THE ACYLATION OF CYCLOHEPTATRIENE.

by

CLIVE JOHN TATE

A Thesis presented for the
degree of Doctor of Philosophy
in
THE UNIVERSITY OF ASTON IN BIRMINGHAM

MARCH, 1971

Summary

The reaction of cycloheptatriene with acyl halides in the presence of a Lewis-acid catalyst has been studied. In particular reaction of benzoyl fluoride and boron trifluoride in methylene chloride, benzoyl-fluoride and borontrifluoride in liquid SO_2 and a series of acyl chlorides and aluminium chloride in methylene chloride, with cycloheptatriene gave tropylium salts in up to 30% yield, without the simultaneous formation of an aldehyde. Thus a process other than direct hydride-ion transfer to the electrophilic acylium species was responsible for the formation of the tropylium salts. A mechanism has been proposed for these reactions.

Additional products have been isolated from the above reactions and by slight variations in the reaction conditions either 1-acylcyloheptatrienes or substituted deoxybenzoins have been prepared. This method is more convenient than any other preparations of acylcycloheptatrienes, and the reaction also provides the first example of the introduction of an electrophilic species into the cycloheptatriene π-electron system. Normally in such reactions only extensive polymerisation and low yields of tropylium salts are recorded.

The preparation of substituted deoxybenzoins is also of synthetic importance, isomerically pure products being conveniently obtained. The normal synthesis, i.e. by Friedel-Crafts acylation of the substituted benzene with phenyl acetyl chloride, leads to mixed products, depending upon the orientating effects of the substituent on the benzene ring.

The identification of a chloro-ketone intermediate allowed a coherent mechanism for the formation of both series of compounds to be postulated. The evidence supporting this mechanism is discussed in detail.

The ready synthesis of 1-benzoylcycloheptatriene by these reactions made possible an investigation of the properties of this compound. Thermolysis of 1-benzoylcycloheptatriene gave deoxybenzoin. Photolysis, provided a convenient synthesis of 2-benzoylcycloheptatriene by a highly specific 1,7 hydrogen shift and hydride-ion transfer to trityl fluoroborate gave the novel benzoyltropylium fluoroborate. The characterisation of this compound by spectroscopic and chemical techniques, is described.

Acknowledgements

I wish to express my sincere thanks to Dr. J. A. Blair for his supervision and encouragement of this work; to Mr. E. Hartland, Mrs. V. Shearsby, Miss M. Sparkes, Mrs. B. Taylor, Mr. M. Houghton and Mr. M. Perry for the various services they provided.

Also to Dr. D. G. Wibberley for use of a Varian A-60 spectrometer and to Mrs. H. B. Hulbert for typing this manuscript.

I wish to acknowledge the support of a Science Research Council Grant.

This work was carried out between 1967 and 1970 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

C. J. Tate

C. J. Tate

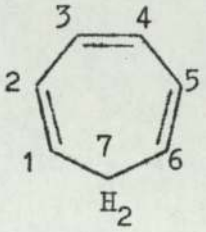
Contents

Figures

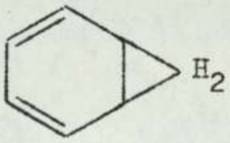
Tables

I Introduction

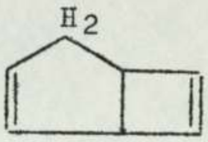
Tropilidene,[1] prepared initially by a degradation of the alkaloid atropine[2,3] was subjected to a thorough investigation by Willstatter. He synthesised tropilidene by an unambiguous route from cycloheptanone,[4] leading him to propose cycloheptatriene I as the correct structure. However this synthesis does not exclude the valence tautomeric bicycloheptadienes II & III.



(I)

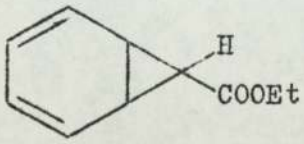


(II)

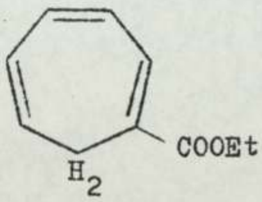


(III)

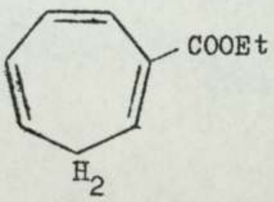
Evidence for the existence of the bicyclo [4.1.0] hepta-2, 4-diene (norcaradiene) structure II had already been described by Buchner.[5] Analysing the products formed from the thermal decomposition of diazo-acetic ester in benzene, he found a mixture of esters ("Buchner esters") that appeared to contain the ester IV a norcaradiene derivative, as well as the esters of three isomeric cycloheptatriene carboxylic acids, V - VII.



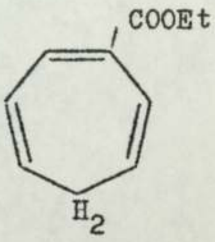
(IV)



(V)



(VI)



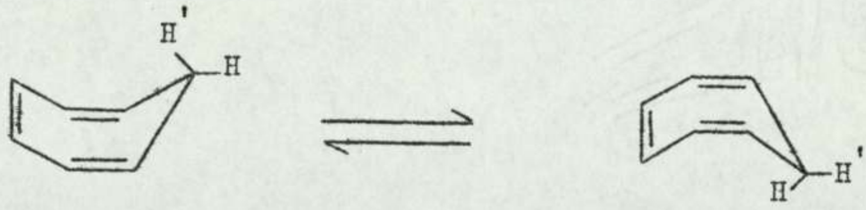
(VII)

Thus early views were that both the norcaradiene and the cycloheptatriene ring systems existed and that neither appeared to show any tendency to change spontaneously to the other.

This view was accepted until 1950 when Doering[6] showed that the photolysis of diazomethane in benzene gave only cycloheptatriene I whereas norcaradiene II was the expected product. Doering also repeated Buchner's experiments and found that all Buchner's esters were isomeric cycloheptatriene esters.[7] Thus the existence of the norcaradiene ring system was discredited.

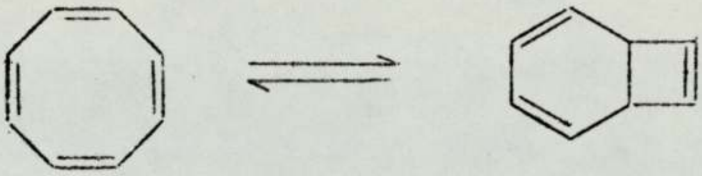
Chemical reactions of tropilidene proved confusing. Hydrogenation gave cycloheptane,[8] but many reactions involved the bicyclic form. Thus Diels-Alder reactions gave tricyclic adducts.[9]

Nuclear magnetic resonance (n.m.r.) examinations of tropilidene showed that it existed mainly as the monocyclic cycloheptatriene, and the separation of the methylene protons at -140° [9,10] was interpreted as evidence for a non-planar "boat" conformation which undergoes rapid ring inversion at normal temperatures :-



No direct evidence has so far been found for the existence of a small amount of norcaradiene in equilibrium with the cycloheptatriene.

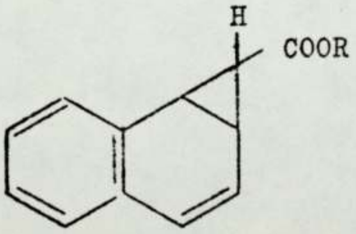
A similar situation existed for cyclooctatetraene VIII and bicyclo [4,2,0] octa-2,4,7 triene IX. Diels-Alder reactions of cyclooctatetraene gave adducts derived from the bicyclic tautomer IX. Kinetic measurements (with a dilatometer) on such reactions with dienophiles of widely differing activity, e.g. maleic anhydride and tetracyanoethylene, can only be interpreted by postulating the prior formation of a small amount of the bicyclic tautomer IX in equilibrium with the cyclooctatetraene[11] VIII :-



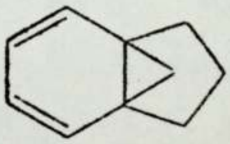
(VIII) (IX)

This verifies the existence of the valence tautomeric equilibrium shown. However attempts to apply this method to tropilidene have failed to demonstrate the existence of the norcaradiene tautomer.[12]

Norcaradiene derivatives have been prepared using special expedients, such as the inclusion of one of the two double bonds of the norcaradiene in an aromatic ring system or by bridging of carbon atoms 1 and 6 with an additional ring. For example decomposition of diazoacetic ester in naphthalene[13] gave X, and Vogel[14] synthesised the hydrocarbon XI.

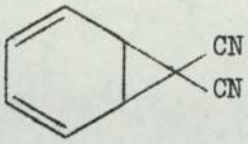


(X)

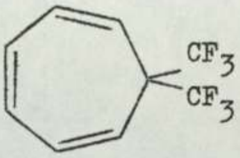


(XI)

7,7-Dicyano norcaradiene XII was the first simple norcaradiene to be synthesised,[15,16] whereas the similar 7,7-bis(trifluoromethyl) compound XIII existed entirely in the cycloheptatriene form.

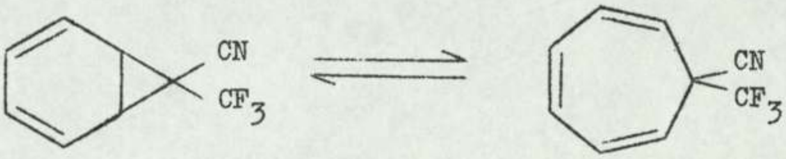


(XII)



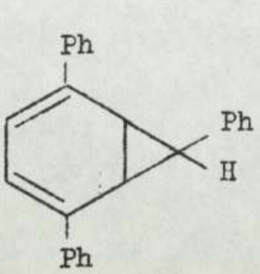
(XIII)

It was not surprising therefore when a temperature dependence n.m.r. study of the 7-cyano-7-trifluoromethyl[17] compound showed the existence of a valence tautomeric equilibrium between 7-cyano-7-trifluoromethylcycloheptatriene XIV and the 7-cyano-7-trifluoromethyl norcaradiene XV.

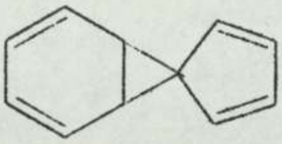


(XIV) (XV)

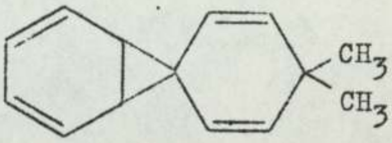
Other simple norcaradiene systems have recently been prepared. They include the 2,5,7-triphenyl norcaradiene[18] XVI and the 7,7-spironorcaradienes XVII[19] and XVIII[20] :-



(XVI)



(XVII)

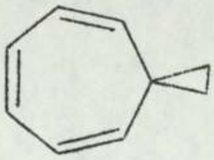


(XVIII)

The factors affecting stability of the norcaradiene ring system are, as yet, not fully understood. Ciganek[16] has advanced two possible explanations :-

i) Stabilisation of the norcaradiene via formation of an intramolecular charge-transfer or π-complex between one cyano group and the planar diene system.[16] Unfortunately u.v. spectra give no indication of a charge-transfer band although the large dipole moment[16] may well be evidence for a charge-transfer complex.

(ii) A large external angle at C_7 ($\angle$ CN-C-CN in XII), and hence a small "contra" angle favours the cyclopropane ring. This explains the stability of the norcaradiene system in 7,7-dicyanonorcaradiene XII, the spironorcaradienes XVII, and XVIII, and the stability of the cycloheptatriene ring system in the spirononatriene XIX.[21]

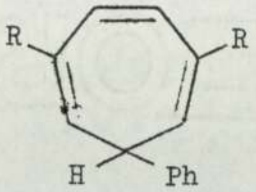


(XIX)

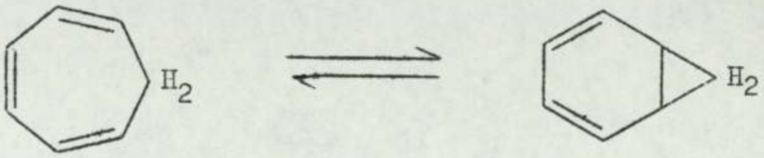
However it does not explain the stability of the triphenyl norcaradiene XVI.

A third explanation which has not been considered to date, is the stabilisation of the cyclopropane ring by the formation of a charge-transfer complex between the p-orbitals of the ring and correctly orientated p-orbitals of a π-electron system at the 7-position. A similar explanation has been advanced to account for the ability of a cyclopropropyl group to stabilise carbonium ions.[22,23] This hypothesis accounts for the stability of the known norcaradienes including the 2,5,7-triphenyl norcaradiene XVI. The role of the 2 and 5 phenyl groups is presumably to give the 7-phenyl group the correct orientation for overlap with the cyclopropyl ring. As with (i) there is no conclusive evidence for the existence of any charge-transfer complex.

Possibly the synthesis of 7-phenyl cycloheptatrienes with bulky groups, R, at the 2 and 5 positions may help to distinguish between the above explanations.



By analogy with the 7-cyano-7-trifluoro methyl compound it is now accepted that tropilidene exists in such a valence-tautomeric equilibrium, with the equilibrium concentration of norcaradiene being, as yet, undetectable.



(I) (II)

This is the only reasonable explanation of the diversity of the chemical reactions of the compound. "Tropilidene" will therefore be replaced by the name "cycloheptatriene" in the remainder of the dissertation.

The major topic of this study is the reaction of cycloheptatriene with acyl halides in the presence of Lewis-acid catalysts. Reactions of cycloheptatriene with a wide range of electrophilic reagents have been described in the literature, tropylium salts usually being isolated in yields varying from 20% to 100%.*

Cycloheptatriene is an efficient hydride-ion donor and such a transfer to the potential carbonium ion centre in these reagents is generally accepted as accounting for the tropylium ion formation.

This hypothesis has been tested for the following systems :-

a) benzoyl fluoride with boron trifluoride in methylene chloride.

b) benzoyl fluoride with boron-trifluoride in liquid SO_2.

---

* For a more detailed discussion, with references, see Chapter II.

c) benzoyl chloride with aluminium chloride in methylene chloride

d) mesitoyl chloride with aluminium chloride in methylene chloride.

In each case the appropriate tropylium salt was isolated in about 30% yield, so if it had been formed by direct hydride-ion transfer the corresponding aldehyde XX must also have been formed :-

$$C_7H_8 \quad + \quad RCO^+ \longrightarrow C_7H_7^+ \quad + \quad \underset{(XX)}{RCHO}$$

This is conveniently checked by obtaining an n.m.r. spectrum of the reaction solution, any aldehydic signal showing at τ 0

The experiments performed with these systems clearly show the absence of any aldehyde signals. Thus it was concluded that the tropylium ion is formed by a route other than direct hydride-ion transfer. A possible alternative is discussed in some detail.

The synthetic possibilities of the reaction were also explored and by variation of the reaction conditions it was possible to obtain either substituted deoxybenzoins or 1-acylcycloheptatrienes in up to 42% yield.

A range of acylcycloheptatrienes and substituted deoxybenzoins prepared by this method are described. The characterisation of these compounds, by i.r., n.m.r. and m.s. is discussed in detail.

Isolation of an intermediate chloro-ketone in the synthesis of 1-benzoylcycloheptatriene allowed a reasonable mechanism to be postulated. Consideration of the stereochemistry of this compound, by analysis of the n.m.r. spectrum allowed a reasonable explanation to be given for the formation of both series of compounds.

The ready availability of 1-benzoylcycloheptatriene from this reaction made possible the study of typical reactions of this compound.

II Hydride-ion-transfer Reactions

1. Introduction

The hydride-ion transfer reaction[24,25] involves the transfer of a hydrogen atom with its pair of electrons from one carbon atom to another. The carbon accepting this hydride-ion must have an actual or potential open sextet of electrons. For example, the triphenyl methyl (trityl) carbonium ion, Ph_3C^+ or a carbonyl group in acid solution.

$$C = O + H^+ \longrightarrow C^+ - OH$$

Hydride-ion transfers involve polar transition states and are promoted by polar solvents.

Cycloheptatriene is an efficient hydride-ion donor and in the presence of acceptors is readily converted to the tropylium ion.[26] Thus trityl fluoroborate,[27] in polar solvents, converts cycloheptatriene I to tropylium fluoroborate, XXI in almost quantitative yield.

$$\underset{(I)}{C_7H_8} + Ph_3C^+ BF_4^- \longrightarrow \underset{(XXI)}{C_7H_7^+ BF_4^-} + Ph_3CH$$

The isolation of an equivalent amount of triphenyl methane shows that direct hydride-ion transfer has taken place.

Boron bromide[28] XXII also gives tropylium salts with cycloheptatriene, (See Figs. I and II).

Figure I. Reaction of Cycloheptatriene and Boron Bromide.

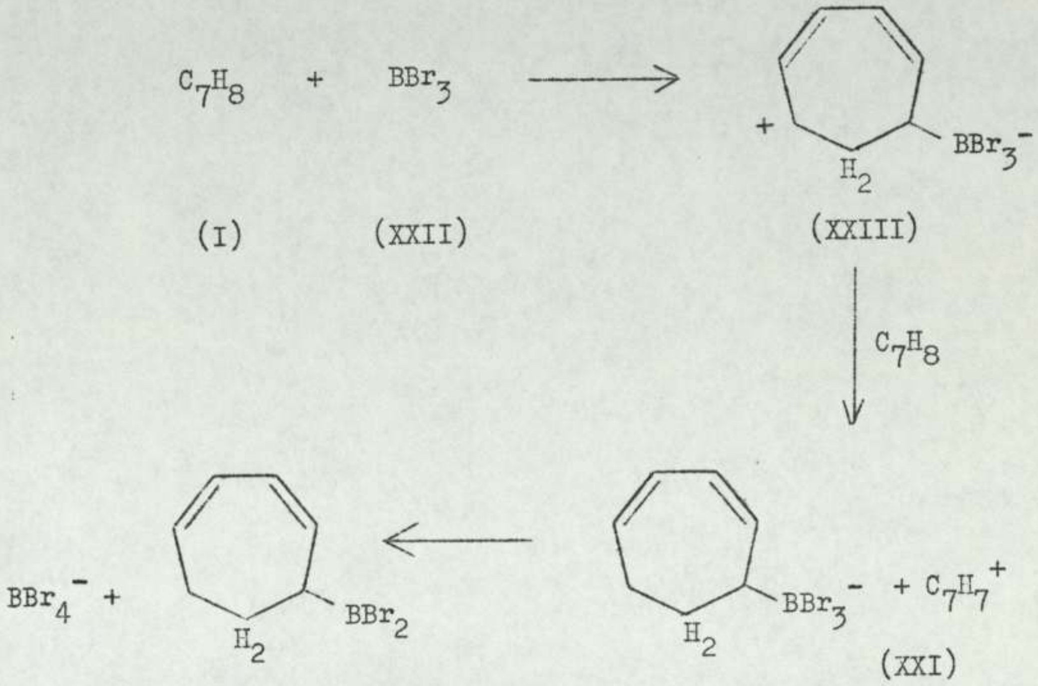


Figure II. Reaction of Cycloheptatriene with Boron Bromide.

$$C_7H_8 \quad + \quad BBr_3 \longrightarrow C_7H_7^{+} \quad BBr_3H^{-}$$

(I) (XXII)

$$C_7H_7^{+} \quad BBr_3H^{-} \quad + \quad BBr_3 \longrightarrow C_7H_7^{+} \quad BBr_4^{-} + BBr_2H.$$

(XXI)

As $HBBr_2$ readily dissociates it was more difficult in this instance to show that hydride-ion-transfer had taken place. Kursanov[29] studied this system and found that by adding water to the reaction mixture molecular hydrogen was obtained in yields up to 40%. The evolution of hydrogen indicated direct hydride-ion-abstraction (see Fig. II). The $HBBr_2$, formed by disproportionation of the BBr_3H^- anion, was decomposed by water :-

$$BBr_2H + 3H_2O \longrightarrow H_3BO_3 + 2HBr + H_2.$$

Harmon et. al. considered both hydride-ion-transfer and addition to the triene system, pointing out that formation of the cycloheptadienyl carbonium ion XXIII would cause extensive polymerisation. In view of the high yield and clean nature of the product, these workers concluded that the direct hydride-ion-transfer was the more likely mechanism. In later work the reaction was extended to the synthesis tropylium chloro-[30] and iodoborates.[31]

The formation of tropylium salts from cycloheptatriene and t-butyl chloride in the presence of Lewis-acid catalysts (Al_2Cl_6, BCl_3, Fe_2Cl_6, $SnCl_6$) has been described.[32,33] A halide-hydride exchange mechanism was postulated :-

$$\underset{(I)}{C_7H_8} + BCl_3 \longrightarrow C_7H_7^+ \ BHCl_3^-$$

$$C_7H_7^+ \ BHCl_3^- + tBuCl \longrightarrow C_7H_7^+ \ BCl_4^- + t\text{-}BuH.$$

The detection of t-butane was not reported, although this would provide a ready test of the above hypothesis.

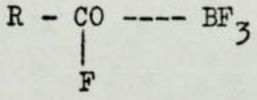
2. Reaction of Cycloheptatriene with the Benzoyl Fluoride - Boron Trifluoride Complex in Methylene Chloride. (expt. 3).

Seel,[34] in 1943, reported the isolation of the first stable, well-identified, oxocarbonium salt, a 1:1 addition-complex of acetyl fluoride and boron trifluoride. Olah[35,36] has since made a wide range of such compounds, and has used infra-red (i.r.) and nuclear magnetic resonance (n.m.r.) techniques to determine the precise structure of the products. He used two methods to synthesise these compounds, namely the"Silver Salt Method" and the "Fluoride Method". Attempts using the "silver salt method" were limited by difficulties encountered in the synthesis of anhydrous silver tetrafluoroborate. Hydration of the silver tetrafluoroborate decreased solubility and reactions using this method to produce the oxocarbonium salt gave poor yields of tropylium fluoroborate.

$$\begin{array}{ccccccc} AgBF_4 & + & RCOCl & \dashrightarrow & AgCl & + & RCO^+ BF_4^- \\ (XXIV) & & (XXV) & & (XXVI) & & (XXVII) \end{array}$$

Thus the "fluoride method" was employed, despite having to use the less convenient acyl fluorides.

The acyl fluoride-boron trifluoride complex exists either as a highly polar, covalent donor-acceptor complex XXXIIA or as a carbonium ion XXVII B :-



$$R - \underset{\displaystyle F}{\underset{|}{CO}} ---- BF_3$$

(XXVII A)

$$RCO^+ \quad BF_4^-$$

(XXVII B)

The precise nature of the adduct varies with the conditions under which it is studied.

The compounds decompose at room temperature and are highly reactive even at low temperatures. It was hoped they would be efficient hydride-ion acceptors at low temperatures and to test this efficiency, benzoyl oxocarbonium fluoroborate was treated with cycloheptatriene.

Benzoyl oxocarbonium fluoroborate XXIX was prepared by the addition of boron fluoride XXVIII to a solution of benzoyl fluoride XXX in methylene chloride at -60°.

Comparison of the position and shape of the aromatic ring protons, with those of similar complexes described by Olah^{35} clearly showed the complex to exist as the donor-acceptor complex XXVII. Addition o cycloheptatriene I to the solution gave tropylium fluoroborate XVI in 30% yield. If this is formed by direct hydride-ion transfer, an equivalent amount of benzaldehyde XXXI must be formed :-

$$\begin{array}{ccccc} C_6H_5COF & + & BF_3 & \xrightarrow{-60^{\circ}} & C_6H_5COBF_4. \\ (XXX) & & (XXVIII) & & (XXIX) \end{array}$$

$$\begin{array}{ccccccc} C_6H_5COBF_4. & + & C_7H_8 & \xrightarrow{-60^{\circ}} & C_7H_7^{+}\ BF_4^{-} & + & C_6H_5CHO \\ (XXIX) & & (I) & & (XVI) & & (XXXI) \end{array}$$

The aldehydic proton resonance occurs at about τ 0.0 making n.m.r. spectroscopy a sensitive method of detecting benzaldehyde. Examination of the reaction filtrate revealed no aldehydic resonance, however, there was an acidic resonance at low field (presumably benzoic acid from hydrolysis of the benzoyl fluoride). Further, benzaldehyde added to the reaction mixture rapidly decomposed to benzoic acid, hence it could not be concluded that benzaldehyde was formed.

Examination of the n.m.r. spectrum of the reaction filtrate at -60°, revealed no aldehydic and no acidic resonance. Presumably at this temperature benzoyl fluoride is not hydrolysed to benzoic acid. However a signal at τ 0.8 shows that tropylium fluoroborate is formed so it is reasonable to assume that the tropylium fluoroborate had not been produced by a direct hydride-ion transfer.

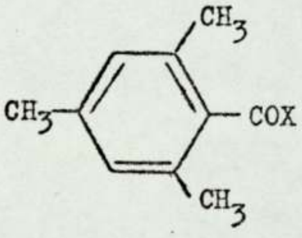
3. Reaction of Cycloheptatriene with Benzoyl Fluoride - Boron Trifluoride Complex in Liquid SO2 (expt. 4).

Examination of the n.m.r. spectrum of a solution of the benzoyl fluoride-boron trifluoride complex at -60°. in liquid SO2, revealed that it was present as the oxocarbonium ion XXVII B. Hydride-ion transfer reactions are promoted by ionic reactants so it was decided to try to detect benzaldehyde in the reaction of this complex with cycloheptatriene.

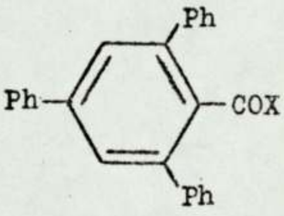
The n.m.r. spectrum of the reaction filtrate at -60° showed no evidence for benzaldehyde although working-up the residue obtained after evaporating off the SO_2, gave tropylium fluoroborate in 30% yield. So again it must be concluded that the tropylium fluoroborate is not formed by a direct hydride-ion-transfer.

4. Reaction of Cycloheptatriene with Acyl Chlorides in the Presence of Aluminium Chloride (expts. 6, 7, 22).

The reactions of cycloheptatriene and the benzoyl fluoride-boron trifluoride complex, show that attack of the electrophilic species on the triene system[28] (Fig. 1) is preferred to the expected hydride-ion-transfer. The transition state for hydride-ion-transfer is less crowded than the addition transition state, thus it is possible that in reactions with sterically hindered acyl halides, hydride-ion-transfer may predominate. It was proposed to study a series of 2,4,6 tri-substituted benzoyl halides, namely the 2,4,6-trimethyl (mesitoyl) XXXIII and 2,4,6-triphenyl XXXIV compounds :-



(XXXIII)



(XXXIV)

These acyl chlorides are more readily available than the corresponding acyl fluorides, and since preliminary experiments showed that the benzoyl chloride/$AlCl_3$ system gave the same results as the benzoyl fluoride/BF_3 system it was decided to use the chloride derivatives. This had other advantages, the greater stability of the acyl chloride to hydrolysis allowed the n.m.r. spectra to be run at normal probe temperatures without interference from benzoic acid formation.

Unfortunately attempts to prepare the 2,4,6-triphenyl benzoyl chloride from the acid gave only diphenylfluorenone as previously recorded[37].

Despite this, the failure to detect any aldehydic signal with the reaction of either benzoyl or mesitoyl chlorides with cycloheptatriene (expts. 6 & 7) shows that direct hydride-ion-transfer does not take place in the systems studied.

