been investigated.

According to Dogadkin[30] 2-mercaptobenzothiazole and sulphur react to give a 2-mercaptobenzothiazoyl radical and a persulphydrile radical; these can then react and pass into 2-sulphurhydrilebenzothiazole and polysulphide diradicals; the 2-mercaptobenzothiazoyl radicals can also react to form dibenzothiazoyldisulphide.



The formation of polysulphide was deduced from spectroscopic work.[31] During the initial stages of vulcanization polysulphides are formed from the accelerator and

sulphur; the active sulphur radicals subsequently liberated play an important part in the cross-linking process. Zinc oxide can react with the polysulphides to give sulphides or sulphur radicals, and the thiol groups can be converted to cross-links by reactions of the type shown below:

(1) $2RSH + ZnO + S \longrightarrow RSSR + ZnS + H_2O$

(2) $R_1SH + ZnO + R_2SH \longrightarrow R_1S - Zn - SR_2 + H_2O$

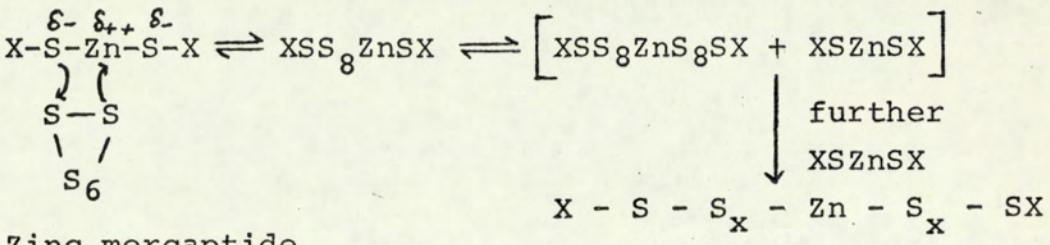
In reaction 2, zinc can split out and give rise to more cross-links, giving a thioether linkage as the product of such a reaction. To explain polysulphide links a third reaction was proposed.

(3) $R_1S_yR_2 + Zn^{++} \longrightarrow R_1S_{y-1}R_2 + ZnS$

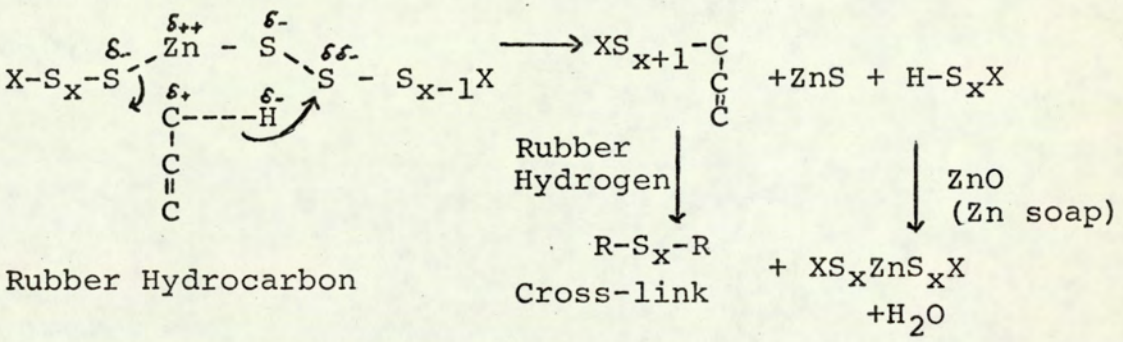
Tsurugi and Nakabayashi[32] using diphenylmethane as a simulated rubber hydrocarbon have concluded that 2-mercapto-benzothiazole and sulphur react in a radical manner with diphenylmethane and by analogy support the general views of Dogadkin.

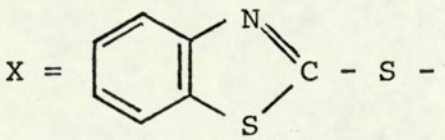
From a study of the sulphur vulcanization of natural rubber accelerated by 2-mercaptobenzothiazole, C. G. Moore and co-workers[33] have proposed that a sequence of reactions occur during vulcanization, which are polar in nature. Following the initial formation of zinc mercaptide of 2-mercaptobenzothiazole the bound sulphur atoms are electro-philic, and for this reason a sulphurating reaction of the

hydrocarbon is probable. Cross-linking may then take place when one modified rubber chain reacts with another rubber hydrocarbon, (see below).



Zinc mercaptide



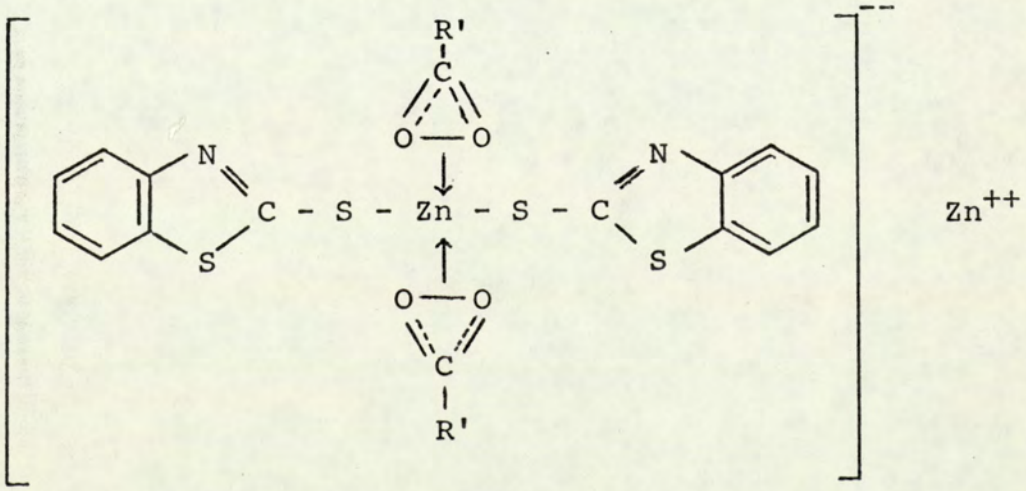


Sulphenamides are unique in that they exhibit relatively long delay periods before cross-linking occurs. Dogadkin[30] has suggested that sulphenamides split homolytically by fission of the benzothiazoyl -N-S- bond, giving the 2-mercaptobenzothiazoyl radical which then reacts with the sulphur ring to yield radical species and initiate the vulcanization process. The splitting of

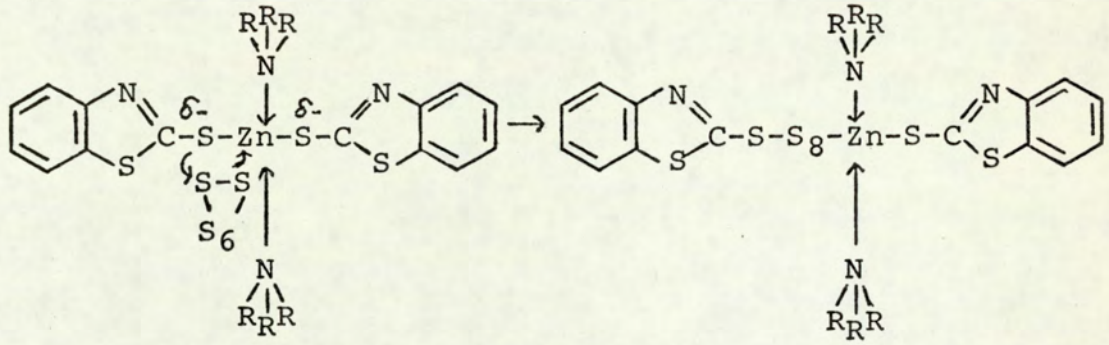
sulphenamides into radicals has been doubted by Morita and Young,[34] who considered that the reaction of sulphur with sulphenamides forms reactive intermediates. The formation of reactive intermediates was offered as an alternative explanation for sulphenamide activity. Fukuda and Tsurugi[35] have studied the reaction of sulphenamides with diphenylmethane and conclude that the reaction is radical in nature and favour the Dogadkin interpretation. In a series of papers Campbell and co-workers[36] studied the reactions of various accelerators in natural rubber gum stocks. The disappearance of the accelerator and the appearance of intermediate species were followed with time. The investigation of the curing system was accomplished using an analytical scheme developed by the above workers. Using the quantitative data obtained and emperical relationships derived in later papers a scheme for vulcanization was proposed which involved complexes and radical species. The scheme explains the delay period in terms of reactions involving complexes of the accelerator and polysulphide intermediates but offers no explanation for the structural properties conferred on the vulcanizate. Scheele has examined the kinetics of various rubber vulcanizing systems but warns that since the detailed chemical reactions between sulphur, rubber, accelerator, and activators are not known the evidence for intermediates

should not be accepted blindly. Dogadkin has noted in agreement with Shelton and McDonald[37] that both polar and radical mechanisms may be operative depending on the type of accelerator, rubber and activators used. Scheele and Dogadkin have reviewed their extensive work.[38,31] A mixed mechanism has been proposed[39] which attempts to accommodate both radical and polar nature of vulcanization with sulphenamides.

As a result of the various investigations great interest has centred on the structure of accelerator complexes. Complexes are capable of forming in the presence of zinc oxide and 2-mercaptobenzothiazole,[33] which have increased activity compared to that of the pure accelerator. When activators are present, the first step in the reaction is assumed to be the generation of a zinc mercaptide, then the bases or fatty acids attach themselves as ligands to the mercaptide forming complexes.[40]



The ligands increase the polarization of the zinc-sulphur bond, increasing the nucleophilicity of the mercaptide towards the sulphur and facilitate the reaction between the complex and the sulphur ring. A similar explanation has been offered by Krebs[41] for the action of amines and this has been expanded by Saville.[42]



Many of the experimental investigations which have been carried out on the sulphur vulcanization of natural rubber were carried out on gum stocks, i.e., stocks which do not contain a reinforcing agent such as carbon black. Information on reinforced stocks is not comprehensive and all further discussion and comments will refer to gum stocks. Most theories explain accelerator activity in terms of intermediates formed from the sulphur and accelerator which may be formed by either a radical or polar mechanism. The activators are seen as reacting rapidly

with the accelerator, e.g. zinc mercaptides, while amines and stearic acid act as ligands which activate adjacent sulphur bonds. The activation of the sulphur bonds enhances the reaction between polymer hydrocarbon and the sulphurating species. The structural properties of the cured vulcanizate have been elucidated in detail and from the structural elucidation of vulcanization an explanation of the vulcanization mechanism has been advanced in terms of polar intermediates. Kinetic schemes have given convincing correlations but as Scheele warns, till the detailed reactions and the sequence in which they occur is understood, care must be exercised in accepting detailed mechanisms. The main deficiency in most theories as the prior comment would indicate is the lack of correlation between the kinetics and detailed mechanism. Many explanations for accelerator activity also lack any correlation between reaction sequence used to explain the delay period and the step or steps responsible for the final structure of the vulcanizate.

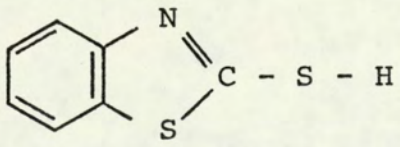
Various classes of compounds have emerged as accelerators and some of these classes were chosen for study within the framework outlined in the Summary.

For the present study the classes chosen were 2-mercaptobenzothiazole, dimethyldithiocarbamates, 0,0 dimethylphosphorodithioates and O-methyldithiocarbonate

derivatives. A brief review of the chemistry of the prior accelerating species will be given but the information described only concerns such data that is of immediate concern to the work described within the thesis.

2-Mercaptobenzothiazole derivatives

2-mercaptobenzothiazole derivatives can exist in two isomeric forms which can be distinguished by ultraviolet spectra and dipole moment measurements. Comparison of the ultraviolet spectra,[43,44,45] and dipole moments[46] of 2-mercaptobenzothiazole and its methyl derivative, indicate that in solutions of organic solvents the parent 2-mercaptobenzothiazole exists wholely in the thiazoline-2-thione form II. Molecular weight determinations show a



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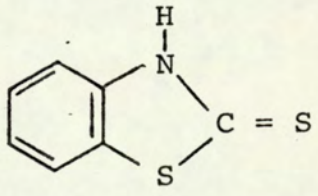

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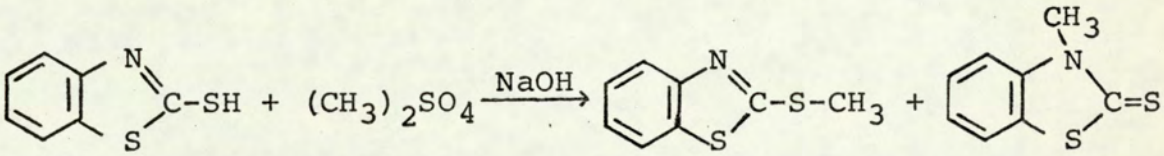
high degree of association;[47] x-ray data[45] on the solid indicate a symmetrical bimolecular structure resulting from hydrogen bonding from the thiazoline-2-thione form. 2-mercaptobenzothiazole undergoes many reactions typical

of thiols; it is a weak acid readily soluble in alkali. Oxidation may follow one of several courses, under mild conditions iodine[48] or hydrogen peroxide[49] in neutral conditions yield the disulphide. Often in substitution reactions atmospheric oxidation may yield the disulphide as an undesirable side product. 2-mercaptobenzothiazole will undergo a variety of substitution reactions and may yield both isomers as products, e.g., methylation with dimethyl sulphate yields a small amount of the thiazoline-2-thione form.[50]



63% 15%

Additional reactions between 2-mercaptothiazoles; benzothiazoles and unsaturated systems are known and the point of substitution is often the ring nitrogen.[51,52]

Dimethyldithiocarbamate derivatives

The infrared spectra of various metal complexes of dimethyldithiocarbamates have been examined[53] and the "thioureide band" which occurs between 1542 and 1480 $cm.^{-1}$ has been explained in terms of various canonical forms,

one of which is postulated as involving a partial C=N bond and this canonical form is thought to be responsible for the thioureide absorption.

Dipole moments have been determined for some esters and related compounds.[54,55] The esters show a high degree of association provided an amine hydrogen is present, replacement of the hydrogen by alkylararyl groups destroys this association.[56] The ultraviolet spectra of dithiocarbamates exhibit intense bonds in the following regions, 250 m μ , 290 m μ , and a weaker absorption occurs at 330 m μ Janssen[57] and Koch[58] have assigned the bond at 250 m μ to be located in the - C(=S) - N - group. However, they disagree on the bond at 290 m μ ; Janssen favours the absorption to arise from the - S=C - N< group, while Koch assigns the absorption as arising from the - S=C - S - group.

Free dimethyldithiocarbamic acid is unstable at room temperature and decomposes very rapidly. Dithiocarbamate metal salts can be readily oxidized to disulphides under mild conditions.[59] Alkyl esters can be prepared by reaction with the appropriate halogen compound.[54]

$$(CH_3)_2NCS_2Na + CH_3I \xrightarrow[\text{Ethanol}]{95\%} (CH_3)_2NCS_2CH_3 + NaI$$

Dialkyldithiocarbamic acids when formed in situ, add to unsaturated systems such as acrylonitrile to form

esters.[60] The uses and properties of dithiocarbamates have been reviewed comprehensively by Thorn and Ludwig[61] particularly in the area of biological applications.

O-Methyldithiocarbonates derivatives

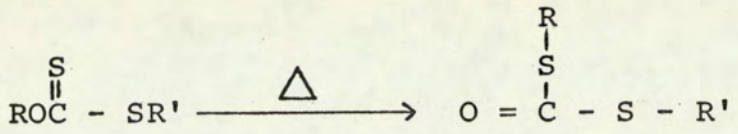
The free acids, commonly called xanthates, unstable at room temperature; the decomposition has been investigated and found to be mono-molecular.[62] The ultraviolet spectra,[53] crystal structure,[63,64] of metal salts of the acids have been investigated. Oxidation of alkali metal salts is facile and can be accomplished with a wide variety of agents to yield the disulphide.[65] The potassium or sodium salts react readily with a wide variety of halogen compounds to give the esters.

$$RO - \overset{S}{\overset{\|}{C}} - SK + EtI \longrightarrow RO\overset{S}{\overset{\|}{C}} - S - Et + KI$$

The esters can be obtained by nucleophilic substitution on the acid chloride.

$$R - O - \overset{S}{\overset{\|}{C}} - Cl + NaSR' \longrightarrow RO - \overset{S}{\overset{\|}{C}} - S - R' + NaCl$$

The esters are known to isomerise when heated, the extent of the isomerisation depending on the molecule forming the S- substituted group.[66, 67]



The ester are particularly useful for introducing unsaturation into molecules and this reaction which entails heating is known as the Chug v reaction. The details of this reaction will be dealt with later in the consideration of cyclic processes. In this study O-methyldithiocarb ates will not be used but the more familiar nomenclature, i.e., methylxanthate, will be used throughout the thesis.

0,0 Dimethylphosphorodithioate derivatives

The infrared spectra[68] of some phosphorodithioates have been investigated and empirical correlations made.

A similar study has been made of the nuclear magnetic resonance spectra,[69] particular attention being paid to phosphorous coupling.

The reaction between phosphorous pentasulphide and alcohols[70] yields as a major product dithiophosphoric acids. The acids are stable and can be titrated with alkali. The sodium salts are easily oxidized to the disulphide[71] and react with a variety of halogen compounds to give esters,[72] e.g.,

$$(RO)_2\overset{S}{\overset{\|}{P}} - SNa + R'BR \longrightarrow (RO)_2\overset{S}{\overset{\|}{P}} - S - R' + NaBr$$

The various synthetic routes to the esters have been reviewed[73] comprehensively. The esters are usually stable thermally, but may isomerise and sometimes decompose violently, often yielding polymeric residues.[74]

Cyclic Processes

Moore and Waight[29] studied the thermal decomposition and isomerisation of 2-substituted thiobenzothiazoles and 3-substituted thiobenzothiazolines and proposed that the decompositions of such molecules proceeded via an elimination pathway analogous to an El elimination. The isomerisation of alkenyl derivatives was considered to proceed by a mechanism similar to that envisaged for the Claisen rearrangement. Of the compounds studied the cyclohex-1-enyl and trans-but-2-enyl derivatives showed a mixed mechanism both isomerising and decomposing. The two reactions were competitive, the relative rates being dependent on the nature of the substituent group. To explain substituent effects on both reactions various transition states were discussed and a cyclic transition state was invoked for the isomerisation after consideration of the activation parameters involved. In this study the

dimethyldithiocarbamate, 0,0 dimethylphosphorodithioate and 0-methyldithiocarbonate (0-methylxanthate) derivatives were prepared and examined. The prior compounds are esters of various acids. The decomposition of carboxylic acid esters has been studied extensively and consideration of the mechanisms and transition states invoked in such reactions will now be considered.

Formal recognition[75,76] of these processes has been made in recent times and various names are given to reactions involving such processes, e.g., circular, four-centred, molecular and no-mechanism. The main problem in such reactions is a description of the transition state (or several in some cases) which results from the electronic sources within the molecule concerned. A precise description is often difficult as the reactions are often thermally induced, show no response to free radical initiators or inhibitors, are insensitive to acid-base catalysis, and often show only small changes in rate with structure and solvent. The electronic shifts which constitute the bond making and bond breaking process are closely synchronized and in some of the processes the reactions are invariably unimolecular, intramolecular, and show definite stereochemical consequences.

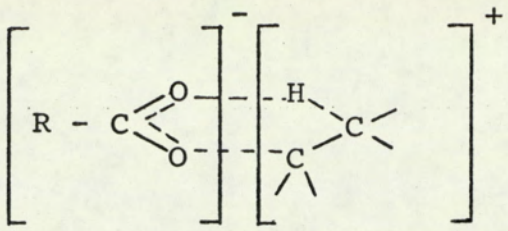
The scope of such mechanisms is a broad one bordering on homolytic dissociation at one extreme, an example of

which is the decomposition of cyclobutane to ethylene.[77] At the opposite end of the spectrum is the gas phase decomposition of esters[78] for which a transition state of considerable ionic character has been advanced. Within this spectrum of reactions fall the Claisen rearrangements of alkenyl aryl ethers and related rearrangements.

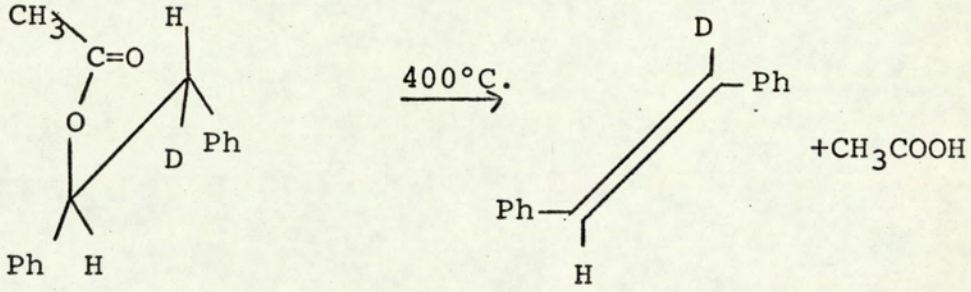
One of the earliest attempts to describe the transition state in an ester decomposition was proposed by Hurd and Blunck[79] who envisaged the abstraction of the β hydrogen taking place via a cyclic transition state, e.g.,

Usually the direction of electron transfer is based on the electronegativity of the atoms but it is not certain that the electrons move in pairs around the system in a particular direction. In such a concerted process the difference between homolytic and heterolytic displacement is minimal, but for convenience the electrons are usually shown to move in pairs when this provides an adequate description. In a comprehensive review Maccoll[78] shows that the transition state of esters is amenable to substituent studies at the α carbon and proposes that the

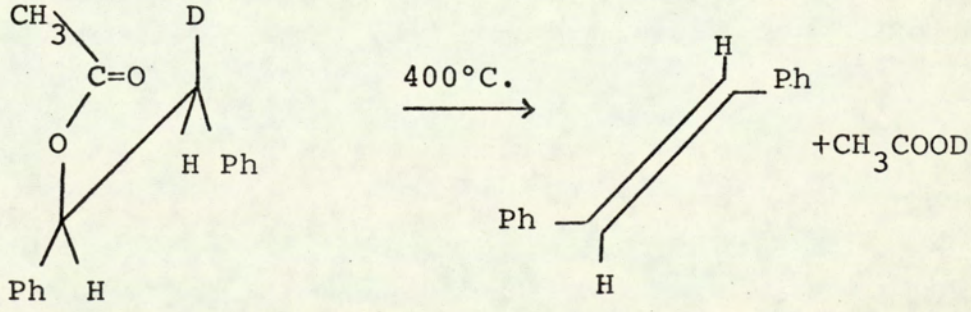
best representation for the mass of data is as follows:



Stereochemical studies and ester decomposition have been undertaken by Curtin and Kellom[80] who studied the enantiomers of Ph.CHD.CH.Ph O.C.O.CH_3. Whereas the erythro form gave trans-stilbene in which almost all the deuterium



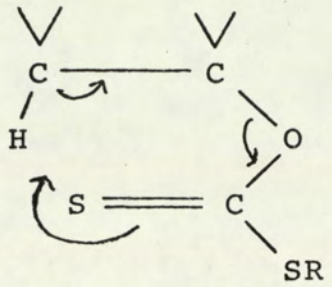
ERYTHRO



THREO

was retained, the threo gave trans-stilbene containing little deuterium. Trans-stilbene formation was explained in terms of a cyclic transition state in which it was postulated that the phenyl groups would avoid eclipsing and by doing so reduce unfavourable steric interactions. The decomposition of linalyl, neryl and geranyl acetates[81] yielded a large variety of products, particularly cyclic products. To explain product formation, homolysis of the carbon-oxygen bond of the alkenyl group was proposed giving an allylic system, in which the alkenyl group then rotates about the acid residue before hydrogen abstraction takes place. A variety of products can be obtained depending on the relative positions of the ester group and acid residue. Kwart and Taagepera[82] have noted in a study of nor-bonyl acetates decomposition that endo-norbonyl acetate decomposition has a large negative entropy of activation and ascribe this to a concerted transition state which is particularly well ordered. In an isotope study of the decomposition of the hydrogen phthalate ester of trans 1,2 dimethylcyclohexanol,[83] ^{18}O enrichment in the undecomposed ester is cited as evidence for an ion pair transition state. The Chugaev reaction was considered to function via a cyclic transition with the sulphur of the thio ether abstracting the β-hydrogen. Isotope studies[84] have shown the following sequence to be

operative, i.e., abstraction via the thione sulphur.



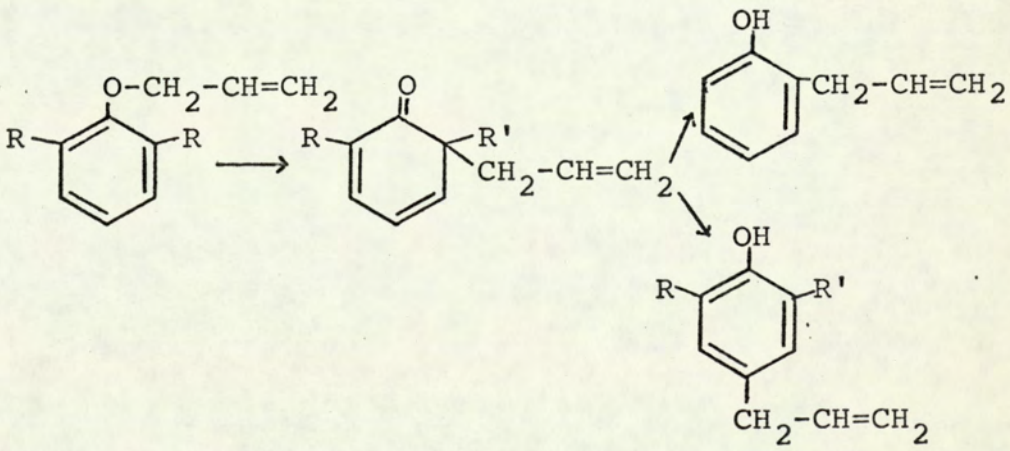
Little kinetic data is available for the thermal decomposition of xanthates and so no detailed mechanistic picture has emerged apart from the prior study[84] which distinguishes two gross possibilities. In the thermal decomposition of t-alkyl N-aryl carbamates,[85] ring substituents were used to probe the mechanism. A cyclic transition state similar to that envisaged for the decomposition of esters was proposed and although the participation of radical intermediates in the decomposition was not disproved, such species were discounted. Diveley[86] and co-workers have noted in a study of 0,0 dimethyl and 0,0 diethylphosphorodithioate derivatives a p-dioxan, that esters which decomposed at lower temperatures were usually those which facilitated a cis elimination process to yield the acid, while those which did not required much higher temperatures for decomposition. The decomposition of some thiocarbonic anhydrides[87] have been investigated and from the measurement of activation parameters and the

effects of various solvents upon the rates of decomposition it was concluded that the transition state was concerted and similar to the processes postulated for ester decompositions.

The original Hurd and Blunck[79] mechanism proposed for the thermal decomposition of esters had many attractive features; it indicated the reaction was unimolecular, homogeneous and proceeded via abstraction of the β-hydrogen in keeping with the observation that β-deuteriated esters show an isotope effect and implied a negative entropy of activation. This truly concerted process did not describe the influence of the acid residues[88,89] upon the reaction rates. The ion-pair as originally postulated by Maccoll[90] was doubted because of the difficulty in accommodating the isotope effect. Scheer[91] points out that the ion-pair need not be in conflict with the isotope effect if the reversal of the ion-pair to the initial state proceeds much more rapidly than the transition to the olefin, then a large isotope effect is quite feasible. Maccoll[78] in a later discussion modified slightly the ion-pair hypothesis to accommodate the bulk of data. The observations of Kraus[92] strongly favour the idea of a polar transition state for esters. After application of the Taft equation to ester pyrolysis data he concluded that high negative values of the slope may be connected

with the polar nature of the transition state and the absence of solvent, or that the reaction centre forms part of the alkyl group. The decomposition of esters, xanthates and amine oxides to produce olefins have been reviewed by DePuy and King.[93]

When part of an aromatic ring provides the vinyl group the rearrangement of allyl vinyl ethers is known as the Claisen rearrangement. The migrations which occur can be summarized as follows: when the allyl ether has an enalisable hydrogen in the ortho-position an o-allyl phenol will probably form. When the ether contains neither hydrogen nor displacable groups in the ortho position the migration of the allyl group is to the para position, e.g.,



Where R' = H, R = alkyl

The existence of the dienone has been shown by heating an allyl ether with maleic anhydride, the isomeric adducts formed were consistent with a dienone intermediate.[94] A dienone has been synthesized directly and shown to revert to the allyl ether and the rearranged phenol.[95] The para rearrangement is preceded by an ortho migration. The second step is probably better classified as a Cope rearrangement and the details of the mechanism have been summarized.[96] In an attempt to elucidate the nature of the transition state the Hammatt relationship has been used on a series of para substituted allyl ethers. The rate data give a ρ value which is negative (-0.609),[97] (see Table 2).

TABLE 2

REARRANGEMENT OF p-x-PHENYL ETHERS IN CARBITOL AT 181°C.[97]

X	10^5 k sec^{-1}
NO_2	1.03
H	2.56
Br	2.77
NHAc	5.79
MeO	9.16
NH_2	21.30

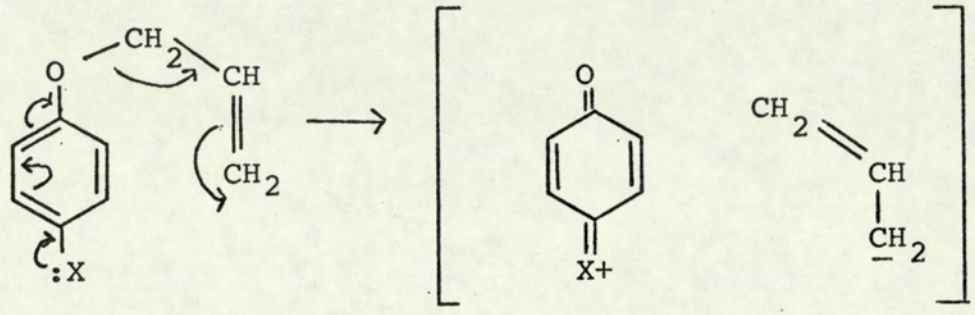
The ρ value is not large and may imply that in the transition state an electron deficiency develops at the oxygen and by helping to compensate this deficiency by electron donation, the electron donating para substituents facilitates the rearrangement. This would imply that carbon-oxygen bond braking is more important than bonding to the ortho position. In various solvents[98] the rate of rearrangement is greater with increasing polarity of the solvent, (see Table 3).

