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Sulphene Formation: New Routes And Mechanisms

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SULPHENE FORMATION

NEW ROUTES AND MECHANISMS

by

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ABSTRACT

Sulphenes are believed to be intermediates in the base promoted dehydrochlorination of sulphonyl chlorides bearing at least one alpha-hydrogen atom. This reaction is well known and the mechanism has been studied. In this thesis two new routes to sulphene are developed and their mechanisms are explored.

Part I presents an investigation of the fragmentation of the alpha-chloroethanesulphinate anion. The intermediacy of methylsulphene is shown by trapping experiments. Rate measurements and labelling experiments show the reaction to be a simple first order decomposition of the sulphinate anion.

Part II presents a study of the base promoted elimination reactions of aryl arylmethanesulphonates. The intermediacy of a sulphene is demonstrated by trapping experiments. The intermediacy of a carbanion is shown by exchange experiments. Kinetic studies include correlations of the exchange and elimination rates with sigma constants and proton chemical shifts, the demonstration of specific and general base catalysis and an investigation of the effect of the conjugate acid of the base on the rates of elimination and exchange.

All the results in part II are fitted to an Elcb mechanism. The arylmethanesulphonate esters of phenols having a pK_a above 5.45 form arylsulphene via a reversible Elcb mechanism and those of phenols having a pKa less than 5.45 via an irreversible Elcb mechanism.

ACKNOWLEDGEMENTS

Many people have contributed directly and indirectly to this thesis and the work that it contains.

I thank Dr. J. F. King for providing many of the ideas incorporated into this thesis and for his guidance throughout the project. I would also like to thank Dr. J. P. Guthrie for his advice on the work contained in the second part of the thesis.

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PART I

THE FORMATION OF METHYLSULPHENE from the ALPHA-CHLOROETHANESULPHINATE ANION

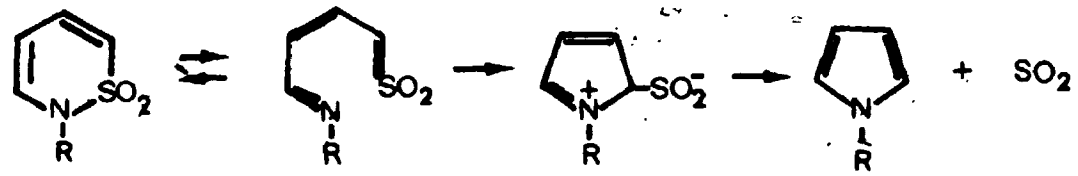
A. INTRODUCTION

It is "normal" for sulphene to react with a nucleophile to give a sulphonate derivative by attack of the nucleophile at sulphur(1). However in several instances "abnormal" nucleophilic attack on a sulphene giving a sulphinate, or a derivative thereof, has been proposed.

For example King and Durst(2) proposed the nucleophilic attack of chloride ion on the carbon of phenylsulphene

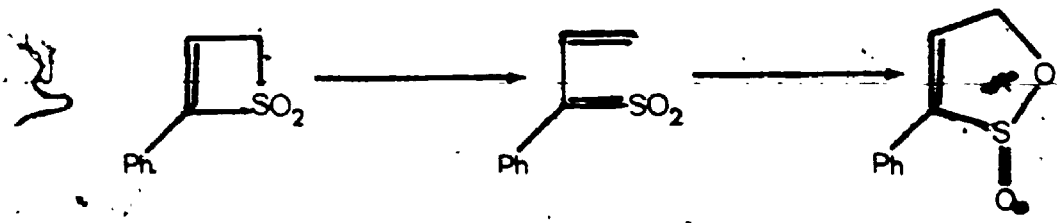
$$PhCH{=}SO_2 + Cl^- \longrightarrow PhCHClSO_2^-$$

to account for the formation of thiobenzoyl chloride S-oxide in the reaction of triethylamine with phenylmethanesulphonyl chloride in cyclohexane. They(3) also proposed an abnormal nucleophilic attack on the carbon atom of a sulphene giving a sulphinate in the photolysis of unsaturated sultams to give pyrroles.

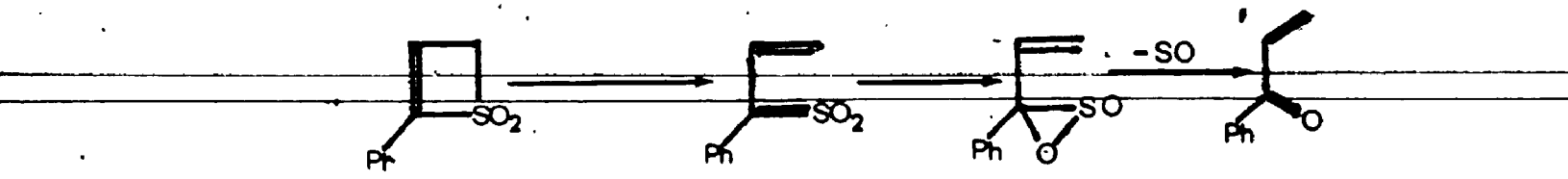


Normal attack at the sulphur would regenerate the starting material.

Abnormal addition of a double bond to the oxygen of sulphene to give sulphinic acid derivatives has been noted in the thermal reactions of thietan derivatives(4). For example the flash thermolysis of 2-phenylthiete 1,1-dioxide at 600° gave the sultine.



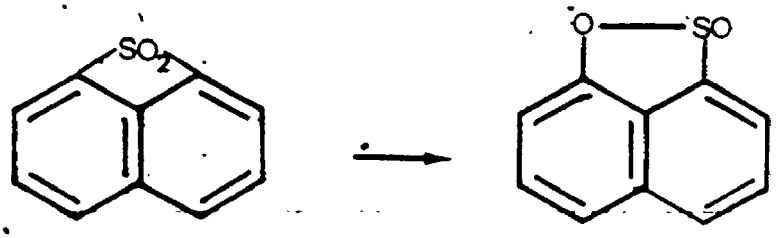
At 950° phenyl vinyl ketone was formed and this mechanism below,



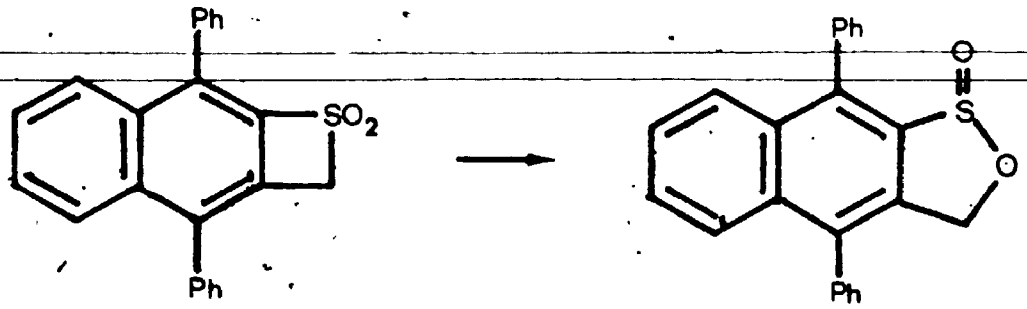
involving the abnormal attack of the oxygen of the sulphene upon its own carbon atom, was used to rationalize the results.

Other analogous reactions in which sulphenes have yielded sultines upon thermolysis have been reported by Hoffmann and Sieber(5), Dittmer(6), King et al(7).

Hoffmann et. al. found that naphtho (1,8-bc) thiete 1,1-dioxide at 300° under vacuum gave naphtho (1,8-cd) (1,2) oxathiol-5-oxide.



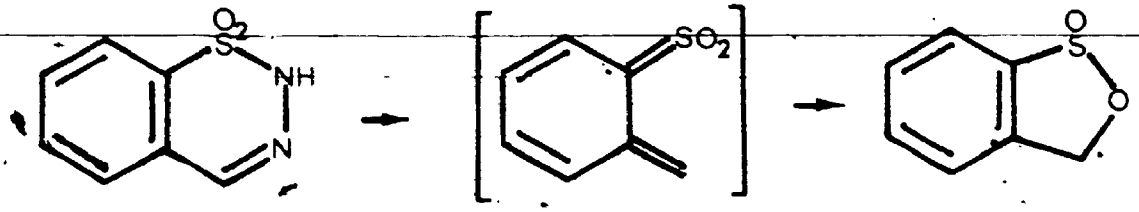
Dittmer discovered that 3,8-diphenyl-2H-naphtho (2,3-b) thiete 1,1-dioxide when thermolysed at 400° under nitrogen in the presence of 9,10-dihydroanthracene gave 4,9-diphenyl-3H-naphtho (2,3-c) 2,1-oxathiole-1-oxide.



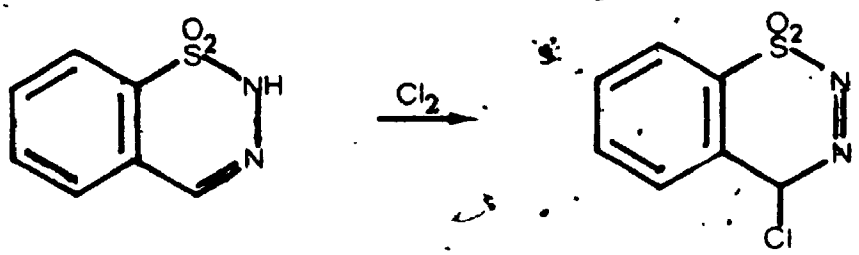
King et al found that a sultine is produced in the thermolysis of 2H-1,2,3-benzothiadiazine 1,1-dioxide

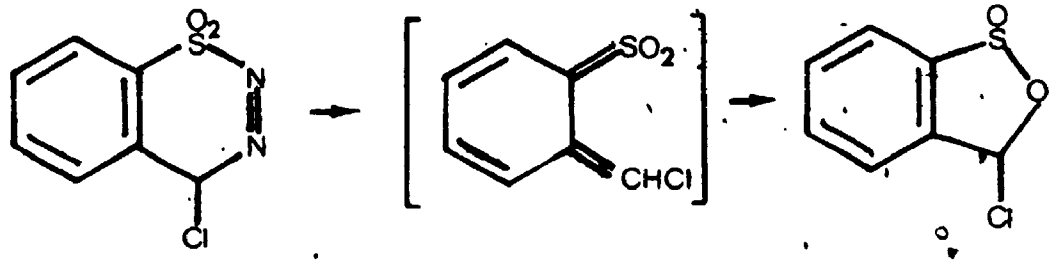
(B.T.D.).

Thermolysis of B.T.D. in a quartz tube with a glass plug at 500° and 1 mm Hg pressure gave a 25% yield of 3H-2, 1-benzoxathiole 1-oxide.



One further example also involves a reaction of B.T.D. King et al(8) believed that chlorination of B.T.D. in dry methylene chloride yielded a sulphinic acid derivative as below.





Two papers, pertinent to this "abnormal" nucleophilic attack, have been published since completion of the work described in part I of this thesis. Kempe and Norin have proposed an "abnormal" nucleophilic attack by the chloride ion on the carbon of dichlorosulphene to give trichloromethanesulphinate(9);

$$Cl_2CHSO_2Cl \xrightarrow[-Cl^-]{Et_3N} [CCl_2{=}SO_2] \xrightarrow{Cl^-} CCl_3SO_2^-$$

Dykman(10) proposed the reverse process, generation of a sulphene from a sulphinate, in a rationalisation of the formation of trichloromethylsulphenylsulphonyldichloromethane in the base treatment of trichloromethanesulphonyl chloride. The relevant step is shown below;

$$Cl_3CSO_2^- \xrightarrow[-Cl^-]{} [Cl_2C{=}SO_2]$$

In 1931 Müller and Raudenbusch(11) found that 1-chloroethanesulphonyl chloride on treatment with zinc dust in ethanol, followed by workup with warm aqueous potassium carbonate, gave potassium ethanesulphonate. This may be envisaged as a reduction of the sulphonyl chloride, by the zinc, to a sulphinate which by the loss of chloride ion, during work up, gives a sulphene which is trapped by water to yield the sulphonic acid. The sulphonic acid is converted to its salt by the potassium carbonate.

$$CH_3CHClSO_2Cl \xrightarrow[\text{Ethanol}]{Zn} CH_3CHClSO_2^-(Zn^{2+})_{\frac{1}{2}}$$

$$CH_3CHClSO_2^- \longrightarrow CH_3CH{=}SO_2 + Cl^-$$

$$CH_3CH{=}SO_2 \xrightarrow[H_2O]{K_2CO_3} CH_3CH_2SO_3K$$

The formation of methylsulphene from 1-chloroethane sulphinate is the formal reverse of the abnormal attack on sulphene by a nucleophile. This process has been termed the "abnormal" route to sulphene(12).

B. RESULTS AND DISCUSSION

The following research was conducted to verify the interpretation of the results of Müller and Raudenbusch which has been proposed in the introduction.

(a) Confirmation of the Results of Müller and Raudenbusch

A modified version of Müller and Raudenbusch's reaction of 1-chloroethanesulphonyl chloride was performed. This involved the conversion of the potassium salts, formed in their procedure, to the acids by using a cation exchange resin (H^+ form). Ethanesulphonyl chloride was isolated in about 8% yield, by treatment of the acid with thionyl chloride. Physical and spectral data of the ethanesulphonyl chloride and the toluidide derivative, prepared by treatment of the ethanesulphonyl chloride with triethylamine and p-toluidine in benzene, were found to be identical to those of authentic samples.

The success of this experiment encouraged attempts to isolate 1-chloroethanesulphinic acid to see if it would give methylsulphene under basic conditions.

(b) The Preparation and Identification of 1-Chloroethanesulphinic Acid

When 1-chloroethanesulphonyl chloride was treated with aqueous sodium sulphite and the solution acidified and extracted with ether, evaporation under reduced pressure and a low temperature, gave a 60% yield of 1-chloroethanesulphinic acid as a quite pure colourless oil.

$$CH_3CHClSO_2Cl \xrightarrow[ii)\ H^+]{i)\ Na_2SO_3} CH_3CHClSO_2H$$

The oil had an i.r. spectrum with strong absorption at 2900 cm^{-1} (O-H of acid) and 1080 cm^{-1} (S-O stretch of a sulphinic acid). The n.m.r. showed 1.75(3H, d, J = 7), 4.75(1H, q, J = 7) 10.5(1H, s). The purity of the acid was checked by potentiometric titration against standardised potassium permanganate solution(13). This indicated that a pure sample had been obtained.

Investigation of the pKa of the acid by potentiometric titrations and conductiometric measurements indicated that the pKa was less than 2.

In order to confirm the identity of the acid two derivatives, methyl 1-chloroethyl sulphone and 1-chloroethanesulphinyl chloride, were prepared and their properties determined.

Methyl 1-chloroethyl sulphone was formed on refluxing methyl iodide with a mixture of 1-chloroethanesulphinic acid

and triethylamine.

$$CH_3CHClSO_2H \xrightarrow[MeI]{NEt_3} CH_3CHClSO_2CH_3 + \overset{+}{N}HEt_3I^-$$

The sulphone had a melting point of 56-57°(reported(14) 62°), bands at 1.85(3H, d, J = 8), 2.98(3H, s) and 4.68(1H, q, J = 8) in the n.m.r. and absorption at 1322(str), 1145 (str) and 960(m) in the i.r. A satisfactory analysis was obtained.

The colourless oil 1-chloroethanesulphinyl chloride was prepared in low yield by refluxing 1-chloroethanesulphinic acid with thionyl chloride.

$$CH_3CHClSO_2H + SOCl_2 \longrightarrow CH_3CHClSOCl + SO_2 + HCl$$

Absorption in the i.r. occurred at 1440(m), 1374(m), 1160(str) and 1035(m). In the n.m.r. the presence of two diastereoisomers was revealed by the superimposed quartets at 5.02 and 5.18(J = 6.5, relative areas 3:5) and doublets at 1.92 and 1.91(J = 6.5). Subsequent to this work Canalini and Maccagnani(15) have found the presence of diastereomers in a series of simple alkylsulphinyl chlorides.

(c) <u>Evidence for Methylsulphene in the reaction of 1-Chloroethanesulphinic Acid with Base</u>

The refluxing of 1-chloroethanesulphinic acid with

aqueous sodium hydroxide followed by evaporation of the water and treatment of the residue with phosphorus pentachloride gave a 50% yield of ethanesulphonyl chloride.

$$CH_3CHClSO_2^- \ Na^+ \longrightarrow [CH_3CH{=}SO_2] \xrightarrow[NaOH]{H_2O} CH_3CH_2SO_3^- \ Na^+$$

$$CH_3CH_2SO_3^- \ Na^+ \longrightarrow CH_3CH_2SO_2Cl$$

This confirmed the participation of the 1-chloroethanesulphinate in the formation of potassium ethanesulphonate observed by Müller and Raudenbusch(11).

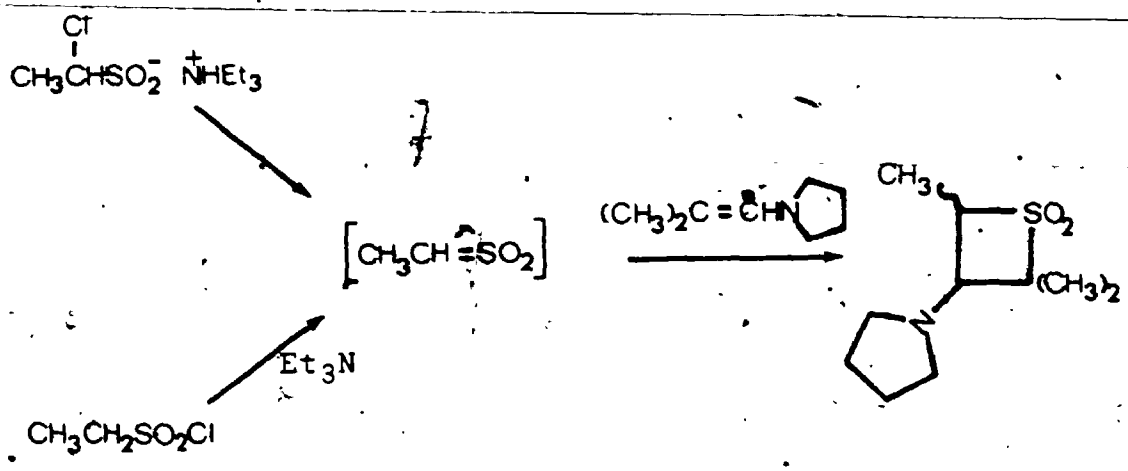
Evidence for the intermediacy of methylsulphene in this reaction was sought by trapping experiments. It was found that 1-chloroethanesulphinic acid in the presence of triethylamine and p-toluidine, at the temperature of refluxing benzene(81°), gave a 7% yield of ethanesulphon-p-toluidide. This yield diminished drastically at reduced temperatures.

$$CH_3CHClSO_2^- \ \overset{+}{N}HEt_3 \xrightarrow[81^\circ]{\Delta} [CH_3CH{=}SO_2] + \overset{+}{N}HEt_3 \ Cl^-$$

$$[CH_3CH{=}SO_2] + NH_2\text{-}C_6H_4\text{-}CH_3 \longrightarrow CH_3CH_2SO_2NH\text{-}C_6H_4\text{-}CH_3$$

When 1-chloroethanesulphinic acid was refluxed in benzene with triethylamine and 1-(2-methylpropenyl)-pyrrolidine, a 15% yield of the methylsulphene-

enamine* cycloaddition product was obtained. This can be compared to a 23% yield of the same product when ethanesulphonyl chloride is treated with the enamine under identical conditions. The formation of the same product in similar yield implies the presence of a common intermediate.



As 1-chloroethanesulphinate undergoes the reactions from which the intermediacy of sulphene is inferred in the reactions of sulphonyl chlorides(1) the evidence for the intermediacy of a sulphene in the reactions of 1-chloro-

*The stereochemistry of the adduct is unknown. The coupling constant of 10 Hz between the methine protons of the thietane ring is not a reliable indication of the stereochemistry(16).

ethanesulphinate is equally compelling.

(d) Kinetic Measurements on the Decomposition of 1-Chloroethanesulphinic Acid to give Methylsulphene

According to the reaction schemes already presented, the formation of sulphene from 1-chloroethanesulphinic acid should be unimolecular. Thus the rate of release of chloride from 1-chloroethanesulphinic acid should be independent of pH, provided all the acid exists as the sulphinate.