5. The Formation of the Tropylium Ion.

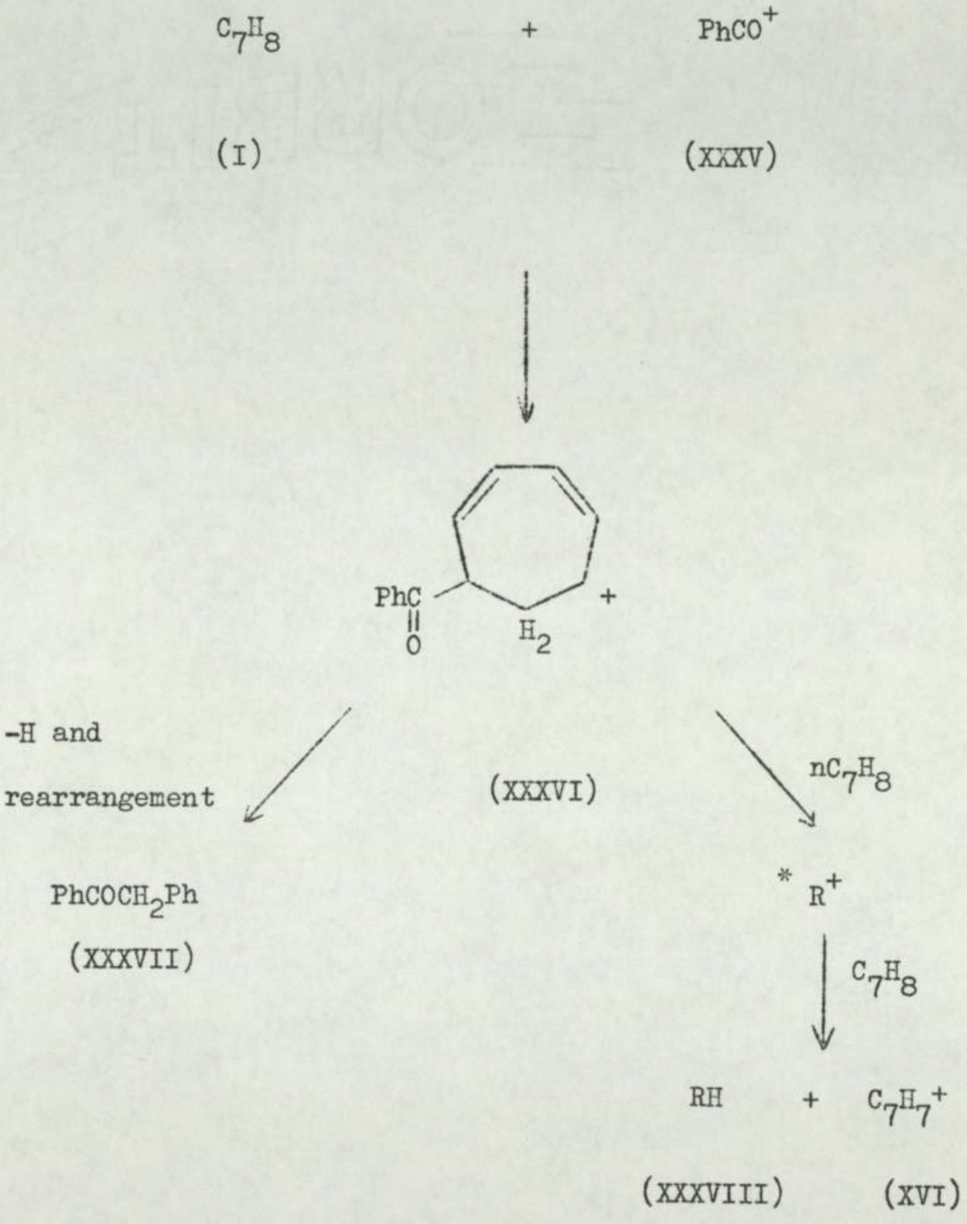
Fig. III summarises the possible reactions of an electrophilic species with cycloheptatriene.[38] The evidence presented in this chapter conclusively rules out a direct hydride-ion-transfer, and electrophilic attack at the triene system is the most reasonable alternative.

The preceding discussion has considered the formation of the tropylium ion only, however other products have been isolated from those reactions, namely desoxybenzoin and an uncharacterised polymeric material.

The synthetic possibilities of the reaction, and a detailed mechanistic study of the formation of these other products are considered in later chapters of this dissertation, meanwhile any overall reaction scheme must consider the formation of these other products.

In Fig. III the attacking species is assumed, for simplicity to be an acylium ion, as its nature does not appear to affect the course of the reaction. The addition of the acylium ion XXXV to cycloheptatriene I gives a cycloheptadienyl carbonium ion XXXVI, which may react in two ways. Firstly, addition of further molecules of cycloheptatriene gives a polymeric carbonium ion R^+, which in the chain termination step accepts a hydride-ion from cycloheptatriene to give a neutral polymer RH and the tropylium ion XVI. Or secondly, XXXVI may rearrange to deoxybenzoin, the details of which are discussed in Chapter V.

Figure III Formation of the Tropylium Ion.



* R^+ represents a polymeric carbonium ion, formed from n cycloheptatriene molecules.

Clearly, dilution of the reaction solution will favour the formation of deoxybenzoin at the expense of the polymerisation and formation of tropylium fluoroborate. To test the proposed scheme the reaction was repeated at varying dilutions and the yields of the products noted. The results, summarised in Table I, clearly support the proposed scheme.

Table I.

Product yields, from the Reaction of Cycloheptatriene and Benzoyl Fluoride-Boron Trifluoride at Varying Dilutions.

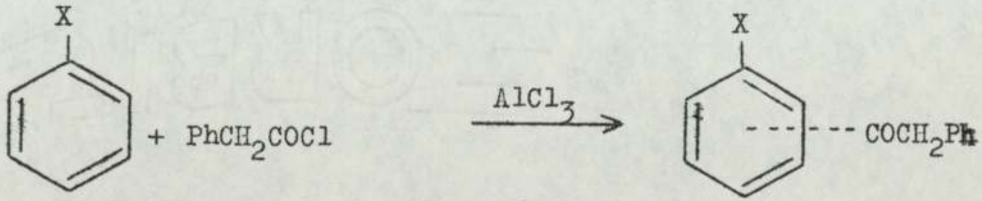
Reactants 0.1 mole		Products, yields g.		
Benzoyl fluoride in x ml. CH_2Cl_2	Cycloheptatriene in x ml. CH_2Cl_2	$C_7H_7^+BF_4^-$	Deoxybenzoin	Polymer
100	-	4.0	1.1	4.0
250	100	1.5	2.9	3.5
50	250	0.7	5.1	1.5

III Synthesis of Deoxybenzoin Derivatives

The reaction of cycloheptatriene with acyl halides in the presence of Lewis-acid catalysts to give tropylium fluoroborate, was described in Chapter II. Removal of solvent from the reaction filtrate followed by vacuum distillation gave deoxybenzoin in low yield (identified by mixed-melting point, infra-red and nuclear magnetic resonance spectra identical with the spectra of an authentic sample). The yield of deoxybenzoin was improved considerably by using the benzoyl chloride-aluminium chloride system and adding the cycloheptatriene at 0°.

Using this reaction a wide range of deoxybenzoin derivatives were prepared. These compounds together with their properties are summarised in Table II. They were identified mainly by their characteristic magnetic resonance (n.m.r.) spectra. Two singlets dominate the spectra, τ 2.8 ± 0.05 p.p.m. ($P\underline{h}$ CH_2) and 6.0 ± 0.3 p.p.m ($CO-C\underline{H}_2-Ph$), making identification of these compounds straightforward. (For further details of the n.m.r. spectra see Appendix I No. 1 and Table IX Chapter VII).

These compounds would usually be prepared by Friedel-Crafts acylation of the substituted benzene with phenyl acetyl chloride[39] :-



Thus the product will depend upon the directing effects of the substituent X. Inevitably mixtures of the isomeric deoxybenzoins will be formed. The method described above gives one product only and hence is important despite the relatively low yields involved.

Far more interesting than these synthetic possibilities, is the addition of the acylium species to the triene ring system, which subsequently rearranges. A large amount of the study consists of investigating the mechanism of this addition and the reactions of the intermediate so formed.[40]

Similar reactions have been reported in the literature but no-one has reported the isolation of substituted products. Presumably such products have been formed in low yields and have not been detected.

Table II

Properties of Deoxybenzoin Derivatives.

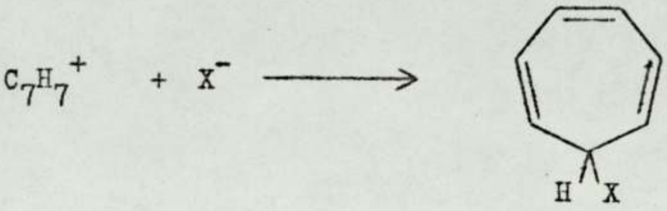
Compound	m.pt.	C/H				Experiment No.
		measured		theoretical		
		C%	H%	C%	H%	
deoxybenzoin	54-55°	86.1	6.1	85.8	6.2	6
benzyl mesityl ketone	b.p. 167-180°/ 6 m.m.	*				7
benzyl 1-naphthyl ketone	64.5-66°	88.2	5.7	87.9	5.7	8
benzyl 2-naphthyl ketone	77-79°	87.2	5.6	87.9	5.7	9
benzyl p-bromophenyl ketone	112-114°	61.5	4.2	61.2	4.0	10
benzyl cinnamyl ketone	65-67°	86.5	6.4	86.5	6.4	11
benzyl p-methoxyphenyl ketone	75-76°	79.1	6.1	79.7	6.2	12
benzyl methyl ketone	b.p. 91-95/ 10 m.m.	*				13

* Peak matching of parent ion only, see experimental section.

IV Synthesis of 1-Acylcycloheptatrienes.

1. Alternative Routes to Acylcycloheptatrienes.

Substituted cycloheptatrienes are readily prepared by the action of nucleophiles (X^-) upon tropylium salts, the 7-substituted cycloheptatriene XXXIX being formed :-

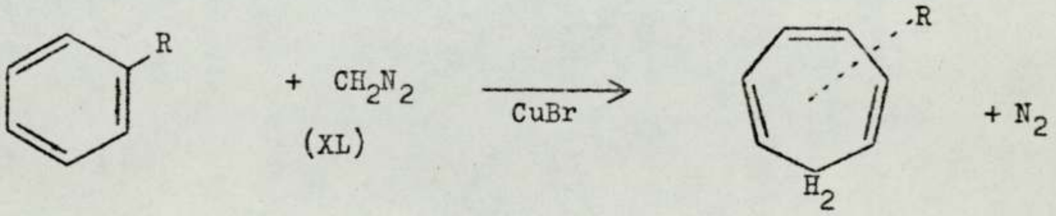


(XXXIX)

7-methyl,[43] 7-phenyl,[42] 7-methoxy[42] and 7-cyanocycloheptatrienes[41] have been prepared by this method.

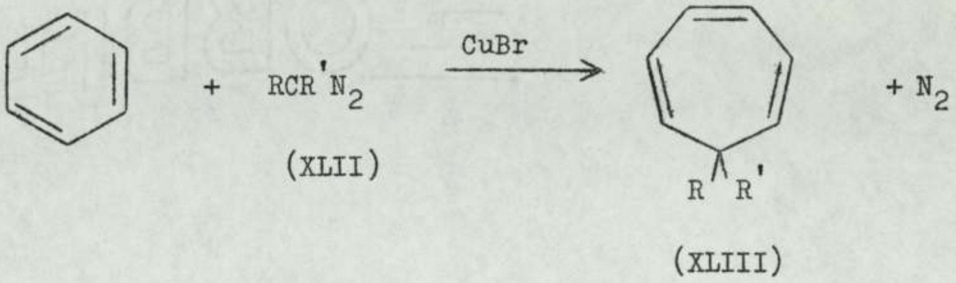
Thermolysis of XXXIX will give a mixture of the isomeric 1, 2 and 3-substituted cycloheptatrienes. Separation, usually by distillation or preparative gas-liquid chromotography (g.l.c.), will give the individual isomers.

The other method widely used in cycloheptatriene chemistry is the addition of a carbene to an aromatic compound. For example (1), addition of diazomethane XL to mono alkyl benzene derivatives gives a mixture of isomeric 1,2 and 3-alkylcycloheptatrienes[44,45] XLI :-



(XLI)

(2) addition of substituted diazocompounds XLII to benzene gives 7-substituted cycloheptatrienes XLIII.



The 1-acylcycloheptatrienes made in this study would be difficult to separate from the isomeric cycloheptatrienes because of their high boiling points, and the ease with which they isomerise to deoxybenzoin derivatives (see Chapter VI). For this reason it is better to prepare a substituted cycloheptatriene which can be readily separated from its isomers and convert this to the acylcycloheptatriene. There are several possibilties :-

a) Convert the appropriate cyanocycloheptatriene XLIV to the ketone XLV with a Grignard[41] reagent

$$\underset{\text{(XLIV)}}{C_7H_7CN} \xrightarrow{\text{PhMgBr}} \underset{\text{(XLV)}}{C_7H_7COPh}$$

b) Convert the cycloheptatriene ester, C_7H_7COOMe, to the ketone, again with a Grignard reagent.[48] One problem with this method is the separation of the ketone from the alcohol also formed.

c) Convert the cycloheptatriene acid chloride,[46] C_7H_7COCl, to the ketone with an organo cadmium derivative.[47]

In theory, any of these methods may be used to prepare acyl cycloheptatrienes, although (b) has the disadvantage of giving the alcohol in comparable yield.

2. Synthesis of 1-Acylcycloheptatrienes.

The reaction conditions were varied as part of an investigation into the mechanism of addition of benzoyl chloride to cycloheptatriene. It was observed that by decomposing the aluminium chloride-complex at 0°, instead of at room temperature, an unstable product was obtained. The nuclear magnetic resonance (n.m.r.) spectrum of the crude material showed that it was neither a deoxybenzoin nor a cycloheptatriene derivative. Attempts to purify the compound caused decomposition, 1-benzoylcycloheptatriene being the product.

Identification of this product was mainly from its n.m.r. spectrum. τ 2.3 - 2.7 (m, 5H) was assigned to the aromatic protons of the benzoyl group, τ 3.3 - 4.5 (m, 5H) consisted of three well defined multiplets, typical of the vinylic protons of the cycloheptatriene ring, and τ 7.3 (d, 2H) was assigned to the methylene protons. The doublet splitting, τ 7.3 is consistent only with a 1-substituted cycloheptatriene, all other isomers giving a triplet splitting. (For further discussion see Chapter VII).

The n.m.r. spectrum also indicated the presence of small amounts of deoxybenzoin and the isomeric 2 and 3-benzoylcycloheptatrienes. These are formed by thermolysis of the 1-isomer (see Chapter VI for details), during decomposition of the intermediate and distillation of the crude product.

Decomposing the intermediate in methylene chloride by passing HCl gas, followed by careful distillation, gave 1-benzoylcycloheptatriene, about 95% pure (estimated from the n.m.r. spectrum).

Chromatography of the crude material on a silica gel column, eluting with chloroform, provides an alternative method of isolating the product. This gave 1-benzoylcycloheptatriene, free from isomeric impurities, (estimated from the n.m.r. spectrum).

The acylcycloheptatrienes made by this method are summarised, together with their properties, in Table III. The addition of mesitoyl chloride differs from the other acyl chlorides in that no intermediate could be isolated, instead 1-mesitoylcycloheptatriene was obtained directly (expt. 15).

Attempts were made to synthesise 1-benzoylcycloheptatriene without having to decompose the intermediate. Using benzoic anhydride instead of benzoyl chloride to provide the electrophilic species, still gave the intermediate and then 1-benzoylcycloheptatriene (expt. 20). Changing the solvent to carbon disulphide (expt. 21) retarded the reaction, so it was therefore necessary to add the cycloheptatriene to the refluxing mixture, and at these temperatures only deoxybenzoin is formed.

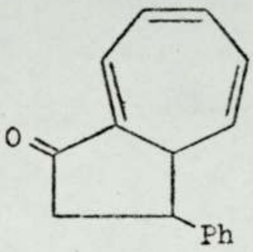
Table III

Properties of Cycloheptatriene Derivatives.

Compound	m.pt./b.p.	M^+		Experiment No.
		measured	theoretical	
1-benzoylcycloheptatriene	45-47°	196.0894	196.0888	14
1-mesitoylcycloheptatriene	30-34°	238.1359	238.1358	15
1-(1-naphthoyl)cycloheptatriene	155-170°/ 0.3 m.m.	246.1022	246.1045	16
1-(p-methoxybenzoyl)-cycloheptatriene	157-163°/ 0.7 m.m.	226.0883	226.0994	17
1-acetylcycloheptatriene	100-110°/ 15 m.m.	134.0718	134.0732	18

3. Reaction of Cycloheptatriene with Cinnamoyl Chloride.

Cinnamoyl chloride adds to cycloheptatriene (expt. 19) to give the intermediate as with the other acyl chlorides, however, decomposition of this compound with HCl gas did not give the expected cycloheptatriene derivative. The most likely product XLVI is shown below :-



(XLVI)

Similar ring closures have been observed in other Friedel-Crafts reactions. These are discussed in Chapter V.

4. Summary.

The method described, provides a convenient synthesis of 1-acylcycloheptatrienes from readily available materials. It is superior to the alternative methods discussed in Section 1, where at some stage in the synthesis the separation of isomeric cycloheptatrienes has to be performed. Further photolysis of this material causes a highly specific 1,7-hydrogen shift, giving 2-benzoylcycloheptatriene as the only product. This extends the range of the reaction to the preparation of two out of the four possible isomers.

The reaction also provides a means of introducing substituents directly into the cycloheptatriene ring. Radical attack is the only other example of this.[49]

V Mechanism for the reaction of acyl chlorides with cycloheptatriene in the presence of aluminium chloride.

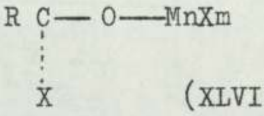
1. Friedel-Crafts Acylation of Olefinic Compounds.[50,51]

Soon after Friedel and Crafts established the alkylation and acylation of aromatic compounds, Kondakov[52] extended the reaction to the acylation of olefins. He investigated the reaction of isobutylene with acetic anhydride or acetyl chloride in the presence of zinc chloride and found the main products were unsaturated ketones and β-chloroketones, respectively.

Although the volume of work done on these reactions is small compared to that done on aromatic compounds the scheme outlined, Fig. IV, is well-established. Extensive evidence has been produced concerning the nature of the electrophilic species in acylation reactions,[53] but this does not affect the mechanism of the reaction and will not be described here. It is sufficient to point out that the acylating agent may exist as an ion pair XLVII or a polarised donor-acceptor complex XLVIII depending upon the medium. The role of the catalyst in the reaction is

$RCO^+ \quad MnX_{\bar{m}+1}$

(XLVII)



$$\begin{matrix} R\,C - O - MnXm \\ \vdots \\ X \end{matrix}$$

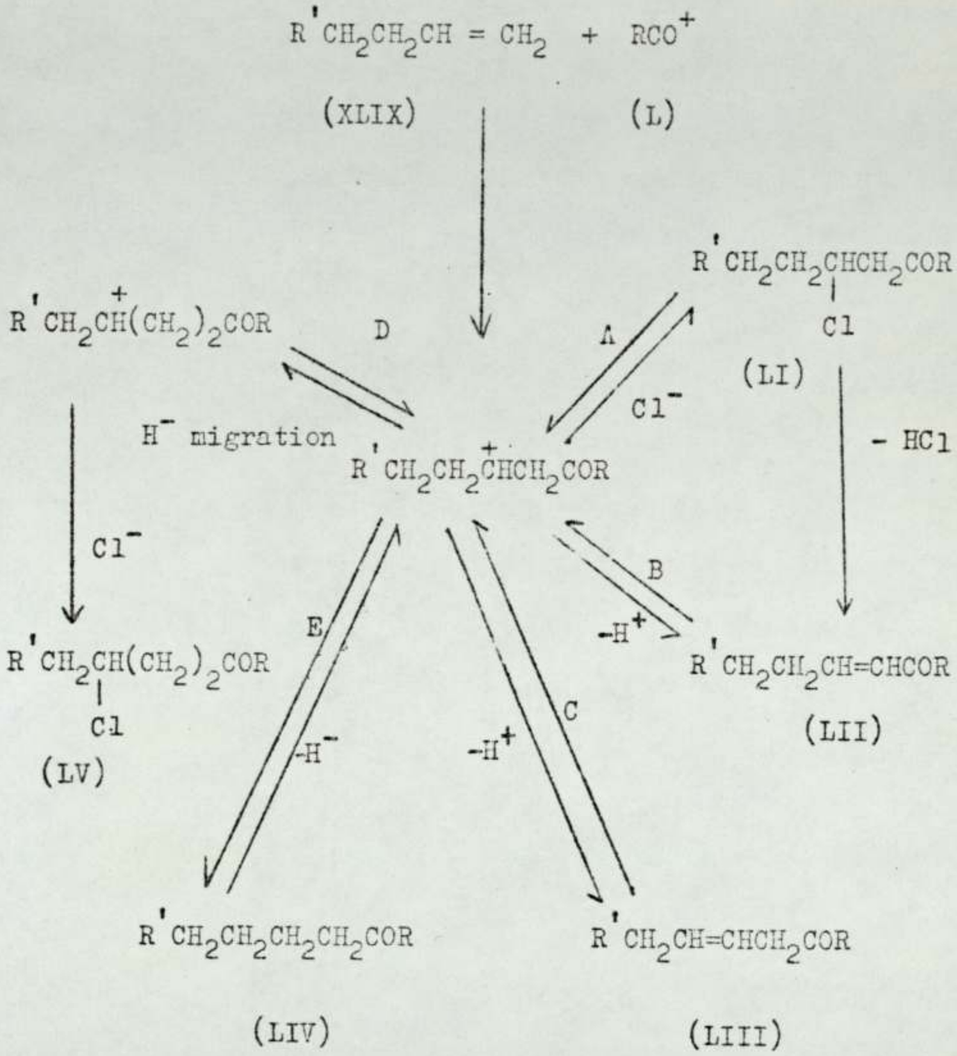
(XLVIII)

to make the acylating species, whatever its form, a more effective electrophile.

The reaction consists of :-

a) the formation of a sufficiently active acylating species (represented RCO^+) from the catalyst and the acyl compound.

Figure IV. Acylation of Olefinic Compounds.



b) the attack of this species on the olefinic substrate and the subsequent behaviour of the intermediate so formed, (see Fig. IV.)

Route A is the most frequent route to α,β-unsaturated ketones, via the intermediate haloketone LI, whereas the importance of B, which corresponds to direct substitution is uncertain. Route C to give the α, β-unsaturated ketone LIII is also very common, and is thought to be due to the formation of a six-membered cyclic transition state. Hydride migration, D, often accounts for the formation of halogenated side products, the haloketone LV not readily losing HX. Route E is often observed in hydrocarbon solvents e.g. the acylation of cyclohexene in cyclohexane, to form a saturated ketone.[50]

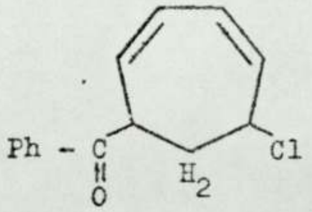
Additional complications can be caused by polymerisation of unstable alkenes. The relative importance of each route varies with the particular system.

2. Intermediate isolated in the Synthesis of 1-Benzoylcycloheptatriene.

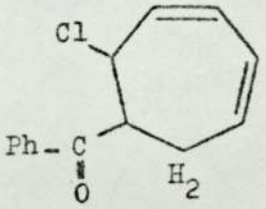
Chapter IV described the synthesis of 1-benzoylcycloheptatriene by decomposition of the intermediate isolated from the reaction of cycloheptatriene and benzoyl chloride at 0°.

Attempts to purify this intermediate failed, rearrangement to 1-benzoylcycloheptatriene occurring too rapidly. Hence physical data had to be obtained with a crude sample prepared by evaporating off the solvent from the reaction mixture. Infra-red (i.r.) and mass spectra (m.s.) showed the benzoyl group (, C=0, 1690 cm.$^{-1}$, m/e 105), Cl^{35}/Cl^{37} isotope ratios in the m.s. indicated one chlorine atom, and the nuclear magnetic resonance (n.m.r.) spectrum at τ 4.0 was similar to reported spectra of conjugated cyclic dienes.[15,54,55] These data coupled with the formation of the compound from, and its ready conversion to, a cycloheptatriene ring, suggested a cycloheptadiene. Peak matching the parent ion in the m.s. as $C_{14}H_{13}O$ confirmed a benzoylchlorocycloheptadiene.

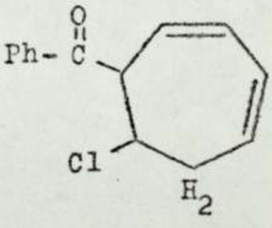
The possible conjugated dienes were the 1-benzoyl- 6-chlorocyclohepta-2,4-diene LVI and the two 1,-2 isomers LVII and LVIII.



(LVI)



(LVII)



(LVIII)

Spin decoupling experiments using the n.m.r. spectrometer in a field sweep mode, showed that the signals at τ 5.15 (CHCl) and τ 5.50 (CHCO) were both coupled to the axial proton of the methylene group τ 7.85 (see chapter VII). Clearly this could only happen for LVI, the 1-benzoyl-6-chlorocyclohepta-2-4-diene.*

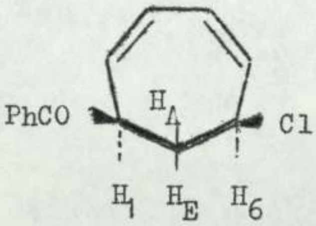
* The numbering used for the cycloheptadiene derivatives is based upon that of the cycloheptatriene ring system. This method was thought to be less confusing than the conventional method, where numbering is from one of the double bonds.

3. Structure of 1-benzoyl-6-chlorocyclohepta-2-4-diene.

Electron diffraction[56] studies on the cycloheptadiene ring system have shown the molecule to be planar, with one carbon atom (C_7) tilted at an angle of 70°. In the following discussion it was assumed that LVI has a similar conformation, with only slight distortions to accommodate substituents.

LVI may have either a cis or trans configuration, both isomers having two conformations. These structures are shown in Fig. V.

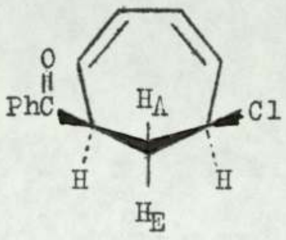
Analysis of the nuclear magnetic resonance (n.m.r.) spectrum (Appendix I, No. 7), in particular the region τ 7-8, assigned to the methylene protons, enables the isomers to be distinguished. By analogy with the cycloheptatriene system H_A (the quasi-axial methylene proton) is shielded by the double bond system[57] and will be to high field of H_E (the quasi-equatorial methylene proton). H_A τ 7.8 appears as an eight line multiplet due to coupling with H_E, H_1 and H_6 (the protons attached to carbon atoms 1 and 6 respectively.



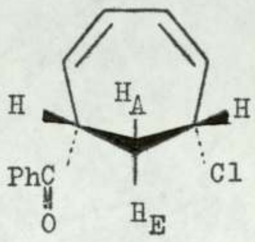
Applying the concepts of the Karplus equation qualitatively to the cis isomer it follows that $J_{1A} = J_{6A}$ (the coupling constants between H_1 and H_A and H_6 and H_A respectively) and similarly $J_{1E} = J_{6E}$. This is so because the appropriate dihedral angles in the cis isomer are identical.

Figure V. Structures of 1-benzoyl -6-chlorocyclohepta-2-4-diene.