TABLE 3

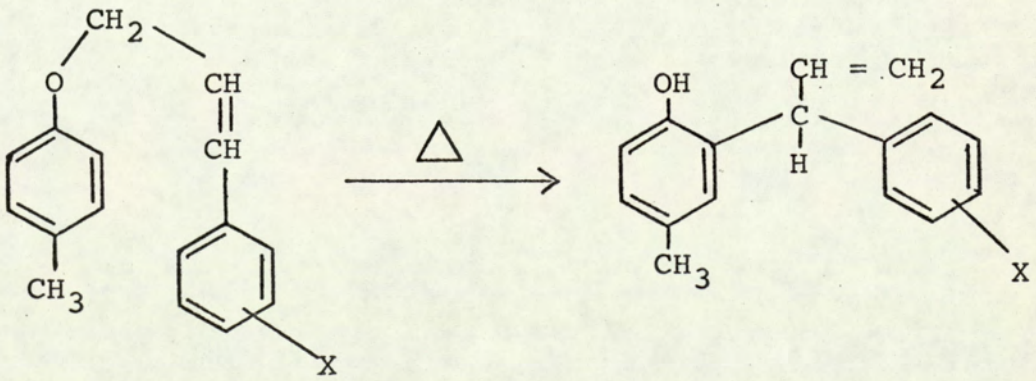
REARRANGEMENT OF ALLYL p-CRESYL ETHER AT 184-85°C.[98]

Solvent	10^5 k sec^{-1}
Phenol	45
1-Octanol	9
Benzonitrile	2.49
Decalin	1.56

Only an illustrative sample of the author's results have been used in Tables 2 and 3. From the kinetics a polar transition can be envisaged with the allyl group obtaining, in the extreme, the negative charge.



Such representation would suggest that electron withdrawing groups on the carbon of the allyl group would enhance the rate. It has been found that for meta and para substituents in the cinnamyl group of cinnamyl tolyl ethers can be fitted by δ^+ constants, giving small negative ρ values.[99]



The rearrangement is enhanced by electron donation from both portions of the ether and this makes the description of the transition state difficult. There are some analogies with the thermal decomposition of substituted benzoyl peroxides[100] and a transition state with considerable homolytic character becomes a tempting explanation.[101] The Woodward and Hoffman rules have been applied to the Claisen rearrangement[102] and the processes were classified as sigmatropic changes.

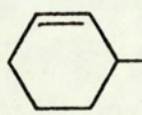
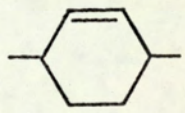
CHAPTER II

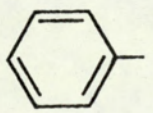
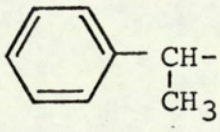
SYNTHESIS AND STRUCTURAL ELUCIDATION

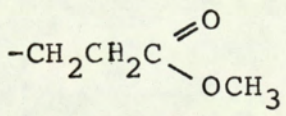
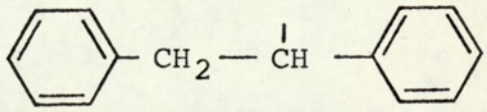
Synthesis

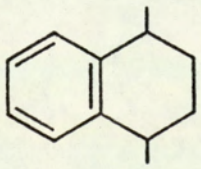
The synthetic methods used are illustrated by the following equation, where R represents the alkyl, alkenyl, or aralkyl group utilized and Ac is the potential accelerating species.

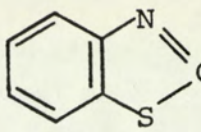
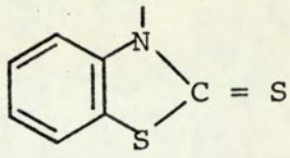
$$RX + Ac - S - Na \longrightarrow Ac - S - R + NaX$$

Where R =  , $-CH_2-CH=CH-CH_2-CH=CH_2$,  ,

 ,  , $-CH_2CH_2CN$,

 ,  ,

 .

Ac = a)  - S - or 

b) $(CH_3)_2N - \overset{|}{C} = S$, $CH_3O\overset{|}{C} = S$, $(CH_3O)_2\overset{|}{P} = S$

Initially only the 2-mercaptobenzothiazole derivatives were synthesised and after various R groups had been evaluated, the two most promising R groups were then selected for further study. The study was then extended to other accelerating species, e.g., series (b). The selection of a group for further study was made by comparing the rate of decomposition, i.e., to yield 2-mercaptobenzothiazole and the corresponding olefin. The two groups with the greatest rates of decomposition were then chosen and were mono-substituted 1,2 diphenylethane and 1,4-bis-substituted tetralin.

Most of the accelerating species (Ac-S-Na), when present in solution as the sodium or potassium salt are prone to oxidation, yielding the corresponding disulphide. In order to minimize this undesirable side reaction, nitrogen was continuously bubbled through the reaction vessel. The sodium or potassium salts of the phosphorodithioates, xanthates and dimethyldithiocarbamates were commercially available but the sodium salt of 2-mercapto-

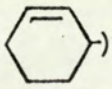
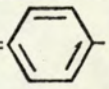
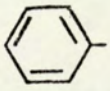
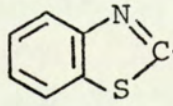
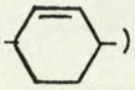
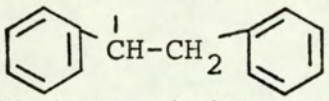
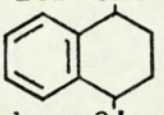
benzothiazole was prepared prior to use. Care was taken in this preparation to avoid excess base. This precaution was taken so that the possibility of any base induced elimination would not seriously lower the synthetic yields. Excess heating was avoided in order to limit elimination reactions that could be induced by indiscriminate heating of the reaction vessel, similarly heat and oxygen were kept to a minimum during work-ups. The solvents used were purified, as needed, by the methods outlined in Vogel.[103] In a study of xanthates Nace, et al[104] found that xanthates containing peroxide impurities decomposed at lower temperatures than those whose peroxides had been removed by washing with ferrous sulphate but both starting materials gave the same products. The ferrous sulphate wash was introduced for all compounds and then the compounds were stored in the dark, under nitrogen at room temperature. The synthetic conditions are summarized in Table 4. The cyclohex-2'-enyl (R= ), 2':5' hexadien-1'-yl (R=CH_2-CH=CH-CH_2-CH=CH_2), α-phenyl ethyl (R= ) and β-phenyl ethyl (R= ) derivatives of 2-mercaptobenzothiazole () were prepared using water as the reaction solvent. The insoluble halide was added dropwise to a solution containing the sodium salt of

TABLE 4

SYNTHETIC CONDITIONS FOR SUBSTITUTED THIOBENZOTHIAZOLES, DITHIOCARBAMATES,[a] XANTHATES,[b] PHOSPHORODITHIOATES[c]

Substituent	Halide	Solvent	Temperature (°C.)	Yield (%)
cyclohex-2'-enyl	Br	Water	80	61
2':5' hexadien-1'-yl	Br	Water	80	71
cyclohex-2'-enyl 3':6' di	Br	Dioxan/ Water	40	49
α-phenylethyl	Br	Water	80	70
β-phenylethyl	Br	Water	80	64
β-cyanoethyl	--	Ethanol	16	20
β-methoxycarbonylethyl	--	Glacial acetic acid	60	48
1',2' diphenylethyl	Cl	Isopropanol (aqueous)	80	76
	Cl	Isopropanol (aqueous)	80	53[a]
	Cl	Isopropanol (aqueous)	80	64[b]
	Cl	Isopropanol (aqueous)	80	71[c]
1,4 bis tetralin	Br	Dioxan/ Water	35	54
	Br	Dioxan/ Water	35	47[a]
	Br	Dioxan/ Water	35	67[b]
	Br	Dioxan/ Water	35	52[c]

2-mercaptobenzothiazole. In all cases the yields were satisfactory. When the cyclohex-2'-enyl 3':6' di derivative (R= ) was prepared, dioxan/water was used as the solvent and the temperature of reaction lowered. The changes were necessary, as the dibromide is liable to hydrolysis, and early attempts to recrystallise the dibromide from alcohol lead to the corresponding diol. The yield was lower than that obtained from the previous reactions. The derivatives of α-chloro 1,2 diphenylethane (R= ) were prepared using reaction conditions similar to those employed in the previous experiments and good yields were obtained. Initial difficulty was encountered in the distillation of α-chloro 1,2 diphenylethane, the chloro compound decomposed to give trans-stilbene. As a result of this difficulty an alternative synthetic route to these derivatives was explored. Trans-stilbene was protonated using perchloric acid and then 2-mercaptobenzothiazole was added; the method was visualised as an initial protonation; nucleophilic attack by the thiol then followed, giving the desired product. The yield was low (27%) and so this method was not pursued any further. In a similar manner, dithiophosphoric acid addition to α-hydroxy 1,2 diphenylethane was attempted as an alternative synthetic route to the 0,0 dimethylphosphorodithioate derivative

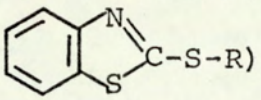
[Ac=$(CH_3O)_2PS_2$-], the result was disappointing. The synthetic procedure used for the 1,4-bis-substituted tetralin derivatives (R= ) was analogous to the method used for the cyclohex-2'-enyl 3':6' di derivative, and this gave satisfactory quantities of pure products. The β-cyanoethyl and β-methoxycarbonylethyl derivatives (R= $-CH_2CH_2CN$, $-CH_2CH_2COOMe$) were prepared by the addition of the thiol to the activated double bond of acrylonitrile and methyl acrylate. The reaction of 2-mercaptobenzothiazole and methyl acrylate was conducted in a large excess of glacial acetic acid in order to avoid any dimerisation,[105] which would be an undesirable side reaction.

Structural Elucidation

Ultraviolet spectroscopy was used to investigate the structure of the various compounds synthesized, as certain absorptions that occur in the ultraviolet region have been associated with accelerator chromophores. The ultraviolet spectra of 2-substituted thiobenzothiazoles have been noted by Morgan[106] but very little fundamental work can be found in the literature; however, 2-mercaptobenzothiazole has been investigated by Koch[58] who tentatively assigned the strong absorption of 2-mercaptobenzothiazole at 325 mμ to the $\geq C=S$ group. The disubstituted thiobenzothiazoles

have extinction coefficients considerably greater than the monosubstituted thiobenzothiazole derivatives (see Tables 5 and 6), which is further evidence to support the proposal that the origin of the various absorptions lies in the thiobenzothiazole ring.

TABLE 5

ULTRAVIOLET ABSORPTIONS OF 2-SUBSTITUTED THIOBENZOTHIAZOLES () IN ETHANOL

Substituent	λ Max (mμ)	ε (max)	$E^{1\%}_{327}$
cyclohex-2'-enyl	282;291;301	13,000;12,500;11,000	60
2':5' hexadien-1'-yl	282;290;301	12,410;11,560;9,600	N 0.1
α-phenylethyl	283;291;301	12,200;11,970;10,650	4
β-phenylethyl	282;290;300	12,800;11,700;9,700	2
β-methoxy-carbonylethyl	279;290;300	11,750;10,400;8,350	10
1',2' diphenyl ethyl	283;294;301	14,400;14,600;13,500	4

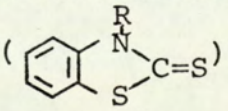
TABLE 6

ULTRAVIOLET ABSORPTIONS OF 2-SUBSTITUTED DITHIOBENZOTHIAZOLES IN ETHANOL

Substituent	λ max (mμ)	ε (max)	$E^{1\%}_{327}$
cyclohex-2'-enyl 3':6' di	283;291;301	27,100;26,800;25,200	1
1,4 bis tetralin	283;292;302	26,900;26,500;26,400	10

The ultraviolet spectra provided firm evidence for the presence of the thiobenzothiazole group and furthermore could be used to determine whether the compound is the tautomeric thiobenzothiazole, as are the examples in Tables 5 and 6 or the benzothiazoline-2-thione, i.e., substituted at the ring nitrogen (see Table 7).

TABLE 7

ULTRAVIOLET ABSORPTIONS OF 3-SUBSTITUTED BENZOTHIAZOLINE-2-THIONE () IN ETHANOL

Substituent	λ max (mμ)	ε (max)	$E^{1\%}_{281}$
cyclohex-2'-enyl	242; 327	12,700; 26,100	89
β-cyanoethyl	242; 325	13,800; 24,600	90

The absorption at ca. 326 mμ can be used to follow the isomerisation of the 2-substituted thiobenzothiazoles to the 3-substituted benzothiazoline-2-thiones providing decomposition[58] does not occur, as background absorption due to the 2-substituted thiobenzothiazoles at 326 mμ is negligible. When the ultraviolet spectra of the S-substituted dimethyldithiocarbamates were examined, the extinction coefficient of the 1,4-bis-substituted tetralin derivative was approximately twice that of the mono-substituted 1,2 diphenylethane derivative (see Table 8). A similar increase in extinction coefficients was observed in the corresponding thiobenzothiazoles. The xanthate derivatives also showed an increase in extinction coefficient when they were further substituted (see Table 9).

TABLE 8

ULTRAVIOLET ABSORPTIONS OF S-SUBSTITUTED DIMETHYLDITHIOCARBAMATES IN ETHANOL

Substituent	λ max (mμ)	ε (max)
1', 2' diphenyl-ethyl	220;251;278	30,500;24,800;17,200
1,4 bis tetralin	225;253;279	58,700;50,400;34,200

TABLE 9

ULTRAVIOLET ABSORPTIONS OF S-SUBSTITUTED METHYLXANTHATES IN ETHANOL

Substituent	λ max (mμ)	ε (max)
1',2' diphenyl-ethyl	225; 287	8,900; 7,900
1,4 bis tetralin	225; 284	17,800;14,700

Information concerning the presence of alkyl, alkenyl, aryl, methoxy and dimethylamine groups can be obtained using infrared spectroscopy. Analysis of the spectra and identification of such groups was aided by the texts indicated in the experimental. Morgan[106] has recorded the infrared data of a small number of 2-substituted thiobenzothiazole and 3-substituted benzothiazoline-2-thione derivatives. This investigation revealed that an absorption at ca. 1000 $cm.^{-1}$ might be useful in identifying such derivatives. O'Sullivan[107] in a study of various fused heterocyclics, concluded that for systems of the benzothiazole type, absorptions near the following frequencies ($cm.^{-1}$) would be expected, 1600, 1460, 1390, 1310, 1270, 1250, 1200, 1160, 1110, 1060, 1020, 950, 890, 850, 800, 750. No assignment of the absorption at ca. 1000 $cm.^{-1}$

was made by O'Sullivan. In order to correlate the absorptions of thiobenzothiazole derivatives it was necessary to examine the data available for thiazoles, so that the large number of absorptions could be resolved and correlated. Many of the absorptions cited by O'Sullivan originate in the 1,2 disubstituted benzene ring, but Mijovic and Walker[108] in a study of thiazoles assign the absorption at ca. 1000 cm.$^{-1}$ to the $-\overset{|}{C}-H$ vibrational modes or ring breathing, while β-ring vibrational modes are assigned to absorptions occurring between 870 and 820 cm.$^{-1}$. Similar studies have been made on ring breathing modes[109] and β-ring vibrational modes.[110] The results obtained from the present work (see Table 10) would indicate that the aromatic-nitrogen stretching (ca. 1320 cm.$^{-1}$) is always strong, while variable intensity absorptions occur at 670 cm.$^{-1}$, i.e., aromatic-sulphur stretching. Ring breathing would be a favoured assignment for the absorption occurring at ca. 1000 cm.$^{-1}$, as the benzothiazole nucleus would not possess the simple $-\overset{|}{C}-H$ vibrational modes that were observed in simple thiazoles. An encouraging observation is that they do not disappear or weaken in the spectra of the benzothiazoline-2-thiones. The absorptions occurring between 900 and 850 cm.$^{-1}$ do not appear to be reliable diagnostic absorptions for the compounds studied. These considerations are only tentative; an exhaustive

TABLE 10

INFRARED ABSORPTIONS OF 2-SUBSTITUTED THIOBENZOTHIAZOLES AND 3-SUBSTITUTED BENZOTHIAZOLINE-2-THIONES

Substituent	1330-1300 $cm.^{-1}$ Vibrations	1010-900 $cm.^{-1}$ Vibrations	900-850 $cm.^{-1}$ Vibrations	710-650 $cm.^{-1}$ Vibrations
cyclohex-2'-enyl (thiazole)	1310 (S)	990(S), 920(M)	860 (S)	670 (M)
cyclohex-2'-enyl (thiazoline)	1310 (S)	1008(S), 950(W)	850 (W)	650 (M)
2':5' hexadien-1'-yl	1320 (S)	1000(S), absent	860 (W)	675 (W)
cyclohex-2'-enyl 3':6' di	1310 (M)	1000(S), 940(W)	absent	660 (W)
α-phenylethyl	1310 (S)	990(S), 945(W)	absent	660 (W)
β-phenylethyl	1310 (S)	998(S), 940(W)	855(V.W.)	670 (W)
β-cyanoethyl (thiazoline)	1320 (S)	980(S), 940(W)	absent	660 (M)
β-methoxycarbonyl-ethyl	1310 (M)	995(S), 940(W)	absent	670 (W)
1',2' diphenyl-ethyl	1310 (S)	995(S), 950(W)	absent	650 (V.W.)
1,4 bis tetralin	1305 (S)	985(S), 930(W)	860 (W)	670 (M)

S = Strong M = Medium W = Weak V.W. = Very Weak intensity absorption

study was not performed and no solvent investigations were carried out. The infrared spectra of 0,0 dimethylphosphorodithioate derivatives have been analysed on the basis of P-O-C, P → S, and P-S-C stretching assignments made by McIvor, et al[68] (see Table 11).

TABLE 11

INFRARED ABSORPTIONS OF S-SUBSTITUTED 0,0 DIMETHYLPHOSPHORODITHIOATES

Substituents	P-O-C ($cm.^{-1}$)	P→S ($cm.^{-1}$)	P-S-C ($cm.^{-1}$)
1',2' diphenylethyl	1020	815	660
1,4 bis tetralin	1015	810	660

Xanthates have not been fully investigated and although dimethyldithiocarbamates possess the "thioureide band" it is of doubtful validity[106] in structural assignments.

Nuclear magnetic resonance spectroscopy provided supplementary structural information. The spectra were recorded in carbon tetrachloride or deuterochloroform using tetramethylsilane as an internal standard. The tautomeric thiobenzothiazole and benzothiazoline-2-thione exhibited different absorption spectra. The S-substituted

α-carbon proton (-S-C-H) absorbing at higher τ values than the N-substituted α-carbon proton (=N-C-H), such shifts have been noted previously by McCall, et al[111] (see Table 12).

TABLE 12

NUCLEAR MAGNETIC RESONANCE ABSORPTIONS OF 2-SUBSTITUTED THIOBENZOTHIAZOLES AND 3-SUBSTITUTED BENZOTHIAZOLINE-2-THIONES

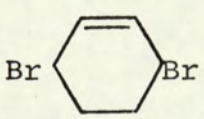
Substituent	τ (-S-C-H)	τ (=N-C-H)
Methyl	7.32	6.19[111]
cyclohex-2'-enyl	5.15	4.10
β-cyanoethyl	-	5.50

The exceptionally low τ values at which absorption occurs for the cyclohex-2'-enyl derivative is probably due to the reinforcing effect of the allylic position which is also the seat of substitution.

Structural resolution of the isomeric allylic bromides and the reaction product obtained from them was necessary because of the possible allylic rearrangement and and nucleophilic rearrangement, i.e., S_N2'. Bateman and co-workers[112] in a study of the allylic bromination of hexa-1:5-diene showed that the product contained 1-bromo-

hex-2:5-diene (90%) and 3-bromohexa-1:5-diene (10%). The isomeric composition was determined by comparing the absorption intensities at 918 cm.$^{-1}$ (CH_2=CHR) and 965 cm.$^{-1}$ (RCH=CHR). Hexa-1:5-diene was brominated and the mixed bromides reacted with 2-mercaptobenzothiazole. It seemed likely that a S_N2' process might be operative, as similar substitutions yielding rearranged products, have been noted by Hwa[113] and so the product obtained was examined for both isomers. The product absorptions at 918 cm.$^{-1}$ were reduced while the absorption at 965 cm.$^{-1}$ increased compared to the mixed bromides. The nuclear magnetic resonance spectra indicated no 3-isomer (CH_2=CH-$\dot{C}$H-CH_2-CH=CH_2) present, confirming the evidence of the infrared, that the 3-isomer concentration must be considerably less than 10%.

The preparation of 3:6 dibromocyclohexene[114] raised similar problems, since allylic bromination could produce the following rearranged products.[115]



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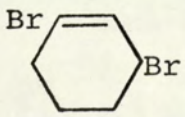

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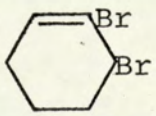
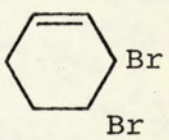


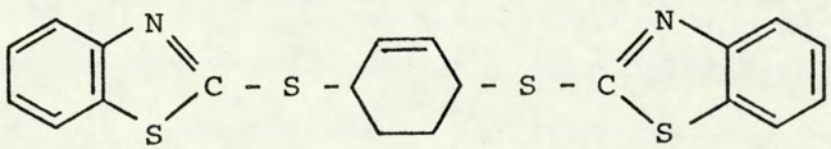
III



IV

Isomer II and III were eliminated by examination of the

nuclear magnetic resonance spectra, the observed proton ratio did not agree with that expected from II and III. The resolution of I and IV was accomplished by strongly irradiating the allylic protons, i.e., spin decoupling. The olefinic protons, which had a pronounced doublet, should decouple reducing the doublet to a different form depending on which isomer was present. The doublet reduced to a single peak indicating I, from IV no such reduction would have been expected as the $-CH_2-$ group adjacent to the olefinic bond would not give a single peak. The bromide was reacted with the sodium salt of 2-mercaptobenzothiazole and the product's structure elucidated from U.V., I.R. and N.M.R. data (see below).



The nuclear magnetic resonance spectra of α and β phenylethyl thiobenzothiazoles gave characteristic spin-spin coupling, e.g., doublet- quadruplet and triplet, respectively. The spectra of 2-(1',2' diphenylethyl)-thiobenzothiazole was unusual giving quadruplet-octet coupling, the expected coupling of the ethyl protons being triplet-doublet. The spectra is very similar to that of

stilbene oxide, which would suggest that rotation about the -C-C- bond of the ethyl group is hindered; when a model was made, rotation was found to be extremely hindered. Phosphorous coupling[69] was observed with the S-substituted 0,0 dimethylphosphorodithioate derivatives, the coupling constant being 15.6 cy./sec. This observation helped considerably in identification of protons on the carbon atom adjacent to the sulphur, which absorbed in a similar region to the methoxy protons. The methyl groups of both xanthate and dithiocarbamate esters were identified by comparison with the salts dissolved in deuterium oxide, in which was dissolved acetone, i.e., internal reference (see Table 13).

TABLE 13

NUCLEAR MAGNETIC RESONANCE ABSORPTIONS OF α-SULPHUR CARBON PROTONS, i.e., -S-C-

Compound	τ
2-(hexa 2':5' dien-1'-yl) thiobenzothiazole	6.05
2-(cyclohex-2'-enyl,3',6') dithiobenzothiazole	5.01
2-(α-phenylethyl) thiobenzothiazole	4.85
2-(β-phenylethyl) thiobenzothiazole	6.95
2-(β-methoxycarbonylethyl) thiobenzothiazole	6.40
2-(1',2' diphenylethyl) thiobenzothiazole	4.75
S-(1,2 diphenylethyl) dimethyldithiocarbamate	4.40
S-(1,2 diphenylethyl) methylxanthates	5.05
S-(1,2 diphenylethyl) 0,0 dimethylphosphorodithioate	5.10
	(J=15.6 cy./sec.)
1,4 bis-(2'-benzothiazoylthio) tetralin	4.01
1,4 bis-(S-dimethyldithiocarbamate) tetralin	4.50
1,4 bis-(S-methylxanthate) tetralin	4.90
1,4 bis-(S-0,0 dimethylphosphorodithioate) tetralin	5.31
	(J=15.6 cy./sec.)

CHAPTER III

THERMAL DECOMPOSITION AND ISOMERISATION

Introduction

In the study of the decomposition of 2-thiobenzothiazole, dimethyldithiocarbamate, methylxanthate and 0,0 dimethylphosphorodithioate derivatives, kinetic methods were employed, to examine the mechanisms of the competitive isomerisation and decomposition reactions. The isomerisation was detected by the appearance of the benzothiazoline-2-thione absorption at approximately 325 mμ (i.e. $\geq C=S$). The 2-substituted thiobenzothiazole decompositions were initially followed by sodium hydroxide titration. The kinetics of the thermal decomposition of the mono-substituted 1,2 diphenylethane and 1,4 bis-substituted tetralin derivatives could not be followed by titration and a chromatographic -U.V. method was developed for this purpose.

The kinetics of the isomerisation reaction were analysed using the reversible first-order rate equation. The kinetic law for a reversible first-order reaction,

$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, is given by the following equation, where x_t is the concentration of A converted into B at time t and

$$\ln xe/(xe - x_t) = (k_1 + k_2)t$$

xe = concentration of A converted into B at equilibrium, the initial concentration of B being zero. The decomposition reaction was analysed by the same procedure, and good kinetic plots were obtained. The decompositions were treated in the same way as a preliminary experiment and showed that the back addition, i.e., 2-mercaptobenzothiazole to olefin occurred readily (see page 64). Although this method of analysis was approximate it provided a convenient way of handling the data obtained from the study of these competitive reactions. Initial rates could have been used but the prior technique gave good reversible first-order plots. The mono-substituted 1,2 diphenylethane and 1,4 bis-substituted tetralins derivatives followed good first-order kinetics, i.e., decomposition and no detectable isomerisation. The kinetics were followed through to approximately 75% of the decomposition, after which scattering of the points used to obtain the rate data occurred. The activation parameters were derived from the Eyring equation for unimolecular reactions, a value of unity being assumed for the transmission coefficient, where k is the rate constant, K = Boltzmann's

constant, T = absolute temperature, h = Plancks constant, $\Delta S^{\ddagger}$ = entropy of activation, R = gas constant, $\Delta H^{\ddagger}$ = heat of activation (or enthalpy).

$$k = \frac{KT}{h} \cdot e^{\frac{\Delta S^{\ddagger}}{R}} \cdot e^{\frac{-\Delta H^{\ddagger}}{RT}}$$

The kinetic plots were subjected to a standard deviation analysis (S.D.); from such an analysis the standard estimate of error[116] can be obtained. If a 95% confidence limit is set, the fractional errors in the rate constants can be obtained from this estimate of error. By using the methods outlined by Wiberg,[117] which utilises the maximum error in rate constants and then evaluates the errors in enthalpy of activation and entropy of activation, assessment of the relevance of the figures obtained can then be made objectively. The fractional error in the rate constant never exceeded 0.2; which is a high upper limit. Reduction of this error bias was attempted by taking the widest possible temperature range, usually 40°C. The analysis based on these figures indicated that the error in enthalpy of activation would be in the region of 5 k.cal.mole.$^{-1}$, while the entropy of activation error would be 6 e.u. The figures quoted in the following chapter are not given to the first decimal place as a result of this analysis.

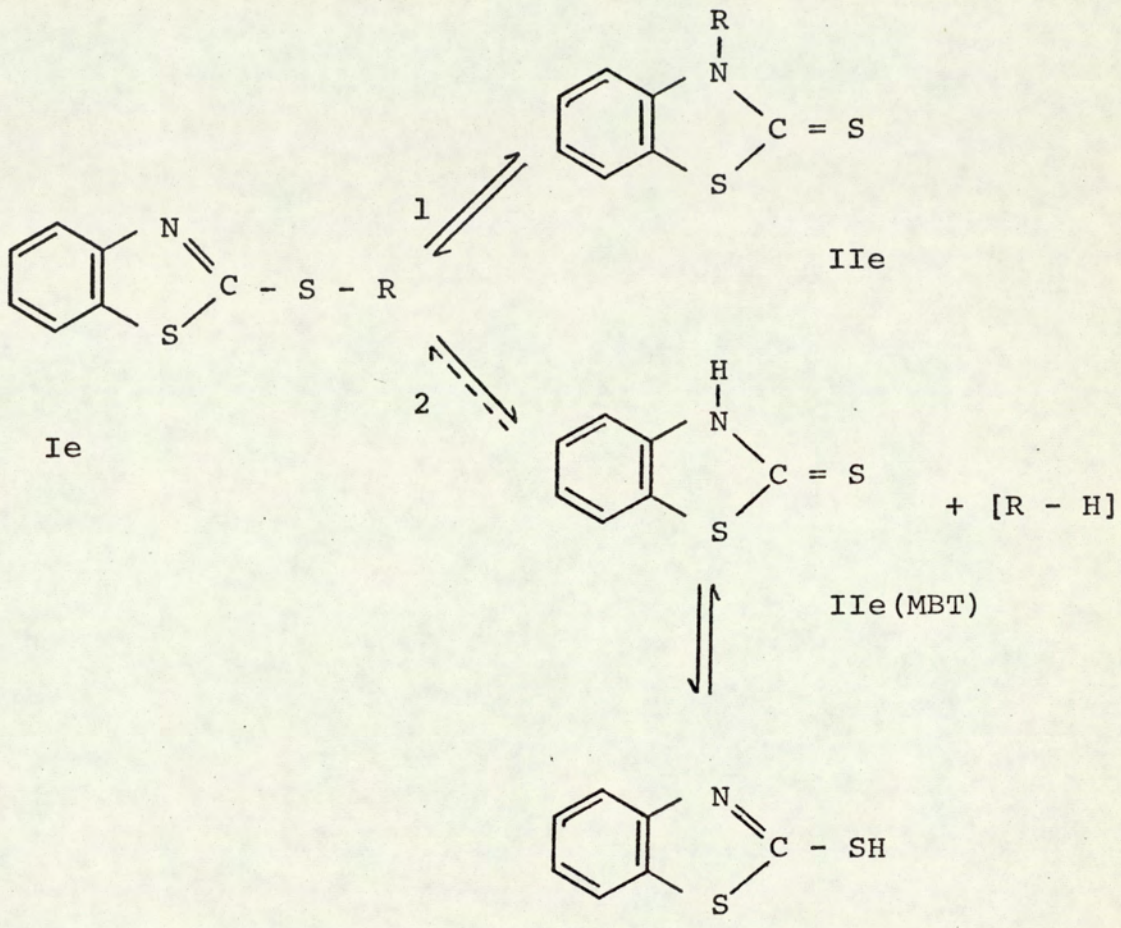
Factors influencing the isomerisation and decomposition reactions

When 2-substituted thiobenzothiazoles are heated two reactions are operative:

1. The reversible isomerisation of the 2-thiobenzothiazole to yield the corresponding 3-benzothiazoline-2-thione.
2. Thermal decomposition to give 2-mercaptobenzothiazole and the hydrocarbon derived from the substituent R by the loss of hydrogen. The latter may subsequently degrade or polymerise.