To test this hypothesis the rate of chloride ion release from 1-chloroethanesulphinic acid in degassed aqueous solutions, thermostated to 60°, and kept under argon, was measured by potentiometric titrations. The solutions were buffered to pH 4.0, 5.0 and 5.9 with acetic acid/sodium acetate buffer and the rate constants from first order plots were 2.5×10^{-5} s^{-1}, 2.7×10^{-5} s^{-1} and 2.6×10^{-5} s^{-1} respectively. This indicates the independence of the rate of the decomposition from the base concentration and is consistent with the reaction mechanisms presented.

(e) The Possibility of the Rearrangement of 1-Chloroethanesulphinic Acid to Ethanesulphonyl Chloride

A remote possibility exsists that the 1-chloroethanesulphinic acid might rearrange to ethanesulphonyl chloride and that the sulphene detected in the reactions of 1-chloroethanesulphinic acid could be derived from the action of

base on the ethanesulphonyl chloride created by this rearrangement.

To investigate the above possibility deuterated 1-chloroethanesulphinic acid($CH_3CHClSO_2D$) was treated with dideuterated toluidine(CH_3ArND_2) in refluxing acetonitrile in the presence of triethylamine. The ethanesulphontoluidide obtained showed no detectable dideuterated sulphonamide($CH_3CD_2SO_2HNC_6H_4CH_3$) by n.m.r. and a negligible amount by mass spectrum(2%, probably zero within the limits of accuracy of the measurements).

The formation of ethanesulphonyl chloride from α-chloroethanesulphinate requires the addition of a proton or deuterium at the α-carbon. In the above medium only the deuterium atoms are labile and thus the rearrangement would yield ethanesulphonyl chloride monodeuterated in the alpha position.

$$CH_3CHClSO_2^- \xrightarrow[+D^+]{} CH_3CHDSO_2Cl$$

Hence any sulphontoluidide formed via this rearrangement must derive from ethanesulphonyl chloride which is monodeuterated in the alpha position.

From an independent experiment it was found that a sample of ethanesulphonyl chloride, 92% monodeuterated at the alpha position, gave the sulphontoluidide which contained 34% of the dideuterated form. Hence the negligible amount

of dideuterated sulphontoluidide formed from the α-chloroethanesulphinate indicates that the rearrangement to ethanesulphonyl chloride plays little or no part in the formation of methylsulphene.

This observation is significant as the route to methylsulphene from α-chloroethanesulphinate has been shown to not require base and thus a sulphene can now be generated in a neutral medium for use in the synthesis of sulphonate esters and sulphonamides of base sensitive compounds.

C. EXPERIMENTAL

Infra red spectra(i.r.) were recorded on a Beckman IR-10 or IR-20A spectrometer. Nuclear magnetic resonance spectra(n.m.r.) were recorded on Varian A-60, T-60 and HA-100 instruments; chemical shifts were expressed in parts per million(p.p.m.) downfield from tetramethylsilane as an internal standard. Melting points were determined on a Kofler hot stage, and are uncorrected.

1,2-Dimethoxyethane(DME) and triethylamine were distilled from calcium hydride. Pyridine was distilled from sodium hydroxide pellets. The DME used in the exchange experiments was further purified by distillation from lithium aluminium hydride.

Micro analyses were performed by A.B. Gygli of Toronto. Deuterium analyses were done by J. Nemeth, Urbana, Ill. by the combustion method.

(a) Experiments Demonstrating the Abnormal Formation of Methylsulphene

(i) The Preparation of β-Trithioacetaldehyde

The procedure for this preparation followed that of Baumann and Fromm(17). Recrystallisation from ethanol yielded white crystals m.p. 122-127°; reported(17) 125-126°. The i.r.($CHCl_3$) included peaks at 2800-3000(m), 1445(m), 1370(w), 1195(w), 1080(w), 1030(w) and 970(w). The n.m.r. ($CDCl_3$) had peaks at 1.7(3H, d, J = 6.5) and 4.5(1H, q, J = 6.5).

(ii) The Preparation of 1-Chloroethanesulphonyl Chloride

1-Chloroethanesulphonyl chloride was prepared from trithioacetaldehyde by the method of Müller and Raudenbusch(11). The 1-chloroethanesulphonyl chloride was obtained in about 50% yield with a b.p. of 51-53° at 5 mm Hg; reported(11) 70-71° at 13 mm Hg. The i.r.(liquid film) showed peaks at 2960-3000(w), 1380(str), 1170(str) and 690(m).

(iii) The Reaction of 1-Chloroethanesulphonyl Chloride with Zinc Dust

This procedure follows that of Müller and Raudenbusch(11). 1-Chloroethanesulphonyl chloride(5.8 g,

35 mmol) was dissolved in 24 ml of absolute ethanol; zinc dust was added in small portions until no more heat was evolved. The mixture was filtered. The ethanol was removed from the filtrate by evaporation. Potassium carbonate solution was added to the liquid residue until it was alkaline. The water was evaporated under reduced pressure. A solid was obtained which was dissolved in water and passed through a column of Dowex 50W-X8(H^+) cation exchange resin. The column was eluted with water until the eluant was no longer acidic. Water was removed from the eluant by evaporation. The residue was refluxed with excess thionyl chloride and the product was distilled under reduced pressure. Ethanesulphonyl chloride(0.36 g, 2.7 mmol, 8%) was obtained. The i.r.(liquid film) showed peaks at 1500(w), 1360(str) and 1160(str). The n.m.r.($CDCl_3$) had peaks at 1.6(3H, t, J = 7.0) and 3.7(2H, q, J = 7.0). Both of the spectra matched those of a sample of ethanesulphonyl chloride from Eastman Organic Chemicals.

(iv) <u>The Formation of Ethanesulphon-p-Toluidide</u>

Ethanesulphonyl chloride(346 mg, 2.69 mmol), prepared from the 1-chloroethanesulphonyl chloride as above, was mixed with a solution of p-toluidine(420 mg, 3.75 mmol) and triethylamine(1 g, 9.9 mmol) in 15 ml of benzene. The mixture was left at room temperature for 1 h. The benzene

was washed with 2M HCl, separated, dried($MgSO_4$) and evaporated. The product obtained was recrystallised from a benzene-petroleum ether mixture to give ethanesulphon-p-toluidide(91 mg, 0.45 mmol, 17% yield) with a m.p. of 74-78°. The i.r.($CHCl_3$) showed peaks at 3365(m), 3225(m), 2840-3020(m), 1510(m), 1330(str), 1150(str) and 915(m). The n.m.r.($CDCl_3$) had peaks at 1.34(3H, t, J = 7), 2.3(3H, s), 3.1(2H, q, J = 7) and 7.15(4H, s).

The m.p. and spectra were identical to a sample of ethanesulphon-p-toluidide prepared from ethanesulphonyl chloride supplied by Eastman Organic Chemicals.

(v) The Preparation of 1-Chloroethanesulphinic Acid

1-Chloroethanesulphonyl chloride(3 g, 18.4 mmol) was stirred for 1 h with a solution of sodium sulphite(4.8 g, 38 mmol) in 50 ml of water. The solution was washed with methylene chloride. Sulphuric acid(2 M) was added to the aqueous layer. This acidic solution was extracted six times with 40 ml portions of ether. The ether extracts were combined, dried($MgSO_4$) and the solvent evaporated at a low temperature(≈40°) to yield 1-chloroethanesulphinic acid(1.8 g, 14 mmol, 60% yield). The i.r.($CHCl_3$) showed bands at 2900(str and broad), 1080(str) and 830(m). The n.m.r.($CDCl_3$) had peaks at 1.75(3H, d, J = 7), 4.75(1H, q, J = 7) and 10.5(1H, s).

(vi) The Determination of the Purity of the 1-Chloroethanesulphinic Acid

The method of P. Allen Jr.(13) was adopted. 1-Chloroethanesulphinic acid(0.132 g, 1.02 mmol) was dissolved in 250 ml of water in a volumetric flask. A 5 ml aliquot(0.0204 mmol of acid) was pipetted into a beaker and the solution was diluted with 140 ml of distilled water plus 200 ml of 0.1 M sodium hydroxide. This solution was titrated potentiometrically(glass and platinum electrodes and a salt bridge) with 0.0066 M potassium permanganate solution to an end point of 3.17 ml. A blank of 0.035 ml was obtained giving a titre of 3.135 ml. This corresponds to 0.0207 mmol of the acid.

(vii) The Reaction of 1-Chloroethanesulphinic Acid with p-Toluidide

p-Toluidine(4.28 g, 40 mmol) and triethylamine (1.2 g, 12 mmol) were dissolved in 30 ml of acetonitrile. The solution was heated to reflux. 1-Chloroethanesulphinic acid(0.516 g, 4 mmol) dissolved in 20 ml of acetonitrile was added to the refluxing solution over a period of 5 min. Refluxing was continued for a further 30 min. The acetonitrile solution was allowed to cool to room temperature. The solution was made acidic with 2 M hydrochloric acid. Most of the acetonitrile was removed by evaporation.

Extraction of the remaining solution with methylene chloride yielded, after drying($MgSO_4$) and evaporation of the solvent, ethanesulphon-p-toluidide(617 mg, 3.09 mmol, 77.5%). Recrystallisation from methylene chloride-petroleum ether gave the ethanesulphon-p-toluidide(532 mg, 2.67 mmol,67% yield) with a m.p. of 77-80°; reported(18) 77.5-78°.

When the above reaction was carried out in benzene at 45° the yield of ethanesulphon-p-toluidide was 10% and at 65° in benzene it was 32%.

(viii) The Preparation of 1-(2-Methylpropenyl)-Pyrrolidine.

The method of Benzing(19) was used giving an 84% yield of 1-(2-methylpropenyl)-pyrrolidine with a b.p. of 69-70° at 40 mm Hg.

(ix) The Reaction of 1-Chloroethanesulphinic Acid with 1-(2-Methylpropenyl)-Pyrrolidine and Triethylamine

Triethylamine(2 g, 20 mmol) was dissolved in 20 ml of acetonitrile and heated to reflux. A solution of the enamine(7.1 g, 56 mmol) in 10 ml of acetonitrile was added to the refluxing mixture. 1-Chloroethanesulphinic acid(713 mg, 5.5 mmol) was dissolved in acetonitrile and added to the stirred, refluxing mixture over a period of 4 min. The reaction was refluxed for a further 35 min.

The mixture was allowed to cool and then acidified with 2 M sulphuric acid. The acidic solution was washed with methylene chloride, made basic with potassium carbonate and extracted with methylene chloride. The layers were separated. The methylene chloride was dried($MgSO_4$) and evaporated to give an oil. A few drops of methanol were added to the oil and the solution was cooled. The cycloadduct(117 mg, 0.82 mmol, 15%) was obtained as a solid with a m.p. of 79-83°. Further recrystallisation of the adduct from methanol gave a white solid with m.p. 83.5-85°. A mixed melting point with the cycloadduct prepared from ethanesulphonyl chloride was 83.5-83°. The spectra were the same as those of the adduct prepared from ethanesulphonyl chloride.

Anal. Calcd. for $C_{10}H_{19}NO_2S$: C, 55.26; H, 8.81; N, 6.45; S, 14.75. Found: C, 55.01, H, 8.89; N, 6.42; S, 14.89.

(x) <u>The Reaction of Ethanesulphonyl Chloride with 1-(2-Methylpropenyl)-Pyrrolidine and Triethylamine</u>

The procedure used was the same as that used with 1-chloroethanesulphinic acid. The yield of the cycloadduct was 23%. The m.p. was 83-84°. The i.r.($CHCl_3$) showed bands at 2970(m), 2700(m), 1460(w), 1300(str) and 1100(str): The n.m.r.($CDCl_3$) gave peaks at 1.48(3H, s),

1.58(3H, d, J = 8), 1.60(3H, s), 1.78(4H, multiplet), 2.50(4H, multiplet), 2.88(1H, d, J = 8.7) and 4.03(1H, d of qs, J = 8, J = 8.7).

(b) Experiments Demonstrating that the Methylsulphene is Formed Directly from the 1-Chloroethanesulphinate

(i) The Preparation of Toluidine-d

p-Toluidine was recrystallised from ethanol-water. The crystals were dissolved in methylene chloride. As the crystals dissolved the solution became cool and water condensed in the methylene chloride. The methylene chloride was separated from the water layer and dried($MgSO_4$). The methylene chloride solution was shaken once with 20 ml then several times with 10 ml portions of deuterium oxide. The methylene chloride was dried(anhydrous potassium carbonate) and the solvent was removed by evaporation. The n.m.r. showed 96% incorporation of deuterium at the nitrogen.

(ii) The Preparation of 1-Chloroethanesulphinic Acid-d

Some 1-chloroethanesulphinic acid was dissolved in diethyl ether. This solution was shaken with several portions of deuterium oxide. The ether was dried($MgSO_4$) and evaporated to give the deuterated sulphinic aicd. The n.m.r. showed that more than 90% exchange of the acidic

proton had occurred.

(iii) The Reaction of 1-Chloroethanesulphinic Acid-d with p-Toluidine-d_2 and Triethylamine

Triethylamine(0.7 g, 7 mmol) and p-toluidine-d_2 (1.4 g, 13 mmol) were dissolved in 20 ml of acetonitrile. The solution was heated to reflux. 1-Chloroethanesulphinic acid-d(0.18 g, 1.4 mmol) dissolved in 10 ml of acetonitrile was added to the stirred refluxing mixture over a period of 4 min. The mixture was refluxed for 35 min. The reaction was cooled and dilute sulphuric acid was added. The acetonitrile was evaporated. The aqueous solution was extracted with methylene chloride. The methylene chloride was dried($MgSO_4$) and evaporated yielding the toluidide(0.17 g, 0.86 mmol, 61% yield).

The toluidide was recrystallised from methanol giving a product with m.p. 81-81.5°. The n.m.r.($CDCl_3$) showed no detectable dideuterated toluidide. The mass spectrum analysed for undeuterated 21±2%, monodeuterated 77±2% and dideuterated 2±2% products. This corresponds to a deuterium analysis of 6.18 atom % excess. Deuterium analysis gave 6.10 atom % excess.

(iv) The Preparation of Monodeuterated Ethanesulphonyl Chloride

Ethanesulphonyl chloride(4.4 g, 34 mmol) was

dissolved in dioxane containing 18 ml of deuterium oxide. Triethylamine(50 ml) was added to the solution over a period of 5 min. The solution was left at room temperature for a further 5 min. The solvent and volatiles were evaporated under reduced pressure and the residue obtained was dissolved in water. The aqueous solution was washed with ether and evaporated to dryness. The residue was suspended in methylene chloride and phosphorus pentachloride (8 g, 38.4 mmol) was added in small portions over a period of 5 min. The methylene chloride was decanted, washed with water, dried($MgSO_4$) and evaporated. Ethanesulphonyl chloride (2.3 g, 18 mmol) was obtained. This product was vacuum distilled(b.p. 72° at 20 mm Hg). Deuterium analysis gave 17.65 atom % excess of deuterium. The theoretical value for monodeuterated ethanesulphonyl chloride is 20 atom % excess. The n.m.r.($CDCl_3$) showed a doublet at 1.55 p.p.m. with J = 6.8 cps, each peak of the doublet being split into three by coupling with the deuterium and a multiplet at 3.7 p.p.m. Integration of the peaks at 1.55 p.p.m. gave the composition of the product as 92% monodeuterated and 8% undeuterated ethanesulphonyl chloride. This corresponds to 18.4 atom % excess of deuterium.

(v) <u>The Reaction of 1-Deuteroethanesulphonyl Chloride with p-Toluidine-d_2 and Triethylamine</u>

The procedure was the same as that used in the

reaction of 1-chloroethanesulphinic acid-d with p-toluidine-d_2 and triethylamine.

The toluidide was obtained in 35% yield. Analysis of the methyl group absorption at 0.9 p.p.m. in the n.m.r.($CDCl_3$) showed that the product contained 22±5% of the undeuterated, 44±5% of the monodeuterated and 34±5% of the dideuterated toluidides.

(c) The Proof of the Structure of 1-Chloroethanesulphinic Acid

(i) The Determination of the pKa of 1-Chloroethanesulphinic Acid

Potentiometric titration of 1-chloroethanesulphinic acid with 0.0428 M sodium hydroxide gave a titration curve indistinguishable from that given by perchloric acid. Attempts to measure the pKa by conductometric measurements also failed. This indicated that the pKa of the acid was less than 2.

(ii) Preparation of Methyl 1-Chloroethyl Sulphone from 1-Chloroethanesulphinic Acid

Triethylamine(1.2 g, 12 mmol) was added to 1-chloroethanesulphinic acid(690 mg, 5.4 mmol). This mixture was stirred whilst methyl iodide(17.5 ml, 38 g, 270 mmol) was added over a period of 12 min. The mixture

was refluxed with continuous stirring for 23 min. Water was added. The mixture was extracted with methylene chloride. The extracts were combined, washed with aqueous thiosulphate, dried($MgSO_4$) and evaporated. Methyl 1-chloroethyl sulphone (0.589 g, 4.1 mmol) was obtained. Recrystallisation from chloroform-petroleum ether gave white crystals of the sulphone(0.573 g, 4.0 mmol, 74% yield) with a m.p. of 56-57°; reported(14) m.p. 62°. The n.m.r.($CDCl_3$) showed peaks at 1.85(3H, d, J = 8), 2.98(3H, s) and 4.68(1H, q, J = 8). The i.r.($CHCl_3$) had absorption maxima at 1322(str), 1145(str) and 960(m).

Anal. Calcd. for $C_3H_7ClSO_2$: C, 25.27; H, 4.95; Cl, 24.86; S, 22.48. Found: C, 25.26; H, 5.02; Cl, 24.66; S, 22.65.

(iii) Preparation of 1-Chloroethanesulphinyl Chloride from 1-Chloroethanesulphinic Acid

Thionyl chloride(8.3 g, 70 mmol) was slowly added to 1-chloroethanesulphinic acid(1.22 g, 9.5 mmol) at 0°. Then the mixture was stirred for 1 h at room temperature. The mixture was refluxed for 1 h. The excess thionyl chloride was distilled off at atmospheric pressure. The product was distilled under reduced pressure. A small amount of 1-chloroethanesulphinyl chloride was obtained as a colourless oil. The i.r.(liquid film) had peaks at

1440(m), 1375(m), 1160(str) and 1035(m). The HA-100 n.m.r.($CDCl_3$) showed quartets at 5.02 and 5.18 with J = 6.5 and relative areas of 3:5 and doublets at 1.92 and 1.91 with J = 6.5.

(d) The Reaction of 1-Chloroethanesulphinic Acid with Aqueous Sodium Hydroxide

1-Chloroethanesulphinic acid(0.73 g, 5.7 mmol) was added to a refluxing solution of sodium hydroxide(0.65 g, 16 mmol) in 20 ml of water. The mixture was stirred under reflux for 35 min. The water was removed by evaporation under reduced pressure.

The residue was suspended in methylene chloride and 8.5 g of phosphorus pentachloride was added in small portions whilst swirling the mixture at room temperature. The methylene chloride was decanted, washed with water, dried($MgSO_4$) and evaporated. Ethanesulphonyl chloride (0.48 g, 2.9 mmol, 52% yield) was obtained. The identity of the product was determined by comparing the n.m.r. and i.r. spectra with those of a sample of ethanesulphonyl chloride supplied by Eastman Organic Chemicals.

(e) The Rate of Release of Chloride Ion from 1-Chloroethanesulphinic Acid in Acetic Acid/Sodium Acetate Buffers

(i) General Procedure

1-Chloroethanesulphinic acid was dissolved in

100 ml of buffer solution. This solution was transferred to a two necked flask and frozen in liquid nitrogen. The solution was degassed and then warmed to 60° in a themostated bath. Argon was admitted into the flask and the flask was fitted with a serum cap. Aliquots(5.00 ml) were removed from the flask at known intervals and quenched by placing in 40 ml of ice-cooled water. The chloride ion content was measured by potentiometric titration(platinum and glass electrodes) with 0.01 M silver nitrate solution as described by Lee(20). The results are shown in the following tables. The first order rate constants were determined graphically.

