A STUDY OF THE REACTIONS BETWEEN HALIDES OF METALLOIDS AND PHENYLACETYLENES

BY

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SUMMARY

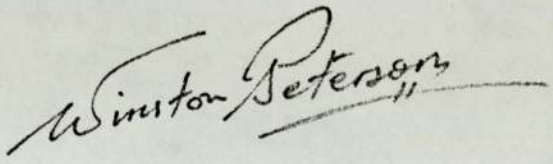
The uncatalysed reactions of phenylacetylenes with arsenic trichloride have been shown to give 1:1 trans-additon products whilst the acetylenic acids and their esters give complex cyclic adducts.

The reactions provide a novel route to compounds like β-chloro-(p-methylstyryl)diphenylarsine, cis-(β-styryl)diphenylarsine and β-chloro-(p-chlorostyryl)dichloroarsine and in all twelve novel organo-arsenic compounds have been prepared.

The stereochemistry of the 1:1 trans-adducts and their derivatives have been established and an attempt has also been made to determine the reaction mechanism from spectroscopically obtained kinetic data.

STATEMENT

The undersigned declares that this thesis has not been carried out in collaboration with others. Neither has the work been submitted for any other award.



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CONTENTS

TABLES

FIGURES

INTRODUCTION

Nieuwland[1] first reported the formation of poisonous, evil-smelling products from the reaction of acetylene with arsenic trichloride in the presence of anhydrous aluminium chloride, but did not identify the compounds formed. During World War I, this reaction was investigated by chemists of the United States Chemical Warfare Service and the addition products of arsenic trichloride and acetylene were isolated. Dafert[2] also obtained a compound to which he ascribed the formula $AsCl_3.2C_2H_2$ by the reaction of arsenic trichloride on acetylene in the presence of aluminium chloride.

Lewis and Perkins[3] employed aluminium halide, or in a few cases mercuric chloride, as an essential catalyst and managed to prepare β-chlorovinyl chlorarsines (Lewisites). An addition compound having the composition $AlCl_3.AsCl_3.3C_2H_2$ was shown to be the intermediate in the reaction of acetylene with aluminium chloride and arsenic trichloride. When the freshly prepared crude product was treated with dilute hydrochloric acid to remove aluminium chloride, the compound ββ′β″-trichlorovinylarsine, $(ClCH{=}CH)_3As$, was found to predominate over the two other derivatives, $(ClCH{=}CH)_2AsCl$ and $(ClCH{=}CH)AsCl_2$, even when an excess of arsenic trichloride was used. On warming with arsenic trichloride, the compound $(ClCH{=}CH)_3As$ or the intermediate containing aluminium chloride yielded a mixture containing the other two derivatives.

Lewis and Steigler[4] found that chlorovinylarsines could also be prepared from arsenic trichloride and acetylene with aluminium bromide as a catalyst and that the corresponding

bromovinylarsines could be prepared from arsenic tribromide and acetylene with aluminium chloride as a catalyst, proving that only halogen from the arsenic halide entered into the composition of the halovinyl groups in the product. The following equations illustrate the mechanisms proposed by Lewis and his co-workers on the basis of this evidence. (SCHEME 1).

SCHEME 1

$$AlBr_3 + 3C_2H_2 \longrightarrow Al(CH{=}CHBr)_3$$

$$Al(CH{=}CHBr)_3 + AsCl_3 \longrightarrow Al(CHCl{-}CHBr)_3As$$

$$Al(CHCl{-}CHBr)_3As \xrightarrow{\text{aq. HCL}} AlBr_3 + (ClCH{=}CH)_3As$$

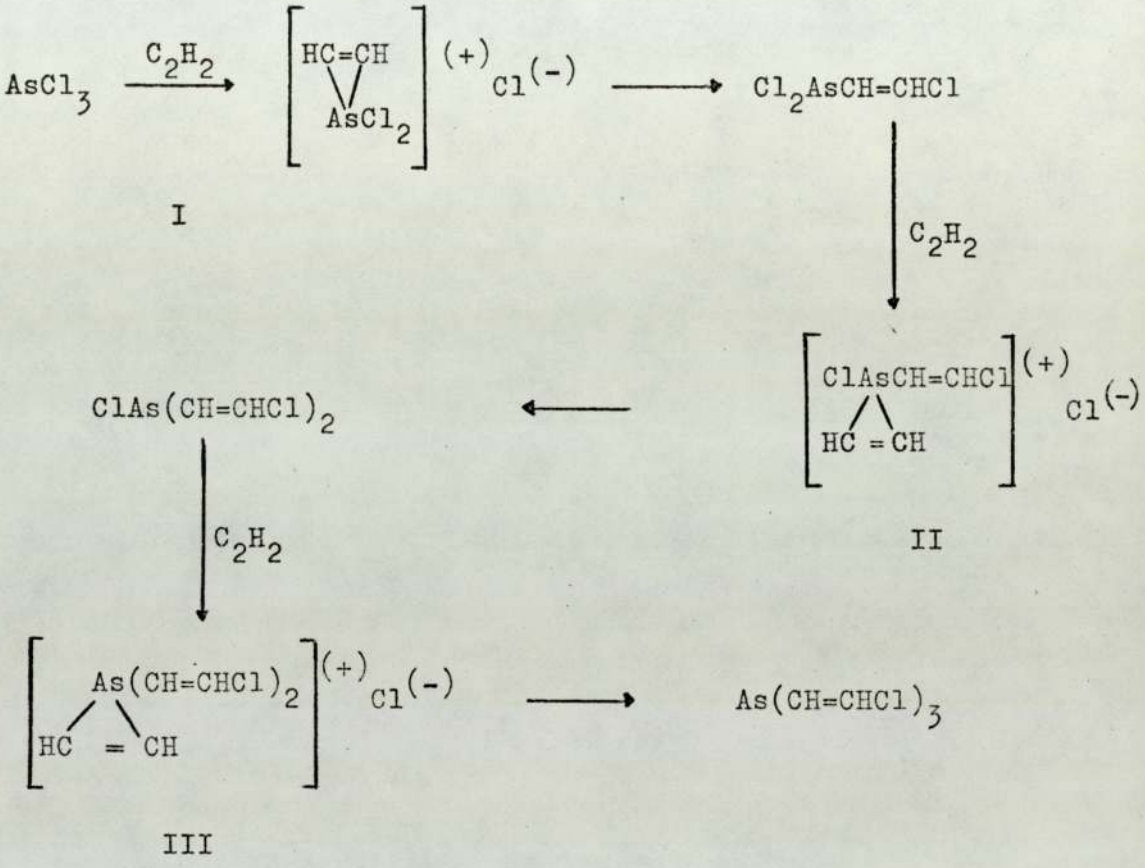
$$(ClCH{=}CH)_3As + AsCl_3 \longrightarrow (ClCH{=}CH)_2AsCl + (ClCH{=}CH)AsCl_2$$

The halogen of the halovinyl groups is quite inert but when halogen atoms remain attached to arsenic they may be replaced readily and the arsenic of all the compounds may be oxidised to the pentavalent state. Lewisites became of great importance as war-gases and the reactions and other characteristics of these compounds have been described by numerous investigators[5].

In 1947, Jean-Pratt[6] suggested an ionic type intermediate for the mechanism of the formation of β-chlorovinylarsines. The addition of acetylene to arsenic trichloride in the presence of aluminium chloride or mercuric chloride proceeds through the formation of arsonium intermediates. Only the tertiary arsonium intermediate (SCHEME 2, III) was isolated and shown to contain pentavalent

arsenic, titratable chloride, and to be soluble in water but insoluble in benzene.

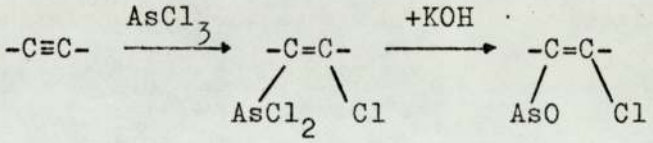
SCHEME 2



The work of Turner and Hunt[7] suggested that an addition product was formed when phenylacetylene was treated with an excess of arsenic trichloride in the absence of a catalyst, and from the heavy green oil obtained, β-chlorostyryldichloroarsine, $C_6H_5CCl{:}CHAsCl_2$, and β β′-dichlorostyrylchloroarsine $(C_6H_5CCl{:}CH)_2AsCl$, were isolated. They found that the presence of aluminium chloride complicated the reaction by polymerising the phenylacetylene and the only product was a yellow amorphous substance containing two chlorine atoms to each atom of arsenic.

A more detailed study of Turner's work by Ipatiew[8] et al., produced a low melting crystalline compound whose structure was not determined. Ipatiew utilised a freezing method to isolate white plate-like crystals with a yellow tinge and recrystallised his material from various solvents to produce white odourless crystals with a melting point of 40.6-41.2°C. Unfortunately, both Turner's and Ipatiew's works must be viewed with some scepticism as the only proof of formulation of the compound was from chlorine and arsenic determinations and a few simple chemical tests. They did not attempt to determine the stereochemistry of the compound or the mechanism of the reaction.

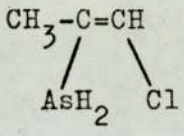
In 1913 E. Fisher and G. Klemperer[9] published a paper on the method of preparing and the pharmacological action of a new arsenic compound called elarson. It was a strontium salt of "chloroarsenobehenolic" acid and was obtained by the action of arsenic trichloride on behenolic acid. In the following year Fisher[10] published more detailed information regarding a new class of aliphatic arsenic compounds and proposed that the reaction of arsenic trichloride and behenolic acid occurred according to the following reaction:-



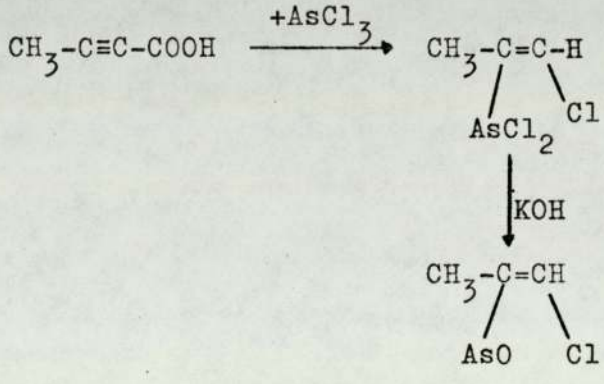
Unfortunately, he was unable to isolate the product of addition because he thought a complex mixture of two structural isomers resulted and his attempt to isolate the reaction products of arsenic trichloride with stearolic and phenylpropiolic acid gave still less satisfactory results because the adduct with

phenylpropiolic acid contained a percentage of arsenic which did not agree with the formula shown above.

Mochnac and Bagniuk[11] followed this line of research and began their investigation by studying the reaction of tetrolic and ethylpropiolic acid with arsenic trichloride. They found that the addition reaction of arsenic trichloride to tetrolic acid at 140°C. gave a product which melted at 91.5 - 92° and corresponded to the formula C_3H_6AsCl with the following structure:-



This product, chloropropenylarsine, may exist in four isomeric forms; however the sharp melting point indicated that it was only one of them. If the addition reaction was carried out under milder conditions, 120-130°C, there was formed an arsinoxy-derivative, but also decarboxylated (chloroarsinoxy-propene), according to the formula:-

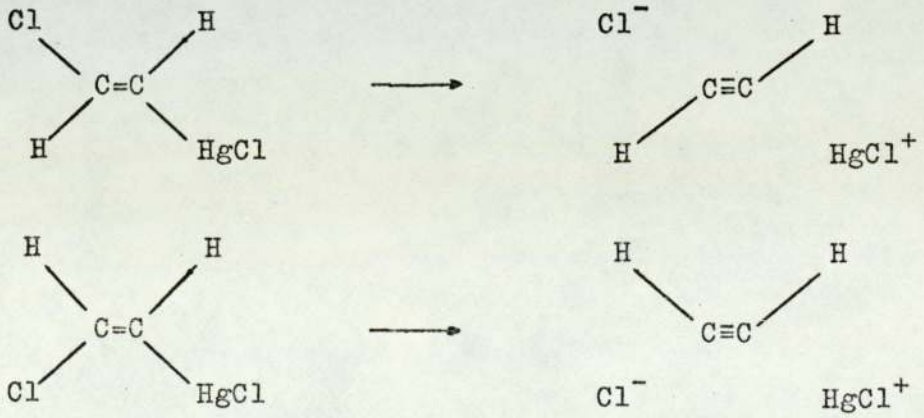


Note

Mochnac's structural formulae for the addition products are incorrect.

Finally, when the temperature is still further lowered the addition reaction proceeds without decarboxylation. The stereochemistry and reaction mechanism of the compounds prepared by Mochnac and Bagniuk have not been elucidated since their work was published although many investigators have studied the products of the reaction between acetylene and arsenic trichloride[9,12,13], and antimony pentachloride[14].

Nesmeyanov[14] managed to prepare the tris(chlorovinyl)stibines by reacting acetylene gas with an alkaline solution of antimony pentachloride in the presence of mercuric chloride and found that the trans-tris-(2-chlorovinyl)antimony dichloride, $(ClCH{=}CH)_3SbCl_2$, had a melting point of 93-4° whilst the cis-compound had a melting point of 61-2°. With mercuric chloride, $HgCl_2$, tris-(2-chlorovinyl)antimony dichloride quantitatively exchanged $SbCl_3$ for HgCl without change of configuration to give ClCH=CHHgCl. He described the mercury and antimony compounds as organometallic but on the other hand they also showed features of complex compounds for which he used the term "quasi-complex". The reasons for this duality showed that there was no tendency to spontaneous dissociation with evolution of acetylene and the explanation proposed assumed resonance of two forms as illustrated in the simplest case by:-



The assumption was corroborated by Raman spectroscopy and dipole moment measurements and the right-hand formulae account for the dissociation with elimination of acetylene whilst the left-hand formulae represent the organometallic behaviour.

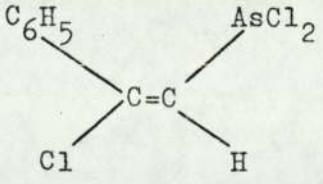
The literature gives numerous examples of additions of simple molecules like hydrogen chloride and hydrogen bromide to acetylene compounds[15,16,17,18], but little information on the addition reactions between halides of metalloids and arylacetylenes.

In as much as the addition products have not only a theoretical interest, but may have also a practical importance, a systematic study of the reaction of phenylacetylene and its para-substituted derivatives with arsenic trichloride, in the absence of any catalyst or solvent, was quite timely. It was hoped that the stereochemistry of the reaction product and the reaction mechanism would be determined with the aid of infrared spectroscopy, nuclear magnetic resonance and mass spectrometry techniques.

The reaction of phenylacetylene with arsenic trichloride was expected to produce an α,β-addition product,

$$C_6H_5C{\equiv}CH + AsCl_3 \longrightarrow C_6H_5CCl{=}CHAsCl_2$$

and the stereochemistry of the compound would be expected to be that of the trans-addition compound by analogy with the Lewisite reaction (90% trans)[19]. Trans-β-chlorostyryldichloroarsine is defined as having the phenyl group and hydrogen atom on opposite sides of the carbon-carbon double bond;



Thus a series of experiments was carried out involving the preparation of the α,β-addition product, its derivative with a Grignard Reagent, and the substituted styrylarsine by reducing the Grignard derivative with a lithium aluminium hydride - lithium hydride mixture. The stereochemistry of the products and derivatives were determined by instrumental methods and the reaction kinetics studied by infrared spectroscopy.

CHAPTER 1

ORGANIC SYNTHESES

Experimental Section

All the para-substituted phenylacetylenes were prepared by well established techniques but in some cases more novel modern methods were used when higher yields were required.

Phenylacetylene and arsenic trichloride are readily available laboratory reagents and were purified by distillation and stored over molecular sieves (TYPE 5A) before use.

Nuclear Magnetic Resonance

Measurements were obtained on a Perkin Elmer R10 spectrometer operating at 60MHz at 33.4°C, or in certain cases where better resolution was required, a Varian Associate HA100D operating at 100MHz at 33.4°C.

Samples were usually examined in carbon tetrachloride solutions and tetramethylsilane was used as an internal standard. (τ=10.0)

Infrared Spectroscopy

Infrared spectra were determined on the neat liquids, and potassium bromide discs or mineral oil mulls of the solids, on a Perkin Elmer 457 grating infrared spectrophotometer operating from 4000cm^{-1} to 250cm^{-1}.

SECTION 1A
PREPARATION OF ARYLACETYLENES

1A (i)
p-Methylphenylacetylene

To phosphorus pentachloride, (47.3g,0.9mole), contained in a 100ml Claisen flask fitted with a dropping funnel and drying tube containing fused calcium chloride and cooled in a bath of ice and salt, p-methylacetophenone, (27.5g,0.83mole), was added during a one hour period.

The reaction mixture was left at room temperature for seventeen hours and the phosphorus oxychloride removed under reduced pressure, (b.p. 45-50°/18mm).

The residue was distilled through a four inch column packed with glass beads and the oily product was collected at 80-85°/10-11mm.

This material, 21.0g, was added to potassium hydroxide, 12.5g, in absolute ethanol, 25mls, and refluxed for twenty-four hours.

The reaction mixture was poured into ice-water, the oil separated and the aqueous layer was extracted with ether.

The oil and ether were combined, dried over potassium hydroxide and the ether was removed. The residue was distilled under reduced pressure to give a 17% yield of p-methylphenylacetylene, (b.p. 79-84°/30-32mm). (Lit. value 79-81°/31-33mm)[20].

Anal.

Calcd. for C_9H_8:	C 93.09%	H 6.89%
Found:	C 92.98%	H 6.69%

N.M.R.

$\tau(CCl_4)$ 7.14 1 proton (≡CH), 7.79 3 protons (CH_3),
2.85 4 protons (Aromatic complex).

I.R.

(thin film) 3300cm^{-1} (≡C-H), 2920cm^{-1}, 1379cm^{-1} (CH_3),
2105cm^{-1} (C≡C), 3030cm^{-1} (aromatic C-H),
1605, 1565, 1450cm^{-1} (aromatic C=C).

1A (ii)
p-Methoxyphenylacetylene

Phosphorus pentachloride, (95g,0.46mole), was treated with p-methoxyacetophenone, (60g,0.40mole), in 150mls dry benzene. The reaction mixture was heated on an oil bath at 60-70°C. for thirty minutes and then allowed to stand at room temperature for twenty-four hours. The phosphorus oxychloride was removed under reduced pressure and the residue was dissolved in 20mls of dry methanol.

This material was added to 125g potassium hydroxide in 500mls of absolute ethanol and the mixture was refluxed on a water bath for twenty-four hours.

On cooling the mixture was poured onto crushed ice, the oil was separated and the aqueous layer was extracted with ether.

The oil and ether were combined, dried over potassium hydroxide and the ether was removed. The residue was distilled under reduced pressure to give a 17% yield of p-methoxyphenylacetylene, (b.p. 109-114°/24mm). (Lit. value 110-114°/24mm)[21].

Anal.

Calcd. for C_9H_8O:	C 81.81%	H 6.06%
Found:	C 81.05%	H 5.99%

N.M.R.

$\tau(CCl_4)$ 6.90 1 proton (≡CH), 6.40 3 protons (CH_3-O-),
2.92 4 protons (Aromatic complex).

I.R.

(thin film) 3290cm^{-1} (≡C-H), 2105cm^{-1} (C≡C),
3010cm^{-1} (aromatic C-H),
1610, 1572, 1508, 1443cm^{-1} (aromatic C=C),
1250cm^{-1} (aromatic C-O), 1030cm^{-1} (C-O).

1A (iii)
p-Chlorophenylacetylene

Phosphorus pentachloride, (107g,0.51mole), and p-chloroacetophenone, (74g,0.48mole), were contained in a 500ml round-bottomed flask provided with a reflux condenser. The flask was heated to 70°C. in an oil bath for fifteen minutes and then allowed to stand at room temperature for twenty-four hours.

The phosphorus oxychloride was removed under reduced pressure and the residue was cooled to room temperature and treated with ethanolic potassium hydroxide, (400g 25% w/v).

After refluxing for four hours, it was poured into ice water, the oil separated and the aqueous portion was extracted with ether.

The oil and ether were combined and dried over potassium hydroxide.

The ether was removed and the residue distilled under reduced pressure, (b.p. 93-95°/4-5mm).

The p-chlorophenylacetylene crystallised in the receiver and was recrystallised from water/methanol (50% v/v), to give a 38% yield, (m.p. 46-7°). (Lit. value 46.5 - 47.0°)[22].

Anal.

Calcd. for C_8H_5Cl:	C 70.34%	H 3.66%
Found:	C 70.31%	H 3.62%

N.M.R.

$\tau(CCl_4)$ 7.0 1 proton (≡CH)

2.56 4 protons (aromatic complex).

I.R.

(Mineral oil mull) 3310cm^{-1} (≡C-H), 2110cm^{-1} (-C≡ C-),

1590, 1485cm^{-1} (aromatic C=C),

1090cm^{-1} (aromatic C-Cl).

1A (iv)

p-Nitrophenylacetylene

Using the method described for p-chlorophenylacetylene, the corresponding p-nitrophenylacetylene was prepared from p-nitroacetophenone.

The product was distilled under reduced pressure, (b.p. 118-123°/22-24mm), and on cooling gave a 12% yield of needle-like crystals which were recrystallised from hot water, (m.p. 151-2°). (Lit. value m.p. 152°)[23].

Anal.

Calcd. for $C_8H_5NO_2$: C 65.31% H 3.40%

Found: C 65.20% H 3.31%

N.M.R.

$\tau(CDCl_3)$ 6.63 1 proton (≡C-H)

2.0 4 protons (aromatic complex).

I.R.

(Mineral oil mull) 3250cm^{-1} (≡C-H), 2110cm^{-1} (C≡C),

1500, 1593cm^{-1} (aromatic C=C),

1510, 1344cm^{-1} (aromatic C-NO_2).

1A (v)
Phenylpropiolic acid

Cinnamic acid, (74g,0.5mole), and carbon tetrachloride, (500mls), were placed in a three-necked flask fitted with a stirrer, reflux condenser and separating funnel.

The mixture was heated to boiling and the addition of bromine, (80g,0.5mole), in carbon tetrachloride, (50mls), begun whilst gently stirring the contents of the flask.

The bromine was added over forty-five minutes. The reactants were heated for an additional fifteen minutes and the stirring continued while the mixture cooled to room temperature.

The fine colourless needles of cinnamic acid dibromide were filtered off and dried.

Cinnamic acid dibromide, (25g), was placed in an evaporating dish and 100mls. of a 25% (w/v) solution of potassium hydroxide in methanol added and the mixture was stirred over boiling water until nearly all the alcohol had evaporated.

Methanol, (75mls), was added and the procedure repeated to ensure complete reaction.

The paste was filtered, washed with a little cold methanol and dissolved in 500mls. ice-water. Iced hydrochloric acid was added to pH6.

As the phenylpropiolic separated as an oil, hydrochloric acid was added slowly with vigorous stirring until the mixture was strongly acid.

The crude phenylpropiolic acid was filtered off and recrystallised from boiling carbon tetrachloride to give a 45% yield, (m.p. 136-137°). (Lit. value m.p. 138°)[24].

Anal.

Calcd. for $C_9H_6O_2$: C 73.96% H 4.11%

Found: C 73.88% H 4.00%

N.M.R.

τ(acetone) -0.9 1 proton (-COOH),

2.5 5 protons (aromatic complex).

I.R.

(KBr disc.) 1675cm^{-1} (C=O), 2200cm^{-1} (C≡C),

2575cm^{-1} (-OH),

1490, 1445cm^{-1} (aromatic C=C).

1A (vi)

Methyl phenylpropiolate

To phenylpropiolic acid, (20g,0.14mole), in 200mls.dry methanol, was added 4-5 drops concentrated sulphuric acid. Dry toluene, 50mls, was added to the mixture which was then refluxed for seven hours.

The excess methanol and toluene was removed until about 50mls. residue remained.

The residue was washed with aqueous sodium bicarbonate, (30% w/v), and extracted with ether.

The ether was dried with magnesium sulphate and removed using a rotary evaporator.

The ester was distilled under reduced pressure, (b.p. 129-131°/16mm). (Lit. value 132-3°/16mm)[25].

Anal.

Calcd. for $C_{10}H_8O_2$: C 75.01% H 5.00%

Found: C 75.49% H 4.15%

N.M.R.

$\tau(CCl_4)$ 6.26 3 protons ($-O-CH_3$),

2.58 5 protons (aromatic complex).

I.R.

(thin film) $2225cm^{-1}$ (C≡C), $1710cm^{-1}$ (C=O),

1600, 1573, 1490, $1443cm^{-1}$ (aromatic C=C),

$2950cm^{-1}$ (CH_3).

1A (vii)

General procedure for the synthesis of arylalkynes via selenadiazoles [26,27].

The semicarbazones were prepared by treating the acetophenones in methanol with aqueous solutions of semicarbazide hydrochloride as described by Vogel.[28]

The powdered semicarbazones were not purified before use as they were found to be sufficiently pure after several washings with methanol.