Cis isomers

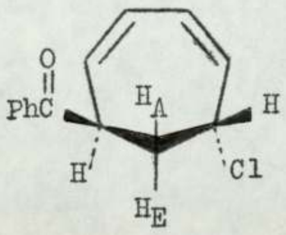


(LVI a)

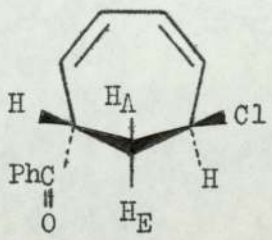


(LVI b)

Trans isomers



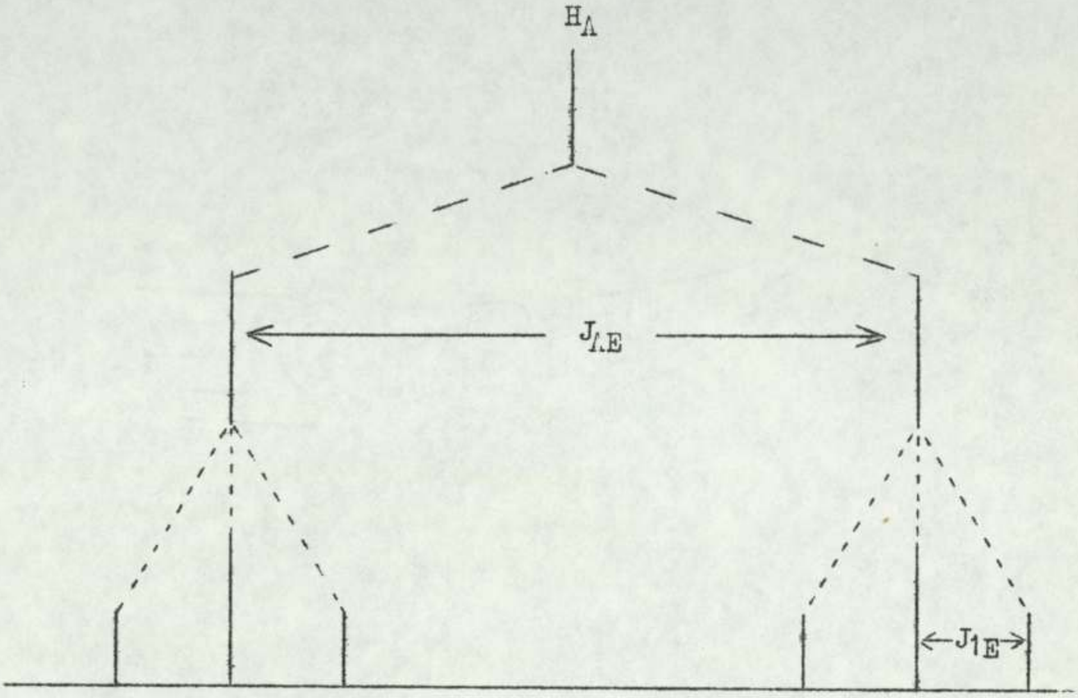
(LVI c)



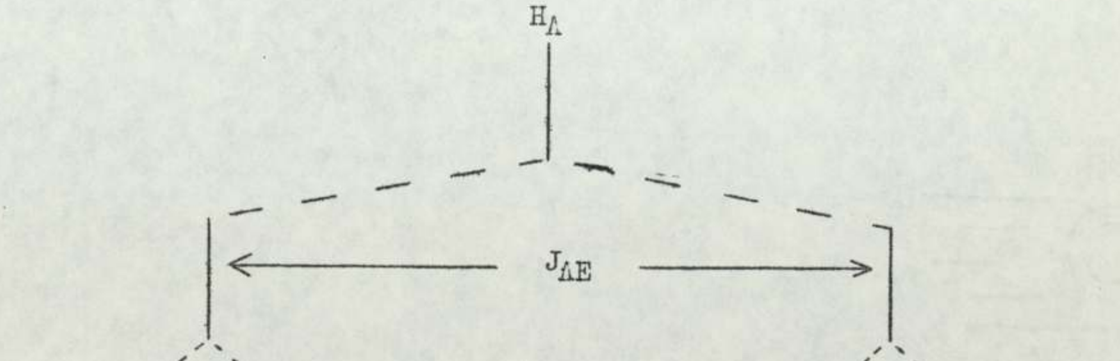
(LVI d)

Figure VI. Predicted N.M.R. Spectrum of the Axial Methylenic Protons in the Isomeric 1-Benzoyl- 6-chlorocyclohepta-2-4-diene.

A Cis isomer



B Trans isomer



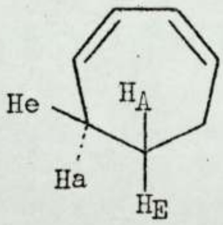
Hence, a doublet of triplets is expected for H_A as shown in Fig. VIA. The observed eight line multiplet indicates that $J_{1A} \neq J_{6A}$ as shown in Fig. VIB.

Evidently the intermediate is not a cis isomer. Of the two trans isomers, that with the bulky benzoyl group equatorial should predominate. Further, since the n.m.r. spectrum shows only one isomer, it must be LVI C.

To verify this it is necessary to calculate the appropriate coupling constants from the Karplus[58] equation. These data, together with the observed constants, are summarised in Table IV. The subscripts used denote the configuration of a particular hydrogen (axial or equatorial), uppercase subscripts referring to the methylene protons and lower case subscripts to the protons H_1 & H_6.

Table IV

Coupling Constants in the Cycloheptadiene Ring.



Coupling Constant	estimated value, Hz.	measured value, Hz.
J_{Ae}	0	3
J_{Aa}	10	10
J_{AE}	12	15
J_{Ee}	4	2
J_{Ea}	0	2

The agreement is reasonable, the largest discrepancies being in the prediction of the small coupling constants.

These deviations are due partly to the approximations inherent in applying the Karplus equation to a seven-membered ring system, partly due to ignoring the electronegativity of the substituents, and partly due to distortion of the ring to accommodate bulky substituents.[58]

The width of the signal at τ 5.50 is 18 Hz, and so it must include the large coupling J_{Aa}, making this proton axial. From its position, to high field of the other methine proton, τ 5.10, this proton must be adjacent to the benzoyl group, which deshields an α-proton less than a chlorine group.[59] Hence the benzoyl group must be equatorial and the chlorine axial, i.e. LVIC, as predicted.

N.m.r. studies at 0° of the solution obtained from the addition of cycloheptatriene to a mixture of benzoyl chloride and aluminium chloride in methylene chloride showed the presence of a benzoylchlorocycloheptadiene intermediate. Warming this solution (still in the n.m.r. tube) to room temperature gave deoxybenzoin.

The n.m.r. spectrum was difficult to interpret because of the poor quality of the spectrum, which was caused by :-

a) the reaction solution being dilute (compared to solutions normally used in n.m.r. work) and low intensity lines were possibly lost in the background noise.

b) spinning side-bands from the protons of the methylene chloride solvent obscuring part of the spectrum.

c) the variable temperature probe (V.T.P.) used "icing up" at the temperature used causing spinning to be irregular which in turn decreases resolution.

However, it could be said with certainty that the isomer was not a trans isomer. Hence it seems reasonable to assume the cis diequatorial conformer LVIa was obtained, since steric interaction would be prohibitive in the cis diaxial conformer. The n.m.r. spectrum in fact resembles that expected for the diequatorial conformer more closely than any of the other possibilities, however, in view of the poor quality of this spectrum any positive identification is impossible.

4. Reaction Scheme for the formation of Deoxybenzoin and 1-Benzoylcycloheptatriene.

The reaction of an electrophilic reagent with cycloheptatriene was expected to give tropylium salts by hydride-ion exchange. Similar reactions reported in the literature* support this view. However, the experiments described in Chapter II show that although tropylium salts were formed, an initial hydride-ion transfer from cycloheptatriene to the electrophilic species had not occurred. The only reasonable alternative was attack at the double bond system.

The introduction to this present chapter describes the attack of Friedel-Crafts reagents on an isolated double bond, to give an intermediate halo-ketone. The isolation of a chloro-ketone intermediate in the synthesis of 1-benzoylcycloheptatriene indicates that the reaction is entirely analogous to this more familiar olefinic acylation.

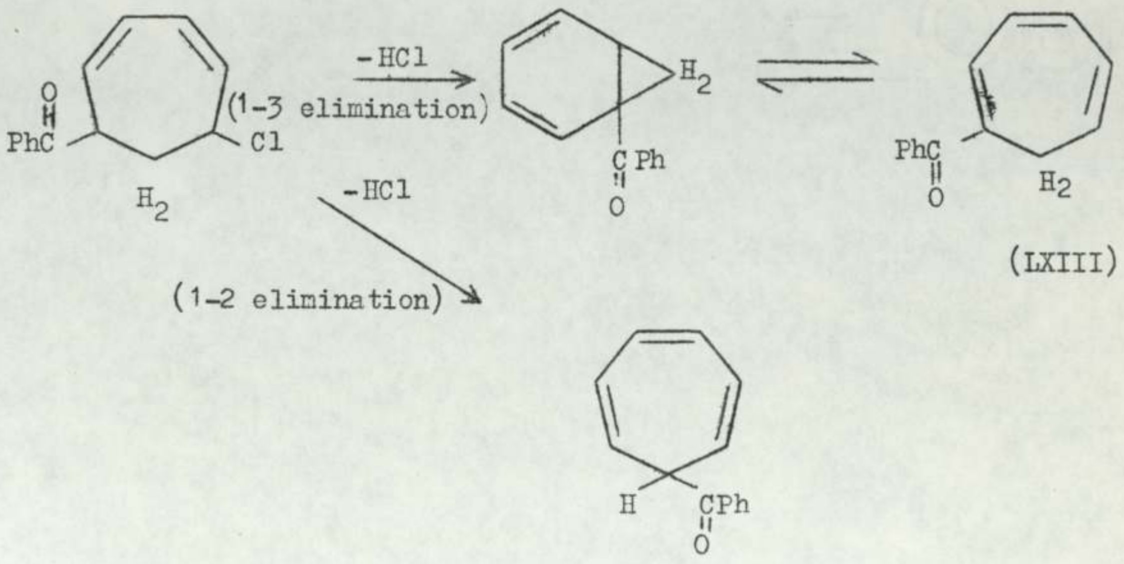
Further since a 1,6-adduct has been isolated (i.e. 1-benzoyl-6-chlorocyclohepta-2-4-diene) 1,6 addition must have occurred. The only other 1,6 additions to cycloheptatriene that have been reported, i.e. addition of nitrosobenzene [55,61] and chlorosulphonyl isocyanate,[60] are cycloadditions. Concerted cycloadditions are governed by the Woodward-Hoffmann[63] rules which allow only 1,4 addition to cycloheptatriene e.g. the more familiar Diels-Alder[65] reactions, hence the 1,6 cycloadditions must be stepwise.[61,62]

The chloro-ketone LVI is an intermediate in the formation of both products. A 1-3 elimination of HCl would give 1-benzoylcyclo-

---

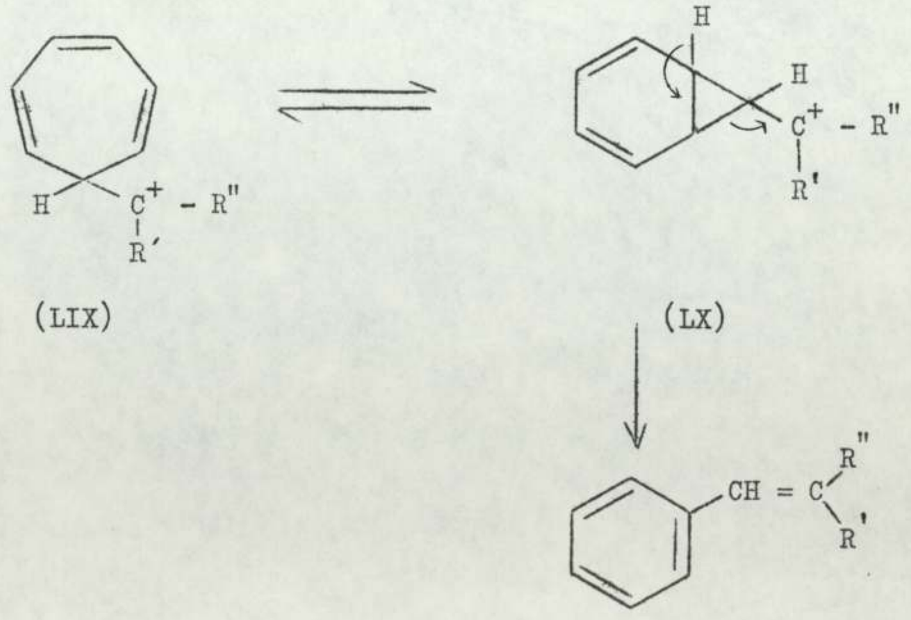
* For examples and references see Chapter II.

heptatriene, while a 1-2 elimination of HCl would give 7-benzoylcycloheptatriene.



(LXIII)

The acid catalysed rearrangement of 7-substituted cycloheptatrienes which are capable of giving rise to ions of the type LIX has been discussed by Ganellin and Pettit.[47] Valence tautomerism to the norcaradiene LX



(LIX)

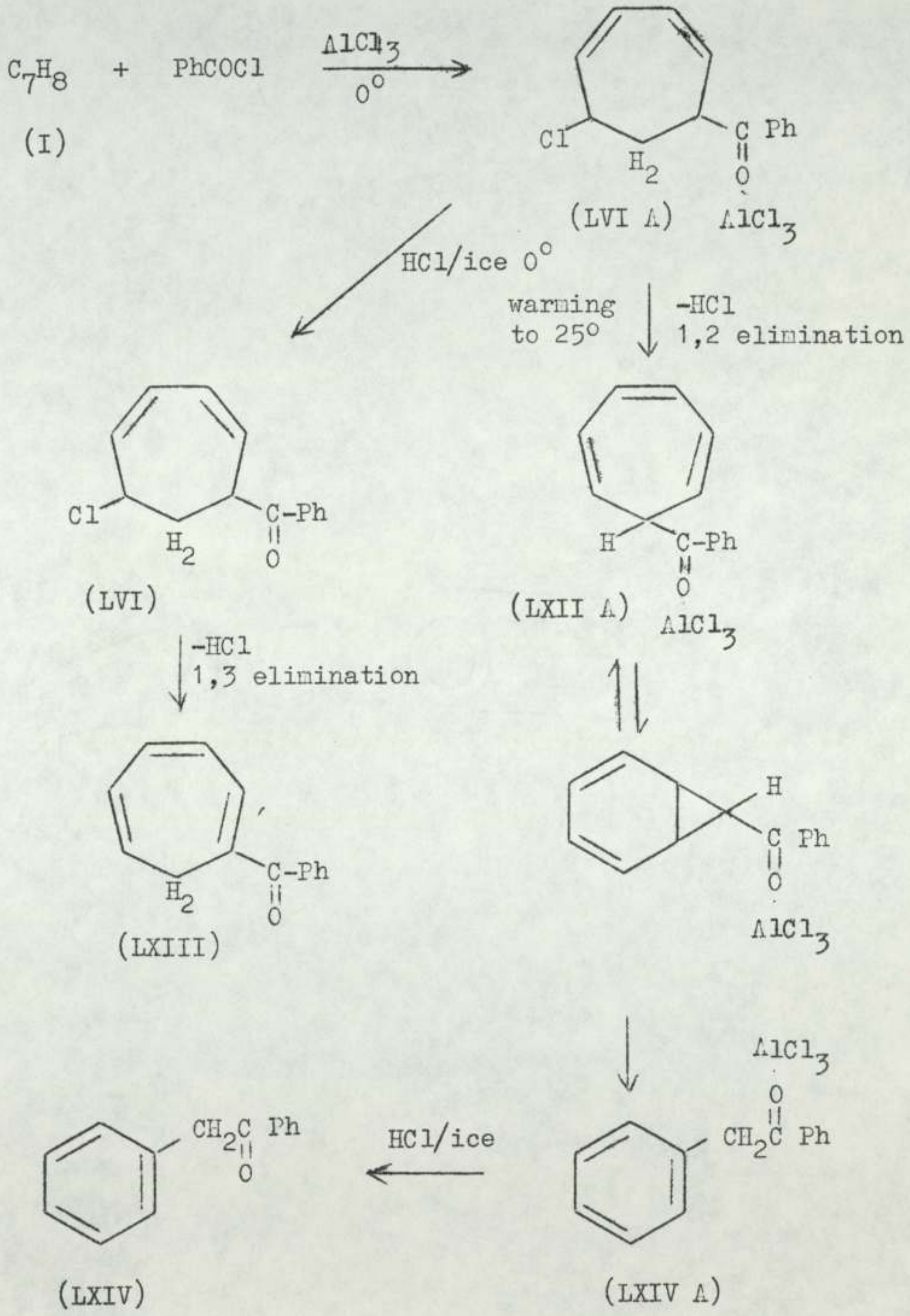
(LX)

(LXI)

and bond cleavage gives the aromatic compound LXI. A 7-keto cycloheptatriene in acid solution would form LIX by protonation ($R' =$ alkyl or aryl, $R'' = OH$), rearranging to LXI which is the enol form of a benzyl ketone. Ganellin and Pettit[38] synthesised 7-acetylcycloheptatriene which in acid solution LIX ($R' = CH_3$, $R'' = OH$) rearranges to benzyl methyl ketone [redacted] Even more relevant to the present study is the work of Doering[41] who added phenyl magnesium bromide to 7-cyanocycloheptatriene in an attempt to prepare 7-benzyoylcycloheptatriene and obtained deoxybenzoin. Thus it seems reasonably certain that 7-benzoylcycloheptatriene, if formed, would rearrange, in the conditions used, to deoxybenzoin. These schemes are outlined in Fig. VII.

The problem remains, however, to explain why the intermediate chloro-ketone LVI should eliminate HCl by two different paths. Considering first the general theories of elimination reactions. Due largely to the work of Hughes and Ingold three principal mechanisms of elimination have been recognised, namely E1 (unimolecular elimination), E2 (bimolecular elimination) and E1cb (carbanion elimination), the nomenclature being that used by these workers.

Figure VII. The Formation of Deoxybenzoin and 1-Benzoylcycloheptatriene.



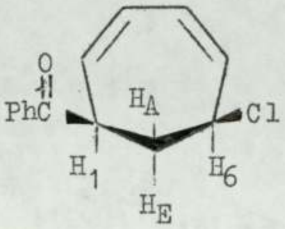
The E_2 mechanism will be operating in the elimination of HCl from the chloro-ketone intermediate, and so only this mechanism will be discussed. Initially it appeared that E_2 eliminations proceeded most rapidly when the leaving groups were arranged trans to one another. The evidence for this mode of elimination is well covered in a number of standard texts.[66,67] It was not until the work of DePuy[68,69] et al in 1962 that this idea was challenged. These workers studied elimination from a series of cis and trans β-aryl cyclopentyl and β-aryl cyclohexyl tosylates, showing that cis eliminations occurred preferentially in the cyclopentyl tosylates, and at rates comparable to the trans elimination in the cyclohexyl tosylates. They concluded that coplanarity of the groups to be eliminated, was of greatest importance in determining the mode of elimination.

Returning to the elimination from LVI, one must conclude that different configurations of the 1,6-chloro-ketone are involved.

Evidence has already been presented, (section 3) for the existence of two isomeric chloro-ketone intermediates. Analysis of the n.m.r. spectrum revealed that the compound isolated in the synthesis of 1-benzoyl cycloheptatriene was LVIc, whereas the compound in solution at 0°, which gave deoxybenzoin on warming, was probably LVIa. The proton eliminated may be either a methylene proton, H_7, forming the cycloheptatriene ring, or the proton adjacent to the benzoyl group, H_1, forming a bond between C_1 and C_6 to give the norcaradiene, which will rapidly tautomerise to the cycloheptatriene. The appropriate dihedral angles between these hydrogen atoms and the chlorine atom are summarised in Table V.

Table V.

Dihedral Angles (α) between the chlorine atom and the adjacent hydrogen atoms.



β-H atom	angle° (α) for LVIa	angle° (α) for LVIc
HA	80	160
HE	40	90
H1	100	0

These results clearly show that in LVIc H1 the cis proton is coplanar with the chlorine atom and will be eliminated preferentially to give 1-benzoylcycloheptatriene LXIII, whereas in LVIa trans-elimination of the equatorial methylene proton is preferred to give 7-benzoylcycloheptatriene LXI which rearranges spontaneously to deoxybenzoin LXIV.

The system studied was particularly suited to rearrangements. For example epimerisation, due to enolisation of the carbonyl group, rapidly interconverts diastereomers, while the large benzoyl group, will always attain an equatorial conformation. Thus while n.m.r. evidence can prove the presence of a species in solution, this species need not necessarily be formed directly from the reactants. Transient intermediates may precede this compound. For these reasons it is difficult to prove any mechanism conclusively, analogies must be made to simpler system

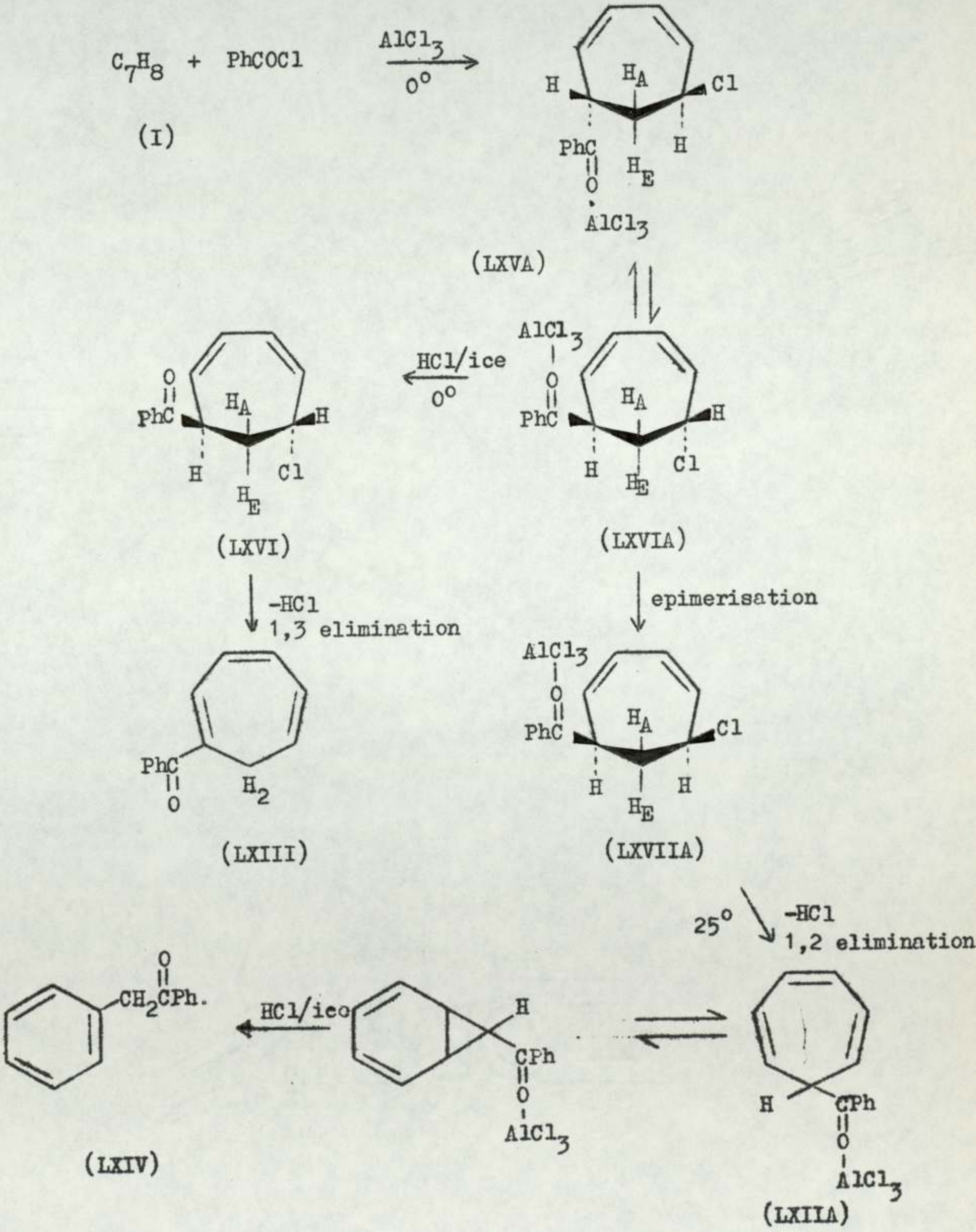
The stereochemistry of addition reactions has recently been studied by Dewar et al and, as with elimination reactions, the improved techniques have revealed that the accepted trans-addition is no longer satisfactory.

Studying the polar addition of DBr to a variety of olefins[70,71] cis addition was shown to be preferred in the examples studied. A classical carbonium ion intermediate was postulated with Br^- attacking from the same side as the electrophile, to give cis addition except when bulky groups were involved, then rotation occurred in the ion pair to give trans addition. It would appear, therefore, that both cis and trans addition of benzoyl chloride to cycloheptatriene are possible, although trans addition should be preferred in view of the crowding in the diaxial transition state.

Firstly considering trans addition, the least hindered position of attack will probably be on the underside of the cycloheptatriene ring, although the subsequent argument is still valid if this is not so. This leads to axial substitution, see Fig. VIII. Trans-addition then gives the chlorine atom in the equatorial position LXVA. Inversion of LXVA gives LXVIA which is isolated LXVI (LVIC) on adding the reaction mixture to HCl/ice at 0°. 1-3 HCl elimination then gives 1-benzoylcycloheptatriene LXIII as described above.

Warming the reaction mixture to room temperature, as in the synthesis of deoxybenzoin, causes epimerisation of the ketone function, to the more stable diequatorial conformer LXVIIA (LVIa) which undergoes a 1,2 elimination of HCl, to give 7-benzoylcycloheptatriene LXIIA and hence deoxybenzoin LXIV. The complete scheme for the formation of both deoxybenzoin and 1-benzoylcycloheptatriene by an initial trans-addition of the benzoyl chloride is summarised in Fig. VIII.