(ii) Results

Concentration of 1-chloroethanesulphinic acid = 4.1×10^{-2} M

Buffer: 82 ml of 0.2 M acetic acid

18 ml of 0.2 M sodium acetate

pH = 4.0 Temperature = 60.0±0.1°

Time/min	Titre/ml	% Reaction	Log(100-%Reaction)
112	3.10	15.5	1.927
215	5.35	26.9	1.864
317	7.25	36.4	1.804
408	8.80	43.2	1.754
502	10.30	52.0	1.681

$k = 2.5 \times 10^{-3}\ s^{-1}$

Concentration of 1-chloroethanesulphinic acid = 4.06×10^{-2} M

Buffer: 29.5 ml of 0.2 M acetic acid

70.5 ml of 0.2 M sodium acetate

pH = 5.0 Temperature = 60.0±0.1°

Time/min	Titre/ml	% Reaction	Log(100-%Reaction)
60	1.80	9.05	1.959
128	3.70	18.5	1.911
304	5.60	28.2	1.856
317	8.05	40.5	1.775
404	9.50	47.6	1.719
497	11.15	56.0	1.644
580	12.15	61.0	1.591

$k = 2.7 \times 10^{-5}\ s^{-1}$

Concentration of 1-chloroethanesulphinic acid = 3.45×10^{-3} M

Buffer: 4.5 ml of 0.2 M acetic acid

95.5 ml of 0.2 M sodium acetate

pH = 5.90 Temperature = 60.0±0.1°

Time/min	Titre/ml	% Reaction	Log(100-%Reaction)
86	2.25	12.7	1.941
129	3.15	18.0	1.914
213	4.90	28.0	1.857
296	6.25	36.0	1.806
410	8.05	46.4	1.729
501	9.30	53.6	1.667
602	10.40	60.0	1.602
3290	17.30	1000.0	1.000

$k = 2.6 \times 10^{-5}\ s^{-1}$

PART II

THE FORMATION OF SULPHENE

by

BASE PROMOTED ELIMINATION FROM ARYL ARYLMETHANESULPHONATES

A. INTRODUCTION

The formation of phenylsulphene has been found to occur in the reactions of base with phenylmethanesulphonyl chloride (1,2), 4-nitrophenyl phenylmethanesulphonate(3,4), and 2,4-dinitrophenyl phenylmethanesulphonate(5).

The above reactions can be summarised in the following equation

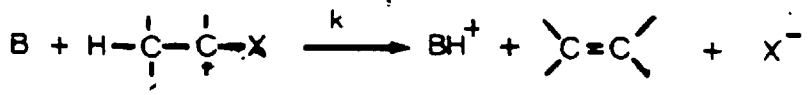
$$B + PhCH_2\text{-}SO_2\text{-}X \longrightarrow BH^+ + PhCH{=}SO_2 + X^-$$

X(leaving group) = Cl, $4\text{-}NO_2ArO$, $2,4\text{-}(NO_2)_2ArO$

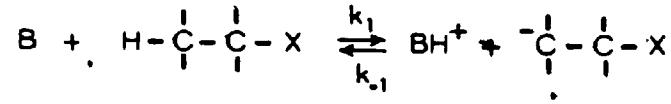
The above are base promoted 1,2-eliminations and previous work has shown, in the case of phenylmethanesulphonyl chloride and 4-nitrophenyl phenylmethanesulphonate, that they are second order reactions. Elimination reactions have been reviewed by Bordwell(6). He placed them into eight cate-

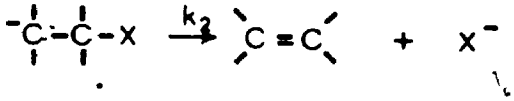
gories, five of these showing second order kinetics. In this introduction I will discuss the three second order reactions which do not involve ion pairs because ion pair intermediates, as the later discussion shows, are not required to explain the experimental data. The three second order mechanisms to be discussed are the reversible Elcb, the irreversible Elcb and E2 mechanisms.

The term E2 is used to signify an elimination involving concomitant attack of the base on the β-hydrogen and loss of the leaving group with its pair of electrons.



The term Elcb denotes a mechanism in which the β-proton is removed to give a carbanion which subsequently loses the leaving group.





The problem now arises of determing which, if any, of these two modes of reaction is occurring.

Kinetic measurements are one of the most valuable

probes of mechanism. The E2 reaction would be first order in both the base and the substrate.

$$\text{Rate} = k[B][RX]$$

In contrast, applying the steady state assumption to the concentration of the carbanion, the following rate expression is obtained for the Elcb reaction.

$$\text{Rate} = \frac{k_1 k_2 [RX][B]}{k_{-1}[BH^+]+k_2}$$

If the anion goes to products much faster than it protonates(irreversible Elcb), $k_2 >> k_{-1}[BH^+]$ and hence

$$\text{Rate} = k_1[RX][B]$$

which is the same form of rate expression as that for an E2 reaction.

When reprotonation of the anion is much more rapid than its decomposition to products(reversible Elcb). $k_{-1}[BH^+] >> k_2$

$$\text{Rate} = \frac{k_1 k_2 [RX][B]}{k_{-1}[BH^+]}$$

Although the reaction is still first order in base, the inverse dependence on the conjugate acid is a kinetically

distinguishing feature. Also, as the reprotonation of the anion is faster than its decomposition, the reprotonation should be detectable by the observation of exchange in the presence of deuterium oxide.

From the above discussion it can be seen that the determination of the kinetic order is extremely valuable in distinguishing between many elimination mechanisms. The major problem which remains is to find a way of distinguishing between the irreversible Elcb and the E2 mechanisms. Once it is realised that these two pathways obey the same rate law other factors must be used to distinguish between the two mechanisms. Although the rate law is the same for both reactions the rate constants have different meanings. The rate constant in the E2 reaction refers to a process in which the β-hydrogen bond is stretched as the bond to the leaving group is weakened but in the irreversible Elcb case only the β-hydrogen bond is broken in the rate determining step.

In an Elcb reaction the only influence of the leaving group on the rate of carbanion formation should be through an inductive or field effect on the stability of the carbanion. In the E2 reaction the weakening of the bond to the leaving group should lower the energy of the transition state below that of the stepwise process. Thus the E2 reaction should be faster than that expected from a simple electrostatic effect of the leaving group. Also in the

irreversible Elcb reaction a change of the leaving group should have a smaller effect on the rate, as the rate is independent of the facility of the loss of the leaving group. Some of these criteria have already been used in the study of 1,2-eliminations yielding phenylsulphene.

King and Lee(1) found that the rate of elimination from phenylmethanesulphonyl chloride was first order in both base and substrate. This indicated either an E2 or Elcb mechanism. The reversible Elcb mechanism was excluded by the observation that only one deuterium atom was incorporated at the benzylic carbon of the product in the reaction of 4-nitrophenylmethanesulphonyl chloride with triethylamine in the presence of deuterium oxide(2). This agreed with an earlier observation by King and Durst(7) when they used phenylmethanesulphonyl chloride as the substrate. In order to distinguish between the E2 and the irreversible Elcb mechanisms Lee(2) assumed the inductive effect of the chlorine in the phenylmethanesulphonyl chloride to be close to that of the phenyl group in phenyl benzyl sulphone. He compared the rate of the elimination reaction of phenylmethanesulphonyl chloride with triethylamine at -25° with the rate of exchange(extrapolated to -25°) of the benzylic protons of the benzyl phenyl sulphone with triethylamine. He found a rate of elimination 10^8-10^9 times faster than the rate of carbanion formation as measured by the exchange rate.

He deduced that carbon-chloride bond cleavage in the transition state must be aiding the elimination and hence an E2 mechanism was operating. Lee concluded that the E2 reaction was Elcb-like from a positive ρ^- value of 2.4 obtained from a study of phenylmethanesulphonyl chlorides.

The mechanism for the generation of phenylsulphene in the reaction of 4-nitrophenyl phenylmethanesulphonates with bases was found to contrast sharply with the mechanism found for the reaction of base with phenylmethanesulphonyl chloride.

Singh(3) found the reaction of 4-nitrophenyl phenylmethanesulphonate to be first order in both base and substrate. Singh excluded the irreversible Elcb and the E2 mechanisms by the observation that the benzylic position of the phenylmethanesulphonic acid, formed in the reaction of 4-nitrophenyl phenylmethanesulphonate with triethylamine in the presence of deuterium oxide, was 95% deuterated at the benzylic position. A ρ value of 0.06 was obtained from a Hammett correlation of the rates of the elimination from substituted 4-nitrophenyl phenylmethanesulphonates with triethylamine. This low ρ value was attributed to the opposing effects of the substituents on the carbanion pre-equilibrium and the decomposition of the carbanion to phenylsulphene.

It has been pointed out(8) that exchange does not necessarily exclude an E2 mechanism, and the ρ value of zero

could certainly be the result of an E2 reaction. Considering the doubt that still remains as to this mechanism, further investigations were required.

Previous to this work no mechanistic investigations had been published on the base catalysed 1,2-eliminations from 2,4-dinitrophenyl phenylmethanesulphonates.

The work presented in this thesis continues the studies of base catalysed eliminations forming phenylsulphene. It includes a more complete investigation of the eliminations from 4-nitrophenyl phenylmethanesulphonates and a study of the base catalysed eliminations from 2,4-dinitrophenyl phenylmethanesulphonates and several other closely related esters.

B. RESULTS AND DISCUSSION

(a) Phenylsulphene Formation in the Reaction of Base with 2,4-Dinitrophenyl Phenylmethanesulphonates

1,2-Dimethoxyethane containing 20% of water* was chosen as the reaction solvent for the investigations because all the reactants and products are highly soluble in this medium. Choice of the above medium also allows a comparison of the results of the present investigation with those of Singh(3) and Lee(2) who both used aqueous DME as the solvent medium for their studies. A further advantage of using 20% aqueous DME as a solvent, over the use of a non-aqueous medium, is that the nitrophenoxides released during the reactions remained as the anions, furnishing a strong and distinct chromophore which could be used to follow the reaction.

Singh(3) and more recently Christensen(4) have shown the presence of phenylsulphene in the reactions of base with 4-nitrophenyl phenylmethanesulphonates. In order to prove the presence of phenylsulphene in the reactions

*This solvent was prepared by mixing 20 ml of water with DME to a volume of 100 ml at room temperature.

2,4-dinitrophenyl phenylmethanesulphonates with base the following experiments were conducted.

2,4-Dinitrophenyl 4-nitrophenylmethanesulphonate was treated with triethylamine in methylene chloride giving a 93% yield of 4,4'-dinitrostilbene. The reaction of 2,4-dinitrophenyl 4-nitrophenylmethanesulphonate with pyridine in a 20% solution of deuterium oxide in DME yielded the sulphonic acid which was converted to the sulphonyl chloride with phosphorus pentachloride. The nmr spectrum showed that this acid chloride was monodeuterated in the benzylic position*. The mass spectrum showed that the 4-nitrophenylmethanesulphonyl chloride contained 98% of the monodeuterated and 3% of the undeuterated compounds. The formation of monodeuterated products(7,9) and the formation of stilbenes(10) are both typical of reactions involving sulphenes.

Another reaction which is taken as evidence for the intermediacy of sulphenes in the reaction of sulphonyl chlorides with base is the formation of a cyclic adduct in the presence of an enamine(10). This criterion for sulphene formation was applied to the reaction of triethylamine with 2,4-dinitrophenyl 4-nitrophenylmethanesulphonate. When this ester was treated with triethylamine in DME containing N-(2-methyl-1-propenyl)-pyrrolidine the cyclo-

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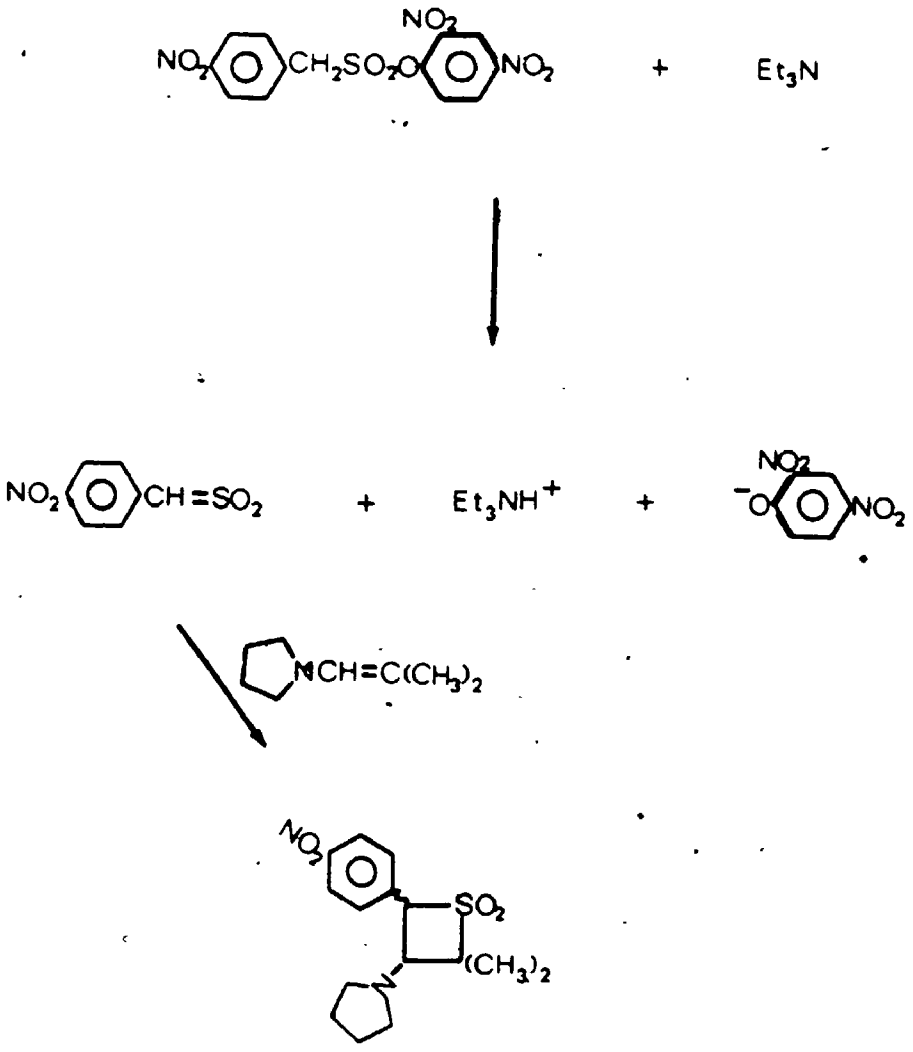
*A similar experiment using 4-acetyl 2-nitrophenyl phenylmethanesulphonate as the ester also gave the monodeuterated sulphonyl chloride.

adduct was obtained in 85% yield.



This is the same adduct* as is formed when 4-nitrophenylmethanesulphonyl chloride is treated with triethylamine in the presence of N-(2-methyl-1-propenyl)-pyrrolidine in methylene chloride.

To confirm that the sulphene was generated under the conditions of the kinetic measurements the trapping experiments were repeated using 20% aqueous DME as the solvent. In both cases, using 4-nitrophenylmethanesulphonyl chloride or 2,4-dinitrophenyl 4-nitrophenylmethanesulphonate, a 12% yield of the adduct was obtained.

Now that the reaction of base with 2,4-dinitrophenyl phenylmethanesulphonates has been shown to give phenylsulphene, as judged by three common criteria, the mode of its formation can be studied.

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*The stereochemistry of the adduct is unknown. The coupling constant of 10 Hz between the methine protons is not a reliable indication of the stereochemistry(11).

(b) The Mechanism of Base Catalysed 1,2-Eliminations from 2,4-Dinitrophenyl Arylmethanesulphonates

(i) The Order of the Reaction

2,4-Dinitrophenyl 4-methylphenylmethanesulphonate was prepared by reacting 4-methylphenylmethanesulphonyl chloride with base in the presence of 2,4-dinitrophenol. This ester, 2,4-dinitrophenyl 4-methylphenylmethanesulphonate, was used to investigate the dependence of the elimination on base and substrate. The rate of release of the 2,4-dinitrophenoxide from the ester, under pseudo first order conditions, on treatment with varying concentrations of triethylamine at a pH of 8.64 and an ionic strength of 0.002 M, was measured. The pH was kept constant by using triethylammonium chloride. The ionic strength was maintained at 0.002 M with tetraethylammonium chloride. The rate was measured by following the change in the absorbance at 405 nm with time. Plots of log(100- percentage reaction) versus time gave good straight lines showing that the reaction was first order in the substrate. The pseudo first order rate constants, obtained from the gradients of these plots, at various concentrations of the base are shown in table I and displayed in Fig 1.

The linear dependence of the pseudo first order rate constant on base concentration shows that the elimination is also first order with respect to the base. A least squares analysis of the data gave a correlation coefficient of 0.999, a gradient of 1.35 and an intercept, where the concentration of the base is zero, of 0.08 s^{-1}.

TABLE I

The Pseudo First Order Rate Constants for the Triethylamine Promoted Elimination from 2,4-Dinitrophenyl 4-Methylphenylmethanesulphonate

Solvent: 20% aqueous DME

Ester concentration: 5×10^{-5} M

Temperature: $20 \pm 0.1^{\circ}$

"pH": 8.64

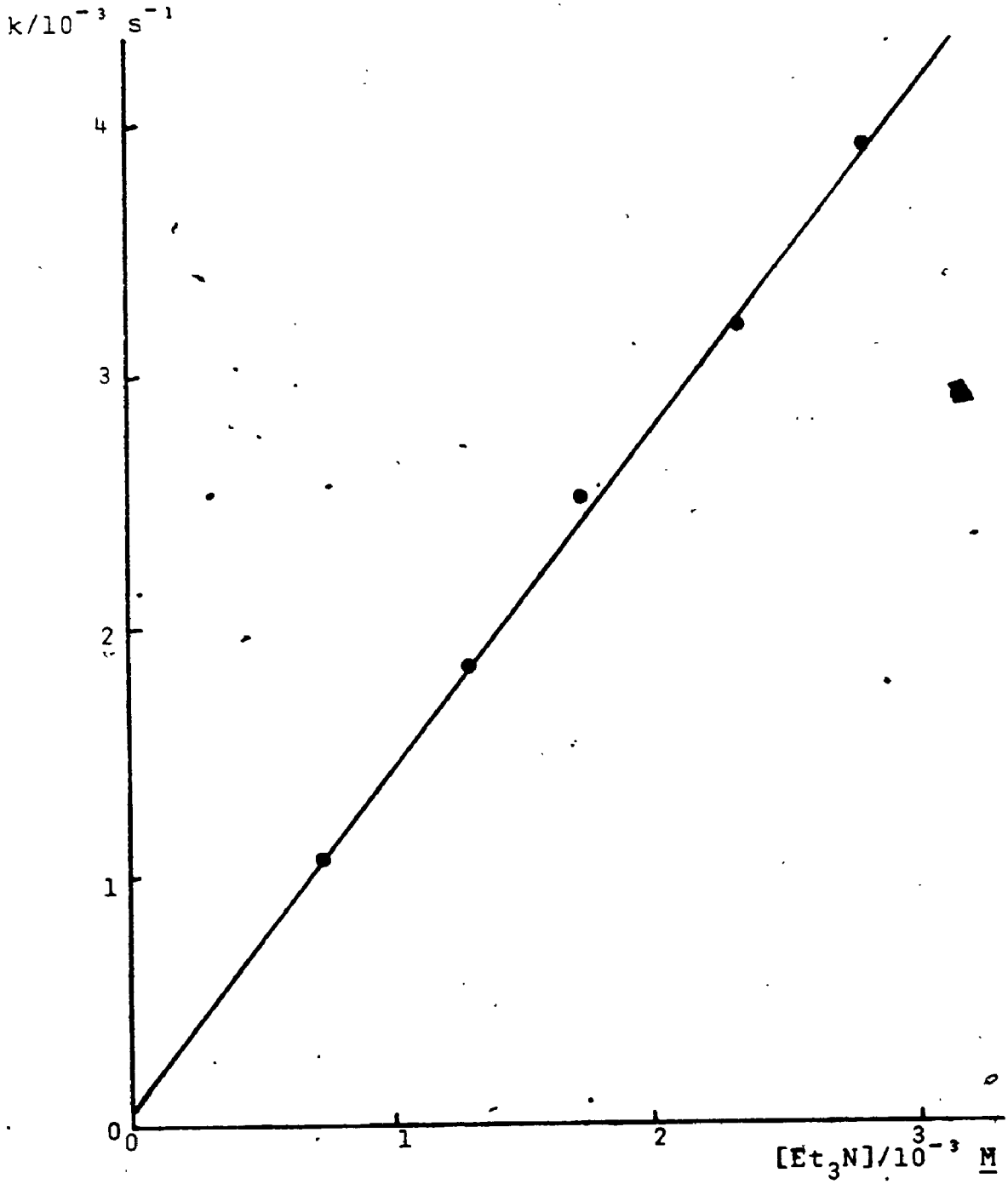
Ionic strength($[Et_3\overset{+}{N}HCl^-] + [Et_4\overset{+}{N}Cl^-]$): 0.002 M

Triethylamine* Concentration/10^{-3} M	Rate Constant(k)/$10^{-3}s^{-1}$
0.74	1.05
1.30	1.82
1.74	2.50
2.34	3.18
2.82	3.88

*Calculated using a 'pKa' of triethylamine in 20% aqueous DME of 8.43. See appendix II.