All the selenadiazoles were prepared by dissolving or suspending the powdered semicarbazone in about 10-15 times its volume of dry glacial acetic acid followed by the slow addition of equimolar quantities of finely powdered selenium dioxide.

Whenever necessary, the solution was warmed gently on a water bath to start the reaction, as shown by the evolution of nitrogen gas.

When the evolution of gas slowed down, the mixture was heated gently on a water bath until evolution ceased and finally, the mixture was filtered to remove the slight amounts of deposited metallic selenium.

The filtrate was added to water and extracted several times with chloroform. The chloroform layer was washed with sodium bicarbonate solution, dried with sodium sulphate and rotary evaporated to leave a reddish oil of the appropriate selenadiazole. All the selenadiazoles were unstable at room temperature and in the light.

For the formation of acetylenes, the selenadiazoles were pyrolysed on sand (washed with glacial acetic acid and dried at 100°C. for two days) and vacuum distilled.

Arylalkynes prepared in this way were obtained in higher yields than from the phosphorus pentachloride method.

	Selenadiazole Method	Phosphorus pentachloride Method
p-$ClC_6H_4C{\equiv}CH$	50%	38%
p-$MeC_6H_4C{\equiv}CH$	38%	17%
p-$NO_2C_6H_4C{\equiv}CH$	30%	12%
p-$CH_3OC_6H_4C{\equiv}CH$	26%	17%

SECTION 1B

TREATMENT OF ARSENIC TRICHLORIDE WITH ARYLACETYLENES

1B (i)

Phenylacetylene

Arsenic trichloride, (21.7g, 0.12mole), and phenylacetylene, (7.4g, 0.073mole), were contained in a 50ml. round bottomed flask fitted with a reflux condenser, guard tube containing fused calcium chloride and inert gas (N_2) by-pass tube.

The mixture was heated to about 90° on an oil bath for two hours and then cooled to room temperature in an inert atmosphere of nitrogen.

The dark brown liquid was cooled to -10°C. (acetone/CO_2) until a paste was formed and then rapidly filtered, pressed between filter pads and stored under vacuum.

The dark brown crystals were recrystallised from dry petroleum ether (b.p. 40-60°) at -20 to -15°C. and vacuum dried, m.p. 39-40°. A further two recrystallisations produced pale golden plate-like crystals in 20% yield, m.p. 40-41°C.

It is important to realise that the product reacts with the atmosphere and all operations in the open were carried out under a blanket of nitrogen.

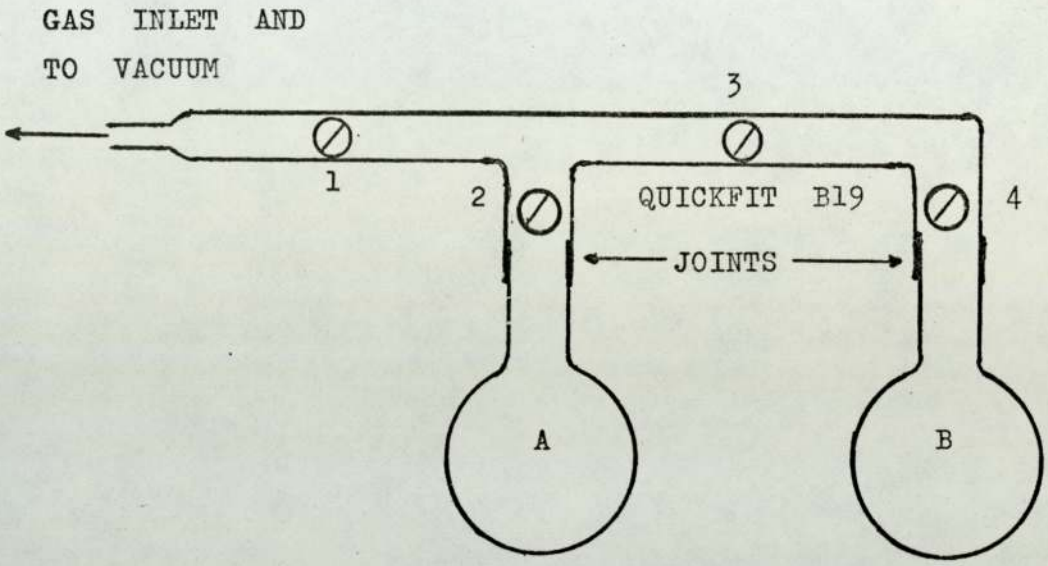
Anal.

Calcd. for $C_8H_6AsCl_3$:	C 33.89%	H 2.13%	Cl 37.58%
Found:	C 33.84%	H 2.10%	Cl 37.47%

See Table 3 page 36 for I.R. data, Table 12 page 45 for N.M.R. data.

A modification of the apparatus has improved the yield of the product and this is based on the principle of recycling the unreacted materials within an inert atmosphere. The apparatus is

shown in the following diagram.



⊘ = QUICKFIT HIGH VAC TAPS

The reactants were introduced into flask A and the apparatus flushed with nitrogen. A guard tube was connected to the gas inlet, tap 3 was closed and the reactants heated to 90° for two hours.

After cooling to room temperature, tap 1 was closed and the reactants cooled in liquid nitrogen for half an hour, tap 3 reopened and the pressure reduced to 1-2mm for fifteen minutes.

Tap 1 was closed, flask B cooled with liquid nitrogen and flask A was gently warmed to 50-60°C. to permit the unreacted phenylacetylene and arsenic trichloride to distill into flask B.

To assist in the rapid removal of the volatiles, it was found necessary to heat the exposed glass tubing between the flasks.

Within thirty minutes distillation was complete and the apparatus was filled with a nitrogen atmosphere.

Taps 3 and 4 were closed and flask A containing the crude product cooled to room temperature and removed from the apparatus.

The whole procedure was repeated again and this time more product collected in flask B.

After only one such 'transference of reactants', a 50% yield was obtained after two recrystallisations using petroleum ether, (b.p. 40-60°).

1B (ii)
p-Chlorophenylacetylene

p-Chlorophenylacetylene, (1.0g,0.0073mole), and arsenic trichloride, (1.99g,0.011mole), were placed in a 20ml. flask fitted with reflux condenser, guard tube and inert gas by-pass tube.

The apparatus was thoroughly flushed with nitrogen and then gently heated to 130-135° for six hours on an oil bath.

The dark brown liquid solidified on cooling to room temperature and an infrared spectrum of this mixture showed no triple bond absorption.

The excess arsenic trichloride was removed under reduced pressure and the tarry residue treated with dry petroleum ether, (b.p. 40-60°).

Using the freezing technique previously described, pale yellow crystals were obtained from the tarry residue. The hygroscopic crystals were vacuum dried and stored over nitrogen.

A 43% yield was obtained, m.p. 45-46°.

Anal.

Calcd. for $C_8H_5AsCl_4$:	C 30.20%	H 1.57%	Cl 44.67%
Found:	C 30.12%	H 1.52%	Cl 44.50%

See Table 4 page 37 for I.R. data, Table 13 page 46 for N.M.R. data.

1B (iii)
p-Nitrophenylacetylene

p-Nitrophenylacetylene, (1.0g,0.0068mole), and arsenic trichloride, (1.85g,0.0102mole), were placed in a 10ml. flask fitted with a reflux condenser, guard tube containing fused calcium chloride and inert gas by-pass tube.

The reactants were heated to 135-140° for six hours on an oil bath and the infrared spectrum of the reaction mixture, a black liquid, still showed a strong triple bond absorption.

The mixture was then heated for another hour by which time a black solid was produced and the flask was cooled to room temperature.

The excess arsenic trichloride was removed under reduced pressure and the residue treated with dry petroleum ether, (b.p. 40-60°).

No crystalline material could be extracted from this black solid, even using boiling petroleum ether.

The black solid was insoluble in hydrocarbon solvents and carbon tetrachloride and only slightly soluble in acetone.

Its infrared spectrum remained unchanged after exposing the solid to the atmosphere for thirty-six hours, and the material did not melt below 350°.

A single absorption band at 1015cm^{-1} suggests the material to be polymeric in nature. The following infrared absorptions due to the aromatic structure are also present, 3070cm^{-1} (C-H), 1600, 1580 and 1500cm^{-1} (C=C).

See Table 5 page 38 for I.R. data, Table 14 page 47 for N.M.R. data.

1B (iv)
p-Methylphenylacetylene

p-Methylphenylacetylene, (2.32g,0.02mole), and arsenic trichloride, (4.36g,0.024mole), were placed in a 20ml. flask fitted with a reflux condenser, guard tube containing fused calcium chloride and inert gas by-pass tube.

The reactants were heated on an oil bath at 60-65° for seven hours and then cooled to room temperature in an atmosphere of nitrogen.

The excess arsenic trichloride was removed under reduced pressure and the residue allowed to solidify.

The golden crystalline material was recrystallised twice from dry petroleum ether, (b.p. 40-60°), vacuum dried and then stored under nitrogen.

A 40% yield was obtained, m.p. 66-67°.

Anal.

Calcd. for $C_9H_8AsCl_3$:	C 36.38%	H 2.70%	Cl 35.91%
Found:	C 36.50%	H 2.50%	Cl 35.70%

See Table 6 page 39 for I.R. data, Table 15 page 48 for N.M.R. data.

1B (v)
p-Methoxyphenylacetylene

p-Methoxyphenylacetylene, (1.32g,0.01mole), and 10ml. dry cyclohexane were contained in a 25ml. flask fitted with a reflux condenser, guard tube containing fused calcium chloride and inert gas by-pass tube.

Arsenic trichloride, (2.72g,0.015mole), in 5ml. dry cyclohexane was gradually added over a period of ten minutes whilst the reactants were kept stirred at about 28°C. in a constant temperature bath.

After five hours all the acetylene had reacted as shown

by the absence of the -C≡C- and ≡C-H bond absorptions in an infrared spectrum taken on the reaction mixture.

The cyclohexane and excess arsenic trichloride were removed under reduced pressure and the dark brown residue cooled to room temperature.

As the viscous dark brown liquid did not solidify, it was treated with dry petroleum ether, (b.p. 40-60°), and the extract cooled to -20° in a acetone/CO_2 mixture. No crystals were isolated and rotary evaporation of the ether showed that very little material had been extracted from the viscous dark brown liquid.

The 'adduct' appeared to decompose when distilled under reduced pressure and as expected, reacted rapidly with the atmosphere.

Because of its reactivity, it was felt that the diphenyl derivative formed with phenylmagnesium bromide would be more stable and hence a better material to isolate and characterise than the dichloroarsine adduct. However, spectral data suggested that the adduct had been produced and that p-methoxy-phenylacetylene reacts very rapidly (exothermically) with arsenic trichloride at much lower temperatures than the other para-substituted acetylenes.

See Table 7 page 40 for I.R. data, Table 16 page 49 for N.M.R. data.

1B (vi)

Phenylpropiolic acid

Phenylpropiolic acid, (2.0g, 0.014mole), and arsenic trichloride, (3.8g, 0.021mole), were contained in a 10ml. flask fitted with a reflux condenser, guard tube containing fused

calcium chloride and inert gas by-pass tube.

The reactants were heated on an oil bath at 120-125° for fifteen hours and the mixture was cooled to room temperature and allowed to solidify after the excess arsenic trichloride had been removed under reduced pressure.

Dry ether, 10mls., was used to wash the product and the white powder was rapidly filtered, washed several times with dry ether, vacuum dried and stored under nitrogen.

N.B. An infrared spectrum of the washings showed the presence of small amounts of unreacted phenylpropiolic acid.

Attempted recrystallisations from cold and hot hydrocarbon and chlorinated solvents failed to achieve satisfactory results as the material was insoluble. However, it was fairly soluble in acetone and even using mixed solvents, recrystallisation was found to be unsatisfactory.

Distillation or sublimation under reduced pressure appeared to change the nature of the material, as indicated by its infrared spectrum which originally showed the solid to probably be a cyclic anhydride.

Purification by column chromatography using alkaline and neutral aluminium oxide and/or silica gel was also unsuccessful.

Repeated washings with a acetone/petroleum (1:3 vols.) mixture produced a white crystalline solid which had a constant melting point and infrared spectrum and it was this material that was chemically and instrumentally characterised, (m.p. 228-230°).

See Table 8 page 41 for I.R. data, Table 20 page 53 for Mass Spectral data.

1B (vii)

Methyl phenylpropiolate

Methyl phenylpropiolate, (3.2g, 0.02mole), and arsenic trichloride, (5.42g, 0.03mole), were contained in a 20ml. flask fitted with reflux condenser, guard tube containing fused calcium chloride and inert gas by-pass tube.

The reactants were gently brought to reflux for seven hours and then cooled in an inert atmosphere of nitrogen.

The triple bond absorption was absent when a sample of the reaction mixture was analysed by infrared spectroscopy.

The dark brown paste was washed with dry petroleum ether, (b.p. 40-60°), filtered and vacuum dried.

The pale yellow powder appeared to be stable in the atmosphere and it was recrystallised from hot benzene, (m.p. 272-274°).

Further recrystallisations did not improve its melting temperature or alter its infrared spectrum.

See Table 10 page 43 for I.R. data, Table 22 page 58 for Mass Spectral data.

SECTION 1C
GENERAL METHOD OF PREPARATION OF THE β-CHLOROSTYRYLDIPHENYLARSINES

An ethereal solution of the dichloroarsine was treated with an excess of phenylmagnesium bromide in an atmosphere of nitrogen.

All the usual precautions were taken to exclude the atmosphere from coming into contact with the reactants and adequate stirring (magnetic) was essential to ensure maximum dispersion of the mixture.

The reaction was terminated with moist ether, acidified with dilute acid, filtered and water washed.

The ether extract was dried with anhydrous magnesium sulphate and rotary evaporated to leave the diphenyl derivative.

The product was readily recrystallised from methanol, ethanol or aqueous mixtures of alcohols.

A typical example of the synthesis of β-chlorostyryldiphenyl arsine was carried out as follows:-

Pure dry magnesium ribbon, (0.48g), was treated with dry bromobenzene, (2.4g,0.153mole), in dry diethyl ether, 40mls. The reaction was catalysed with a trace of iodine and allowed to stand at room temperature for twenty-four hours after the complete addition of the bromide.

Pure dry β-chlorostyryldichloroarsine, (1.88g,0.0515mole), in 20mls. dry diethyl ether was added dropwise over a period of ten minutes with continuous stirring of the reaction mixture. The rate of addition was such that the ether only just refluxed. Sometimes cooling was necessary to avoid overheating. When the addition was completed, the reaction mixture was stirred for a further hour at room temperature and the excess Grignard Reagent destroyed with moist ether. Dilute hydrochloric acid was added and the etheral layer was separated, water washed and dried with anhydrous

magnesium sulphate. Removal of the ether by rotary evaporation left a pale yellow paste which on recrystallisation from methanol gave a 57% yield of β-chlorostyryldiphenylarsine, (m.p. 97-8°).

Yields between 50-60% were obtained in all cases where such a derivative could be prepared and recrystallised from methanol.

Table 1 lists the melting points of some of the derivatives prepared.

See Tables 3-7 pages 36-40 for I.R. data, Tables 12-16 pages 45-49 for N.M.R. data.

SECTION 1D

GENERAL METHOD OF PREPARATION OF THE CIS-(β-STYRYL)DIPHENYLARSINES

The method adopted was a modified version of Johnson[29] who studied the reduction of alkyl halides by lithium aluminium hydride.

A mixture of lithium aluminium hydride, (0.87 mole), lithium hydride, (1.56mole), was treated with the β-chlorodiphenyl compound, (1.0mole), in dry tetrahydrofuran in an atmosphere of inert gas.

The mixture was magnetically stirred for seventeen hours at 45-50°, treated with moist ether, washed with dilute acid and extracted with diethyl ether.

The product was readily recrystallised from methanol and in most cases 65-70% yields were obtained.

A typical example for the synthesis of a cis-(β-styryl)-diphenylarsine was as follows:-

Lithium hydride, (0.17g 0.0214mole), and lithium aluminium hydride, (0.45g 0.87mole), were contained in a 100ml. flask fitted with a reflux condenser, guard tube containing fused calcium chloride and side arm for a dropping funnel.

β-chlorostyryldiphenylarsine, (5.0g,0.137mole), in 50mls. dry tetrahydrofuran (distilled from calcium hydride) was added dropwise to the stirred mixture over a period of ten minutes and then the flask was gently heated on an oil bath at 45-50° for about seventeen hours.

The mixture, red in colour, was cooled to room temperature in an inert atmosphere of nitrogen and then water was added cautiously with stirring, keeping the temperature below 20°.

The mixture was concentrated by removing the tetrahydrofuran under reduced pressure and then the residue was treated with

about 20ml. ether.

The ethereal layer was washed with dilute sulphuric acid, then with water until neutral and finally dried with anhydrous magnesium sulphate.

Removal of the ether by rotary evaporation left a pale yellow paste which was readily recrystallised from methanol to give a 70% yield of a white crystalline solid, m.p. 90-91°.

Yields between 60-70% were obtained in all cases where such a derivative could be prepared and recrystallised from methanol.

Table 1 lists the melting points of the cis-(β-styryl)-diphenylarsines prepared by the above method.

Table 2 summarises the elemental analytical data and Tables 3-7 pages 36-40 for I.R. data, Tables 12-16 pages 45-49 for N.M.R. data.

TABLE 1

Melting Points

Alkyne	β-chlorostyryldichloroarsine	β-chlorostyryldiphenylarsine	cis-(β-styryl)diphenylarsine
$C_6H_5-C\equiv CH$	40-1°	97-8°	90-1° (d)
$p-Cl-C_6H_4C\equiv CH$	45-6°	72-3°	75-6°
$p-CH_3-C_6H_4C\equiv CH$	66-7°	79-80°	76-7°
$p-CH_3O-C_6H_4C\equiv CH$	Too unstable to isolate	B.p. 145-150/0.3m.m. Slight decomposition.	The viscous yellow liquid product decomposed when vacuum distilled.
$p-NO_2-C_6H_4C\equiv CH$	350° (a)	-	-
$C_6H_5-C\equiv C-COOH$	228-30° (b)	-	-
$C_6H_5-C\equiv C-COOCH_3$	272-4° (c)	-	-

(a) The adduct was polymeric. See discussion on Page 94.

(b) The adduct was probably a cyclic anhydride. See discussion on Page 95.

(c) The adduct was probably a lactone. See discussion on Page 99.

(d) Trans-(β-styryl)diphenylarsine has a melting point of 194-5°C when recrystallised from carbon tetrachloride.

TABLE 2

Analytical Data

Alkyne	β-chlorostyryldichloroarsine		β-chlorostyryldiphenylarsine		cis-(β-styryl)diphenylarsine	
	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)
$C_6H_5C\equiv CH$	C 33.89 H 2.13 Cl 37.58	C 33.84 H 2.10 Cl 37.47	C 65.49 H 4.37 Cl 9.69	C 65.38 H 4.20 Cl 9.45	C 72.31 H 5.12 Cl -	C 72.45 H 5.20 Cl -
$p\text{-}ClC_6H_4C\equiv CH$	C 30.20 H 1.57 Cl 44.67	C 30.12 H 1.52 Cl 44.50	C 59.85 H 3.74 Cl 17.71	C 59.70 H 3.61 Cl 17.50	C 71.36 H 4.76 Cl 10.55	C 71.20 H 4.68 Cl 10.59
$p\text{-}CH_3C_6H_4C\equiv CH$	C 36.38 H 2.70 Cl 35.71	C 36.50 H 2.50 Cl 35.70	C 66.24 H 4.73 Cl 9.33	C 66.30 H 5.0 Cl 9.30	C 72.86 H 5.49 Cl -	C 72.50 H 5.74 Cl -
$p\text{-}CH_3OC_6H_4C\equiv CH$	Too unstable to isolate		C 63.57 H 4.54 Cl 8.96	C 66.84 H 4.76 Cl 6.13	C 69.63 H 5.25 Cl -	C 68.98 H 4.79 Cl -

Cont....

T A B L E 2 (Continued)

Analytical Data

Alkyne	β-chlorostyryldichloroarsine		β-chlorostyryldiphenylarsine		cis-(β-styryl)diphenylarsine	
	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)
$p\text{-}NO_2C_6H_4C{\equiv}CH$	—	C 40.15 H 2.49 N 6.02 (a) Cl 19.04	-	-	-	-
$C_6H_5C{\equiv}C\text{-}COOH$	C 55.59 H 2.87 Cl 19.10	C 56.65 H 2.41 (b) Cl 19.52	-	-	-	-
$C_6H_5C{\equiv}C\text{-}COOCH_3$	C 54.40 H 3.63 Cl 16.10	C 54.24 H 2.77 (c) Cl 8.12	-	-	-	-

(a), (b), (c). See Table 1 for references.

SECTION 1E

GENERAL METHOD OF HYDROLYSIS OF THE REACTION PRODUCT FROM THE REACTION OF (i) PHENYLPROPIOLIC ACID AND (ii) METHYL PHENYL-PROPIOLATE WITH ARSENIC TRICHLORIDE

About 0.5g of the suspected (i) anhydride or (ii) lactone was dissolved in excess 4N sodium hydroxide by gently warming and then the solution, about 25mls, was refluxed for twenty-four hours.

The reaction mixture was cooled in ice water and then acidified with 8N hydrochloric acid to about pH4 using universal indicator paper.

The solid material was filtered off, washed several times with water until neutral, recrystallised from hot water and then vacuum dried.

The melting point of the acid derived from the suspected anhydride was 255-7° and that from the suspected lactone, 252-4°. The infrared data for the hydrolysed anhydride is shown in Table 9 page 42 and for the hydrolysed lactone in Table 11 page 44.

Anal.

Acid derived from the suspected anhydride.

Calcd. for $C_{26}H_{18}O_4AsCl_3$:	C 54.23%	H 3.13%	Cl 18.50%
Found:	C 52.98%	H 3.01%	Cl 16.79%

Acid derived from the suspected lactone.

Calcd. for $C_{29}H_{24}O_7AsCl_3$:	C 52.30%	H 3.62%	Cl 16.01%
Found:	C 57.94%	H 3.67%	Cl 14.14%

SECTION 1F
ISOMERISATION OF CIS-(β-STYRYL)DIPHENYLARSINE

The following methods of isomerisation were carried out according to the method of Aguiar.[30]

(i) n-Butyl-lithium

A solution of cis-(β-styryl)diphenylarsine, (0.5g 0.0015mole), in 25mls. of dry tetrahydrofuran was treated with 30ml. of 10% (w/v) solution of n-butyl-lithium in hexane and refluxed for three hours.

The mixture was allowed to stand under argon for twenty-four hours and analysed by nuclear magnetic resonance spectroscopy. There was no trans isomer present. (J = 18cps)
trans

(ii) Phosphorus Trichloride

When the cis-(β-styryl)diphenylarsine, (0.5g 0.0015mole), was refluxed for about two hours with phosphorus trichloride, (2g 0.015mole), in 200ml. dry tetrahydrofuran no isomerisation occurred as shown by nuclear magnetic resonance spectroscopy.

(iii) Phosphorus Pentachloride

A solution of cis-(β-styryl)diphenylarsine, (0.5g 0.0015mole), in 20mls. dry tetrahydrofuran was treated with phosphorus pentachloride, (0.1g 0.00056mole), and then refluxed for two hours.

The 100MHz nuclear magnetic resonance spectrum showed an aromatic complex at $\tau(CDCl_3)$ 2.5 and one half of the proton signals at $\tau(CDCl_3)$ 3.1, J = 17cps, due to the trans-β-styryl diphenylarsine isomer.

See Table 1 (d) page 30 and Table 12 page 45 gives the N.M.R. data for the cis-compound.

SECTION 1G
THE EFFECT OF INFRARED RADIATION ON
β-CHLORO(p-CHLOROSTYRYL)-DICHLOROARSINE IN ARSENIC TRICHLORIDE

A reaction mixture consisting of β-chloro(p-chlorostyryl)-dichloroarsine , (1.59g 1.0mole), and arsenic trichloride, (0.91g 1.0mole), was carefully transferred by syringe to the reaction cell at 110°C. and exposed to the infrared radiation at 2100cm^{-1}, by placing it in the sample beam of the instrument.

The spectrometer settings were the same as those used for the kinetic experiments and after two hours exposure at this temperature and frequency, no carbon-carbon triple bond was observed although the reaction mixture had turned dark brown in colour.

Similar experiments were carried out using solutions of β-chlorostyryldichloroarsine and β-chloro-(p-methylstyryl)-dichloroarsine in arsenic trichloride at 100°and 80° respectively and in both cases, no carbon-carbon triple bond absorption was observed, indicating that the reaction of the arylacetylenes with arsenic trichloride is not reversible under the influence of infrared radiation.

SECTION 1H

EXAMINATION OF THE REACTION PRODUCTS BY THIN LAYER CHROMATOGRAPHY

The β-chlorostyryldichloroarsines, β-chlorostyryldiphenylarsines and β-(cis-styryl)diphenylarsines isolated were dissolved in dry carbon tetrachloride to give 5%(w/v) solutions and commercially available Camlab Cambridge 20cm x 3cm Polygrams, SIL.G, (0.25mm SILICA GEL) were used as the chromatography plates.