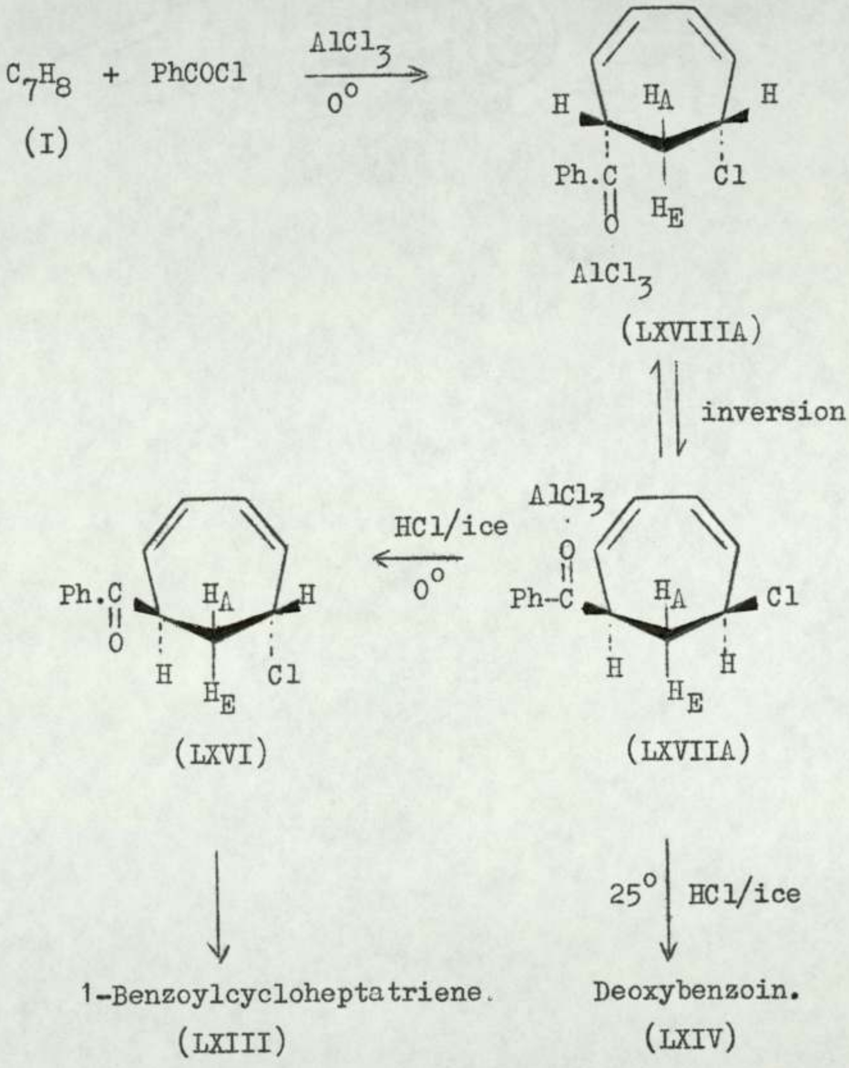
Figure VIII. Reaction of Benzoyl Chloride with Cycloheptatriene, Initial trans-addition.



The alternative cis-addition of the benzoyl chloride, outlined in Fig. IX, gives initially the diaxial chloro-ketone LXVIII which inverts to the more stable diequatorial conformer LXVI. 1,2 HCl elimination followed by rearrangement of the 7-benzoylcycloheptatriene gives deoxybenzoin as with trans-addition. To form 1-benzoylcycloheptatriene the diequatorial chloro-ketone must isomerise to the axial-equatorial configuration LXVI and it is difficult to see what driving force there is for this conversion.

Hence trans-addition explains the formation of deoxybenzoin and 1-benzoylcycloheptatriene far better than the alternative cis addition, and in view of the crowding in the cis transition state, is the most likely mode of addition.

Figure IX. Reaction of Benzoyl Chloride with Cycloheptatriene, Initial Cis Addition.



5. Related Acylations of Cycloheptatriene.

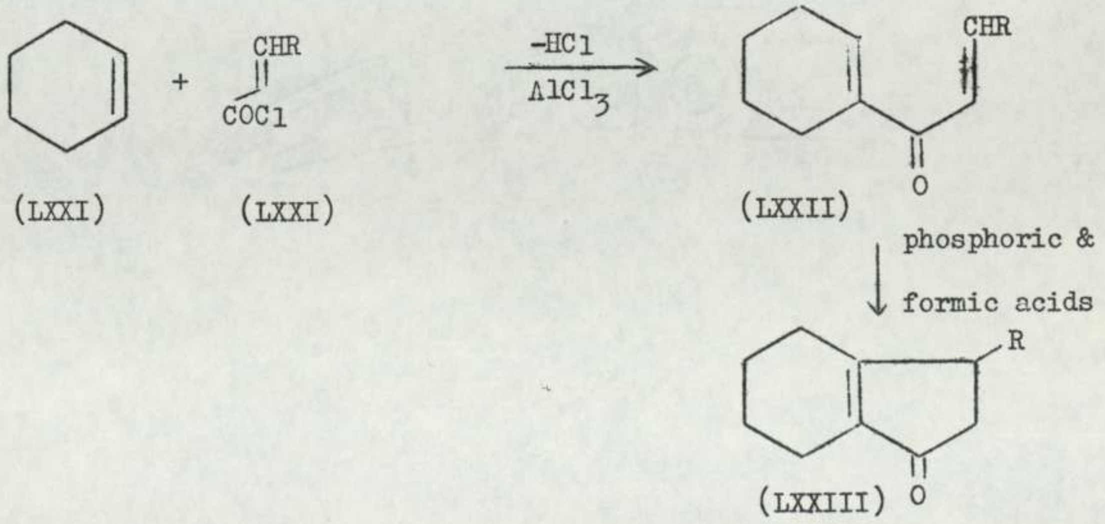
a) Acid chlorides in the presence of aluminium chloride.

The acid chlorides used are summarised in Table III, Chapter IV. In general the appropriate haloketone intermediate was detected, by its characteristic n.m.r. spectrum. This intermediate decomposed readily to the 1-acylcycloheptatriene, presumably as in the benzoyl chloride reaction discussed at length in section 4. Thus it is reasonable to suppose that in these cases the same reaction scheme is operating.

Mesitoyl chloride is the only acyl halide for which the chloro-ketone adduct could not be detected, 1-mesitoyl cycloheptatriene being obtained directly by decomposing the aluminium chloride-complex at 0°. It is most likely that the chloro-ketone complex is in fact formed in the normal way, but that steric crowding favours the elimination of HCl, which now occurs spontaneously at room temperature.

Cinnamoyl chloride adds normally to cycloheptatriene and the intermediate chloro-ketone is observed. However, passage of HCl gas does not give the expected 1-cinnamoylcycloheptatriene.

The acylation of alkenes by unsaturated acyl halides has been studied, cyclisation frequently occurring. For example, divinyl ketones were prepared by the addition of unsaturated acyl halides LXXII to cyclohexene LXXI in the presence of aluminium chloride.[72] . Treatment with phosphoric and formic acids then causes cyclisation.



The analogous reaction with cinnamoyl chloride is outlined in Fig. X. giving the bicyclic product LXXVI.

1-Cinnamoylcycloheptatriene would be expected to cyclise more readily than 7-cinnamoylcycloheptatriene. Loss of the adjacent proton is stabilised by the resonance structures LXXVII a and LXXVII b., in 1-cinnamoylcycloheptatriene, whereas in the 7-substituted compound proton loss is not stabilised to the same extent, see Fig. XI.

Thus the proposed scheme explains the formation of benzyl cinnamyl ketone, while attempts to prepare 1-cinnamoylcycloheptatriene lead only to the bicyclic product LXXVI.

Figure X. Reaction of Cycloheptatriene and Cinnamoyl Chloride.

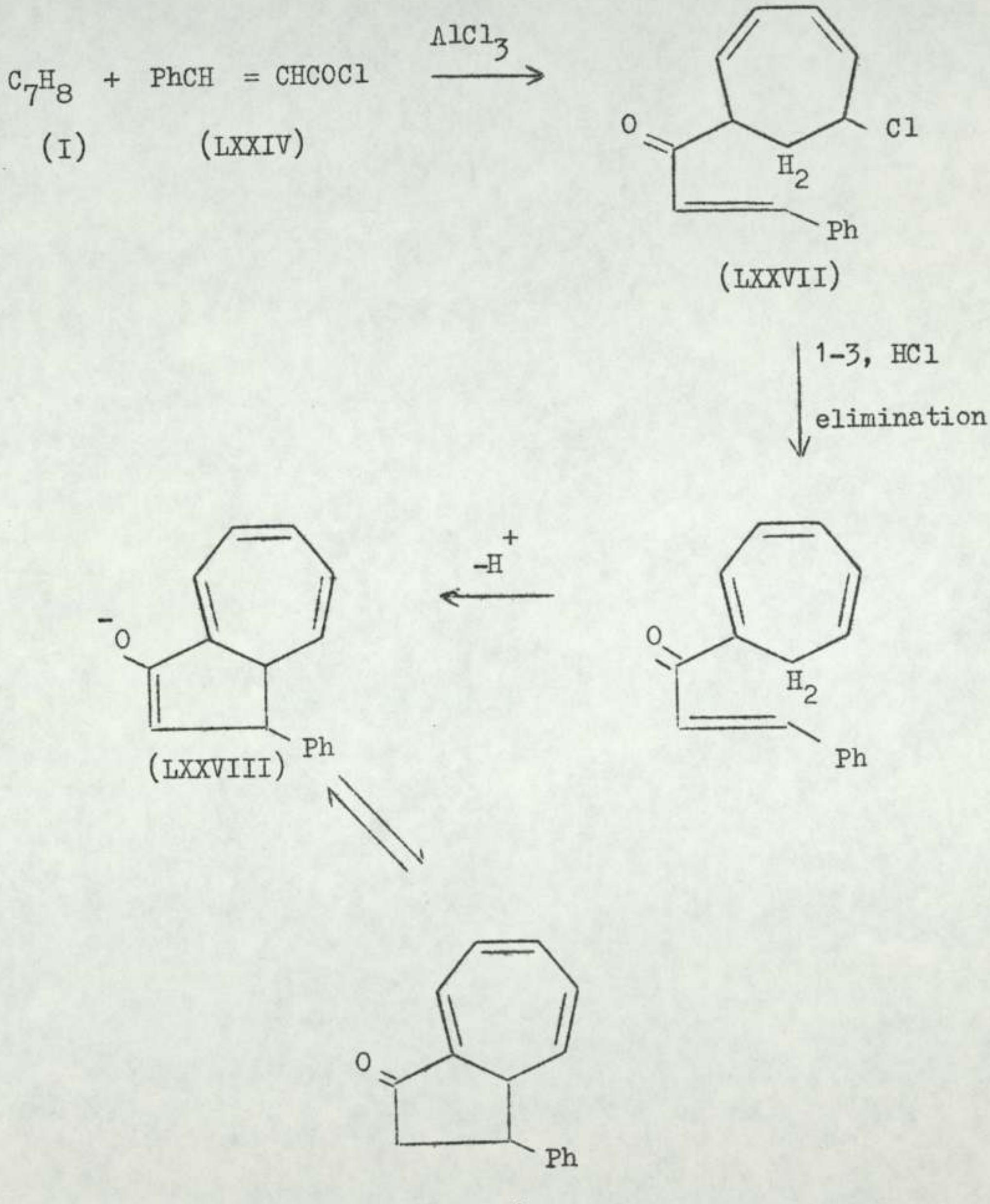
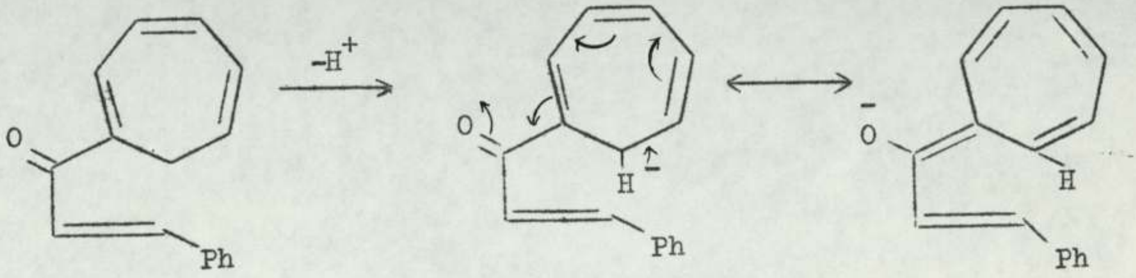
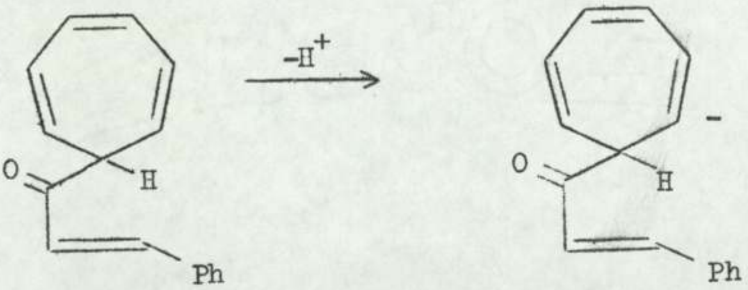


Figure XI. Resonance Structures Stabilising Proton Loss from Acylcycloheptatrienes.

A. 1-cinnamoylcycloheptatriene.



B. 7-cinnamoylcycloheptatriene.



(LXXV)

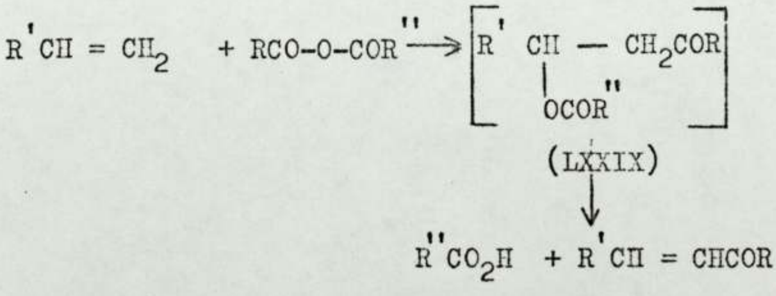
The physical data obtained for the product are in agreement with LXXVI. Peak matching the parent ion in the mass spectrum gives $C_{16}H_{15}O$, while the infra-red (i.r.) spectrum shows the presence of carbonyl and aromatic groups. The n.m.r. spectrum can be assigned as follows :-

τ 2.5 - 3.0 (m, P$\underline{h}$, - 5H), 3.6 - 4.6 (m, vinylic, 4H), 6.0 (m, Ph C$\underline{H}$, 1H), 7.0 - 7.8 (m, CO - CH_2, 2H and m, methylenic, 1H).

b) <u>Acid Anhydrides in the Presence of Aluminium Chloride</u>.

Benzoic anhydride was treated with cycloheptatriene in the presence of aluminium chloride (expt. 20) in an attempt to prepare 1-benzoylcycloheptatriene without isolating the intermediate chloroketone.

This seemed reasonable since acylation of alkenes with acid anhydrides is well-established, and in general the unsaturated ketone is obtained directly. It is assumed that addition across the double bond takes place to give LXXIX which is unstable, decomposing spontaneously to the unsaturated ketone LXXX.



$$R'CH = CH_2 + RCO\text{-}O\text{-}COR'' \longrightarrow \left[R'\underset{\displaystyle OCOR''}{CH} - CH_2COR \right] \;(LXXIX) \longrightarrow R''CO_2H + R'CH = CHCOR$$

(LXXX)

Under special conditions the intermediate LXXIX can be isolated, for example, with acetic-trifluoroacetic anhydride,[73] LXXIX (where R = CH_3 and R'' = CF_3).

However, anhydride acylation of cycloheptatriene unexpectedly gives the intermediate LXXIX (R = R'' = Ph), (according to n.m.r. evidence), contrasting with the normal acylation by acid anhydrides.

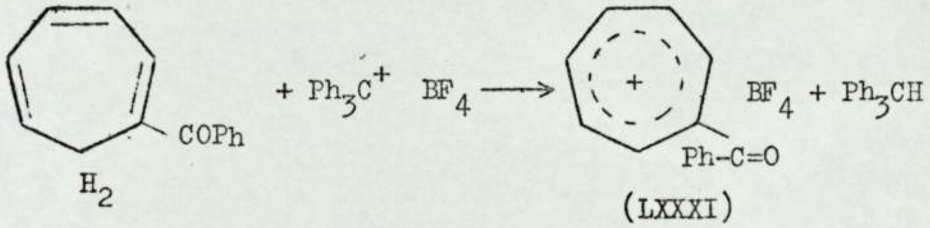
VI Reactions of 1-Benzoylcycloheptatriene[74]

1. Hydride-ion Transfer (expt. 23).

The use of cycloheptatriene as a hydride-ion donor has been discussed in chapter 1. 1-Benzoylcycloheptatriene would be expected to react in a similar way to give benzoyltropylium fluoroborate LXXXI.

Normally the carbon atom of a carbonyl function will be electron deficient, so LXXXI has potentially two adjacent positive charges. The effects of this feature on the stability of the compound could be interesting.

1-Benzoylcycloheptatriene was treated with trityl fluoroborate to give a pale yellow precipitate



(LXXXI)

Filtration at the pump, followed by thorough washing with methylene chloride was necessary to remove excess triphenylmethane, detected by m/e 244 in the mass spectrum of the product.

Working up the reaction filtrate gave triphenylmethane, (Infra-red and nuclear magnetic resonance spectra are identical with authentic material) confirming a hydride-ion transfer. Benzoyltropylium fluoroborate LXXXI is the only reasonable product and the spectral data obtained support this claim.

The nuclear magnetic resonance (n.m.r.) spectrum in trifluoroacetic acid (Me_4Si external reference) shows τ 0.9 (s, $C_7\underline{H_6}$-CO, 6H), 2.7 (m, $\underline{Ph}$CO, 5H). A singlet for the tropylium ring protons was unexpected. A carbonyl function normally deshields the α-protons, which would lead to a complex multiplet for the tropylium ring protons.

This occurs with phenyl tropylium fluoroborate. As the signal is not split this possibly indicates that there is no electron transfer between the ring and the carbonyl group, the polarising effects of the two groups cancelling so that the resultant transfer is zero.

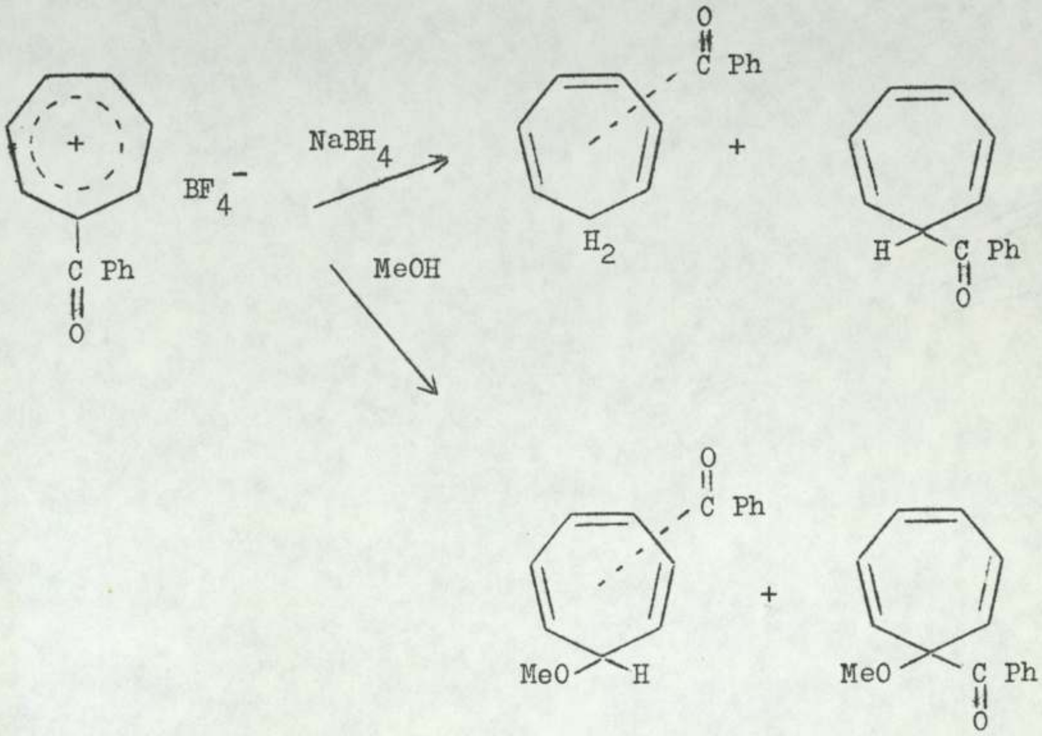
The infra-red (i.r.) spectrum shows the carbonyl ν 1655 and the fluoroborate ν 1050 cm.$^{-1}$ (broad), vibrations while the mass spectrum (m.s.) shows the parent ion at m/e 195, and the P + 1 ion is $C_{14}H_{12}O$.

Reaction with sodium methoxide in methanol (expt. 26) produced an oily residue which was investigated by n.m.r. and i.r. spectroscopy. The n.m.r. spectrum τ 3.2 - 4.6 is typical of the vinylic proton of a cycloheptatriene ring, while its complexity, together with the peaks at τ 7.0 - 8.0, indicates that several isomeric cycloheptatrienes have been formed. Signals at τ 2.2 - 2.9 (m) and 6.7 (s) are assigned to the benzoyl and methoxy groups respectively. The i.r. spectrum confirms this data. The proposed reaction is summarised in Fig. XII.

Reaction with sodium borohydride[76] gave an oily residue that was also analysed by n.m.r. and i.r. spectroscopy. The n.m.r. spectrum showed the characteristic signals of the cycloheptatriene ring protons, τ 3.2 - 4.6 with overlapping multiplets in the region τ 7.0 - 8.0, indicating a mixture of isomeric cycloheptatrienes. The similarity of the i.r. spectrum with that of benzoylcycloheptatriene prepared in this study confirmed this. The i.r. spectrum also shows that only a small amount of the compound is reduced to the alcohol when the sodium borohydride is not present in a large excess. Presumably hydride-ion transfer to the tropylium ion takes place rapidly, and the resulting compounds, being insoluble in water, are removed from the reaction site.

The product was unstable, being observed to decompose slowly at room temperature.

Figure XII. Reactions of Benzoyltropylium Fluoroborate with Nucleophiles.

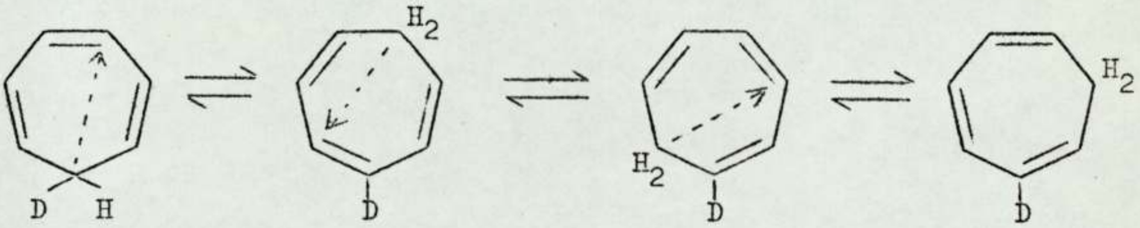


2. Thermolysis. (expt. 24).

The thermal rearrangements of cycloheptatriene and its derivatives have been extensively studied over the temperature range -150° to above 400°.

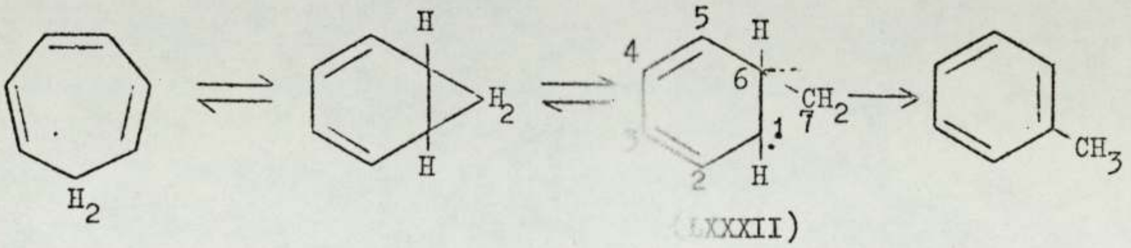
The most facile change is the conformational ring inversion of the two boat forms of the parent compound[9,10] (page 2). At a slightly higher energy of activation is the much-discussed cycloheptatriene-norcaradiene interconversion.*

At temperatures of 130° upwards randomisation of the label in 7-deuterocycloheptatriene takes place by a series of 1-5 sigmatropic hydrogen shifts.[77,78] The precise nature of these rearrangements was confirmed by n.m.r. spectroscopy, randomisation occurring as shown :-



The 1-5 sigmatropic hydrogen shifts are now well established and have been observed for a large number of 7-substituted cycloheptatriene derivatives,[79,80] and reaction parameters have been obtained for the individual reactions.[84]

At much higher temperatures (≃ 400°C) isomerisation of cycloheptatriene to toluene takes place.[81,82] Woods postulated cleavage of the 1,7 bond in the valence tautomeric norcaradiene to form a diradical intermediate LXXXII. A hydrogen shift then gives toluene.[81]

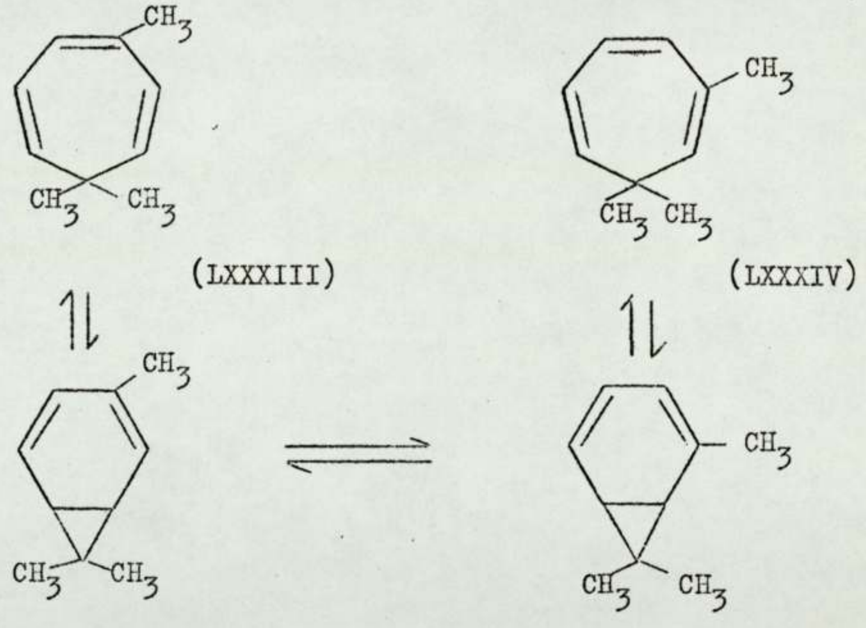


(LXXXII)

---

* for discussion see chapter I and references therein.