FIG 1

General Base Catalysis in the Reaction of Triethylamine with 2,4-Dinitrophenyl 4-Methylphenylmethanesulphonate



The intercept close to zero, at zero triethylamine concentration, indicates little involvement in the reaction of any base but triethylamine.

(ii) Exchange Measurements

When 2,4-dinitrophenyl phenylmethanesulphonate was treated with pyridine or triethylamine, in DME containing 20% of deuterium oxide, only undeuterated products and products monodeuterated at the benzylic position were detected. The ester therefore cannot be exchanging before the elimination occurs. Hence a reversible Elcb mechanism is not occuring and now the task is to distinguish between the irreversible-Elcb and E2 mechanisms.

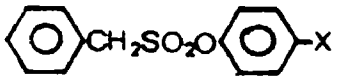
(iii) The Inductive and Field Effects of the Nitro Groups on the Rate of the Formation of the Benzylic Carbanion

As discussed in the introduction the only way the rate of carbanion formation can be affected by the group which subsequently leaves, in an Elcb reaction, is by the inductive and field effects. If these effects can be estimated for the nitro groups the rate of formation of the carbanion in 2,4-dinitrophenyl phenylmethanesulphonate can be estimated. If this rate of carbanion formation is the same as the rate of the elimination, then the reaction most likely occurs via an irreversible-Elcb mechanism, for an E2

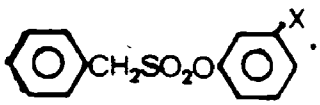
type reaction should be more rapid.

In order to estimate the rate of carbanion formation in the 2,4-dinitrophenyl phenylmethanesulphonate the rates of exchange of the benzylic protons in aryl phenylmethanesulphonates, bearing different substituents on the phenoxy moiety, were measured.

The following aryl phenylmethanesulphonates were prepared.



X = OCH_3, H, Cl, CN, NO_2



X = OCH_3, Cl, NO_2

Each of these esters was dissolved in DME containing 20% of deuterium oxide and triethylamine(0.2 M) at 20°. The ester was recovered after a known time interval and the amount of exchange that had occurred was measured by mass and nmr spectroscopy. The rate of exchange per hydrogen was calculated from the percentage of deuterium incorporated(%D) at the benzylic position. The percentage of deuterium incorporated at time t was defined by the following equation

$$\%D = [D]_t \times 100/[H]_o$$

where $[D]_t/[H]_o$ is the ratio of the amount of deuterium incorporated at the benzylic position to the initial amount of hydrogen.

The rate constant(k) for the carbanion formation, the rate of exchange per hydrogen, at the benzylic position, was calculated from the following equation*

$$\ln 1/(1-\%D/100) = kt/2$$

The rate constants derived from one point nmr measurements and those derived from plots of log $1/(1-\%D/100)$ versus t, using the results obtained from mass spectroscopy, are shown in table II. Both of the above methods of analysis yield approximately the same values of k.

When a Hammett correlation is constructed(Fig 2) a good straight line is obtained using σ_n for the substituent constants. A least squares analysis of the results in table II gives a ρ value of 1.9 ± 0.1 with a correlation coefficient of 0.988. This good correlation over such a wide array of substituents allows the extrapolation to higher σ_n values, such as that for 2,4-dinitrophenyl phenylmethanesulphonate, to be done with confidence.

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*For derivation of the equation see appendix I.

TABLE II

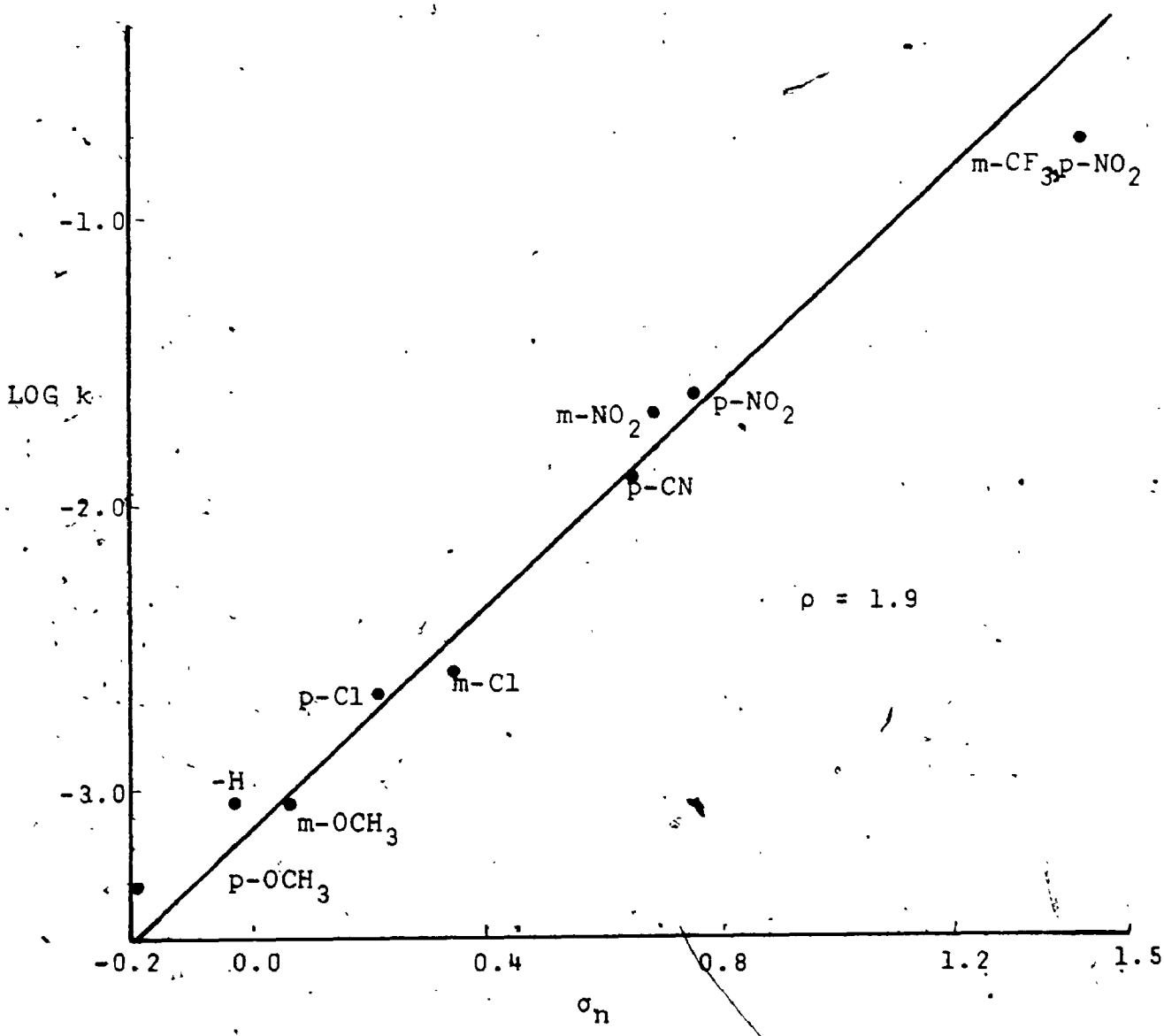
The Rate Constants for Carbanion Formation in the Reaction Triethylamine with Phenyl Phenylmethanesulphonates at 20°

Ester	$k/10^{-3}$ M s^{-1} From nmr	From mass spec.	log $k_{mass\ spec.}$ ξ	σ_n ψ
$C_6H_5CH_2SO_3C_6H_4OCH_3$-4	0.38 ± 0.05	0.48 ± 0.02	-3.31_9	-0.18
$C_6H_5CH_2SO_3C_6H_5$	0.87 ± 0.1†	0.75 ± 0.04	-3.12_5	0
$C_6H_5CH_2SO_3C_6H_4OCH_3$-3	0.64 ± 0.07	0.67 ± 0.03	-3.11_9	0.08
$C_6H_5CH_2SO_3C_6H_4Cl$-4	2.1 ± 0.2	2.38 ± 0.02	-2.62_0	0.24
$C_6H_5CH_2SO_3C_6H_4Cl$-3	2.7 ± 0.3§		-2.56_9	0.37
$C_6H_5CH_2SO_3C_6H_4CN$-4	15 ± 1.5	14.0 ± 0.7	-1.85_4	0.67
$C_6H_5CH_2SO_3C_6H_4NO_2$-3	19 ± 2	22 ± 1	-1.65_8	0.71
$C_6H_5CH_2SO_3C_6H_4NO_2$-4	27 ± 3	25 ± 1	-1.60_2	0.78
$C_6H_5CH_2SO_3C_6H_4CF_3$-3,NO_2-4	220 ± 20		-0.69_9	1.25¶

†From Ref. 2(base strength 0.5 M)
§Dual measurements at differing base strengths.
ξFor all except the meta chloro, derived from the mass spec. measurements.
ψFrom Ref. 12.
¶The sum of σ_n(para nitro) and σ_n(meta CF_3).

FIG 2

Hammett Correlation for the Triethylamine Promoted Exchange of Aryl Phenylmethanesulphonates



(iv) The Rates of Elimination of Nitrophenoxides from Nitroaryl Phenylmethanesulphonates

The rate at which 2,4-dinitrophenyl phenylmethanesulphonate, and four other nitroaryl phenylmethanesulphonates, released the nitroaryloxy moiety at 20°, when treated with triethylamine in DME containing 20% of deuterium oxide, was followed by u.v. spectroscopy. The pseudo first order rate constants(k') were obtained by plotting log $(A_\infty/(A_\infty-A_t))$ versus t the gradient being k'/2.303 in accordance with the following equation

$$\log (A_\infty/(A_\infty - A_t)) = \frac{k'}{2.303} t$$

where t is the time, A_t is the absorbance at time t and A_∞ is the absorbance at infinity.

The second order rate constants(k) derived from k', log k and the substituent constants for the esters are shown in table III. The Hammett correlation from this data is displayed in Fig 3. Again a good straight line is obtained. A least squares analysis of the data gave a ρ value of 1.9±0.2 and a correlation coefficient of 0.992.

If the results from the exchange and u.v. measurements are combined(see Fig 4) a good straight line can be drawn to fit the data from both sources. A least squares analysis of the combined data gave a ρ value of 2.03±0.05 and a correlation coefficient of 0.997. Thus the rate of carbanion formation predicted from the exchange measurements

TABLE III

The Rate Constants for the Triethylamine Promoted Eliminations from Nitroaryl Phenylmethanesulponates at 20° in DME containing 20% of Deuterium Oxide

Ester	Rate Constant(k)/$\underline{M}^{-1}$ s^{-1}	log k	σ^{*}†
$PhCH_2SO_3C_6H_3(NO_2)_2$-2,4	2.34	0.368	1.72
$PhCH_2SO_3C_6H_3Cl$-2,NO_2-4	0.139	-0.857	1.09
$PhCH_2SO_3C_6H_3CF_3$-3,NO_2-4	5.89×10^{-2}	-1.23	1.25
$PhCH_2SO_3C_6H_3(NO_2)_2$-3,4	0.895	-0.063	1.49
$PhCH_2SO_3C_6H_3COCH_3$-4,NO_2-2	0.502	-0.299	1.44

†Calculated by summing the sigma values for each substituent, σ_n(12) was used for the meta and para substituents and σ_o(13) for the ortho substituents.

FIG 3

Hammett Correlation for the Triethylamine Promoted Elimination from Nitroaryl Phenylmethanesulphonates

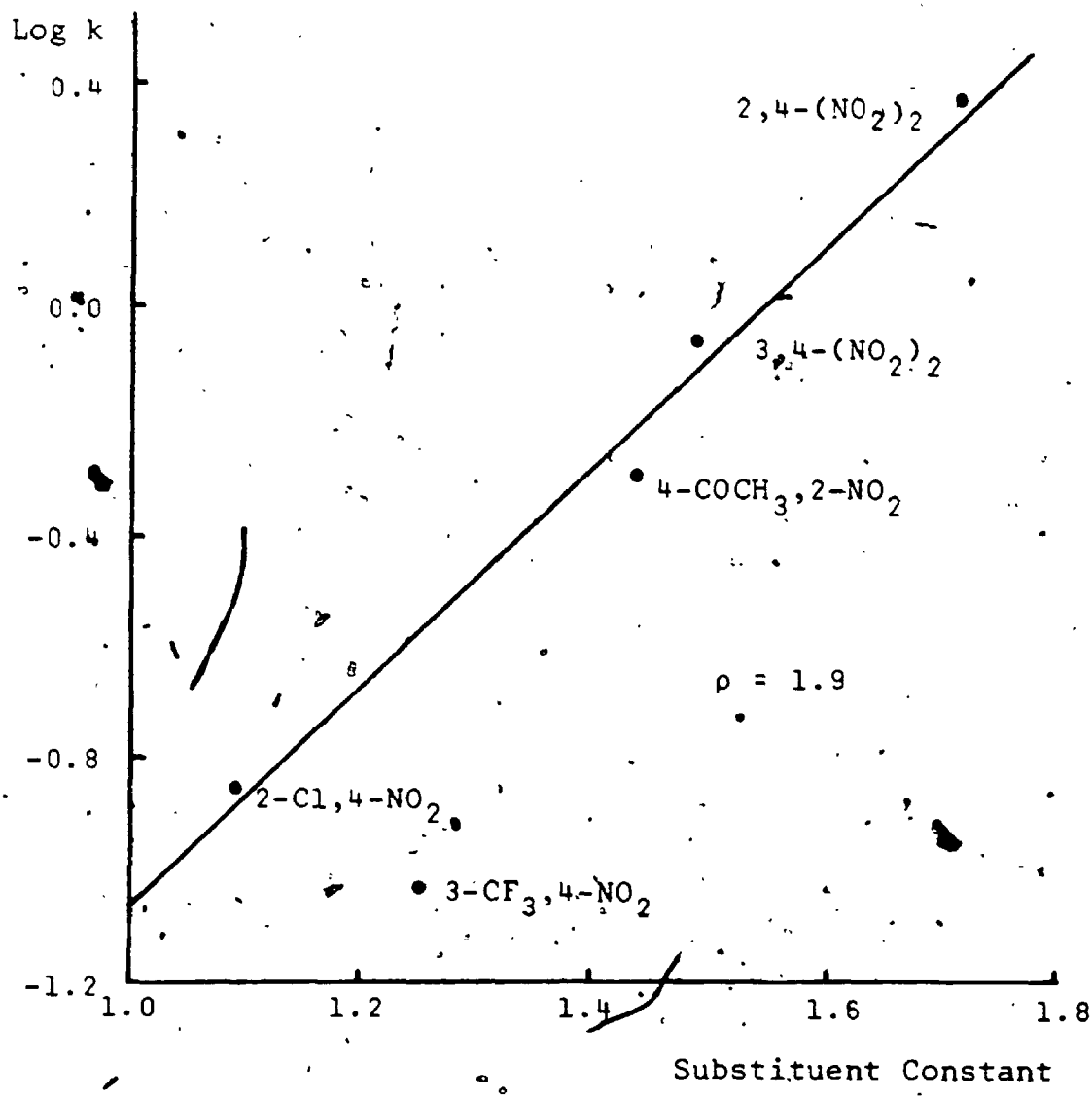
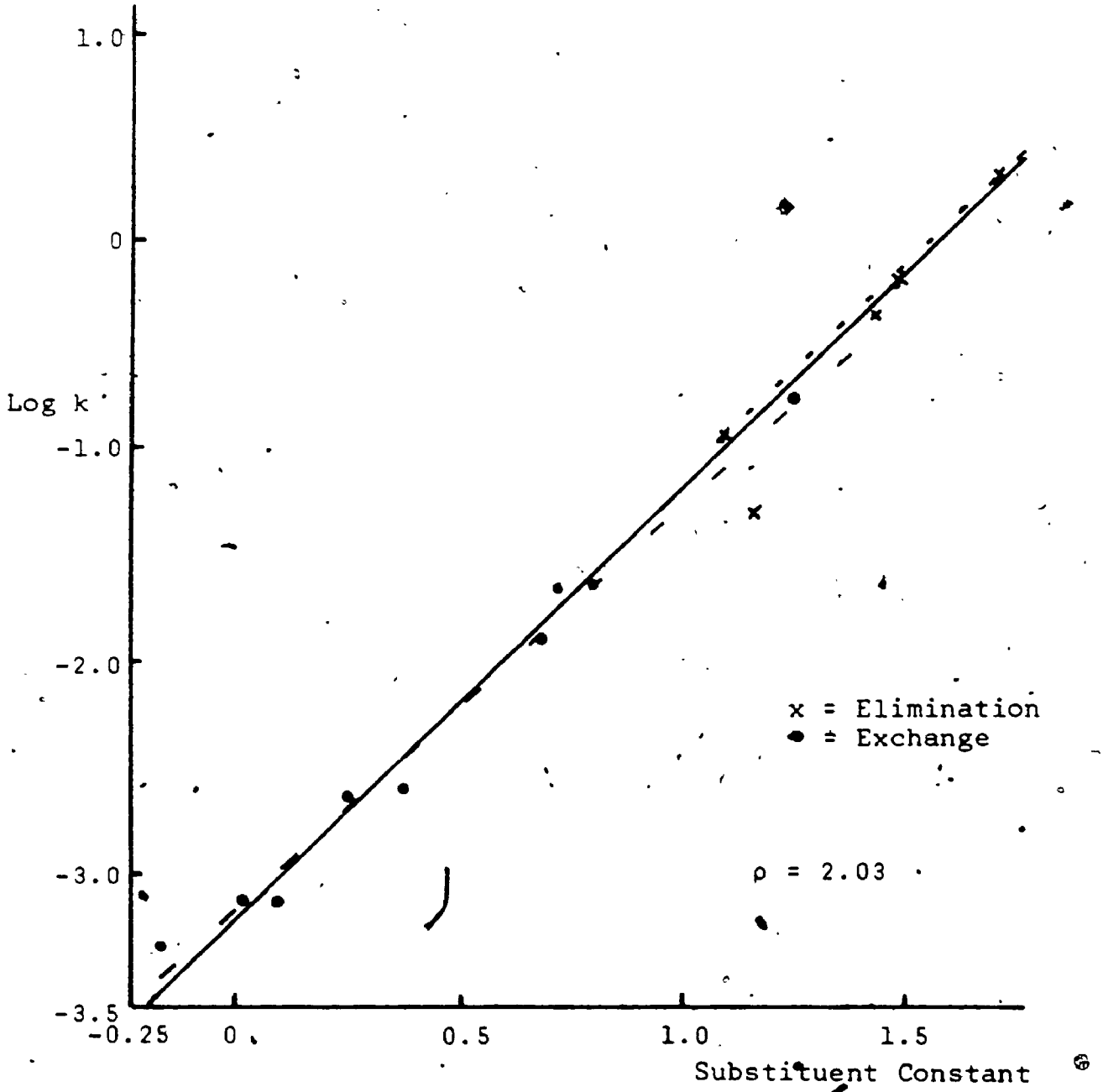


FIG 4

Hammett Correlation of the Rate Constants for the Triethylamine Promoted Exchange and Elimination from Aryl Phenylmethanesulphonates



coincides with the rate of elimination. Hence it would appear that only inductive and field effects are affecting the rate of the elimination reactions of 2,4-dinitrophenyl phenylmethanesulphonate and the other nitro esters. There is no evidence for any weakening of the bond between the group that subsequently leaves and the sulphur in the transition state, since this would be expected to lead to a faster reaction than that occurring by an Elcb process. Therefore the Elcb mechanism shown below fits the data for elimination from the esters with good leaving groups.

$$PhCH_2SO_2OAr + Et_3N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ph\bar{C}HSO_2OAr + Et_3\overset{+}{N}H$$

$$Ph\bar{C}HSO_2OAr \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PhCH{=}SO_2 + \bar{O}Ar$$

$$PhCH_2SO_3H \xleftarrow[k_3]{H_2O} PhCH{=}SO_2 + Et_3\overset{+}{N}H + \bar{O}Ar$$

where $k_1 < k_2 > k_{-1}$ and $k_3 > k_{-2}$

Further information about the reaction can be obtained from a detailed analysis of these data.