The solvents employed were chloroform, carbon tetrachloride, benzene and mixtures of diethyl ether - petroleum ether (b.p. 40-60°), 50:50(v/v) and benzene - methanol, 90:10(v/v) and the spots on the chromatograms rendered visible with iodine vapour.

All the products examined, except the adducts of arsenic trichloride with p-methoxyphenylacetylene, p-nitrophenylacetylene, phenylpropiolic acid and methyl phenylpropiolate, gave single spots indicating pure materials and the absence of any isomers, in agreement with the sharp melting points, Table 1, page 30, and nuclear magnetic resonance data, Tables 12-16, pages 45-49.

TABLE 3

INFRARED DATA

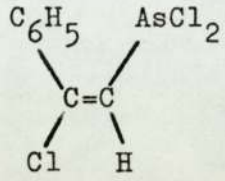
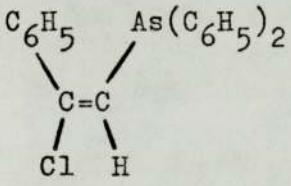
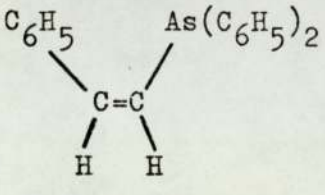
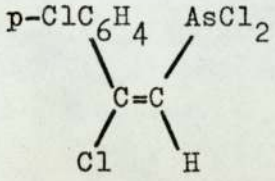
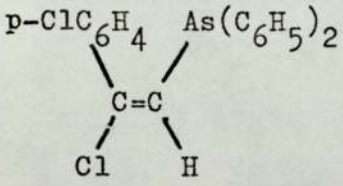
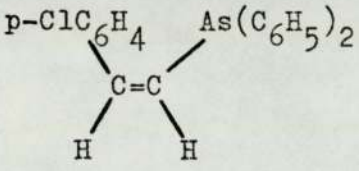
COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
	3030-3040	Aromatic C-H and alkene C-H stretching vibrations.
	1600, 1585, 1490, 1447.	Aromatic C=C skeletal vibrations.
β-chlorostyryl-dichloroarsine (KBr disc)	1562	Probably C=C of trisubstituted alkene. It is possible that the expected double bond stretching frequency at 1600-1700cm^{-1} has been lowered due to the degree of conjugation.
	890cm^{-1}	Carbon-chlorine stretching frequency probably due to >C=C< structure. Cl
	3030-3040	Aromatic C-H and alkene C-H stretching vibrations.
	1600-1445	Aromatic C=C skeletal vibrations.
β-chlorostyryl-diphenylarsine (KBr disc)	1560	Probably due to the >C=C< structure of the alkene .
	890	Probably C-Cl of >C=C< Cl
	3030-3055	Aromatic CH and alkene CH stretching vibrations.
	1600-1445	Aromatic skeletal vibrations.
cis-β-styryldiphenyl-arsine (KBr disc)	1562	Probably >C=C< of alkene. Note The absorption at 890cm^{-1} was absent - the band assigned to the >C=C< structure. Cl

TABLE 4

INFRARED DATA

COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
	1590, 1575	Aromatic C=C skeletal vibrations.
	1559	Probably alkene C=C. Lowered frequency due to conjugation.
	890	Probably carbon-chlorine absorption due to >C=C< structure. (Cl)
β-chloro-p-chloro-styryldichloroarsine		
(Mineral Oil Mull)	830	Aromatic C-Cl absorption.
	3030	Aromatic C-H.
	1590, 1480	Aromatic C=C skeletal vibrations.
	1560	Probably alkene >C=C<
β-chloro-p-chloro-diphenylarsine	890	Probably carbon-chlorine of >C=C< group. (Cl)
(KBr disc)	830	Aromatic C-Cl.
		The absorption bands were not well defined probably due to an imperfect disc.
	1480, 1580	Aromatic C=C.
β-(cis-p-chlorostyryl) diphenylarsine		The expected 1560cm^{-1} probably due to C=C of the alkene was not clearly visible but the 890cm^{-1}, was definitely absent - the band assigned to the >C=C< (Cl) structure.
(KBr disc)		

T A B L E 5

INFRARED DATA

COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
Probably a polymeric material from the reaction of p-nitrophenylacetylene and arsenic trichloride. M.p.> 350°	3030	Aromatic CH.
	1600, 1580, 1505, 1455.	Aromatic C=C skeletal vibrations.
	1515, 1345.	Aromatic C-NO_2.
(KBr disc)	1015	Probably the absorption due to the polymeric material of a trans-configuration.[32]

TABLE 6

INFRARED DATA

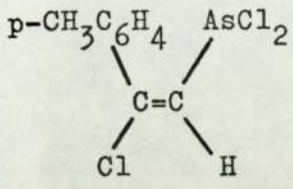
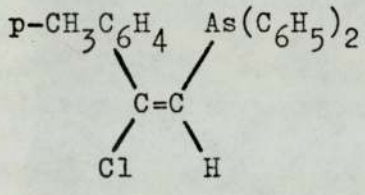
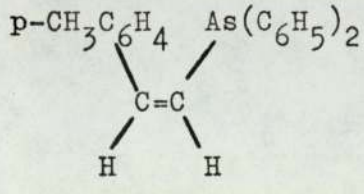
COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
	3035	Aromatic CH.
	2920	Aliphatic CH.
	1380 (sym)	$C-CH_3$ Methyl attached to an aromatic carbon atom.
β-chloro-p-methyl-styryldichloroarsine	1608, 1575, 1500, 1450.	Aromatic C=C skeletal vibrations.
(KBr disc)	1555	Probably alkene C=C, lower frequency due to conjugation.
	890	Probably C-Cl of >C=C< (Cl) structure.
	3035	Aromatic CH.
	2920	Aliphatic CH.
	1595, 1505, 1580, 1433.	Aromatic C=C skeletal vibrations.
β-chloro-p-methyl-styryldiphenylarsine	1568	Probably alkene C=C.
(KBr disc)	889	Probably C-Cl of >C=C< (Cl) structure.
	3030	Aromatic CH.
	3050	Alkene CH.
	2980	Aliphatic CH.
β-(cis-p-methylstyryl) diphenylarsine	1590, 1510, 1438.	Aromatic C=C skeletal vibrations.
(KBr disc)		Note: The 890cm^{-1} band, probably due to C-Cl was absent.

TABLE 7

INFRARED DATA

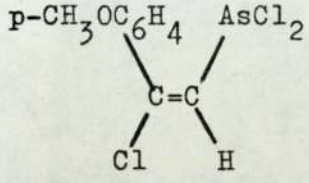
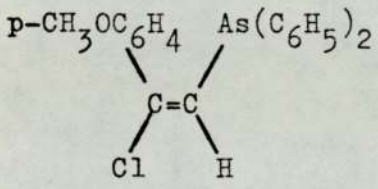
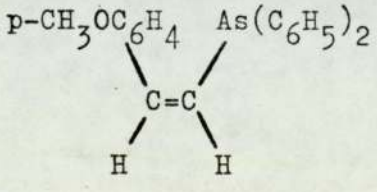
COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
 β-chloro-p-methoxystyryldichloroarsine (Thin film)	1605, 1580, 1503, 1440.	Aromatic C=C skeletal vibrations.
	2960	Aliphatic CH.
	3030	Aromatic CH.
	1310, 1255, 1230.	Ether-type vibrations, C-O-C.
	1552	Probably C=C
	894	Probably C-Cl of the >C=C< / Cl structure.
 β-chloro-p-methoxystyryldiphenylarsine (Thin film)	1608, 1583, 1505, 1438.	Aromatic C=C skeletal vibrations.
	3035	Aromatic CH.
	2960	Aliphatic CH.
	1300, 1255, 1230.	Ether-type vibrations, C-O-C.
	1565	Probably C=C
	891	Probably C-Cl of the >C=C< / Cl structure.
 β-(cis-p-methoxystyryl) diphenylarsine (Thin film)	3070-3050 2960.	Aromatic and alkene CH and Aliphatic CH respectively.
	1605, 1580, 1508, 1433.	Aromatic skeletal C=C vibrations.
	1300, 1258.	Ether-type vibrations, C-O-C.
		Note: The 890cm^{-1} band, probably due to C-Cl was absent.

TABLE 8

INFRARED DATA

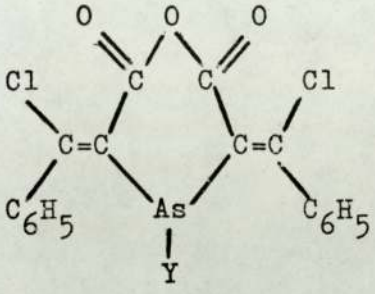
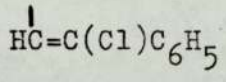
COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
Possibly a cyclic anhydride with the structure:-  where Y is probably  (KBr disc)	3048	Aromatic C-H stretching vibrations.
	2930 2830	Region of C-H vibrations due to aliphatic groups - cannot be accounted for on the basis of proposed structure since no such groups are present in the starting materials i.e. $C_6H_5C{\equiv}C.COOH$ and $AsCl_3$
	1704	Difficult to assign with certainty - could be due to C=C.
	1837 and 1769	Anhydride, cyclic, the $1769cm^{-1}$ band more intense. Could be conjugated or unconjugated, as in both cases the band separation is about $60cm^{-1}$ with the lower frequency band the more intense.[33]
	1610	Probably alkene C=C.
	1597, 1580, 1499, 1444.	Aromatic C=C skeletal vibration region.
	1518	Unidentifiable.
	1368	Unidentifiable.
	1238, 1213, 1174, 951, 905.	Probably stretching vibrations. from C-C-O-C-C structure of a cyclic anhydride.
	886	Probably C-Cl obsorption of >C=C< structure. Cl
	450-800	Bands in this region were not of great diagnostic value.

TABLE 9

INFRARED DATA

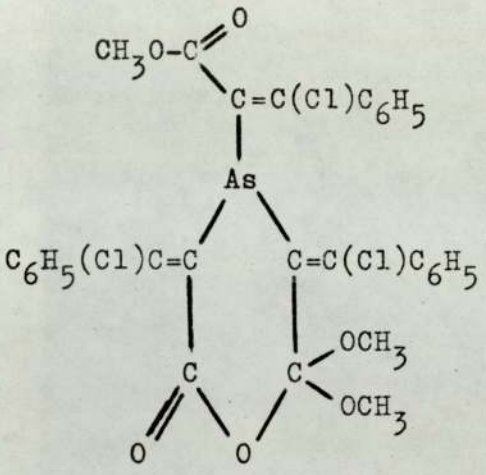
Base hydrolysed reaction product* between phenylpropiolic acid and arsenic trichloride. The acidified material was recrystallised from hot water.

COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
See Discussion on page 97.	3500, 2920.	Broad absorption bands due to -OH of carboxylic acid.
	3050	Aromatic C-H stretching vibration.
	2600	Broad absorption band due to OH of carboxylic acid (bonded). The wide range of the OH absorptions is due to intermolecular hydrogen bonding between carboxyl groups.
	1835, 1770.	Anhydride, cyclic, the 1770cm^{-1} band more intense. The formation of the anhydride probably occurred during recrystallisation of the acid.
	1700	Carboxyl absorption of a carboxylic acid.
	1610, 1590.	Aromatic C=C skeletal vibrations.
	1450	Aromatic C=C skeletal vibration or C-O vibration coupled with OH. This band is broader than the corresponding absorption of the suspected anhydride where C-O and OH interactions are not possible.[34b]
	1300, 1200.	Absorptions probably due to carboxyl and hydroxyl interactions.
	900	Probably C-Cl absorption of >C=C< structure. Cl

* The material was too insoluble for an N.M.R. integrated spectrum to be obtained.

T A B L E 10

INFRARED DATA

COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
Possibly a lactone with the following structure:- 	3035	Aromatic CH vibrations.
	2953	Aliphatic CH vibrations.
	1749	Probably the C=O of a six membered ring lactone.[34a,b]
	1705	Probably the ester C=O in conjugation with carbon-carbon double bond.
	1615	Probably alkene C=C in a conjugated system.
	1575, 1505, 1448.	Aromatic C=C skeletal vibration region.
	1300-1000	Nine strong absorptions in this region probably due to the C-O-C stretching mode of esters, ethers and lactones. Difficult to assign to be of diagnostic value.
	860	Probably C-Cl absorption of $>C=C<$ (Cl) structure.
	700-400	Region of little diagnostic value.

T A B L E 11

INFRARED DATA

Base hydrolysed reaction product* between methyl phenylpropiolate and arsenic trichloride. The acidified material was recrystallised from hot water.

COMPOUND	FREQUENCY (cm^{-1})	FUNCTIONAL GROUP AND COMMENTS
See Discussion on page 101, Structure F.	3600-2600	OH stretching vibrations (free) of alcohols and carboxylic acids - broad absorption bands.
	2550-2650	OH stretching vibrations (bonded) of carboxylic acid - weak broad absorption bands.
	3060	Aromatic C-H vibrations.
	1700	C=O vibrations of carboxylic acid probably aryl. Strong broad absorption.
	1600, 1580.	Aromatic C=C skeletal vibrations.
	1450	Could be due to C=C skeletal vibrations of aromatic rings, although the absorptions in the 1600cm^{-1}, 1500cm^{-1}, and 1580cm^{-1} region were not clearly visible, or possibly the vibration due to interaction of the carboxyl groups. This absorption is broader than the corresponding band of the suspected lactone.[34b]
	1300, 1260.	The higher frequency band is probably derived from the coupled C-O and O-H modes but the origin of the second band (1260) is less certain.
	855	Probably C-Cl absorption of >C=C< structure. Cl

* The material was too insoluble for an N.M.R. integrated spectrum to be obtained.

T A B L E 12

NUCLEAR MAGNETIC RESONANCE DATA

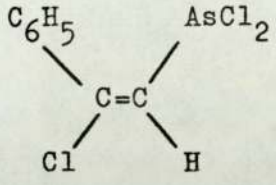
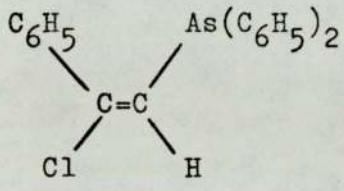
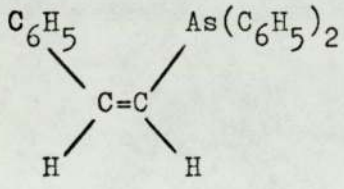
COMPOUND	$\tau(CCl_4)$	COMMENTS
 β-chlorostyryl-dichloroarsine	2.6(m)	Aromatic complex. The vinyl proton expected in τ =3-4 region has probably shifted downfield under the aromatic complex due to the deshielding effect of the $AsCl_2$ group.[31]
 β-chlorostyryl-diphenylarsine	2.5(m) 3.04(s)	Aromatic complex due to 15 protons. Vinyl proton, 1 proton, moved upfield because of the shielding effect of the aromatic nuclei on the arsenic atom.
 cis-β-styryl-diphenylarsine	2.6(m) 3.35(d)	Aromatic complex. One half of the proton signals, J = 12cps. The other half of this signal is hidden under the aromatic complex as indicated by the relative ratios of 16:1. See discussion on Page 106.

TABLE 13

NUCLEAR MAGNETIC RESONANCE DATA

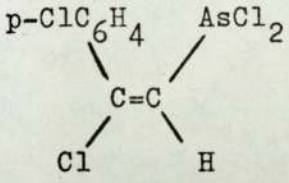
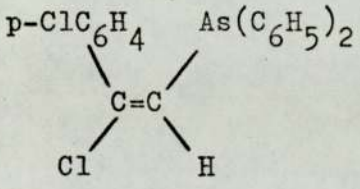
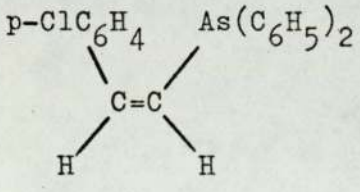
COMPOUND	$\tau(CCl_4)$	COMMENTS
 β-chloro-p-chloro-styryldichloroarsine	2.5(m)	Aromatic complex. Vinyl proton probably hidden under the aromatic complex due to the deshielding effect of the $AsCl_2$ group.
 β-chloro-p-chloro-styryldiphenylarsine	2.7(m) 3.1(s)	Aromatic complex corresponding to 14 protons, and the vinyl proton, now upfield due to the shielding effect of the aromatic nuclei on the arsenic atom.
 β(cis-p-chlorostyryl) diphenylarsine	2.9(m) 3.5(d)	Aromatic complex. One half of the proton signal, J = 12cps, and the other half hidden under the aromatic complex as indicated by the relative ratios of 15:1.

TABLE 14

NUCLEAR MAGNETIC RESONANCE DATA

COMPOUND	τ (acetone)	COMMENTS
Probably a polymeric material from the reaction of p-nitrophenylacetylene and arsenic trichloride. M.p. $> 350^{\circ}$	2.0(m) 4.9(s)	Aromatic complex. Probably due to C-H of a polymer. Solubility problems made it impossible to obtain a high resolution integrated spectrum.

TABLE 15

NUCLEAR MAGNETIC RESONANCE DATA

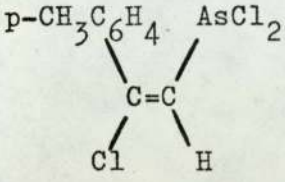
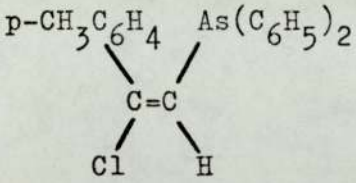
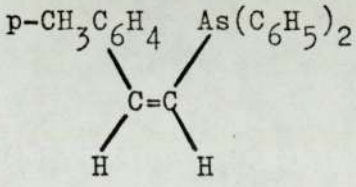
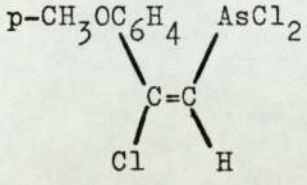
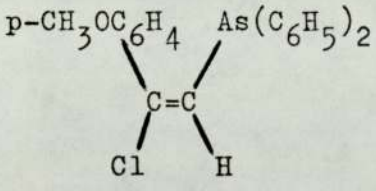
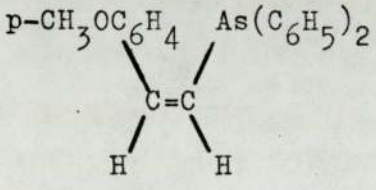
COMPOUND	$\tau(CCl_4)$	COMMENTS
 β-chloro-p-methyl styryldichloroarsine	2.43 and 2.80	Two doublets due to the aromatic protons, (4).
	2.68(s)	The vinyl proton (1) - singlet.
	7.6(s)	Methyl protons (3).
 β-chloro-p-methyl-styryldiphenylarsine	2.7(m)	Aromatic complex, 15 protons.
	3.16(s)	Vinyl proton (1).
	7.69(s)	Methyl protons (3).
 β-(cis-p-methylstyryl) diphenylarsine	2.75(m)	Aromatic complex.
	3.5(d)	One half of the proton signal, J = 10cps, the other half is hidden under the aromatic complex as indicated by the relative ratios of 15:1.
	7.7(s)	Methyl protons (3).

TABLE 16

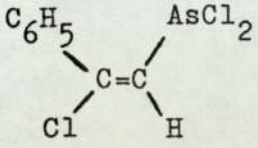
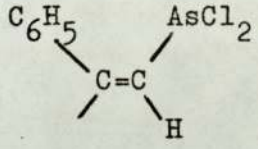
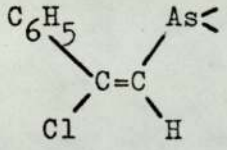
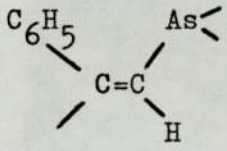
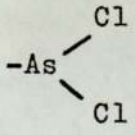
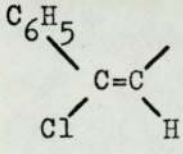
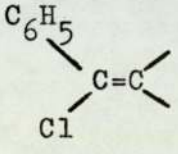
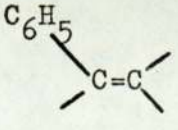
NUCLEAR MAGNETIC RESONANCE DATA

COMPOUND	$\tau(CCl_4)$	COMMENTS
 β-chloro-p-methoxy-styryldichloroarsine	2.4 and 3.15	Two aromatic doublets, 4 protons.
	2.75(s)	Vinyl proton (1).
	6.2(s)	Methyl protons (3).
		The spectrum was obtained on the reaction mixture because the adduct was too reactive to isolate.
 β-chloro-p-methoxy-styryldiphenylarsine	2.7(m)	Aromatic complex, 15 protons. (Theoretical value, (14), indicating some degree of impurity.)
	3.27(s)	Vinyl proton (1).
	6.38(s)	Methyl protons (3).
 β-(cis-p-methoxystyryl) diphenylarsine	2.75(m)	Aromatic complex.
	3.53(d)	One half of the proton signal, J = 10cps, the other half is hidden under the aromatic complex.
	6.4(s)	Methyl protons.
		The relative ratios of vinyl: aromatic: aliphatic protons of 1:16:2 indicate some degree of impurity of the material.
		Theoretical ratios: 1:15:3.

T A B L E 17

MASS SPECTRAL DATA

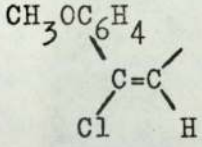
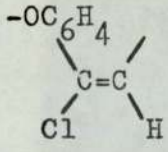
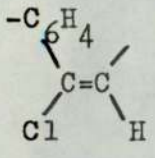
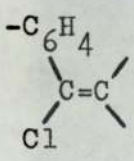
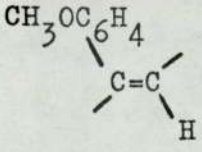
β-CHLOROSTYRYLDICHLOROARSINE

Fragment	Mass-to-charge ratio
	282
	247
	212
	177
	145
	137
	136
	101
C_6H_5-	77

T A B L E 18

MASS SPECTRAL DATA

β-CHLORO-(p-METHOXYSTYRYL)DIPHENYLARSINE

Fragment	Mass-to-charge ratio
$(C_6H_5)_2As-$	229
	167
	152
	136
	135
	132
$CH_3OC_6H_4-$	107
$-OC_6H_4-$	92

T A B L E 19

MASS SPECTRAL DATA

β-(CIS-p-METHOXYSTYRYL)DIPHENYLARSINE

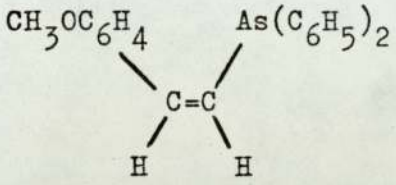
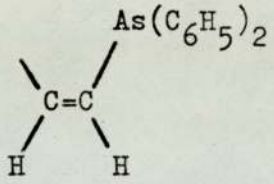
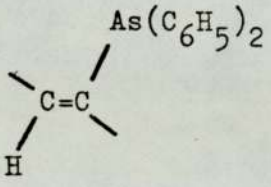
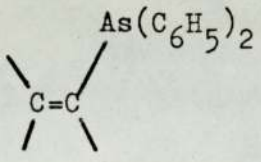
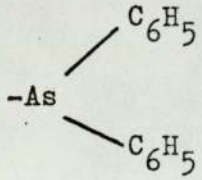
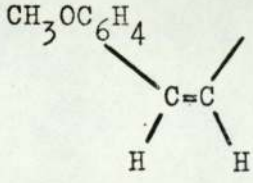
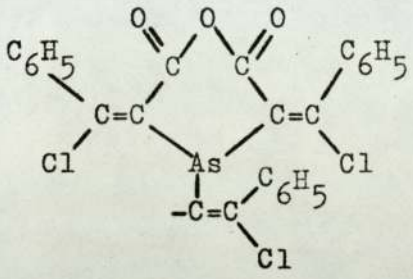
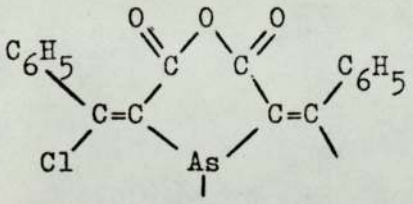
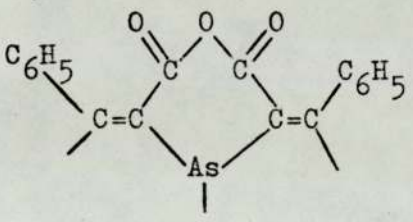
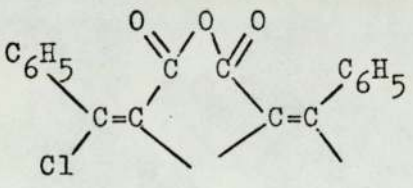
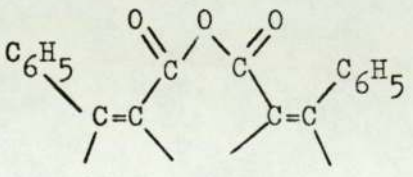
Fragment	Mass-to-charge ratio
	362
	255
	254
	253
	229
$-As-C_6H_5$	152
	133
C_6H_5-	77

TABLE 20

MASS SPECTRAL DATA

REACTION PRODUCT OF PHENYLPROPIOLIC ACID AND ARSENIC TRICHLORIDE

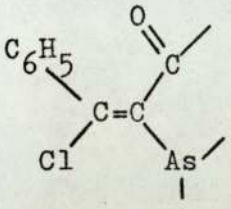
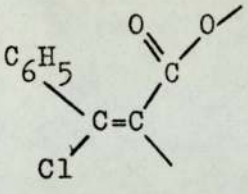
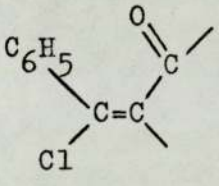
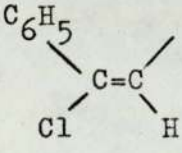
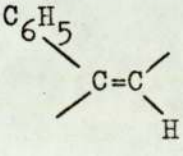
Fragment	Mass-to-charge ratio
	555
	384
	349
	309
	274

Cont...