If step 2-3 is reversible it is possible that bond formation may take place between C_7 and C_5 as well as between C_7 and C_1. Thus in a substituted cycloheptatriene isomerisation might take place. Berson and Willcott[83,84] investigated these possibilities. A suitable molecule must be disubstituted at the 7-positions (to prevent the facile 1,5 sigmatropic hydrogen migrations) and one more position to provide asymmetry. 3,7,7-trimethylcycloheptatriene LXXXIII was chosen, being readily available,[85] and its thermolysis studied. The results are complex, several competing reactions occurring, but 2,7,7-trimethyl cycloheptatrienes can be isolated LXXXIV showing the anticipated isomerisation. The postulated mechanism is shown below :-


(LXXXIII)

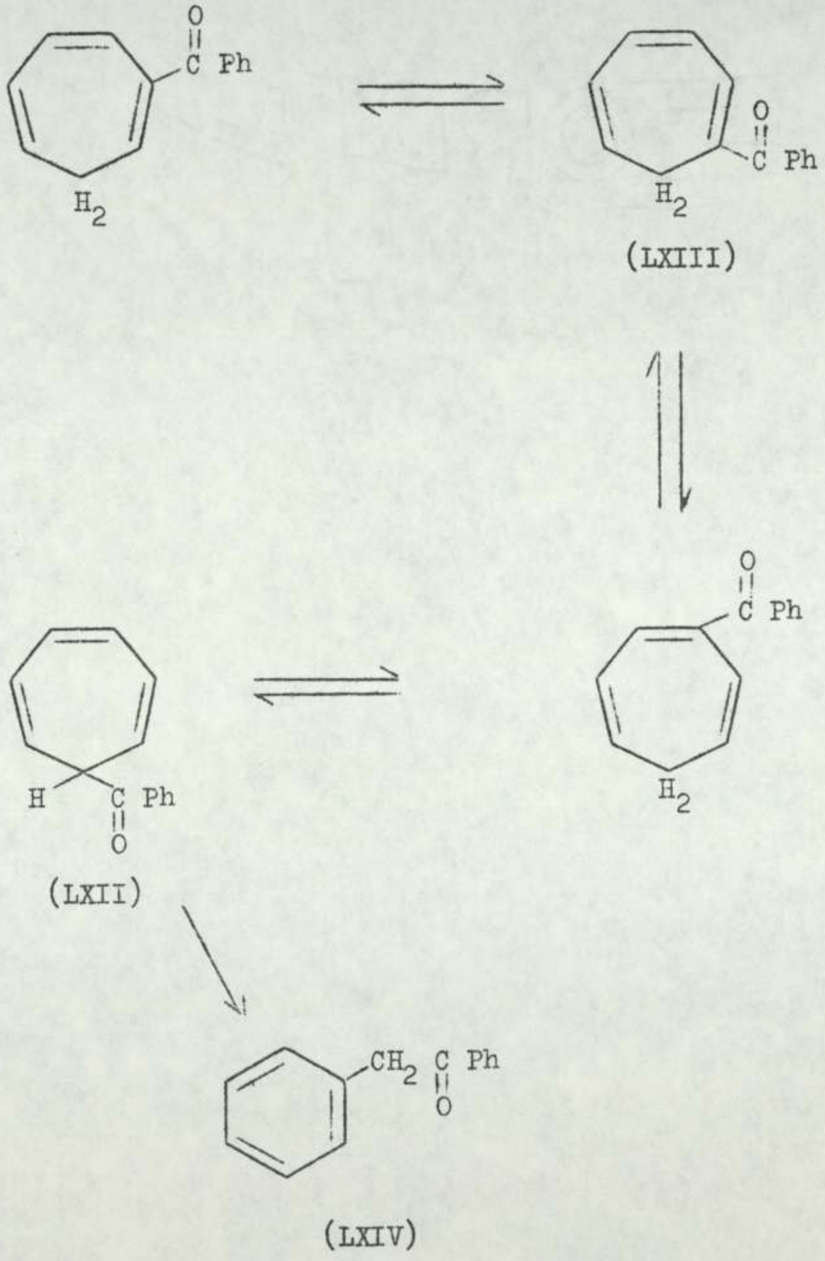
(LXXXIV)

This reaction illustrates 1-5 sigmatropic rearrangement of a carbon atom and raises the possibilities of studying the stereochemistry of these sigmatropic rearrangements. The consequences of this have been outlined in two recent reviews of the subject.[86,87]

As part of an investigation of the properties of 1-benzoylcycloheptatriene, thermolysis was performed to observe the 1-5 sigmatropic hydrogen shifts. Heating (184°, 24 hrs.), gave deoxybenzoin as the only isolable product., (i.r. n.m.r. identical with authentic material).

Samples taken at intermediate times, and examined by n.m.r. spectroscopy showed the formation of isomeric 2 and 3 benzoylcycloheptatrienes. Unfortunately the spectra of these compounds at τ 7.8 overlap and as they are formed in only small amounts it was impossible to say in which order they were formed. However, since 1,5 sigmatropic hydrogen shifts are so well established it is possible to rationalise the formation of deoxybenzoin. (See Fig. III). 7-benzoylcycloheptatriene LXII formed by a series of 1-5 hydrogen shifts, isomerises to deoxybenzoin LXIV. This reaction parallels the isomerisation of cycloheptatriene to toluene described by Woods[81] (see above). The irreversibility of this process accounts for deoxybenzoin being the only product. The drop in temperature of about 240° for this isomerisation illustrates the lower activation energy for the conversion of 7-benzoylcycloheptatriene to the norcaradiene valence-tautomer, compared to the parent molecule.

Figure XIII. Thermolysis of 1-Benzoylcycloheptatriene.



3. Photolysis (expt. 25).

The photolysis of cycloheptatriene and its derivatives has been shown to give 1,7 sigmatropic hydrogen migrations[88,89] and/or valence tautomerism to bicycloheptadiene derivatives.[90] These possibilities are outlined in Fig. XIV. In addition to these reactions Jones et al observed a 1,7 methyl migration on photolysis of 3,7,7-trimethylcycloheptatriene[91] and related compounds.[92,93]

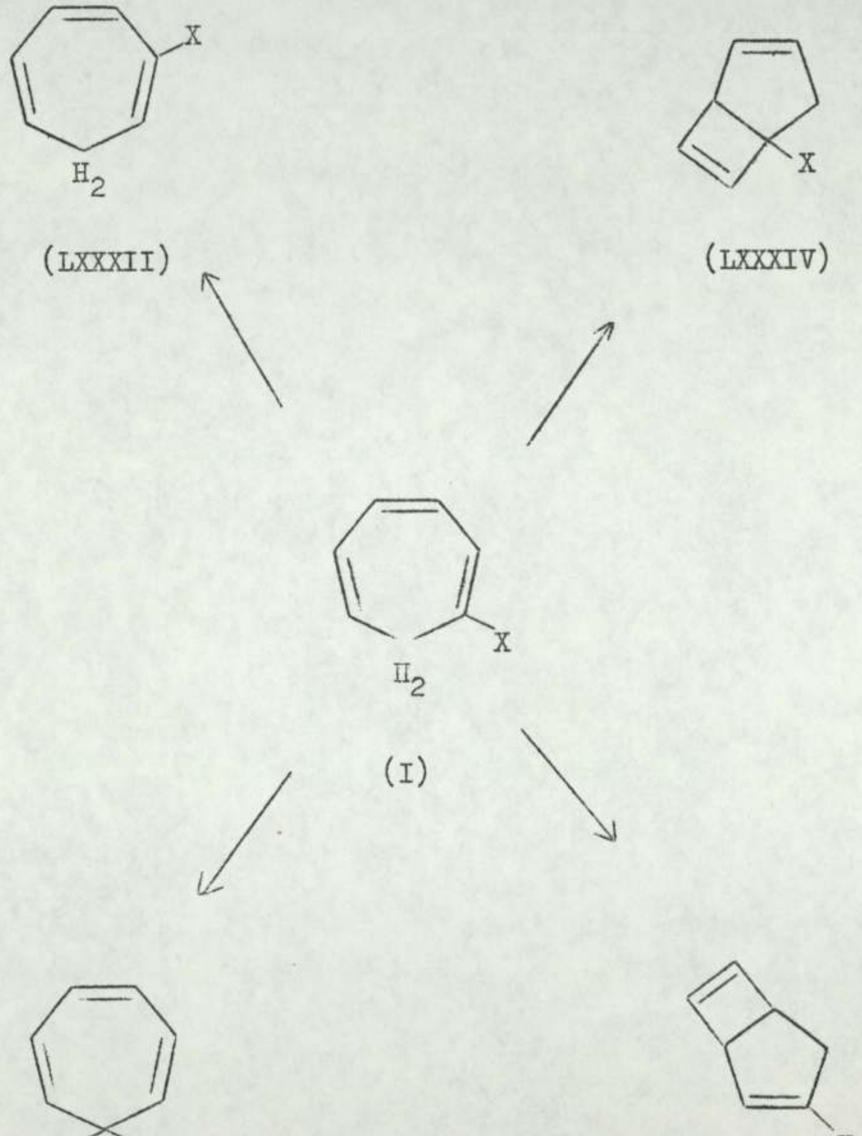
These photolytic reactions are often characterised by a high degree of specificity, e.g. Chapman[94] et al showed that photolysis of 1-methoxycycloheptatriene gave 1-methoxybicyclo [3.2.0] hepta-3,6-diene (valence tautomerism) and 7-methoxycycloheptatriene (1,7 hydrogen shift) (see Fig. XIV. X = OMe), but no 2-methoxycycloheptatriene.

Similarly the 1,7 methyl shifts observed by Jones et al for 3,7,7-trimethylcycloheptatriene[91] were also highly specific only one of the two possible isomers being formed.

Photolysis of 1-benzoylcycloheptatriene in benzene (30 hrs.) using a Hanovia 125-W medium pressure mercury lamp, gave 2-benzoylcycloheptatriene as the product. I.r. n.m.r. and m.s. data were consistent with a benzoylcycloheptatriene, and the position of substitution was obtained from the n.m.r. spectrum. (For discussion see chapter VII).

No valence tautomerism was observed and the direction of the 1-7 hydrogen shift was highly specific. 1-Cyanocycloheptatriene behaves similarly[95] the specificity of its reactions being attributed to the electron-withdrawing capacity of the substituent.

Figure XIV. Photolysis of 1-Benzoyl Cycloheptatriene.



4. Rationalisation of the Cycloheptatriene Rearrangements.

The thermal and photolytic rearrangements described above for cycloheptatriene involve two main classes of reaction, namely sigmatropic and electrocyclic reactions. Woodward and Hoffmann have introduced a most useful theoretical approach to the qualitative description of these and other reactions,[63,64] in the form of a set of rules based on orbital symmetry considerations. The application of the Woodward-Hoffmann rules to both classes of reaction will be outlined for the cycloheptatrienyl system.

(i) Sigmatropic Reactions.

Sigmatropic rearrangements involve the migration of a σ-bonded atom or group (R) in a polyenylic (n = 2,3 ...) chain :-

$$R - C - (C = C)_n \longrightarrow (C = C)_n - C - R$$

For the purpose of this discussion only hydrogen migration, i.e. R = H, will be considered, when the orbital concerned is always the completely symmetrical 1s orbital. If the migrating hydrogen atom is assumed to remain bonded to both ends of the unsaturated system throughout (i.e. a concerted reaction), then the orbital symmetry constraints are derived from the form of the highest occupied molecular orbital (M.O.) of the hydrocarbon radical corresponding to the polyenylic chain. For the cycloheptatriene system molecular orbitals of the linear heptatrienyl radical provide a satisfactory approximation (used by both Chapman[94] et al and Jones[91-93] et al.).

The energy levels of this system are shown in Fig. XV and if the seven electrons of the radical are placed in the lowest energy levels it can be seen that Ψ_4 is the highest occupied M.O. in the ground state. Exciting this electron the Ψ_5 becomes the highest occupied M.O. in the first excited state with Ψ_4 empty. The form of Ψ_4 and Ψ_5 is included in the energy level diagram (Fig. XV).

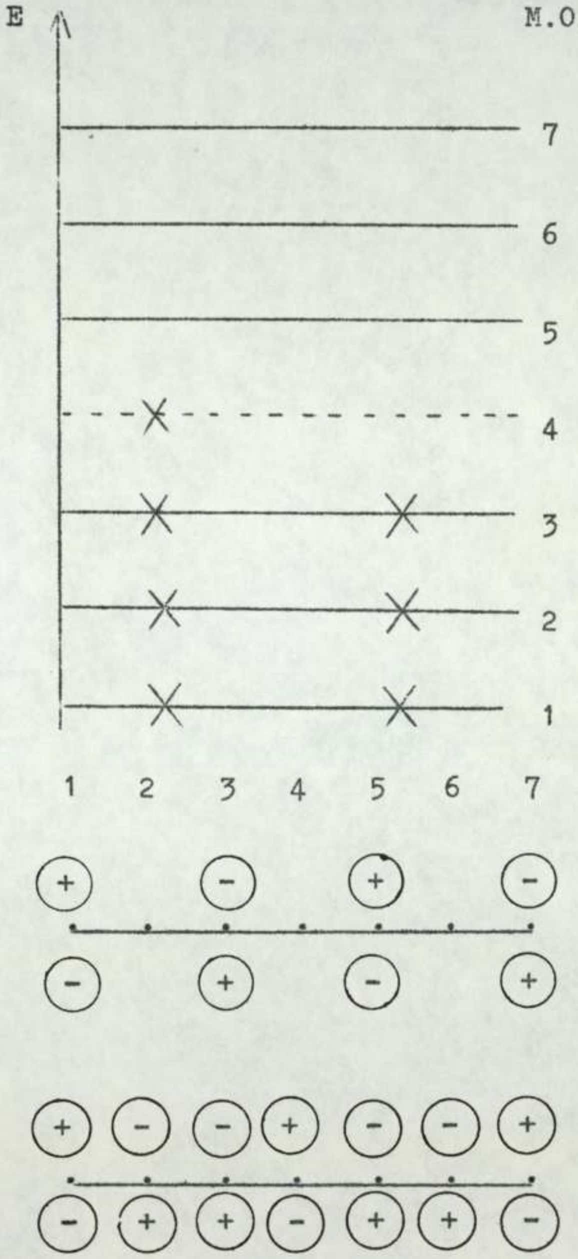
In practice only suprafacial sigmatropic rearrangements (i.e. where group R is always bonded to one face of the π-electron system) are possible for small ring systems, antarafacial migrations (i.e. where group R bonds to both sides of the π-electron system) being geometrically improbable.

Considering thermal migrations, Ψ_4 is the appropriate M.O., and of the possible migrations (i.e. 1-3, 1-5, 1-7) only the 1-5 migration has the correct orbital symmetry requirements. Similarly Ψ_5 is the appropriate orbital for the photolytic migrations, and inspection shows that only 1,7 migrations* have the correct symmetry requirements.

---

* See ref. 91 footnote 9.

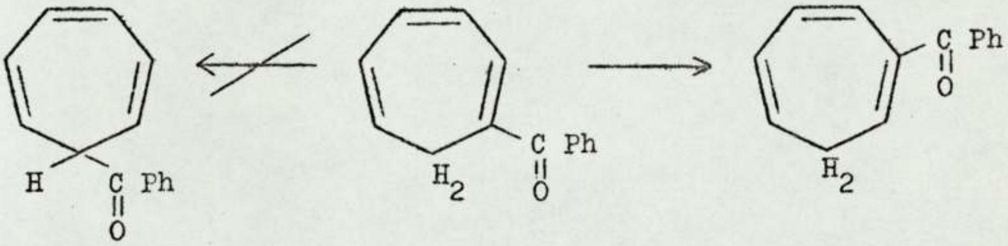
Figure XV. Molecular Orbital Energies of the Linear heptatrienyl Radical.



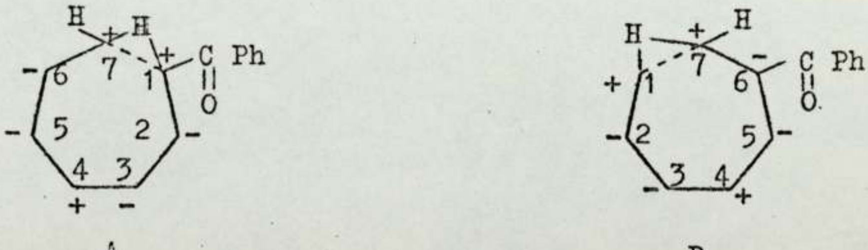
These predictions were in agreement with the rearrangements known at the time of the publication,[96] and have explained the consistency of the rearrangements observed in later years.

Extending these arguments a qualitative explanation of the stereospecificity of the photolytic rearrangements can be proposed. Jones et al[91-93] have outlined such a method to explain the specific 1,7-methyl migrations in trimethylcycloheptatrienes.* Similar arguments can be used to explain the rearrangements of 1-benzoylcycloheptatriene observed by the author.

There are two possible products from a 1,7 hydrogen migration in 1-benzoylcycloheptatriene, namely 2-benzoyl- and 7-benzoylcycloheptatriene. Only the 2-isomer was isolated from the photolysis in benzene :-



The transition states are shown below :-



A, for the formation of 7-benzoylcycloheptatriene and B, for 2-benzoylcycloheptatriene. The benzoyl substituent, an electron-withdrawing group, will stabilise a high electron density at the "1" position. Charge density calculations[97,91,92] show that C_7 and hence C_1

---

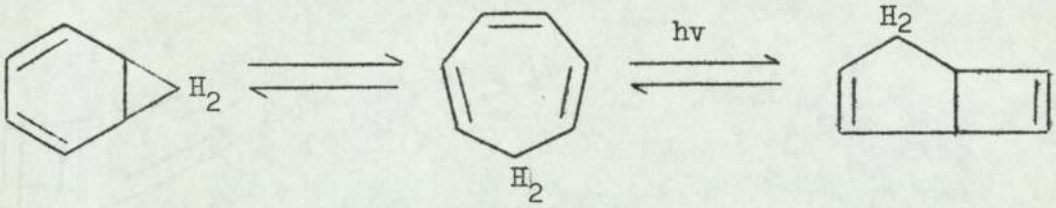
* For an alternative explanation see A. P. ter Borg & H. Kloosterziel, Rec. Trav. Chim., 1969, 88, 266.

are slightly positive, whereas C_6 and C_2 have a large charge density (i.e. relatively negative), hence transition state B. where the negative charge coincides with the benzoyl group is stabilised, explaining why 2-benzoylcycloheptatriene is the preferred product.

It follows from the above argument that an electron donating substituent at the same position should produce the opposite migration. Chapman[94] et al have shown that photolysis of 1-methoxycycloheptatriene gives only 7-methoxycycloheptatriene in agreement with the theoretical predictions.

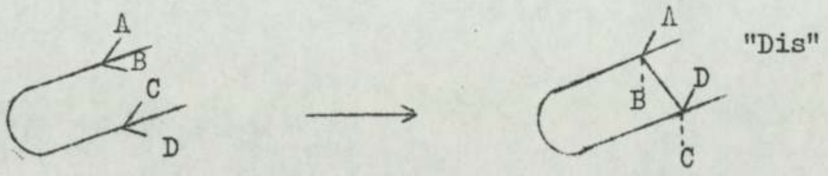
(ii) Electrocyclic Reactions.

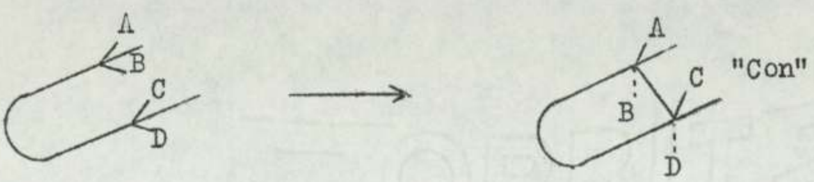
The conversion of cycloheptatriene, and its derivatives, to the valence tautomeric bicycloheptadienes are electrocyclic reactions :-



Typically these reactions involve the conversion of a linear polyene to the cyclic-ene containing two less π-electrons.

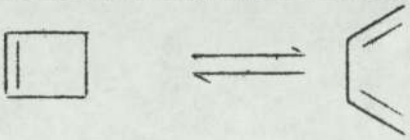
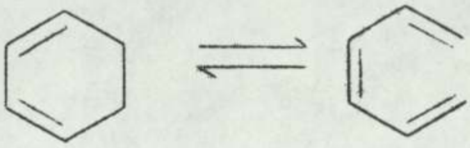
This cyclisation may involve a "conrotatory" or "disrotatory" ring closure :-





For valence-tautomeric changes where B and C form part of a ring system only the disrotatory reaction is possible. Woodward and Hoffmann have summarised the rules governing these reactions. (see table VI).

Table VI. Rules for Electrocyclic Reactions.

	Δ	hv
	con	dis
	dis	con

Thus it can be predicted that conversion to norcaradiene, involving the cyclohexadiene ring, should be thermally allowed, and conversion to bicyclo [3.2.0] heptadiene, involving the cyclobutene ring should be photolytically allowed.

These predictions compare fairly well with experimental observations.

Thermolysis of cycloheptatriene gives toluene[81,82] via cleavage of the norcaradiene species, and no bicyclo [3.2.0] heptadiene while photolysis of cycloheptatriene in solution[90] gives bicyclo [3.2.0] heptadiene and no toluene. Srinivasan [98] has photolysed cycloheptatriene in the gas phase to give mainly toluene, an apparent contradiction of the above principles, but reported that this probably involved a vibrationally excited ground state so that the reaction resembles a thermochemical rather than a photochemical change.

A further anomaly is the thermolysis of bicyclo [3.2.0] heptadienes at temperatures above 200°. Willcott et al[99] discuss this in terms of the Woodward-Hoffmann rules pointing out that symmetry rules do not indicate the difference in activation energy between preferred and forbidden ring openings. Hence if sufficient thermal energy is supplied unfavourable reactions may take place.

VII Discussion of the Physical Data Compiled for the Deoxybenzoin and Cycloheptatriene Derivatives.

1. Infra-Red Spectra.[100,101]

a) Substituted Deoxybenzoins.

The infra-red (i.r.) spectra of deoxybenzoin derivatives are straightforward, being dominated by vibration of the two aromatic nuclei, and the carbonyl stretching band. In Table VII the main vibrations are assigned for deoxybenzoin.[100,101] Vibrations in the region 1400-1000 are mainly the C-H "inplane bends". They have been omitted because of the difficulties in distinguishing these vibrations from the C-H "inplane vibrations" of the cycloheptatriene ring in such compounds as 1-benzoylcycloheptatriene.

b) Acyl-substituted Cycloheptatrienes.

Table VIII summarises the main bands, with assignments, for 1-benzoylcycloheptatriene. These bands have been assigned mainly by reference to the work of Evans and Lord on cycloheptatriene[102] itself, and by reference to the spectra of a limited number of cycloheptatriene derivatives prepared by the author. The most obvious distinction between the spectra of the isomeric compounds is the position of the carbonyl stretch. This has approximately 50 $cm.^{-1}$ lower energy for 1-benzoylcycloheptatriene because of the α-β double bond.

Other vibrations unique to the cycloheptatriene spectrum are the ring stretching bands, 1580 and 1525 $cm.^{-1}$, the bending modes associated with the methylene group, 1450, 1275 and 975 $cm.^{-1}$, and the out-of-plane bending vibrations of the hydrogens associated with the triene system, 800, 780 and 750 $cm.^{-1}$.

However, the differences in the i.r. spectra of the two series of compounds are small compared to those of the nuclear magnetic resonance (n.m.r.) spectra, and so i.r. spectroscopy is rarely used to distinguish the isomers.

Table VII.

Assignment of the Major Vibrational Frequencies in Deoxybenzoin.

Observed frequency (cm.$^{-1}$)	Description of Vibration.
3080 3060 3020	CH stretching phenyl
2900	CH_2 stretching
1690	C=O stretching
1600 1580 1500 1450	C-C stretching of phenyl nuclei
1450	CH_2 scissor
750 730 700 690	C-H out of plane bends for two mono substituted aromatic ring.

Table VIII

Assignment of the Major Vibrational Frequencies in 1-BenzoylCycloheptatriene.

Observed Frequency (cm.$^{-1}$)	Description of vibration
3080	CH stretching, aromatic and olefinic
3050	
3020	
2880	CH_2 stretching, symmetric & anti-symmetric.
2840	
1640	C=O stretching
1600	C-C stretching of phenyl nucleus
1580	C=C stretching of cycloheptatriene ring
1520	
1450	C-C stretching of phenyl nucleus
1450	CH_2 bending
1275	CH_2 wagging
970	CH_2 twisting
950	C-C ring (cycloheptatriene) stretch
930	
900	
870	C-H out of plane bend (cycloheptatriene
800	
780	
750	
740	C-H out of plane bend (aromatic).
700	

2. Nuclear Magnetic Resonance Spectra.

a. Substituted Deoxybenzoins.

The main features of the nuclear magnetic resonance (n.m.r.) spectra of these compounds are summarised in Table IX, and the spectrum of benzyl p-bromophenyl ketone is reproduced in Appendix I No. 1.

It can readily be seen that this spectrum is dominated by two singlets, one at τ 2.8 ($\underline{\mathrm{Ph}}\mathrm{CH_2}$) and the other at τ 5.85 ($\mathrm{Ph\underline{CH_2}CO}$), which are characteristic of all compounds in this series. The remainder of the spectrum is due to the aryl group and naturally depends upon the particular compound.

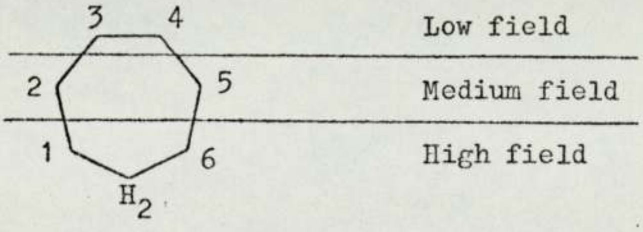
Table IX

N.M.R. Spectra of substituted deoxybenzoins.

Compound	$\underline{\mathrm{Ph}}\mathrm{CH_2}$	$\mathrm{Ph\underline{CH_2}CO}$
deoxybenzoin	2.80 (s)	5.90 (s)
benzyl mesityl ketone	2.80 (s)	6.05 (s)
benzyl 1-naphthyl ketone	2.70 (s)	5.73 (s)
benzyl 2-naphthyl ketone	2.70 (s)	5.70 (s)
benzyl p-bromophenyl ketone	2.70 (s)	5.85 (s)
benzyl cinnamyl ketone	2.70 (s)	6.18 (s)
benzyl p-methoxyphenyl ketone	2.75 (s)	5.90 (s)
benzyl methyl ketone	2.80 (m)	6.45 (s)

b. Acyl substituted Cycloheptatrienes.

The n.m.r. spectra of cycloheptatriene and several substituted cycloheptatrienes are reproduced in Appendix I Nos. 2-6. For cycloheptatriene the assignment of the various absorption bands to individual protons is well-established being represented diagramatically below :-



The triplet coupling of the methylene protons, τ 7.8 (equivalent due to rapid oscillation between the two possible boat forms) is due to the H_1 and H_6 protons ($J_{17} = J_{67} = 7.0$ Hz.).

The vinylic protons show second order effects and must strictly be analysed by AA' BB' XX' mathematics.[103] However, far more useful to the organic chemist is the restricted first order analysis, employed by Egger and Moser[104] to describe the spectra of the isomeric methylcycloheptrienes.

H_1 and H_6 are chemically equivalent and will have superimposable spectra. Thus H_1 couples with the two H_7 protons to give a triplet ($J_{17} = 7.0$ Hz.), which is split further by the H_2 proton ($J_{12} = 9.0$ Hz.) giving the observed doublet of triplets. By similar considerations one would predict that H_2 and H_5 would be a quartet, H_2 coupling to H_1 ($J_{12} = 9.0$ Hz.) and H_3 ($J_{23} = 6.5$ Hz.), while H_3 and H_4 would be a doublet, H_3 coupling only to H_2.

However, the observed spectrum shows a doublet of triplets for H_2, H_5 and a triplet for H_3, H_4. Egger and Moser[104] suggested that this system would illustrate "virtual coupling".[105] This is not a physical phenomenon but merely a convenient term for a well-understood spectral effect.

For an ABX spectrum where $J_{AX} = 0$ and protons A & B are very strongly coupled, e.g. when they have the same chemical shift, one observes X appearing to couple equally to both A and B, i.e. a triplet coupling for X.

With cycloheptatriene, H_2, H_3, H_4 and H_3, H_4, H_5, provide two virtually coupled systems. H_3 & H_4 have the same chemical shift while J_{24} and J_{35} are zero. Thus the spectrum will appear as though H_2 and H_5 couple equally to both H_3 and H_4 to give superimposable triplets, and further coupling to the H_1 or H_6 proton gives the observed doublet of triplets. H_3 and H_4 simultaneously participate in both virtually coupled systems giving superimposable spectra, H_3 coupling equally to H_2 and H_5 to give a triplet as is observed.