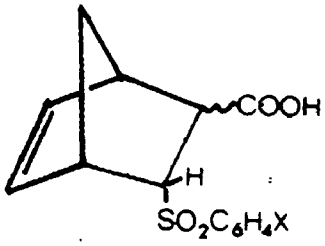
(v) The Rho Value and the Correlation with σ_n

The rho value of 2 is positive and as such is consistent with the build-up of negative charge in the transition state of the rate determining step. However the value of 2 seems to be rather high as the inductive effect of the substituent must be transmitted through two atoms to reach the proposed centre of negative charge build-up, the benzylic carbon. It is possible that this high ρ value is a consequence of the exchange occurring by a reversible sulphene formation as shown below,

$$B + ArCH_2SO_2OAr \underset{D_2O}{\rightleftharpoons} ArCH{=}SO_2 + BH^+ + ArO^-$$

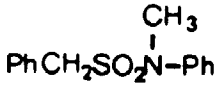
and that all the Hammett plot signifies is the absence of a change in mechanism and thus the elimination is occurring by an E2 mechanism.

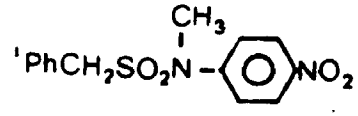
However several observations combine to exclude such a mechanism. The sulphone grouping and the oxygen can transmit substituent effects to a carbon bearing a negative charge to a certain extent. For example in the exchange of 3-arylsulphonyl bicyclo[2,2,1]hept-5-ene 2 carboxylic acid



a value of 2.8 was obtained(14). Also a ρ value of 1.5 was obtained for the tertiary butoxide promoted E2 reaction (with a carbanion like transition state) of β-phenoxyethyl chlorides(15).

In order to obtain an estimate of the inductive and field effects of the substituents on the rate of exchange at the benzylic carbon of the esters the following amides were prepared.





Using these amides as substrates exchange via an elimination-addition mechanism seems extremely unlikely.

The rates of exchange of these amides, at 50° with triethylamine in DME containing 20% of deuterium oxide, were measured. These results gave a ρ value of 1.8. As a case in which there is little doubt that the exchange is occurring via a carbanion gives a ρ value of 1.8, the value of 1.9 found for the exchange in the sulphonate esters is reasonable for a carbanion mechanism.

These ρ values of ~2 found for the exchange and elimination reactions are much less than the ρ^- value of 4.04 found by Douglas and Williams(16) in the elimination of phenols from phenyl N-methylaminosulphonates,

$$MeNHSO_2OArX \overset{Ka}{\rightleftharpoons} Me\bar{N}SO_2OArX \xrightarrow{k} MeN{=}SO_2 + {}^-OArX$$

where the weakening of the bond between the sulphur and the leaving group is involved in the rate determining process. Again this is consistent with no weakening of the bond between the sulphur and the group which subsequently leaves in the sulphonate esters.

It is interesting to note that the correlation for the exchange and elimination reactions in the sulphonate

esters decreases from 0.997 to 0.989 when σ^-, instead of σ_n, is used for the para chloro, nitro and acetyl substituents. This observation implies that the negative charge in the transition state cannot be on the oxygen of the phenol moiety. If the negative charge were on this oxygen the rates should correlate better with σ^- (σ^- is defined using the ionisation of phenols as the standard reaction) as is the case with phenyl N-methylaminosulphonates where a correlation coefficient of 0.9998 is obtained with σ^-.

Although resonance stabilisation of the negative charge on the phenolic oxygen has no apparent effect on the rate of the reactions it should determine the leaving ability of the phenoxide. The more stable the phenoxide the easier it should depart. This explains the observation that 3-trifluoromethyl 4-nitrophenyl phenylmethanesulphonate (σ = 1.25) forms the carbanion more readily than 2-chloro 4-nitrophenyl phenylmethanesulphonate(σ = 1.09) but the former favours exchange and the latter elimination in accordance with the stability of the phenoxides(pKa of 3-trifluoromethyl 4-nitrophenol is 6.36; pKa of 2-chloro 4-nitrophenol is 5.45, see table XI).

The elimination-addition process as a source of deuterium incorporation in the esters was further discounted by the following observations.

For the exchange of the esters to occur by this process the phenoxide must be reacting with the sulphene

much faster than it is trapped by the deuterium oxide ($k_{-2}[^{-}OArX][Et_3\overset{+}{N}D] > k_3[D_2O]$). However when phenylsulphene was generated from phenylmethanesulphonyl chloride and triethylamine in the presence of an equimolar quantity of triethylammonium 4-nitrophenoxide, at approximately the same concentration as used in the exchange experiments, in [redacted]% aqueous DME, only 2% of the crude 4-nitrophenyl phenylmethanesulphonate was produced. Similarly an attempt to trap phenylsulphene, generated as above, with triethylammonium 4-methoxyphenoxide failed. These results agree with the deductions of Lee(2) that phenylsulphene is not involved in the exchange of the benzylic protons of phenyl phenylmethanesulphonate.

The source of the small amount of 4-nitrophenyl phenylmethanesulphonate will be discussed in a later section.

(vi) Correlation of the Rate Constant for Carbanion Formation with the Chemical Shift of the Benzylic Protons in the pmr

If, as already deduced, the rates of elimination and the rates of exchange are measures of the rate of removal of the benzylic proton it is reasonable to expect that this rate is a function of the electronegativity of the group attached to the benzylic carbon. It is known that the electronegativity of a group can often be estimated from the chemical shift of the proton on the carbon to which it is

TABLE LV

The Chemical Shift and the Rate Constant for Removal of the Benzylic Protons of Phenylmethanesulphonyl Compounds

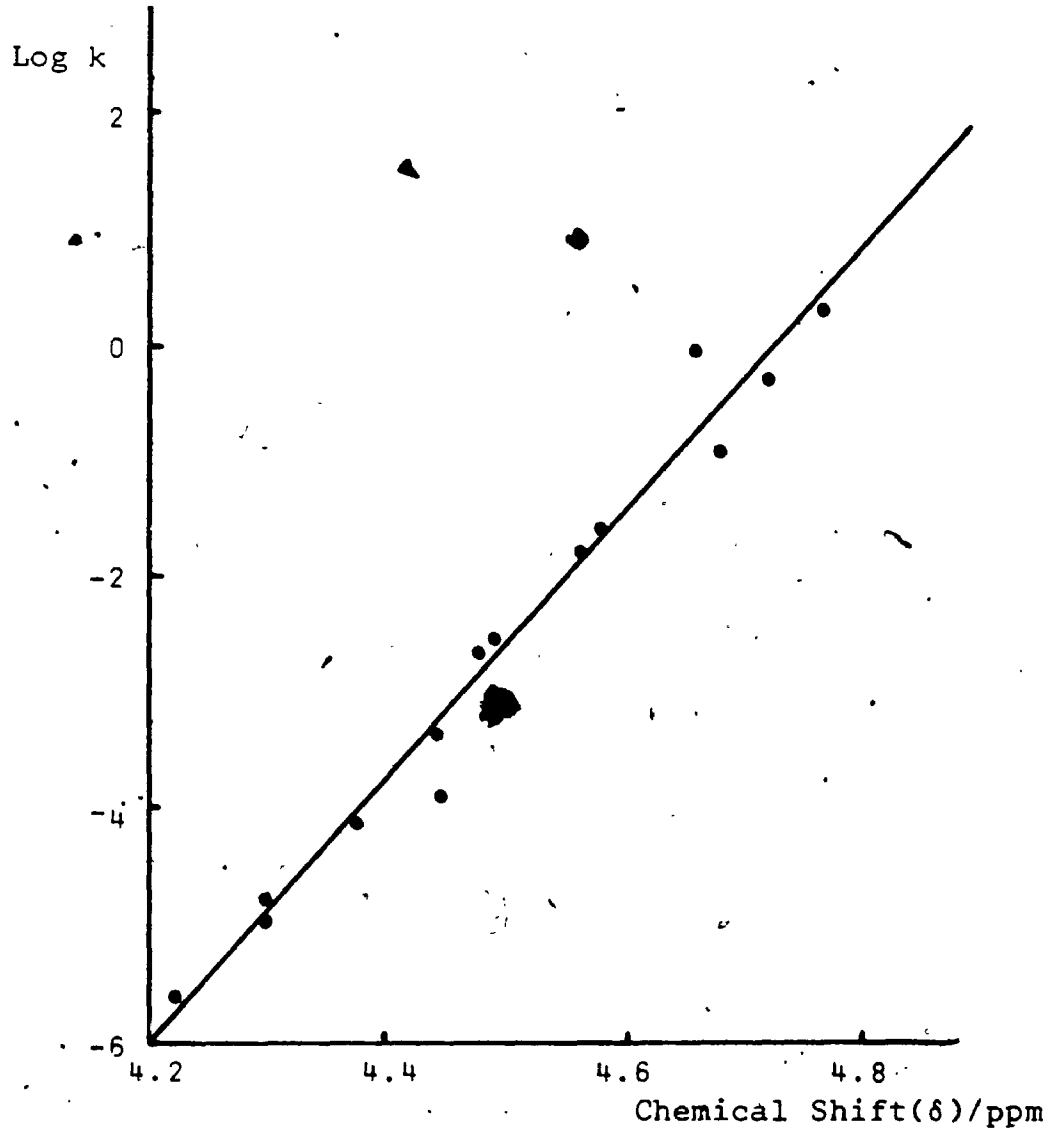
Compound (XSO_2CH_2Ph) X	δ/ppm	$Log(k/M^{-1}s^{-1})$
$C_6H_5N(CH_3)$-	4.242	-5.62†
$(CH_3)_2CHO$-	4.288	-5.07*
$4\text{-}NO_2C_6H_4N(CH_3)$-	4.373	-4.14†
C_6H_5-	4.296	-4.80*
CF_3-	4.460	-3.96*
$4\text{-}CH_3OC_6H_4O$-	4.443	-3.32
$4\text{-}ClC_6H_4O$-	4.478	-2.62
$3\text{-}ClC_6H_4O$-	4.480	-2.57
$4\text{-}CNC_6H_4O$-	4.564	-1.85
$4\text{-}NO_2C_6H_4O$-	4.582	-1.60
$2\text{-}Cl,4\text{-}NO_2C_6H_3O$-	4.679	-0.86
$2\text{-}CH_3CO,4\text{-}NO_2C_6H_3O$-	4.722	-0.30
$3,4\text{-}(NO_2)_2C_6H_3O$-	4.658	-0.06
$2,4\text{-}(NO_2)_2C_6H_3O$-	4.768	0.37

* From reference 2

† Adjusted to 20° by dividing the rate constant measured at 50° by 10

FIG 5

Correlation Between the Rate Constants for Carbanion Formation and the Chemical Shift of the Benzylic Protons



attached(17). Thus the rate of carbanion formation, as measured by the rates of exchange and elimination, might correlate with the chemical shift of the benzylic protons.

Table IV shows the proton chemical shift, relative to T.M.S. in $CDCl_3$, and the rate of carbanion formation deduced from the exchange or elimination rates measured at 20° for a series of compounds with the formula $XSO_2CH_2C_6H_5$. The results are displayed graphically in Fig 5. The correlation is good (r=0.997) except for $X=CF_3$ and $X=3,4\text{-}(NO_2)_2C_6H_3O$. Using all the results a correlation coefficient(r) of 0.983 is obtained from the least squares analysis.

This reasonable correlation confirms the deduction that the rate of elimination is indeed governed solely by the rate of removal of the benzylic proton.

(vii) <u>The Effect of Substitutents in 2,4-Dinitrophenyl Phenylmethanesulphonate on the Rate of Elimination</u>

Another probe into the nature of the elimination reaction is the effect of substituents, in the phenyl ring attached to the carbon, on the rate of elimination. To determine this a series of suitable substrates were prepared by treating substitued phenylmethanesulphonyl chlorides with base in the presence of 2,4-dinitrophenol. The series of esters so prepared were treated with 0.2 M pyridine in 20% aqueous DME at 20°. The rate of phenoxide release was

followed by monitoring the increase in the absorbance, with time, at 405 nm. The results are not a true measure of the rate of sulphene formation since the hydrolysis, in some cases, is also occurring by a non-sulphene route.

Any phenylmethanesulphonic acid formed in this reaction via a sulphene mechanism should be monodeuterated at the benzylic position(7,9) when the reaction is conducted in the presence of excess deuterium oxide. However the phenylmethanesulphonyl chloride, obtained from the phenylmethanesulphonic acid, was found to consist of both monodeuterated and undeuterated products. This undeuterated acid could be formed by either of the routes found by Maccoll (18) in the pyridine catalysed methanolysis of 2,4-dinitrophenyl toluene-p-sulphonate as neither leads to exchange. Since both these routes are first order in base and ester, assuming that one or both of these routes give rise to the undeuterated material, the rate constant for the hydrolysis via the sulphene route can be obtained by multiplying the observed rate constant for 2,4-dinitrophenoxide release by the fraction of the hydrolysis going by the sulphene route. This fraction, determined from the mass spectra of the phenylmethanesulphonyl chlorides derived from the reactions conducted in the presence of deuterium oxide, is shown in table V.

The correction is only significant for the less reactive esters, 2,4-dinitrophenyl phenylmethanesulphonate and 2,4-dinitrophenyl 3-chlorophenylmethanesulphonate. In

the case of the more reactive esters all the hydrolysis appears to take place via a sulphene mechanism. These corrected rate constants, their logarithms and the σ^- values for the esters are shown in table VI. The Hammett correlation of these results is shown in Fig 6. The least squares analysis of the data gives a ρ^- of 2.38±0.04 and a correlation coefficient of 0.9995.

The rates of elimination from the three less reactive esters, using triethylamine rather than pyridine, were also measured. These results are shown in table VII and displayed in Fig 7. A least squares analysis of the data gave a ρ^- value of 2.7±0.2.

The positive ρ^- values of 2.4 and 2.7 are consistent with an increase in the negative charge in the formation of the transition state of the rate determing step. The better correlation with σ^-(0.995) than with σ_n(0.9389) indicates that the charge is resonance stabilised. This is consistent with the charge being on the carbon adjacent to the phenyl ring bearing the substituents. The ρ^- value is higher when the stronger base is used to promote the elimination reaction. This contradicts the Swain-Thornton rules (19) which are obeyed in many E2 eliminations(20). However the published literature yields two examples of irreversible Elcb reactions in which ρ increases with increasing base strength. For example in the irreversible Elcb elimination from aryl carbamoyl chlorides, when N,N-dimethyl 4-bromoaniline(pKa=4.23) is used as the base ρ = 0.86 and when

TABLE V

The Fraction of 2,4-Dinitrophenoxide Formed by the Sulphene Route in the Pyridine Promoted Hydrolysis of 2,4-Dinitrophenyl Phenylmethanesulphonates at 20° in DME containing 20% of Deuterium Oxide

Ester	Fraction of Hydrolysis by the Sulphene Route
$C_6H_5CH_2SO_3C_6H_3(NO_2)_2$-2,4	0.62
4-$ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	0.82
3-$ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	0.90
4-CN $C_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	1
4-$NO_2C_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	1

TABLE VI

The Data for the Hammett Correlation of σ^- with the Logarithm of the Rate Constant ($\log k_s$) for the Pyridine Promoted Hydrolysis of 2,4-Dinitrophenyl Phenylmethanesulphonates Occurring via a Sulphene Route in 20% Aqueous DME at 20°

Ester	$k_t/10^{-3}$ M^{-1} s^{-1} †	$k_s/10^{-3}$ M^{-1} s^{-1} §	$\log k_s$	σ^-
$C_6H_5CH_2SO_3C_6H_3(NO_2)_2$-2,4	0.106	0.066	-4.18	0
4-$ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	0.251	0.207	-3.68	0.23
3-$ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	0.593	0.535	-3.27	0.37
3-$NO_2C_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	3.10	3.01	-2.52	0.71
4-$CNC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	14.3	14.3	-1.85	1.00
4-$NO_2C_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	73.4	73.4	-1.13	1.27

†k_t is the measured rate constant for the hydrolysis.
§k_s is the rate constant for the hydrolysis via the sulphene route.

FIG 6

Hammett Correlation for the Reaction of Pyridine with 2,4-Dinitrophenyl Arylmethanesulphonates