TABLE 20

MASS SPECTRAL DATA

REACTION PRODUCT OF PHENYLPROPIOLIC ACID AND ARSENIC TRICHLORIDE

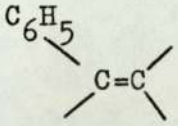
Fragment	Mass-to-charge ratio
	239
	175
	164
	137
	102

Cont...

T A B L E 20

MASS SPECTRAL DATA

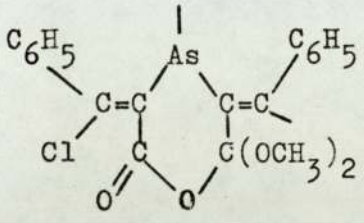
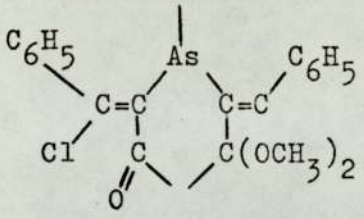
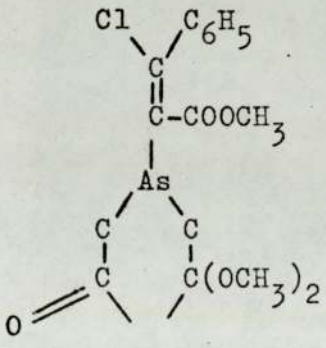
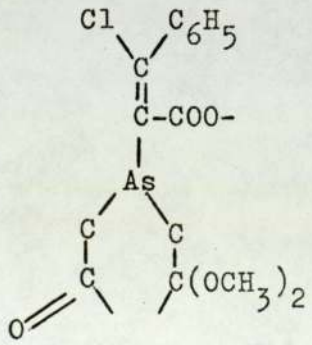
REACTION PRODUCT OF PHENYLPROPIOLIC ACID AND ARSENIC TRICHLORIDE

Fragment	Mass-to-charge ratio
	101
C_6H_5—	77
CO_2	44
CO	28

T A B L E 21

MASS SPECTRAL DATA

REACTION PRODUCT OF METHYL PHENYLPROPIOLATE AND ARSENIC TRICHLORIDE

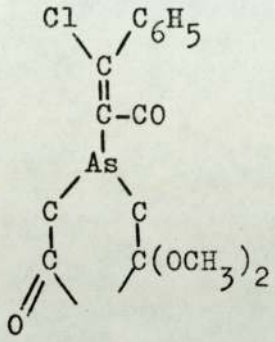
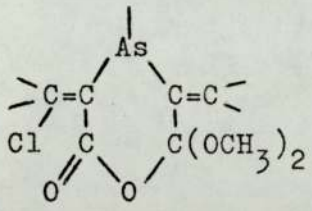
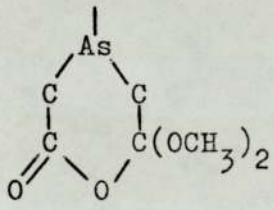
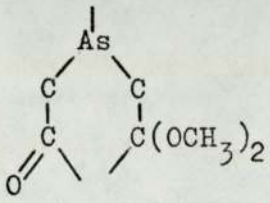
Fragment	Mass-to-charge ratio
	430
	414
	395
	381

Cont...

T A B L E 21

MASS SPECTRAL DATA

REACTION PRODUCT OF METHYL PHENYLPROPIOLATE AND ARSENIC TRICHLORIDE

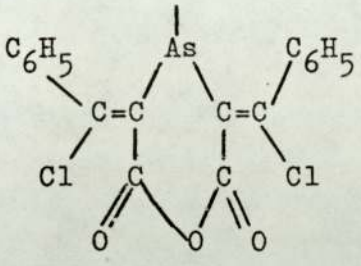
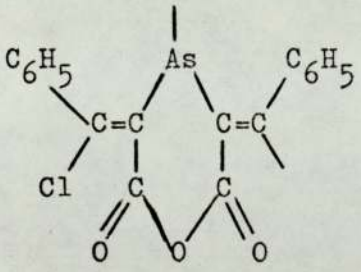
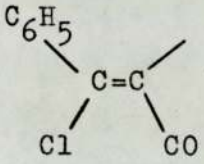
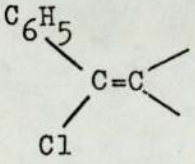
Fragment	Mass-to-charge ratio
	365
	276
	217
	201
C_6H_5—	77
CO_2	44
CH_3O—	31
CO	28

T A B L E 22

MASS SPECTRAL DATA

HYDROLYSED REACTION PRODUCT OF PHENYLPROPIOLIC ACID AND ARSENIC TRICHLORIDE

No molecular ion peak at 574 mass units.

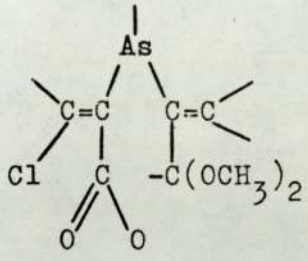
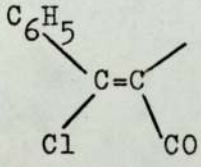
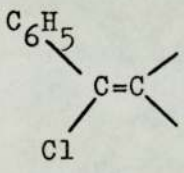
Fragment	Mass-to-charge ratio
	419
	384
	164
	136
C_6H_5	77
COOH	45
CO_2	44
CO	28
H_2O	18
OH	17

T A B L E 23

MASS SPECTRAL DATA

HYDROLYSED REACTION PRODUCT OF METHYL PHENYLPROPIOLATE AND ARSENIC TRICHLORIDE

No molecular ion peak at 664 mass units.

Fragment	Mass-to-charge ratio
	276
	164
	136
C_6H_5	77
$-\overset{\vert}{\underset{\vert}{C}}-(OCH_3)_2$	74
COOH	45
CO_2	44
$-\overset{\vert}{\underset{\vert}{C}}-O-CH_3$	43
$-O-CH_3$	31
CO	28
OH	17

CHAPTER 2
SECTION 2A
REACTION KINETICS

Experimental

The reaction rates were followed by measuring the decrease in peak height (absorbance) of the carbon-carbon triple bond at about 2100cm^{-1} of the infrared region.

The instrument used was a Perkin Elmer 457 Grating Spectrometer operating at the following settings:-

Slit width = 2

Speed = Slow at 10X

Gain = At a setting that gave a constant peak height at 909.1cm^{-1} (11.03μ) for a standard polystyrene film supplied by the manufacturers of the instrument.

Throughout the work, the reference beam contained only air and the baseline was altered by adjusting the reference beam attenuator. Logarithmic chart paper was used to measure the peak height (absorbance) and the instrument allowed to scan the 2200-1900cm^{-1} region after the spectrometer had been calibrated by comparing the spectrum of a standard polystyrene film with the calibration data in the manufacturers manual, (Perkin Elmer).

The reaction mixture was contained in a demountable Beckman RIIC.FH01 cell, fitted with an inlet and outlet port and a thermocouple orifice. The path length of the cell was varied by using various Teflon gaskets of known thickness and the gasket was secured between the sodium chloride windows by means of four screws. The cell thickness (path length) was measured by observing the interference fringes which resulted

when the spectrum of the empty cell was taken. This method of determining the path length of a cell is only possible if the cell windows are sufficiently flat, clean and parallel, because the infrared beam which is twice reflected inside the cell is retarded by twice the cell thickness relative to the unreflected beam. The thickness 'b' in centimetres may be calculated by:

$$2b = \frac{N}{V_1 - V_2}$$

where N is the number of fringes found between V_1 and V_2 (frequencies in cm^{-1})[34b] and an example of a calculation is shown on page 65. The cell was electrically heated and the heating controlled by an Isomantle Control (Type ERN/1), whilst the temperature of the cell was kept constant by means of a water jacket connected to an electrical water pump and monitored on a Bristol chart-recorder by using an Iron-Constantan thermocouple. The 'hot' junction was placed in the sodium chloride windows through a hole in the metal case of the cell and the 'cold' junction placed in ice, contained in a vacuum flask.

The thermocouple was calibrated by measuring the boiling points of a few common solvents such as acetone (Analar Grade - b.p. 56.5°C), benzene (Analar Grade - b.p. 80.1°C) and toluene (Analar Grade - b.p. 110.6°C) and comparing the values with those from tables in The Handbook of Chemistry and Physics.[35] The cell was maintained at the required reaction temperature for at least fifteen minutes before the reactants were transferred into the reaction chamber.

The phenylacetylenes were accurately weighed (ca. one gram) in a clean, dry, capped weighing bottle and then the corresponding

amount of arsenic trichloride added to give a 1:1 mole reaction mixture. The bottle was flushed with nitrogen, capped and weighed again. The reactants were thoroughly mixed by shaking the bottle and a portion withdrawn using a clean and dry hypodermic syringe and transferred into the reaction chamber of the cell in an atmosphere of nitrogen. The inlet port was sealed by a Teflon stopper and any excess reactants wiped clean from the outlet port before being sealed by a similar Teflon stopper.

Note It only required two to three drops of mixture to fill the reaction chamber and any air bubbles that were trapped had to be expelled by adding more reactants until the chamber was completely filled with liquid.

The cell was immediately secured in the clamp of the sample beam and the time clock and instrument started simultaneously. The whole operation from transferring the reactants into the cell until the first measurement of the C≡C absorption at 2100cm^{-1} was about one and a half minutes. The peak height (absorbance) of the carbon-carbon triple bond was measured at regular intervals and the measurements stopped when the value had decreased to at least one-half its initial value. The reaction cell was then allowed to cool to room temperature and washed several times with dry analar carbon tetrachloride, dried with warm dry nitrogen gas and immediately stored in a desiccator containing silica gel. From a plot of peak height (absorbance) and time, the rate of reaction was determined as shown on page 76.

Using the same cell and operating with the same instrument settings, the absorbance values of the reaction mixtures of

aryacetylene and arsenic trichloride (1:1 mole) were measured at room temperature so that absorbtivity (ϵ) values could be measured. An example of the calculation is shown on page 67. and the results tabulated on page 68 Table 24.

Note The rate of reaction at room temperature between the arylacetylenes and arsenic trichloride is so slow that it is reasonable to assume that no reaction occours within the short space of time the measurement is being made. The average absorbance value from three readings was calculated from the logarithmic chart paper and the results shown in Table 25 page 70.

Since p-methoxyphenylacetylene reacts rapidly with arsenic trichloride at room temperature, it was difficult to obtain any kinetic data for this reaction. Cooling the reaction cell below room temperature would have caused condensation on the cell windows and damage to the sodium chloride plates.

The temperature required to study the rate of reaction of p-nitrophenylacetylene with arsenic trichloride was too high (ca. 130-140°C) and as an insoluble polymeric material was produced, cleaning of the cell would have been difficult, apart from the fact that the cell windows had a tendency to crack at temperatures around 120-130°C. For similar reasons, the kinetics of addition of arsenic trichloride to phenylpropiolic acid and methyl phenylpropiolate were not studied.

2A (i)

Calculation of the concentration of Phenylacetylene in arsenic trichloride for 1:1 mole ratio

Mass of Phenylacetylene	= 1.020g.
Mass of Arsenic trichloride	= 1.814g.
Density of Phenylacetylene	= 0.93g/cc.
Density of Arsenic trichloride	= 2.21g/cc.
∴ Volume of Phenylacetylene	= 1.10mls.
∴ Volume of Arsenic trichloride	= 0.82mls.
∴ Total volume of mixture	= 1.92mls.

i.e. 1.9168mls. reaction mixture contains 1.02g phenylacetylene.

∴ 1000mls. reaction mixture contains $\frac{1000 \times 1.02g}{1.9168}$ phenylacetylene.

or $\frac{1000 \times 1.02}{1.9168 \times 1\ 02}$ moles phenylacetylene.

= 5.22 moles.

∴ Concentration of phenylacetylene = 5.22 moles per litre of reaction mixture.

The concentrations of p-chloro- and p-methylphenylacetylene are given in Table 24 page 68.

2A (ii)
Calculation of the internal cell length (path length), b.

The internal cell length (path length), b , was calculated from the equation:

$$2b = \frac{N}{V_1 - V_2} \text{ cm} \qquad \text{where}$$

N, is the number of fringes, i.e. 20, found between

V_1, and V_2, the frequencies in cm^{-1}, i.e. 1900 and 813cm^{-1}

Substituting these values into the above equation:

$$b = \frac{20}{2(1900-813)} \text{ cm}$$

$$= \frac{20}{2 \times 1087} \text{ cm}$$

$$= 9.20 \times 10^{-3} \text{ cm}$$

2A (iii)
Calculation of the Absorptivity (ε) value for Phenylacetylene in arsenic trichloride at room temperature

The fundamental law relating the absorption at a particular wavelength of radiation to the number and type of molecules is known as Beer's Law.

When a single component is responsible for the absorption of a certain amount of radiation, the law can be written as follows:-

$$\log \frac{(P_o)}{(P)} = A = \varepsilon \cdot b \cdot c \cdot$$

where,

P_o = incident radiation

P = transmitted radiation

A = absorbance

ε = absorptivity, a constant for a given material at a given wavelength

b = internal cell length or path length

c = concentration of the absorbing component.

The absorbance value of phenylacetylene in arsenic trichloride at room temperature (23°C) was 0.480. Since the concentration and path length are known, Table 24 page 68, the absorptivity value is given by,

$$\epsilon = \frac{A}{b.c.}$$

where,

$$A = 0.480$$

$$b = 9.20 \times 10^{-3} \text{cm}$$

$$c = 5.22 \text{ moles per litre}$$

$$\therefore \quad \epsilon = \frac{0.480}{9.20 \times 10^{-3} \times 5.22}$$

$$= 9.99 \text{ (absorbance) moles}^{-1} \text{ lit cm}^{-1}$$

The absorptivity values for p-chloro and p-methylphenylacetylene are given in Table 24 page 68.

When a series of solutions of known concentration of arylacetylene in arsenic trichloride were measured under the same experimental conditions, a plot of absorbance (A) versus concentration was found to be a straight line. See Figure 1, Page 71. Thus, phenylacetylene and its para-substituted derivatives, obey Beer's Law and the absorbance is directly proportional to the concentration of the arylacetylene, (PA).

T A B L E 24

ABSORBANCE VALUES FOR REACTION MIXTURES AT ROOM TEMPERATURE (23°)

Phenylacetylene in arsenic trichloride, 1:1 mole,	0.480
p-Chlorophenylacetylene in arsenic trichloride, 1:1 mole,	0.343
p-Methylphenylacetylene in arsenic trichloride, 1:1 mole,	0.730

PATH LENGTH (b)

Path length of cell = 9.20×10^{-3}cm

ABSORPTIVITY VALUES (ε) AT 2110cm^{-1} AND AT ROOM TEMPERATURE (23°)

Phenylacetylene in arsenic trichloride, 1:1 mole,	9.99
p-Chlorophenylacetylene in arsenic trichloride, 1:1 mole,	3.22
p-Methylphenylacetylene in arsenic trichloride, 1:1 mole,	16.66

CONCENTRATIONS (C) OF ARYLACETYLENES IN ARSENIC TRICHLORIDE FOR 1:1 MOLE RATIOS

Phenylacetylene	5.22 moles per litre
p-Chlorophenylacetylene	11.57 moles per litre
p-Methylphenylacetylene	4.76 moles per litre

2A (iv)
The Rate Equation

The Differential Method suggested by J.H. van't Hoff depends on the fact that the rate of a reaction of the n^{th} order is proportional to the n^{th} power of the concentration, viz.,

$$-\frac{dc}{dt} = kc^n \qquad (1)$$

where c is the concentration of the arylacetylene at any instant and k, the rate constant. Taking logarithms,

$$\log\left(-\frac{dc}{dt}\right) = \log k + n \log (c) \qquad (2)$$

Hence, a plot of $\log\left(-\frac{dc}{dt}\right)$ i.e. log (Rate) against log (c) will be linear and the slope of the straight line will be equal to n, the order of the reaction with respect to the arylacetylene.

The rate constant, k, was obtained by substituting values of $\log\left(-\frac{dc}{dt}\right)$ and log (c) into equation (2), and the values of $\frac{dc}{dt}$ were obtained from a plot of concentration (absorbance) against time by measuring the slopes of the tangents at several places. See note on page 77.

The example on page 76 for the reaction of phenylacetylene and arsenic trichloride at 90°C is a typical calculation illustrating the method.

TABLE 25

CONCENTRATION AND ABSORBANCE VALUES

PHENYLACETYLENE IN ARSENIC TRICHLORIDE AT ROOM TEMPERATURE (23°C)

Concentration (moles per litre)	Absorbance
6.50	0.581
5.22	0.480
4.25	0.410
2.61	0.252
1.25	0.112

p-CHLOROPHENYLACETYLENE IN ARSENIC TRICHLORIDE AT ROOM TEMPERATURE (23°C)

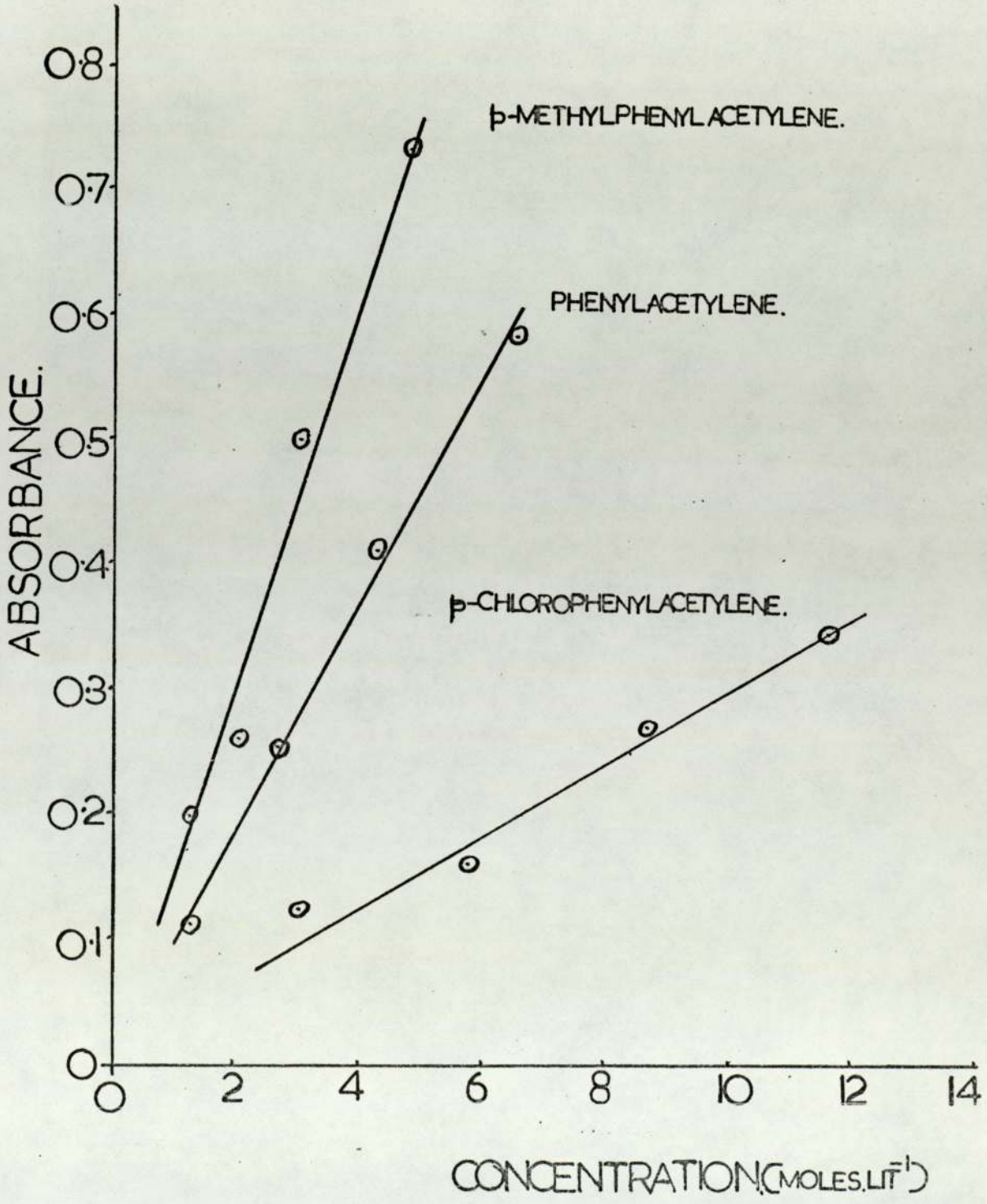
1.57	0.343
8.60	0.270
5.70	0.160
3.0	0.125

p-METHYLPHENYLACETYLENE IN ARSENIC TRICHLORIDE AT ROOM TEMPERATURE (23°C)

4.76	0.730
3.00	0.500
2.00	0.260
1.2	0.200

FIG. 1

PLOT OF ABSORBANCE vs CONCENTRATION OF ARYLACETYLENES AT ROOM TEMPERATURE. 23°C



T A B L E 26

TIME AND ABSORBANCE VALUES FOR THE REACTION OF PHENYLACETYLENE AND ARSENIC TRICHLORIDE AT 90°C AND 1:1 MOLE RATIO

Time (mins.)	Absorbance or concentration of Phenylacetylene (PA)
0	0.400
3	0.380
6	0.360
10	0.340
14	0.325
24	0.290
29	0.270
35	0.259
40	0.245
46	0.235
52	0.228
57	0.224
65	0.209
70	0.205
77	0.200
86	0.195
96	0.182
106	0.175
116	0.170
121	0.170

From the above data, Fig.2 was obtained. See page 73.