These reactions are competitive and this study was carried out in order to determine the factors which would facilitate the thermal decomposition (reaction 2) at the expense of reaction 1. A typical example of this two way process is provided by the isomerisation and decomposition of 2-(cyclohex-2'-enyl)thiobenzothiazole at 200°C., (see Table 14). The decomposition reaction is accompanied by a significant contribution from the isomerisation reaction.

A preliminary study of the factors influencing the isomerisation was attempted, in the hope that the structural features which favoured isomerisation could be detected, and then by eliminating these from the compounds the isomerisation process could be suppressed.



Where: Ie = mole % of 2-thiobenzothiazole at equilibrium

IIe = mole % of benzothiazoline-2-thione at equilibrium

IIe(MBT) = mole % of 2-mercaptobenzothiazole at equilibrium

TABLE 14

ISOMERISATION AND DECOMPOSITION OF 2-(CYCLOHEX-2'-ENYL)THIOBENZOTHIAZOLE AT 200° C.

Time (hours)	0.5	1.0	3.0	6.0	12.0	24.0	48.0	96.0
$E^{1\%}_{281}$	210.1	209.8	204.1	198.2	201.2	193.0	190.1	192.4
$E^{1\%}_{326}$	708.1	672.2	608.2	528.1	494.5	444.6	431.0	432.6
Mole % MBT*	4.2	6.7	17.4	25.2	28.3	37.4	36.5	35.8
Mole %N-isomer	68.3	65.5	58.0	51.0	47.2	42.3	41.1	41.3
Mole %S-isomer	26.5	25.8	24.0	23.0	23.4	21.4	20.8	21.2
	99.0	98.0	99.4	99.2	98.9	101.1	98.4	98.3

*MBT = 2-mercaptobenzothiazole
N-isomer = 3-(cyclohex-2'-enyl)benzothiazoline-2-thione
S-isomer = 2-(cyclohex-2'-enyl)thiobenzothiazole

The isomerisation rates of 2-(cyclohex-2'-enyl) thiobenzothiazole, and 2-(hexa-2',5'-dienyl-1'-yl)thiobenzothiazole were measured at 140°C. and 160°C. During each kinetic run aliquots of the ethanol solution were titrated with sodium hydroxide to ensure that the decomposition reaction was not taking place; no 2-mercaptobenzothiazole could be detected. The results of the kinetic runs are summarised in Tables 15 and 16; while the activation parameters are summarised in Table 17.

TABLE 15

RATE DATA FOR THE THERMAL ISOMERISATION OF 2-(CYCLOHEX-2'-ENYL)THIOBENZOTHIAZOLE - U.V. ESTIMATION

140°C.

$(k_1+k_2)x10^{-4}sec.^{-1}$	Mole %*		k_1/k_2	$10^4k_1sec.^{-1}$	$10^4k_2sec.^{-1}$
	Ie	IIe			
1.39 (S.D. = 0.02)	35	65	1.855	0.922	0.468

160°C.

$(k_1+k_2)x10^{-3}sec.^{-1}$	Mole %*		k_1/k_2	$10\ k_1sec.^{-1}$	$10^3k_2sec.^{-1}$
	Ie	IIe			
1.22 (S.D. = 0.02)	43	57	1.325	0.695	0.525

*Ie = 100- IIe on the basis of the benzothiazoline-2-thione absorption at 327 mμ.

Both compounds possess an allylic side chain adjacent to the sulphur atom and such reactions are analogous to the Claisen rearrangement of alkenyl aryl ethers. Two unimolecular mechanisms need to be considered for the isomerisation in the present discussion, (a) an intramolecular rearrangement involving a cyclic transition state, in which both bond making and breaking occur synchronously, and (b) an ionic process in which the mesomeric 2-thiobenzothiazoyl anion and alkenyl cation are

formed.

TABLE 16

RATE DATA FOR THE THERMAL ISOMERISATION OF 2-(HEXA-2',5'-DIEN-1'-YL)THIOBENZOTHIAZOLE - U.V. ESTIMATION

140°C.

$(k_1+k_2)x10^{-8}sec.^{-1}$	Mole %*		K_1/k_2	$10^8k_1sec.^{-1}$	$10^8k_2sec.^{-1}$
	Ie	IIe			
4.43 (S.D. = 0.08)	34	66	1.94	2.92	1.51

160°C.

$(k_1+k_2)x10^{-7}sec.^{-1}$	Mole %*		K_1/k_2	$10^7k_1sec.^{-1}$	$10^7k_2sec.^{-1}$
	Ie	IIe			
3.40 (S.D. = 0.06)	36	64	1.78	2.18	1.22

*Ie = 100-IIe on the basis of the benzothiazoline-2-thione absorption.

In order to determine which mechanism was operative the activation parameters were calculated from the rates at 140°C. and 160°C. (see Table 17).

In both cases the entropies of activation would indicate a cyclic transition state. The activation enthalpies are similar suggesting that the same type of charge dispersal occurs in the transition state. When

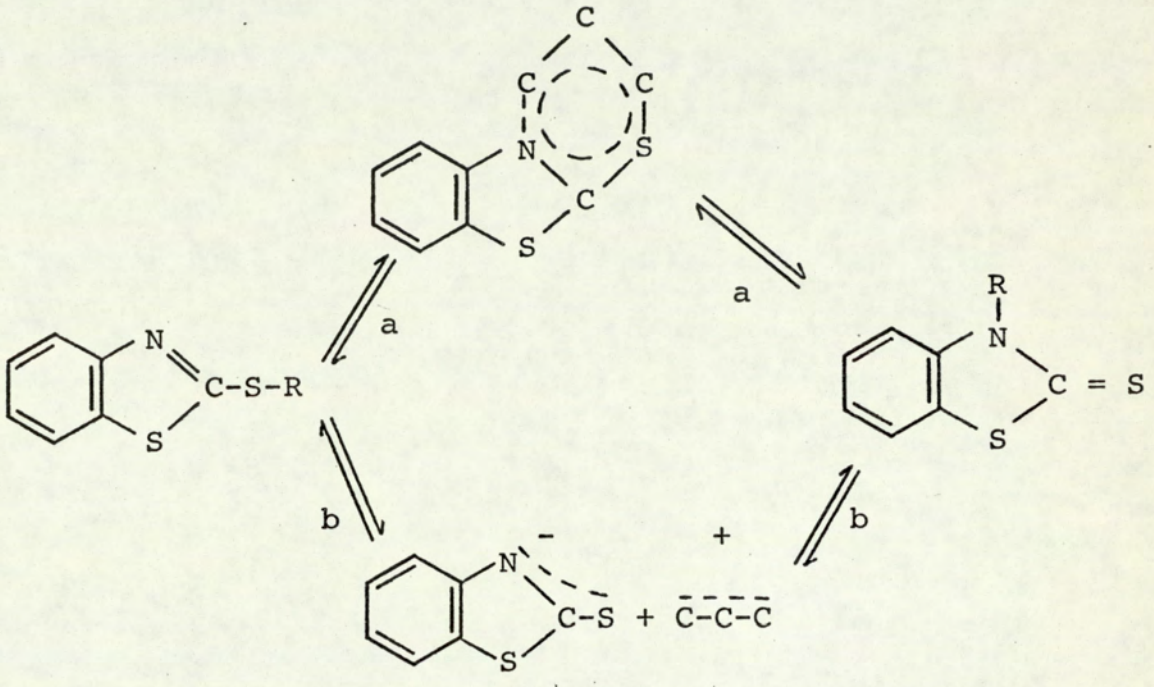


TABLE 17

ACTIVATION PARAMETERS FOR THE THERMAL ISOMERISATION OF 2-SUBSTITUTED THIOBENZOTHIAZOLES

Compound	$\Delta H^{\ddagger}$ (K.cal.mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\log_{10} A$
2-(cyclohex-2'-enyl) thiobenzothiazole	28	-29	11.87
2-(hexa-2':5'-diene-1'-yl)thiobenzothiazole	30	-13	9.70

2-(cyclohex-2'-enyl)thiobenzothiazole rearranges, the allylic substituent can orientate above the planar heterocyclic ring, this would involve considerable strain in the transition state compared to the starting configuration.

As 2-(cyclohex-2'-enyl)thiobenzothiazole has adjacent $-CH_2-$ groups pinned back, steric interactions with the heterocyclic benzene ring should be minimised, thereby favouring a more concerted transition state. Bateman and co-workers[112] have indicated that the α-allylic group of 1-bromohexa-2:5-diene is mainly the trans isomer. When 2-(hexa-2':5'-dien-1'-yl)thiobenzothiazole rearranges the trans configuration will help to keep the other allylic group of the alkenyl side chain pushed away from the ring, but on forming the cyclic transition state, carbon 4 being sp^3 hybridised can rotate freely, bringing into steric interaction the other allylic group of the substituent with the heterocyclic aromatic system, and as a result of this the transition state will be destabilised. If in this system more electron charge is centred on the thiobenzothiazoyl nucleus, particularly at the $-\overset{|}{\underset{|}{C}}-S-$ bond, i.e., the forming $>C=S$ function; any effect which could reduce or inhibit $>C=S$ bond formation would also effect the transition state in a similar manner. Such an effect may play a part in the rearrangement of 2-(hexa-2':5'-dien-1'-yl)thiobenzothiazole, the two double bonds

are not conjugated, and when heated the bonds could attempt to conjugate. This competing electron reorganisation would then oppose the forces of rearrangement again destabilising the transition state. When comparing the rearrangement of 2-(hexa-2':5'-dien-1'-yl)thiobenzothiazole with that of 2-(cyclohex-2'-enyl)thiobenzothiazole, it can be seen that influences such as steric interactions and the opposing forces of conjugation would destabilise the transition state of the non-cyclic substitutent, giving a less ordered transition state, as observed in Table 17.

The thermal behaviour of typical allylic derivatives are listed in Table 18, the benzyl derivative was included for comparison. It can be seen that allylic groups in the substituent portion of the molecule enhance the decomposition but unfortunately they also facilitate the competitive isomerisation. The benzyl derivative reduced the isomerisation considerably. A pattern emerges from the experimental results; allylic groups facilitate decomposition and isomerisation, and a way to control the isomerication was needed. The isomerisation could be controlled in the following manner:

1. make the transition state sterically hindered
2. position the double bond in a molecular structure where freedom of movement or conjugation is limited.

TABLE 18

THERMAL DECOMPOSITION AND ISOMERISATION OF 2-SUBSTITUTED THIOBENZOTHIAZOLES AT 200°C. FOR 48 HOURS

Substituent	Mole % 2-Thiobenzothiazole	Mole % 3-Benzothiazoline-2-thione	Mole % 2-Mercaptobenzothiazole
Cyclohex-2'-enyl	20.8	41.1	36.5
Hexa-2':5'-dien-1'-yl	24.4	37.8	34.2
Benzyl[29]	76.0	3.5	20.1
Cyclohex-2'-enyl, 3':6' di	18.3	49.6	31.5*

*This figure is divided by 2 as 200 mole % is liberated from the disubstituted molecule.

It was hoped that by using these methods, it would be possible to increase decomposition relative to isomerisation.

The rates of decomposition were obtained from the equilibrium data and the methods used are those indicated in the introduction; only the rate of decomposition was determined even though isomerisation did occur at the same time. The concurrent isomerisations were not studied as the aim of this research was to study the effects of

various substituent on the rate of decomposition. The first compounds studied were the isomeric forms, 2-(cyclohex-2'-enyl)thiobenzothiazole and 3-(cyclohex-2'-enyl)benzothiazoline-2-thione and the results are summarised in Tables 19 and 20. The rates of decomposition are similar but the magnitude of k_2 is appreciable. A feature of this decomposition reaction was the equilibrium, which might be explained by assuming that the axial or equatorial β-hydrogens are fixed in the transition state relative to the ring nitrogen; once such a conformational proportion has been utilised the equilibrium was established. To test this postulate, a portion of the isomers which had been previously heated, and from which the 2-mercaptobenzothiazole had been removed, were re-heated and equilibrium was again re-established. The above result agrees with the findings of DePuy and King,[118] who observed that elimination utilizing an axial or equatorial position is not appreciably different in product or rate. The hydrocarbon products obtained from the decomposition were unusual, being benzene (59%), cyclohexene (36%), and cyclohexa-1:3-diene (5%), the expected product cyclohexa-1:3-diene was a minor product. A mechanistic scheme[29] has been proposed for the formation of the products. However, Erofee[119] observed that cyclohexa-1:3-diene disproportionates to yield benzene and cyclohexene

on heating. This may indicate that in the decomposition reactions studied, cyclohexa-1:3-diene was initially formed and equilibrium being established by 2-mercapto-benzothiazole back-addition to the olefin, i.e., k_2, the remainder of the diene disproportionating to the products indicated. To examine and verify that the back-addition was facile, cyclohexa-1:3-diene was heated with 2-mercapto-benzothiazole; and 2-(cyclohex-2'-enyl)thiobenzothiazole and 3-(cyclohex-2'-enyl)benzothiazoline-2-thione were obtained in good yield (64%). The detailed balance of the reaction was not investigated any further. When 2-(hexa-2':5'-dien-1'-yl)thiobenzothiazole was examined the rate of decomposition was slower than the previous compounds studied (see Table 21). This compound was synthesised since it would yield on decomposition the conjugated triene. According to DePuy and King,[93] the strength of

TABLE 19

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(CYCLOHEX-2'-ENYL)THIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)\times10^{-5}$ sec.$^{-1}$	Mole %*		k_1/k_2	10^5k_1 sec.$^{-1}$	10^5k_2 sec.$^{-1}$
	Ie	IIe(MBT)			
4.30 (S.D. = 0.07)	66	34	0.515	1.46	2.84

*MBT = 2-mercaptobenzothiazole
Ie = Initial sulphide and is estimated by Ie = 100 - IIe.

TABLE 20

RATE DATA FOR THE THERMAL DECOMPOSITION OF 3-(CYCLOHEX-2'-ENYL)BENZOTHIAZOLINE-2-THIONE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)x10^{-5}sec.^{-1}$	Mole %		k_1/k_2	$10^5k_1sec.^{-1}$	$10^5k_2sec.^{-1}$
	Ie	IIe(MBT)*			
4.90 (S.D.=0.12)	63	37	0.586	1.82	3.08

*MBT = 2-mercaptobenzothiazole
Ie = Initial sulphide and is estimated by Ie = 100-IIe.

TABLE 21

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(HEXA-2':5'-DIEN-1'-YL)THIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)x10^{-5}sec.^{-1}$	Mole %		k_1/k_2	$10^5k_1sec.^{-1}$	$10^5k_2sec.^{-1}$
	Ie	IIe(MBT)*			
1.10 (S.D.=0.07)	62.4	37.6	0.603	0.41	0.69

the forming double bond strongly influences the rate of decomposition, so that a product with greater resonance stabilisation should decompose more rapidly than a similar product with a lower degree of stabilisation. Gas phase chromatography indicated that hexatriene was the olefin product, but this was accompanied by polymerisation and

degradation products. The idea that stabilisation during double bond formation strongly influenced the rate was the main reason for the investigation of 2-(cyclohex-2'-enyl, 3':6')dithiobenzothiazole. The decomposition would be expected to produce benzene, which having considerably greater resonance stabilisation than the previous products, i.e., cyclohexa-1:3-diene, hexatriene and should therefore decompose at a greater rate. The kinetic data indicated a rate of decomposition similar to 2-(cyclohex-2'-enyl)thiobenzothiazole (see Table 22).

TABLE 22

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(CYCLOHEX-2'-ENYL, 3':6')DITHIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)x10^{-5}sec.^{-1}$	Mole %		k_1/k_2	$10^5k_1sec.^{-1}$	$10^5k_2sec.^{-1}$
	Ie	IIe(MBT)			
4.60 (S.D.=0.12)	68	32*	0.470	1.50	3.10

*Based on 100 mole %.

Gas phase chromatography indicated that the olefin product was benzene and the U.V. absorption spectra confirmed these findings. It was apparent that the hypothesis which had been used so far, i.e., that the

resonance stabilisation of the forming double bond strongly influenced the rate of decomposition, could not be used in a predictive manner for these systems and this disagreed with the general findings of DePuy and King.[93]

A new approach was investigated, namely to examine the effect of substituent groups at the seat of elimination. Accordingly, 2-(β-phenylethyl)thiobenzothiazole was synthesised and the rate of decomposition determined (see Table 23). The rate of decomposition was faster than expected; being approximately one-tenth of the activated allylic compounds. Product analysis using gas phase chromatography indicated the product to be styrene but this was accompanied by polymeric species. Mayo[120] noted that when styrene was heated, a complex mixture of products was obtained.

TABLE 23

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(β-PHENYLETHYL)THIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)\times10^{-6}sec.^{-1}$	Mole %		k_1/k_2	$10^6k_1sec.^{-1}$	$10^6k_2sec.^{-1}$
	Ie	IIe(MBT)			
4.68 (S.D.=0.11)	74.9	25.1	0.335	1.17	3.50

The rate data for the decomposition of 3-(β-cyano-

ethyl)benzothiazoline-2-thione and 2-(β-methoxycarbonyl-ethyl)thiobenzothiazole are summarised in Tables 24 and 25.

TABLE 24

RATE DATA FOR THE THERMAL DECOMPOSITION OF 3-(β-CYANOETHYL)BENZOTHIAZOLINE-2-THIONE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)x10^{-7}sec.^{-1}$	Mole %		k_1/k_2	$10^7k_1sec.^{-1}$	$10^7k_2sec.^{-1}$
	Ie	IIe(MBT)			
2.3 (S.D.=0.05)	87	13	0.148	0.30	2.00

Product analysis of the residues from the thermal decomposition of 3-(β-cyanoethyl)benzothiazoline-2-thione revealed that acrylonitrile was formed but thermal degradation and polymerisation reactions contaminated the products considerably. The rate of decomposition was slower than that of β-substituted derivatives examined previously and the yield of free 2-mercaptobenzothiazole was correspondingly lower. Similar results were obtained when 2-(β-methoxycarbonylethyl)thiobenzothiazole was examined at 200°C.

Product analysis indicated that methyl acrylate was formed but soon degraded or polymerised. The β-

TABLE 25

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(β-METHOXYCARBONYLETHYL)THIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ESTIMATION

$(k_1+k_2)x10^{-7}sec.^{-1}$	Mole %		k_1/k_2	$10^7k_1sec.^{-1}$	$10^7k_2sec.^{-1}$
	Ie	IIe(MBT)			
5.60 (S.D.=0.11)	84	16	0.19	0.90	4.70

substituent effects observed, although small, were surprising when compared to compounds such as 2-N-octyl thiobenzothiazole[29] which hardly decomposes on heating. When this compound was heated at 200°C. for forty-eight hours only 1% of 2-mercaptobenzothiazole could be detected.

The increase in rate caused by β phenyl substitution was encouraging and so the substituent study was extended to include α phenyl substituents. 2-(α-phenylethyl)thiobenzothiazole was synthesised and the decomposition reaction studied; the results being summarised in Table 26. The results indicated that α phenyl substitution increased the rate of decomposition appreciably, while product analysis indicated that the products obtained were very similar to those obtained when 2-(β-phenylethyl) thiobenzothiazole decomposed. The experimental observations showed that α phenyl substitution increased the rate

of decomposition substantially when compared to the effect of β phenyl substitution. A substituent group (i.e., the group from which elimination takes place and not the 2-mercaptobenzothiazole nucleus), which would combine both α and β phenyl substituent effects was chosen, namely 1,2 diphenylethane and then the corresponding 2-thiobenzothiazole derivative was prepared. The decomposition of 2-(1',2' diphenylethyl)thiobenzothiazole gave good first order kinetic plots and the rate was appreciably greater than any of the other derivatives studied (see Table 27).

TABLE 26

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(α-PHENYLETHYL)THIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ANALYSIS

$(k_1+k_2)x10^{-5}sec.^{-1}$	Mole %		k_1/k_2	$10^5 k_1 sec.^{-1}$	$10^5 k_2 sec.^{-1}$
	Ie	IIe(MBT)			
8.47 (S.D.=0.32)	70	30	0.429	2.52	5.95

The competitive isomerisation reaction was suppressed and product analysis indicated that trans-stilbene was the olefin produced from the decomposition reaction. The decomposition products were almost free of degradation and polymeric residues and olefin analysis for both cis- and trans-stilbene was carried out using the absorbance

ratio method.[121,122]

The success obtained using substituents, especially phenyl groups prompted a re-examination of the allylic derivatives. The problem was to preserve the enhancement

TABLE 27

FIRST ORDER RATE CONSTANT FOR THE THERMAL DECOMPOSITION OF 2-(1',2'-DIPHENYL-ETHYL)THIOBENZOTHIAZOLE AT 200°C.- TITRIMETRIC ESTIMATION

$k = 7.60 \times 10^{-5}$ $sec.^{-1}$ (S.D. = 0.12)

of the thermal decomposition reaction, but at the same time suppress any possible isomerisations which might occur. The candidate, i.e., 1,4 bis-(2'-benzothiazoylthio) tetralin was then synthesised and the decomposition was studied at 200°C., (see Table 28). The rate of decomposition was greater than the corresponding 2-(1',2' diphenyl-ethyl)thiobenzothiazole and good first-order kinetic plots were obtained. Product analysis indicated that the olefin product obtained from the decomposition was napthalene and the decomposition was almost free of degradation and polymeric residues.

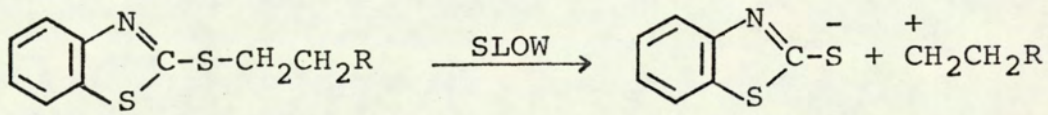
The accumulated evidence obtained so far would suggest that the decomposition reaction is ionic in

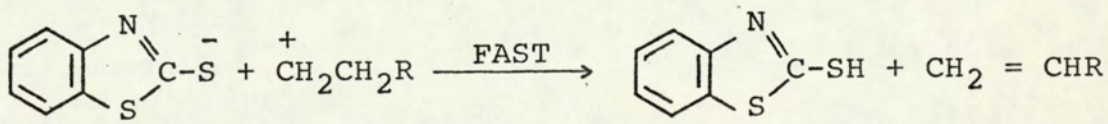
TABLE 28

FIRST ORDER RATE CONSTANT FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(2'-BENZO-THIAZOYLTHIO)TETRALIN AT 200°C. - TITRIMETRIC ESTIMATION

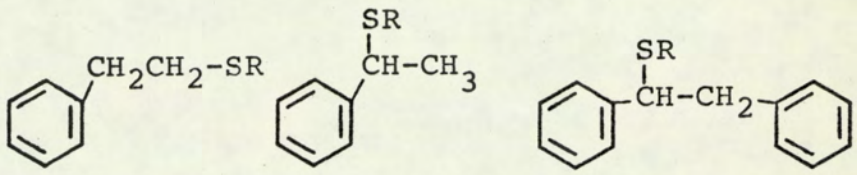
$k = 6.13 \times 10^{-4}$ sec.$^{-1}$ (S.D. = 0.06)

nature, the rate determining step being heterocyclic fission of the $\geq$C-S- bond to yield the thiobenzothiazoyl anion and carbonium ion. The heterocyclic fission is then followed by rapid proton abstraction to give the olefin and 2-mercaptobenzothiazole the effect of α phenyl



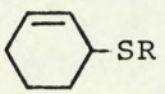
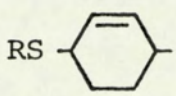
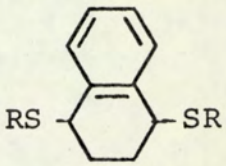


substitution could be explained in terms of resonance stabilisation of the carbonium ion, for example consider the following series, where -SR is the 2-thiobenzothiazole group. Substitution at the β position of the ethyl group



k_{200} sec.$^{-1}$	1.17×10^{-6}	2.52×10^{-5}	7.60×10^{-5}
$k_{rel.}$	1.00	21.6	65.0
R.E.[123] product (k.cal.mole^{-1})	38	38	77

provides an intervening methylene group which probably prevents resonance stabilisation with the aromatic phenyl ring; however, when substitution is in the α position conjugation can take place effectively. The small supplementary effect of β phenyl substitution can be seen when the relative rates are compared, whereas α phenyl substitution increases the rate twenty fold, additional β substitution only doubles the relative rate. A similar situation is found with the allylic derivatives, again α. phenyl substitution leads to a forty-fold increase in rate and also appears to suppress the isomerisation reaction completely. The resonance energies of the products are included to test the postulations of DePuy and King;[93] that the rate of decomposition is strongly influenced by

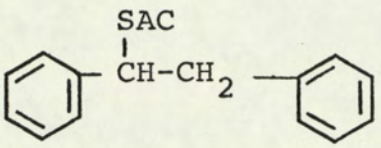
			
k_{200} sec.$^{-1}$	1.46×10^{-5}	1.50×10^{-5}	6.13×10^{-4}
$k_{rel.}$	1.00	1.03	42.0
R.E.[123] product (K.cal. mole^{-1})	1	39	75.0

the stabilisation gained from the forming double bond which is in turn related to the resonance energy of the product. It is evident that no correlation exists between the relative rates and the resonance energy of the conjugated product. The occurrence of degradation and polymeric residues indicated that a radical process might be occurring but it was not possible to measure any induction period prior to decomposition. In a study[124] of the reaction of dibenzothiazoyldisulphide with cyclohexene a radical chain mechanism was proposed, the products of such a reaction being 2-(cyclohex-2'-enyl) thiobenzothiazole and 3-(cyclohex-2'-enyl)benzothiazoline-2-thione. The decomposition of 2-(1',2' diphenylethyl) thiobenzothiazole and 1,4 bis-(2'-benzothiazoylthio) tetralin were performed in cyclohexene and no products

could be isolated which would have indicated the formation of the 2-thiobenzothiazoyl radical. The experimental evidence would suggest that the thermal decomposition reactions are best accommodated by an E1 type reaction mechanism, thereby explaining the pronounced effect of substituent groups in terms of the resonance stabilisation of the incipient carbonium ion. The finding of hydrocarbon groups which would lead to decomposition as opposed to isomerisation had been accomplished. To accommodate the technological aims of the study, variations in the accelerating species were now considered, e.g., dimethyldithiocarbamate, xanthates and phosphorodithioates. The principle which had governed the work, i.e., eliminate the accelerator, can now be extended to other accelerating species. To accomplish this aim, the most successful hydrocarbon groups were chosen for further study, e.g., mono-substituted 1,2 diphenylethanes and 1,4 bis-substituted tetralins.

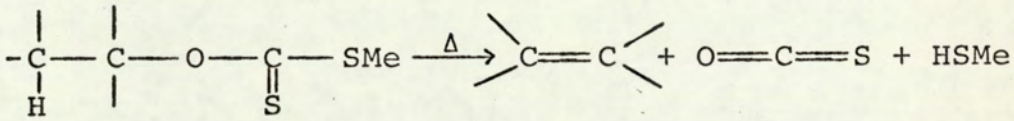
Mono-substituted 1,2 diphenylethanes

The accelerator species which replaced the 2-thiobenzothiazole nucleus in 2-(1',2'diphenylethyl)thiobenzothiazole were dimethyldithiocarbamate, methylxanthate and 0,0 dimethylphosphorodithioate, e.g.,



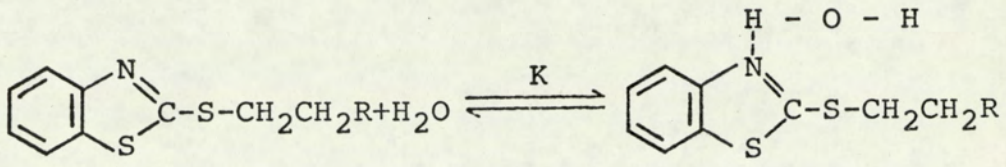
Where Ac = $(CH_3)_2$-N-C(=S)-, CH_3O-C(=S)-, $(CH_3O)_2$-P(=S)-.

The choice of methyl and methoxy groups was dictated by the possibility of a Chugaev elimination taking place with the xanthate derivative and competing with the desired elimination pathway, e.g.,



When 2-mercaptobenzothiazole derivatives decomposed, the concentration of the free thiol, which was stable, could be estimated by titrimetric methods; however, when the above accelerating species were studied, these species gave free acids which were unstable and not amenable to rapid estimation. In order to overcome this difficulty the following method was used, impurities which might interfere with olefin estimation were separated using column chromatography and then the concentration of the olefin, i.e., stilbene, was determined by ultraviolet

spectroscopy. Using the decomposition reaction of 2-(1',2' diphenylethyl)thiobenzothiazole as a standard, a comparison of the titration method and column procedure was performed, giving the following results: titrimetric analysis $k_{200} = 7.60 \times 10^{-5}$ sec.$^{-1}$; column procedure $k_{200} = 7.79 \times 10^{-5}$ sec.$^{-1}$. The results indicated that both procedures gave similar results, and so the column procedure was used for the following studies. The results obtained for the decomposition of 2-(1',2' diphenylethyl) thiobenzothiazole are summarised in Table 29. The solvent studies were undertaken to illustrate that an E1 reaction was operative, and it would be anticipated that a large change in rate would result from increasing the solvent polarity. When the solvent was changed from dioxan to dioxan/water (70:30) the rate decreased slightly, an effect that would not be expected from an ionic process. A possible explanation offers itself; during a cyclic elimination process, the ring nitrogen could act as a basic centre, now if the water hydrogen bonds to the ring nitrogen a competitive process with β-hydrogen abstraction ensues, and depending on the magnitude of K, kobs will be affected proportionately.



$$k_{obs} = K \times k_{actual}$$

The small reduction in rate observed is very suggestive that this type of process may be very small in magnitude.