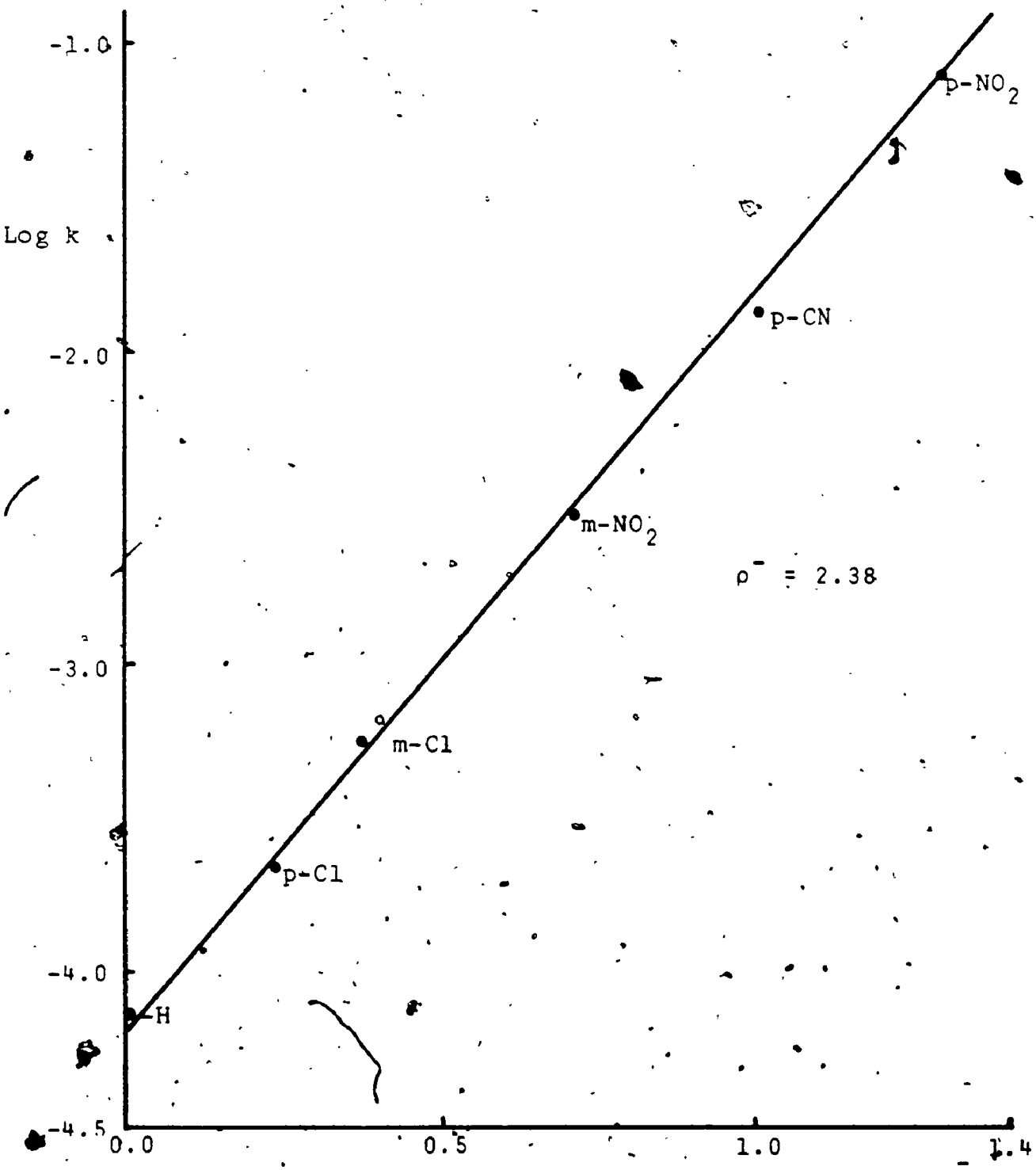


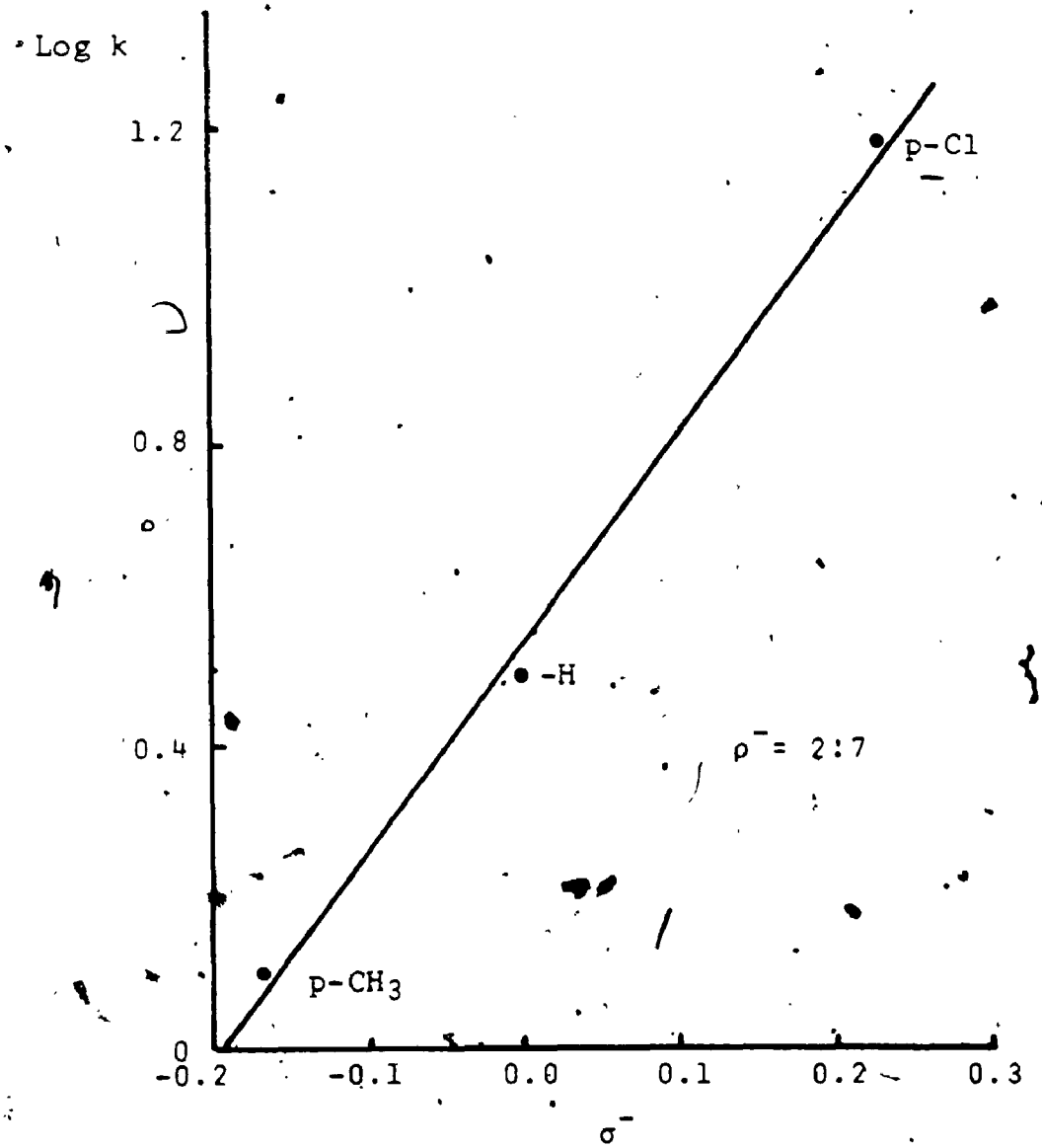
TABLE VII

The Data for the Hammett Correlation of σ with the Logarithm of the Rate Constant for the Triethylamine Catalysed Elimination from 2,4-Dinitrophenyl Phenylmethanesulphonates in 20% Aqueous DMF at 20°

Ester	Rate Constant for Elimination $k/M^{-1}\ s^{-1}$	log k	σ
$4\text{-}CH_3C_6H_4CH_2SO_3C_6H_3(NO_2)_2\text{-}2,4$	1.27	0.104	-0.17
$C_6H_5CH_2SO_3C_6H_3(NO_2)_2\text{-}2,4$	3.03	0.481	0
$4\text{-}ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2\text{-}2,4$	15.2	1.184	0.23

FIG 7

Hammett Correlation for the Reaction of Triethylamine with 2,4-Dinitrophenyl Arylmethanesulphonates



N,N-dimethylaniline(pKa=5.07) is used as the base $\rho = 2.7$(21). Also in the irreversible Elcb elimination from p-substituted phenyl β-chloroethylsulphones with tertiary amines in acetonitrile the same effect is observed(22), see table VIII.

The ρ^- values of 2.4 and 2.7 for the rate determining formation of the carbanion can be compared to the ρ of 4.0 obtained by Strietweiser(23) for the exchange of substituted toluenes with lithium cyclohexamide in cyclohexamine at 50° and the ρ^- value of 2.4 obtained by Lee(2) for the "Elcb like" dehydrohalogenation of phenylmethanesulphonyl chloride.

(c) The Mechanism of Base Catalysed 1,2-Eliminations from 4-Nitrophenyl Phenylmethanesulphonates

In extending the studies of Singh(3) the reversibility of the carbanion formation was confirmed by recovering exchanged 4-nitrophenyl phenylmethanesulphonate from the reaction of the ester with triethylamine in DME containing 20% of deuterium oxide at 20°. The rate of exchange (2.48×10^{-2} $\underline{M}^{-1}$ s^{-1}, see table II) is much faster than the rate of 4-nitrophenoxide release(8.1×10^{-4} $\underline{M}^{-1}$ s^{-1}) found by Singh in DME containing 2.2 $\underline{M}$ water at 45°. These observations are consistent with the reversible Elcb mechanism and as such the rate of phenoxide release should show an inverse dependence on the conjugate acid of the base(see introduction).

TABLE VIII

Substituent Effect in the Reaction of

$XArSO_2CH_2CH_2Cl$ with the Amines in CH_3CN at 50°

Bases	pKa	ρ†	r§
NEt_3	19.0	1.81	0.991
$Et_2N(CH_2CH_2OH)$	17.9	1.75 1.76	0.994 0.995
$EtN(CH_2CH_2OH)_2$	16.9	1.72 1.73	0.995 0.994
$N(CH_2CH_2OH)_3$	15.3	1.65 1.64	0.982 0.989

X: CH_3O, CH_3, H and Cl.
†These values were calculated from the method of least square.
§Coefficient of correlation.

$$\text{Rate} = \frac{k_1 k_2 [RX][B]}{k_{-1}[BH^+]}$$

modifying this equation

$$\text{Rate} = \frac{k_1 k_2 K_a^{BH^+} [RX][OH^-]}{k_{-1} K_w}$$

This last equation indicates that for a reversible Elcb mechanism the rate of the elimination should be first order in the substrate and the hydroxide ion concentrations and independent of the triethylamine concentration. In other words a reversible Elcb reaction should be specific base catalysed.

(i) Specific Base Catalysis in the Elimination from 4-Nitrophenyl 4-Nitrophenylmethanesulphonate

4-Nitrophenyl 4-nitrophenylmethanesulphonate was chosen for this investigation since, from the results of Singh(3), it had the largest rate constant of the esters that were available and was thus more convenient for the many rate measurements required for this analysis.

4-Nitrophenyl 4-nitrophenylmethanesulphonate was treated with different concentrations of triethylamine in 20% aqueous DME. The pH of the solutions was maintained at 9.40 by using triethylammonium chloride. The ionic strength was maintained at 0.05 M by the use of tetraethylammonium

chloride. The ester was injected into these solutions and the rate of 4-nitrophenoxide release was determined by following the increase in absorbance at 405 nm with time. The results are shown in table IX and are displayed in Fig 8. A least squares analysis of the data gave a line with slope 2.7×10^{-4} M^{-1} s^{-1} and an intercept(k) of 1.08×10^{-4} s^{-1}. As can be seen from Fig 8, within experimental error, the rate remains constant as the triethylamine concentration varies. This observation plus the observation that as the pH increases so does the rate (pH = 9.9, $k = 3.1 \times 10^{-4}$ s^{-1}, ionic strength 0.005 M) confirms specific base catalysis.

Now that the dependence of the reaction on pH had been established it was deemed necessary to repeat the Hammett correlation of the rate of phenoxide release from 4-nitrophenyl phenylmethanesulphonates carried out by Singh (3) but now using a buffered system.

(ii) The Effect of Substituents in 4-Nitrophenyl Phenylmethanesulphonate on the Rate of the Specific Base Catalysed Elimination

The 4-nitrophenyl phenylmethanesulphonates, substituted on the phenyl attached to the methylene, available from the work of Singh, were treated with triethylamine in 20% aqueous DME, the pH being maintained at 9.39 with triethylammonium chloride. The ionic strength was maintained at 0.05 M using tetraethylammonium chloride. The rate of the appearance of 4-nitrophenoxide was followed by u.v. spectro-

TABLE IX

The Pseudo First Order Rate Constants for the Triethylamine Promoted Elimination from 4-Nitrophenyl 4-Nitrophenylmethanesulphonate

Solvent: 20% aqueous DME

Ester concentration: 4×10^{-5} M

Temperature: $20 \pm 0.1^{\circ}$

pH: 9.40

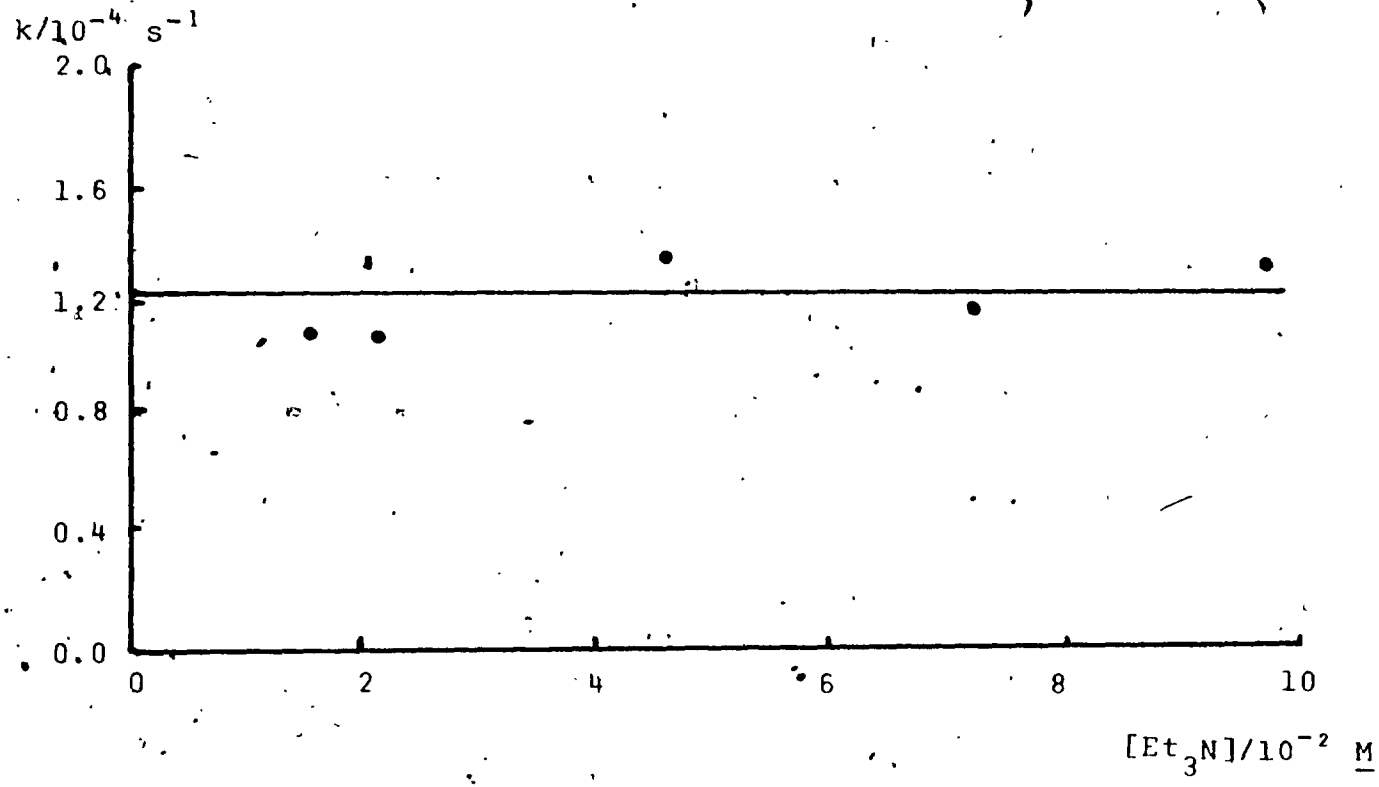
Ionic strength: 0.05 M

Triethylamine* Concentration/10^{-2} M	Rate Constant $k/10^{-4}$ s^{-1}
1.54	1.10
2.15	1.08
4.66	1.37
7.24	1.18
9.73	1.34

*Corrected using a 'pKa' for triethylamine of 8.43 in 20% aqueous DME, see appendix II.

FIG 8

Specific Base Catalysis in the Reaction of Triethylamine with 4-Nitrophenyl 4-Nitrophenylmethanesulphonate



scopy. The rate constants so obtained are listed on table X along with the σ^- values for the esters. The correlation with σ^- is displayed in Fig 9. A least squares analysis of the data gave a ρ^- of 0.54±0.04 with a correlation coefficient of 0.992.

The better correlation with σ^- than with σ_n (correlation coefficient with σ_n = 0.917) indicates that there is resonance stabilisation of the forming negative charge at the benzylic position by the substituents on the adjacent phenyl ring. The low positive ρ^- value is consistent with the rate expression derived at the beginning of this section. The ρ^- value is the sum of the ρ^- for the equilibrium constant ($K = k_1/k_{-1}$) for the formation of the carbanion, which will be positive and the ρ^- value for the rate constant (k_2) for the formation of the sulphene form the carbanion, which will be negative. The net positive value reflegts the greater sensitivity to the substituents of the equilibrium constant.

(iii) <u>The Absence of Reversible Sulphene Formation</u>

The general equation for the reversible sulphene formation is as shown below

$$B^- + ArCH_2SO_2OAr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCH{=}SO_2 + BH^+ + {}^-OAr$$

$$\downarrow k_2 \; H_2O$$

$$ArCH_2SO_3H$$

TABLE X

The Data for the Hammett Correlation of the Logarithm of Pseudo First Order Rate Constants for Triethylamine Promoted Elimination from 4-Nitrophenyl Phenylmethanesulphonates with σ^-

"pH": 9.39

Ionic Strength: 0.05 M

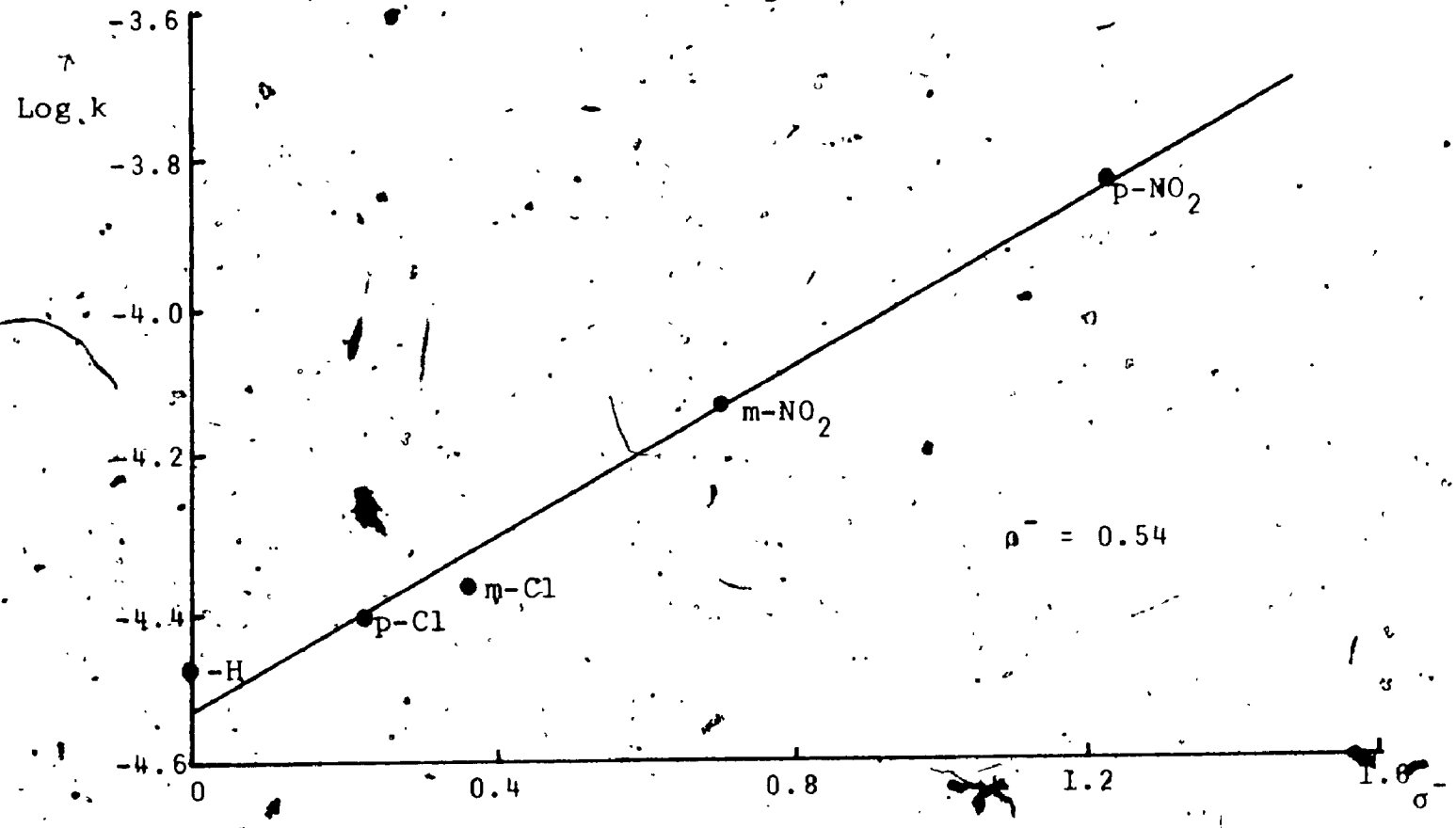
Triethylamine Concentration: 0.059 M

Ester Constration: ≈1 x 10^{-4} M

Ester	Rate Constant $k/10^{-5}$ s^{-1}	log k	σ^-
$PhCH_2SO_3C_6H_4NO_2$-4	3.31	-4.48	0
4-$ClC_6H_4CH_2SO_3C_6H_4NO_2$-4	3.92	-4.41	0.23
3-$ClC_6H_4CH_2SO_3C_6H_4NO_2$-4	4.25	-4.37	0.37
3-$NO_2C_6H_4CH_2SO_3C_6H_4NO_2$-4	7.46	-4.13	0.71
4-$NO_2C_6H_4CH_2SO_3C_6H_4NO_2$-4	14.5	-3.84	1.24

FIG 9

Hammett Correlation for the Reaction of Triethylamine with 4-Nitrophenyl Arylmethanesulphonates



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Applying the steady state assumption to the concentration of sulphene, the rate of the elimination is given by

$$\text{Rate} = \frac{k_1 k_2[B][ArCH_2SO_3Ar]}{k_{-1}[^-OAr][BH^+] + k_2}$$

Since the rate measurements show that the exchange is much faster than the formation of products $k_{-1}[^-OAr][BH^+] > k_2$ and

$$\text{Rate} = \frac{k_1 k_2[B][ArCH_2SO_3Ar]}{k_{-1}[^-OAr][BH^+]}$$

This equation necessitates a decrease in the rate of the elimination, in buffered solution, as the reaction proceeds, because $[^-OAr]$ is steadily increasing. However this behaviour was not observed, the kinetic measurements giving good straight lines to 90% reaction.

(d) <u>The Mechanism of Base Catalysed Elimination from 4-Nitro 2-Chlorophenyl Phenylmethanesulphonate</u>

As discussed in section (b), whether these esters exchange or eliminate depends upon the pK_a of the conjugate acid of the phenoxide being released. This relationship is shown in table XI. From the table it appears that 4-nitro 2-chlorophenyl phenylmethanesulphonate is in the border

TABLE XI

The Relationship Between pKa of the Phenol and Reaction Mode of the Ester

PHENOL	pKa	Ref	
3-NO_2Phenol	8.28	24	Exchange only
4-CNPhenol	7.97	25	
4-NO_2Phenol	7.15	24	Exchange and Sulphene Formation
3-CF_3,4-NO_2Phenol	6.36	26	
2-Cl,4-NO_2Phenol	5.45	27	
3,4-$(NO_2)_2$Phenol	5.37	28	Sulphene Formation only
2-NO_2,4-CH_3COPhenol	5.09	29	
2,4-$(NO_2)_2$Phenol	4.07	29	

Above pKa 7.9 only the exchange of the ester was observed.