The other spectra presented in the Appendix show the same basic form as the cycloheptatriene spectrum. They all consist of a complex vinylic region τ 3-5 with the methylene protons to high field. 7-cyanocycloheptatriene (No. 6) is included as an example of a mono-substituted cycloheptatriene that can be analysed using the "virtual coupling" approximation described above. It differs from cycloheptatriene in that the 1,6 protons now only couple to one methylene proton and so appear as a quartet and not a doublet of triplets.

1-Benzoylcycloheptatriene (No. 3) is typical of the spectra of the 1-aroylcycloheptatrienes prepared. (see Table X for details of these spectra). The high field doublet, τ 7.3, assigned to the methylene protons, characterises 1-substituted cycloheptatrienes, which can only couple with the lone H_6 proton. The H_6 proton is a doublet of triplets, τ 4.4 as in cycloheptatriene, while the H_5 proton is now a quartet τ 3.7. Clearly, "virtual coupling" is not operating in this system since H_5 would show a triplet pattern, and the H_3 and H_4 protons would not appear so complex. Presumably the benzoyl substituent deshields the H_3 proton with respect to the H_4 proton so that the conditions for "virtual coupling" no longer apply. In fact there is no simple explanation of the observed spectrum and a second order analysis must be employed to derive any further information.

1-Acetylcycloheptatriene (No. 5) differs from the 1-aroylcycloheptatrienes in that the H_2 proton is now clear of other signals appearing at τ 2.9 as a doublet. This is simpler than 1-benzoylcycloheptatriene when it was difficult to decide the exact position of this proton. It could have been either with the aromatic or with the H_3 and H_4 protons. However, the H_3 and H_4 protons in 1-acetylcycloheptatriene still show a second order pattern.

2-benzoylcycloheptatriene (No. 4) illustrates an example of an entirely first order spectrum. Presumably the H_3 proton is now deshielded to such an extent by the adjacent benzoyl group that $\Delta(H_4 - H_3)$ is sufficient for the coupling to be first order. Thus H_3 is a doublet, coupling only with H_4, and H_4 is a quartet coupling to H_3 and H_5, H_5 and H_6 are a quartet, and doublet of triplets respectively, as in 1-benzoylcycloheptatriene, while H_1 is a triplet, coupling only to the methylene protons.

These compounds conveniently illustrate different approaches to the analysis of the spectra of substituted cycloheptatrienes. Although at first sight the vinylic region is complex, analysis or even partial analysis of the region, provides an unambiguous assignment of the substitution pattern, which is virtually impossible to make by any other method.

Table X

N.M.R. Spectra of 1-Acylcycloheptatrienes.

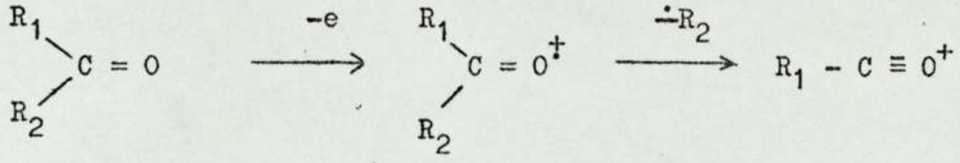
Compound	PROTONS			
	H_7	H_6	H_5	H_4, H_3, H_2
1-benzoyl-cycloheptatriene	7.30 (d)	4.40 (m)	3.70 (m)	3.1 - 3.5 (m)
1-mesitoyl-cycloheptatriene	7.25 (d)	4.40 (m)	3.75 (m)	3.3 - 3.6 (m)
1-(1-napthoyl)-cycloheptatriene	7.15 (d)	4.30 (m)	3.70 (m)	3.1 - 3.6 (m)
1-(p-methoxybenzoyl)-cycloheptatriene	7.30 (d)	4.40 (m)	3.70 (m)	3.1 - 3.4 (m)
1-acetyl-cycloheptatriene	7.4 (d)	4.50 (m)	3.70 (m)	2.9 - 3.4 (m)

3. Mass Spectra.

a. Substituted Deoxybenzoins

1) Fragmentation of the Parent Ion.

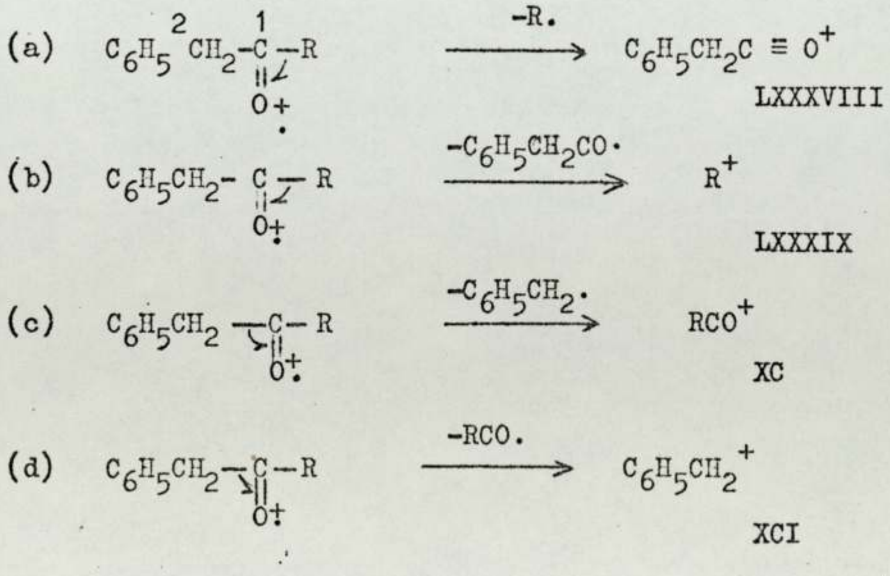
Ionisation of a ketone LXXXVI by electron loss leads to ion LXXXVIa with the positive charge localised on the oxygen atom. This molecular or "parent" ion is a radical species. Such an ion, either parent or fragment, with an unpaired electron, is called an "odd-electron ion", and is designated by the symbol $\overset{+}{\cdot}$. On the same system an "even-electron ion" is designated +.[107,108] The major fragmentation process of this ion is α-cleavage, resulting in the formation of an acylium ion LXXXVII and a neutral radical, R_2.



(LXXXVI) (LXXXVIa) (LXXXVII)

The positive charge is usually retained by the electronegative hetero-atom, as shown.

Substituted deoxybenzoins may undergo α-cleavage to give 4 different ions (LXXXVIII - XCI) :-



$$\text{(a)}\quad C_6H_5\overset{2}{C}H_2-\overset{1}{C}(=\overset{+}{\dot{O}})-R \xrightarrow{-R.} C_6H_5CH_2C\equiv O^+ \quad \text{LXXXVIII}$$

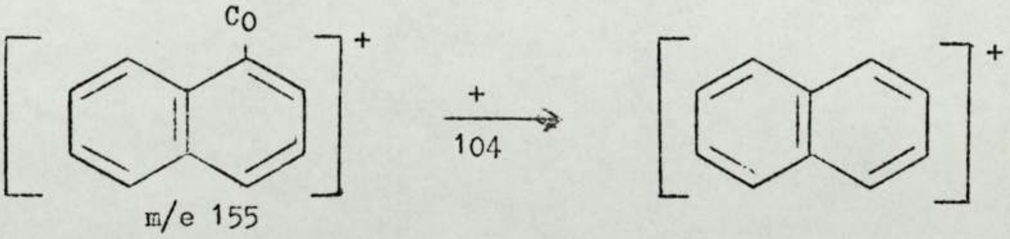
$$\text{(b)}\quad C_6H_5CH_2-C(=\overset{+}{\dot{O}})-R \xrightarrow{-C_6H_5CH_2CO\cdot} R^+ \quad \text{LXXXIX}$$

$$\text{(c)}\quad C_6H_5CH_2-C(=\overset{+}{\dot{O}})-R \xrightarrow{-C_6H_5CH_2.} RCO^+ \quad \text{XC}$$

$$\text{(d)}\quad C_6H_5CH_2-C(=\overset{+}{\dot{O}})-R \xrightarrow{-RCO.} C_6H_5CH_2^+ \quad \text{XCI}$$

The acylium (RCO) and tropylium (C_7H_7) fragments produced by cleavage of the 1,2 bond are clearly more stable than the benzoylium ($C_6H_5CH_2CO$) and alkyl, or aryl (R) fragments produced by the alternative α-cleavage. Thus one would predict the acylium ion XC to be the most abundant ion, charge localisation normally being at the hetero atom. Competition of the tropylium and acylium ions for this positive charge is reflected by an increase in the abundance of the tropylium ion whenever there is a decrease in the ability of the acylium ion to stabilise the positive charge.

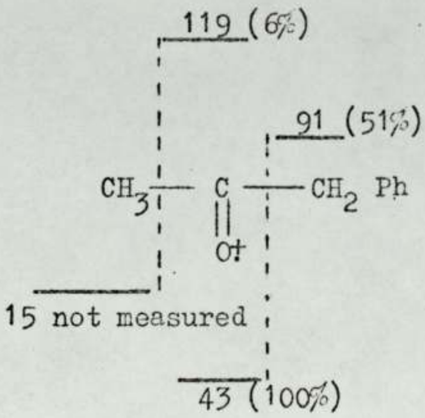
Fig. XVI shows the fragmentation of the parent ion for typical deoxybenzoins, illustrating the principles outlined above. Thus in both examples the acylium ion is the most abundant ion, and the relative abundance of m/e 91, the tropylium ion, is far higher for benzylmethyl ketone XCII ("acetyl deoxybenzoin") where the methyl group is less capable of stabilising the positive charge. m/e 127 in benzyl 1-naphthyl ketone XCIII has an abundance of 53%. This does not indicate the alternative α-cleavage is more favoured, because m/e 127 is formed from m/e 155 by loss of CO, and not from the parent ion.



The abundance of m/e 119 gives a more accurate picture of the probabilities of the two alternative α-cleavages.

Figure XVI. Fragmentation of the Parent Ion for the Deoxybenzoins.

A. Benzyl Methyl Ketone.



B. Benzyl 1-Naphthyl Ketone

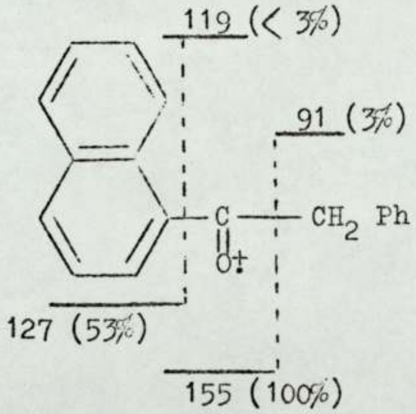


Table XI Metastables showing the origins of the most abundant ions in the spectra of substituted deoxybenzoins.

Compound				M^* obs.	M^* calc.
A	196 (P)	M - 91	105	56.2	56.25
deoxybenzoin	105 (RCO)	M - 28	77	56.5	56.47
	77 (R)	M - 26	51	33.8	33.78
	91 (C_7H_7)	M - 26	65	46.4	46.43
B	238 (P)	M - 91	147	89.5	90.79
benzyl mesityl ketone	147 (RCO)	M - 28	119	96.0	96.33
	119 (C_7H_7CO)	M - 28	91	69.5	69.59
	91 (C_7H_7)	M - 26	65	46.4	46.43
C	246 (P)	M - 91	155	97.8	97.66
benzyl 1-naphthyl	155 (RCO)	M - 28	127	104.0	104.06
	127 (R)	M - 26	101	80.2	80.32
ketone	101 (R)	M - 26	75	55.7	55.69
D	91 (C_7H_7)	M - 26	65	46.4	46.43
E	*274 (P)	M - 91	183	-	-
benzyl p-bromophenyl	183 (RCO)	M - 28	155	131.2	131.28
ketone	155 (R)	M - 80	76	-	-
F	222 (P)	M - 91	131	-	
benzyl cinnamyl	131 (RCO)	M - 28	103	81.0	80.98
	103 (R)	M - 26	77	57.5	57.56
ketone	77 (C_6H_5)	M - 26	51	33.8	33.78
	91 (C_7H_7)	M - 26)	65	46.5	46.43
	65 (C_5H_5)	M - 26	39	23.5	23.40
G	226 (P)	M - 91	135	80.8	80.64
benzyl p-methoxy-	135 (RCO)	M - 28	107	85.0	84.81
phenyl ketone	107 (R)	M - 15	92	-	-
	92 ($R-CH_3$)	M - 28	64	44.5	44.52
	91 (C_7H_7)	M - 26	65	46.4	46.43
H	134 (R)	M - 15	119	105.8	105.68
benzylmethyl ketone	119 (C_7H_7CO)	M - 28	91	69.6	69.59
	91 (C_7H_7)	M - 26	65	46.4	46.43

* for Br^{79} only, similar fragmentation was observed for ions with Br^{81}.

ii) Fragmentation of the acylium ion.

The fragmentation patterns of the compounds synthesised are summarised in Appendix II Table I. The origins of the major fragment ions in each spectrum, with metastable peaks to verify these origins, are tabulated in Table XI. From this data it is possible to construct the fragmentation patterns for the individual deoxybenzoins.

The fragmentation of deoxybenzoin Fig. XVIII will suffice to illustrate the basic fragmentation processes of these compounds. Superimposed upon this is any fragmentation induced by substituents on the aryl ring. The fragmentation of benzyl p-methoxyphenyl ketone Fig. XVII. shows how the methoxy group alters the course of the fragmentation process.

Firstly deoxybenzoin, the acylium ion m/e 105 is the most abundant ion. This fragments by loss of CO to give m/e 77 followed by loss of successive molecules of acetylene (M-26) giving m/e 51. Metastable peaks are included in Fig. XVIII.

The fragmentation of benzyl p-methoxyphenyl ketone is summarised in Fig. XVII. Loss of CO from the acylium ion, m/e 135 to give m/e 107 is identical to deoxybenzoin. Then instead of loss of acetylene, typical of unsubstituted aromatic compounds, a methyl radical is lost from the other linkage giving m/e 92. This loses another CO molecule as shown. Again all metastables observed are included in Fig. XVII.

Figure XVII. Fragmentation of Benzyl p-Methoxyphenyl Ketone.

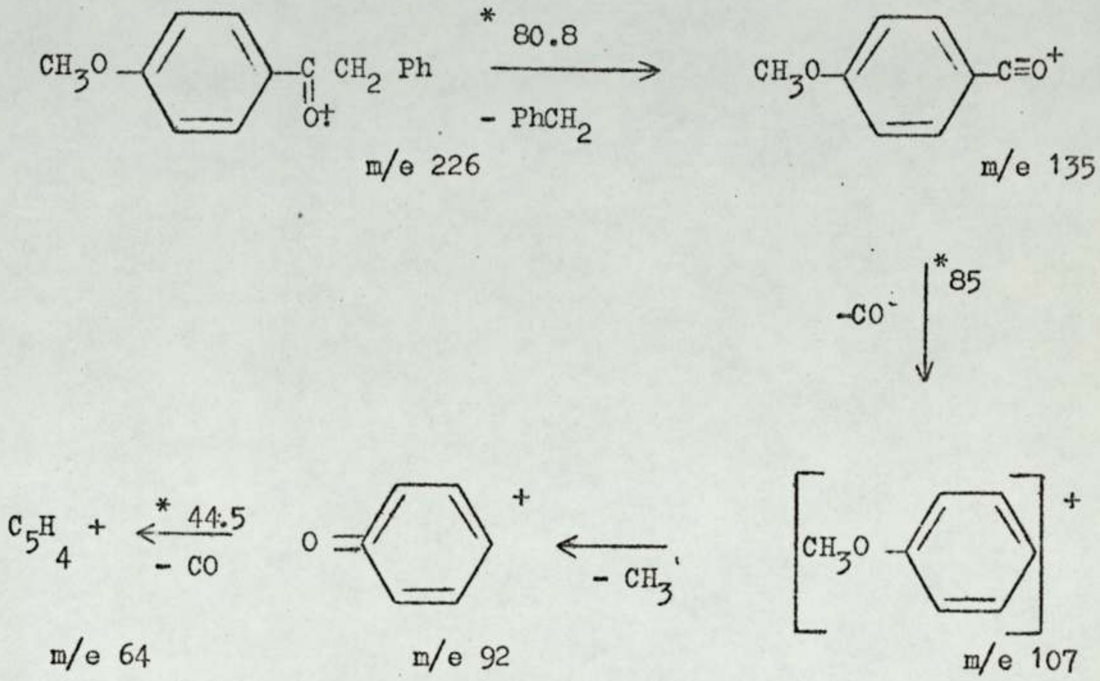
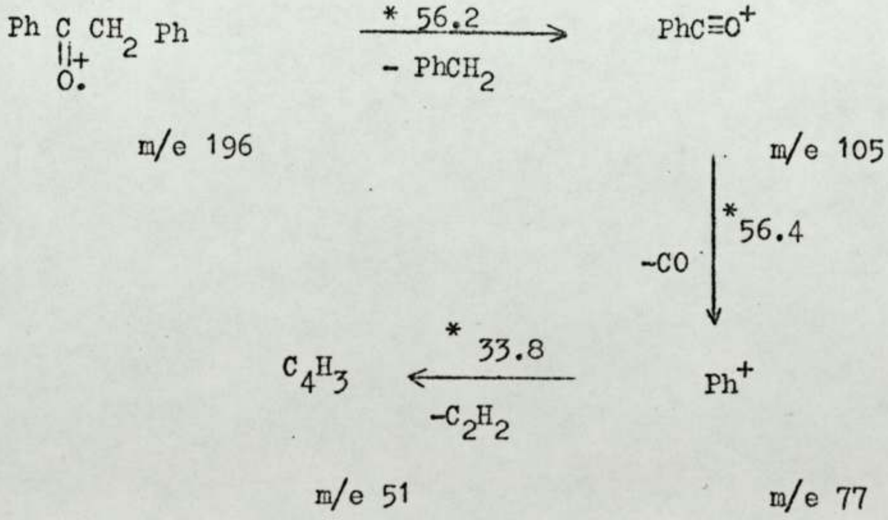


Figure XVIII. Fragmentation of Deoxybenzoin.



(iii) Further Fragmentation Processes.

Every compound studied shows m/e $91 \xrightarrow{*}$ m/e 65 [M - 26], i.e. loss of acetylene. However no metastables have been detected showing the formation of the tropylium ion, m/e 91. The most likely process is directly from the parent ion as discussed in section 1.

Metastable ions also suggest the process, m/e $77 \xrightarrow{*}$ m/e 51 [M - 26]. although there are no metastables connecting m/e 77 to any other ion. From a knowledge of fragmentation processes in ketonic compounds,[107] m/e 77 is most likely to arise from the parent ion by β-cleavage.

b. 1-Acylcycloheptatrienes.

These spectra are summarised in Appendix II, Table II. They show only quantitative differences from the isomeric deoxybenzoins, and metastable ions indicate that the same fragmentation processes are operating in both series of compounds. Thus a table of the origins of the most abundant ions for the cycloheptatrienes would be identical to Table XI and so is not duplicated.

These results are not surprising since the 1-acyl cycloheptatriene could isomerise thermally to the deoxybenzoin (see Chapter VI) with the sampling conditions used. Also spectra of the C_7H_8 isomers, cycloheptatriene and toluene, are known to be identical.[106]

Experimental.

The Melting points were determined with a Kofler block apparatus and are uncorrected. Infra-red (i.r.) spectra were recorded on a Perkin-Elmer 257 or 457 spectrometer, nuclear magnetic resonance spectra (n.m.r.) on a Varian A-60 or Perkin-Elmer R14 spectrometer, mass spectra (m.s.) on an A.E.I. MS9 and Ultra-Violet (u.v.) spectra on a Unicam S.P. 700.

Mathieson[59] was used to assign the n.m.r. spectra and and Bellamy[100] the i.r. spectra.

Anhydrous sodium sulphate was used for drying and a rotary evaporator for removing solvents.

The cycloheptatriene, kindly supplied by Shell, was distilled prior to using,(and still contained about 8% of toluene). A.R. solvents were used in the Friedel-Crafts reactions, further purification being unnecessary. The acid chlorides used were either bought as the acid chloride or as the acids. The acids were converted to the acid chloride by reaction with thionyl chloride.[109]

1. Synthesis of Silver Fluoride. AgF.[110]

40% HF (47 g.) was added in small portions, with stirring to silver carbonate (11.0 g.) contained in a platinum dish. When the initial evolution of CO_2 was finished the dish was heated on a steam bath (30 mins.) to complete the reaction. The AgF solution was separated from excess silver carbonate by filtration and the solution evaporated from a platinum dish until 115 g. were left. The remaining water was removed by washing with 100 ml. of anhydrous methanol and decanting supernatant liquid (3 times), followed by 100 ml. anhydrous diethyl ether (3 times). Traces of ether can be removed with a water pump.

The ether used for washing, together with an additional 300 ml. is added to the methanol. The yellow precipitate is treated with 25 ml. of methanol (2 times) and 50 ml. of ether (3 times) and the moist AgF dried as before.

The combined yield was 55 g. 55%. This material was used in the synthesis of silver tetrafluoroborate.

2. Synthesis of Silver Tetrafluoroborate.[111]

Manipulations that involved exposing the materials to the atmosphere were performed in a dry-box. Silver fluoride (34 g.) was suspended in dry nitromethane (40 g.) and boron trifluoride was passed into the stirred suspension (30 min.), keeping the system at 60°C by immersing the reaction flask in water. Dry nitrogen was passed through this solution (1 hr.) to remove excess BF_3 and the solution filtered under reduced pressure (50 mm.) into an evacuated flask held at 70°, which removed the nitro-methane leaving the solid silver tetrafluoroborate behind.

The $AgBF_4$ obtained from this reaction was to be used to prepare the benzoyl oxocarbonium fluoroborate in methylene chloride. However low solubility of the $AgBF_4$ in the solvent (due to the presence of the hydrated compound, $AgBF_4 . H_2O$) reduced yields, measured by the AgCl precipitated, drastically.

For this reason the method was abandoned in favour of the more straightforward "Fluoride method", (expt. 3).

3. Reaction of Benzoyl Oxocarbonium Fluoroborate (generated in situ from $PhCOF + BF_3$[26]) with Cycloheptatriene in Methylene Chloride.

Cycloheptatriene (9.2 g.) was slowly added, with stirring, to a solution prepared by bubbling BF_3 gas through benzoyl fluoride (12.4 g.) in methylene chloride (100 ml.) at -60°. Samples of the solution were examined at -60° by n.m.r. spectroscopy, and the remainder allowed to warm to room temperature.

Filtration gave tropylium fluoroborate, yield 4.0 g, 22%, recrystallised from methyl cyanide/ethyl acetate, m.p. 210 - 236° (with decomposition)[27] λmax. (conc. H_2SO_4). 273.5 (4330), $\nu_{max.}$ 1050 $cm.^{-1}$ (broad, BF_4^-) τ (MeCN), 0.8 (s).

The filtrate was poured onto a HCl/ice mixture, washed with sodium bicarbonate and water, then dried. Addition of ether (50 ml.) precipitated an uncharacterised polymeric material, yield 4.0 g.

Evaporating off the solvent followed by vacuum distillation gave deoxybenzoin, 1.1 g., 6% recrystallised from pet.ether 40/60°, m.p. 54 - 55°, mixed m.p. 54 - 56°, i.r. and n.m.r. identical with an authentic sample.

4. Reaction of Benzoyl Oxocarbonium Fluoroborate (generated in situ from $PhCOF + BF_3$) with Cycloheptatriene in Liquid SO_2.

Cycloheptatriene (9.2 g.) was slowly added, with stirring, to a solution prepared by bubbling BF_3 gas through benzoyl fluoride (12.4 g.) in liquid SO_2 (100 ml.) at -60°. Samples of the solution were examined at -60^{o} by n.m.r. spectroscopy. Cold methylene chloride was added to the solution which was allowed to warm to room temperature, the SO_2 boiling off.

Filtration gave tropylium fluoroborate, yield m.p. i.r. u.v. and n.m.r. identical with material in expt. 3.

The filtrate was poured onto a HCl/ice mixture, washed with sodium bicarbonate and water, then dried. Addition of ether (50 ml.) precipitated an uncharacterised polymeric material.

Evaporating off the solvent followed by vacuum distillation gave deoxybenzoin, recrystallised from pet-ether, $40/60^{o}$, m.p. $54 - 55^{o}$, mixed m.p. $54 - 56^{o}$, i.r. and n.m.r. identical with an authentic sample.

5. Reaction of Benzoyl Chloride with Cycloheptatriene in the Presence of Aluminium Chloride in Methylene Chloride.

Cycloheptatriene (9.2 g.) was slowly added, with stirring, to a solution of benzoyl chloride (14.1 g.) and aluminium chloride (13.4 g.) in methylene chloride (100 ml.) at -60^{o}. The solution allowed to warm to room temperature and samples examined by n.m.r. spectroscopy.

Filtration of the remaining solution gave tropylium chloroaluminate,[33]

The filtrate was poured onto a HCl/ice mixture, washed with sodium bicarbonate and water, then dried. Addition of ether (50 ml.) precipitated an uncharacterised polymeric material.

Evaporating off the solvent followed by vacuum distillation gave deoxybenzoin, 5% yield recrystallised from pet-ether, $40/60^{o}$, m.p. $54 - 55^{o}$, mixed m.p. $54 - 56^{o}$, i.r. and n.m.r. identical with an authentic sample.

6. Synthesis of Deoxybenzoin.

Cycloheptatriene (9.2 g.) was slowly added with stirring to a solution of benzoyl chloride (14.1 g.) and aluminium chloride (13.4 g.) in methylene chloride (100 ml.) at 0°. The solution was allowed to warm to room temperature, then poured into HCl-ice mixture. The organic phase was washed with water, dried and the methylene chloride evaporated off. Vacuum distillation of the residue gave deoxybenzoin 8.4 g., 43%, recrystallised from 40/60° pet.-ether, m.p. 54-55°, mixed m.p. 54 - 56°, i.r. and n.m.r. identical with authentic sample.

7. Synthesis of Benzyl Mesityl Ketone.

Prepared in a similar manner to deoxybenzoin. This gave benzyl mesityl ketone 3.0 g., 13%, b.p. 167 - 180°(6 mm.) M^+ 238.1350, $C_{17}H_{18}O$ requires 238.1358. $\nu_{max.}$ 1700 cm.$^{-1}$ (ν C=O), τ 2.80 (s, $\underline{Ph}CH_2$, 5H), 3.20 (s, $\underline{Ar}CO$, 2H), 6.05 (s, $Ph\underline{CH_2}CO$, 2H), 7.75 (s, $Ar\underline{CH_3}$, 3H), 7.90 (s, $Ar\underline{CH_3}$, 6H).

8. Synthesis of Benzyl 1-Naphthyl Ketone.

Prepared in a similar manner to deoxybenzoin. This gave benzyl 1-naphthyl ketone 5.5 g. 23% recrystallised from 40/60 pet.-ether, m.p. 64.5 - 66.0° Found C, 88.2; H, 5.7, $C_{18}H_{14}O$ requires C, 87.9; H, 5.7, M^+, 246.0980 $C_{18}H_{14}O$, 246.1046, $\nu_{max.}$ 1690 cm.$^{-1}$ (ν C=O), τ 1.30 - 2.60 (m, ArCO, 7H) 2.70 (s, $\underline{Ph}CH_2$, 5H) 5.73 (s, $Ph\underline{CH_2}CO$, 2H).