TABLE 29

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF 2-(1',2' DIPHENYLETHYL) THIOBENZOTHIAZOLE

Temp. °C.	k sec^{-1}	S.D.	k sec^{-1} (in dioxan)	S.D.	k sec^{-1} (in dioxan 70, water 30)	S.D.
200	7.79×10^{-5}	0.30	-	-	-	-
180	1.40×10^{-5}	0.08	6.63×10^{-6}	0.56	3.4×10^{-6}	0.12
160	3.31×10^{-6}	0.09	-	-	-	-

$\Delta H^{\ddagger}$ (K.cal.$mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)	$\log_{10} A$
31	-19	10.8

The activation parameters obtained from the decomposition in the melted form indicate that a cyclic process is feasible and the absorbance ratio indicated that the olefin product was predominantly trans-stilbene.

When S-(1,2 diphenylethyl)dimethyldithiocarbamate was examined a similar pattern emerged as in the previous study. The kinetic data is summarised in Table 30.

TABLE 30

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL)DI-METHYLDITHIOCARBAMATE

Temp. °C.	k $sec.^{-1}$	S.D.	k $sec.^{-1}$ (in dioxan)	S.D.	k $sec.^{-1}$ (in dioxan 70, water 30)	S.D.
200	7.58×10^{-5}	0.35	-	-	-	-
180	2.24×10^{-5}	0.06	1.21×10^{-5}	0.08	4.31×10^{-5}	0.10
160	3.63×10^{-5}	0.06	-	-	-	-
	$\frac{\Delta H^{+} (K.cal.mole^{-1})}{30}$		$\frac{\Delta S^{+} (e.u.)}{-19}$		$\frac{\log_{10} A}{10.15}$	

Product analysis indicated that the olefin product was predominantly trans-stilbene and the volatile acid fraction was analysed by gas phase chromatography

techniques. The results indicated that a mixture of dimethylamine and carbon disulphide had been formed. Studies[125] on free dimethyldithiocarbamic acid indicated that the products of decomposition were mainly the free amine and carbon disulphide.

When S-(1,2 diphenylethyl)methylxanthate was examined, no solvent work was undertaken. Since a technological evaluation had indicated that the 2-thiobenzothiazoles and S-substituted dimethyldithiocarbamate derivatives showed the greatest promise as delayed action accelerators more attention was focused on these derivatives at the expense of the methylxanthate and 0,0 dimethyl phosphorodithioate derivatives. The kinetic data obtained for the decomposition reaction of S-(1,2 diphenylethyl) methylxanthate is summarised in Table 31.

TABLE 31

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL)METHYLXANTHATE

Temp. °C.	k sec.$^{-1}$	S.D.
200	1.51×10^{-4}	0.07
180	3.21×10^{-5}	0.11
160	6.91×10^{-6}	0.06
$\frac{\Delta H^{\ddagger}(k.cal.mole^{-1})}{30}$	$\frac{\Delta S^{\ddagger}(e.u.)}{-21}$	$\frac{\log_{10} A}{10.50}$

Product analysis revealed that the olefin product was mainly trans-stilbene, while gas phase chromatographic analysis of the volatile products indicated two major components. These components were identified as methanol and carbon disulphide, another possible product carbon oxysulphide could not be detected.

The entropy of activation which was observed in the thermal decomposition reaction of S-(1,2 diphenylethyl) 0,0 dimethylphosphorodithioate was slightly larger than those of the previous compounds studied. The kinetic data and the derived parameters are summarised in Table 32. Product analysis indicated that the olefin was trans-stilbene, while evaporative distillation of the decomposition products yielded a small amount of free acid which was contaminated with a higher molecular weight material. Product analysis of the residue revealed substantial amounts of a white polymeric material, which was not identified. Similar types of degradation products have been noted in studies on the thermal decomposition of metal salts of phosphorodithioates.[126]

TABLE 32

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL) 0,0 DIMETHYL PHOSPHORODITHIOATE

Temp. °C.	k $sec.^{-1}$	S.D.
200	1.35×10^{-3}	0.05
140	1.29×10^{-5}	0.10

$\Delta H^{\ddagger}$ (k.cal.$mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)	$\log_{10} A$
29	-25	11.05

1,4 Bis-substituted tetralins

The study of the 1,4 bis-substituted tetralins was analogous to the previous study of the mono-substituted 1,2 diphenylethane derivatives in kinetic procedure and product analysis.

When 1,4 bis-(2'-benzothiazoylthio)tetralin was studied the activation parameters obtained from the kinetic data were greater than the corresponding 1',2' diphenylethyl derivative. The kinetic data and activation parameters are summarised in Table 33. A small reduction in rate was observed when the solvent polarity was increased by the addition of water. The products of decomposition were 2-mercaptobenzothiazole and naphthalene,

these were separated using sodium hydroxide and then instrumental techniques were used to identify each component.

The kinetic data obtained from the thermal decomposition of 1,4 bis-(S-dimethyldithiocarbamate)tetralin revealed that this derivative was similar to the previous derivatives; however, the kinetic data yielded activation parameters which were slightly greater in magnitude than any which had been obtained previously. The kinetic data is summarised in Table 34.

TABLE 33

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(2'-BENZOTHIAZOYLTHIO)TETRALIN

Temp. °C.	k $sec.^{-1}$	S.D.	k $sec.^{-1}$ (in dioxan)	S.D.	k $sec.^{-1}$ (dioxan 70, water 30)	S.D.
200	6.03×10^{-4}	0.12	-	-	-	-
180	8.83×10^{-5}	0.04	3.28×10^{-5}	0.11	1.90×10^{-5}	0.07
160	1.03×10^{-5}	0.09	-	-	-	-
140	1.51×10^{-6}	0.04	-	-	-	-

$\Delta H^{\ddagger}$ (K.cal.$mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)	$\log_{10} A$
37	-25	12.10

TABLE 34

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(S-DIMETHYLDITHIOCARBAMATE) TETRALIN

Temp. °C.	k $sec.^{-1}$	S.D.	k $sec.^{-1}$ (in dioxan)	S.D.	k $sec.^{-1}$ (dioxan 70, water 30)	S.D.
200	3.63×10^{-4}	0.18	-	-	-	-
180	4.40×10^{-5}	0.14	2.85×10^{-5}	0.19	6.90×10^{-5}	0.48
160	6.91×10^{-5}	0.05	-	-	-	-
140	6.76×10^{-7}	0.36	-	-	-	-

$\Delta H^{\ddagger}$ (K.cal.$mole^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)	$\log_{10} A$
37	-24	11.90

Product analysis indicated that naphthalene was the olefin that resulted from thermal decomposition. Analysis of the volatile component using gas phase chromatography showed that the volatile material was a mixture of dimethylamine and carbon disulphide. The decomposition reaction was remarkably free of degradation products.

1,4 bis-(S-methylxanthate)tetralin was unusual in that the entropy of activation was the largest observed in the kinetic studies. The kinetic data is summarised in Table 35. Product analysis showed that naphthalene,

methyl alcohol and carbon disulphide were the major products obtained from the thermal decomposition.

TABLE 35

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(S-METHYLXANTHATE)TETRALIN

Temp. °C.	k. $sec.^{-1}$	S.D.
180	2.87×10^{-4}	0.02
160	7.84×10^{-4}	0.03
140	1.35×10^{-5}	0.06
$\frac{\Delta H^{+}(k.cal.mole^{-1})}{30}$	$\frac{\Delta S^{+}(e.u.)}{-35}$	$\frac{\log_{10} A}{10.98}$

The activation parameters obtained from the kinetic study of 1,4 bis-(S-0,0 dimethylphosphorodithioate) tetralin were surprising; the activation enthalpy being the lowest of the series. The main product was a white polymeric material, but a small amount of the free acid was obtained, together with naphthalene. The kinetic data is summarised in Table 36.

The molecules which have been examined in this work were intended to function as delayed action accelerators in the sulphur vulcanization of rubber. Therefore, some

TABLE 36

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(S-O, O DIMETHYLPHOSPHORODITHIOATE)TETRALIN

Temperature °C.	k. $sec.^{-1}$	S.D.
180	2.29×10^{-3}	0.07
160	6.46×10^{-4}	0.12
140	2.02×10^{-4}	0.08

$\Delta H\ddagger$ (K.cal.$mole^{-1}$)	$\Delta S+$ (e.u.)	$\log_{10} A$
22	-28	8.6

of the thermal decomposition reactions were studied in the presence of zinc oxide and stearic acid to ascertain the effects of such materials, i.e., complex formation. The rates of decomposition did not change appreciably when zinc oxide and stearic acid were present. The results of these experiments are listed in Table 37.

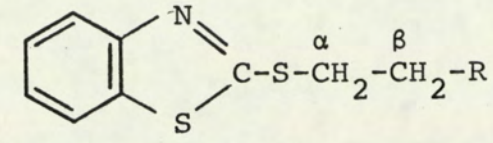
TABLE 37

RATE CONSTANTS FOR THE THERMAL DECOMPOSITION OF 2-(1',2' DIPHENYLETHYL)THIOBENZOTHIAZOLE AND 1,4 BIS-(2'-BENZOTHIAZOYLTHIO)TETRALIN IN THE PRESENCE OF ZINC OXIDE AND STEARIC ACID AT 180°C.

	k. $sec.^{-1}$	S.D.
2-(1',2' diphenylethyl)thio-benzothiazole	7.73×10^{-5}	0.03
1,4 bis-(2'-benzothiazoylthio) tetralin	2.90×10^{-5}	0.09

Discussion

The initial study of 2-mercaptobenzothiazole derivatives indicated that the rate of decomposition was influenced by substituent groups, particularly α phenyl groups which increased the rate considerably compared to an unsubstituted compound. When phenyl groups were used as β-substituents a much smaller increase in the rate of decomposition was observed but this increase was quite large if it was compared to the rate of decomposition of normal alkyl derivatives of 2-mercaptobenzothiazole.



Accelerating Species

Ac

Ac = $(CH_3)_2$-N-C(=S)-S-, CH_3O-C(=S)-S-, $(CH_3O)_2$-P(=S)-S-.

Initially, an E1 reaction scheme was offered to explain the thermal decomposition of the 2-mercaptobenzothiazole derivatives, where the slow rate determining step was identified with α carbon-sulphur bond heterolysis, which was then followed by rapid hydrogen abstraction, the basic species being the 2-thiobenzothiazoyl anion. The activation entropies determined for these compounds raised doubts about the porposed description of the reaction sequence. This was further compounded when the rates of decomposition of the various derivatives in dioxan were compared to the rate in dioxan/water (70:30) and no significant change in rate was observed. The activation parameters for the decomposition of 2-(1',2' diphenylethyl)thiobenzothiazole and 1,4 bis-(2'-benzothiazoylthio)tetralin were calculated and negative

entropies of activation were obtained, this would imply a loss in freedom on going from reactant to transition state, which is in direct conflict with the reaction sequence proposed. It could be argued that for an ionic reaction of the type proposed, that when free ions were formed they could be strongly solvated by the surrounding molecules causing a reduction in the translational freedom of the bulk solvent molecules. Such an effect if sufficiently large would yield rate data from which negative entropies of activation would be obtained. An implicit assumption in the previous agrument is that the surrounding solvent molecules would have a dipole function which could orientate itself around the ionic intermediates thereby producing negative values for the entropy of activation. The 2-thiobenzothiazole derivatives do have the potential to isomerise, yielding the corresponding benzothiazoline-2-thiones, which possess a thiocarbonyl group and this group could act as a powerful dipole species, particularly when it is present as the solvent. The possibility of 2-thiobenzothiazole derivatives isomerising prior to decomposition offered a plausible explanation, which was evaluated. All attempts to detect isomerisation or obtain any evidence for isomerisation prior to decomposition of the mono-

substituted 1,2 diphenylethane and 1,4 bis-substituted tetralin derivatives failed. If solvent effects of the type previously considered were operative some manifestations of these effects should be seen in the rates of decomposition of the two isomers, in fact the rates of decomposition of the isomeric cyclohex-2-enyl derivatives are very similar. It has been proposed previously[29] that solvation effects in reactions involving melts of 2-mercaptobenzothiazole derivatives are minimal. In an ionic decomposition of the type initially proposed an appreciable change in rate would be anticipated when the solvent was changed from melt to dioxan and then to dioxan/water, very little change in the rate was observed and once more doubts are raised about the original description of the decomposition reaction. It is doubtful whether the negative entropy effects caused by preferential solvation could completely outweigh the positive entropy contributions that would arise from the formation of an ionic species, as Frost and Pearson[127] point out, from calculations based on a simple electrostatic model, solvents of medium polarity (e.g., dioxan, dioxan/water) usually have the greatest effect on changes in entropy. In the prior treatment of entropy effects, no distinction has been drawn between bulk dielectric and molecular

dielectric properties other than to consider the possible influence of dipole interactions. The magnitude and effect of these properties upon the rate data, and in particular the entropy values, have not been dwelt upon because it is extremely unlikely that dielectric properties as measured, i.e., bulk dielectric constant, can be related to the molecular dielectric and that would be needed if any meaningful correlation is to be made in this study. An interesting example of solvent effects can be found in the Menschutkin reaction,[117] where changes in solvent modify the entropies of activation slightly despite the development of change in the transition state and product. The conclusions which can be drawn from such activation parameters must be tentative; solvents undoubtedly modify entropies of activation but in a case where completely free ionic species are formed it would seem unlikely that solvent effects could completely suppress the positive contributions that free ions would give to the entropy of activation.

The rate data obtained on S-substituted dimethyldithiocarbamate and methylxanthate derivatives indicated that these compounds behaved in a similar manner to the corresponding 2-mercaptobenzothiazole derivatives, exhibiting little change in the rate of decomposition with

a change in solvent, and the rate data yielded negative entropies of activation. The 0,0 dimethylphosphorodithioate derivatives were similar to the previous compounds studied but certain significant differences were apparent. In both series of compounds chosen for further study the hydrocarbon group had as substituents various accelerating species, this then maintained a "constant" hydrocarbon group, i.e., 1,2 diphenylethane within each series. As the hydrocarbon group remained identical within a series it would be anticipated that on thermal decomposition by the ionic mechanism originally proposed, the same carbonium ion should be generated. The inference drawn would be that the rates of decomposition should also be similar within a given series, as the primary carbonium ion would be the same but also dependent upon the leaving group. Table 38 reveals that although the 2-thiobenzothiazole, dimethyldithiocarbamate, and 0-methylxanthate derivatives have similar rates, the relative rate of the 0,0 dimethylphosphorodithioate is considerably greater than the later derivatives. A similar set of data is obtained with the 1,4 bis-substituted tetralins (see Table 39).

To rationalise the experimental data obtained in the prior study the following observations must be

explained:

1. Marked α substituent effects, particularly with phenyl groups
2. Small β substituent effects
3. Negative entropies of activation
4. Insensitivity of the rate of decomposition to changes in solvent
5. Effect of various accelerating species upon the rate of decomposition

TABLE 38

RELATIVE RATES OF DECOMPOSITION OF α-SUBSTITUTED 1,2 DIPHENYLETHYL DERIVATIVES AT 200°C.

Substituent	2-thiobenzo-thiazole	Dimethyl-dithio Carbamate	Methyl xanthate	0,0 dimethyl-phosphoro-dithioate
k_{200} $sec.^{-1}$	7.79×10^{-5}	7.58×10^{-5}	1.51×10^{-4}	1.35×10^{-3}
$k_{rel.}$	1.03	1.00	1.99	17.80

All the parent accelerating species used in this study are acids except 2-mercaptobenzothiazole; however, the thiol does dissolve readily in sodium hydroxide. When the ρKa values of the various species are examined (see Table 40) it becomes apparent that 0,0 dimethyldithio-

phosphoric acid is a considerably stronger acid than any of the other species.

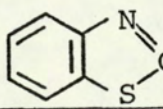
TABLE 39

RELATIVE RATES OF DECOMPOSITION OF 1,4 BIS-SUBSTITUTED TETRALINS AT 180°C.

Substituent	2-thiobenzo-thiazole	Dimethyl-dithio carbamate	Methyl xanthate	0,0 dimethyl-phosphoro-dithioate
k_{180} $sec.^{-1}$	8.83×10^{-5}	6.91×10^{-5}	2.87×10^{-4}	2.29×10^{-3}
$k_{rel.}$	1.28	1	4.15	33.2

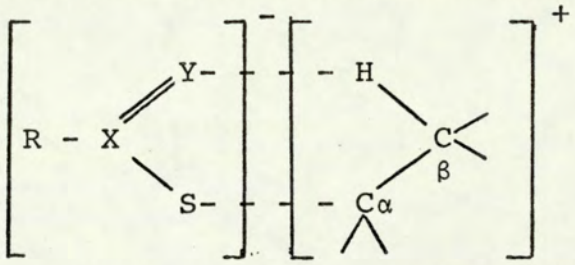
TABLE 40

ρKa VALUES OF THE ACCELERATING SPECIES

	$(CH_3)_2NC(=S)-SH$	$CH_3OC(=S)-SH$	$(CH_3O)_2P(=S)-SH$
ρKa 8.0[128]	3.66[129]	3.53[130]	1.62[131]

The conjugate base, i.e., anion formed from the strongest acid, should be more stable than the anion derived from the weaker acids and the relative rate data indicate that 0,0 dimethylphosphorodithioates exhibit the largest

relative rates. 2-mercaptobenzothiazole is unusual, although the weakest acid as measured by a ρKa value, this weakness is not extrapolated to the relative rate data; however, a nullifying factor which may explain this anomaly, could be the aromatic nature of the thiol coupled with the availability of the ring nitrogen which may influence the rates of decomposition considerably. To explain the observations which have been made, the following decomposition transition state is offered.

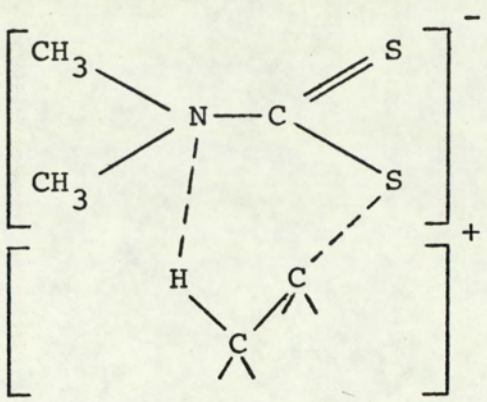


where X = P or C
Y = N or S

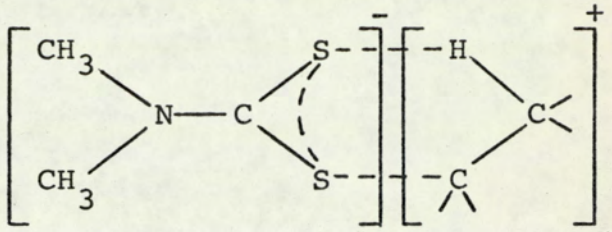
The marked α substituent effects can be interpreted by assuming phenyl groups aid carbon-sulphur bond heterolysis via conjugative stabilisation of the developing carbonium ion. Small β effects which would aid hydrogen abstraction could be visualised as an inductive effect. If the ions were not separated to a great extent then negative entropies of activation would be implied as would the insensitivity of the decomposition rate to a change in solvent. The role of the acid residue becomes clearer in terms of anion stabilisation, the stronger acid stabilising the anion much more effectively than the weaker acids. This stabilisation would increase the

decomposition rate by aiding carbon-sulphur bond heterolysis. The work does not provide any information on the relative separation of the ions and does not lead to an insight of the subtle details of structure such as the role of the ring nitrogen in 2-thiobenzothiazole derivatives decomposition reactions. Although trans-stilbene was formed when mono-substituted 1,2 diphenyl-ethane derivatives decomposed this does not lead to a proof of the stereochemistry of the reaction as various conformations could yield trans-stilbene via a cis or trans elimination pathway. The isomerisation of cis-stilbene in the presence of 2-mercaptobenzothiazole was investigated and it was found that the rate of isomerisation to trans-stilbene was considerably slower than the rate of formation of trans-stilbene from the thermal decomposition reaction.

When dimethyldithiocarbamate derivatives are considered, two transition states seem likely; II would be similar to the transition proposed, while with I the similarity to 2-thiobenzothiazole derivatives is noticeable, i.e., nitrogen participation. If in I heterolysis was almost complete then a "zwitterion" of the type below could be postulated. It would seem likely that type I is operative, since the rate data for the

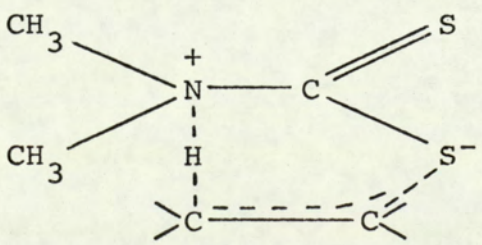


I



II

dimethyldithiocarbamates is similar to the other compounds studied. It has been noted that on passing from monoalkylamino to dialkylamino dithiocarbamates bascity and particularly association is considerably reduced.[65] Similar reasoning can be used for the methylxanthate and 0,0 dimethylphosphorodithioate derivatives both of which are accommodated most effectively by the "ion-pair" transition state.



CHAPTER IV

RUBBER TECHNOLOGY

Introduction

The compounds which exhibited the greatest rates of decomposition, i.e., mono-substituted 1,2 diphenylethane and 1,4-bis substituted tetralin derivatives, were evaluated for accelerating behavior by comparing the activities of these compounds with known accelerators in a sulphur cured natural rubber vulcanizate. Known concentrations of the compounds under evaluation were added to a natural rubber stock containing zinc oxide, stearic acid and sulphur (see Table 41). The experimental stocks were tested using a Wallace-Shawbury Curometer Mk III and the temperature of the upper and lower platens were controlled thermostatically to ±1°C. In order to maintain experimental consistency from run to run a standard mixing procedure was adopted and then if it was necessary, the experimental stocks were stored at -28°C. in sealed polyethylene bags.

The treatment of the experimental data obtained from

the curometer evaluation is based on the work of Pinfold,[132] who showed that the shear modulus can be related to the measurements obtained from the curometer by the following equation:

$$\text{Shear Modulus} = t \frac{(\lambda 1 + \lambda 2)}{2A} \cdot \frac{(ao - 1)}{a}$$

Where t = the thickness of the sample, i.e., the distance between platens

$\lambda 1$, $\lambda 2$ are the Young's moduli of the springs in the instrument

A = the area of the sample

ao= trace width for a minimum load on the paddle

a = trace width at a time t when the "modulus" is M.

From the above equation and depending on the instrument, i.e., the springs $\lambda 1$ and $\lambda 2$, the shear modulus derivative (M) was related to the trace by the following equation:

$$M = f \frac{(ao - 1)}{a}$$

Where f is a constant

TABLE 41

FORMULATIONS FOR COMPOUNDS CHOSEN FOR EVALUATION

Accelerator	Molecular Weight	Amount Added (g)	Moles	Index
Stock	-	-	-	A
2-mercaptobenzothiazole	167	1.00	0.006	B
0,0 dimethylthiothionophosphoric acid	158	0.95	0.006	C
Potassium methylxanthate	146	0.88	0.006	D
Sodium dimethyldithiocarbamate	143	0.86	0.006	E
2-(1',2' diphenylethyl)thiobenzothiazole	347	2.08	0.006	F
S-(1,2 diphenylethyl) 0,0-dimethylphosphorodithioate	338	2.03	0.006	G
S-(1,2 diphenylethyl) methyl xanthate	288	1.73	0.006	H
S-(1,2 diphenylethyl) dimethyldithiocarbamate	301	1.81	0.006	I
1,4 bis-(2'-benzothiazoylthio)tetralin	462	1.39	0.003	J
1,4 bis-(S-0,0 dimethylphosphorodithioate) tetralin	444	1.33	0.003	K
1,4 bis-(S-methyl xanthate) tetralin	344	1.03	0.003	L
1,4 bis-(S-dimethyldithiocarbamate) tetralin	370	1.11	0.003	M

Natural Rubber - 100 g.
Zinc oxide - 5.0 g.
Sulphur - 2.5 g.
Accelerator - See above.

In a second paper, Robinson and Pinfold[133] related the cross-link density to the shear modulus derivative. During vulcanization the cross-link density increases with time, whilst the rate decreases and only when the vulcanization reaction is completed can an estimate of the cross-link density be made. To simplify the treatment it is more convenient to consider the potential cross-links, i.e., those still to be added at any given stage of the reaction. If M_∞ is the modulus when all the cross-links have been formed then $M_\infty - M$ is a measure of the potential cross-links at the time when the modulus is equal to M. This yields the following first order expression:

$$M_\infty - M = M_\infty e^{-kt}$$

Where k = the rate constant

t = the time taken to reach a cross-link density $M_\infty - M$

If the shear modulus derivative is substituted, then the following equation is obtained:

$$\frac{(ao}{a_\infty} - 1) - \frac{(ao}{a} - 1) = \frac{(ao}{a_\infty} - 1)\, e^{-kt}$$

Which becomes:

$$\left(\frac{1}{a_\infty} - \frac{1}{a}\right) = \left(\frac{1}{a_\infty} - \frac{1}{ao}\right)e^{-kt}$$

TABLE 42

COMPARATIVE VULCANIZATION KINETICS OF 2-(1',2' DIPHENYLETHYL)THIOBENZOTHIAZOLE (F) AND 1,4 BIS-(2'-BENZOTHIAZOYLTHIO) TETRALIN (J)

Vulcanizate	A	S.D.	B	S.D.	F	S.D.	J	S.D.
180°								
$k.min.^{-1}$	0.28	0.02	0.64	0.05	0.30	0.02	0.28	0.02
k.rel.	1.00		2.28		1.07		1.03	
a_∞-ao	14.00		30.00		13.00		12.00	
$(a_\infty$-ao) rel.	1.00		2.14		0.93		0.86	
200°								
$k.min^{-1}$	0.89	0.09	3.21	0.35	1.09	0.09	1.62	0.22
k.rel.	1.00		3.61		1.23		1.82	
a_∞-ao	22.00		31.00		15.00		17.00	
$(a_\infty$-ao) rel.	1.00		1.41		0.68		0.77	
220°								
$k.min^{-1}$	1.18	0.05	9.37	2.00	3.23	0.82	5.27	0.95
k. rel.	1.00		7.95		2.74		4.47	
a_∞-ao	25.00		24.00		30.00		30.00	
$(a_\infty$-ao) rel.	1.00		0.96		1.20		1.20	

from which the rate constant can be evaluated. The actual slope of the line will vary with the concentration of curatives, accelerator used and the temperature. In the

treatment of the experimental data a_∞ - ao was taken as a measure of the total number of cross-links inserted during vulcanization.

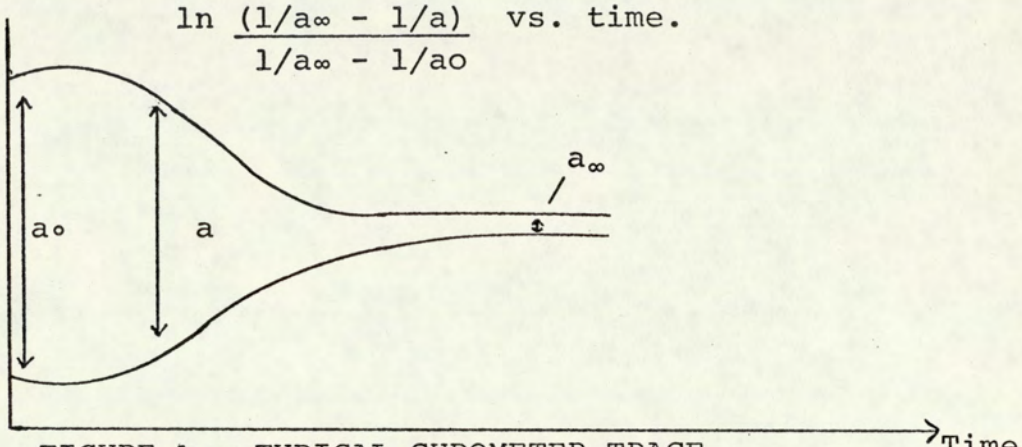


FIGURE 1 - TYPICAL CUROMETER TRACE

Evaluation of the vulcanization activity of 1',2' diphenylethyl and 1,4-bis tetralin derivatives

When the experimental data obtained from the curometer was analysed, the deviations (S.D. = standard deviation) which occurred from run to run were considered too large for a meaningful comparison to be made on the basis of the vulcanization rate constants of individual experimental stocks. Two additional stocks were prepared for comparative purposes, the first stock contained no accelerating species and from the kinetic measurements made on this stock, the lowest level of activity that

could be expected was found.

TABLE 43

COMPARATIVE VULCANIZATION KINETICS OF S-(1,2 DIPHENYLETHYL)DIMETHYLDITHIOCARBAMATE (I) AND 1,4 BIS-(S-DIMETHYLDITHIOCARBAMATE) TETRALIN (M)

Vulcanizate	A	S.D.	E	S.D.	I	S.D.	M	S.D.
180°								
$k.min.^{-1}$	0.28	0.02	0.95	0.16	0.33	0.02	0.38	0.01
k.rel.	1.00		3.39		1.18		1.36	
a_∞-ao	14.00		44.00		14.00		21.00	
(a_∞-ao) rel.	1.00		3.14		1.00		1.50	
200°								
$k.min.^{-1}$	0.89	0.09	4.04	0.25	1.13	0.06	0.96	0.08
k.rel.	1.00		4.54		1.27		1.08	
a_∞-ao	22.00		42.00		21.00		24.00	
(a_∞-ao) rel.	1.00		1.91		0.96		1.09	
220°								
$k.min.^{-1}$	1.18	0.05	5.38	0.88	4.66	0.99	3.76	0.45
k.rel.	1.00		4.55		3.96		3.18	
a_∞-ao	25.00		33.00		31.00		34.00	
(a_∞-ao) rel.	1.00		1.32		1.24		1.36	

The second stock contained the accelerating species which the compounds under investigation were designed to liberate, e.g., 2-mercaptobenzothiazole derivatives would be compared to the parent compound 2-mercaptobenzothiazole,

and from a comparison of the kinetic data obtained an indication of the highest level of activity that might be expected was obtained.

Some of the compounds liberated were unstable acids, in these cases the stable sodium or potassium salts were used for evaluation purposes. The compounds under evaluation were compared on an equimolar basis (see Table 41). The vulcanizations were carried out at 180°C., 200°C. and 220°C., as it was hoped that molecules of the type synthesized in this work would be active in this temperature range, particularly as decompositions at 200°C. were rapid. The experimental data obtained is summarised in tables throughout the chapter. The first column in each table reports the data obtained on a vulcanizate which does not contain an accelerating species, the second column gives the results obtained on a stock which contained a known accelerating species, e.g., 2-mercaptobenzothiazole, while the third and fourth columns list the experimental results obtained on the compounds under evaluation. For an index of the experimental stock, A to M, see Table 41.