Below pKa 5.4 only the formation of phenylsulphene was observed.

region between exchange and elimination. Assuming an Elcb process is occurring, in this case $k_2=k_{-1}[BH^+]$ and as a result of this balance an increase in $[BH^+]$ should increase $k_{-1}[BH^+]$ over k_2 with an observable increase in the rate of exchange. Also in a case where $k_2=k_{-1}[BH^+]$ the rate of the elimination should be in accordance with the following equation

$$\text{Rate} = \frac{k_1 k_2 [RX][B]}{k_{-1}[BH^+] + k_2} \qquad \text{(see section (a))}$$

Hence an increase in $[BH^+]$ should reduce the rate of phenoxide release:

(i) The Effect of Triethylammonium Chloride on the Rate of Exchange of 4-Nitro 2-Chlorophenyl Phenyl methanesulphonate

When 4-nitro 2-chlorophenyl phenylmethanesulphonate was recovered from the incomplete reaction of the ester with triethylamine in DME containing 20% of deuterium oxide no exchange of the benzylic protons was observed. However when the experiment was repeated in the presence of 0.07 M triethylammonium chloride the ester recovered after 70% reaction was 20% deuterated in the benzylic position. This is consistent with the Elcb mechanism.

(ii) The Effect of Triethylammonium Chloride on the Rate of the Elimination Reaction

The rate of phenoxide release, when 4-nitro 2-chlorophenyl phenylmethanesulphonate was treated with triethylamine in 20% aqueous DME in the presence of different concentrations of triethylammonium chloride at a constant ionic strength of 0.1 M, was measured. The results are shown in table XII. From this table the depression of the observed second order 'rate constant' ($k_{obs}/[Et_3N]$) as the triethylammonium ion concentration was increased is immediately apparent.

This effect should follow the equation below, derived from the equation on p82.

$$\frac{k_{obs}}{[Et_3N]} = \frac{A(1)}{A(2)[BH^+] + 1}$$

A(1) and A(2) are the constants k_1 and k_{-1}/k_2. A non-linear least squares fit of the data to the above equation gave $k_1 = 0.16 \pm 0.01\ M^{-1}\ s^{-1}$ and $k_{-1}/k_2 = 14 \pm 2\ M^{-1}$.

TABLE XII

The Effect of the Triethylammonium Cation on the Pseudo First Order Rate Constants for the Triethylamine Promoted Elimination from 2-Chloro 4-Nitrophenyl Phenylmethanesulphonate

Solvent: 20% aqueous DME

Temperature: 20.0 ± 0.1^{0}

Ionic strength: 0.1 M

$[Et_3N]^{*}/10^{-2}M$	$[Et_3NH^{+}]^{*}/10^{-2}M$	$kobs/10^{-4}s^{-1}$	$(kobs/[Et_3N]^{*})/M^{-1}s^{-1}$
0.33	0.87	4.96	0.15
0.97	0.99	14.4	0.15
0.84	1.56	9.82	0.12
2.36	1.84	29.0	0.12
3.14	2.46	37.6	0.12
2.25	3.75	22.1	0.10
5.58	4.22	67.5	0.10
4.59	7.41	36.4	0.08

*Concentrations adjusted using a 'pKa' of 8.43 for triethylamine in 20% aqueous DME. See appendix II.

(iii) The Absence of Reversible Sulphene Formation Directly from the Ester

The analysis on pages 77 and 80 can also be applied to the reaction of 4-nitro 2-chlorophenyl phenylmethanesulphonate with base. In the region where the rate of the elimination depends upon $[BH^+]$, the rate of the reaction should decrease as the reaction proceeds. Again this behaviour was not observed.

A study of the exchange rates confirms the absence of the reversible sulphene formation mechanism. If the reversible sulphene mechanism was the source of the exchange the rate of the exchange would be governed by the following equation

$$\text{Rate} = \frac{k_1[ArCH_2SO_2OAr][B]}{1 + k_2/(k_{-1}[BH^+][^-OAr])}$$

(for assignment of rate constants see p.77)

From this equation the rate of exchange is dependent on the product of $[BH^+]$ and $[^-OAr]$. Thus if the concentration of ^-OAr is doubled, under conditions where the reaction is dependent on $[BH^+]$, the $k_{-1}[BH^+][^-OAr]$ term should have a significant effect on the rate. Three experiments were conducted to test this theory.

The ester(6×10^{-3} M) was treated with triethylamine

(4.9×10^{-2} M) and triethylammonium chloride(7.1×10^{-2} M), in the absence of 2-chloro 4-nitrophenoxide, in the presence of 3×10^{-3} M phenoxide and in the presence of 6×10^{-3} M phenoxide over a period of 1.72 min. The amount of exchange was measured by mass spectroscopy. The results are shown in table XIII.

It can be seen that the rate of exchange is almost constant. The variation of the amount of exchange from 22% to 26% when the concentration of the phenoxide is at least doubled is not consistent with the reversible sulphene mechanism. The small upward drift of the amount of exchange may be assigned to the reversibility of the formation of phenylsulphene from the carbanion, as is discussed in the following section.

(e) The Reversibility of the Formation of Phenylsulphene from the Carbanion

The assumption that the formation of the phenylsulphene from the carbanion is substantially irreversible has been made in all the analyses of the data so far presented. However as the esters were prepared by the trapping of the sulphene by the phenoxides, albeit in a different solvent medium, it is obvious that the assumption may not be valid under all conditions.

To test the range of validity of this assumption a few experiments, testing the ability of the phenoxide to

TABLE XIII

The Percentage of Exchange of the Methylene Protons of 2-Chloro 4-Nitrophenyl Phenylmethanesulphonate in the Presence of Triethylamine and Triethylammonium 2-Chloro 4-Nitrophenoxide in DME containing 20% of Deuterium Oxide

Temp : 20°

Time : 1.72 min

$[Et_3\overset{+}{N}HCl^-]$: 0.071 M

Ester concentration : 6.0×10^{-3} M

$[NEt_3]$/M	[Phenoxide]/M	CH_2:CHD:CD_2	Percentage Exchange
4.6×10^{-2}	ZERO	101: 59: 7	21.9
4.9×10^{-2}	3×10^{-3}	102: 65: 8	23.3
4.9×10^{-2}	6×10^{-3}	95: 72: 11	26.6

trap the phenylsulphene, in 20% aqueous DME, were conducted. Phenylsulphene was generated from phenylmethanesulphonyl chloride and base in 20% aqueous DME in the presence of phenoxides. The results are summarised in table XIV.

From this table it can be seen that, at concentrations close to those used in the measurement of the exchange rates(5×10^{-3} M), there is a small amount of phenylsulphene trapping by the 4-nitrophenoxide. Thus the assumption in this case is only an approximation but the error is within the error of the experiment. The assumption is certainly valid for the measurements of the elimination rates where the concentrations of the esters were approximately 5×10^{-5} M.

The results, when 2-chloro 4-nitrophenol was used indicate that at 5×10^{-3} M a small amount of trapping of the phenylsulphene(3%) by the phenol might occur. This could explain the small increase in the amount of exchange of 2-chloro 4-nitrophenyl phenylmethanesulphonate as the phenoxide concentration was increased(see p. 87 , table XIII). Again the effect of the phenoxide on the rate of the eliminations would be negligible since these determinations were conducted at an ester concentration of approximately 5×10^{-5} M.

TABLE XIV

The Trapping of Phenylsulphene, Generated from Phenylmethanesulphonyl Chloride and Triethylamine, by Phenols in 20% Aqueous DME

Phenol	[Phenol]/M	[$PhCH_2SO_2Cl$]/M	[Et_3N]/M	Time/min	Yield of Ester
4-Methoxyphenol	5.37×10^{-3}	5.35×10^{-3}	0.198	30	0
4-Nitrophenol	7.00×10^{-3}	6.98×10^{-3}	0.198	1	2%
2-Chloro 4-Nitrophenol	7.20×10^{-2}	7.10×10^{-2}	0.232	0.1	38%

The absence of the ester in the experiment with 4-methoxyphenol demonstrates that the trapping of the phenylsulphene by this phenol does not occur under the conditions of the exchange experiments. Hence none of the exchange detected with 4-methoxyphenyl phenylmethanesulphonate derives from a trapping of the phenylsulphene.

(f) The Mechanism of Phenylsulphene Formation from Phenylmethanesulphonyl Chlorides and Their Esters

All the experimental evidence gleaned in this study of the elimination and exchange reactions of phenyl phenylmethanesulphonates can be adequately rationalised by the following model, an Elcb mechanism;

$$B + ArCH_2SO_2OAr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\bar{C}HSO_2OAr + BH^+$$

$$Ar\bar{C}HSO_2OAr \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArCH{=}SO_2 + {}^-OAr$$

$$ArCH{=}SO_2 \xrightarrow[k_3]{H_2O} ArCH_2SO_3H$$

in which $k_{-2}[^-OAr]$ is smaller than k_3 under the conditions used. The differing behaviour of the esters is a result of the increase in $k_2/k_{-1}[BH^+]$ as the phenoxide becomes a better leaving group.

It is important to compare my deductions and results with the recently published papers of Williams et al

concerning his concurrent studies of the reaction of base with aryl phenylmethanesulphonates(30,31). My results and conclusions agree with those of Williams published in the first paper(30). However in the second paper(31) Williams deduced that, with phenylmethanesulphonate esters of phenols with a pKa of less than 6, if the carbanion is formed during the alkaline hydrolysis it would have an estimated lifetime of less than the vibration time of the S-OAr bond. This prompts these workers to conclude that, with these esters, carbanions do not exist as identifiable species and thus according to this criterion the reaction is a concerted E2 reaction.

If one accepts that Williams' linear correlation of the rate of unimolecular carbanion decomposition with the pKa of the phenol can be extrapolated into the region of the vibration limit, a model to fit my data and that of Williams must be found. Such a model is one in which the transition state is that expected for carbanion formation but this transition state fragments without forming an intermediate carbanion. We have progressed smoothly from an irreversible E1cb reaction to a second order single step elimination in which the bond to the group that subsequently leaves is intact in the transition state. This type of reaction no longer fits into the generally accepted class of E2 reactions, members of which are envisaged as having a weakened bond to the leaving group in the transition state.

It is informative to compare my results with those of Lee(2) for the base catalysed eliminations from phenylmethanesulphonyl chloride. The rate constant for the pyridine promoted dehydrochlorination of phenylmethanesulphonyl chloride at 20° in 1% aqueous DME is 7×10^{-4} $\underline{M}^{-1}$ s^{-1} a value which is close to the value of 6.60×10^{-5} $\underline{M}^{-1}$ s^{-1}, measured at 20° in 20% aqueous DME, found for the rate constant for the pyridine promoted elimination from 2,4-dinitrophenyl phenylmethanesulphonate. It seems likely that this small rate increase can be explained by greater stabilisation of the transition state by the inductive and field effects of the chlorine rather than a lowering of the transition state energy by a weakening of the bond to the leaving group.

The correlation of the chemical shift of the methylene protons in phenylmethanesulphonyl compounds with the kinetic acidity in their reactions with triethylamine (see p.62) enables one to predict the inductive and field effects of the chlorine in phenylmethanesulphonyl chloride on this acidity. The chemical shift of the benzylic protons of phenylmethanesulphonyl chloride is 4.480 ppm which corresponds to a rate constant of 20 $\underline{M}^{-1}$ s^{-1} for its' reaction with triethylamine. This rate constant is 8.5 times greater than that found for the triethylamine promoted elimination from 2,4-dinitrophenyl phenylmethanesulphonate. If a similar enhancement of the rate constant is found in the pyridine promoted eliminations a rate constant of 5.6×10^{-4} $\underline{M}^{-1}$ s^{-1},

8.5 times that found for the pyridine promoted elimination from 2,4-dinitrophenyl phenylmethanesulphonate, is predicted. This is very close to the value of $.7 \times 10^{-4}$ $\underline{M}^{-1}$ s^{-1} found by Lee for the dehydrochlorination of phenylmethanesulphonyl chloride by pyridine. Thus it seems that it is not necessary to invoke a weakening of the bond to the group that subsequently leaves to explain the rate of the base promoted dehydrochlorination of phenylmethanesulphonyl chloride.

Further comparison of the results obtained by Lee(2) reveals that the same ρ^- value of 2.4 is found for the pyridine promoted eliminations from both 2,4-dinitrophenyl phenylmethanesulphonates and phenylmethanesulphonyl chlorides. This implies that both reactions are proceeding by an irreversible Elcb mechanism for in E2 reactions the ρ value increases the poorer the leaving group(20), whereas if the formation of a carbanion is the rate determining step in both cases, similar ρ values might be expected*.

Thus it seems that the pyridine promoted dehydrochlorination of phenylmethanesuphonyl chloride could be proceeding via an irreversible Elcb mechanism. This conclusion is antagonistic to King and Lee's deduction(1), that the triethylamine dehydrochlorination of phenylmethanesulphonyl chloride was via an "Elcb like" E2 mechanism. King and Lee based their deduction on a

---

*Solvent effects on ρ values in elimination reactions are usually small(20).

difference of 10^8 between the estimated (by extrapolation of the rate of exchange of benzyl phenyl sulphone to -25°) rate of carbanion formation and the measured rate of the dehydrochlorination(1,2). Provided the change in base is not causing a change in mechanism, the source of the differing conclusions must be inaccuracy in the models chosen for estimating the rate of carbanion formation. Inaccuracy in the models used for estimating carbanion formation rates has previuosly led to confusion in determining the mechanism of elimination reactions(32;33).

Summarising, it is now evident that base promoted eliminations from phenylmethanesulphonates of phenols with a pKa of 5.45 (the pKa of 2-chloro 4-nitrophenol) or greater occur via a reversible Elcb mechanism. The esters of phenols with a pKa of less than 5.45, and perhaps even phenylmethanesulphonyl chloride, eliminate according to an irreversible Elcb mechanism or possibly by an E2 mechanism in which the bond to the leaving group is intact in the transition state. The distinction between this new type of E2 mechanism and the irreversible Elcb mechanism depends upon evidence for the existence of a carbanion which has a lifetime of less than about 10^{-9} s*.

*Estimated lifetime of the carbanion formed from 2-Cl, 4-NO_2phenyl phenylmethanesulphonate.

C. EXPERIMENTAL

Infra red spectra(i.r.) were recorded on a Beckman IR-10 or IR 20A. Nuclear magnetic resonance spectra(n.m.r.) were recorded on Varian T-60 and HA-100 instruments; chemical shifts were expressed in parts per million(p.p.m.) downfield from tetramethylsilane as an internal standard. Mass spectra were obtained on a Varian M66 instrument. Melting points were determined on a Kofler hot stage, and are uncorrected.

1,2-Dimethoxyethane(DME), pyridine and triethylamine were distilled from calcium hydride. The DME used in exchange experiments was further purified by distillation from lithium aluminium hydride.

(a) Preparations

(i) The General Method for the Preparation of the Phenylmethanesulphonyl Chlorides

The benzyl halide(0.05 mol) was stirred in a solution of anhydrous sodium sulphite(6.3 g, 0.05 mol) in 100 ml of water at 70° for several hours, until the mixture

was homogeneous. The aqueous solution was washed three times with methylene chloride. The aqueous layer was evaporated to dryness under reduced pressure. The residue was dried over phosphorus pentoxide in a vacuum dessicator.

The dried solid was suspended in methylene chloride and, whilst stirring, an excess of phosphorus pentachloride was slowly added. The methylene chloride was decanted onto ice and this mixture was stirred for about 1 hour. The water layer was removed. The methylene chloride was washed three times with water, dried ($MgSO_4$), filtered and the solvent evaporated. A yield of around 80% was usually obtained.

This procedure was followed for the phenylmethanesulphonyl chlorides listed below.

3-Nitrophenylmethanesulphonyl Chloride

M.p. 98-100°; reported(34) 100-101°

4-Nitrophenylmethanesulphonyl Chloride

M.p. 90-91°; reported(34) 89-90°

4-Chlorophenylmethanesulphonyl Chloride

M.p. 90-91°; reported(35) 89-91°

4-Cyanophenylmethanesulphonyl Chloride

M.p. 93-95°; reported(2) 90-91°

4-Methylphenylmethanesulphonyl Chloride

M.p. 80-81°. The i.r. spectrum(CH_2Cl_2) showed peaks

at 1600(m), 1370(str) and 1168(str). The n.m.r.($CDCl_3$) had peaks at 2.40(3H, s); 4.83(2H, s) and 7.30(4H, AB pattern, $\delta_A = 7.25$, $\delta_B = 7.35$, $J_{AB} = 8$, $\Delta\nu_{AB} = 6$).

Anal. Calcd. for $C_8H_9ClO_2S$: C, 46.95; H, 4.43; Cl, 17.32; S, 15.67. Found: C, 46.90; H, 4.39; Cl, 17.60, S, 15.63.

3-Chlorophenylmethanesulphonyl Chloride

M.p. 73-74°. The i.r. spectrum($CHCl_3$) showed peaks at 1370(str) and 1160(str). The n.m.r.($CDCl_3$) had peaks at 4.78(2H, s) and 7.30-7.50(4H, multiplet).

Anal. Calcd. for $C_7H_6Cl_2O_2S$: C, 37.35; H, 2.69; Cl, 31.50; S, 14.24. Found: C, 37.45; H, 2.74; Cl, 31.35; S, 14.27.

(ii) Preparation of 4-Cyanobenzyl Bromide

This procedure follows that of Coleman and Honeywell(36). 4-Tolunitrile(11.7 g, 0.1 mol) was brominated with 16 g (0.1 mol) of bromine by adding the bromine slowly, from a dropping funnel, to the 4-tolunitrile which was being heated by an oil bath at 140-150°. When the addition was complete the reactants were left for 1 h at 140-150°. The solid obtained was dissolved in methylene chloride. The methylene chloride was washed twice with 2% sodium bisulphite and then twice with water. The methylene chloride was dried($MgSO_4$), filtered and the solvent evaporated. The yield of the crude bromide was 16.4 g (84%).

Recrystallisation from methylene chloride-petroleum ether gave the product with m.p. 113-114°; reported(33) 114-116°.

(iii) Preparation of 3-Nitro 4-Hydroxyacetophenone

The procedure of Brown(38) was followed. The product had a m.p. 126-128°; reported(38) 132.5-135°.

(iv) Method I for the Preparation of Phenylmethanesulphonates from Phenylmethanesulphonyl Chloride and the Phenol

Phenylmethanesulphonyl chloride(10.5 mmol) was dissolved in 30 ml of methylene chloride. This solution was mixed with a solution of the phenol(28.8 mmol) and a little triethylamine in 30 ml of methylene chloride. Triethylamine(5 ml) was poured into the mixture. The mixture was stirred for 30 min. at room temperature and then poured into 100 ml of water. The layers were separated and the methylene chloride layer was washed with dilute hydrochloric acid, dilute sodium hydroxide and finally with water. Drying ($MgSO_4$), followed by evaporation of the solvent gave the ester. When the above method was used for the preparation 3-trifluoromethyl 4-nitrophenyl phenylmethanesulphonate and 2-chloro 4-nitrophenyl phenylmethanesulphonate, saturated sodium bicarbonate was used as the basic wash instead of the dilute sodium hydroxide.

The data obtained for the phenyl phenylmethane-

sulphonates is shown below.

4-Chlorophenyl Phenylmethanesulphonate

Yield 88%. Recrystallisation from methylene chloride-pentane gave the ester with m.p. 85-86°; reported(39) 85-86°. The i.r. spectrum(CH_2Cl_2) showed peaks at 1500(str), 1390 (m), 1165(str), 880(str). The n.m.r.($CDCl_3$) had peaks at 4.44(2H, s), 6.91-7.36(9H, multiplet).

4-Nitro 2-Chlorophenyl Phenylmethanesulphonate

Yield 79%. Recrystallisation from methylene chloride-petroleum ether gave the ester with m.p. 102-104°. The i.r. (CH_2Cl_2) gave peaks at 1535(str), 1350(str), 1175(str), 850(str). The n.m.r.($CDCl_3$) gave peaks at 4.70(2H, s), 7.30(1H, d, J = 9), 7.43(5H, s), 8.08(1H, d of d, J = 9, J = 2.5), 8.31(1H, d, J = 2.5).

Anal. Calcd. for $C_{13}H_{10}ClNO_5S$: C, 47.64; H, 3.06; Cl, 10.82; N, 4.27; S, 9.78. Found: C, 47.85; H, 3.02; Cl, 11.03; N, 4.25; S, 9.82.