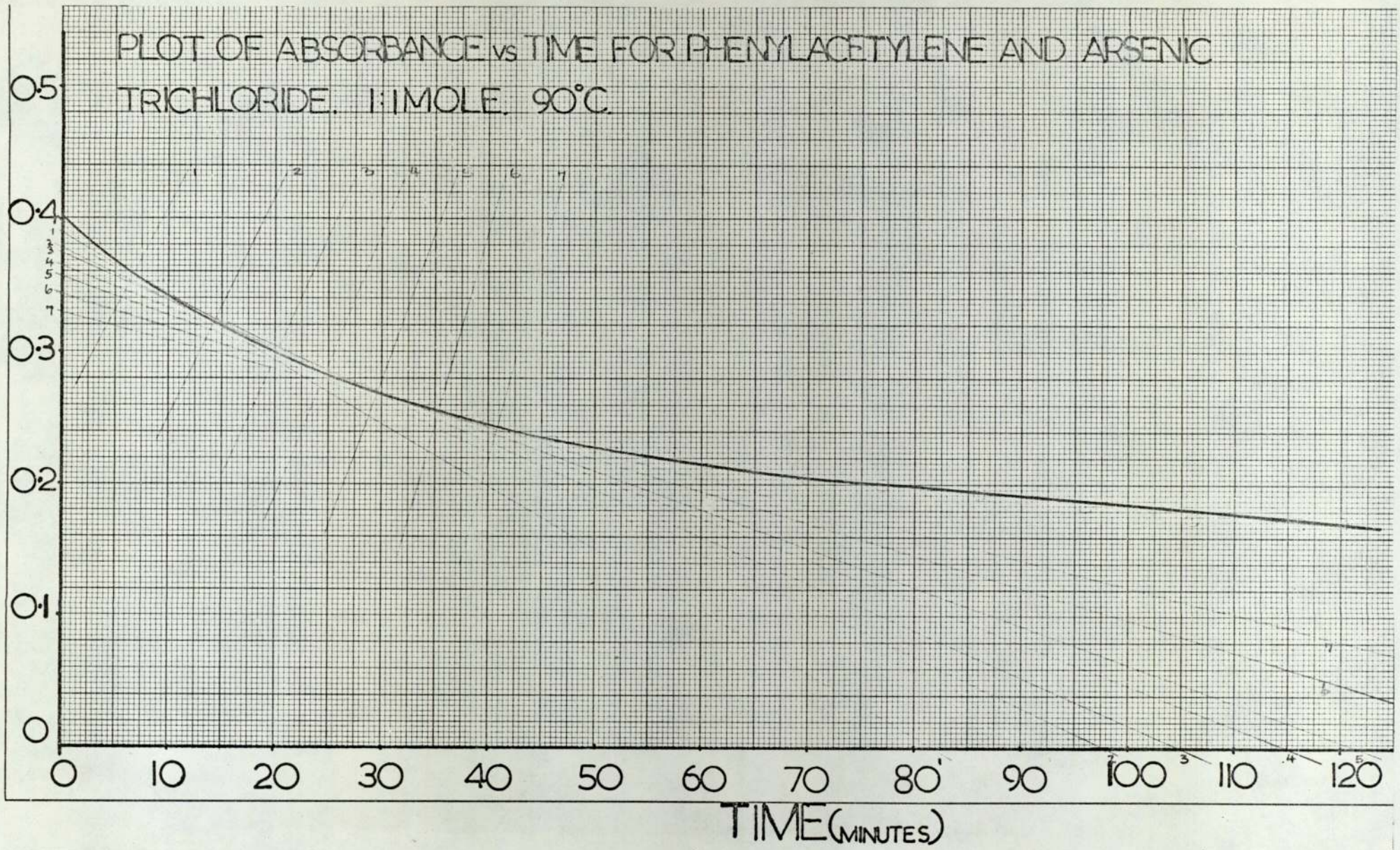

PLOT OF ABSORBANCE vs TIME FOR PHENYLACETYLENE AND ARSENIC TRICHLORIDE. 1:1 MOLE. 90°C.
ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)

FIG. 2

T A B L E 27

THE REACTION OF PHENYLACETYLENE AND ARSENIC TRICHLORIDE

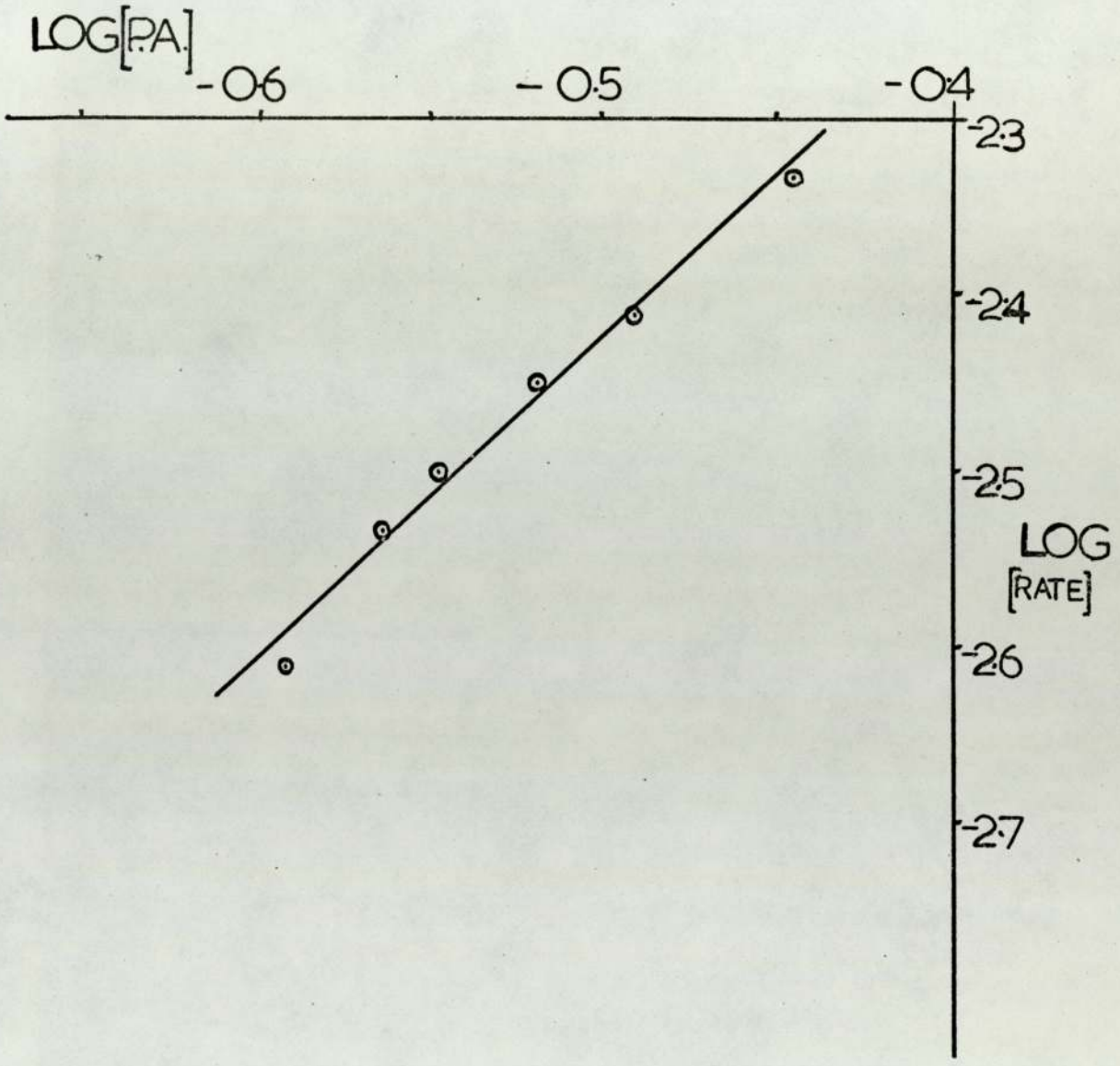
1:1 MOLE AND 90°C

Absorbance (PA)	Log (PA)	Rate $\frac{(dc)}{(dt)}$	Log (RATE)
0.357	$\bar{1}.5527$ -0.4473	$\frac{0.384}{81.7}$	$\bar{3}.6721$ -2.3279
0.322	$\bar{1}.5079$ -0.4921	$\frac{0.380}{98}$	$\bar{3}.5886$ -2.4114
0.302	$\bar{1}.4800$ -0.5200	$\frac{0.372}{105}$	$\bar{3}.5493$ -2.4507
0.283	$\bar{1}.4518$ -0.5482	$\frac{0.362}{115}$	$\bar{3}.4980$ -2.5020
0.272	$\bar{1}.4346$ -0.5654	$\frac{0.357}{122}$	$\bar{3}.4663$ -2.5337
0.255	$\bar{1}.4065$ -0.5935	$\frac{0.342}{140}$	$\bar{3}.3879$ -2.6121

From the above data, Fig. 3 was obtained. See page 75.

FIG. 3

PLOT OF LOG[P.A.] vs LOG[RATE] FOR PHENYLACETYLENE AND ARSENIC TRICHLORIDE. 90°C.



From the plot of log (PA) vs log (RATE), Fig. 3.

$$\text{Slope (n)} = \frac{2.66 - 2.35}{0.63 - 0.46}$$

$$= \frac{0.31}{0.17}$$

$$= 1.82$$

i.e. the order of the reaction is 1.82.

Now, from the equation:

$$\log (\text{RATE}) = \log k + n \log (\text{PA}).$$

when $\log (\text{RATE}) = -2.46$,

$\log (\text{PA}) = -0.52$ as obtained from Fig. 3.

and $n = 1.82$.

Hence,

$$-2.46 = \log k + 1.82\ (-0.52)$$

$$-2.46 = \log k - 0.946$$

$$\therefore \log k = -1.514$$

$$= \bar{2}.486$$

$$\therefore k = 3.06 \times 10^{-2} \text{ absorbance}^{-1} \text{ min.}^{-1}$$

and k expressed in litres mole^{-1} min.^{-1} will be:

$$3.06 \times 10^{-2} \times \text{absorptivity} \times \text{path length}$$

i.e. $3.06 \times 10^{-2} \times 9.99 \times 9.20 \times 10^{-3}$

$= 2.82 \times 10^{-3}$ litres mole^{-1} min.^{-1}

The half-life, $t_{1/2}$, of a second order reaction is given by:-

$$t_{1/2} = \frac{1}{kc}$$

where $k = 2.82 \times 10^{-3}$ litres $mole^{-1}$ min^{-1}

$c = 5.22$ moles lit^{-1} i.e. the concentration of phenylacetylene in the reaction mixture

$$\therefore \quad t_{1/2} = \frac{10^3}{2.82 \times 5.22} \text{ mins.}$$

$$= 68.1 \text{ mins.} \quad \text{(Found 75 mins.)}$$

Table 28 page 81 shows the results obtained for p-chloro and p-methylphenylacetylene.

Note The alternative method of determining the value of k, the rate constant, is to use equation 2, page 69, for when log (C) = 0 then log k = $\log \left\{ \frac{-dc}{dt} \right)$ and the intercept of the straight line with the $\log \left\{ \frac{-dc}{dt} \right)$ axis gives the value of log k.

The data for the calculation of the rate constants for the reaction of arsenic trichloride with phenylacetylene (80° and 100°), p-methylphenylacetylene (60°, 70° and 80°) and p-chlorophenylacetylene (90°, 100° and 110°) is given in Tables 27a - 27c, pages 77a - 77c.

T A B L E 27a

THE REACTION OF PHENYLACETYLENE AND ARSENIC TRICHLORIDE 1:1 MOLE

80°		100°	
Log (PA)	Log (RATE)	Log (PA)	Log (RATE)
-0.4200	-2.6020	-0.4935	-2.2541
-0.4318	-2.6156	-0.5317	-2.3072
-0.4559	-2.6486	-0.5735	-2.3665
-0.4685	-2.6784	-0.6021	-2.4318
-0.4908	-2.7130	-0.6517	-2.4921
-0.5157	-2.7550	-0.6925	-2.6596

TABLE 27b

THE REACTION OF p-METHYLPHENYLACETYLENE AND ARSENIC TRICHLORIDE

1:1 MOLE

60°		70°		80°	
Log (PA)	Log (RATE)	Log (PA)	Log (RATE)	Log (PA)	Log (RATE)
-0.2204	-2.3103	-0.2518	-2.0255	-0.2993	-1.8305
-0.2503	-2.3603	-0.2840	-2.1319	-0.3655	-2.0905
-0.2882	-2.4200	-0.3188	-2.2369	-0.4547	-2.1060
-0.3279	-2.4945	-0.3565	-2.3112	-0.5302	-2.2098
-0.3747	-2.5566	-0.3979	-2.3610	-0.6234	-2.3533
		-0.4353	-2.4349	-0.7352	-2.5273
		-0.4685	-2.5013		
		-0.4976	-2.5852		

T A B L E 27c

THE REACTION OF p-CHLOROPHENYLACETYLENE AND ARSENIC TRICHLORIDE

1:1 MOLE

90°		100°		110°	
Log (PA)	Log (RATE)	Log (PA)	Log (RATE)	Log (PA)	Log (RATE)
-0.5017	-2.8645	-0.5100	-2.6666	-0.5031	-2.5383
-0.5229	-2.8846	-0.5346	-2.7245	-0.5346	-2.6112
-0.5482	-2.9313	-0.5702	-2.8168	-0.5817	-2.7256
-0.5735	-2.9504	-0.6091	-2.9199	-0.6308	-2.8421
-0.6055	-3.0000	-0.6517	-3.0259	-0.6778	-2.9513
-0.6440	-3.0481	-0.6968	-3.1400	-0.7144	-2.9858
-0.6799	-3.1002				

2A (v)

The determination of the Energy of Activation

The relationship between the rate constant, k, of a reaction and the energy of activation, E, is best expressed in the form of the Arrhenius equation,

$$k = Ae^{-E/RT}$$

where R is the gas constant, 1.987 cal.deg.$^{-1}$ mole^{-1}, T the absolute temperature, and A a constant called the frequency factor. Talking logarithms of the equation,

$$\log k = \log A - \frac{E}{2.303\ RT}$$

Thus, a plot of log k against 1/T will be linear, the slope being equal to $-\frac{E}{2.303\ R}$ and the constant E, the activation energy of the reaction can thus be calculated from the values of k, the rate constant, at different temperatures.

The following calculation is a typical example of the method used to determine the activation energy of the reaction between phenylacetylene and arsenic trichloride. See page 79.

2A (vi)

THE REACTION OF PHENYLACETYLENE AND ARSENIC TRICHLORIDE

1:1 MOLE RATIO

The determination of the Activation Energy of the reaction was obtained from the following data:-

Temperature (°C)	Temperature (°K)	$\frac{1}{(T^{\circ}K)}$	Rate Constant (k litres $mole^{-1}$ min^{-1})	Log k
80	353.15	2.83×10^{-3}	1.17×10^{-3}	$\bar{3}.0677$
				-2.9323
90	363.15	2.76×10^{-3}	2.82×10^{-3}	$\bar{3}.4495$
				-2.5505
100	373.15	2.68×10^{-3}	5.86×10^{-3}	$\bar{3}.7675$
				-2.2325

From the graph of log k against $1/T^{\circ}K$, Fig.4 page 80.

$$\text{Slope} = \frac{E}{2.303R} = \frac{0.6}{0.126 \times 10^{-3}}$$

where $R = 1.987$ cal deg^{-1} $mole^{-1}$

$$\therefore E = \frac{2.303 \times 1.987 \times 0.6}{0.126 \times 10^{-3}} \text{ cals mole}^{-1}$$

$$= 21790 \text{ cals mole}^{-1}$$

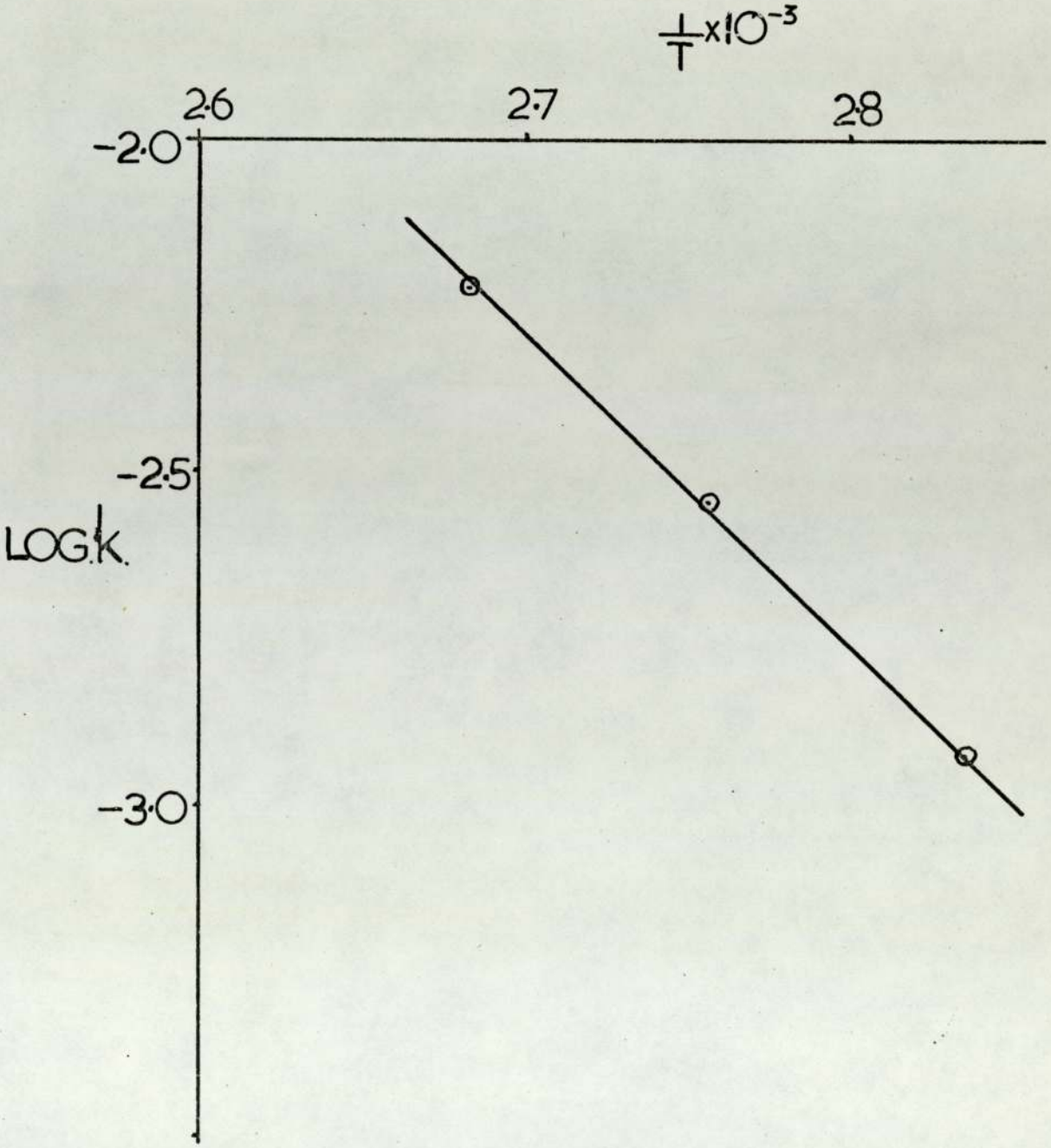
$$= 21.79 \text{ k cals mole}^{-1}$$

The activation energies for p-chloro and p-methylphenylacetylene were obtained in a similar manner and the results are shown in Table 28 page 81.

FIG. 4

ACTIVATION ENERGY.

PHENYLACETYLENE AND ARSENIC TRICHLORIDE.



T A B L E 28

SUMMARY OF THE KINETIC DATA

PHENYLACETYLENE AND ARSENIC TRICHLORIDE 1:1 MOLE

Temp. (°C)	Order of (n)	Rate Constant (k) (litres mole^{-1} min^{-1})	Half-Life* (t0.5)mins Cal.	Found	Activation Energy (E) (k cal mole^{-1})
60		Too Slow			
80	1.67	1.17×10^{-3}	163.9	160	
90	1.82	2.82×10^{-3}	68.1	75	21.79
100	2.09	5.86×10^{-3}	32.7	43	

p-METHYLPHENYLACETYLENE AND ARSENIC TRICHLORIDE 1:1 MOLE

60	1.67	1.76×10^{-3}	119.1	114	
70	2.12	4.56×10^{-3}	46.1	62.5 (a)	15.78
80	1.59	6.70×10^{-3}	31.4	27.5	

p-CHLOROPHENYLACETYLENE AND ARSENIC TRICHLORIDE 1:1 MOLE

90	1.35	1.95×10^{-4}	443.7	186 (b)	
100	1.97	5.75×10^{-4}	150.3	148	29.87
110	2.24	1.13×10^{-3}	76.9	108 (c)	

* For a second order reaction (n=2) the half-life of the reaction, t0.5 is given by $t0.5 = \frac{1}{kc}$ where k = rate constant, c = concentration of reactant. The differences in the calculated and observed value of t0.5 is mainly due to the value of n, the order of reaction. If the calculated value of $n > 2$, the calculated half-life will be less than the found value and if the calculated value of $n < 2$, the calculated

T A B L E 28 (Continued)

* half-life will be greater than the found value.

(a) If n = 2, k = 4.13×10^{-3} litres $mole^{-1}$ min^{-1} and $t_{0.5}^{70^\circ}$ = 50.9 mins.

(b) If n = 2.0, k = 4.61×10^{-4} litres $mole^{-1}$ min^{-1} and $t_{0.5}^{90^\circ}$ = 187.4 mins.

See discussion on page 113.

(c) If n = 2, k = 0.82×10^{-3} litres $mole^{-1}$ min^{-1} and $t_{0.5}^{110^\circ}$ = 105.8 mins.

FIG. 5

PLOT OF ABSORBANCE vs TIME FOR THE REACTION OF PHENYLACETYLENE AND ARSENIC TRICHLORIDE.

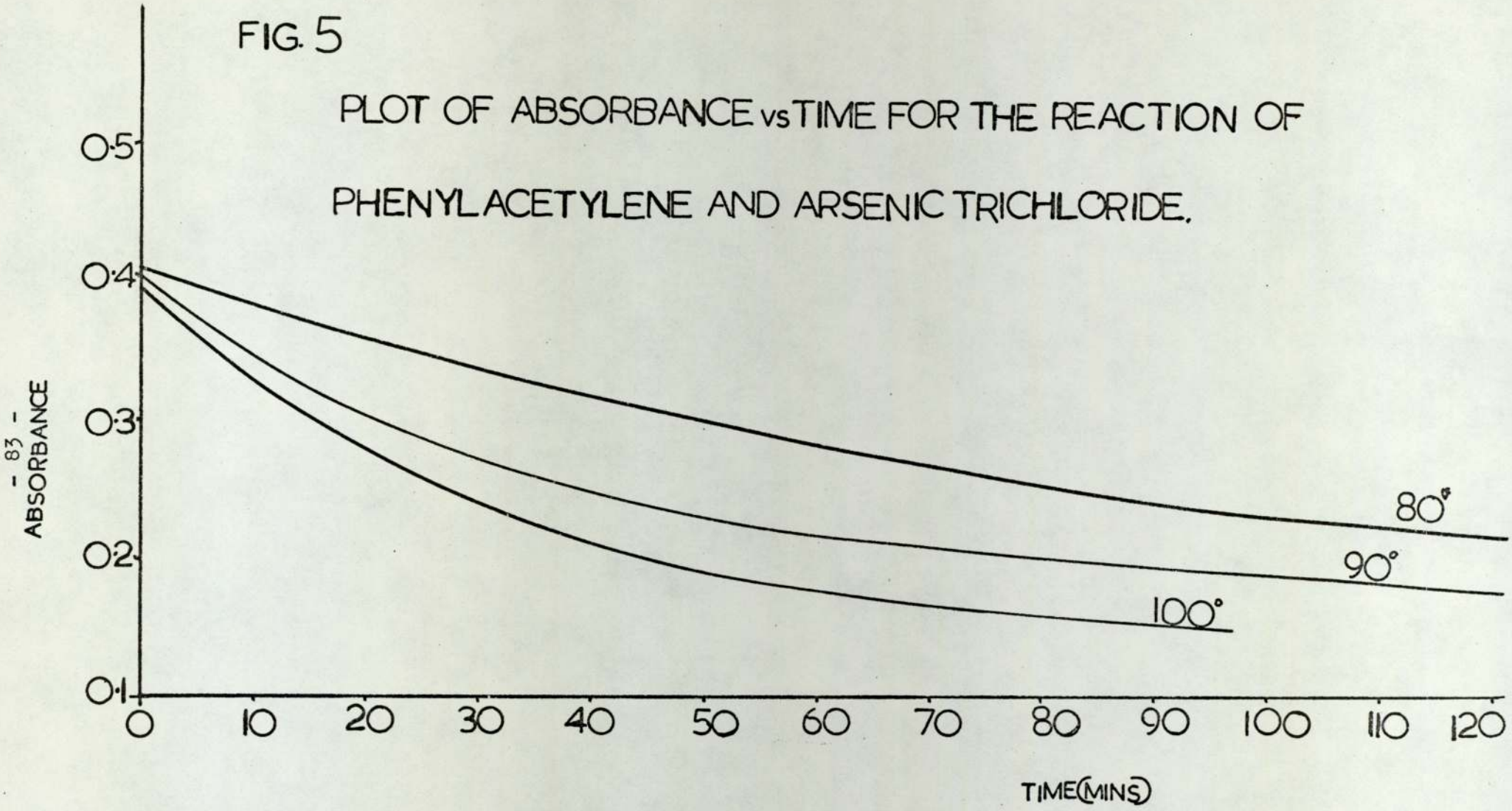


FIG. 6

PLOT OF ABSORBANCE vs TIME FOR THE REACTION OF p-CHLOROPHENYLACETYLENE AND ARSENIC TRICHLORIDE.