In the analysis of the curometer data, two relative measurements were used:

1. Krel was used to measure the relative acceleration

of the compounds under evaluation. The lower level of activity was taken as that of a stock which contained no accelerating species and this rate was used as the denominator in the Krel expression. The second level of activity, i.e., the upper level, was obtained by using a stock containing a known accelerator. A comparison of the relative rate data of these two stocks with those in columns three and four gave a measure of the accelerating behavior of the 1',2' diphenyl-ethyl and 1,4-bis tetralin derivatives.

2. (a_∞-ao) rel. was used in a similar manner to compare the structural efficiency induced by the test compounds, again column one will represent the lower level of activity, and column two the upper level of activity.

The prior screening was based upon the knowledge that presently available accelerators accelerate the rate of vulcanization and produce a network in which the sulphur is more efficiently utilized than it would be if an accelerator were not present. Evaluation of 2-(1',2' diphenylethyl)thiobenzothiazole (F) and 1,4 bis-(2'-benzothiazoylthio)tetralin (J) (see Table 42), showed that little acceleration took place at 180°C. or 200°C.

However, the stock containing 2-mercaptobenzothiazole (B) showed an appreciable increase in the relative rate, but the utilization of sulphur for cross-linking purposes as measured by $(a_\infty - ao)$rel. did not show a correspondingly large increase. At 220°C. both test compounds (F and J) increased the relative rate but this increase was less than that of the parent compound (B), while sulphur utilization as measured by $(a_\infty - ao)$rel. was similar to the parent compound (B). Similar results were obtained when S-(1,2 diphenylethyl)dimethyldithiocarbamate (I) and 1,4 bis-(S-dimethyldithiocarbamate)tetralin (M) were evaluated, see Table 43. At 220°C., both test compounds (I and M) approach the level of activity displayed by the parent compound, sodium dimethyldithiocarbamate (E). The evaluation of S-(1,2-diphenylethyl)methyl xanthate (H) and 1,4 bis-(S-methyl xanthate) tetralin (L) (see Table 44), revealed that these compounds were capable of minor accelerating behavior. Similar results were obtained from the evaluation of S-(1,2-diphenylethyl) 0,0-dimethyl-phosphorodithioate (G) and 1,4 bis-(S-0,0 dimethyl-phosphorodithioate) tetralin (K), see Table 45.

Discussion

The 2-mercaptobenzothiazole and dimethyldithiocarbamate derivatives gave the highest level of accelerator

TABLE 44

COMPARATIVE VULCANIZATION KINETICS OF S-(1,2 DIPHENYLETHYL)METHYLXANTHATE (H) AND 1,4 BIS-(S-METHYLXANTHATE) TETRALIN (L)

Vulcanizate	A	S.D.	D	S.D.	H	S.D.	L	S.D.
180°								
$k.min.^{-1}$	0.28	0.02	1.15	0.03	0.40	0.03	0.35	0.02
k.rel.	1.00		4.10		1.43		1.25	
a_∞-ao	14.00		43.00		6.00		10.00	
(a_∞-ao) rel.	1.00		3.17		0.43		0.71	
200°								
$k.min.^{-1}$	0.89	0.09	1.83	0.29	2.55	0.20	2.12	0.08
k.rel.	1.00		2.06		2.86		2.32	
a_∞-ao	22.00		37.00		10.00		18.00	
(a_∞-ao) rel.	1.00		1.68		0.45		0.82	
220°								
$k.min.^{-1}$	1.18	0.05	6.95	0.13	3.20	0.17	5.10	0.69
k.rel.	1.00		5.90		2.71		4.31	
a_∞-ao	25.00		30.00		11.00		15.00	
(a_∞-ao) rel.	1.00		1.20		0.44		0.60	

activity in a sulphur cured natural rubber vulcanizate but the level of activity only approached that of the parent compounds. Lower levels of activity were obtained with the methylxanthate and 0,0-dimethylphosphorodithioate derivatives. Rate data obtained from the thermal decomposition reactions of the prior derivatives indicated a relative order almost opposite to that shown in the

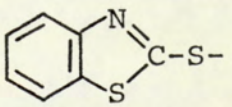
TABLE 45

COMPARATIVE VULCANIZATION KINETICS OF S-(1,2 DIPHENYLETHYL) 0,0-DIMETHYLPHOSPHORODITHIOATE (G) AND 1,4 BIS-(S-0,0 DIMETHYLPHOSPHORODITHIOATE) TETRALIN (K)

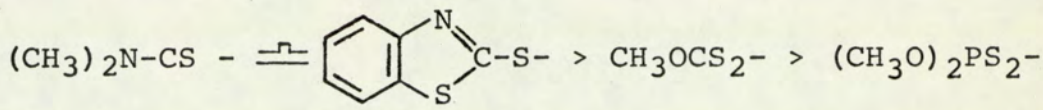
Vulcanizate	A	S.D.	C	S.D.	G	S.D.	K	S.D.
180°								
$k.min.^{-1}$	0.28	0.02	1.34	0.13	0.31	0.02	0.57	0.08
k.rel.	1.00		4.80		1.10		2.04	
a_∞-ao	14.00		12.00		10.00		11.00	
(a_∞-ao) rel.	1.00		0.85		0.71		0.79	
200°								
$k.min.^{-1}$	0.89	0.09	2.00	0.38	0.97	0.05	2.19	0.35
k.rel.	1.00		2.24		1.09		2.46	
a_∞-ao	22.00		13.00		16.00		10.00	
(a_∞-ao) rel.	1.00		0.59		0.73		0.45	
220°								
$k.min.^{-1}$	1.18	0.05	5.14	0.74	2.75	0.40	3.01	0.35
k.rel.	1.00		4.30		2.33		2.55	
a_∞-ao	25.00		10.00		12.00		6.00	
(a_∞-ao) rel.	1.00		0.40		0.48		0.24	

vulcanization study below:

Thermal decomposition

$(CH_3O)_2PS_2^-$ > $CH_3OCS_2^-$ > $(CH_3)_2N\text{-}CS_2^-$ > 

Vulcanization



The vulcanization study revealed that the level of accelerator activity is not related to the rate of decomposition of the test compounds. The rate determining step or steps occurring during accelerated sulphur vulcanization used in this study are not the thermal decomposition steps which have been determined in Chapter III, or a similar activity sequence would have been expected in both the thermal and decomposition studies.

Initially, it was hoped that the high temperature vulcanization study would be analogous to vulcanization at 144°C., i.e., a normal cure temperature. When the sequence of activities was reversed, it became necessary to consider if any effects resulting from the higher vulcanization temperatures used could have modified or even reversed the vulcanization sequence. A possible constraint may be acting, namely a phenomenon called reversion which becomes operative at higher temperatures and is usually manifested by a loss in modulus or cross-link density. Gee and Morrel[134] postulated that the unstable cross-links broke down at a slower rate than at which they were formed, while Dogadkin[135] attributed cross-

linking to the action of the curing system and the loss in modulus to oxygen attack. Other workers[136,137] have represented the reversion process in terms of a consecutive reaction sequence and concluded that additional terms are needed in the rate equations but also conclude that the reversion process does not appreciably effect the formation of cross-links.

The sulphur vulcanization of natural rubber in the presence of an accelerator at normal curing temperatures is usually seen in terms of reactive intermediates, that promote efficient attachment of the sulphur to the rubber hydrocarbon backbone. It has been postulated by various workers[31,138] that one of the initial reactions which occurs in accelerated vulcanization is that of ring opening of the sulphur ring by an accelerator or its activator complex. In the 200°C. region, the prior mechanistic route may not be feasible and a consideration of the behavior of sulphur over a range of temperatures illustrates the marked differences in the composition of sulphur between 140°C. and 200°C. When sulphur is heated to 120°C., it exists as eight-membered rings. At approximately 159°C., the eight-membered rings undergo thermal scission to yield linear sulphenyl diradicals. These then attack other sulphur rings which leads to

sulphur-based polymers, the formation of polymeric sulphur is indicated by an increasing viscosity of the liquid sulphur. Above 188°C., the viscosity of the liquid sulphur rapidly decreases and an explanation has been offered which proposes that the polymeric sulphur chains cleave rapidly and thereby reduce the viscosity of the molten sulphur yielding low molecular weight species.[139] When the test compounds eliminated an accelerator species at 200°C., the reaction of the accelerator with sulphur may be seriously impaired; as most of the sulphur will probably have depolymerized and formation of reactive intermediates suitable for efficient cross-linking may not take place. Efficient incorporation of sulphur as cross-links would be reduced as much of the sulphur may react to form cyclic modifications of the main chain. The accelerating species may be incapable of effective reaction with the depolymerized sulphur at these temperatures. Such temperature-dependent effects may have rendered the utility of sulphur as a curing agent questionable, and also influenced the activity sequence considerably.

The initial evaluation yielded promising results in terms of the accelerator behavior of the test compounds, but in retrospect, the choice of polymer and curing

system was poor. A polymer more suitable for these temperature ranges would have been desirable as would a curing system that possessed high temperature stability. An evaluation of more suitable systems would require a considerable technical effort, but initially an ethylene propylene terpolymer and a cross-linking agent other than elemental sulphur would be a more promising choice. High temperature vulcanization which yields sulphur cross-links may be accomplished by using compounds capable of introducing sulphur cross-links via a delayed action accelerator species thus avoiding the use of elemental sulphur. However, this area must remain speculative until further experimental work is undertaken.

CHAPTER V

AN INITIAL MASS SPECTROSCOPY STUDY OF 2-SUBSTITUTED THIOBENZOTHIAZOLES, 3-SUBSTITUTED BENZO-THIAZOLINE-2-THIONES AND RELATED COMPOUNDS

Introduction

The study of the above compounds or perhaps a better description would be survey, was undertaken with two principle aims.

1. To examine the fragmentation patterns of the compounds under study and correlate molecular structure with any consistent peaks in the spectra.
2. To determine whether there existed any correlation between the mass spectroscopic behavior of the compounds and their thermal and accelerator activity.

The compounds studied are listed in Table 46, while the spectroscopic data is presented in tabular form (see Tables 47, 48, 49, 50, 51, 52, 53 and 54). The base peak

was used as the relative standard for intensity measurements and most peak intensities below 2% were not recorded unless they had special significance in the discussion of the spectra.

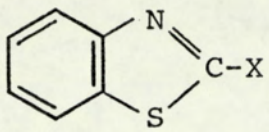
Discussion of Spectra

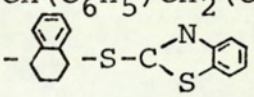
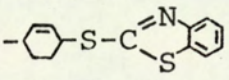
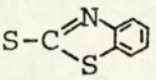
In the spectrum of compound I, the base and molecular ion peak occurred at m/e 169. The peak at m/e 134 may arise from the molecular ion via the loss of chlorine, i.e., (M-35). The structure of the ion occurring at m/e 108 is uncertain; however, the presence of a metastable peak at m/e 87 (calc. 87.04) indicates that the ion was directly related to the ion occurring at m/e 134, i.e., 134 → 108 + 22. The ions occurring at m/e 82, 69, and 63 were difficult to interpret; however, similar peaks have been observed in the mass spectrum of benzothiazole, e.g., m/e 135, 108, 82, 69, and 63. It seems likely that the ions are derived from the heterocyclic nucleus but their relationship to the peaks at m/e 134 and 108 remains obscure.

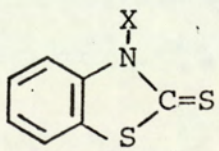
The peaks which occurred at m/e 181 in the spectrum of compounds III and XIX were identified as the molecular ion peaks and were also used as the base peak for intensity measurements. Rearrangement of the molecular ion prior to fragmentation was indicated by the presence of an ion

TABLE 46

THE 2-SUBSTITUTED THIOBENZOTHIAZOLES, 3-SUBSTITUTED BENZOTHIAZOLINE-2-THIONE AND RELATED COMPOUNDS USED IN THE MASS SPECTROMETRY STUDY



Compound	X	Compound	X
I	-Cl	X	$-SCH_2CH_2 \cdot C_6H_5$
II	-SH	XI	$-SCH(CH_3) \cdot C_6H_5$
III	$-SCH_3$	XII	$-SCH(C_6H_5)CH_2(C_6H_5)$
IV	$-SCH(CH_3)_2$	XIII	
V	$-SCH_2CH=CH_2$	XIV	$-SN(C_6H_{11})_2$
VI	$-SCH_2CH=CHCH_2CH=CH_2$	XV	$-SNH(C_6H_{11})$
VII	$-SCH_2CH_2CO_2CH_3$	XVI	$-SNH \cdot C(CH_3)_3$
VIII		XVII	
IX		XVIII	



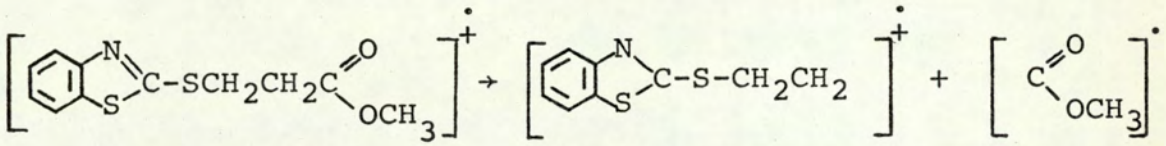
Compound	X
XIX	$-CH_3$
XX	

at m/e 148 which may have arisen via the following route, M = (M-33) + SH. Ions of the (M-SH) type have been investigated by Bowie and co-workers[140] who considered that the occurrence of such ions in a spectrum usually indicated skeletal rearrangements were taking place. The formation of the m/e 166 ion in the spectrum of both compounds is typical of α-cleavage. The β activating effect of sulphur[141] was reflected in the spectrum of compound III by the occurrence of a relatively intense peak at m/e 180, and the intensity of the analogous ion in the spectrum of compound XIX was reduced, which would be expected as ring attachment is via nitrogen and not sulphur.

Compound V gave a molecular ion peak at m/e 207 while the base peak occurred at m/e 192. The presence of a metastable peak 178.1 (calc. 178.08) corresponds to the transition 207 → 192 + 15 which could only have arisen via suitable hydrogen rearrangement. Substantial skeletal rearrangements were indicated by the presence of the m/e 174 ion which may have arisen from the following transition: 207 → 167 + 40 and it is possible that the transition represents an electron induced elimination; however, it could be argued that compound V, thermally decomposed prior to electron bombardment as the injection

temperature was approximately 200°C. This is unlikely as compound V is stable at 200°C.[29] The spectrum of compound VI was similar to that of compound V.

The molecular ion peak occurred at m/e 253 in the spectrum of compound VII while the base peak was found at m/e 194. The combined activating effect of both the sulphur atom and ester grouping would enhance a β fragmentation pattern thereby yielding the ion at m/e 194.



m/e 253 m/e 194 m/e 59

The $(M-OCH_3)$ ion is usually found in the spectrum of methyl esters and the ion occurring at m/e 222 can be correlated with such a process. The intense peak of m/e 167 indicated that an electron induced elimination had taken place and as additional proof for such a process, was the presence of a metastable peak at 110 (calc. 110.23) which corresponds to the following transition: 253 → 167 + 86.

The spectrum of compound VIII was characterized by a low intensity molecular ion peak at m/e 247. The

fragmentation was dominated by α-cleavage of the parent compound which yielded the base peak at m/e 81. Fragmentation via elimination was operative and the transition was manifested by the appearance of an m/e 167 ion in the spectrum. Rearrangement prior to fragmentation was not a major decomposition pathway as the (M-SH) peak at m/e 214 was a low intensity peak. The spectrum of the isomeric compound XX was very similar.

Compound X gave a low intensity molecular ion peak at m/e 271 while the base peak at m/e 167 characterized an induced elimination process. The m/e 180 ion indicated that a small sulfur β activating effect was operative. Cleavage of the aliphatic carbon-carbon bond of the parent molecular ion yielded a moderately intense peak at m/e 91. The resulting benzyl ion is stabilized by expansion into the mesomeric tropylium ion.

Compound XII was unusual as the molecular ion peak could not be detected. The spectrum is dominated by an apparent induced elimination which yielded the thiol at m/e 167 and the hydrocarbon fragment, i.e., stilbene, at m/e 180. Decomposition of it in compound XII within the injection system, prior to electron impact seems likely particularly as the molecular ion peak could not be detected. Similar results were obtained for compound XIII

which yielded naphthalene, i.e., m/e 128, as the hydrocarbon species.

Compound XIV gave a low intensity molecular ion peak at m/e 346. The base peak occurred at m/e 55 and this ion is probably derived from the cyclohexylamine portion of the molecule.[142] The m/e 167 ion indicated that an induced elimination had taken place while cleavage of the sulphur nitrogen bond of the parent ion was manifested by the presence of the ion at m/e 180. The spectrum of compound XV was similar to that of compound XIV.

The base peak in the spectrum of compound XVI occurred at m/e 58 and the ion was probably derived from the amine portion of the molecule. The molecular ion peak occurred at m/e 238 and the peak which occurred at m/e 223 was derived from the molecular ion via the loss of a methyl group. The presence of a metastable peak at 209.0 (calc. 208.95) corresponds to the transition $238 \rightarrow 223 + 15$. The m/e 167 ion was characterized by a low intensity peak indicating that prior thermal decomposition was unlikely. Compound XVII behaved in a similar manner to the other sulphenamides studied.

Conclusions

The thermal decomposition data, accelerator activity

TABLE 47

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS I, II, III, AND IV

I	m/e	39	41	42	43	44	45	50	51	54	58	62	63	64	69	74	75
	I%	6	3	3	2	3	6	5	2	5	5	2	8	3	18	3	2
	m/e	76	82	89	108	134	169(M^+)										
	I%	6	7	4	27	19	100										
II	m/e	37	38	39	44	45	50	51	54	58	61	62	63	69	70	74	75
	I%	3	3	5	2	7	5	3	3	5	2	4	9	20	4	3	2
	m/e	76	82	91	108	135	167(M^+)										
	I%	4	10	8	33	100	16										
III	m/e	37	38	39	41	43	44	45	46	47	50	51	55	57	58	62	63
	I%	2	5	14	4	6	12	19	4	4	6	7	5	5	5	4	17
	m/e	64	69	70	71	74	75	76	77	81	82	90	91	95	102	108	
	I%	8	25	4	4	3	5	6	4	6	9	5	5	4	6	31	
	m/e	122	135	148	166	180	181(M^+)										
	I%	11	23	50	14	26	100										
IV	m/e	38	39	41	42	43	44	45	50	51	58	59	63	64	65	69	70
	I%	2	7	9	2	9	4	3	2	2	2	2	3	2	2	9	2
	m/e	76	82	91	96	102	103	108	109	122	123	135	140	167			
	I%	2	3	4	3	2	2	10	7	5	3	5	3	100			
	m/e	176	194	209(M^+)													
	I%	17	3	27													

TABLE 48

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS V AND VI

V	m/e	36	37	38	39	40	41	42	43	44	45	50	51	52	54	55	57
	I%	6	5	7	30	4	25	2	4	7	16	8	7	2	3	5	4
	m/e	58	61	62	63	64	65	69	70	71	72	73	74	75	76	77	78
	I%	8	2	5	15	6	3	30	5	4	2	2	4	5	9	5	3
	m/e	81	82	83	90	91	95	96	102	103	108	109	122	135	139		
	I%	4	12	2	4	8	3	5	8	4	50	10	13	68	3		
	m/e	140	148	149	160	162	166	167	174	180	192	207(M^+)					
	I%	2	4	8	3	8	23	23	23	7	100	33					
VI	m/e	37	38	39	40	41	42	44	45	50	51	52	53	54	55	58	62
	I%	2	4	32	4	42	2	3	10	8	13	7	35	5	8	4	2
	m/e	63	64	65	66	67	69	70	71	75	76	77	78	79	80	81	82
	I%	10	4	9	8	5	18	3	3	2	3	16	6	44	41	33	7
	m/e	90	91	95	96	102	103	108	109	122	133	134	135	140			
	I%	3	4	3	4	7	4	33	8	12	2	2	16	2			
	m/e	148	149	162	166	167	173	180	181	186	193	194	200				
	I%	3	8	3	18	100	8	2	2	5	15	23	3				
	m/e	206	214	218	232	247(M^+)											
	I%	12	26	2	3	6											

TABLE 49

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS VII AND VIII

VII	m/e	38	39	41	42	43	44	45	47	50	51	55	57	58	59	62	63
	I%	2	7	3	2	3	3	9	2	4	4	29	3	5	16	2	10
	m/e	64	65	69	70	75	76	77	78	81	82	83	85	90	91	95	96
	I%	4	3	17	2	3	7	5	3	3	7	9	6	4	7	2	3
	m/e	102	103	104	105	107	108	109	122	133	134	135	136				
	I%	6	4	2	3	2	34	8	12	3	3	31	15				
	m/e	140	148	149	160	161	162	166	167	180	188	192	193				
	I%	3	3	5	5	2	2	23	95	13	5	5	27				
	m/e	194	220	222	253(M^+)												
	I%	100	3	16	44												
VIII	m/e	37	38	39	40	41	42	44	45	50	51	52	53	54	55	57	58
	I%	10	9	42	6	29	3	10	19	12	13	11	30	6	7	4	4
	m/e	59	62	63	64	65	66	67	68	69	70	71	72	74	75	76	77
	I%	4	4	13	5	10	9	11	3	21	8	5	8	3	3	13	20
	m/e	78	79	80	81	82	83	91	95	96	102	108	109	122	123		
	I%	10	54	64	100	11	4	6	3	2	5	22	7	7	7		
	m/e	131	135	140	152	154	162	166	167	194	214	232					
	I%	7	44	6	2	2	2	35	43	3	6	4					
	m/e	247(M^+)															
	I%	9															

TABLE 50

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS IX, X AND XI

IX	m/e	37	38	39	41	45	50	51	52	53	58	62	63	64	65	69	70
	I%	2	4	12	2	8	8	11	7	5	5	3	12	5	6	23	3
	m/e	71	74	75	76	77	78	79	80	81	82	90	91	92	93	95	96
	I%	2	3	4	4	33	14	26	3	10	2	4	8	2	2	2	7
	m/e	102	103	108	109	122	123	133	134	135	139	160	166				
	I%	7	5	40	17	11	7	3	6	23	7	2	21				
	m/e	167	168	192	212	221	244	245	246	268	300	332	386				
	I%	100	83	2	6	2	25	26	49	38	5	2	2				
	m/e	412(M^+)															
	I%	1															
X	m/e	39	41	44	45	50	51	52	63	65	69	74	75	76	77	78	79
	I%	6	2	2	4	4	8	2	5	4	5	2	2	3	15	7	8
	m/e	82	91	92	102	103	104	105	106	108	122	135	136	138			
	I%	2	15	2	2	11	17	16	2	7	2	12	6	2			
	m/e	166	167	168	180	271(M^+)											
	I%	2	100	10	6	2											
XI	m/e	38	39	41	45	50	51	52	53	58	62	63	64	65	69	74	75
	I%	2	7	2	3	5	10	3	3	2	2	6	2	3	6	2	2
	m/e	76	77	78	79	80	82	91	102	103	104	105	106	108	109		
	I%	2	19	11	13	3	3	15	4	15	25	100	13	10	2		
	m/e	122	135	166	167	168	271(M^+)										
	I%	3	10	4	33	4	12										

TABLE 51

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS XII AND XIII

XII	m/e	39	41	43	45	50	51	52	55	59	62	63	64	65	69	74	75
	I%	11	3	3	4	7	17	5	13	5	3	11	3	6	7	4	5
	m/e	76	77	78	79	82	88	89	90	91	92	102	103	104	105		
	I%	14	19	7	11	8	4	16	6	12	13	13	5	2	6		
	m/e	107	108	115	122	126	127	128	135	138	149	150	151				
	I%	22	12	5	3	2	2	2	18	4	5	3	6				
	m/e	152	165	166	167	178	179	180	181	194	214(M^+)						
	I%	11	35	6	22	63	88	100	16	16	4						
XIII	m/e	38	39	41	43	44	45	50	51	52	53	54	55	56	57	58	59
	I%	10	10	19	3	2	9	16	9	9	9	7	5	4	7	13	4
	m/e	62	63	65	67	68	69	71	76	77	78	79	80	81	82	83	84
	I%	8	7	9	5	7	7	11	3	6	13	4	16	23	10	7	8
	m/e	91	94	102	106	108	110	111	112	123	126	127	128				
	I%	6	14	6	3	11	2	5	6	62	8	12	100				
	m/e	135	146	148	166	167	180	202	213	247	248	258	269				
	I%	23	10	4	7	70	3	5	8	4	4	4	10				
	m/e	295	412	429(M^+)													
	I%	3	4	3													

TABLE 52

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS XIV, XV AND XVI

XIV	m/e	37	38	39	40	41	42	43	44	45	50	51	52	53	54	55	56
	I%	3	12	25	4	99	14	16	20	6	3	4	2	13	30	100	37
	m/e	57	58	62	63	64	65	66	67	68	69	70	77	79	80	81	82
	I%	5	3	2	6	2	3	2	15	12	21	7	4	5	7	16	17
	m/e	83	91	94	96	97	98	108	122	123	124	125	135	136			
	I%	33	3	4	15	10	80	15	5	5	6	4	11	35			
	m/e	137	138	150	151	166	167	179	180	221	268	346(M^+)					
	I%	7	26	6	4	8	25	14	67	4	11	1					
XV	m/e	37	38	39	40	41	42	43	44	45	50	51	52	53	54	55	56
	I%	2	4	27	4	58	15	24	5	9	4	6	3	6	24	37	47
	m/e	57	58	62	63	64	65	67	68	69	70	75	76	77	78	79	81
	I%	6	4	2	8	4	4	3	4	12	5	3	2	2	2	2	5
	m/e	82	83	90	91	96	97	98	99	102	108	122	135	136	149		
	I%	8	4	4	4	2	4	100	10	4	21	6	10	4	8		
	m/e	150	154	162	166	167	181	182	221	264(M^+)							
	I%	6	4	3	11	45	4	12	4	2							
XVI	m/e	37	38	39	40	41	42	43	45	58	50	51	55	56	57	58	59
	I%	3	5	21	4	42	36	5	8	7	4	4	2	9	35	100	6
	m/e	62	63	64	69	81	82	90	91	102	108	122	135	148	149		
	I%	9	9	9	15	2	6	3	3	3	23	5	28	7	15		
	m/e	154	166	167	182	223	238(M^+)										
	I%	3	7	5	39	15	16										

TABLE 53

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS XVII AND XVIII

XVII	m/e	36	37	38	39	40	41	42	43	44	45	48	50	51	52	54	55
	I%	33	2	10	17	2	12	12	2	10	10	2	5	6	2	6	7
	m/e	56	57	58	63	64	69	70	75	76	80	81	82	86	87	90	91
	I%	18	24	8	13	4	28	3	3	2	3	3	17	21	14	8	5
	m/e	93	94	95	96	102	106	107	108	121	122	133	134	135			
	I%	5	3	5	8	11	3	9	100	3	22	5	16	15			
	m/e	139	140	149	150	151	163	166	167	182	223	252(M^+)					
	I%	3	2	5	4	2	2	13	68	13	6	2					
XVIII	m/e	36	38	39	40	41	42	43	44	45	47	49	50	51	52	54	55
	I%	21	11	43	3	13	3	3	5	35	2	2	17	19	10	2	14
	m/e	56	57	58	59	61	62	63	64	65	68	69	70	71	72	74	75
	I%	5	5	19	2	3	6	43	16	5	2	82	13	6	2	5	11
	m/e	76	77	78	79	81	82	83	84	88	90	91	93	94	95	96	97
	I%	10	4	23	2	6	32	5	4	2	9	4	5	3	6	6	2
	m/e	98	102	108	122	133	134	135	139	140	152	154	158				
	I%	3	19	100	28	6	9	6	5	5	4	4	2				
	m/e	160	165	166	184	186	197	224	229	242	256	268	300				
	I%	3	4	74	3	3	2	6	4	4	2	31	2				
	m/e	332(M^+)															
	I%	4															

TABLE 54

THE RELATIVE ABUNDANCIES OF THE MAIN FRAGMENTS FROM COMPOUNDS XIX AND XX

XIX	m/e	38	39	44	45	46	50	51	52	58	62	63	64	65	69	70	72
	I%	5	8	7	15	3	7	11	3	3	3	11	5	3	13	3	2
	m/e	74	75	76	77	78	82	90	91	95	96	102	104	108	121		
	I%	5	3	8	10	11	6	3	3	3	3	3	10	13	8		
	m/e	122	135	136	148	166	180	181(M^+)									
	I%	6	9	18	30	3	4	100									
XX	m/e	38	39	40	41	42	43	44	45	50	51	52	53	54	55	56	57
	I%	6	39	10	34	4	11	22	7	8	15	21	27	5	10	4	9
	m/e	58	59	63	64	65	66	67	69	71	72	74	75	76	77	78	79
	I%	6	5	13	10	12	9	12	22	5	3	4	7	11	24	20	54
	m/e	80	81	82	83	84	88	91	94	95	96	102	103	108	109		
	I%	66	100	19	8	8	5	13	5	3	6	3	5	18	15		
	m/e	115	122	123	135	139	140	148	150	152	160	166	167				
	I%	7	15	4	27	4	4	3	3	2	2	43	67				
	m/e	180	193	214	247(M^+)												
	I%	3	4	3	17												

TABLE 55

CORRELATION OF THE RELATIVE ABUNDANCIES AND MOST FREQUENTLY FOUND FRAGMENTS WITH MOLECULAR ION ABUNDANCE, THERMAL AND VULCANIZATION ACTIVITY

m/e	63	69	82	108	135	166	167	Molecular Ion	Mole % of MBT* @ 200° C.	Vulcanization Activity
I	8	18	7	27	19	-	-	100	-	-ive
II	9	20	10	33	100	-	16	16	-	++ive
III	17	25	9	31	23	14	-	100	1.0	-ive
IV	3	9	3	10	5	-	100	27	17.0	-ive
V	15	30	12	50	68	23	23	33	0.0	-ive
VI	10	18	7	33	16	18	100	6	34.0	-ive
VII	10	17	7	34	31	23	95	44	16.0	-ive
VIII	13	21	11	22	44	35	43	9	37.0	-ive
IX	12	23	2	40	23	21	100	1	32.0	-ive
X	5	5	2	7	12	2	100	2	25.0	-ive

* = 2-mercaptobenzothiazole
\- = no accelerator activity
++ = large accelerator activity
\+ = minor accelerator activity

TABLE 56

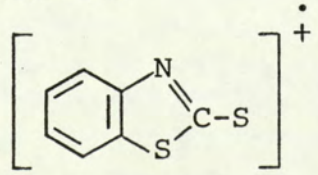
CORRELATION OF THE RELATIVE ABUNDANCIES AND MOST FREQUENTLY FOUND FRAGMENTS WITH MOLECULAR ION ABUNDANCE, THERMAL AND VULCANIZATION ACTIVITY

m/e	63	69	82	108	135	166	167	Molecular Ion	Mole % of MBT* @ 200° C.	Vulcanization Activity
XI	6	6	3	10	10	4	33	12	25.0	-ive
XII	11	7	3	12	18	6	22	-	100.0	+ive
XIII	7	7	10	11	23	7	70	-	100.0	+ive
XIV	6	21	17	15	11	8	25	1	-	++ive
XV	8	12	8	21	10	11	45	2	-	++ive
XVI	9	15	6	23	28	7	5	16	-	++ive
XVII	13	28	17	100	15	13	68	2	-	++ive
XVIII	43	82	32	100	6	74	-	4	-	++ive
XIX	11	13	6	13	9	3	-	100	1.0	-ive
XX	13	22	19	18	27	43	67	17	37.0	-ive

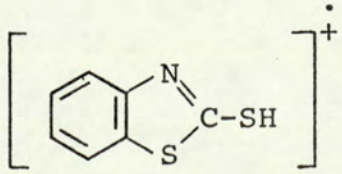
* = 2-mercaptobenzothiazole
\- = no accelerator activity
++ = large accelerator activity
\+ = minor accelerator activity

and most commonly found fragments have been tabulated in Tables 55 and 56. The following designations have been used to describe accelerator activity; -ive indicates a complete lack of accelerator activity; +ive indicates some accelerator activity; and, ++ive was arbitrarily assigned to known commercial accelerators.