9. Synthesis of Benzyl 2-Naphthyl Ketone.

Prepared in a similar manner to deoxybenzoin. This gave benzyl 2-naphthyl ketone, 3.6 g., 15% recrystallised from 40/60 pet.-ether, m.p. 97 - 99°. Found C, 87.2; H, 5.7, $C_{18}H_{14}O$ requires C, 87.9; H, 5.7, M^+, 246.0968, $C_{18}H_{18}O$, 246.1046, $\nu_{max.}$ 1685 cm.$^{-1}$ (ν C=O), τ 1.50 - 2.50 (m, $\underline{Ar}CO$, 7H), 2.70 (s, $\underline{Ph}CH_2$, 5H), 5.70 (s, $Ph\underline{CH_2}CO$, 2H).

10. Synthesis of Benzyl p-Bromophenyl Ketone.

Prepared in a similar manner to deoxybenzoin. This gave benzyl p-bromophenyl ketone, 1.2 g., 4%, recrystallised from 40/60°pet.-ether, m.p. 112 - 114° Found C, 61.5; H, 4.2, $C_{14}H_{11}OBr$ requires C, 61.2; H, 4.0 M^+, 273.9790 $C_{14}H_{11}OBr$, 273,9994, $\nu_{max.}$ 1690 cm.$^{-1}$ (ν C=O). τ 2.07 - 2.42 (AB multiplet, <u>Ar</u>CO, 4H), 2.10 (s, <u>Ph</u>CH$_2$, 5H), 5.85 (s, Ph<u>CH$_2$</u>CO, 2H).

11. Synthesis of Benzyl Cinnamyl Ketone.

Prepared in a similar manner to deoxybenzoin. This gave benzyl cinnamyl ketone 2.6 g., 12%, recrystallised from 40/60° pet.-ether m.p. 65 - 68° Found, C, 86.5; H, 6.4, $C_{16}H_{14}O$ requires C, 86.5, H, 6.4, M^+, 222.0981, $C_{16}H_{14}O$, 222.1045, $\nu_{max.}$ 1660 cm.$^{-1}$ (ν C=O), τ 2.40 - 2.70 (m, <u>Ar</u>-CH, 5H) 2.4 and 3.3 (AB multiplet CH=CH, 2H), 2.70,(s, <u>Ph</u>CH$_2$, 5H), 6.18 (s, Ph<u>CH$_2$</u>CO, 2H).

12. Synthesis of Benzyl p-Methoxyphenyl Ketone

Prepared in a similar manner to deoxybenzoin. This gave benzyl p-methoxyphenyl ketone 4.4 g., 20%, recrystallised from 40 / 60° pet.-ether, m.p. 75 - 76°, Found C, 79.1; H, 6.1, $C_{15}H_{14}O_2$ requires C, 79.7; H, 6.2, M^+ 226.0851, $C_{15}H_{14}O_2$, 226.0994, $\nu_{max.}$ 1680 cm.$^{-1}$ (ν C=O), τ 2.05 and 3.15 (AB multiplet, <u>Ar</u>CO, 4H), 2.75 (s, <u>Ph</u>CH$_2$, 5H), 5.90 (s, Ph<u>CH$_2$</u>CO, 2H), 6.20 (s, ArO<u>CH$_3$</u>, 3H).

13. Synthesis of Benzyl Methyl Ketone

Cycloheptatriene (9.2 g.) was slowly added with stirring to a solution of acetyl chloride 7.8 g.) and aluminium chloride (13.4 g.) in methylene chloride (100 ml.) at -20°. The remainder of the reaction is identical to expt. 6. This gave benzyl methyl ketone, 2.9 g., 22% b.p. 91 - 95° (10 mm.) M^+ 134.0712, $C_9H_{10}O$ 134.0732, $\nu_{max.}$ 1710 cm.$^{-1}$ (ν C=O), τ 2.80 (m, <u>Ph</u>CH$_2$, 5H) 6.45 (s, Ph<u>CH$_2$</u>CO, 2H) 8.00 (s, <u>CH$_3$</u>CO, 3H).

14. Synthesis of 1-Benzoylcycloheptatriene.

Cycloheptatriene (9.2 g.) was slowly added, with stirring, to a solution of benzoyl chloride (14.1 g.) and aluminium chloride (13.4 g.) in methylene chloride (100 ml.) at 0°.

The solution was poured into HCl-ice mixture, the organic phase washed with water and dried. Evaporating off the methylene chloride gave the crude intermediate chloro-ketone LVI. Identification was made on this crude product. M^+ 232.0656, $C_{14}H_{13}ClO$, 232.0655, $\nu_{max.}$ 1690 cm.$^{-1}$ (ν C=O), τ 2.3 (m, aromatic), 4.0 (m, vinylic), 5.05 (m, C$\underline{H}$Cl), 5.5 (m, C$\underline{H}$CO), 7.8 (m, C$\underline{H}_2$)

Bubbling HCl gas through the methylene chloride solution of LVI (10 min.) and evaporating off the methylene chloride gave crude 1-benzoylcycloheptatriene. This was purified :-

(i) Chromatography on a silica gel column, eluting with chloroform, and recrystallisation from hexane giving pure 1-benzoylcycloheptatriene (estimated from the n.m.r. spectrum).

(ii) Vacuum distillation, product 8.3 g., 42%, m.p. 45 - 47°, Found C, 85.4, H, 6.1 $C_{14}H_{12}O$ requires C, 85.8, H, 6.2, M^+ 196.0894, $C_{14}H_{12}O$, 196.0888, $\nu_{max.}$ 1640 cm.$^{-1}$, (ν C=O) τ 2.30 - 2.77 (m, Ph$\underline{H}$CO, 5H), 3.10 - 3.50 (m, H_2, H_3, H_4, 3H), 3.70 (m, H_5, 1H), 4.40 (m, H_6, 1H) 7.30 (d, H_7, 2H).

15. Synthesis of Mesitoylcycloheptatriene.

Cycloheptatriene (9.2 g.) was slowly added, with stirring to a solution of mesitoyl chloride (18.0 g.) and aluminium chloride (13.4 g.) in methylene chloride (100 ml.) at 0°C. The solution was poured into HCl-ice mixture, the organic phase washed with water and dried. Evaporating off the methylene chloride followed by vacuum distillation gave 1-mesitoylcycloheptatriene, 9.0 g., 38%, recrystallisation from, m.p. 30 - 34°, M^+ 238.1359 $C_{17}H_{18}O$, 238.1358, $\nu_{max.}$ 1650 cm.$^{-1}$ (ν , C=O), τ 3.20 (s, $\underline{Ar}$CO, 2H)

3.10 - 3.50 (m, H_2, H_3, H_4, 3H), 3.70 (m, H_5, 1H), 4.40 (m, H_6, 1H), 7.25 (d, H_7, 2H), 7.80 and 8.0 (s, Ar$\underline{CH_3}$, 9H).

16. Synthesis of 1-(1-Naphthoyl)cycloheptatriene.

Prepared in a similar manner to 1-benzoylcycloheptatriene and isolated by chromatography. 16.0 g. 65%, M^+ 246.1022, $C_{18}H_{14}O$, 246.1045, $\nu_{max.}$ 1640 cm.$^{-1}$ (ν, C=O), τ 1.90 - 2.70 (m, $\underline{Ar}$CO, 7H), 3.1 - 3.6 (m, H_2, H_3, H_4) 3.70 (m, H_5, 1H), 4.30 (m, H_6, 1H) 7.15 (d, H_7, 2H).

(Impurities in the sample largely from the column, prevented recrystallisation of the sample.)

17. Synthesis of 1-(p-Methoxybenzoyl)cycloheptatriene.

Prepared in a similar manner to 1-benzoylcycloheptatriene and isolated by vacuum distillation. 8.6 g. 38%, M^+ 226.0983, $C_{15}H_{14}O_2$, 226.0994, $\nu_{max.}$ 1640 cm.$^{-1}$ (ν, C=O), τ 2.35 and 3.15 (AB multiplet, $\underline{Ar}$CO, 4H) 3.10 - 3.40 (m, H_2, H_3, H_4, 3H), 3.70 (m, H_5, 1H), 4.40 (m, H_6, 1H), 7.30 (d, H_7, 2H).

18. Synthesis of 1-Acetylcycloheptatriene.

Reaction performed at -20°, cf. expt. 13, otherwise prepared in a similar manner to 1-benzoylcycloheptatriene. Isolated by vacuum distillation, 2.0 g., 15%, b.p. 100 - 110° at 15 m.m., M^+ 134.0718, $C_9H_{10}O$, 134.0732, $\nu_{max.}$ 1660 cm.$^{-1}$ (ν C=O), τ 2.90 (d, H_2, 1H), 3.05 - 3.4 (m, H_3, H_4, 2H), 3.70 (m, H_5, 1H), 4.50 (m, H_6, 1H), 7.40 (d, H_7, 2H) 7.73 (s, $\underline{CH_3}$CO, 3H).

19. Reaction of Cinnamoyl Chloride with Cycloheptatriene.

The reaction was performed in a similar manner to 1-benzoyl cycloheptatriene. However vacuum distillation did not give the expected cycloheptatriene. It is suggested that the physical data is in accord with

LXXVI. (Chapter 5, section 5), 7.8 g., 35%, b.p. 164 - 168°, (0.7 m.m.), M^+ 222.1035, $C_{16}H_{14}O$, 222.1045, $\nu_{max.}$ 1690 cm.$^{-1}$ (ν, C=0) τ 2.50 - 3.0 (m, PhCH, 5H), 3.60 - 4.60 (m, vinylic, 5H), 6.00 (m, PhCH, 1H), 7.00 - 7,80 (m, $COCH_2$, 2H and m, methine, 1H).

20. Reaction of Benzoic Anhydride with Cycloheptatriene.

Cycloheptatriene 4.6 g. was slowly added, with stirring, to a solution of benzoic anhydride (11.3 g.) and aluminium chloride (13.4 g.) in methylene chloride (100 ml.) at 10°C. The solution was stirred at this temperature (5 hrs.) then poured into HCl-ice mixture. The organic phase was washed with water and dried. Evaporating off the solvent gave a crude material and examination of the n.m.r. spectrum showed it to be a mixture of deoxybenzoin and the chloro-ketone intermediate. Passing HCl gas through this mixture converted the intermediate chloro-ketone to 1-benzoylcycloheptatriene, (identified by comparison of n.m.r. spectrum with that of an authentic specimen).

21. Acylation of Cycloheptatriene with Benzoyl Chloride in Carbon Disulphide.

Cycloheptatriene (9.2 g.) was slowly added with stirring, to a solution of benzoyl chloride (14.1 g.) and aluminium chloride (13.4 g.) in carbon disulphide at 40°. The solution was poured into HCl-ice mixture, the organic phase washed with water, dried and the carbon disulphide evaporated off. Vacuum distillation of the residue gave deoxybenzoin identical to material prepared in previous reactions.

22. Synthesis of 2,4,6-triphenyl benzoyl chloride.[37]

The synthesis of 2,4,6-triphenyl benzoic acid was performed by the method of Kohler[37] et al. The acid was isolated in 81% yield. Attempts to convert this to the acid chloride gave a yellow solid m.p. 185 - 187°. 1,3-Diphenyl fluorenone m.p. 183°.[37]

23. 1-Benzoylcycloheptatriene; Hydride-exchange.[27]

1-benzoylcycloheptatriene (1.2 g.) in methylene chloride (5 ml.) was added to a solution of trityl fluoroborate (2.0 g.) in methylene chloride (10 ml.). The heavy precipitate (20 mins.) was filtered and washed giving a pale yellow product, 0.75 g., 48%, m.p. 150° (decomposition) $(M + 1)^+$ 196.0862, $C_{14}H_{12}O$, 196.0888, $\nu_{max.}$ 1655 (C=O), 1050 cm.$^{-1}$ (BF_4), τ (trifluoracetic acid, Me_4Si external reference) 0.9 (s, $C_7\underline{H}_6CO$ 6H), 2.7 (m, $\underline{Ph}$-CO 5H).

24. 1-Benzoylcycloheptatriene; Thermolysis.

1-benzoyl cycloheptatriene was heated (24 hrs.) in aniline vapour (184°). Samples were taken at 6 hr. intervals for analysis by n.m.r. spectroscopy. Vacuum distillation of the residue gave deoxybenzoin (identical with samples prepared previously) as the only isolateable product.

25. 1-Benzoylcycloheptatriene; Photolysis.

Photolysis of 1-benzoyl cycloheptatriene in benzene (30 hrs.) using a Hanovia 125-W medium pressure mercury lamp, gave 2-benzoyl cycloheptatriene as sole product (from the n.m.r. spectrum). Evaporating off the solvent gave a sample of the crude material which could not be recrystallised from any of the normal solvents. M^+ 196.0878, $C_{14}H_{12}O$ 196.0888, $\nu_{max.}$(1680 cm.$^{-1}$ (ν C=O), τ 1.90(d, H_3, 1H) 2.50 (m, $\underline{Ph}CO$, 5H), 3.30 (m, H_4, 1H), 3.80 (m, H5, 1H), 4.15 (t, H_1, 1H) 4.55 (m, H_6, 1H), 7.75 (t, H_7, 2H).

26. Reaction of Benzoyl Tropylium Fluoroborate with Sodium Borohydride.

The method used was that described by Conrow [76], and the product isolated by separation of the organic layer, washing with water drying and evaporating off the pet.-ether. The residue was analysed by n.m.r. (in CCl_4) and i.r. (thin-film) spectroscopy. A discussion of these results is included in the text, and although the spectra appear complex, due to the presence of several products, it can be concluded with certainty that these are isomeric benzoyl cycloheptatrienes.

27. Reaction of Benzoyl Tropylium Fluoroborate with sodium methoxide in methanol.

The method is described by Dauben.[112] A solution of NaOMe (1 g. in MeOH (10 ml.) was slowly added to the benzoyl tropylium fluoroborate (1 g.) in methanol (10 ml.)

The solution was diluted with carbon tetrachloride (20 ml.) and washed several times with water. The carbon tetrachloride layer was retained, dried and concentrated to obtain an n.m.r. spectrum. The remainder of the carbon tetrachloride was evaporated off and the residue analysed by i.r. spectroscopy.

By similar considerations to expt. 26 it was concluded that the product was a mixture of isomeric benzoyl, methoxy cycloheptatrienes.

References.

1. Reviewed by :-

   a) G. Maier, Angew Chem. internat. Edit. 1967, 402.

   b) R. M. Willcott, Ph.D. Dissertation, Yale University, 1963.

2. A. Ladenberg, Chem. Ber., 1881, 14, 2126.

3. A. Ladenberg, Annalen, 1883, 217, 115.

4. R. Willstätter, Annalen, 1901, 317, 204.

5. E. Buchner and T. Curtius, Chem. Ber., 1885, 18, 2377 and references in the review articles mentioned in reference 1.

6. W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 1950, 72, 2305.

7. W. von E. Doering, G. Laber, R. Vanderwahl, N. F. Chamberlain and R. B. Williams, J. Amer. Chem. Soc., 1956, 78, 5448.

8. G. O. Schenck and H. Ziegler, Annalen, 1953, 548, 221.

9. F. A. L. Anet, J. Amer. Chem. Soc., 1964, 86, 458.

10. F. R. Jensen and L. A. Smith, J. Amer. Chem. Soc., 1964, 86, 956.

11. R. Huigsen and F. Mietzsch, Angew. Chem. internat. Edit, 1964, 3, 83.

12. T. Tsuji, S. Teratake, M. Tainda, Bull. Chem. Soc. Jap., 1969, 2033.

13. E. Buchner and S. Hediger, Ber., 1903, 36, 3502.

14. E. Vogel, W. Wiedemann, H. Kiefer and V. F. Harrison, Tetrahedron Lett., 1963, 673.

15. E. Ciganek, J. Amer. Chem. Soc., 1965, 87, 652.

16. E. Ciganek, J. Amer. Chem. Soc., 1967, 89, 1454.

17. E. Ciganek, J. Amer. Chem. Soc., 1965, 87, 1149.

18. T. Mukai, H. Kubota, and T. Toda, Tetrahedron Lett. 1967, 37, 3581.

19. D. Schönleber, Angew Chem. internat. Edit., 1969, 8, 76.

20. M. Jones, Angew Chem. internat. Edit., 1969, 8, 76.

21. M. Jones, Tetrahedron Lett., 1969, 39, 3953.

22. C. U. Pittman, Jr., and G. A. Olah, J. Amer. Chem. Soc., 1965, 87, 5123.

23. N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, J. Amer. Chem. Soc., 1965, 87, 4533.

24. N. C. Deno, H. J. Paterson and G. S. Saines, Chem. Rev., 1960, 60, 7.

25. C. D. Nenitzescu, in G. A. Olah and P. von R. Schleyer "Carbonium Ions", Vol. II Chap. 13, Interscience 1970.

26. G. D. Kolomnikova and Z. N. Parnes, Russ. Chem. Rev., 1967, 36, 735.

27. H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, J. Amer. Chem. Soc., 1957, 79, 4557.

28. K. M. Harmon and A. B. Harmon, J. Amer. Chem. Soc., 1961, 83, 865.

29. Z. N. Parnes, M. I. Kalinkiu and D. N. Kursanov., Dok. Akad. Nauk. S.S.S.R., 1965, 165, 1194.

30. K. M. Harmon, A. B. Harmon and F. E. Cummings, J. Amer. Chem. Soc., 1961, 83, 3912.

31. K. M. Harmon and F. E. Cummings, [illegible]er. Chem. Soc., 1962, 84, 1751.

32. D. Bryce-Smith and N. A. Perkins, Chem. and Ind., 1959, 1022.

33. D. Bryce-Smith and N. A. Perkins, J. Chem. Soc., 1961, 2320.

34. F. Seel, Z. Anorg. Allgem. Chem., 1943, 250, 331.

35. G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, J. Amer. Chem. Soc., 1962, 84, 2733 and succeeding articles entitled "Stable Carbonium Ions."

36. Reviewed in a forthcoming publication :- G. A. Olah and P. von R. Schleyer, "Carbonium Ions", Vol. IV. Wiley.

37. E. P. Kohler and L. W. Blanchard, J. Amer. Chem. Soc., 1935, 57, 367.

38. J. A. Blair, G. P. McLaughlin, and J. Paslawski, Chem. Comm., 1967, 1

39. T. I. Temnikova and V. S. Karavan, J. Gen. Chem. U.S.S.R., 1964, 34, 3204.

40. J. A. Blair and C. J. Tate, Chem. Comm., 1969, 1506.

41. W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 1957, 79, 352.

42. W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 1954, 76, 3203

43. E. W. Abel, J. Chem. Soc., 1958, 4559.

44. E. Müller, H. Fricke and W. Rundel, Z. Naturforsch, 1960, 15b, 753.

45. E. Müller, H. Fricke and H. Kessler, Tetrahedron Lett., 1963, 1501.

46. M. J. S. Dewar and R. Pettit, J. Chem. Soc., 1956, 2026.

47. C. R. Ganellin and R. Pettit, J. Chem. Soc., 1958, 576.

48. G. Linstrumelle, Bull. Soc. Chim. France, 1970, 920.

49. K. Weiss and Sister M. Lalande, J. Amer. Chem. Soc., 1960, 82, 3117.

50. C. D. Nenitzescu and A. T. Balaban, in G. A. Olah "Friedel-Crafts and Related Reactions", Vol. III, Part 2, Chapter XXXVII Interscience, 1964.

51. D. P. N. Satchell and R. S. Satchell in S. Patai "The Chemistry of the Carbonyl Group", Chapter 5, Interscience, 1966.

52. I. L. Kondakov, J. Russ. Phys. Chem. Soc., 1892, 24, 309.

53. G. A. Olah "Friedel-Crafts and Related Reactions" Vol.I. Interscience 1963.

54. W. E. Parham, J. Amer. Chem. Soc., 1962, 84, 1755.

55. J. Hutton and W. A. Waters, Chem. Comm., 1966, 634.

56. J. F. Chiang and S. H. Bauer, J. Amer. Chem. Soc., 1966, 88, 420.

57. J. A. Elvidge, in D. W. Mathieson "Nuclear Magnetic Resonance for Organic Chemists", Chapter 3, Academic Press, Inc. 1967.

58. S. Sternhell, Quart. Rev. 1969, 23, 236.

59. D. W. Mathieson "Nuclear Magnetic Resonance for Organic Chemists, Appendix. Academic Press, Inc. 1967.

60. E. J. Moriconi, C. F. Hummel and J. F. Kelly, Tetrahedron Lett., 1969, 5325.

61. P. Burns and W. A. Waters, J. Chem. Soc. "C", 1969, 27.

62. H. M. R. Hoffmann, Annual Reports Chem. Soc., 1966, 63, 333.

63. R. Hoffmann and R. B. Woodward, Accounts Chem. Research, 1968, 1, 17.

64. R. Hoffmann and R. B. Woodward, Angew. Chem. internat. Edit. 1969, 8, 78

65. K. Alder and F. G. Jacobs, Chem. Ber., 1953, 86, 1528.

66. J. Hine, "Physical Methods in Organic Chemistry", Mc.Graw-Hill, New York, 1956.

67. D. V. Banthorpe in E. D. Hughes "Reaction Mechanisms in Organic Chemistry", Volume II, "Elimination Reactions", Elsevier, 1963.

68. C. H. Depuy, R. D. Thurn and G. F. Morris, J. Amer. Chem. Soc., 1962, 84, 1314.

69. C. H. Depuy, G. F. Morris, J. S. Smith and R. J. Smatt, J. Amer. Chem. Soc., 1965, 87, 2421.

70. M. J. S. Dewar and R. C. Fahey, J. Amer. Chem. Soc., 1962, 84, 2012.

71. M. J. S. Dewar and R. C. Fahey, J. Amer. Chem. Soc., 1963, 85, 2245, 2248 and 3645.

72. G. Baddeley, H. T. Taylor and W. Pickles, J. Chem. Soc., 1953, 124.

73. D. P. N. Satchell and R. S. Satchell, in S. Patai "The Chemistry of the Carbonyl Group", Chapter 5, p. 260, Interscience, 1966.

74. J. A. Blair and C. J. Tate, J. Chem. Soc. "D", 1970, 1319.

75. J. W. Wilt and D. Piszkiewicz, Chem. and Ind., 1963, 1761.

76. K. Conrow, J. Amer. Chem. Soc., 1961, 83, 2543.

77. A. P. ter Borg, H. Kloosterziel and N. van. Meurs, Rec. Trav. Chim., 1963, 82, 717.

78. E. Weth and A. S. Dreiding, Proc. Chem. Soc., 1964, 59.

79. A. P. ter Borg, E. Razenberg and H. Kloosterziel, Rec. Trav. Chim., 1965, 84, 1230.

80. A. P. ter Borg and H. Kloosterziel, Rec. Trav. Chim., 1965, 84, 245.

81. W. G. Woods, J. Org. Chem., 1958, 23, 110.

82. K. N. Klump and J. P. Chesick, J. Amer. Chem. Soc., 1963, 85, 130.

83. J. A. Berson and M. R. Willcott, J. Amer. Chem. Soc., 1965, 87, 2751 and 2752 ibid., 1966, 88, 2494.

84. K. W. Egger, J. Amer. Chem. Soc., 1967, 89, 3688. ibid., 1968, 90, 1.

85. E. J. Corey, H. J. Burke and W. A. Reimers, J. Amer. Chem. Soc., 1956, 78, 180.

86. J. A. Berson, Accounts Chem. Research, 1968, 1, 152.

87. J. A. Berson and M. R. Willcott, Record. Chem. Prog., 1966, 27, 139.

88. W. von E. Doering and P. Gaspar, J. Amer. Chem. Soc., 1963, 85, 3043.

89. A. P. ter Borg and H. Kloosterziel, Rec. Trav. Chim., 1965, 84, 241.

90. W. G. Dauben and R. L. Cargill, Tetrahedron, 1961, 12, 186.

91. L. B. Jones and V. K. Jones, J. Amer. Chem. Soc., 1967, 89, 1880.

92. L. B. Jones and V. K. Jones, J. Amer. Chem. Soc., 1968, 90, 1540.

93. L. B. Jones and V. K. Jones, J. Org. Chem., 1969, 34, 1298.

94. G. W. Borden, O. L. Chapman, R. Swindell and T. Tezuka, J. Amer. Chem. Soc., 1967, 89, 2979.

95 A. P. ter Borg, E. Razenberg and H. Kloosterziel, Chem. Comm., 1967, 1210.

96. R. B. Woodward and R. Hoffmann,J. Amer. Chem. Soc., 1965, 87, 375, 2511, 2046, 4388 and 4389.

97. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley, New York, 1961.

98. R. Srinivasan, J. Amer. Chem. Soc., 1962, 84, 3432.

99. R. M. Willcott and E. Goerland, Tetrahedron Lett., 1966, 51, 6341.

100. L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen 1958.

101. K. Nakanishi, "Infra-Red Absorption Spectroscopy," Holden-Day Inc. 1962.

102. M. V. Evans & R. C. Lord, J. Amer. Chem. Soc., 1960, 82, 1876.

103. J. B. Lambert, L. J. Durham, P. Lepautere, and J. D. Roberts, J. Amer. Chem. Soc., 1965, 87, 3896.

104. K. W. Egger and W. R. Moser, J. Phys. Chem., 1967, 71, 3699.

105. J. I. Musher and E. J. Corey, Tetrahedron, 1962, 18, 791.

106. S. Meyerson, J. D. McCallum and P. N. Rylander, J. Amer. Chem. Soc., 1961, 83, 1401.

107. H. Budzikiewicz, C. Djerassi,D. H. Williams, "Mass Spectrometry of Organic Chemistry", Holden-Day, Inc. 1967.

108. F. W. McLafferty, "Interpretation of Mass Spectra", W. A. Benjamin, Inc., 1967.

109. A. I. Vogel, "Practical Organic Chemistry" Longmans, 3rd Edition, 1956, p. 792.

110. F. A. Andersen, B. Bak and A. Hillebert, Acta. Chem. Scand. 1953, 7, 236.

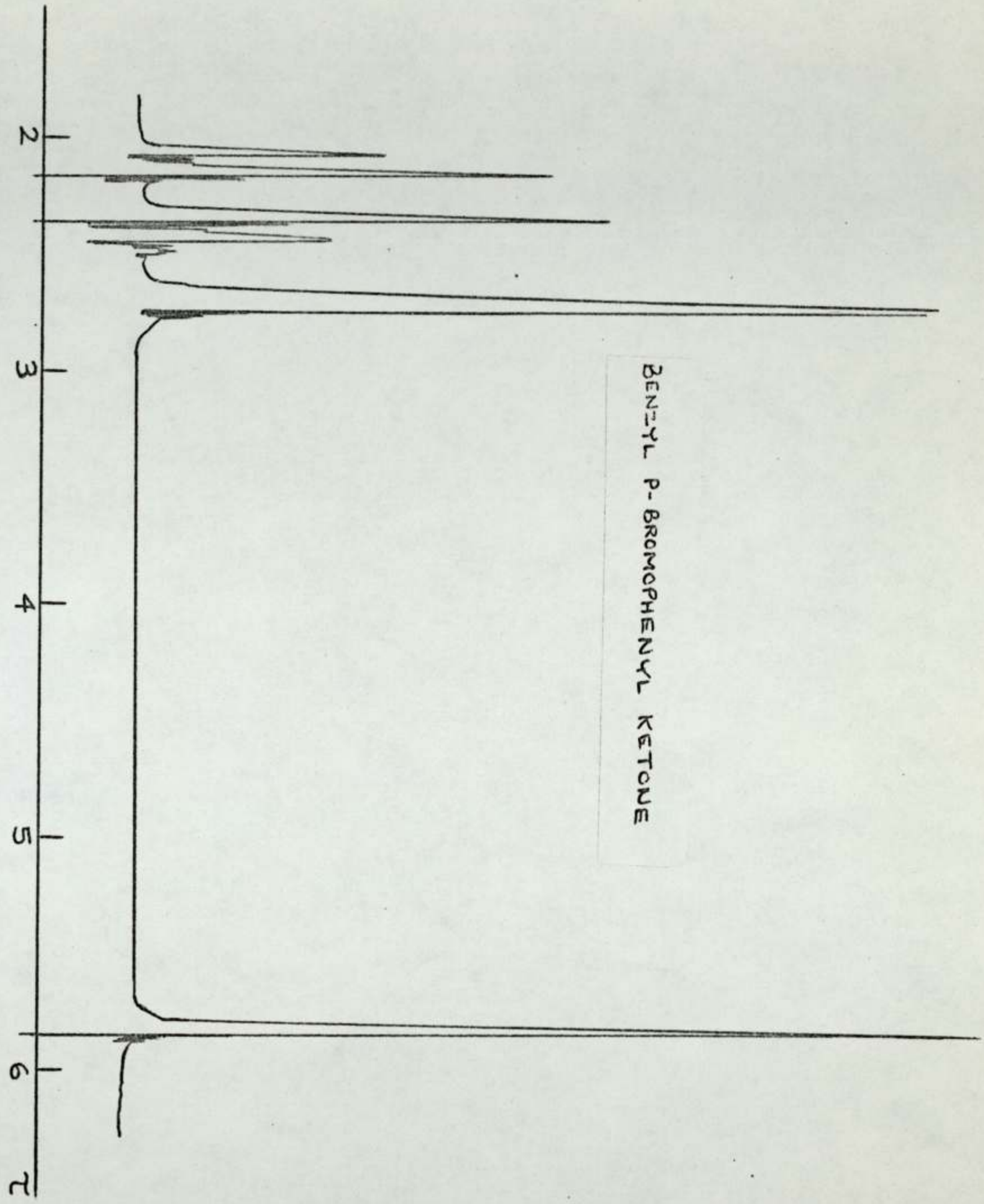
111. G. A. Olah and H. W. Quinn, J. Inorg. Nucl. Chem., 1960, 295.