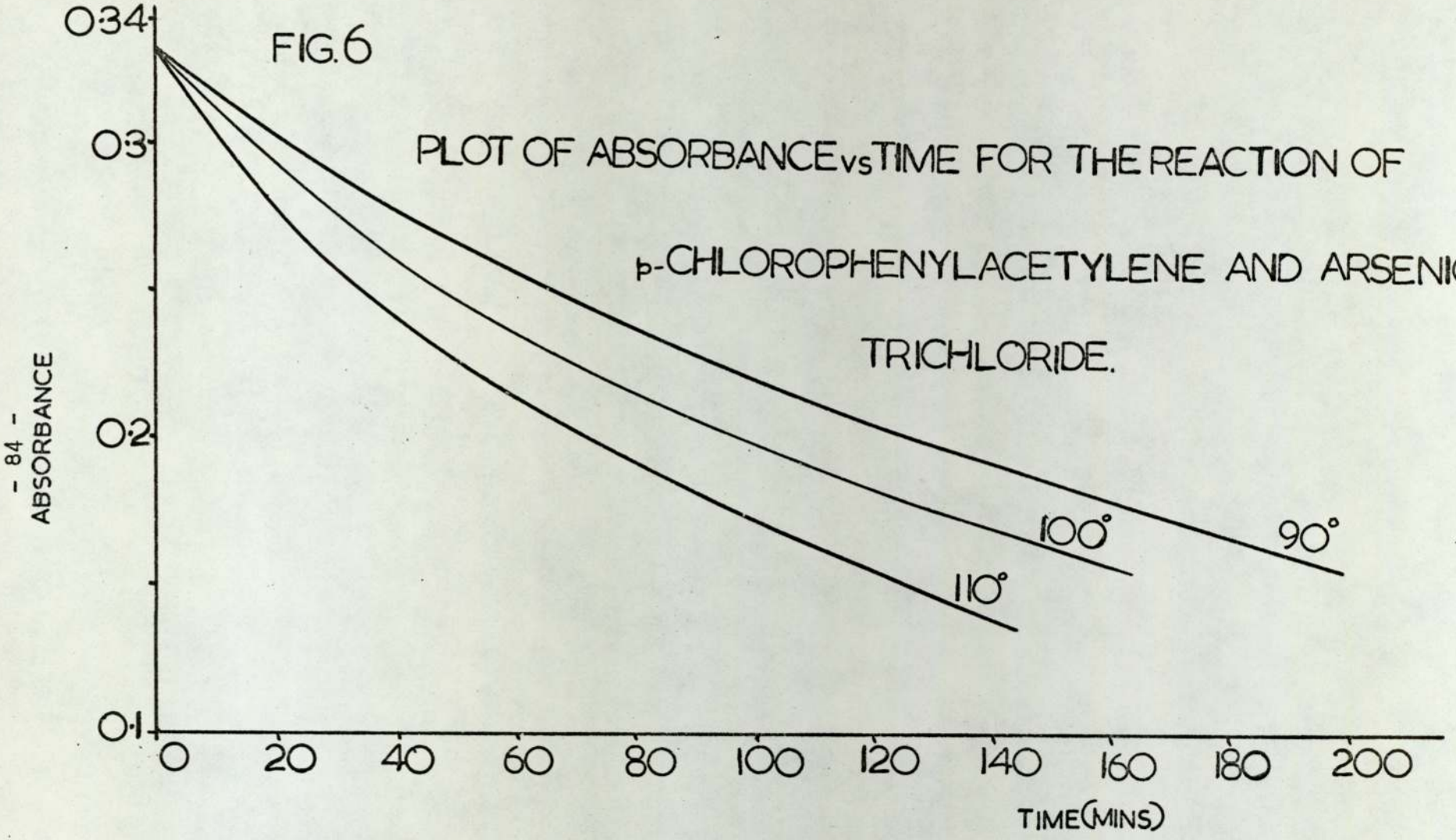
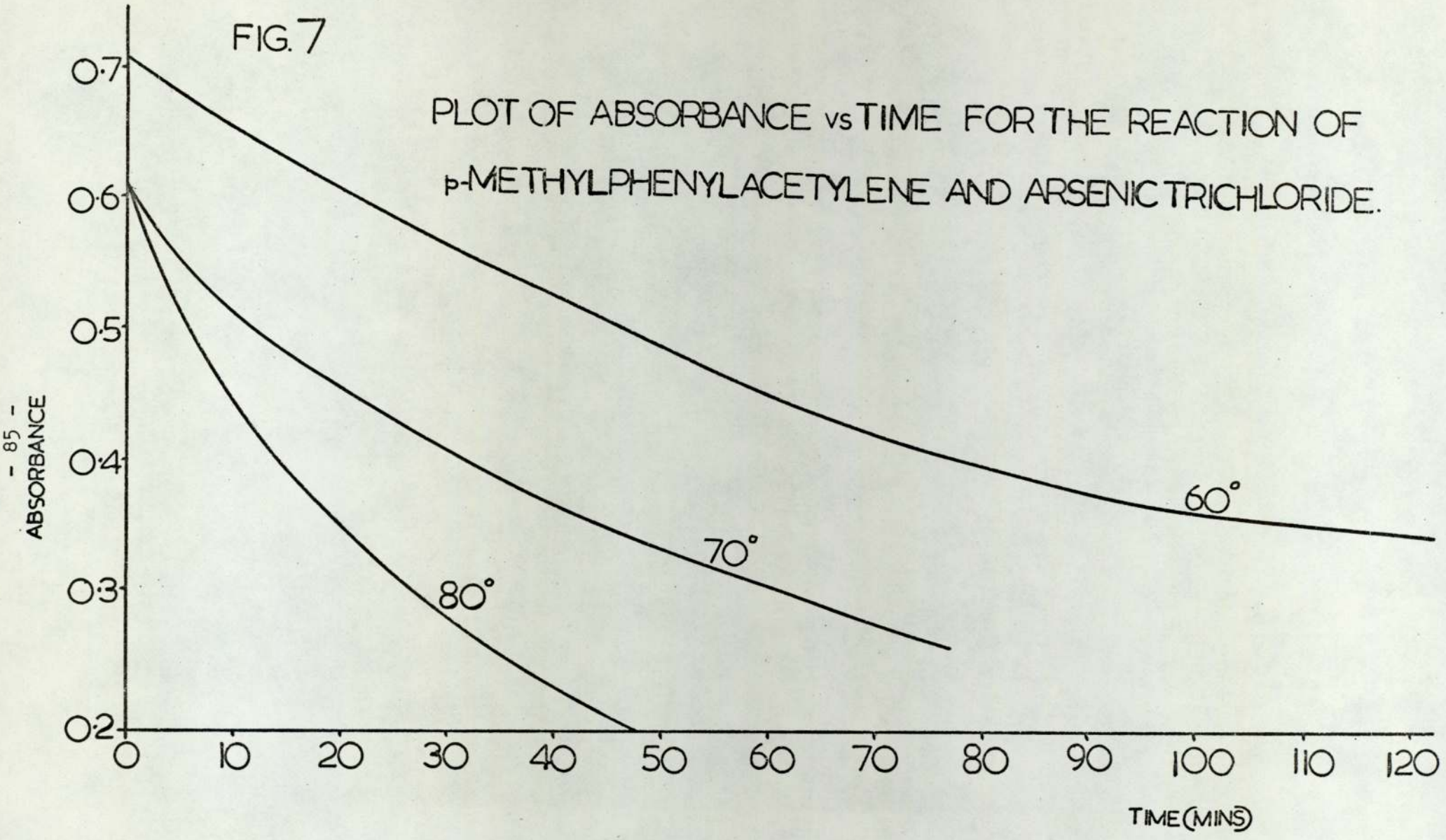


FIG. 7

PLOT OF ABSORBANCE vs TIME FOR THE REACTION OF p-METHYLPHENYLACETYLENE AND ARSENIC TRICHLORIDE.



2A (vii)
The Hammett Equation

The Hammett Equation which relates structure to both equilibrium constants and rate constants for the reactions of meta- and para- substituted benzene derivatives may be written:-

$$\log \left(\frac{k}{ko}\right) = \rho\sigma$$

where k and ko are the rate constants for the reaction of the substituted and unsubstituted compound respectively,

ρ, a parameter characteristic of the reaction series, i.e. the reaction of arylacetylenes with arsenic trichloride, and is a measure of the sensitivity of this type of reaction to ring substitution and

σ, is characteristic of the substituent and represents the ability of the group to attract or repel electrons by a combination of its Inductive and Resonance effects.

The σ values[36] for the p-Methyl and p-Chloro groups are -0.17 and +0.23 respectively and by substituting these values into the Hammett equation the ρ values for the reaction of p-Methyl and p-Chloro-phenylacetylene with arsenic trichloride were calculated. The following calculation is a typical example:-

Rate Constant for
Phenylacetylene at 100°C = 5.86×10^{-3} lit. mole.$^{-1}$ min.$^{-1}$

Rate Constant for
p-Chlorophenylacetylene at 100°C = 5.75×10^{-4} lit. mole.$^{-1}$ min.$^{-1}$

σ for the p-Chloro group = +0.23

Hence, from the Hammett Equation,

$$\log \left(\frac{5.75 \times 10^{-4}}{5.86 \times 10^{-3}}\right) = \rho \times 0.23$$

$$\bar{2}.9923 = 0.23\rho$$

$$-1.0077 = 0.23\rho$$

$$\therefore \rho = \frac{-1.0077}{0.23}$$

$$= -4.38$$

Similarly, the ρ value for the reaction of p-Methylphenylacetylene and arsenic trichloride at 80°C was found to be -4.46.

The negative ρ values indicate that the reactions of para-substituted arylacetylenes and arsenic trichloride are aided by electron donating groups like methyl and methoxy, or made more difficult by electron withdrawing groups like the chloro and nitro group.

Note A plot of log (k/ko) vs σ would have been a better method of obtaining the ρ value for the reaction series but due to the lack of data at the required temperatures, this method was not possible.

T A B L E 28

INTEGRATED SECOND ORDER EQUATION

PHENYLACETYLENE AND ARSENIC TRICHLORIDE 1:1 MOLE 90°C

Time (mins.)	$\frac{1}{\text{Absorbance}}$
0	2.50
3	2.63
6	2.78
10	2.94
14	3.08
24	3.45
29	3.70
35	3.86
40	4.08
46	4.26
52	4.39
57	4.46
65	4.79
70	4.88
77	5.00
86	5.13
96	5.50
106	5.71
116	5.88
121	5.88

From the plot of time vs $\frac{1}{\text{absorbance}}$ for the integrated second order equation;

$$\text{Slope} = \frac{1}{k} = \frac{60}{2.10}$$

$$\therefore \quad k = \frac{2.10}{60.0} = 3.50 \times 10^{-2} \text{ absorbance}^{-1} \text{ min.}^{-1}$$

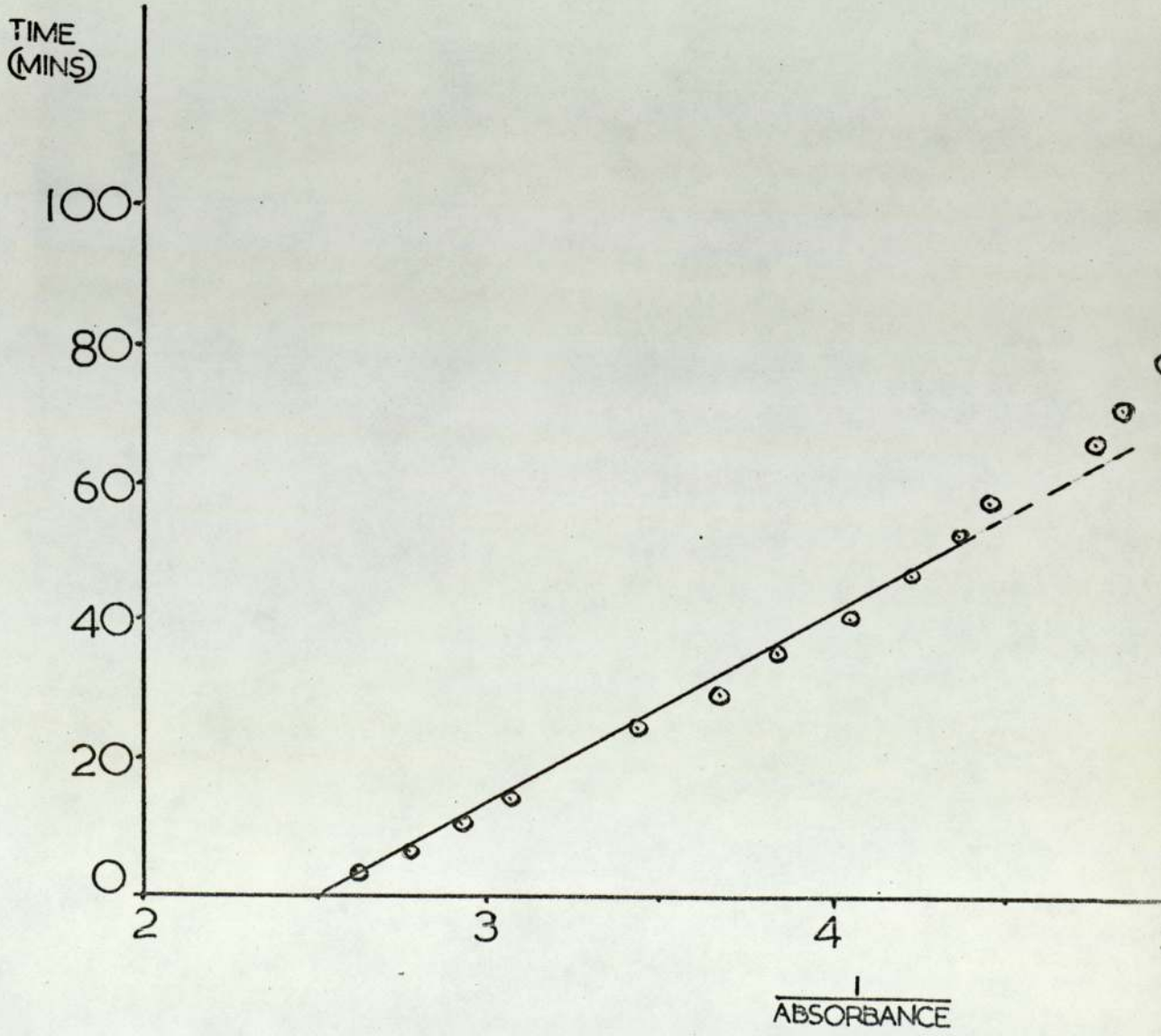
$$= 3.21 \text{ litres mole}^{-1} \text{ min.}^{-1}$$

(van't Hoff method : $k = 2.82$ litres mole^{-1} min.$^{-1}$)

FIG. 8

INTEGRATED SECOND ORDER EQUATION.

THE REACTION OF PHENYLACETYLENE AND ARSENIC TRICHLORIDE. 90°C AND 1:1 MOLE.



CHAPTER 3

SECTION 3A

DISCUSSION

ORGANIC SYNTHESES

3A (i)
Substituted Arylacetylenes

The preparation of the substituted phenylacetylenes from the corresponding ketones did not present any experimental difficulties apart from the fact that low yields were obtained after purification.

The reaction of phosphorus pentachloride with carbonyl compounds gives reaction products which include the monochloroethylenes as well as the expected dichlorides; hydrogen chloride is always produced.

$$R.CO.CH_2R' + PCl_5 \longrightarrow R.CCl_2.CH_2R' + POCl_3$$

$$R.CO.CH_2R' + PCl_5 \longrightarrow RCCl = CHR' + HCl + POCl_3$$

Maximum yields of chlorides for acetylene synthesis were obtained by adding the ketone dropwise to a slight excess of finely powdered phosphorus pentachloride so that evolution of hydrogen chloride was not vigorous. In all cases a tarry residue, probably a polymer, remained in the flask when phosphorus oxychloride and the chlorocompounds were isolated by vacuum distillation.

Dehydrohalogenation with ethanolic potassium hydroxide was used to prepare the para-substituted arylacetylenes whilst methanolic potassium hydroxide was used to prepare phenylpropiolic acid because a lower temperature was required to minimise the side reaction of decarboxylation. This side reaction also occurred readily during acidification of the alkaline reaction mixture, hence the use of

iced hydrochloric acid and iced water.

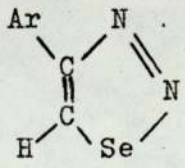
$$(-)_{O-C(=O)-C\equiv C-R} \longrightarrow CO_2 + R-C\equiv C^{(-)} \xrightarrow{H^{(+)}} R-C\equiv C-H$$

Further quantities of tarry material, probably of polymeric nature, were obtained under the influence of ethanolic potassium hydroxide and this may be due to polymerisation of the vinyl ethers formed by the addition of alcohol to the triple bond that is activated by conjugation with phenyl or carboxyl groups.[37]

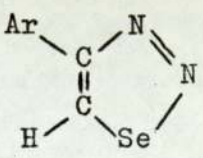
As the yields of arylacetylenes were very low, an alternative method utilising arylselenadiazoles was adopted because this was reported to give improved yields.[26,27] The method involved the preparation of the semicarbazone from the aryl ketone and then treating it with finely divided selenium dioxide in dry glacial acetic acid. Pyrolysis of the selenadiazole gave the arylacetylene which was then purified to remove traces of selenium. The reaction scheme may be represented as follows:-

$$Ar.CO.CH_3 + NH_2.NH.CO.NH_2 \longrightarrow Ar.C(=N.NHCO.NH_2).CH_3$$

$$Ar.C(=N.NH.CONH_2).CH_3 \xrightarrow[\text{glacial acetic acid}]{SeO_2}$$



4-Phenyl,1,2,3 Selenadiazole



$\xrightarrow{\text{Heat}}$ $Ar.C\equiv CH$

The crude selenadiazoles were gently pyrolysed under reduced pressure and yields were sufficiently high in comparison with

the phosphorus pentachloride method to justify the pyrolysis of the crude, rather than the pure, selenadiazole. The table on page 17 gives the yields obtained by both methods.

The main impurity in the arylacetylenes prepared via their selenadiazoles was finely powdered selenium which was removed by filtration and vacuum distillation in the case of liquid arylacetylenes and by repeated recrystallisations for the solid arylacetylenes. The purified materials were stored in an atmosphere of dry nitrogen and sealed in dark coloured bottles containing molecular sieves for the phenyl, p-methyl and p-methoxyphenylacetylenes.

3A (ii)
The Reaction of the Arylacetylenes with Arsenic Trichloride

The reaction may be generally represented by the following chemical equation :-

$$R.C{\equiv}CH + AsCl_3 \longrightarrow R.C(Cl) = CHAsCl_2$$

where $R = C_6H_5$, $p\text{-}CH_3C_6H_4$-, $p\text{-}CH_3O.C_6H_4$, $p\text{-}ClC_6H_4$-.

The syntheses of the β-chlorostyryldichloroarsines were carried out under anhydrous conditions and in an inert atmosphere as described in the experimental section. Thus, it was essential that all the reagents and apparatus were dried before use so that the hydrolysis of arsenic trichloride and the adduct was reduced to a minimum.

Isolation and recrystallisation of the adduct under anhydrous conditions was rather more difficult because the method involved cooling the petroleum ether below room temperature. This also meant that the product had to be filtered rapidly when its temperature was below room temperature and as several recrystallisations were necessary, the final product was probably slightly hydrolysed by the atmosphere. However, with sufficient care and working in an atmosphere of dry nitrogen, pure products were obtained as evident from their sharp melting points, spectra and elemental analysis. The yield from the reaction of phenylacetylene and arsenic trichloride was improved from twenty percent to about fifty percent by the use of the 'transference method' described on page 18. The method had the advantage of continously working in an inert atmosphere and recycling and combining the unreacted reagents without exposing them to air. Recrystallisations in an inert atmosphere were possible when using this apparatus, provided

the cold petroleum ether was decanted with caution from one flask to the other.

With the exception of the p-methoxy and p-nitrophenylacetylene, the dichloroarsines of p-chloro, p-methyl and phenylacetylene were easily isolated and recrystallised from petroleum ether, (b.p. 40-60°C). The adducts formed pale golden plate-like crystals which readily hydrolysed in the atmosphere. The sharp melting points were indicative of pure single substances and this was confirmed by thin layer chromatography. The analysis of the mass spectrum of β-chlorostyryldichloroarsine, showing a molecular ion peak at 282 mass units, is shown in Table 17 page 50.
Attempts to isolate the p-methoxy-adduct failed as it appeared to be too unstable when subjected to the purification conditions of vacuum distillation or recrystallisation. It was thought that the material had polymerised or decomposed when subjected to heat treatment and attempts to isolate the adduct were abandoned. When the reaction of p-methoxyphenylacetylene and arsenic trichloride was carried out in dry cyclohexane at about 28°C, spectral data, Table 7, page 40, showed infrared absorption bands characteristic of the dichloroarsine whilst the nuclear magnetic resonance spectrum confirmed the ratio of vinyl: aromatic: aliphatic protons to be in the region of 1:4:3.

The reaction of p-nitrophenylacetylene with arsenic trichloride was more difficult, as expected, and even heating the reaction mixture for twenty-four hours at 120-130°C did not produce any appreciable reaction as shown by spectral analysis on the reaction mixture. A black crystalline material of indefinite melting point was obtained at a reaction temperature of 140°C and the infrared

spectrum indicated that the material was probably polymeric, Table 5 page 38.

The absence of the 890cm^{-1} absorption band suggested that there was probably no vinylic carbon-chlorine bonds in the structure and the single peak at 1015cm^{-1} was probably attributable to a polymer with essentially a trans-configuration.[32] The material appeared to be stable in the atmosphere although it changed colour from black to dark brown after two days exposure. Nuclear magnetic resonance data was not easily obtainable because it was insoluble in most organic solvents and although only sparingly soluble in acetone, the concentration of this solution was too low for a suitable integrated spectrum to be obtained. See Table 14 page 47. Purification of this material was difficult because of its insolubility and it was decided that further analysis of the adduct would not provide conclusive evidence of its exact identity. Thus, the reaction of p-nitrophenylacetylene with arsenic trichloride gave a high melting ($>350^{\circ}C$) black crystalline solid which was probably polymeric.

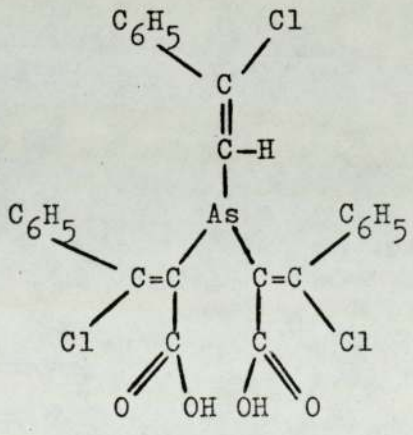
The reaction of phenylpropiolic acid and arsenic trichloride did not produce the expected β-chlorostyryldichororarsine but gave a stable off-white crystalline material, m.p. 228-30°, whose infrared spectrum indicated that it was probably a cyclic anhydride, see Table 8, page 41. The material was stable in the atmosphere, indicating the absence of readily hydrolysable chlorine atoms and although easily soluble in warm dilute sodium hydroxide, was insoluble in hot water, dilute hydrochloric acid and most organic solvents, excluding boiling acetone in which it was sparingly soluble. These solutions of the material in acetone

were too dilute for any integrated nuclear magnetic resonance spectra to be obtained and even warm trifluoroacetic acid did not give a sufficiently concentrated solution suitable for instrumental analysis.

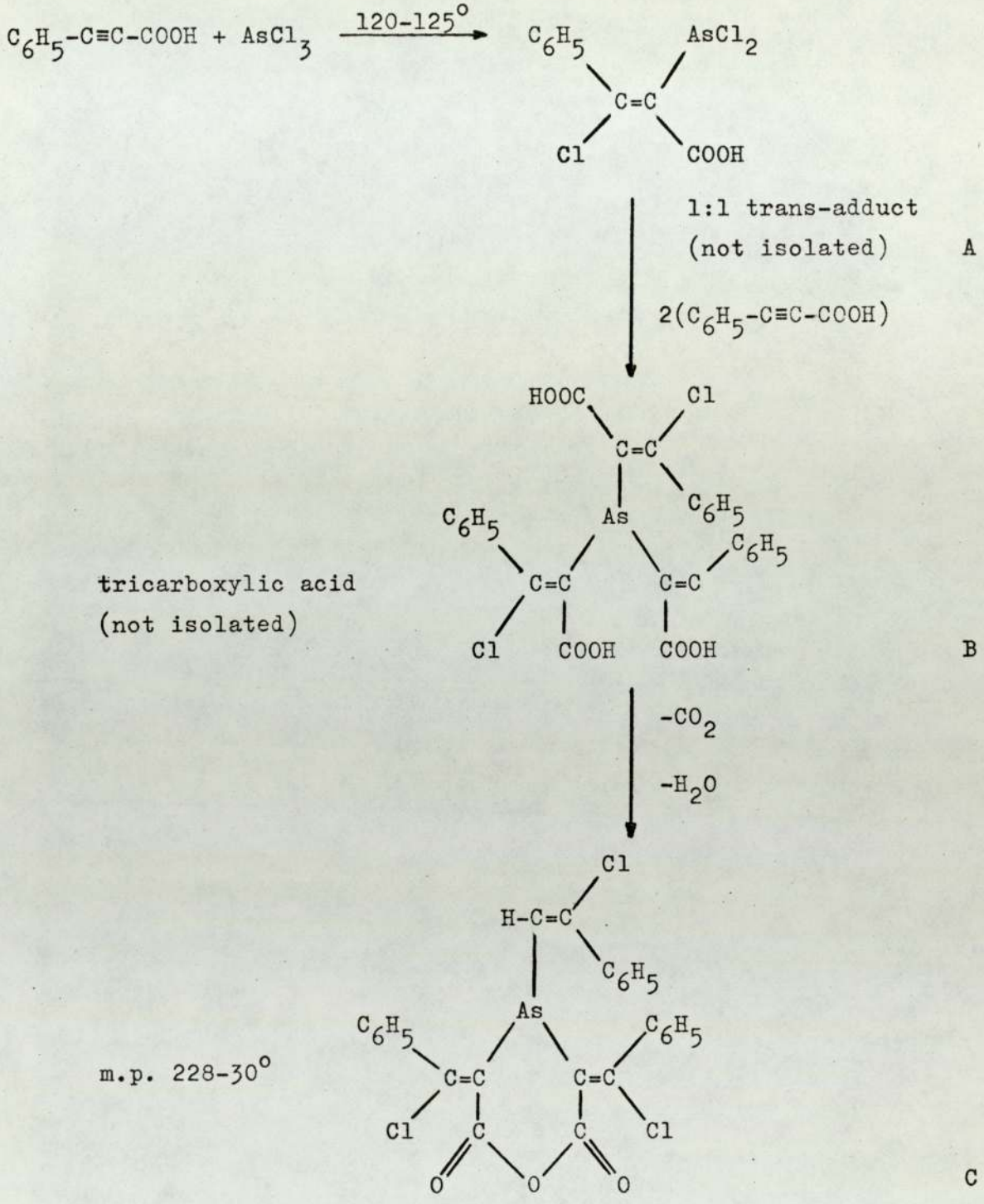
An attempt to determine the equivalent weight of the material by dissolving it in an excess of sodium hydroxide and back titrating the excess alkali with dilute hydrochloric acid was inconclusive because the titre values were very inconsistent. This may have been due to the fact that the material was slightly impure or incompletely hydrolysed and that the 'end-point' was not well defined because of the absorption effects of the precipitated acid. Several attempts were made to determine the equivalent weight of the material and even boiling the solutions, to ensure complete hydrolysis, failed to give consistent and reliable results. Typical values ranged from 40 to 80 and as the equivalent weight of phenylpropiolic acid is 146 this would have meant that the suspected anhydride would have had a molecular weight less or slightly greater than that of the parent acid and since at least two molecules of acid are required to form one molecule of anhydride, the values obtained were obviously incorrect. The analysis of the mass spectrum of the suspected cyclic anhydride, (c) page 98, did not show a molecular ion peak at 556 mass units, see Table 20 page 53, but instead a molecular ion fragment at 555 mass units probably corresponding to the removal of the vinylic proton, compound C, page 98.