The ions which occurred most frequently in the spectra of compounds I to XX were found at m/e 63, 69, 82, 108, 135, 166 and 167. Some of the previous ions may be absent in the spectra of a particular compound studied. Further examination of the specific compound usually indicated that the molecule in question was lacking the necessary structural unit, which would give rise to the missing ion; for example, compound I gave no ions at m/e 166 and 167. The mechanism by which the ions at m/e 63, 69, and 82 were formed is uncertain but it seems likely that the ions arose from the heterocyclic nucleus. The part of the molecule which was responsible for the occurrence of the ions at m/e 166 and 167 was probably the thiobenzothiazole unit and the ions can be visualized as follows:

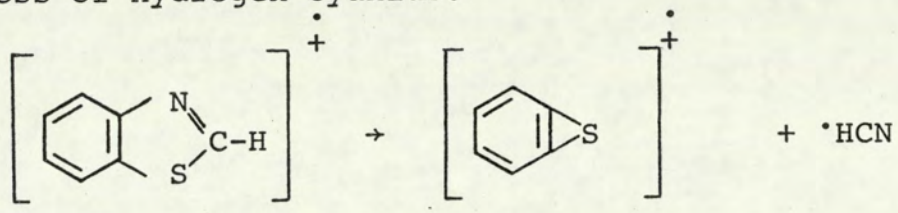


m/e 166



m/e 167

Similarly, the ion which occurs at m/e 135 must be the benzothiazole ion, while the ion occurring at m/e 108 could easily have derived from the m/e 135 ion by the loss of hydrogen cyanide.



m/e 135 m/e 108 m/e 27

No accurate relationship could be found between molecular ion intensity and the mole percentage of 2-mercaptobenzothiazole liberated by the test compounds after forty-eight hours at 200°C. A general correlation can be made, inasmuch as those compounds which decompose rapidly at 200°C. do not possess in their mass spectrum a detectable molecular ion. Accelerator activity correlation is equally ambiguous but most active accelerators do not exhibit intense molecular ion peaks.

The conclusions drawn are tentative and much of the work needs refining before any definitive conclusions concerning the mechanism of fragmentation and correlation of activities can be made. The absence of certain molecular ions was disturbing and further experimental work will be needed to establish that prior decomposition

within the injection system was not responsible for the absence of the molecular ions. The following experiments might be undertaken to investigate the points raised:

... Study the effect of varying the temperature of the injection system on selected compounds, i.e. XII and XIII.

... Determine the appearance potential of the molecular ions.

... Undertake high resolution measurements on all major peaks.

Without the above refinements the appearance of the ions at m/e 63, 69, 82, 108, 135, 166 and 167 provided strong evidence for the presence of the thiobenzothiazole nucleus. The information derived from other structural techniques, the knowledge of the mass spectral behavior of these molecules, proved valuable in the characterization of the test compounds.

CHAPTER VI

EXPERIMENTAL

Introduction

Melting points and boiling points are uncorrected and in degrees Centigrade. Physical constants quoted as lit. without qualification are from the "Dictionary of Organic Compounds" and the "Handbook of Chemistry and Physics."

N.M.R. spectra were determined on a Perkin-Elmer R10 (60 Mc), I.R. spectra on a Perkin-Elmer Infracord 237, the U.V. spectra on a Perkin-Elmer Infracord 137-UV, mass spectra on an A.E.I. M.S.9 double focusing mass spectrometer operating at 70 e.v. G.L.C. were carried out on a Pye Pan chromatograph.

I.R. interpretations are based on the texts of Bellamy,[143] Nakanishi[144] and the individual references as cited; N.M.R. on Jackman,[145] U.V. on Rao,[146] Jaffe and Orchin.[147] The I.R. and U.V. spectra are deposited in the Chemistry Department collection.

The vulcanization kinetics were followed on a

Wallace Shawbury Curometer Mk. III, all rubbers and chemicals were used without purification unless stated.

Micro analysis by Mr. S. Williams and Mrs. B. Taylor, Department of Chemistry, University of Aston in Birmingham, Drs. G. Weiler and F. B. Straus Oxford.

Synthesis

Preparation of 2-(cyclohex-2'-enyl)thiobenzothiazole (I) and 3-(cyclohex-2'-enyl)benzothiazoline-2-thione (II)

a) 3-bromocyclohexene was prepared by refluxing N-bromosuccinimide (73.2 g.) and cyclohexene (206 ml.) in carbon tetrachloride (300 ml.) with a trace of benzoyl peroxide. 3-bromo-cyclohexene (38.5 g., 60%) was distilled under nitrogen b.p. 64° - 67°/16 mm. N^{D}_{25} = 1.5276 (lit. 58° - 60°/12 mm., $N^{D}_{18.5}$ = 1.5309). Found 6% 44.70, H% 5.60 C_6H_9Br required C% 44.75, H% 5.65.

b) To a stirred aqueous solution (200 ml.) of sodium hydroxide (8.0 g., 0.2 mol.) with nitrogen bubbling through, 2-mercaptobenzothiazole (23.4 g., 0.2 mol.) was added. The temperature of the reaction vessel was adjusted to 80°C. and 3-bromocyclohexene (32.0 g., 0.2 mol.) was added dropwise over three hours and the reaction was maintained at 80°C. for a further five hours and

left to cool overnight. The products were extracted with ether (3 x 200 ml.) and the ether washed with water till neutral to litmus and then with ferrous sulphate (10%, 2 x 200 ml.) and again with water (2 x 200 ml.). The ether was dried over sodium sulphate and the ether removed under vacuo. The crude yellow viscous oil was distilled to give a light yellow oil (33.0 g., 61%), b.p. 168° - 173°/0.002 mm., N^{D}_{20} 1.6670, (lit.[29] 162° - 170°/0.005 mm., 1.6660). Alkali titration indicated the liquid contained 6.9 mole % of 2-mercaptobenzothiazole. This was removed by alkali extraction and treated as above. After three weeks of storage under nitrogen a white solid crystallised, this was filtered. Recrystallisation of the solid from ethanol gave white stumpy crystals (II)(12.0 g., 24%), m.p. 148° - 149° (lit[29] 148°). U.V. absorption in ethanol mμ (ε max); 242 (12,700), 327 (26,100). I.R. absorption 1005 $cm.^{-1}$ N.M.R. absorptions τ(H ratio); 2.5(4), 3.4 - 4.4 (3.0), 7.9 (6.0). The mass spectrum gave an M^{+} ion at 247, $E^{\%}_{81}$ 17.2. Found C% 63.05, H% 5.20, N% 5.35, S% 25.8. The filterate (I) (17.0 g., 34.2%), N^{D}_{20}

1.6657. U.V. absorption mμ (ε max); 282 (13,000), 291 (12,500), 301 (11,000, $E^{1\%}_{327}$ = 60, which indicates 6.0% of isomer II, the figures for pure I on this basis would be 282 (13,575), 291 (12,792), 301 (11,486). I.R. absorption 1000 $cm.^{-1}$ N.M.R. absorptions τ(H ratio); 1.9 - 2.9 (4.2), 4.1 (2.0), 5.15 (1), 8.10 (6.1). The mass spectrum gave an M^+ ion at 247 $E^{\%}_{81}$ 9.0. Found C% 63.0, H% 5.45, N% 5.80, S% 25.71 $C_{13}H_{13}NS_2$ requires C% 63.10, H% 5.30, N% 5.70, S% 25.90.

Preparation of 2-(hexa-2',5'-dien-1'-yl)thiobenzothiazole

a) Hexa 1:5 diene was purified by distillation through a packed column, b.p. 58.5° - 59.7°/758 mm., N^D_{20} 1.4039). Gas phase chromatography indicated a purity greater than 95%. Hexa 1:5 diene (61.4 g., 0.75 mol.) was refluxed with N-bromosuccinimide (44.5 g., 0.24 mol.) in carbon tetrachloride (120 ml.) with a trace of benzoyl peroxide. The mixed bromides (13.5 g., 28%) were distilled through a column b.p. 48° - 54°/15 mm., N^D_{20} 1.4981 (lit.[112] 39° - 41°/11 mm., 1.4996).

b) The bromides (20.0 g., 0.125 mol.) were reacted

with 2-mercaptobenzothiazole (21.0 g., 0.126 mol.) as for 2-(cyclohex-2'-enyl)thiobenzothiazole and purified in the same way. The product (22.1 g., 71%), a brown viscous oil was distilled using a molecular still to give a pale yellow oil b.p. 106° - 110°/0.002 mm., N_{20}^{D} 1.6384. Alkali titration indicated that 2-mercaptobenzothiazole was absent. U.V. absorption in ethanol mμ (ε max); 282 (12,410), 290 (11,560), 301 (9600), $E_{327}^{1\%}$ = 0.1. I.R. absorptions, neat liquid, the absorption at 918 $cm.^{-1}$ (CH_2=CHR) was reduced in going from the bromides to the product, while the absorption at 965 $cm.^{-1}$ (RCH=CHR trans) increased. Comparison of the absorption at 995 $cm.^{-1}$ (CH_2=CHR) was not practicalable because of the strong absorption at 1005 $cm.^{-1}$ (benzothiazole ring) N.M.R. absorptions τ(H ratio); 2.0 - 2.6 (4.0), 4.2 (3), 4.8 - 5.1 (2), 6.1 (2), 7.3 (2). The mass spectrum gave an M^{+} ion at 247 $E_{167}^{\%}$ 6.3. Found C% 63.10, M% 5.40, N% 5.80, S% 27.50, $C_{13}H_{13}NS_2$ requires C% 63.11, H% 5.27, N% 5.66, S% 25.90.

Preparation of 2-(cyclohex-2'-enyl, 3':6') dithiodibenzothiazole

a) 3:6 dibromocyclohexene was prepared by refluxing N-bromosuccinimide (146.0 g., 0.82 mol.) with cyclohexene (40.0 g., 0.45 mol.) in carbon tetrachloride (500 ml.) with a trace of benzoyl peroxide. The dibromide (37.0 g., 34%) crystallised after two days at 8.0° and was recrystallised from acetone by cooling in a dri cold-acetone bath m.p. 106° - 108° (lit.[114] 108°). N.M.R. absorptions τ(H ratio); 3.95 (1), 5.05 (1), 7.6 (2). The olefinic proton absorption at 3.95τ was a doublet, the 3:6 protons at 5.05τ were strongly irradiated, i.e., spin decoupling and the doublet reduced to a single line. If substitution had been 3:4 more than one resonance would have been expected. Found C% 30.40, H% 3.45, Br% 66.70 $C_6H_8Br_2$ required C% 30.04, H% 3.43, Br% 66.60.

b) To a stirred solution of dioxan (200 ml.) with nitrogen bubbling through sodium hydroxide (8.0 g., 0.2 mol.) was added as a 25% solution and this was followed by 2-mercaptobenzothiazole (23.4 g., 0.2 mol.). The temperature of the reaction vessel was adjusted to 40° and then 3:6 dibromocyclohexene (24.0 g., 0.1 mol.) was dissolved in

dioxan (25 ml.) and added over four hours the reaction was maintained at 40° for a further four hours and left to cool overnight. The dioxan was removed under vacuo and the products taken up in ether (200 ml.), extracted with sodium hydroxide (10%, 2 x 150 ml.) and washed with water till neutral to litmus. The ether extract was washed with ferrous sulphate (10%, 2 x 200 ml.) and again with water (2 x 100 ml.) and dried over sodium sulphate. The ether was removed under vacuo. A brown solid remained contaminated with viscous oil, the solid was recrystallised from ethanol: water (90:10) to give a white crystalline solid (20.3 g., 49%), m.p. 114° - 115°. U.V. absorption in ethanol mμ (ε max); 283 (27,100), 291 (26,800), 301 (25,200), $E^{1\%}_{327} = 1.0$. I.R. absorption 990 $cm.^{-1}$, 1310 $cm.^{-1}$ N.M.R. absorption τ(H ratio); 2.0 - 2.6 (7.7), 3.8 (2), 5.0 (2), 7.7 (4.0), the absorption at 3.8τ was a doublet. The mass spectrum gave an M^+ ion at 412, $E^{\%}_{167}$ 0.8. Found C% 58.3, H% 3.9, N% 6.7, S% 31.2 $C_{20}H_{16}N_2S_4$ requires C% 58.2, H% 3.9, N% 6.8, S% 31.1.

Preparation of 2-(α-phenylethyl)thiobenzothiazole

a) α-phenylethyl bromide (Koch-Light Ltd.) was purified by fractional distillation and the fraction taken was b.p. 78° - 81°/10 mm., N_{25}^{D} 1.5598 (lit. 78° - 82°/10 mm., 1.5595). Gas phase chromatography indicated a purity greater than 95%.

b) α-phenylethyl bromide (12.0 g., 0.065 mol.) was reacted with 2-mercaptobenzothiazole (12.5 g., 0.075 mol.) and worked up as for 2-(cyclohex-2'-enyl)thiobenzothiazole. The product (12.0 g., 70%), a dark brown viscous oil was distilled using a molecular still to give a clear brown oil b.p. 129° - 131°/0.002 mm., N_{20}^{D} 1.6716. Alkali titration indicated 2-mercaptobenzothiazole was absent. U.V. absorption in ethanol mμ (ε max); 283 (12,200), 291 (11,970), 301 (10,650, $E_{327}^{1\%}$ = 4. I.R. absorption at 1306 $cm.^{-1}$, 1000 $cm.^{-1}$ N.M.R. absorption τ(H ratio); 2.3 - 2.9 (9), 4.85 (1) quartet, 7.9 (3) doublet. The mass spectrum gave an M^{+} ion at 271 $E_{105}^{\%}$ 12.2. Found C% 66.5, 66.5; H% 4.8, 4.7; N% 5.1, 4.9; S% 23.3 $C_{15}H_{13}NS_2$ requires C% 66.5, H% 4.8, N% 5.1, S% 23.6.

Preparation of 2-(β-phenylethyl)thiobenzothiazole

a) β-phenylethyl bromide (Koch-Light) was purified by fractional distillation, and the fraction taken was b.p. 90° - 92°/11 mm., N_{25}^{D} 1.5543 (lit. 92°/11 mm., 1.5546). Gas phase chromatography indicated a purity of 95%.

b) β-phenylethyl bromide (12.0 g., 0.065 mol.) was reacted with 2-mercaptobenzothiazole (12.5 g., 0.075 mol.) as for 2-(cyclohex-2'-enyl)thiobenzothiazole and worked up in the same way. The product (11.0 g., 64%), a brown oil was distilled using a molecular still to give a brown mobile oil b.p. 68° - 71°/0.002 mm., N_{20}^{D} 1.6672. Alkali titration indicated that 2-mercaptobenzothiazole was absent. U.V. absorption in ethanol mμ (ε max); 282 (12,800), 290 (11,700), 300 (9,700), $E_{327}^{1\%}$ = 2. N.M.R. absorption τ(H ratio); 2.5 - 3.0 (9.0), 6.5 (2.0), 6.95 (2.0). The mass spectrum gave an M^{+} ion at 271, $E_{167}^{\%}$ 2.0. Found C% 66.3, H% 4.8, N% 4.8, S% 23.4 $C_{15}H_{13}NS_2$ requires C% 66.5, H% 4.8, N% 5.1, S% 23.6.

Preparation of 3-(β-cyanoethyl)benzothiazoline-2-thione

Sodium hydroxide (4.0 g., 0.1 mol.) was added as a 25% solution to a stirred solution of ethanol (100 ml.) containing 2-mercaptobenzothiazole (16.7 g., 0.1 mol.).

Nitrogen was bubbled through the reaction vessel and the temperature adjusted to 16° - 18°. Acrylonitrile (7.0 g., 0.13 mol.) was added, dropwise, over one hour then the reaction vessel was maintained at this temperature for a further seven hours and then allowed to reach room temperature overnight. The product was filtered off and recrystallised from ethanol to yield pale yellow crystals (4.4 g., 20%) m.p. 158° - 160° (lit.[52] 162° - 165°). U.V. absorption in ethanol mμ (ε max); 242 (13,800), 325 (24,600), $E^{1\%}_{281}$ = 90. I.R. absorption 1320 $cm.^{-1}$, 980 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 1.8 - 2.3 (4.1), 5.5 (2.2) triplet, 7.4 (2.0) triplet. Found C% 54.5, H% 3.4, N% 12.8, S% 29.2 $C_{10}H_8N_2S_2$ requires C% 54.5, H% 3.7, N% 12.7, S% 29.1.

Preparation of 2-(β-methoxycarbonylethyl)thiobenzothiazole

To a stirred solution of glacial acetic acid (300 ml.) and perchloric acid (4 ml. of 72%), 2-mercaptobenzothiazole (16.7 g., 0.1 mol.) was added and the reaction vessel adjusted to 60°. Methyl acrylate (8.6 g., 0.1 mol.) was added dropwise over four hours and then reaction was maintained at 60° for a further four hours and left to cool overnight. The acetic acid was removed under vacuo and the resultant product carefully neutralised with sodium hydroxide (25%) and then extracted with ether

(200 ml.). The etherial solution was washed with sodium hydroxide (10%, 2 x 100 ml.) and with water till neutral, then with ferrous sulphate (10%, 2 x 100 ml.) and finally with water (3 x 100 ml.). The ether was dried over sodium sulphate and removed under vacuo and the product dissolved in a minimum of ethanol, stored for two weeks at 0°, this gave a light brown crystalline product (12.5 g., 48%), m.p. 43° - 45°. U.V. absorption in ethanol mμ (ε max); 279 (11,750), 290 (10,400), 300 (8,350), $E^{1\%}_{327}$ = 10. I.R. absorption, potassium bromide disc, 1730 $cm.^{-1}$, 1310 $cm.^{-1}$, 995 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 2.1 - 2.8 (4.1), 6.4 (5.2), 7.3 (2) triplet. The mass spectrum gave an M^+ ion at 253, $E^{\%}_{194}$ 44. Found C% 52.48, 52.30; H% 4.40, 4.50; N% 5.32, 5.60; S% 25.88 $C_{11}H_{11}NO_2S_2$ requires C% 52.20, H% 4.36, N% 5.53, O% 12.64, S% 25.37.

Preparation of 2-(1',2' diphenylethyl)thiobenzothiazole

a) To a stirred solution of glacial acetic acid (350 ml.) and concentrated sulphuric acid (60 ml.) with nitrogen bubbling through, 2-mercaptobenzothiazole (16.7 g., 0.1 mol.) was added and then the reaction vessel was adjusted to 65°. Transstilbene (14.6 g., 0.08 mol.) was dissolved in glacial acetic acid (100 ml.) then added over a

period of four hours, heating continued for a further four hours and the reaction mixture was left to cool overnight. A precipitate formed which was filtered and washed with water (2000 ml.) and dissolved in ether (150 ml.). The etherial solution was extracted with sodium hydroxide (10%, 2 x 100 ml.), washed with water till neutral and dried over magnesium sulphate. The ether was removed under vacuo and the product dissolved in benzene (15 ml.), chromatographic separation was attempted using aluminum oxide (170 g.) and benzene as the eluant. The first 200 ml. after removal of benzene under vacuo gave a white crystalline solid (10.6 g.) which when recrystallised from aqueous ethanol m.p. 121° - 123° and mixed m.p. with trans-stilbene 123° - 124°. U.V. absorption in ethanol mμ (ε max); 228 (17,800), 294 (28,800), 306 (27,800). Found C% 93.1, H% 6.65, $C_{14}H_{12}$ requires C% 93.3, H% 6.7. The next 200 ml. gave a yellow solution which yielded a yellow solid (11.0 g.), m.p. 179° - 180°, after recrystallisation from benzene. Found C% 50.80, H% 2.55, N% 8.40, S% 38.45 $C_{14}H_8N_2S_4$ requires C% 50.6, H% 2.4, N% 8.4, S%

38.6, i.e., 2,2'-dibenzothiazoyldisulphide. A further 400 ml. gave a yellow oil (7.8 g., 27%), which would not distill or crystallise immediately. U.V. absorption in ethanol mμ ($E^{1\%}$); 249 (435), 284 (515), 292 (520), 292 (520), 302 (515). I.R. absorption 1310 $cm.^{-1}$, 997 $cm.^{-1}$. Found C% 71.8, H% 4.8, N% 4.6, S% 18.4, $C_{21}H_{17}NS_2$ requires C% 72.59, H% 4.93, N% 4.03, S% 18.46.

b) α-hydroxy 1,2 diphenylethane (Eastman-Kodak) m.p. 67° - 68° (lit. 67° - 68°). Found C% 86.4, H% 6.9 $C_{14}H_{14}O$ requires C% 84.1, H% 7.12.

Thionyl chloride (99.0 g., 0.83 mol.) was added dropwise, with caution, to α-hydroxy 1,2 diphenylethane (55.0 g., 0.27 mol.), after the addition the reactants were refluxed for four hours. The resultant product was distilled using a vigreaux column, after preliminary distillation of thionyl chloride, to give a clear colourless liquid (48.0 g., 75%), b.p. 100° - 102°/0.04 mm., N^{D}_{25} 1.5830. I.R. absorption 3090 $cm.^{-1}$, 3070 $cm.^{-1}$, 3040 $cm.^{-1}$, 2940 $cm.^{-1}$, 2920 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 2.8 (9.7), 5.0 (1.0) triplet, 6.7 (1.9) doublet. Found C% 77.85, H% 5.94, Cl% 16.55 $C_{14}H_{13}Cl$ requires C% 77.60, H%

6.04, Cl% 16.36.

c) Sodium hydroxide (3.9 g., 0.097 mol. as a 25% solution) was added to stirred isopropanol (300 ml.) with nitrogen bubbling through and this was followed by 2-mercaptobenzothiazole (16.0 g., 0.096 mol.). The temperature of the reaction vessel was adjusted to 80°. The α-chloro 1,2 diphenylethane (18.5 g., 0.086 mol.), was added dropwise over three hours and the reaction was maintained at 80° for a further three hours and left to cool overnight. The isopropanol was removed under vacuo to give a viscous liquid which was dissolved in ether (100 ml.) and extracted with sodium hydroxide (10%, 2 x 50 ml.) washed with water till neutral. The etherial solution was washed with ferrous sulphate (10%, 2 x 50 ml.) and again with water (3 x 50 ml.) and dried over magnesium sulphate. The ether was removed under vacuo and yielded a viscous oil which was taken up in a minimum of isopropanol (7 ml.) this solution was stored under nitrogen at approximately 0° for a month. A pale yellow solid crystallised (16.0 g., 76%), m.p. 53° - 55°. U.V. absorption in ethanol mμ (ε max);

283 (14,400), 294 (14,600), 301 (13,500), $E^{1\%}_{327}$ = 4. I.R. absorption, potassium bromide disc, 1310 $cm.^{-1}$, 1000 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 2.9 (14.0), 4.75 (1.0) quadruplet, 6.6 (2.0) octet. The mass spectrum gave no M^+ ion. Found C% 72.40, H% 5.06, N% 3.82, S% 18.40 $C_{12}H_{17}NS_2$ requires C% 72.59, H% 4.93, N% 4.03, S% 18.46.

Preparation of S-(1,2 diphenylethyl)dimethyldithiocarbamate

Potassium dimethyldithiocarbamate (12.9 g., 0.09 mol.) was reacted with α-chloro 1,2 diphenylethane (15.0 g., 0.069 mol.) as for 2-(1',2' diphenylethyl)thiobenzothiazole and worked up in the same way. The product was recrystallised from aqueous ethanol to yield a white crystalline solid (10.95 g., 53%), m.p. 94° - 95°. U.V. absorption in ethanol mμ (ε max); 220 (30,500), 251 (24,800), 278 (17,200). I.R. absorption potassium bromide disc, 2840 $cm.^{-1}$, 1245 $cm.^{-1}$, 1150 $cm.^{-1}$. N.M.R. absorptions τ(H ratio); 2.85 (10.2), 4.4 (0.9), 6.55 (8.0). Found C% 67.35, H% 6.21, N% 4.52, S% 21.20 $C_{17}H_{19}NS_2$ requires C% 67.77, H% 6.33, N% 4.63, S% 21.27.

Preparation of S-(1,2 diphenylethyl)methylxanthate

a) Potassium methyl xanthate was prepared by the

method of Vogel[148].

b) Potassium methyl xanthate (17.6 g., 0.12 mol.) was reacted with α-chloro 1,2 diphenylethane (20.0 g., 0.092 mol.) as for 2-(1',2' diphenylethyl)thiobenzothiazole and worked up in the same way. The product obtained was distilled using a molecular still to give a pale yellow oil (17.1 g., 64.5%), b.p. 70° - 72°/0.001 mm., N^{D}_{20} 1.6270. U.V. absorption in ethanol mμ (ε max); 225 (8,900), 287 (7,900). I.R. absorption, neat, 3060 $cm.^{-1}$, 3050 $cm.^{-1}$, 3040 $cm.^{-1}$, 2920 $cm.^{-1}$, 2850 $cm.^{-1}$. N.M.R. absorptions τ(H ratio); 2.8 (10.1), 5.05 (0.9) triplet, 6.8 (5.2). Found C% 66.40, 66.39; H% 5.62, 5.58; S% 22.10, 22.08; $C_{16}H_{16}OS_2$ requires C% 66.56, H% 5.51, O% 5.57, S% 22.26.

Preparation of S-(1,2 diphenylethyl) 0,0 dimethylphosphorodithioate

a) α-hydroxy 1,2 diphenylethane (6.0 g., 0.03 mol.) was dissolved in a stirred solution of toluene (100 ml.) through which nitrogen was bubbling. The reaction was maintained at 40°, over a period of four hours 0,0 dimethylthiothionophosphoric acid (6.0 g., 0.038 mol., 60% solution in toluene)

was added and then the reaction was left to cool overnight. The reactants were extracted with sodium hydroxide (10%, 3 x 50 ml.) washed with water till neutral and then washed with ferrous sulphate (10%, 3 x 20 ml.) and dried over magnesium sulphate. The toluene was removed under vacuo and the oil distilled using a molecular still to give a pale yellow oil (2.0 g., 19%), b.p. 72° - 76°/0.005 mm. I.R. absorption at 3400 $cm.^{-1}$(s), indicated considerable contamination by the alcohol and the N.M.R. spectrum also indicated major proportions of the alcohol. The impure product was not purified.

b) Potassium 0,0 dimethylphosphorodithioate (23.6 g., 0.12 mol.) was reacted with α-chloro 1,2 diphenylethane (20.0 g., 0.092 mol.) as for 2-(1',2' diphenylethyl)thiobenzothiazole, but was heated for forty-eight hours and then worked up in the same way. The dark coloured oil was distilled using a molecular still to give a pale brown oil (22.0 g., 71%), b.p. 87° - 92°/0.001 mm., N^{D}_{20} 1.5740. I.R. absorption, neat, 1020 $cm.^{-1}$, 815 $cm.^{-1}$, 660 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 2.7 - 3.0 (10.1), 5.1 (0.9) triplet, 6.5 (6)

doublet J = 15 cy/sec.,[69] 6.8 (2.1) doublet. Found C% 56.53, 56.61; H% 5.48, 5.77; P% 9.38, 9.31; S% 18.88, 18.91 $C_{16}H_{19}O_2PS_2$ requires C% 56.72, H% 5.67, P% 9.47, O% 9.16, S% 18.98.

Preparation of 1,4 bis-(2'-benzothiazoylthio)tetralin

a) Tetralin (44.0 g., 0.3 mol.) was added to a stirred solution of anhydrous carbon tetrachloride (800 ml.) through which nitrogen was bubbling. Finely ground N-bromosuccinimide (119.0 g., 0.6 mol.) was added together with a trace of benzoyl peroxide and the reactants were heated carefully, a vigorous reaction ensued, which was moderated by cooling and after this had subsided the reactants were refluxed for thirty minutes. The succinimide (58.0 g., calc. 59.4 g.) was filtered off and the carbon tetrachloride removed under vacuo to yield the crude dibromide, which was recrystallised from hexane to give pale yellow crystals (50.0 g., 58%), m.p. 93° - 94° (lit.[114] 94° - 95°). The bromide was stored under nitrogen at -20° as it appeared to decompose slowly at room temperature.

b) Sodium hydroxide (2.9 g., 0.12 mol. as 25% solution) was added to a stirred solution of

dioxan (100 ml.) with nitrogen bubbling through and this was followed by 2-mercaptobenzothiazole (19.6 g., 0.12 mol.). The temperature of the reaction vessel was adjusted to 35° and then 1,4 dibromotetralin (17.0 g., 0.058 mol.) was dissolved in dioxan (20 ml.) and added over five hours, then the reaction was left overnight to cool. The dioxan was removed under vacuo and the residue dissolved in ether (100 ml.), extracted with sodium hydroxide (10%, 3 x 30 ml.), and washed with water till neutral to litmus. The etherial solution was washed with ferrous sulphate (10%, 3 x 50 ml.) and water (3 x 50 ml.) and then dried over magnesium sulphate. The ether was removed under vacuo and the residue recrystallised from ethyl acetate/ethanol/water mixture to give pale yellow stumpy crystals (14.7 g., 54%), m.p. 139° - 141°. U.V. absorption in ethanol mμ (ε max); 283 (26,900), 292 (26,500), 302 (26,400); $E^{1\%}_{327}$= 10. I.R. absorption, ceasium iodide disc, 1305 $cm.^{-1}$, 985 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 2.3 (12.2), 4.0 (2.0), 6.8 (4.1). Found C% 62.15, H% 3.80, N% 6.25, S% 27.60 $C_{24}H_{18}N_2S_4$ requires C% 62.25, H% 3.89,

N% 6.05, S% 27.70.