112. A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, J. Amer. Chem. Soc., 1960, 82, 5593.

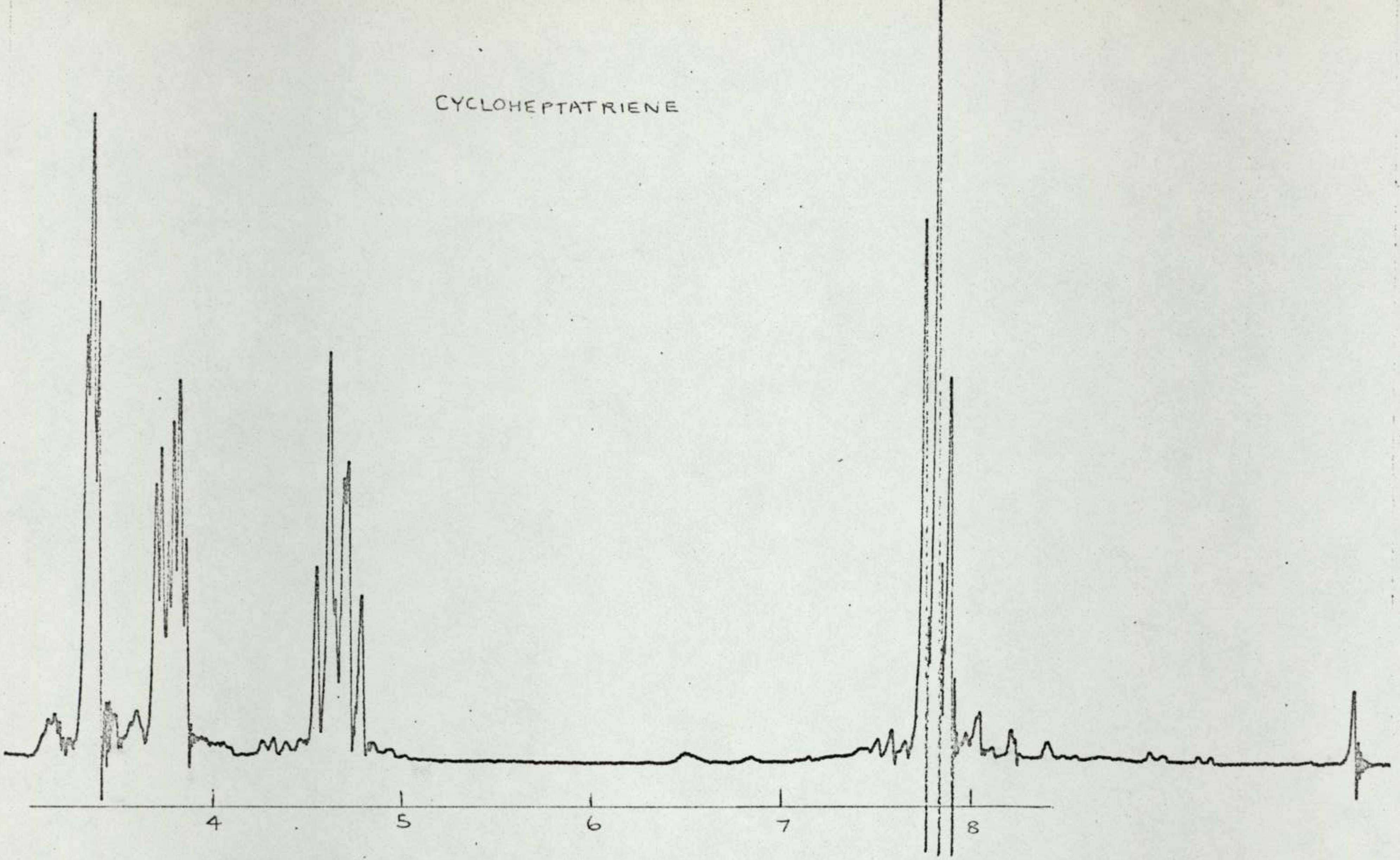
Appendix I.

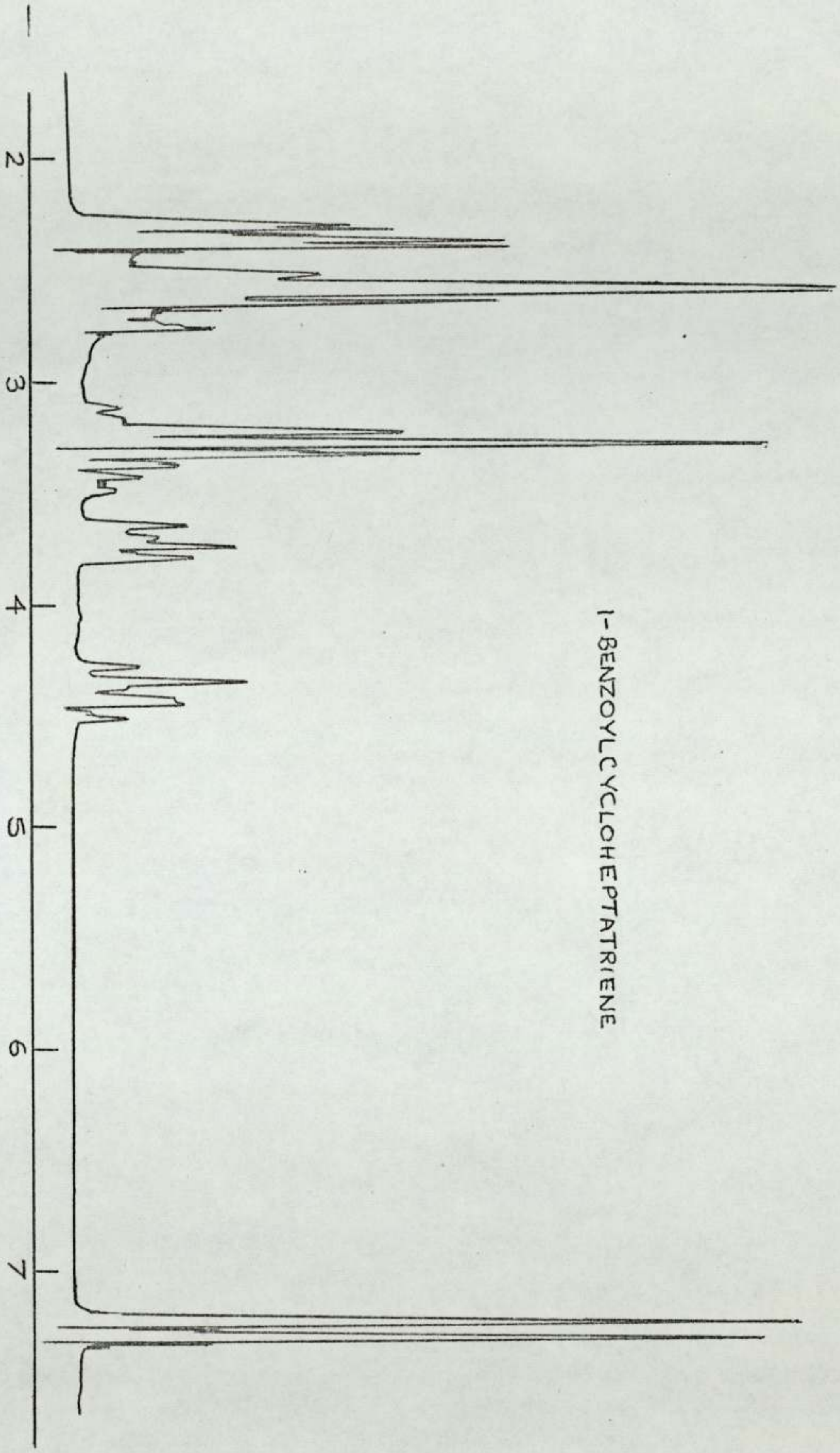
Index.

Appendix II.

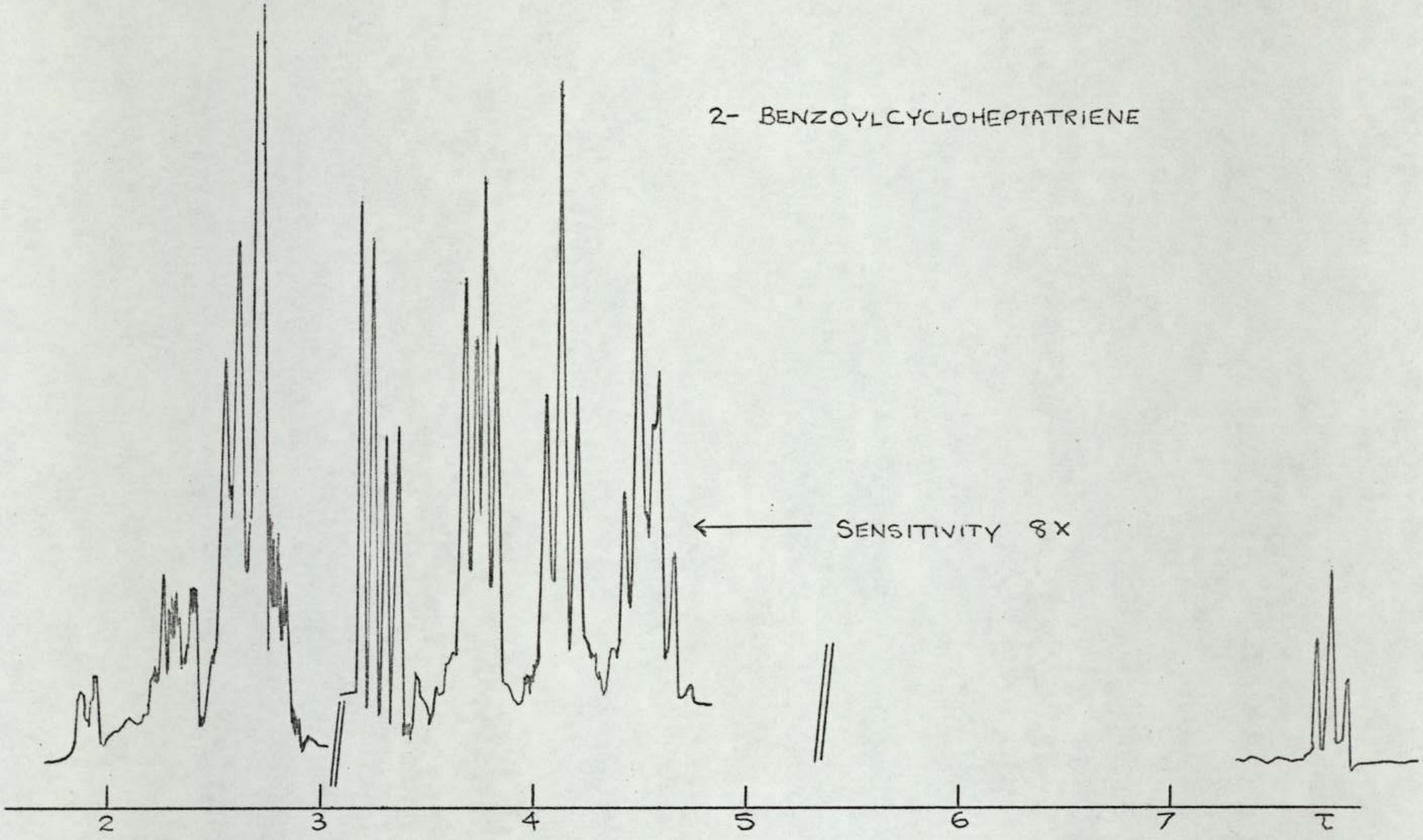


BENZYL P-BROMOPHENYL KETONE

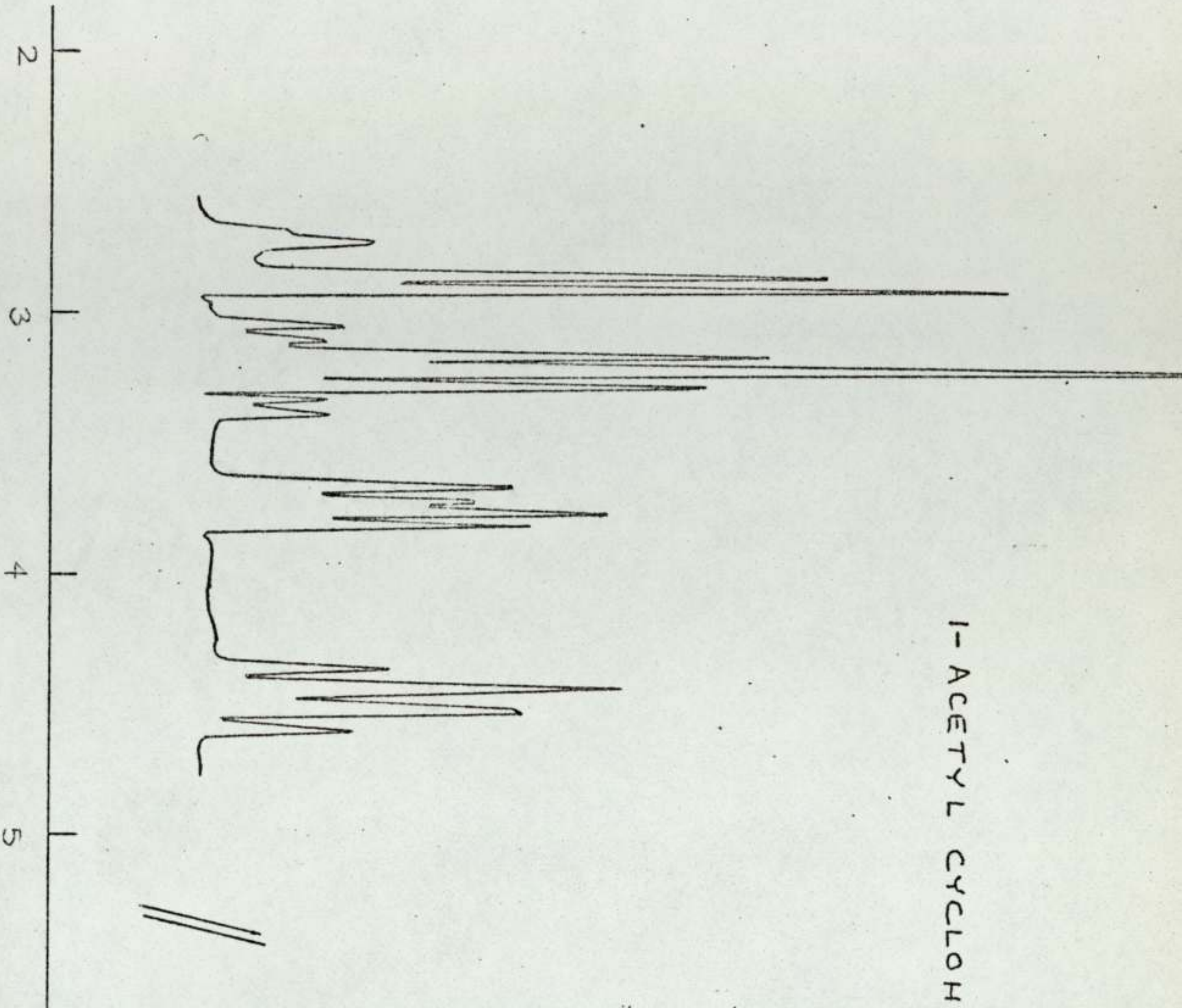

CYCLOHEPTATRIENE
4
5
6
7
8

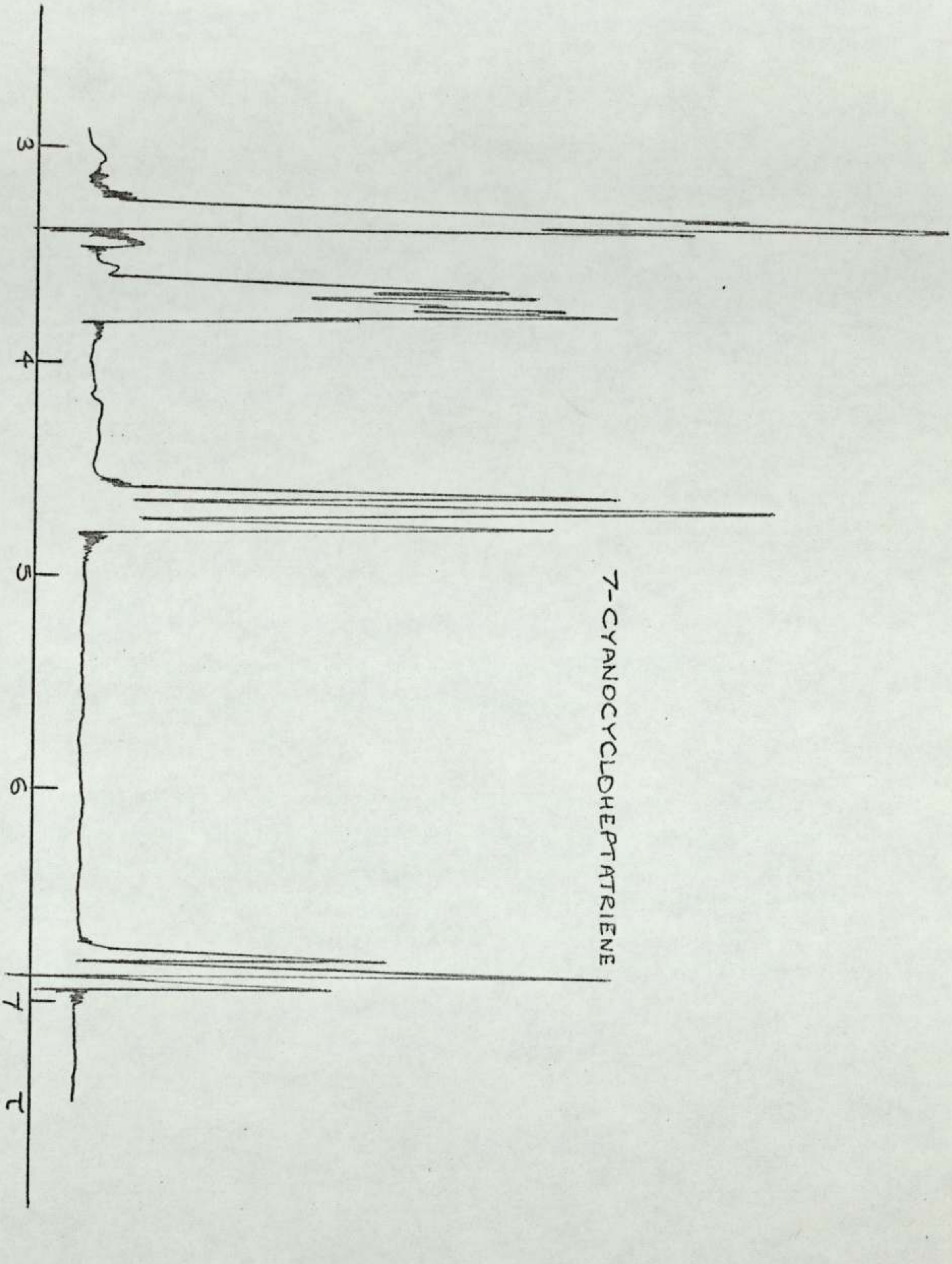


1-BENZOYLCYCLOHEPTATRIENE

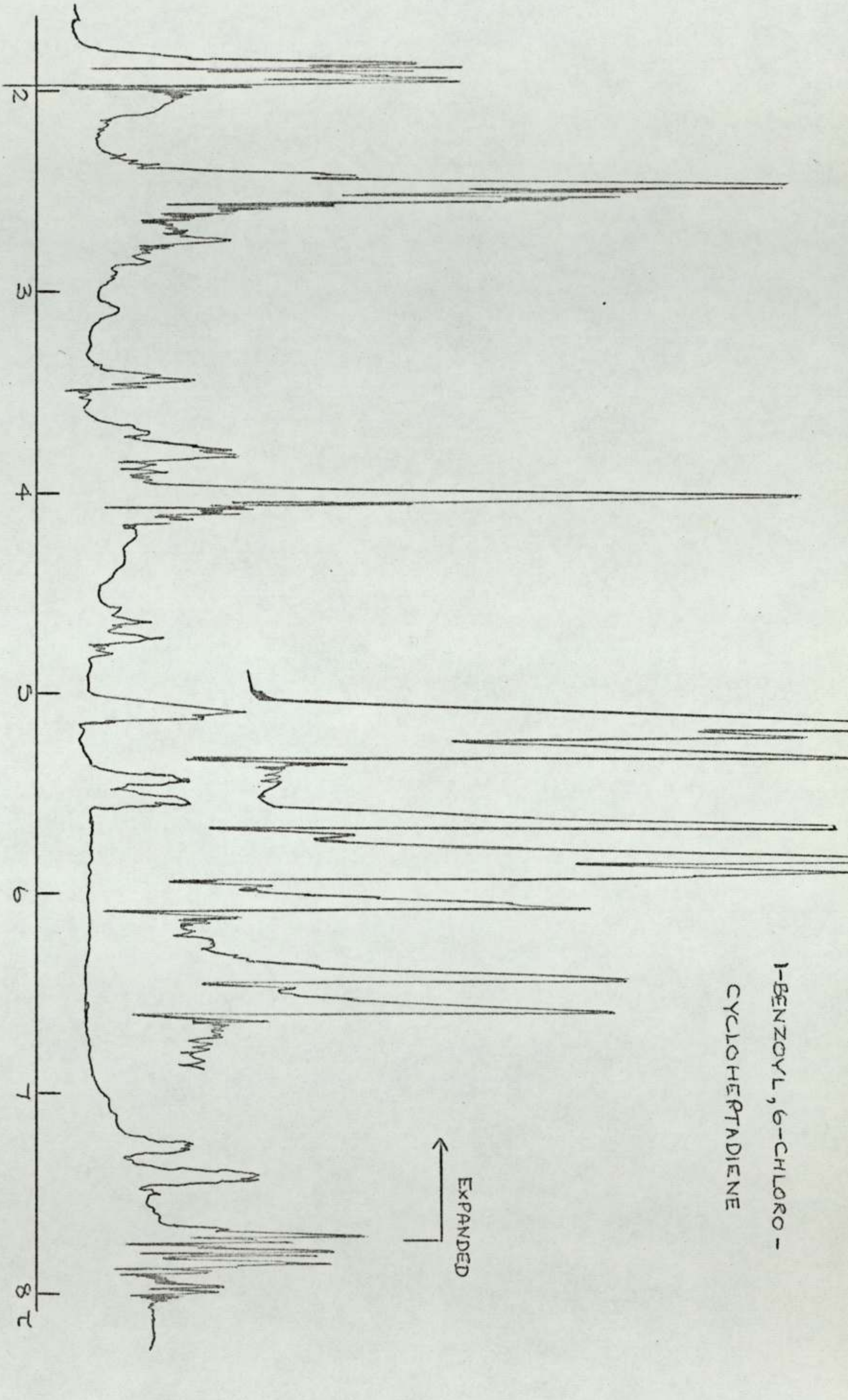


2- BENZOYLCYCLOHEPTATRIENE


1- ACETYL CYCLOHEPTATRIENE



7-CYANOCYCLOHEPTATRIENE



1-BENZOYL, 6-CHLORO-CYCLOHEPTADIENE

Mass spectra of substituted deoxybenzoins, relative abundance as a percentage of the base peak.

m/e	A	B	C	D	E	F	G	H *
39	5	3	3	5	11	6	2	10
43	-	41 5			50 14	-		100
51	3		3	7	10	9	1	5
63		2			6	-	3	5
64	-					-	5	
65	6	4	3		18	6	3	11
75			4		15	-		
76					18	-		
77	39	5	6	7	13	25	14	4
91	6	13	3	4	23	8	4	51 *
92			101 3			-	10	20
103		3				37		
104		3						
105	100	2						
106	8							
107							6	
115		2						
117		2						
118		2						
119		22						
126			6	7				
127			53	60				
128			7	8				
131						100		
132						10		

Mass spectra of substituted deoxybenzoins, relative abundance as a percentage of the base peak. (Cont'd.)

m/e	A	B	C	D	E	F	G	H
134							-	16
135							100	
136							9	
147	100						-	
148	11						-	
155			100	100	21			
156			12	12	-			
157					19			
183					100			
185					95			
196	(1.5)							
222						(0.5)		
226							(0.5)	
238		(0.4)						
246			3	6				
274					1.8			
276					1.8			
	(3)	(2)	(3)	(4)	(10)	(5)	(1)	(5)

Mass spectra of 1-acyl cycloheptatrienes, relative abundance as a percentage of the base peak.

	A	B	C	G	H*
39	15	64	5	7	17
41		41			
43					100
51	23	33	7	4	7
63		26	9	7	8
64				8	
65	15	57		8	26
75					
76					
77	53	47	21	25	7
91	52	90 71	9	90 11	66
92	26	100	8	19	11
103					
104		20			
105	100	20			
106	10			10	
107					
115		21			
119		48			10
126			12		–
127			74		
128			14		
131					
132					133 8
134					22

Mass spectra of 1-acyl cycloheptatrienes, relative abundance as a percentage of the base peak. (Cont'd.)

	A	B	C	G	H*
135				100	
136				10	
147		63			
148				152 7	
155			100		
156			22		
157					
183					
185	195 13			195 5	
196	29				
222				225 19	
226				64	
238		15		227 11	
246		–	0.3		
274		–	–		
	(10)	(20)	(5)	(4)	(7)

* See table XI. p. 77