The material was hydrolysed as described on page 33 and the infrared data of the product is shown in Table 9 page 42. The characteristic carbonyl absorption at 1700cm^{-1} and hydroxyl

absorptions in the 3500 - 2600cm^{-1} region indicated that the hydrolysed product was a carboxylic acid, m.p. 255-7°. The acid was sparingly soluble in hot water and effervesced with an aqueous solution of sodium bicarbonate. Recrystallisation from hot water was difficult because of the formation of the insoluble anhydride during the heating operation, see infrared data in Table 9 page 42, and prolonged heating in hot water eventually converted most of the acid to the anhydride, thus probably indicating that at a temperature of about 100° the dicarboxylic acid was unstable and readily reformed the anhydride. The mass spectrum of the crude hydrolysed material, Table 22 page 58, showed no molecular ion peak at 574 mass units, but a number of small fragments probably arising from the following structure:-



Further evidence for the possible structure of the cyclic anhydride was based on infrared (Table 8 page 41) and elemental data, see page 32, and although conclusive proof was not obtained, one can postulate the method of formation of such a compound by considering the following series of reactions between phenylpropiolic acid and arsenic trichloride.



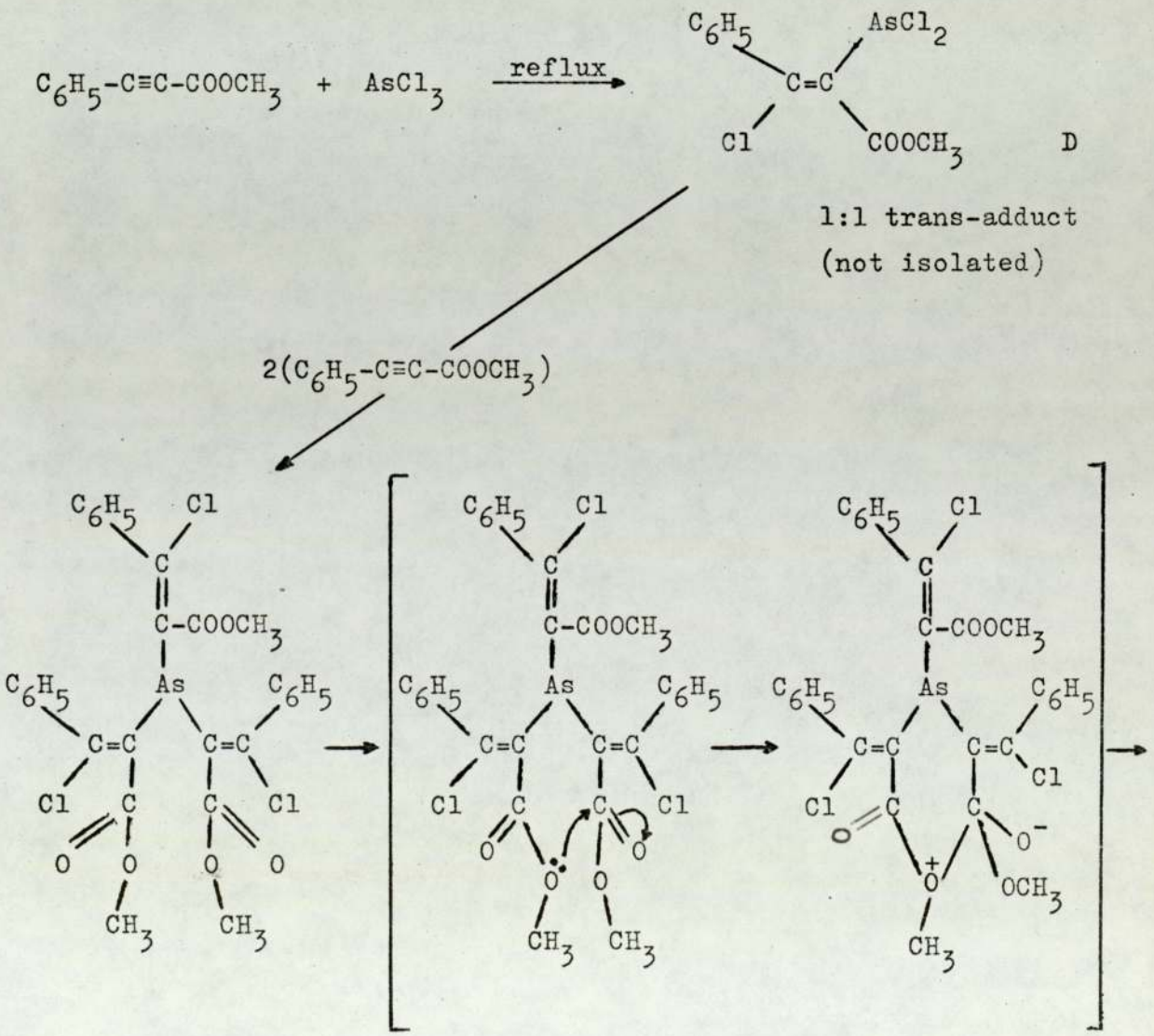
It is reasonable to assume that the acid reacts initially with the arsenic trichloride to form the 1:1-addition product, (A), and as the above reaction scheme shows, this subsequently reacts with more phenylpropiolic acid to give the trisubstituted acid derivative, (B), which then cyclises to form the anhydride, (C). The other possible

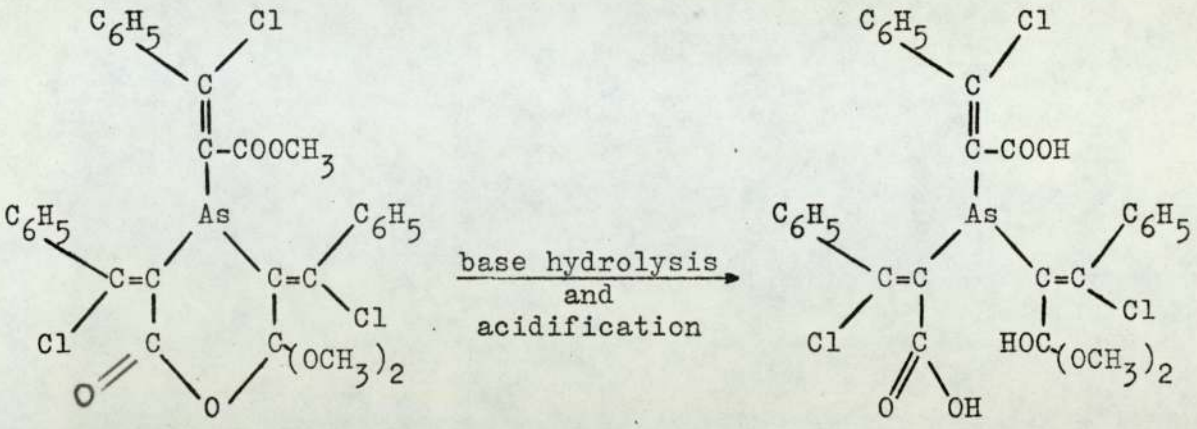
reaction is that of phenylacetylene, formed by decarboxylation of the phenylpropiolic acid, with arsenic trichloride, but as no β-chlorostyryldichloroarsine was isolated, this side-reaction is probably insignificant.

To eliminate the possibility of decarboxylation, the ester, methyl phenylpropiolate, was treated with arsenic trichloride as described on page 25. Here again, the product was found to be insoluble in most organic solvents except in boiling benzene. Attempts to obtain nuclear magnetic resonance spectra at elevated temperatures, (60-70°), using benzene as solvent, failed to give satisfactory high resolution integrated spectra because the concentrations of these solutions were too low. Only the infrared data, see Table 10 page 43, indicating possibly a lactone, and a complex mass spectrum, Table 21 page 56, showing no molecular ion peak at 660 mass units, but several smaller fragments probably arising from the proposed structure, (E) page 101, were obtained for the adduct which, when recrystallised from boiling benzene, had a melting point of 272-4°C.

The suspected lactone was hydrolysed as described on page 33 and the product, m.p. 252 - 4°, which was recrystallised from boiling water, readily effervesced with aqueous sodium bicarbonate. Its infrared spectrum, Table 11 page 44, was characteristic of a carboxylic acid with the strong broad carbonyl absorption at 1700cm^{-1} together with the absorptions in the 3400 - 2600cm^{-1} region due to hydroxyl groups. The bands at 1160cm^{-1} and 1140cm^{-1} are probably due to the C-C-O group of a tertiary alcohol or the C-O-C group of an aliphatic ether and the similarity of the spectrum to that of the hydrolysed anhydride, Table 9 page 42,

suggests that these hydrolysed materials have very similar structures. The mass spectrum, Table 23 page 59, showed no molecular ion peak at 664 mass units, but a large number of small fragments which could arise from the fragmentation of the proposed structure, (F) page 101. Although the elemental analysis, page 32, did not correspond closely with the calculated values of the proposed structure, the following reaction scheme between methyl phenylpropiolate and arsenic trichloride may be a possible mechanism for the formation of the complex lactone (E) via the 1:1 adduct (D).





E - lactone m.p. 272-4°C.

F - m.p. 252-4°C.

It is clear from the experimental data that the reactions of arsenic trichloride with phenylpropiolic acid and methyl phenylpropiolate, do not stop at the simple 1:1 trans-addition products but lead to the formation of complex insoluble cyclic adducts. Further work is necessary to establish the exact nature of the proposed structures of these materials.

3A (iii)

The Reaction of the β-Chlorostyryldichloroarsines with Phenylmagnesium Bromide

One molecule of β-chlorostyryldichloroarsine reacts with two molecules of phenylmagnesium bromide to give one molecule of β-chlorostyryldiphenylarsine as represented by the following chemical equation:-

$$RC(Cl) = CHAsCl_2 + 2C_6H_5MgBr \longrightarrow RC(Cl) = CHAs(C_6H_5)_2 + 2MgClBr$$

β-chlorostyryldiphenylarsine

where R = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4.

The exothermic reactions were carried out in diethyl ether under anhydrous conditions and the stable white crystalline β-chlorostyryldiphenylarsines were readily recrystallised from alcohol to give sharp melting points, (Table 1 page 30), and in good yields, (page 20). The sharp melting points and thin layer chromatography confirmed that the products were single substances.

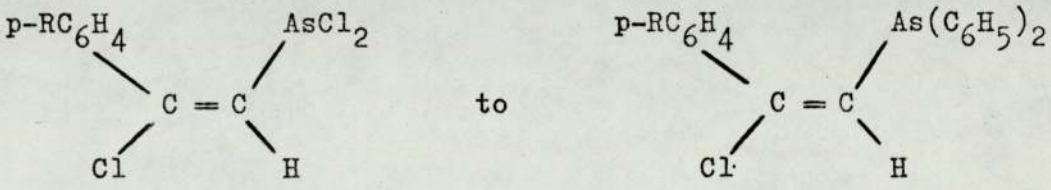
The p-methoxy-compound was a viscous liquid which decomposed slightly when vacuum distilled but the infrared, Table 7 page 40, and nuclear magnetic resonance spectrum, Table 16 page 49, and mass spectral data, Table 18 page 51, confirmed the structure of the compound as β-chloro-p-methoxystyryldiphenylarsine. As expected from the structure of the dichloroarsines, the vinylic chlorine was unreactive towards the phenylmagnesium bromide and spectroscopic measurements on the reaction mixtures confirmed the absence of any trisubstituted styrylarsine as a by-product.

The β-chlorostyryldiphenylarsine derivatives of p-nitrophenylacetylene, phenylpropiolic acid and methyl phenylpropiolate could not be prepared because these compounds did not react with

arsenic trichloride to form the β-chlorostyryldichloroarsine adduct.

The infrared spectra of the β-chlorostyryldiphenylarsines were not of great diagnostic value and the observed frequencies could not be assigned with certainty due to the absence of data published in the current literature. For instance, the expected carbon-carbon double bond frequency is usually in the 1600-1700cm^{-1} region, but due to the degree of conjugation of the molecule, the β-chlorostyryldichloroarsines and β-chlorostyryldiphenylarsines probably have this absorption lowered to 1560 ± 9cm^{-1} whilst that for the carbon-chlorine bond (vinylic) is probably around the 890cm^{-1} region. No attempt was made to assign the absorption frequency due to the carbon-arsenic bond because the low frequency region, 590-620cm^{-1}, contained a number of weak ill-defined bands.

The nuclear magnetic resonance spectra of the β-chlorostyryldiphenylarsines were of greater diagnostic value because the expected proton shift due to enviromental changes of the molecule from,



did produce a strong singlet absorption at $\tau(CCl_4)$ = 3.1(ca) due to the shielding effects of the aromatic nuclei on the arsenic atom. The aromatic complex, centered around $\tau(CCl_4)$ = 2.7, had not altered its position significantly and in all cases the correct ratio of aromatic to vinylic protons was obtained, see Tables 12-16 pages 45-49.

3A (iv)

The Reduction of the β-Chlorostyryldiphenylarsines

The initial attempts to reduce the β-chlorostyryldiphenylarsines with lithium aluminium hydride in diethyl ether did not produce the required product even though the experiments were carried out for a reasonable length of time (ca. 16 hours) in refluxing solvent. This difficulty was overcome by adopting J.E. Johnson's method which employed solvents such as tetrahydrofuran and a mixture of lithium aluminium hydride and lithium hydride.[29] The use of tetrahydrofuran permits a higher working temperature and it is also a suitable reaction medium because it is a good solvent for the reducing agents.[38] Johnson found that not all four hydrogen atoms showed the same reactivity towards alkyl halides and that the reaction probably proceeded in at least two steps as represented by the equations:-

$$LiAlH_4 + RX \longrightarrow RH + LiX + AlH_3$$

$$AlH_3 + 3RX \longrightarrow 3RH + AlX_3$$

Of these steps, he assumed the first to be more rapid than the second and that when the molar ratio of the reagent to the active halide was greater than one, the reactions proceeded rapidly and to completion, but when the ratio was about 0.25, the calculated value to replace all four hydrogens, the reactions were sluggish. The stepwise course of the reaction would account for the fact that more than one hydrogen per mole of the reagent is consumed and that all four hydrogens are not replaced in a reasonable time.

Aluminium hydride reacts with lithium hydride in ether to produce lithium aluminium hydride,[39] and it was considered by Johnson that reduction by means of lithium hydride would be possible under such conditions. This he found to be correct and the

reaction proceeded rapidly to completion, and under these conditions the reaction may be represented as:-

$$RX + LiH \xrightarrow{LiAlH_4} RH + LiX$$

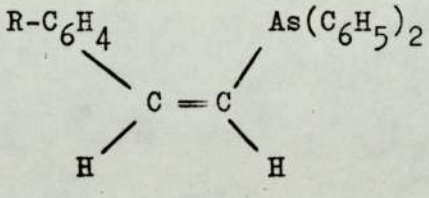
The conclusion that lithium aluminium hydride acts as a hydrogen carrier was shown by the fact that no reaction occurred with lithium hydride alone.

The experimental work on the reduction of the β-chlorostyryldiphenylarsines also confirmed that no reaction occurs with lithium hydride and the optimum molar ratios of β-chlorostyryldiphenylarsine to lithium aluminium hydride to lithium hydride was 1:0.87:1.56.

The reduction of the vinylic chloride in dry tetrahydrofuran was carried out at a lower temperature of 45-50°C because it was feared that refluxing conditions would cleave the carbon-arsenic bond with the formation of undesirable side products. Under such anhydrous conditions, a reaction time of seventeen hours gave the most satisfactory yields of 60-70% of pure cis-(β-styryl)-diphenylarsine and no trans-isomer as evident from the sharp melting points and thin layer chromatography. The p-methoxy-compound was a viscous yellow liquid which was found to decompose slightly when vacuum distilled and purification by column chromatography using silica gel or neutral alumina was also unsatisfactory. The infrared and nuclear magnetic resonance data on the unpurified compound showed that the material was predominantly β-(cis-p-methoxystyryl)diphenylarsine. The mass spectrum, Table 19 page 52, showed a molecular ion peak at 362 mass units and the mass-to-charge ratios of the fragments were in good agreement with

the proposed structure. The infrared spectra of these compounds were not of great diagnostic value although the absence of the absorption in the 890cm^{-1} region, which is probably due to the carbon-chlorine bond, was a convenient method of following the reduction to completion. In all cases, the absorption position of the carbon-carbon double bond was assumed to be in the 1562cm^{-1} region due to the enhanced degree of conjugation of the molecule and no attempt was made to identify the carbon-arsenic absorption frequency.

Nuclear magnetic resonance data was conclusive in assigning the structure of the molecule as cis-(β-styryl)diphenylarsine,



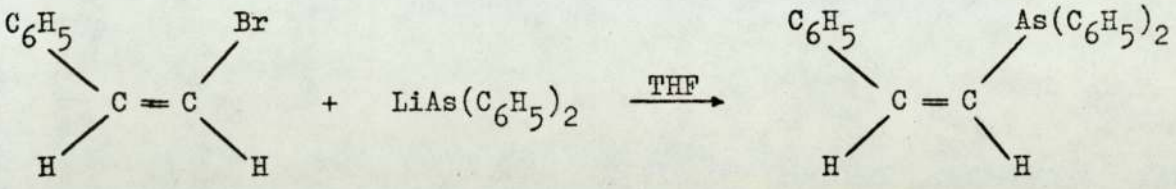
R = H, CH_3, Cl or CH_3O. (J = 12 cps)

and the results were in agreement with Aguiar, et al.[30] The nuclear magnetic resonance spectrum showed a phenyl complex at τ = 2.6 and one-half of the vinyl proton signal at τ = 3.35 (J = 12 cps). The other half of this signal was hidden under the phenyl complex as indicated by their integrated relative ratios. The coupling constants for vinyl proton signals found by Cullen[40] for $(CH_3)_2AsCH=CHCF_3$ were $J_{(cis)}$ = 13 cps and $J_{(trans)}$ = 18 cps, and comparison of these values with the coupling constant (J = 12 cps) found, confirmed the material to be the cis-isomer.

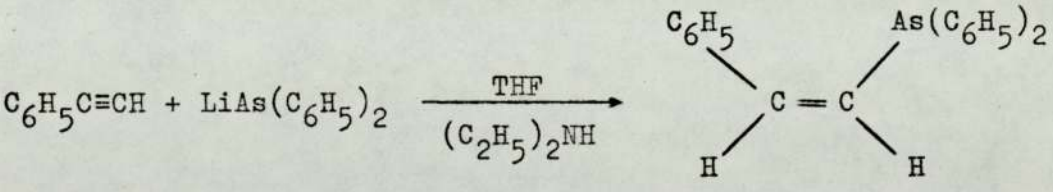
When the cis-(β-styryl)diphenylarsine was treated with n-butyllithium or phosphorus trichloride in tetrahydrofuran, no isomerisation was found to occur and these observations are in

agreement with reports in the literature.[30]

It is interesting to note that Aguiar prepared his material by treating lithium diphenylarsenide with cis-β-bromostyrene in tetrahydrofuran,[41]

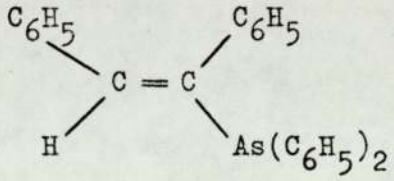


or by treating phenylacetylene with a solution of lithium diphenylarsenide in the presence of either a primary or secondary amine,



and that lithium diphenylarsenide adds to alkynes to give stereochemically pure vinylarsines.

The stereochemistry of addition was found to be controlled by the addition of amines. Diphenylacetylene in the presence of diethylamine reacted with lithium diphenylarsenide in tetrahydrofuran to give cis-1,2-diphenylvinyldiphenylarsine,



whilst in the presence of n-butylamine, the trans-compound was obtained. Nuclear magnetic resonance spectroscopy and dipole moment measurements were used to elucidate the structure of the compounds produced by this novel method.

Aguiar's work has been of valuable assistance in establishing

the stereochemistry of the addition products of arsenic trichloride to the phenylacetylenes and it is reassuring to know that the same conclusions have been reached about the compounds prepared by two different methods.

SECTION 3B
REACTION KINETICS

3B (i)
Volumetric Method

The hydrolysis of β-chlorostyryldichloroarsine with water was expected to produce two molecules of hydrochloric acid according to the following equation and by analogy with Lewisite I[42].

$$C_6H_5C(Cl) = CHAsCl_2 + 2H_2O \underset{\text{fast}}{\rightleftharpoons} C_6H_5C(Cl) = CHAs(OH)_2 + 2HCl$$

$$C_6H_5C(Cl) = CHAs(OH)_2 \underset{\text{slow}}{\rightleftharpoons} H_2O + C_6H_5C(Cl) = CHAsO$$

$$\Big\Downarrow \text{slow}$$

$$(C_6H_5C(Cl) = CHAsO)_n$$

polymeric material

β-chlorostyrylarsinoxide.

However, in the attempt to determine the molecular weight of the β-chlorostyryldichloroarsine by titrating the liberated acid with dilute sodium hydroxide, it was found that the values obtained were not consistent and were generally between forty to fifty percent lower than the theoretical value of 283.4. Similar results were obtained when the material was hydrolysed with excess dilute sodium hydroxide and the excess base titrated with dilute hydrochloric acid using phenolphthalein as indicator.

When the β-chlorostyryldichloroarsine was treated with an excess of $\frac{N}{5}$ silver nitrate solution and the excess back titrated with aqueous $\frac{N}{10}$ sodium chloride using potassium dichromate/ potassium chromate as indicator, (Mohr's Method)[43], inconsistent results were also obtained but this time varying between seventy to eighty percent of the theoretical value. In this case some difficulty was experienced in obtaining a clear 'end-point' even when the solution was vigorously stirred to disperse the precipitate during the titration.

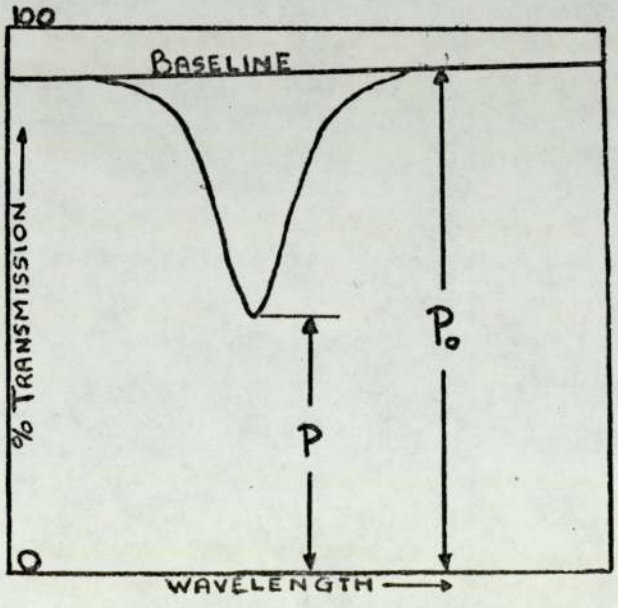
From the results of the preliminary volumetric work, it was concluded that β-chlorostyryldichloroarsine probably did not hydrolyse according to the equations and that the second chlorine atom is not readily hydrolysed once the first chlorine atom has reacted. Its reaction with two moles of silver nitrate appeared to be quantitative but the method was not accurate enough to enable the reaction of phenylacetylene and arsenic trichloride to be studied. No attempt was made to determine the nature of the products of the partially hydrolysed β-chlorostyryldichloro-arsine although the formation of a sticky insoluble material suggested that probably some polymeric substance was formed during the aqueous hydrolysis of β-chlorostyryldichloroarsine.

Sampling hot reaction mixtures of arylacetylene and arsenic trichloride at temperatures between 80-110°C was extremely difficult because of the volatile nature of arsenic trichloride and so for these reasons, it was decided that the reaction kinetics should be spectroscopically studied by measuring the decrease in absorbance of the carbon-carbon triple bond of the arylacetylene in the infrared region.