Preparation of 1,4 bis-(S-dimethyldithiocarbamate)tetralin

Potassium dimethyldithiocarbamate (28.6 g., 0.2 mol.) was reacted with 1,4 dibromotetralin (20.0 g., 0.07 mol.) as for 1,4 bis-(2'-benzothiazoylthio)tetralin and worked up in the same way. The product was recrystallised from isopropanol to give white flakey crystals (12.2 g., 47%), m.p. 218° - 220°. U.V. absorption in ethanol mμ (ε max); 225 (58,700), 253 (50,400), 279 (34,200). I.R. absorption, potassium bromide disc. 2860 $cm.^{-1}$, 1250 $cm.^{-1}$, 1150 $cm.^{-1}$. N.M.R. absorption τ(H ratio); 2.5 - 2.7 (4.1), 4.5 (2.0), 6.5 (12.0), 7.8 (4.2). Found C% 51.71, H% 5.82, N% 7.40, S% 34.31 $C_{16}H_{22}N_2S_4$ requires C% 51.84, H% 5.97, N% 7.55, S% 34.64.

Preparation of 1,4 bis-(S-methylxanthate)tetralin

Potassium methyl xanthate (29.2 g., 0.2 mol.) was reacted with 1,4 dibromotetralin (20.0 g., 0.07 mol.) as for 1,4 bis-(2'-benzothiazoylthio)tetralin and worked up in the same way. The product, a very viscous oil which was distilled using a molecular still to give a yellow viscous oil (16.1 g., 67%), b.p. 128° - 132°/0.001 mm., N^{D}_{20} 1.6280. U.V. absorption in ethanol mμ (ε max); 225 (17,800), 284 (14,700). I.R. absorption, neat, 2860 $cm.^{-1}$,

1230 cm.$^{-1}$, 1150 cm.$^{-1}$. N.M.R. absorption τ(H ratio); 2.85 (3.9), 4.90 (1.9), 5.95 (6.0), 7.90 (4.1). Found C% 48.59, H% 4.82, S% 37.61 $C_{14}H_{16}O_2S_4$ requires C% 48.82, H% 4.68, O% 9.28, S% 37.22

Preparation of 1,4 bis-(S-0,0 dimethylphosphorodithioate) tetralin

Potassium 0,0 dimethylphosphorodithioate (39.2 g., 0.2 mol.) was reacted with 1,4 dibromotetralin (20.0 g., 0.07 mol.) as for 1,4 bis-(2'-benzothiazoylthio) tetralin and worked up in the same way but was reacted for forty-eight hours. The product was recrystallised from iso-propanol, the crystallisation was facilitated by vigorous scratching and seeding with a small piece of dri-cold, this gave a white solid (16.0 g., 52%), m.p. 76° - 78°. I.R. absorption potassium bromide disc, 1015 cm.$^{-1}$, 810 cm.$^{-1}$, 660 cm.$^{-1}$. N.M.R. absorption τ(H ratio); 2.75 (3.9), 5.3 (2.0) broad doublet, J=15.6 cy/sec; 6.3 (12.2) doublet, J=15.6 cy/sec; 7.8 (4.0). Found C% 37.71, H% 4.78, P% 13.81, S% 28.47 $C_{14}H_{22}O_4P_2S_4$ requires C% 37.90, H% 4.96, O% 14.41, P% 13.90, S% 28.83.

Synthetic materials and other compounds for ancillary studies

Pure samples of 2-mercaptobenzothiazole (Thiotax); N-tertbutyl-benzothiazole-2-sulphenamide (Santocure N.S.);

2-(Morpholinothiobenzothiazole (Santocure MOR); and 2,2' Dithiobisbenzothiazole (Thiofide) were obtained from the Monsanto Company. N.N'-dicyclohexylbenzothiazole-2-sulphenamide (Vulkacit DZ) was obtained from Farbenfabriken Bayer AG. Potassium 0,0 dimethylphosphorodithioate, and 0,0 dimethylthiothionophosphoric acid were obtained from Robinson Brothers (West Bromwich). 2-methylthiobenzothiazole, 3-methylbenzothiazoline-2-thione, 2-isopropylthiobenzothiazole, 2-allylthiobenzothiazole were obtained from Dr. C. G. Moore, The Natural Rubber Producers Research Association.

Decomposition and Isomerisation Studies

Alkali extraction procedure for 2-mercaptobenzothiazole

Samples of 2-mercaptobenzothiazole were dissolved in chloroform (50 ml.) and extracted, by vigourous shaking, for five minutes with sodium hydroxide (10%, 2 x 25 ml.) and then washed with water (3 x 20 mls.). The extracts and washings were retained, acidified with concentrated hydrochloric acid, and then left overnight at approximately 8°. The precipitated 2-mercaptobenzothiazole was filtered off (sintered glass cruicible) washed with water (3 x 50 ml.) and dried to constant weight of 110° - 120°. The results in Tables 57 and 58 indicate the

level of accuracy attainable for the determination of 2-mercaptobenzothiazole by the prior procedure.

TABLE 57

ESTIMATION OF 2-MERCAPTOBENZOTHIAZOLE

2-mercaptobenzo-thiazole (g)	% Recovered	2-mercaptobenzo-thiazole (g)	% Recovered
0.1069	96.4	0.80666	98.4
0.1512	97.1	1.7334	99.1
0.1902	96.8	2.6718	99.6
0.4022	97.8		

TABLE 58

ESTIMATION OF 2-MERCAPTOBENZOTHIAZOLE IN MIXTURES

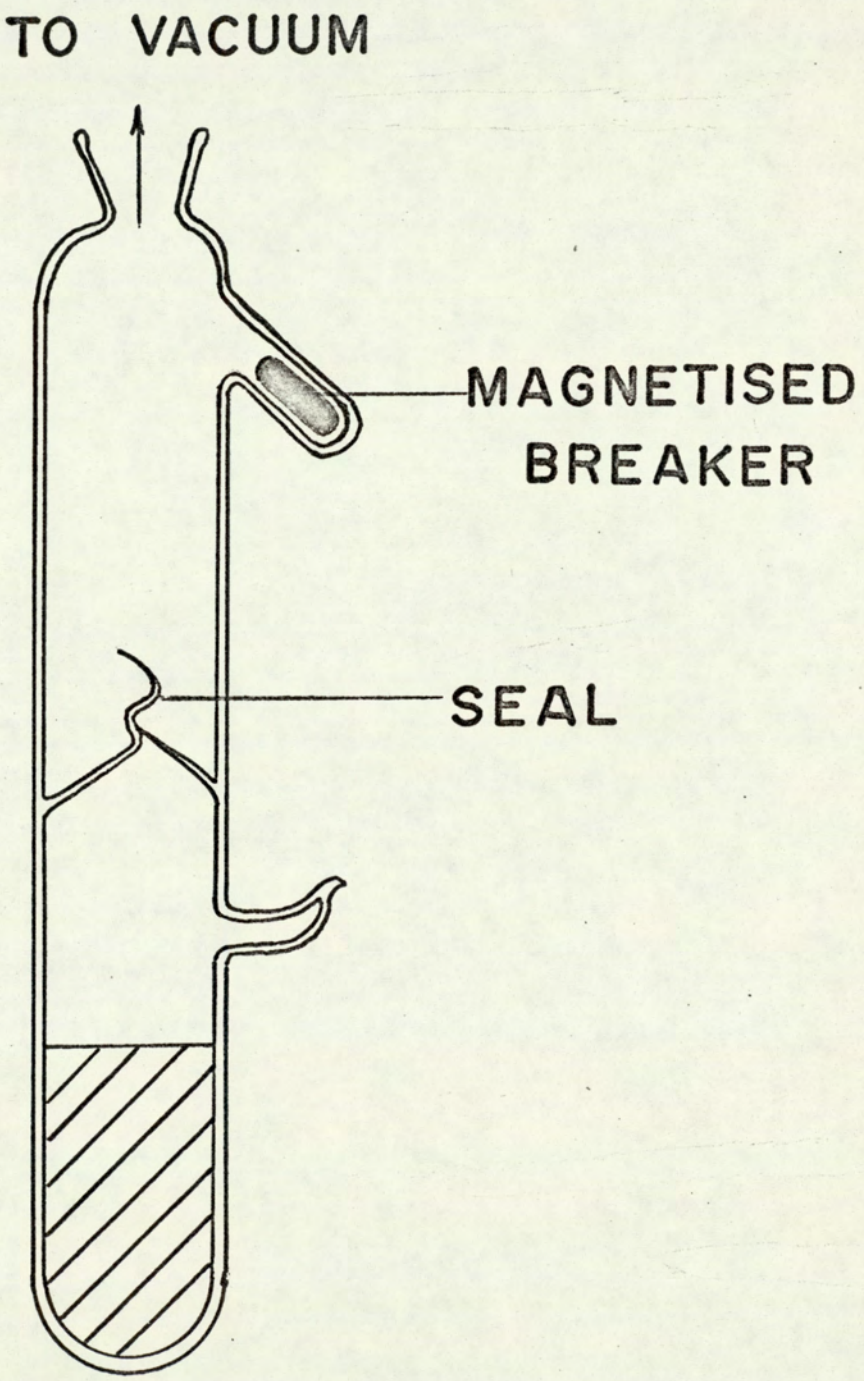
2-mercapto-benzo-thiazole(g)	Naphthalene(g)	2-methyl-thiobenzo-thiazole(g)	% Recovered of 2-mercapto-benzothiazole
0.1210	0.6106	0.7121	98.2
0.1560	0.8108	0.4121	99.1
0.3512	0.3781	0.3106	101.1
0.9100	0.1671	0.2210	101.8
2.3411	0.8171	0.1610	100.8

Thermal decomposition and isomerisation of 2-(cyclohex-2'-enyl)thiobenzothiazole

a) The sulphide (2.89 g., 0.0117 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus shown in Figure II. This was connected to a

FIGURE 2

EVAPOURATIVE DISTILLATION APPARATUS



weighed tube, then the apparatus was evacuated and isolated from the line. After the seal was broken the volatiles were transferred to the weighed tube by cooling in liquid nitrogen. Evaporative distillation gave a colourless liquid (0.27 g.), N_{20}^{D} 1.4812. The I.R. absorptions indicated the presence of an aromatic and alkyl component. Gas phase chromatography (column-squalane 10% on celite, at 20°, nitrogen carrier pressure 150 mm. of Hg.) indicated three components which were identified by reference to known materials.

Peak	Retention Index	Reference	Retention Index
1	1069, 1067	Benzene	1065, 1067
2	1126, 1124	cyclo-hexa-1:3-diene	1123, 1128
3	1201, 1198	cyclo-hexene	1196, 1198

The composition indicated was benzene (59%), cyclohexa-1:3-diene (5%), cyclohexene (36%). The non-volatile products were dissolved in chloroform (50 ml.) and extracted with sodium hydroxide (10%, 3 x 25 ml.). The extracts were retained and neutralised with hydrochloric acid

and the 2-mercaptobenzothiazole (0.58 g., 0.0035 mol.) estimated gravimetrically, m.p. 175° - 177°, recrystallised from benzene m.p. 177° - 178°, mixed m.p. 178° - 179°. The chloroform solution was washed with water till neutral and dried over magnesium sulphate and then the chloroform was removed under vacuo. The alkali insoluble product (1.96 g.) was analysed using U.V. spectrometry. The composition indicated was 3-(cyclohex-2'-enyl)benzothiazoline-2-thione (59%, $E^{1\%}_{326}$ = 621), 2-(cyclohex-2'-enyl)thiobenzothiazole (32%, $E^{1\%}_{281}$ = 236) and the remainder was unidentified.

b) A portion of the alkali insoluble mixture (1.01 g., c.a. 0.0041 mol.) from the first decomposition was heated at 200° ±1° for forty-eight hours. Evaporative distillation gave a colourless liquid (0.08 g.), N^{D}_{20} 1.4809. Gas phase chromatography indicated the composition to be benzene (55%), cyclohexa-1:3-diene (5%) and cyclohexene (39%).

Peak	Retention Index		Reference	Retention Index	
1	1073,	1067	Benzene	1065,	1067
2	1128,	1123	cyclo-hexa-1:3-diene	1123,	1128
3	1200,	1196	cyclo-hexene	1196,	1198

The non-volatile products were worked up using sodium hydroxide extraction and then a gravimetric determination was used to estimate 2-mercaptobenzothiazole (0.23 g., 0.0014 mol.), m.p. 174° - 176°, a small amount was recrystallised from benzene m.p. 178° - 179°, mixed m.p. 178° - 179°. The alkali insoluble product (0.65 g.) was analysed using U.V. spectrometry. The composition indicated was 3-(cyclohex-2'-enyl)benzothiazoline-2-thione (44%, $E^{1\%}_{327} = 480$), 2-(cyclohex-2'-enyl)thiobenzothiazole (37%, $E^{1\%}_{281} = 240$); the remainder being unidentified polymeric hydrocarbon.

Thermal decomposition and isomerisation of 3-(cyclohex-2'-enyl)benzothiazoline-2-thione

a) The thiazoline (2.99 g., 0.012 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus shown in Figure II. This was connected

to a weighed tube then the apparatus was evacuated and isolated from the line, after breaking the seal the volatiles were transferred by cooling the weighed tube in liquid nitrogen. Evaporative distillation gave a colourless liquid (0.31 g.), N^{D}_{20} 1.4802. The I.R. spectra indicated the presence of an aromatic and alkyl components. Gas phase chromatography (column-squalane 10% on celite, at 20°, nitrogen carrier pressure 150 mm. of Hg.) indicated three components which were identified by reference to known materials.

Peak	Retention Index	Reference	Retention Index
1	1070, 1069	Benzene	1065, 1067
2	1123, 1127	Cyclo-hexa-1:3-diene	1125, 1123
3	1200, 1210	Cyclo-hexene	1198, 1202

The composition was benzene (60%), cyclohexa-1:3-diene (4%), cyclohexene (37%). The non-volatile products were dissolved in chloroform (50 ml.) and extracted with sodium hydroxide (10%, 3 x 25 ml.). The extracts were retained and neutralised with hydrochloric acid and the

2-mercaptobenzothiazole (0.83 g., 0.0049 mol.) estimated gravimetrically, m.p. 174° - 175° recrystallised from benzene m.p. 178° - 179°, mixed m.p. 178° - 179°. The chloroform solution was washed well with water till neutral and dried over magnesium sulphate, the chloroform was removed under vacuo. The alkali insoluble product (1.76 g.) was analysed using U.V. spectrometry and the composition was 3-(cyclohex-2'-enyl)benzothiazoline-2-thione (60.6%, $E^{1\%}_{327}$ = 625), 2-(cyclohex-2'-enyl)thiobenzothiazole (22.6%, $E^{1\%}_{281}$ = 194) and the remainder being unidentified hydrocarbon polymer.

b) A portion of the alkali insoluble mixture (1.80 g., ca. 0.0073 mol.) from the first decomposition was heated at 200° ±1° for forty-eight hours. Evaporative distillation gave a clear colourless liquid (0.13 g.), N^{D}_{20} 1.4795. Gas phase chromatography indicated the composition to be benzene (56%), cyclohexa-1:3-diene (6%), cyclohexene (39%).

Peak	Retention Index		Reference	Retention Index	
1	1071,	1065	Benzene	1066,	1062
2	1120,	1127	Cyclo-hexa-1:3-diene	1123,	1127
3	1196,	1201	Cyclo-hexene	1198,	1192

The non-volatile products were worked up using the sodium hydroxide extraction and then a gravimetric determination was used to estimate 2-mercaptobenzothiazole (0.46 g., 0.0026 mol.) m.p. 175° - 176°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. The alkali insoluble product (1.20 g.) was analysed by U.V. spectrometry to give the following composition: 3-(cyclohexa-2'-enyl)benzothiazoline-2-thione (51%, $E^{1\%}_{326} = 540$), 2-(cyclohexa-2'-enyl)thiobenzothiazole (26%, $E^{1\%}_{281} = 220$), the remainder being unidentified.

Thermal decomposition and isomerisation of 2-(hexa-2':5-diene-1'-yl)thiobenzothiazole

The sulphide (4.20 g., 0.017 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus previously described. Evaporative distillation gave a colourless liquid (0.26 g.), N^{D}_{20} 1.4478. The I.R. absorptions

indicated the presence of alkene groups while the U.V. in ethanol mμ (ε max); 257 (28,000), was indicative of 1,3,5 hexatriene, i.e., 258 (35,000). Gas phase chromatography (column-squalane 10% on celite, at 25°, nitrogen carrier gas pressure 150 mm. of Hg.) indicated three components. The major peak (ca. 80%) was reinforced when an authentic sample of 1,3,5 hexatriene was mixed with a portion of the distillate. The other peaks were not investigated. The non-volatile products were worked up in the usual way to give 2-mercaptobenzothiazole (0.97 g., 0.0058 mol.), m.p. 173° - 175°, a small amount was recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed, the I.R. was identical with that of pure 2-mercaptobenzothiazole. The alkali insoluble-product product (2.89 g.) was analysed by U.V. spectrometry and the composition indicated was 3-(hexa-1':3'-dien-3'-yl)benzothiazoline-2-thione (55%, $E^{1\%}_{327}$ = 520), 2-(hexa-2':5'-dien-1'-yl)thiobenzothiazole (35%, $E^{1\%}_{281}$ = 150) the remainder being unidentified polymeric residues.

Decomposition and Isomerisation of 2-(cyclohex-2'-enyl, 3', 6')dithiobenzothiazole

The sulphide (3.12 g., 0.0075 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus previously described. Evaporative distillation gave a colourless

liquid (0.18 g.), N_{20}^{D} 1.5014, which had an aromatic smell. The I.R. spectra indicated an aromatic hydrocarbon, U.V. absorption in ethanol mμ (ε max); 204 (7,200), 254 (199). Gas phase chromatography (column-silicone S.E. 30 (20%) on chromasorb G, at 30°, nitrogen carrier gas pressure 300 mm. of Hg.) indicated a single substance, this peak was reinforced by an authentic sample of benzene. A small sample of the distillate was nitrated to give a crystalline material m.p. 88° - 89° (lit. benzene 89° - 90°). The non-volatile products were worked up in the usual way to give 2-mercaptobenzothiazole (0.81 g., 0.0048 mol.), m.p. 176° - 178°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. The alkali insoluble product (2.10 g.) was analysed by U.V. spectrometry and the following composition was indicated 3-(cyclohex-2'-enyl-3',6')dibenzothiazoline-2-thione (ca. 73%, $E_{281}^{1\%}$ = 1220), 2-(cyclohex-2'-enyl,3',6')dithiobenzothiazole (27%, $E_{281}^{1\%}$ = 177). The isomers could not be separated so that only the absoprtion at 281 mμ could be used for estimation and the % composition for the benzothiazoline-2-thione was obtained by deduction.

Thermal decomposition and isomerisation of 2-(α-phenylethyl)thiobenzothiazole

The sulphide (4.01 g., 0.0148 mol.) was heated at

200° ±1° for forty-eight hours in the apparatus previously described. Evaporative distillation gave a clear liquid (0.11 g.), N^{D}_{20} 1.5191. The I.R. spectra indicated an aromatic hydrocarbon, U.V. in ethanol mμ (ε max); 247 (6,300), 281 (322). Gas phase chromatography (column-squalane 10% on celite, at 50°, nitrogen carrier gas pressure 300 mm. of Hg.) indicated three peaks, the major peak (60%) was reinforced by an authentic sample of styrene. The other peaks were not investigated. The non-volatile products were worked up in the usual way to give 2-mercaptobenzothiazole (0.74 g., 0.0044 mol.), m.p. 172° - 174°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. The alkali insoluble product (3.09 g.) was contaminated with dark residues and U.V. analysis was not attempted due to the lack of maximum at 281 and 327, probably due to the background of the polymeric residues, $E^{1\%}_{327} = 720$.

Thermal decomposition and isomerisation of 2-(β-phenyl-ethyl)thiobenzothiazole

The sulphide (3.20 g., 0.0118 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus previously described. Evaporative distillation gave a clear liquid (0.07 g.), N^{D}_{20} 1.5231. U.V. in ethanol mμ (ε max); 247 (6,400), 281 (350). Gas phase chromatography (column as

for 2-(α-phenylethyl)thiobenzothiazole indicated four components, the major component (55%) was reinforced by an authentic sample of styrene. The other components were not identified. The non-volatile products were worked up in the usual way to give 2-mercaptobenzothiazole (0.28 g., 0.00165 mol.), m.p. 174° - 176°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. The alkali insoluble product (2.75 g.) was considerably darkened with unidentified polymeric residues rendering U.V. analysis inaccurate, $E^{1\%}_{327} = 700$.

Thermal decomposition and isomerisation of 3-(β-cyanoethyl)benzothiazoline-2-thione

The thiazoline (1.30 g., 0.0059 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus previously described. Evaporative distillation gave a clear liquid (0.022 g.), N^{D}_{20} 1.4210. The I.R. spectra indicated a vinyl compound. Gas phase chromatography [column-as for 2-(α-phenylethyl)thiobenzothiazole] indicated three components, the major component (60%) was reinforced by an authentic sample of acrylonitrile, the other components were not identified. The non-volatile products were worked up in the usual way to give 2-mercaptobenzothiazole (0.138 g., 0.00082 mol.), m.p. 174° - 177°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed.

The alkali insoluble product (1.10 g.) was darkened making U.V. analysis unreliable, $E^{1\%}_{281}$ = 135, the polymeric residues were not identified.

Thermal decomposition and isomerisation of 2-(β-methoxycarbonylethyl)thiobenzothiazole

The sulphide (3.50 g., 0.0139 mol.) was heated at 200° ±1° for forty-eight hours in the apparatus previously described. Evaporative distillation gave a colourless liquid (0.11 g.), N^{D}_{20} 1.3871. The I.R. spectra indicated a vinyl and carbonyl group. Gas phase chromatography [column as for 2-(α-phenylethyl)thiobenzothiazole] indicated two components the major component (70%) was reinforced by mixing an authentic sample of methyl acrylate with the distillate. The other component was not identified. The non-volatile component was worked up in the usual way, to give 2-mercaptobenzothiazole (0.37 g., 0.0022 mol.), m.p. 175° - 177°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. The alkali insoluble product (2.92 g.) was slightly darkened but was analysed by U.V.; the composition indicated was 3-(β-methoxycarbonylethyl)benzothiazoline-2-thione (ca. 36%, $E^{1\%}_{327}$ = 340) this was obtained by subtraction and must include polymeric residues as the isomers were not separated, 2-(β-methoxycarbonylethyl)thiobenzothiazole

(64%, $E^{1\%}_{279}$ = 300).

Thermal decomposition of 2-(1',2' diphenylethyl)thiobenzothiazole

The sulphide (3.80 g., 0.011 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. Evaporative distillation yielded no volatile products. The non-volatile products were worked up in the usual way to give 2-mercaptobenzothiazole (1.75 g., 0.0105 mol.), m.p. 176° - 177°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. The slightly discoloured alkali insoluble product (1.95 g.) was analysed by U.V. in ethanol mμ (ε max); 228 (17,800), 294 (28,800), 306 (27,800), i.e., indicative of trans-stilbene, greater than 95%. The ethanol was removed under vacuo, a white solid crystallised, m.p. 123° - 124°, mixed m.p. with trans-stilbene undepressed. Found C% 93.10, H% 6.65, $C_{14}H_{12}$ requires C% 93.3, H% 6.70.

Thermal decomposition of 2-(1',2' diphenylethyl)thiobenzothiazole in cyclohexene

Cyclohexene was distilled from sodium before use b.p. 82° - 83°/762 mm., N^{D}_{20} 1.4470 (lit. 83°, 1.4450). Cyclohexene (8.20 g. , 0.1 mol.) and 2-(1',2' diphenylethyl)thiobenzothiazole (3.47 g., 0.01 mol.) were heated at ca. 0.005 mm., in a thick walled tube at 200° ±1°

for twenty-four hours. After removal of the olefin (8.10 g.) the product (3.51 g.) was dissolved in chloroform (100 ml.) and extracted with sodium hydroxide (10%, 3 x 50 ml.), worked up in the usual way to give 2-mercaptobenzothiazole (1.62 g., 0.0097 mol.), m.p. 175° - 176°, recrystallised from benzene m.p. 178° - 179°, mixed m.p. undepressed. Chromatographic separation of the residue (1.80 g.) with heptane/ether (90:10 by volume) on silica (150 g.) was attempted. The first 200 ml. gave a white crystalline solid (1.75 g.), m.p. 122° - 124°, U.V. in ethanol, mμ (ε max); 228 (17,800), 294 (28,800), 306 (27,800), i.e., trans-stilbene. The column was stripped with benzene (400 ml.) the benzene was removed under vacuo and then the flask was washed with hot ethanol and the ethanol subjected to U.V. analysis, no absorptions characteristic of 2-alkyl thiobenzothiazoles could be detected.

Thermal decomposition of S-(1,2 diphenylethyl)dimethyldithiocarbamate

The dithiocarbamate (3.10 g., 0.013 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. The normal procedure was followed but in the weighed tube, ethanol (2.50 g.) was added and then the volatiles (1.23 g.) were transferred as before

using liquid nitrogen. The volatiles were stored at -28° until analysed.* Gas phase chromatography [column-silicone S.E. 30 (20%) on chromasorb G, at 20°, nitrogen carrier gas pressure 75 mm. of Hg.] indicated two major components apart from ethanol. Comparison with a standard solution of carbon disulphide and dimethylamine in ethanol indicated the major peaks to be carbon disulphide and dimethylamine. The components were reinforced when the volatiles were mixed with a small amount of the standard solution. The relative composition of the volatiles indicated was carbon disulphide (61%), dimethylamine (32%), and a small peak (7%) which was unidentified. The non-volatile product (1.84 g.) was analysed by U.V. in ethanol mμ (ε max); 228 (17,600), 294 (28,900), 306 (27,500) and then worked up as before to give white flaky crystals, m.p. 123° - 124°, mixed m.p. with trans-stilbene undepressed. The I.R. spectrum was identical with that of trans-stilbene.

*In a preliminary experiment the amine vapourised while analysis was conducted at room temperature.

Thermal decomposition of S-(1,2 diphenylethyl)methyl-xanthate

The xanthate (3.60 g., 0.0125 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. Evaporative distillation gave a pale yellow liquid (1.29 g.), the I.R. spectra indicated a hydroxy compound. Gas phase chromatography [column - as for S-(1,2 diphenylethyl)dimethyldithiocarbamate] indicated three components, the two major components were identified as methyl alcohol (28%), and carbon disulphide (62%) by reference to authentic compounds, while the third component was not identified. The non-volatile product (2.27 g.) was analysed by U.V. in ethanol mμ (ε max); 228 (17,400), 294 (28,750), 306 (27,500) and the solid obtained as usual, m.p. 123° - 124°, mixed m.p. with trans-stilbene 122.5° - 124°.

Thermal decomposition of S-(1,2 diphenylethyl) 0,0 di-methylphosphorodithioate

The phosphorodithioate (2.91 g., 0.0086 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. Evaporative distillation gave a clear liquid (0.71 g.), the I.R. of which indicated a dithiophosphoric acid, i.e., a strong P=O absorption. Gas phase chromatography [column-silicone S.E. 30 (20%) on Chromasorb G, at 160°, nitrogen carrier gas pressure

300 mm. of Hg.] indicated two components, the major component was identified by reference to an authentic compound as 0,0 dimethylthiothionophosphoric acid (60%), i.e., peak reinforcement while the second component was not identified. The non-volatile product (2.15 g.) was washed well with ethanol, leaving a white polymeric residue (0.60 g.). The ethanol was analysed by U.V. mμ (ε max); 228 (17,500), 294 (28,700), 306 (27,200) and worked up as usual to give a white crystalline solid, m.p. 122° - 124°, mixed m.p. undepressed. The I.R. spectra was identical with that of trans-stilbene. Found C% 93.2, H% 6.50 $C_{14}H_{12}$ requires C% 93.30, H% 6.70.

Thermal decomposition of 1,4 bis-(2'-benzothiazoylthio) tetralin

The sulphide (4.62 g., 0.01 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus described in Figure II. Evaporative distillation yielded no volatile products. Extraction with sodium hydroxide gave 2-mercaptobenzothiazole (3.30 g., 0.0198 mol.), m.p. 177° - 178°, recrystallised from benzene, m.p. 178° - 179°, mixed m.p. undepressed. The slightly discoloured alkali insoluble product (1.27 g.) was dissolved in ethanol and analysed by U.V. mμ (ε max); 220 (100,000), 275 (5,700) some of the product was reclaimed m.p. 79° -

80°, mixed m.p. with naphthalene 79° - 80°. The picrate derivative was prepared, m.p. 150° - 151° (lit. 150°). Found C% 93.40, H% 6.53 $C_{10}H_8$ requires C% 93.71, H% 6.29.

Thermal decomposition of 1,4 bis-(2'-benzothiazoylthio) tetralin in cyclohexene

Cyclohexene (8.4 g., 0.102 mol.) and 1,4 bis-(2'-benzothiazoylthio)tetralin (4.6 g., 0.00995 mol.) were heated at ca. 0.005 mm., in a thick walled tube at 200° ±1° for twenty-four hours. After the removal of the olefin (8.3 g.) the product (4.6 g.) was dissolved in chloroform (100 ml.) and extracted with sodium hydroxide (10%, 3 x 5 ml.), worked up in the usual way to give 2-mercaptobenzothiazole (3.30 g., 0.0198 mol.), m.p. 177° - 178°, mixed m.p. undepressed. Chromatographic separation of the residue (1.25 g.) with heptane/benzene (70:30 by volume) on silica (150 g.) was attempted. The first 100 ml. gave a white crystalline solid (1.20 g.), m.p. 79° - 80° mixed m.p. undepressed U.V. in ethanol mμ (ε max); 220 (99,990), 275 (5,600), picrate derivative m.p. 150° - 151° (lit. 150°), i.e., naphthalene. The column was stripped with benzene (400 ml.), this was removed under vacuo then the flask washed with warm ethanol and the solution analysed by U.V., no characteristic absorption of 2-alkylthiobenzothiazoles could be detected.