3B (ii)
Spectroscopic Method

The choice of a slow scan speed was necessary to obtain a reproducible measurement of the absorption band in the 2100cm^{-1} region and as the carbon-carbon triple bond absorption was sharp a narrow slit width was used because a large slit setting would have decreased the apparent absorption as the slits opened.

The analytical wavelength chosen was free from neighbouring absorptions and its position was outside the spectral region where water vapour and carbon dioxide absorb. This also made the measurement of absorbance relatively simple as the baseline from which the value of Po (incident radiation) and P (transmitted radiation) were measured was very near the apparent 100% transmission point at the analytical wavelength. The baseline method of measuring absorbance is best illustrated by the following diagram:-



where,

Absorbance, $A = \log \left(\frac{Po}{P}\right)$

and since a log scale chart paper was used, the values of Po and P were read directly off the trace. The advantages of the baseline method are,

a) Cell absorptions and other absorptions are minimised

b) It shows unexpected impurities, and

c) The method can be used to detect small quantities of material.

As was discussed on page 60 the pathlength of the cell was measured by the interference fringe pattern that resulted when the empty cell was scanned through a fixed infrared region ($2500cm^{-1}$ to $800cm^{-1}$), and the fringes appeared as a series of maxima of gradually increasing spacing from short to long wavelengths. If the salt plates had not been optically flat or the cell windows not parallel, a complete absence of fringes would have resulted.

The absorptivity value, ε, varies with the instrumental conditions and its observed value with an infrared spectrophotometer is determined by the band of wavelengths that the instrument passes at the analytical wavelength which in turn is related to the resolution used for analysis. This constant, ε, is also dependent on the bandwidth of the absorbing material as a large bandwidth will give an average of absorptivity constants nearer the true value whilst a narrow absorption band, approaching the width of the band of wavelengths passed by the slits, will show a much lower value. Thus, it is difficult to measure the true absorbance (A) of a band because of the finite width of the band of wavelengths that an infrared spectrometer must pass in order to operate properly and the absorptivity values quoted for the arylacetylenes in arsenic trichloride are best called 'apparent absorptivity values' under the given experimental conditions.

The rate of reaction between arsenic trichloride and phenylacetylene at $80^{o}C$. was determined on three separate experiments to check the reproducibility of the instrument's performance and each measurement gave the same rate curve with only a three to five percent variation in absorbance values up

to fifty to sixty percent conversion. Beyond this point, the carbon-carbon triple bond absorption became progressively distorted and the baseline 'noisy' probably due to the partial precipitation of the β-chlorostyryldichloroarsine adduct. This effect was very noticable for the reaction of p-chlorophenylacetylene at 90°C. when it was observed that a precipitate formed after about thirty percent reaction and the experiment was terminated before fifty percent conversion because the reaction mixture solidified. The effect of precipitation of solid material caused a rapid decrease in absorbance and hence an apparent increase in the rate of reaction resulting in the abnormal values for the order (n) and half-life (t0.5) for the reaction. See Table 28 page 81.

At a higher temperature of 110°C, no precipitate was observed but the reaction mixture turned dark brown in colour at about forty percent conversion probably because of some undesirable side reactions such as polymerisation of the adduct. If the arylacetylene had polymerised, there would have been an increase in the rate of reaction as shown by a corresponding increase of slope of the rate curve but as this was not observed, some other reaction occurred when the reaction had reached about fifty percent conversion. As it has been shown that the reaction is not reversible under the experimental conditions, page 35, it is reasonable to assume that the premature levelling off of the rate curve at about fifty percent conversion is due to changes in the optical properties of the reaction mixture caused by the increased concentration of the dichloroarsine adduct. Other probable reasons are given on page 115 in connection with the integrated second order equation. Hence, the data for the calculation of

the rate constant was obtained from absorbance values corresponding to a reaction up to about fifty percent conversion.

Note The use of inhibitors, e.g. hydroquinone, to prevent polymerisation reactions, was not possible because arsenic trichloride was found to react with them and this would have complicated the reactions under study.

The choice of reaction temperatures was mainly one of convenience because of the differences in reactivity of the arylacetylenes towards arsenic trichloride. The temperature difference for a given reaction was only ten degrees and although a larger temperature difference and several more experiments would have been preferred, it was found that difficulties arose due to the increased rate of reaction causing a rapid darkening of the reaction mixtures when higher temperatures were used. This effect decreased the sensitivity of the instrument and as the settings had to remain constant, the amount of transmitted radiation was reduced beyond which reliable readings could be taken.

Above temperatures of 110°C, the windows of the cell became sensitive to pressure changes when closing the inlet and outlet ports resulting in the fracture of expensive sodium chloride plates and contamination by poisonous arsenic trichloride vapours. Despite this temperature limitation, the values for the Energy of Activation and Hammett ρ parameter for the reaction series are what one might expect for a second order electrophilic reaction. Arranged in decreasing order of reactivity, one can say that p-methylphenylacetylene is more reactive than phenylacetylene than p-chlorophenylacetylene towards the electrophilic addition

of arsenic trichloride.

Generally, from the observations of the organic syntheses and the kinetic data, the reactivity of the para-substituted arylacetylenes depends on the substituent group and when arranged in the following order of decreasing activity,

$$CH_3O > CH_3 > H > Cl > NO_2$$

is in agreement with the fact that the electron donating ability of the groups decrease from left to right in the series.

The difference in the observed and calculated values for the half-life (t0.5) for the reactions is due to the fact that the observed order of reaction is not exactly two, whereas the formula used to calculate the half-life of a second order reaction depends on the fact that n = 2.[44] However, the results in Table 28 page 81 clearly indicated that the reaction of the substituted arylacetylenes with arsenic trichloride is of the second order and in good agreement with the value obtained by the integrated second order plot of time vs $\frac{1}{\text{concentration}}$ for phenylacetylene and arsenic trichloride at 90°C, see Table 28, page 88. The integrated second order equation, Fig. 8 page 89 shows considerable deviation from linearity from about fifty percent conversion of the arylacetylene to the β-chlorostyrylarsine adduct. This is probably due to the fact that undesirable side reactions, like polymerisation, cause the solution to darken in colour and partially precipitate either the polymeric material or the reaction product. Fine solid particles in the reaction mixture would alter the infrared transmission properties of the solution and increase

the apparent absorbance values because of the reduced amount of radiation falling on the detector. Hence, absorbance values after fifty percent conversion are probably unreliable.

SECTION 3C
THE REACTION MECHANISM

3C (i)
Introduction

The stereochemistry of electrophilic addition to acetylenes is still somewhat confusing and was thought to be stereospecifically a trans-process.[45] Recent studies[46] have shown that this theory is incorrect and that certain additions are not stereospecific and yield a mixture of cis- and trans-adducts.[47]

Many of the observed variations in the steric course of additions can be understood in terms of modern mechanistic concepts and hence a brief account of the mechanisms involved will now be given.

Carbonium ion Intermediate

Electrophilic additions to double or triple bonds that do not give stereospecific reaction products can be readily understood if addition occurred via carbonium ion intermediates that are formed in polar media.[48]

The rate-determining step of the reaction depends on how fast this species collapses to form the products, and mechanisms of this type are classified as Ad_{E2} (addition, electrophilic, bimolecular) using Ingolds'[49] notation:-

$$A + XY \xrightarrow{slow} AX^+ + Y^- \xrightarrow{fast} AXY$$

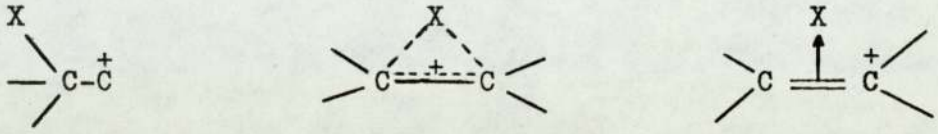
Ad_{E2} MECHANISM

A = alkyne or alkene

XY = reagent.

Addition via this mechanism can lead to either cis- or trans-adducts

depending upon the structure of the intermediate AX^+. For convenience, consider the following carbonium ions derived from alkenes:-



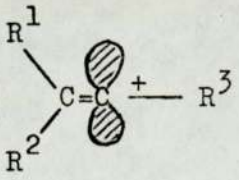
I II III

Cation I, will give a mixture of cis- and trans-adducts because of its open structure[50] but ion-pairing can cause formation of a cis-adduct and electronic and steric effects may result in attack on one or the other side of the carbonium p-orbital.

The bridged structure or onium structure II[51] was called a π-complex III by Dewar[52] and is opened stereospecifically to a trans-adduct.[51]

Fahey and Lee[45] have shown that the electrophilic additions to triple bonds are, in general, also stereospecific and that these reactions occur via linear vinyl cations.

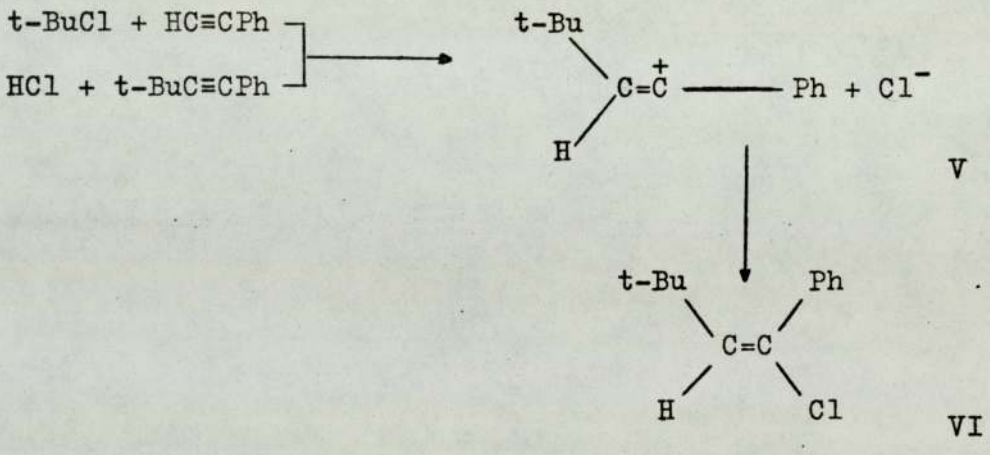
Linear vinyl cations, IV:-



have a planar geometry with the empty p-orbital lying in the plane of the molecule[53] and attack of a nucleophile on the positive centre should occur in the plane and be sensitive to the size and electronic character of the bonded groups to the adjacent carbon atom.

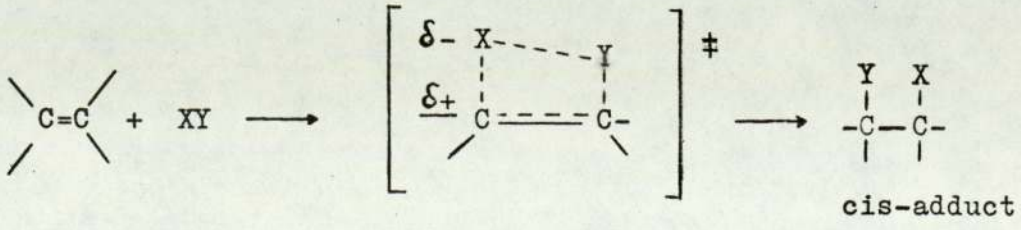
Maroni and Modena[54] have clear evidence that the relative size of the β-groups determines the direction of attack of the

nucleophile and therefore the configuration of the products. The addition of t-butyl chloride to phenylacetylene and of hydrogen chloride to t-butylphenylacetylene in the presence of a Lewis acid ($ZnCl_2$) gave only (E)1-chloro-3,3,dimethyl-1-phenylbutene VI and since electrophilic addition to phenylacetylenes occurs via a linear cation[53] it was assumed that both reactions proceeded via the formation of the same cationic intermediate V which gave the adduct by reacting with the chloride ion.



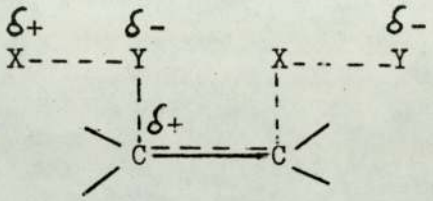
Cyclic Intermediate

The formation of a cyclic intermediate leads exclusively to a cis-adduct and the rate determining step is bond formation between the alkene or alkyne and reagent, (XY). Such transition states are probably formed in non-radical gas-phase reactions and have been described in terms of an electrostatic model by Benson.[55]

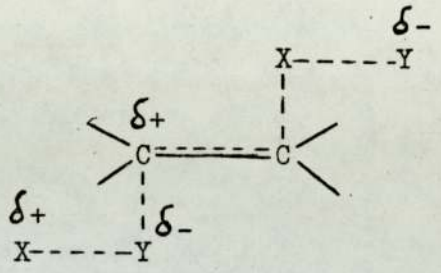


Termolecular Transition State

This type of mechanism is termolecular because the transition state is composed of three reactants and is denoted as an Ad_E3 mechanism.[49] Either cis-, via transition state VII or trans-, via VIII, adducts can result and here again it is assumed that the C-X and C-Y bonds are simultaneously formed.

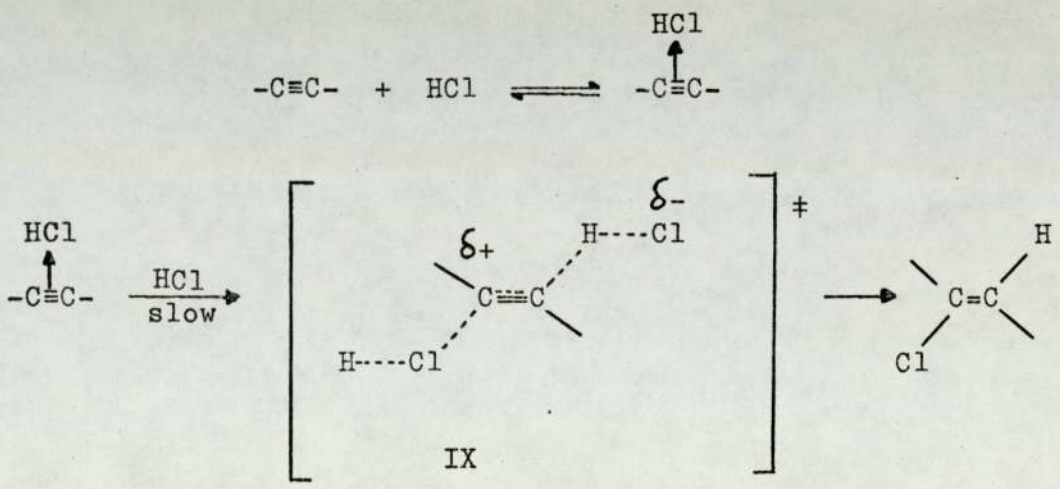


VII



VIII

Fahey and Lee studied the hydrochlorination of 3-hexyne in acetic acid and have shown that trans-addition occurred via transition state VIII. Their mechanism can be formulated as follows:-



Alkynes and other unsaturated hydrocarbons are known to form weak complexes with hydrogen chloride[56] and as the first step of this reaction is probably rapid and reversible attack by hydrogen chloride via the transition state IX leads to a trans-adduct.

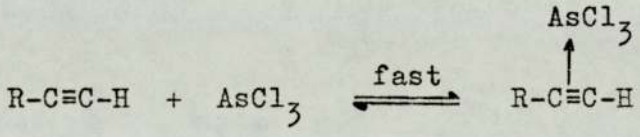
Their results provide no insight into the steps which precede the formation of IX and provide no knowledge as to what extent C-H bond formation precedes the formation of the transition state.

3C (ii)

Addition of Arsenic Trichloride to Phenylacetylenes

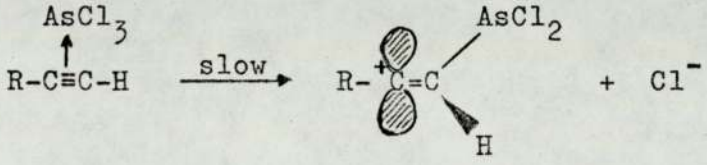
Very little is known about either the stereochemistry or the mechanism of the addition of the halides of metalloids to acetylenes and the present study was carried out to gain some insight into the mechanism of addition of arsenic trichloride to phenylacetylenes in the absence of solvent and catalyst.

The experimental results show that trans-adducts are formed by a bimolecular electrophilic process, possibly via a π-complex and linear vinyl cation, for phenylacetylene, p-methyl and p-chloro-phenylacetylenes. p-methoxyphenylacetylene was found to react too rapidly with arsenic trichloride at room temperature for the reaction kinetics to be studied.



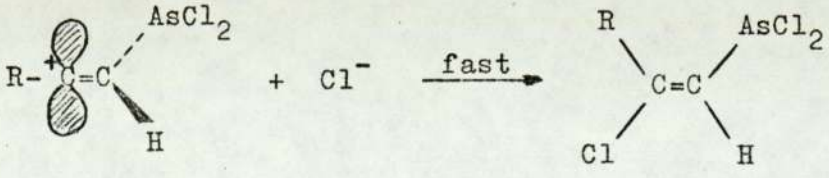
π-complex

X



Linear vinyl cation transition state

XI



trans-adduct

XII

The infrared spectrum of phenylacetylene shows the characteristic -C≡C- absorption band at 2109cm^{-1} whilst an equimolar mixture of phenylacetylene and arsenic trichloride shows the same absorption at a lower frequency of 2105cm^{-1}. The addition of arsenic trichloride lowers the frequency of this band by approximately 4cm^{-1}, possibly due to the formation of a weak complex (I) by a charge transfer mechanism, the phenylacetylene acting as an electron donor and the arsenic trichloride as an electron acceptor.

Acetylenes are known to form weak complexes with hydrochloric acid[56] and the work of J. Gerbier and V. Lorenzelli[57] has shown that antimony trichloride, $SbCl_3$, also forms complexes with phenylacetylenes. Gerbier and Lorenzelli observed frequency shifts in the order of 5cm^{-1} for phenylacetylene with antimony trichloride and iodine and concluded that these molecules were attached to the triple bond.

The first step in the postulated reaction mechanism is probably the rapid and reversible formation of the π-complex (X), page 122, followed by the slow rate determining step leading to the linear vinyl cation transition state (XI) with a high positive charge on the benzylic carbon in accordance with the calculated negative ρ value from the Hammett equation (see page 87). The linear vinyl cation would have a planar geometry with the empty p-orbital lying in the plane of the molecule and rapid nucleophilic attack by the chloride ion on the positive centre would occur in this plane from the least hindered side leading to the trans-adduct (XII). The rate determining step is the formation of the linear vinyl cation (XI) and is proportional to the concentrations of arylacetylene and arsenic trichloride. The

rate data for the phenylacetylenes correlate with the fact that the rate of reaction increases with the electron donating capacity of the para-substituent ($CH_3O > CH_3 > H > Cl > NO_2$) and the average ρ value of -4.42 is of the right order for electrophilic additions and in good agreement with a value -4.79 obtained by D.S. Noyce[48] for the acid-catalysed hydration of phenylpropiolic acids and phenylacetylenes.

The present kinetic study does not clarify with certainty, the course of the reaction leading to the trans-adduct, but all the evidence suggests that such a mechanism is likely at the present time and further studies are needed to confirm this aspect of organo-arsenic chemistry. The kinetics of the reaction between p-nitrophenylacetylene and arsenic trichloride was not studied because there was apparently little or no reaction within the temperature range suitable for kinetic study. This is in agreement with the theory that strong electron withdrawing groups in the para-position of the aromatic ring will retard the electrophilic addition of arsenic trichloride to the para-substituted arylacetylenes.

For similar reasons, the reaction kinetics of the addition of arsenic trichloride to phenylpropiolic acid and methyl phenylpropiolate were not studied because of the high reaction temperatures required to initiate a suitable rate of reaction. As mentioned in section 3A (ii) page 101 the expected 1:1 trans-adducts were not isolated but it is reasonable to assume that product formation is probably also via a transition state preceeded by a similar π-complex (I).

The reaction scheme on page 98 shows that a mixture of products is possible when phenylpropiolic acid reacts with arsenic trichloride but the only product isolated was possibly a cyclic anhydride of uncertain structure. Similarly, methyl phenylpropiolate and arsenic trichloride did not give the expected 1:1 adduct and the only product appeared to be a high melting solid whose infrared spectrum and chemical properties indicated that it was possibly a lactone. The reaction scheme on page 100 shows a possible route to its formation. It is obvious that further research must be carried out to clarify this aspect of the electrophilic addition of arsenic trichloride to acetylenic acids and esters.

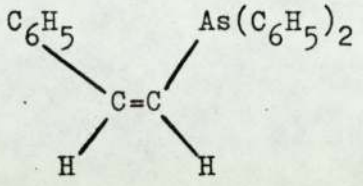
3C (iii)
Determination of Configuration

The configuration of the β-chlorostyryldichloroarsines was based on the preparation and nuclear magnetic resonance data of two derivatives. The first derivative was the diphenyl compound prepared by treating the adduct with an excess of phenylmagnesium bromide as described in section 1C page 26.

The product isolated had a sharp melting point and the nuclear magnetic spectrum and elemental analysis confirmed that the chlorine atoms attached to arsenic had been replaced by aromatic groups. No isomerisation had occurred during the reaction because only one product was isolated as evident from its sharp melting point and thin layer chromatogram. The shielding effect caused by the phenyl groups [58,31] on the arsenic caused the vinyl proton signal to move upfield to τ =3.0-3.3 and away from under tne phenyl complex. This observation confirmed the theory that the vinyl proton of the adduct was deshielded by the chlorine atoms on the arsenic and that the signal was probably hidden under the phenyl complex at τ =2.5-2.7. These observations were still insufficient evidence to determine the configuration of the diphenyl derivative and hence that of the β-chlorostyryldichloro-arsine adduct.

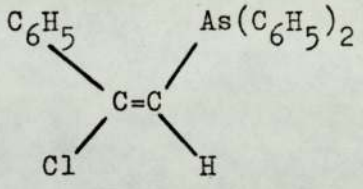
Reduction of the β-chlorostyryldiphenylarsine derivative with a mixture of lithium aluminium hydride and lithium hydride gave only a single substance whose melting point and nuclear magnetic resonance spectrum page 45 was identical to the cis-(β-styryl)-diphenylarsine prepared by Agiuar. The structure of this compound

may be written as:-

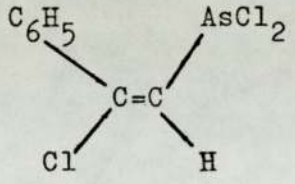


with J = 12 cps for cis-protons.

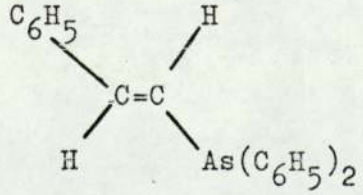
Thus, since no isomerisation occurred during the reduction reaction the configuration of the β-chlorostyryldiphenylarsine must be:-



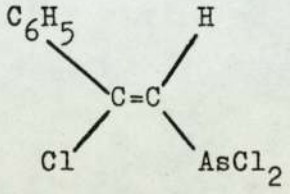
and that of the α, β-adduct, β-chlorostyryldichloroarsine,



The data obtained for p-methyl, p-chloro and p-methoxyphenylacetylenes also confirm an electrophilic trans-addition mechanism for the uncatalysed addition of arsenic trichloride to phenylacetylenes. Had the reaction occurred via a cis-addition mechanism the product from the lithium aluminium hydride - lithium hydride reduction would have been trans-(β-styryl)diphenylarsine,



with J = 17 cps, see section 1F page 34, and the β-chlorostyryl-dichloroarsine adduct would have had the following configuration:-



The data obtained shows that addition is not by a cis-mechanism.

CONCLUSIONS

The most important feature of the present study is the demonstration of a second order trans-electrophilic mechanism for the addition of arsenic trichloride to phenylacetylenes. Thus, the phenylacetylenes give β-chlorostyryldichloroarsines except p-nitrophenylacetylene which forms an insoluble black polymeric material, and good yields can be obtained if sufficient care is taken to exclude moisture because these compounds are very hygroscopic and reactive. The synthetic work affords a novel and convenient route for the preparation of a variety of substituted styrylarsines and the spectroscopic data provides useful diagnostic information for further research into organo-arsenic chemistry. The use of lithium aluminium hydride - lithium hydride mixtures to reduce the vinylic halogen of the β-chlorostyryldiphenylarsines is novel because many researches[59,60], have failed to reduce vinylic halogens using lithium aluminium hydride or lithium hydride. The infrared band in the region of 890cm^{-1} appears to be characteristic of the β-chlorostyrylarsines possibly due to the absorption frequency of the carbon-chlorine bond. The deshielding effect of the chlorine atom and the shielding effect of the aromatic ring on the vinyl proton, has been conclusively demonstrated in the nuclear magnetic resonance spectra of these compounds. The use of spectroscopy has not only been useful as a means of identification of unknown compounds but also as a method of studying the kinetics of a reaction that involves both volatile and toxic compounds.

Further research on the reaction mechanism is necessary in order to establish the nature of the π-complex and transition state. The complete identification of the complex adducts of arsenic trichloride with the acetylenic acids and esters would help to extend the limited work being carried out on this aspect of arsenic chemistry.

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