Thermal decomposition of 1,4 bis-(S-dimethyldithiocarbamate)tetralin

The dithiocarbamate (3.70 g., 0.01 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. The normal procedure was followed but in the weighed tube, ethanol (2.70 g.) was added, then the volatiles (2.35 g.) were transferred as before using liquid nitrogen. The volatiles were stored at -28° until analysed. Gas phase chromatography [as for S-(1,2 diphenylethyl)dimethyldithiocarbamate] indicated two major components carbon disulphide (59%) and dimethylamine (29%), the other two components (ca. 12%) were not identified. The discoloured non-volatile product (1.30 g.) was dissolved in ethanol and analysed by U.V. mμ (ε max); 220 (99,870), 275 (5,360) some of the product was reclaimed in the usual way, m.p. 79° - 80°, mixed m.p. with naphthalene 79° - 80°. The I.R. spectrum was identical with that of naphthalene. The picrate derivative was prepared, m.p. 148° - 149° (lit. 150°).

Thermal decomposition of 1,4 bis-(S-methylxanthate) tetralin

The xanthate (3.44 g., 0.01 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. Evaporative distillation gave a pale yellow liquid (2.09 g.), the I.R. spectrum of which, indicated a

hydroxy compound and also had strong absoprtions at 2350 $cm.^{-1}$, 2100 $cm.^{-1}$. Gas phase chromatography [as for S-(1,2 diphenylethyl)methylxanthate] indicated two major components, carbon disulphide (60%), methanol (27%) which were identified by peak reinforcement. The other components (ca. 13%) were not identified. The non-volatile product (1.31 g.) was dissolved in ethanol U.V., mμ (ε max); 220 (100,720), 275 (5,810) and the product was reclaimed to give a white crystalline solid, m.p. 79° - 80°, mixed m.p. with naphthalene undepressed. Found C% 93.30, H% 6.27 $C_{10}H_8$ requires C% 93.71, H% 6.29. The picrate derivative was prepared m.p. 148° - 149° (lit. 150°).

Thermal decompoisiton of 1,4 bis-(S-0,0 dimethylphosphorodithioate)tetralin

The phosphorodithioate (4.44 g., 0.01 mol.) was heated at 200° ±1° for twenty-four hours in the apparatus previously described. Evaporative distillation gave a clear liquid (1.08 g.), the I.R. spectra of which indicated a dithiophosphoric acid, i.e., a strong P=O absorption. Gas phase chromatography (as for S-(1,2 diphenylethyl) 0,0 dimethylphosphorodithioate indicated two major components, the major component was identified as 0,0 dimethylthiothionophosphoric acid (58%) by

reference to authentic materials and peak reinforcement, the second peak was not identified. The non-volatile product (3.28 g.) was washed with ethanol leaving a white polymeric residue (2.02 g.). The ethanol solution was analysed by U.V. mμ (ε max); 220 (100,190), 275 (5,500) part of the product was reclaimed m.p. 77° - 78°, recrystallised 79° - 80°, mixed m.p. with naphthalene undepressed. Found C% 93.41, H% 6.61 $C_{10}H_8$ requires C% 93.71, H% 6.29. The picrate derivative was prepared m.p. 149° - 150° (lit. 150°).

Kinetic methods and procedures

Analytical method for the kinetics of decomposition of 1,4 bis-substituted tetralins

Separation of the decomposition products was accomplished by absorption chromatography on silica (Whatman Chromedia S.G. 31, particle size 100-200 B.S.S.). The columns were 160 mm. by 13 mm. and approximately 100 g. of silica was used for each determination, this was washed with 200 ml. of the eluting solvent, i.e., benzene/heptane (30:70 by volume) before each determination. The sample was dissolved in 10 ml. of the solvent and transferred quantitatively to the column and eluted with benzene/heptane (30:70), the flow rate was on average 8 ml. per min. The first 75 ml. contained

naphthalene which was transferred to a 250 ml. volumetric flask made up and analysed after the appropriate dilution by U.V. spectrometry with the aid of the calibration determinations. The 1,4 bis-substituted tetralins were removed from the column by eluting with ethanol (300 ml.), the ethanol was carefully removed and the sample weighed and constitution checked by U.V. and I.R. In kinetic runs only naphthalene was estimated, the substituted derivatives and decomposition products remained on the column, with the exception of methanol.

TABLE 59

CALIBRATION OF NAPHTHALENE AT 279 mμ
USING BENZENE/HEPTANE (30:70)

Conc. in moles per cc. x 10^{-8}	Abs.	Conc. in moles per cc. x 10^{-8}	Abs.
3.72	0.16	14.86	0.59
7.44	0.34	18.58	0.69
11.15	0.46	22.29	0.73

TABLE 60

ANALYSIS OF STANDARD MIXTURES OF 1,4-BIS-SUBSTITUTED TETRALINS AND NAPHTHALENE

0,0 dimethylphosphorodithioate (moles)			Naphthalene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-5}$	Found $x10^{-5}$	Recovered (%)
1.25	1.11	88.8	1.02	0.99	97.1
1.15	1.11	96.5	4.76	4.50	95.2
1.35	1.20	89.0	16.90	16.20	95.8
1.19	1.01	86.1	30.10	30.10	100.0
Methylxanthate (moles)			Naphthalene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-5}$	Found $x10^{-5}$	Recovered (%)
1.40	1.38	98.5	1.00	0.97	97.0
1.60	1.56	97.5	4.60	4.40	95.8
1.50	1.42	94.6	30.00	29.00	96.7
1.71	1.68	98.1	49.00	46.00	94.0
Dimethyldithiocarbamate (moles)			Naphthalene (moles)		
Added $x10^{-5}$	Found $x10^{-5}$	Recovered (%)	Added $x10^{-5}$	Found $x10^{-5}$	Recovered (%)
3.81	3.60	94.5	4.68	4.52	96.6
4.00	3.80	95.2	29.70	28.90	96.7
2.70	2.60	96.0	35.20	35.00	99.5
1.84	1.79	97.0	70.40	70.00	99.6
2-thiobenzothiazole (moles)			Naphthalene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-5}$	Found $x10^{-5}$	Recovered (%)
1.20	1.14	95.0	1.10	1.06	96.1
1.62	1.50	92.5	5.60	5.44	97.0
1.51	1.41	93.5	13.10	12.80	98.0
1.41	1.32	93.5	62.10	61.00	98.2

Analytical method for the kinetics of decomposition of mono-substituted 1,2 diphenylethanes

The analysis procedure adopted was the same as for the 1,4 bis-substituted tetralins but the eluting solvent was changed to heptane/ether (90:10 by volume). Cis- and trans-stilbene are eluted in the first 150 ml. and were analysed as usual. The analysis was based on the absorption of trans-stilbene as this was the product of decomposition usually greater than 95% and therefore the procedure was calibrated with trans-stilbene. Each determination was checked for the presence of cis-stilbene using the absorbence ratio method, taking the isoabsorptive point as 266 mμ, the calibration data are included in Tables 61 and 62.

TABLE 61

CALIBRATION OF TRANS-STILBENE AT 295 mμ
USING HEPTANE/ETHER (90:10)

Conc. in moles per cc. x 10^{-11}	Abs.	Conc. in moles per cc. x 10^{-11}	Abs.
4.14	0.12	19.3	0.56
7.25	0.21	21.4	0.62
12.40	0.36		

TABLE 62

ABSORBENCE RATIO CALIBRATION FOR
CIS- AND TRANS-STILBENE

Absorbence Ratio $\frac{A296}{A266}$	% Cis-Stilbene	Absorbence Ratio $\frac{A296}{A266}$	% Cis-Stilbene
2.02	0	1.50	46.3
1.85	11.1	1.43	55.9
1.76	22.0	1.04	85.4
1.57	40.0	0.82	100.0

Purification of dioxan for kinetics

Dioxan was refluxed for eight hours with 10% by volume of a solution consisting of 14 ml. of concentrated hydrochloric acid in a 100 ml. of water, nitrogen being bubbled through to remove acetaldehyde. After cooling potassium hydroxide pellets were added until the aqueous layer was saturated, it was then removed. The dioxan was dried by standing over potassium hydroxide pellets and then refluxed with sodium, and then distilled from sodium and stored under nitrogen and kept away from light.

Procedure for kinetics

Kinetics were carried out in constant temperature baths controlled within ±0.2°. Pyrex tubes 20 mm. i.d., 20 cm. in length were drawn out at ca. 14 cm. for

TABLE 63

ANALYSIS OF STANDARD MIXTURES OF MONO-SUBSTITUTED 1,2 DIPHENYLETHANES AND TRANS-STILBENE

0,0 dimethylphosphorodithioate (moles)			Trans-stilbene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-6}$	Found $x10^{-6}$	Recovered (%)
1.35	1.20	89.1	7.91	7.60	96.0
1.48	1.35	91.2	5.76	5.57	96.6
1.21	1.10	91.0	2.69	2.61	96.8
1.57	1.46	93.0	1.81	1.68	93.0
Methylxanthate (moles)			Trans-stilbene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-6}$	Found $x10^{-6}$	Recovered (%)
1.32	1.21	92.0	8.62	8.30	96.2
1.18	1.04	88.1	6.13	5.94	97.1
1.24	1.12	90.4	4.28	4.30	100.7
1.88	1.73	91.9	1.03	0.97	94.0
Dimethyldithiocarbamate (moles)			Trans-stilbene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-6}$	Found $x10^{-6}$	Recovered (%)
1.43	1.25	87.4	9.11	8.95	98.2
1.61	1.45	90.0	7.20	7.01	97.3
1.11	1.01	91.4	3.19	2.99	93.6
1.52	1.38	90.7	1.26	1.27	100.5
2-thiobenzothiazoles (moles)			Trans-stilbene (moles)		
Added $x10^{-4}$	Found $x10^{-4}$	Recovered (%)	Added $x10^{-6}$	Found $x10^{-6}$	Recovered (%)
1.29	1.18	91.5	8.14	7.95	97.8
1.31	1.19	90.6	7.03	6.61	94.0
1.48	1.29	87.2	5.21	5.26	101.0
1.72	1.52	88.4	1.02	0.99	98.0

convenient sealing and degassing and cleaned with sodium dichromate solution by soaking overnight. The tubes were washed well with distilled water, then dilute ammonium hydroxide, finally with water and dried overnight in an oven at ca. 120°. Into each tube a known amount of material was introduced by weighing. The tubes were then attached to the vacuum line and the air slowly displaced with dry nitrogen. The liquids or solutions were degassed by freezing the tubes in liquid nitrogen under a pressure of ca. 0.005 mm., the solid compounds being evacuated without freezing. The tubes were sealed under this pressure and stored in a refrigerator until carrying out the kinetic runs. Usually eight to ten tubes were placed in a metal rack which was immersed completely in a silicone oil bath. It took about two minutes for the temperature of the tube contents to reach equilibrium with the bath temperature. This was taken as zero time for the reaction; one tube was withdrawn and immersed carefully (to avoid cracking) in crushed ice, this was taken as the zero time sample. The other tubes were removed in the same way at the appropriate times, and stored in a refrigerator until analysis was carried out.

The analysis of 2-mercaptobenzothiazole in the

decompositions was carried out by titration of an ethanolic solution with standard sodium hydroxide (phenolphthalein), the hydrocarbon analysis by absorption chromatography and U.V. spectrometry; while the isomerisation were analysed directly by U.V. from mole % or $E^{1\%}$ of the product at time t. The equilibrium reactions rate constants were evaluated by the least-square slope through the points and then subjected to a standard deviation analysis. The first-order rate constants were evaluated individually and subjected to standard deviation analysis. The computations were carried out by an Olivetti Desk Top Computer Programma 101. The activation parameters were evaluated from the Eyring equation by plotting ln.(k/t) vs. I/T. The entropy of activation $\Delta S^{\ddagger}$ was calculated from the intercept of the plot.

Reaction of cyclohexa-1:3-diene and 2-mercaptobenzothiazole

Cyclohexa-1:3-diene (Eastman-Kodak) was redistilled, with nitrogen bubbling through, b.p. 81°, N_{20}^{D} 1.4742 (lit. 81°, 1.4740). Cyclohexa 1:3 diene (0.38 g., 0.0047 mol.) and 2-mercaptobenzothiazole (0.89 g., 0.0054 mol.) were added to the apparatus described in Figure II, and attached to a vacuum line, then purged gently with dry nitrogen. The reactants were degassed by freezing with

TABLE 64

RATE DATA FOR THE THERMAL ISOMERISATION OF 2-(CYCLOHEX-2'-ENYL)THIOBENZOTHIAZOLE AT 140°C. - U.V. ESTIMATION

$$Xe = 783\ (E^{1\%}_{327})$$

Time (minutes)	$X\ (E^{1\%}_{327})$	$\text{Log}_{10}\ \frac{(Xe)}{(Xe-X)}$
30.0	207	0.1319
45.0	268	0.1818
60.0	327	0.2343
90.0	424	0.3385
120.0	505	0.4487
150.0	566	0.5563
180.0	619	0.6776

$(k_1+k_2)x10^{-4}sec.^{-1}$	Mole % * Ie	IIe	k_1/k_2	$10^4 k_1 sec.^{-1}$	$10^4 k_2 sec.^{-1}$
1.39 (S.D. =0.02)	35	65	1.855	0.922	0.468

*Ie = 100 - IIe on the basis of the thiazoline absorption at 327 mμ.

TABLE 65

RATE DATA FOR THE THERMAL ISOMERISATION OF 2-(CYCLOHEX-2'-ENYL)THIOBENZOTHIAZOLE AT 160°C. - U.V. ESTIMATION

$Xe = 783\ (E^{1\%}_{327})$

Time (minutes)	$X\ (E^{1\%}_{327})$	$\text{Log}_{10}\ \frac{(Xe)}{(Xe-X)}$
10.0	200	0.1750
14.0	265	0.2500
18.0	319	0.3250
22.0	368	0.4050
26.0	408	0.4900
30.0	437	0.5550
34.0	462	0.6250
38.0	492	0.7250
42.0	505	0.7800

$(k_1+k_2)\times10^{-3}\text{sec.}^{-1}$	Mole % * Ie	IIe	k_1/k_2	10^3k_1sec.^{-1}	10^3k_2sec.^{-1}
1.22 (S.D.=0.02)	43	57	1.325	0.695	0.525

*Ie = 100 - IIe on the basis of the thiazoline absorption at 327 mμ

TABLE 66

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(α-PHENYLETHYL)THIOBENZOTHIAZOLE AT 200°C. - TITRIMETRIC ANALYSIS

Time (minutes)	(Xe - X)	$\text{Log}_{10} \frac{(Xe)}{(Xe - X)}$
30.0	29.13	0.0128
60.0	26.80	0.0492
120.0	17.50	0.2343
180.0	12.50	0.3802
240.0	10.00	0.4771
420.0	6.50	0.8637

$(k_1+k_2) \times 10^{-5}$ sec.$^{-1}$	Mole % Ie	Mole % IIe(MBT)	k_1/k_2	$10^5 k_1$ sec.$^{-1}$	$10^5 k_2$ sec.$^{-1}$
8.47 (S.D.=0.32)	70	30	0.429	2.52	5.95

TABLE 67

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(1',2' DIPHENYLETHYL)THIOBENZOTHIAZOLE AT 200°C. - COLUMN PROCEDURE

Time (minutes)	Trans-stilbene (mole %)	$\frac{A296}{A266}$	k $sec.^{-1}$
50.0	20.0	1.95	7.45×10^{-5}
60.0	24.0	1.96	7.50×10^{-5}
85.0	32.0	1.95	7.55×10^{-5}
100.0	38.0	1.98	7.95×10^{-5}
120.0	42.0	2.00	7.53×10^{-5}
135.0	48.0	1.97	7.75×10^{-5}
150.0	52.0	1.99	8.15×10^{-5}
175.0	58.0	1.98	8.25×10^{-5}
200.0	66.0	1.97	8.00×10^{-5}

mean = 7.79×10^{-5}

$k = 7.79 \times 10^{-5}$ $sec.^{-1}$ (S.D. = 0.30)

TABLE 68

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(1',2' DIPHENYLETHYL)THIOBENZOTHIAZOLE AT 180° C. IN DIOXAN, CONC. = 0.046 MOLE LITRE^{-1} - COLUMN PROCEDURE

Time (hours)	Trans-stilbene (mole %)	$(\frac{A296}{A266})$	k sec.$^{-1}$
15.0	28.0	1.97	6.10×10^{-6}
20.0	34.0	1.97	5.75×10^{-6}
22.0	40.0	1.98	6.40×10^{-6}
25.0	42.0	1.99	6.01×10^{-6}
27.5	49.0	1.98	6.85×10^{-6}
30.0	54.0	1.96	7.10×10^{-6}
35.0	59.0	1.99	7.05×10^{-6}
37.5	65.0	2.00	7.20×10^{-6}
40.0	69.0	1.99	7.20×10^{-6}

mean = 6.63×10^{-6}

$k = 6.63 \times 10^{-6}$ sec.$^{-1}$ (S.D. = 0.56)

TABLE 69

RATE DATA FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL)DIMETHYLDITHIOCARBAMATE AT 180°C. - COLUMN PROCEDURE

Time (minutes)	Trans-stilbene (mole %)	$(\frac{A296}{A266})$	k $sec.^{-1}$
368.0	37.0	1.96	2.14×10^{-5}
447.0	44.0	1.98	2.14×10^{-5}
537.0	52.0	1.99	2.26×10^{-5}
627.0	58.1	1.97	2.29×10^{-5}
717.0	63.2	2.00	2.29×10^{-5}
816.0	67.6	1.98	2.28×10^{-5}
895.0	70.2	1.97	2.24×10^{-5}

mean = 2.24×10^{-5}

$k = 2.24 \times 10^{-5}$ $sec.^{-1}$ (S.D. = 0.06)

TABLE 70

RATE DATA FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL)DIMETHYLDITHIO-CARBAMATE AT 180°C. IN DIOXAN, CONC. = 0.038 MOLES LITRE^{-1}, COLUMN PROCEDURE

Time (minutes)	Trans-stilbene (mole %)	$(\frac{A296}{A266})$	k sec.$^{-1}$
453.0	24.1	1.97	1.00×10^{-5}
532.0	30.3	1.97	1.12×10^{-5}
638.0	38.0	1.98	1.24×10^{-5}
744.0	42.0	1.96	1.19×10^{-5}
850.0	47.5	1.99	1.25×10^{-5}
958.0	53.5	2.00	1.27×10^{-5}
1062.0	58.2	1.97	1.26×10^{-5}
1110.0	64.0	1.98	1.27×10^{-5}
1280.0	70.0	1.98	1.31×10^{-5}

mean = 1.21×10^{-5}

$k = 1.21 \times 10^{-5}$ sec.$^{-1}$ (S.D. = 0.08)

TABLE 71

RATE DATA FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL)METHYLXANTHATE AT 180°C. - COLUMN PROCEDURE

Time (minutes)	Trans-stilbene (mole %)	$(\frac{A296}{A266})$	k $sec.^{-1}$
166.0	27.0	1.99	3.18×10^{-5}
193.0	32.4	1.98	3.38×10^{-5}
221.0	33.2	1.99	3.07×10^{-5}
248.0	38.1	1.97	3.25×10^{-5}
276.0	41.3	1.98	3.20×10^{-5}
314.0	43.7	1.99	3.19×10^{-5}
332.0	46.6	1.96	3.16×10^{-5}
359.0	50.3	1.98	3.26×10^{-5}

mean= 3.21×10^{-5}

$k = 3.21 \times 10^{-5}$ $sec.^{-1}$ (S.D. = 0.10)

TABLE 72

RATE DATA FOR THE THERMAL DECOMPOSITION OF S-(1,2 DIPHENYLETHYL) 0,0 DIMETHYL-PHOSPHORODITHIOATE AT 140°C. - COLUMN PROCEDURE

Time (minutes)	Trans-stilbene (mole %)	$(\frac{A296}{A266})$	k sec.$^{-1}$
400	23.9	1.98	1.07×10^{-5}
501	29.8	1.98	1.19×10^{-5}
600	38.0	1.97	1.32×10^{-5}
702	42.1	1.96	1.27×10^{-5}
800	47.4	1.99	1.33×10^{-5}
900	53.5	1.97	1.36×10^{-5}
1000	58.6	1.98	1.34×10^{-5}
1100	63.9	2.00	1.36×10^{-5}
1200	70.0	1.99	1.40×10^{-5}

mean = 1.29×10^{-5}

$k = 1.29 \times 10^{-5}$ sec.$^{-1}$ (S.D. = 0.08)

TABLE 73

RATE DATA FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(2'-BENZOTHIAZOYLTHIO)TETRALIN AT 180°C. - COLUMN PROCEDURE

Time (minutes)	Naphthalene (mole %)	$k.sec.^{-1}$
45.0	20.6	8.51×10^{-5}
50.0	24.1	9.15×10^{-5}
60.0	27.6	8.95×10^{-5}
70.0	30.8	8.75×10^{-5}
80.0	33.9	8.60×10^{-5}
90.0	38.3	8.91×10^{-5}
100.0	41.1	8.86×10^{-5}
110.0	46.3	9.65×10^{-5}
120.0	46.3	8.65×10^{-5}
130.0	47.5	8.25×10^{-5}
180.0	38.0	8.95×10^{-5}

mean = 8.83×10^{-5}

$k = 8.83 \times 10^{-5}$ $sec.^{-1}$ (S.D. = 0.85)

TABLE 74

RATE DATA FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(2'-BENZOTHIAZOYLTHIO)TETRALIN AT 180°C. IN DIOXAN CONC. = 0.028 MOLES LITRE^{-1} - COLUMN PROCEDURE

Time (minutes)	Naphthalene (mole %)	k. sec.$^{-1}$
187.0	29.0	3.06×10^{-5}
233.0	32.1	2.75×10^{-5}
285.0	41.0	3.06×10^{-5}
326.0	47.0	3.13×10^{-5}
374.0	50.9	3.18×10^{-5}
420.0	56.0	3.25×10^{-5}
465.0	63.0	3.56×10^{-5}
512.0	66.0	3.50×10^{-5}
560.0	70.1	3.57×10^{-5}
605.0	73.9	3.70×10^{-5}

mean = 3.28×10^{-5}

$k = 3.28 \times 10^{-5}$ sec.$^{-1}$ (S.D. = 0.15)

TABLE 75

RATE DATA FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(S-DIMETHYLDITHIOCARBAMATE)TETRALIN AT 180° C. - COLUMN PROCEDURE

Time (minutes)	Naphthalene (mole %)	k. $sec.^{-1}$
60.0	14.0	4.60×10^{-5}
80.0	18.0	4.60×10^{-5}
100.0	23.0	4.32×10^{-5}
120.0	27.0	4.37×10^{-5}
140.0	32.4	4.65×10^{-5}
160.0	33.2	4.23×10^{-5}
180.0	38.1	4.48×10^{-5}
201.0	41.3	4.41×10^{-5}
240.0	46.6	4.35×10^{-5}
260.0	50.3	4.48×10^{-5}

mean = 4.40×10^{-5}

$k = 4.40 \times 10^{-5}$ $sec.^{-1}$ (S.D. = 0.15)

TABLE 76

RATE DATA FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(S-DIMETHYLDITHIOCARBAMATE)TETRALIN AT 180° C. IN DIOXAN, CONC. = 0.031 MOLES LITRE^{-1} - COLUMN PROCEDURE

Time (minutes	Naphthalene (mole %)	k. sec.$^{-1}$
120.0	16.1	2.61×10^{-5}
150.0	22.0	2.74×10^{-5}
180.0	26.0	2.77×10^{-5}
210.0	32.0	3.03×10^{-5}
240.0	36.0	2.50×10^{-5}
270.0	39.0	3.02×10^{-5}
299.0	43.5	3.01×10^{-5}
330.0	47.0	2.82×10^{-5}
360.0	54.0	2.77×10^{-5}
390.0	56.0	3.01×10^{-5}
420.0	61.0	3.06×10^{-5}

mean = 2.85×10^{-5}

$k = 2.85 \times 10^{-5}$ sec.$^{-1}$ (S.D. = 0.19)

TABLE 77

RATE DATA FOR THE THERMAL DECOMPOSITION OF 1,4 BIS-(S-METHYLXANTHATE)TETRALIN AT 180°C. - COLUMN PROCEDURE

Time (minutes)	Naphthalene (mole %)	k. $sec.^{-1}$
18.0	25.8	2.50×10^{-4}
20.0	30.0	2.97×10^{-4}
26.1	36.0	2.86×10^{-4}
30.1	40.0	2.83×10^{-4}
35.0	44.0	2.74×10^{-4}
40.0	48.0	2.72×10^{-4}
45.0	53.8	2.84×10^{-4}
50.1	59.1	2.98×10^{-4}
54.3	62.2	2.98×10^{-4}
60.0	68.0	3.14×10^{-4}
65.0	70.0	3.06×10^{-4}

mean = 2.87×10^{-4}

$k = 2.87 \times 10^{-4}$ $sec.^{-1}$ (S.D. = 0.05)

TABLE 78

RATE DATA FOR THERMAL DECOMPOSITION OF 1,4 BIS-(S-0,0 DIMETHYLPHOSPHORODITHIOATE)TETRALIN AT 180°C. - COLUMN PROCEDURE

Time (seconds)	Naphthalene (mole %)	k. $sec.^{-1}$
132.0	26.0	2.27×10^{-3}
194.0	36.0	2.29×10^{-3}
271.0	44.0	2.13×10^{-3}
338.0	54.0	2.41×10^{-3}
362.0	58.0	2.39×10^{-3}
394.0	61.0	2.39×10^{-3}
438.0	63.1	2.27×10^{-3}
500.0	67.2	2.21×10^{-3}
524.0	70.0	2.30×10^{-3}

mean = 2.29×10^{-3}

$k = 2.29 \times 10^{-3}$ $sec.^{-1}$ (S.D. = 0.07)

TABLE 79

RATE DATA FOR THE THERMAL DECOMPOSITION OF 2-(1',2' DIPHENYLETHYL)THIOBENZOTHIAZOLE IN THE PRESENCE OF ZINC OXIDE AND STEARIC ACID AT 180° C. - COLUMN PROCEDURE

Time (minutes)	Trans-stilbene (mole %)	$(\frac{A296}{A266})$	k sec.$^{-1}$
60.1	24.1	1.99	7.60×10^{-5}
90.3	34.0	1.98	7.95×10^{-5}
120.0	42.0	1.99	7.56×10^{-5}
156.0	50.0	1.99	7.45×10^{-5}
180.0	55.0	1.98	7.45×10^{-5}
210.0	62.1	2.00	7.69×10^{-5}
240.0	67.8	1.98	7.85×10^{-5}
270.0	72.0	1.97	7.85×10^{-5}
300.0	78.0	1.97	8.20×10^{-5}

mean = 7.73×10^{-5}

$k = 7.73 \times 10^{-5}$ sec.$^{-1}$ (S.D. = 0.03)

liquid nitrogen at 0.005 mm. pressure and then sealed. The apparatus was heated at 200° ±1° for eight hours. Evaporative distillation gave a clear liquid (0.14 g.) which was not examined. The residue was dissolved in chloroform and extracted with sodium hydroxide (10%, 4 x 10 ml.) and treated as usual to give 2-mercaptobenzothiazole (0.37 g., 0.0022 mol.). The chloroform was removed under vacuo to give a yellow coloured oil and white solid (0.75 g., 0.003 mol.). U.V. in ethanol indicated the following composition, 3-(cyclohex-2'-enyl) benzothiazoline-2-thione (51%, $E^{1\%}_{327}$ = 518), 2-(cyclohex-2'-enyl)thiobenzothiazole (38%, $E^{1\%}_{281}$ = 278), the remainder not being identified. A small amount of 3-(cyclohex-2'-enyl)benzothiazoline-2-thione was isolated m.p. 148° - 149°, mixed m.p. undepressed. Found C% 63.15, H% 5.61, N% 5.90, S% 25.80 $C_{13}H_{13}NS_2$ requires C% 63.10, H% 5.30, N% 5.70, S% 25.90. The I.R. spectra of the composite sample was almost identical to the known compounds except for a peak of medium intensity at 790 $cm.^{-1}$.

Thermal decomposition of 2-substituted thiobenzothiazoles in the presence of zinc oxide and stearic acid

The zinc oxide used was No. 3 Normal French Process grade, purified, Amalgamated Oxides Limited, Stearic Acid as supplied by B.D.H. Limited.

A typical procedure is described which applies to all the compounds studied.

1,4 bis-(2'-benzothiazoylthio)tetralin (0.231 g., 0.0005 mol.) was weighed into a clean dry decomposition tube, stearic acid (0.142 g., 0.0005 mol.) was added and finally zinc oxide (0.405 g., 0.005 mol.). The tube was degassed and evacuated and sealed in the usual way. The amounts of stearic acid and zinc oxide being adjusted with sample weight to maintain a molar ratio of 2-thio-benzothiazole derivative:zinc oxide:stearic acid of 1:10:1, which is similar to that used in the vulcanization processes.

Vulcanization kinetics

The natural rubber used was R.S.S.I. (Yellow circle) grade; zinc oxide No. 3 Normal French Process grade (Amalgamated Oxides Limited); stearic acid as supplied by B.D.H. Ltd. sulphur normal technical grade, accelerators as prepared or used in experimental.

Natural rubber was fragmented and batches (1000 g.) were masticated in a water cooled Banbury internal mixer for three minutes, the temperatures being kept below 145°, to give a Mooney viscosity of 76-78 (ML4, 100°). The natural rubber was further fragmented and homogenised on a two roll mill, so that intercomparison of results could

be made with confidence, i.e., the same composition and pre-treatment history. Further batches of natural rubber (300 g.) were taken and a masterbatch prepared by mixing on a water cooled two roll mill. The composition and mixing times are indicated in Table 80. The concentration of "accelerators" was such that they would have a molar equivalent of 1 p.p.h. of 2-mercaptobenzothiazole. After identical mixing the compounds were milled into thin sheets; sealed in polythene and stored at -28° till used.

The studies were conducted using a Wallace Shawbury Curometer Mk III, the lower and upper platens were controlled to ±1°. Each compound was tested three times and the mean reading with time taken. The kinetic treatment was similar to Robinson and Pinfold[133] which gave the "first order" plots. The "first order" slope was obtained by the least-square slope through the points and subjected to standard deviation analysis. The computations were performed on an Olivetti Desk Top Computer, Programma 101.

TABLE 80

COMPOSITION AND MIXING ORDER AND TIMES
FOR TEST VULCANIZATES

Material	Added (g)	Mixing Time (minutes)
Natural Rubber	100.0	2
Zinc oxide	5.0	10
Stearic acid	2.0	15
Sulphur	2.5	12
"Accelerator"	Variable	5

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