3-Nitrophenyl Phenylmethanesulphonate

Yield 56%. Recrystallisation from chloroform-petroleum ether gave the ester with m.p. 81-83°. The i.r. (CH_2Cl_2) had peaks at 1525(str), 1350(str), 1160(str). The n.m.r.($CDCl_3$) gave peaks at 4.60(1H, s), 7.38-8.20(8H, multiplet).

Anal. Calcd. $C_{13}H_{11}NO_5S$: C, 53.24; H, 3.78; N, 4.78; S, 10.93. Found: C, 53.18; H, 4.02; N, 4.84; S, 11.22.

4-Nitro 3-Trifluorophenyl Phenylmethanesulphonate

Yield 60%. Recrystallisation from methylene chloride-petroleum ether gave the ester with m.p. 97-98°. The i.r. (CH_2Cl_2) had peaks at 1550(str), 1360(str), 1297(m), 1170 (str), 920(m). The n.m.r.($CDCl_3$) showed peaks at 4.65(2H, s), 7.25-7.93(8H, multiplet).

Anal. Calcd. for $C_{14}H_{10}F_3NO_5S$: C, 46.55; H, 2.79; N, 3.88; F, 15.79; S, 8.88. Found: C, 46.56; H, 2.89; N, 3.80; F, 15.99; S, 9.12.

4-Cyanophenyl Phenylmethanesulphonate

Yield 84%. Recrystallisation from methylene chloride-petroleum ether gave the ester with m.p. 113-114°. The i.r. (CH_2Cl_2) showed peaks at 2247(m), 1625(m), 1505(str), 1400 (str), 1175(str). The n.m.r.(HA 100 in $CDCl_3$) showed peaks at 4.56(2H, s), 7.12(2H, AB system, J_{AB} = 9), 7.64(2H, AB system, J_{AB} = 9).

Anal. Calcd. for $C_{14}H_{11}NO_3S$: C, 61.53; H, 4.06; N, 5.13; S, 11.73. Found: C, 61.44; H, 4.05; N, 4.97; S, 11.80.

3-Chlorophenyl Phenylmethanesulphonate

Recrystallisation from methylene chloride-petroleum ether(difficult) gave some crystals with m.p. 57-58°. The

i.r.(CH_2Cl_2) showed peaks at 1590(m), 1470(m), 1380(str), 1160(str). The n.m.r.(HA 100, $CDCl_3$) showed peaks at 4.50 (2H, s), 6.92-7.26(4H, multiplet), 7.41(5H, s).

Anal. Calcd. for $C_{13}H_{11}ClO_3S$: C, 55.22; H, 3.92; Cl, 12.54; S, 11.34. Found: C, 55.32; H, 3.78; Cl, 12.81; S, 11.38.

4-Nitrophenyl Phenylmethanesulphonate

Yield 67%. Recrystallisation from chloroform-petroleum ether gave the ester with m.p. 108-109°; reported (40) 100°. The i.r. spectrum(CH_2Cl_2) showed peaks at 1535 (str), 1355(str), 1160(str). The n.m.r.($CDCl_3$), showed peaks at 4.58(2H, s), 7.37(5H, s), 7.67(4H, AB pattern, $\delta_A = 6.85$, $\delta_B = 8.49$, $J_{AB} = 9$, $\Delta\nu_{AB} = 49.2$ cps).

Anal. Calcd. for $C_{13}H_{11}NO_5S$: C, 53.24; H, 3.78; N, 4.78; S, 10.93. Found: C, 53.42; H, 3.77; N, 4.76; S, 10.96.

4-Methoxyphenyl Phenylmethanesulphonate

Yield 66%. Recrystallisation from methylene chloride-petroleum ether gave the ester with m.p. 97-98°. The i.r. (CH_2Cl_2) showed peaks at 1505(str), 1375(m), 1148(str). The n.m.r.(HA 100, $CDCl_3$) had peaks at 3.86(3H, s), 4.66(2H s), 6.82(2H, A_2B_2 system), 7.03(2H, A_2B_2 system), 7.41(5H, s). For the A_2B_2 system $J_{AB} = 9$, $J_{AA'} = 3$, $J_{BB'} = 2$.

Anal. Calcd. for $C_{14}H_{14}O_4S$: C, 60.42; H, 5.07; S, 11.52. Found: C, 60.53; H, 5.15; S, 11.46.

3-Methoxyphenyl Phenylmethanesulphonate

Recrystallisation from methylene chloride-petroleum ether gave the ester with m.p. 64-68°. The i.r. spectrum (CH_2Cl_2) gave peaks at 1610(m), 1490(m), 1370(str), 1120 (str). The n.m.r. spectrum(HA 100, $CDCl_3$) showed peaks at 3.73(3H, s), 4.47(2H, s), 6.60-6.84(3H, multiplet), 7.17 (1H, d, J = 8), 7.40(5H, s).

Anal. Calcd. for $C_{14}H_{14}O_4S$: C, 60.41; H, 5.07; S, 11.52. Found: C, 60.45; H, 5.09; S, 11.66.

4-Nitrophenyl 3-Nitrophenylmethanesulphonate

Yield 59%. Recrystallisation from chloroform gave the ester with m.p. 141-142°; reported(3) 139-140°.

4-Nitrophenyl 4-Nitrophenylmethanesulphonate

Yield 89%. Recrystallisation from chloroform gave the ester with m.p. 147-148°; reported(3) 148°.

(v) Method II for the Preparation of Phenyl Phenylmethanesulphonate Esters from Phenylmethanesulphonyl Chloride and the Phenol

The phenol(17.7 mmol) and tributylamine(3.71 g, 20 mmol) were mixed in 100 ml of ether(some solid remained undissolved). Phenylmethanesulphonyl chloride(0.2 g, 1 mmol) dissolved in 20 ml of ether was added slowly to the well stirred mixture of base and phenol. After the addition, the

mixture was stirred for a further 5 min at room temperature. The reaction mixture was poured into water, then filtered. The ether layer was washed with 6 M hydrochloric acid (5 times) and with 5% sodium bicarbonate(3 times). The ether was dried($MgSO_4$), filtered and evaporated to yield the crude ester.

The above method was used to prepare the following two compounds.

4-Acetyl 2-Nitrophenyl Phenylmethanesulphonate

Yield 72%. Recrystallisation from methylene chloride-pentane gave the ester with m.p. 100-101°. The i.r.($CHCl_3$) showed peaks at 1700(str), 1610(m), 1540(str), 1370(str), 1250(m), 1170(m). The n.m.r.($CDCl_3$) showed peaks at 2.67 (3H, s), 4.77(2H, s), 7.45(5H, s), 7.48(1H, d, J = 8), 8.13(1H, d of d, J = 8, J = 2), 8.50(1H, d, J = 2).

Anal. Calcd. for $C_{15}H_{13}NO_6S$: C, 53.73; H, 3.91; N, 4.18; S, 9.56. Found: C, 53.76; H, 3.88; N, 4.09; S, 9.58.

3,4-Dinitrophenyl Phenylmethanesulphonate

Recrystallisation from methylene chloride-pentane followed by recrystallisation from chloroform, gave the ester with m.p. 101-102°. The i.r.($CHCl_3$) had peaks at 1550(str), 1360(m), 1170(m). The n.m.r.($CDCl_3$) gave peaks at 4.67(2H, s), 7.23-7.93(8H, aromatic).

Anal. Calcd. for $C_{13}H_{10}N_2O_7S$: C, 46.16; H, 2.98;

N, 8.28; S, 9.48. Found: C, 46.15; H, 3.03; N, 8.17; S, 9.40.

(vi) The General Method for the Preparation of the 2,4-Dinitrophenyl Phenylmethanesulphonates

The phenylmethanesulphonyl chloride(4 mmol) was dissolved in methylene chloride(20 ml) and added to a solution of 2,4-dinitrophenol(32 mmol) and triethylamine in 30 ml of methylene chloride. The mixture was stirred for 30 min at room temperature. The mixture was poured into 100 ml of water. The water layer was removed and the methlyene chloride solution was washed three times with 5% sodium bicarbonate and twice with water. Drying with magnesium sulphate, followed by evaporation of the solvent gave the ester. The yields varied between 40% and 80%. The esters so prepared are given below with the relevant data.

2,4-Dinitrophenyl 4-Nitrophenylmethanesulphonate

Yield 37%. Recrystallisation from methylene chloride-pentane gave the ester with m.p. 174-175°. The i.r.($CHCl_3$) showed peaks at 1608(str), 1520(str), 1380(m), 1350(str), 1170(m). The n.m.r. showed peaks at 5.4(2H, s), 7.83-8.96 (7H, multiplet).

Anal. Calcd. for $C_{13}H_9N_3O_9S$: C, 40.74; H, 2.37; N, 10.96; S, 8.37. Found: C, 40.78; H, 2.37; N, 10.82; S, 8.52.

2,4-Dinitrophenyl 3-Chlorophenylmethanesulphonate

Yield: 55%. Recrystallisation from chloroform-pentane gave the ester with m.p. 81-83°. The i.r.($CHCl_3$) showed peaks at 1615(m), 1543(str), 1382(str), 1352(str), 1179(m). The n.m.r.($CDCl_3$) showed peaks at 4.83(2H, s), 7.33-7.57 (4H, multiplet), 7.73(1H, d, J = 9), 8.53(1H, d of ds, J = 9, J = 3), 8.91(1H, d, J = 3).

Anal. Calcd. for $C_{13}H_9ClN_2O_7S$: C, 41.89; H, 2.43; N, 7.52; S, 8.60; Cl, 9.51. Found: C, 41.84; H, 2.63; N, 7.76; S, 8.64; Cl, 9.68.

2,4-Dinitrophenyl 4-Cyanophenylmethanesulphonate

Yield 34%. Recrystallisation from methylene chloride-petroleum ether gave the ester with m.p. 156-157°. The i.r.($CHCl_3$) had peaks at 1607(m), 1541(str), 1376(m), 1345 (str), 1168(m). The n.m.r.($CDCl_3$) had peaks at 5.25(2H, s), 7.45(4H, s), 7.46(1H, d, J = 9), 8.21(1H, d of ds, J = 9, J = 3), 8.50(1H, d, J = 3).

Anal. Calcd. for $C_{14}H_9N_3O_7S$: C, 46.28; H, 2.50; N, 11.57; S, 8.83. Found: C, 46.25; H, 2.62; N, 11.69; S, 8.86.

2,4-Dinitrophenyl Phenylmethanesulphonate

Yield: 90%. Recrystallisation from methylene chloride gave the ester with the m.p. 113-114°, reported(5) 111-114.5°. The n.m.r. was as recorded in the reference. The i.r. showed peaks at 1608(m), 1538(str), 1372(str), 1344(str), 1170(m),

2,4-Dinitrophenyl 4-Methylphenylmethanesulphonate

Yield: 60%. Recrystallisation from chloroform-pentane gave the ester with m.p. 98-100°. The i.r.($CHCl_3$) showed peaks at 1610(m), 1540(str), 1375(m), 1350(str), 1170(m). The n.m.r.($CDCl_3$) showed peaks at 2.40(3H, s), 4.72(2H, s), 7.30(4H, AB system, $\Delta\nu_{AB}$ = 11.2, J_{AB} = 9), 7.52(1H, d, J = 9), 8.40(1H, d of ds, J = 3), 8.82(1H, d, J = 3).

Anal. Calcd. for $C_{14}H_{12}N_2O_7S$: C, 47.73; H, 3.43; N, 7.95; S, 9.10; Found: C, 47.92; H, 3.40; N, 8.10; S, 9.02.

2,4-Dinitrophenyl 4-Chlorophenylmethanesulphonate

Yield: 66%. Recrystallisation from methylene chloride-pentane gave the ester with m.p. 117-118°. The i.r.($CHCl_3$) showed peaks at 1611(m), 1545(str), 1380(m), 1350(str), 1175(m). The n.m.r. showed peaks at 4.73(2H, s), 7.40(4H, s), 7.63(1H, d, J = 9), 8.45(1H, d of ds, J = 3, J = 9), 8.83(1H, d, J = 3).

Anal. Calcd. for $C_{13}H_9ClN_2O_7S$: C, 41.89; H, 2.43; N, 7.52; S, 8.60; Cl, 9.51. Found: C, 41.98; H, 2.46; N, 7.39; S, 8.80; Cl, 9.64.

2,4-Dinitrophenyl 3-Nitrophenylmethanesulphonate

Yield: 75%. Recrystallisation from chloroform gave the ester with m.p. 164-165°. The i.r.(KBr disc) showed peaks at 1609(m), 1527(str), 1349(str), 1177(m). The n.m.r. (d_6-acetone) gave peaks at 4.93(1H, s), 7.21-8.43(7H, multi-

plet).

Anal. Calcd. for $C_{13}H_9N_3O_9S$: C, 40.74; H, 2.37; N, 10.96; S, 8.37. Found: C, 40.69; H, 2.33; N, 10.88; S, 8.38.

(vii) The Preparation of N-Methyl Phenylmethanesulphonanilide

The procedure of Lee(2) was employed. A crude yield of 83% of the sulphonanilide was obtained. Recrystallisation from methylene chloride-pentane gave white plates with m.p. 104-105°; reported(41) m.p. 102-104°.

(viii) The Preparation of Phenylmethanesulphon-(N-Methyl 4-Nitro)-Anilide.

Phenylmethanesulphon-(N-methyl)-anilide(0.261 g, 0.001 mol) was dissolved in 15 ml of acetic anhydride at 0°. Concentrated nitric acid(3 ml) was added whilst stirring and maintaining the temperature at 0°. The mixture was stirred at 0° for 140 min after the completion of the addition. The cooling bath was removed and the mixture was stirred for a further 30 min. The contents of the flask were poured onto ice. The resulting mixture was warmed on a steam bath to hydrolyse any remaining acetic anhydride. The acid formed was neutralised with potassium hydroxide. The solution was extracted with methylene chloride. The methylene chloride was dried($MgSO_4$), filtered and evaporated to give 0.34 g of

a yellow oil.

The product was placed on a neutral alumina column and eluted with methylene chloride. The first fraction was recrystallised from methylene chloride-pentane to give yellow crystals with a m.p. of 128-135°; reported(42) m.p. 140-141°. The usual yield of the sulphonanilide was about 10%. The i.r. and n.m.r. of the anilide were the same as those of the phenylmethanesulphon-(N-methyl 4-nitro)-anilide prepared by Harding(42).

(b) The Evidence for the Presence of Sulphenes in the Reactions of Bases with the Sulphonate Esters

(i) The Reaction of 4-Nitrophenylmethanesulphonyl Chloride with Triethylamine and N-(2-Methyl-1-Propenyl)-Pyrrolidine in Methylene Chloride

4-Nitrophenylmethanesulphonyl chloride(0.5 g, 2.1 mmol) was dissolved in 10 ml of methylene chloride. A solution of triethylamine(0.61 g, 6.1 mmol) and N-(2-methyl-1-propenyl)-pyrrolidine* in 30 ml of methylene chloride was added dropwise, over a period of 20 min, to the stirred sulphonyl chloride at room temperature. After the addition the solution was allowed to stand for 5 min and then extracted with 2 M hydrochloric acid. The acid layer was allowed to stand for 2 h to hydrolyse the excess enamine. The solution was neutralised with sodium bicarbonate then extracted

*Prepared by the method of Benzing; Angew. Chem. 71,521,(1959).

with methylene chloride. The methylene chloride was dried ($MgSO_4$), filtered and evaporated. Recrystallisation of the residue from methanol gave the adduct in a 67% yield with a m.p. of 167-169°. The i.r. spectrum($CHCl_3$) showed peaks at 2980(w), 2810(w), 1605(w), 1525(m), 1350(str), 1310(str), 1155(m) and 1100(m). The n.m.r.($CDCl_3$) had peaks at 1.70 (10H, multiplet), 2.37(4H, multiplet), 3.10(1H, d, J_{AB} = 10), 5.25(1H, d, J_{AB} = 10), 7.67(2H, AB system, J_{AB} = 9), 8.32 (2H, AB system, J_{AB} = 9).

Anal. Calcd. for $C_{15}H_{20}N_2O_4S$: C, 55.54; H, 6.21; N, 8.64; S, 9.88. Found: C, 55.41; H, 6.28; N, 8.58; S, 9.75.

(ii) <u>The Reaction of 2,4-Dinitrophenyl 4-Nitrophenyl-methanesulphonate with Pyridine and N-(2-Methyl-1-Propenyl)-Pyrrolidine in DME</u>

The ester(192 mg, 0.5 mmol) was dissolved in 20 ml of DME. This solution was added dropwise to a stirred solution of pyridine(5.2 g, 66 mmol) and the enamine(1.25 g, 1 mmol) in 10 ml of DME at room temperature over a period of 30 min. The solution was stirred for a further 2 h. An excess of 2 M hydrochloric acid was added. Most of the DME was removed by evaporation under reduced pressure. The remaining solution was washed with ether. The aqueous layer was made basic with sodium bicarbonate then extracted with methylene chloride. The methylene chloride was washed with

water, dried($MgSO_4$), filtered and evaporated giving a pale yellow solid(181 mg). Recrystallisation from methanol gave 138 mg (85% yield) of the white adduct with m.p. of 162—167°. The properties of the adduct were identical to those of the adduct obtained from 4-nitrophenylmethanesulphonyl chloride.

(iii) The Trapping of 4-Nitrophenylsulphene with N-(2-Methyl-1-Propenyl)-Pyrrolidine in 20% Aqueous DME

(1) When the 4-nitrophenylsulphene was generated from 4-nitrophenylmethanesulphonyl chloride and pyridine.

Pyridine(1.58 g, 20 mmol) and the enamine (6 g, 48 mmol) were dissolved in 100 ml of 20% aqueous DME and 4-nitrophenylmethanesulphonyl chloride(50 mg, 0.21 mmol) was added. The solution was left at room temperature for 30 min, acidified with dilute hydrochloric acid and the DME was removed by evaporation under reduced pressure. The aqueous residue was washed with ether, made basic with solid potassium carbonate and extracted with methylene chloride. The methylene chloride was dried($MgSO_4$), filtered and evaporated to give a brown oil. A few drops of methanol were added to the oil and the solution was cooled over night. The cycloadduct(8.3 mg, 0.026 mmol, 12%) was obtained as white crystals with a m.p. of 168-171°. The properties of the adduct were the same as those of the adduct obtained when methylene chloride was used as the reaction solvent.

(2) When the 4-nitrophenylsulphene was generated from 2,4-dinitrophenyl 4-nitrophenylmethanesulphonate and pyridine

The above procedure was repeated using 2,4-dinitrophenyl 4-nitrophenylmethanesulphonate(50 mg, 0.13 mmol). The same cycloadduct(5 mg, 0.0154 mmol, 12%) with m.p. 167-169^{o} was obtained in the same yield.

(iv) The Reaction of Pyridine with 2,4-Dinitrophenyl 4-Nitrophenylmethanesulphonate in DME containing 20% of Deuterium Oxide

2,4-Dinitrophenyl 4-nitrophenylmethanesulphonate (200 mg, 0.52 mmol) was dissolved in a mixture of 120 ml of DME and 30 ml of deuterium oxide. Pyridine (10.35 g, 131 mmol) was added and the reaction stirred for 25 m. The reaction solution was evaporated down to reduce the volume. The solution was extracted with ether. The ether extracts were dried($MgSO_4$), filtered and evaporated to give dinitrophenol(100%). The aqueous layer was evaporated to dryness on a rotovap. The residue was suspended in methylene chloride and treated with excess phosphorus pentachloride in the normal manner. Work-up gave 4-nitrophenylmethanesulphonyl chloride(91 mg, 0.39 mmol, 74%). The product was recrystallised from methylene chloride and pentane. The nmr and the mass spectrum showed monodeuteration at the benzylic position.

The 4-nitrophenylmethanesulphonyl chloride obtained in a second run using the same method as above was sent for deuterium analysis. It contained 16.75 atom % excess deuterium.

(v) The Reaction of Triethylamine with 2,4-Dinitrophenyl 4-Nitrophenylmethanesulphonate in Methylene Chloride

2,4-Dinitrophenyl 4-nitrophenylmethanesulphonate (191 mg, 0.5 mmol) was dissolved in methylene chloride. Triethylamine(0.8 g, 0.8 mmol) was added. The solution immediately became yellow. The solution was stirred for 1 h at room temperature. The methylene chloride was washed twice with 2 M hydrochloric acid, four times with saturated bicarbonate and twice with water. The methylene chloride was dried($MgSO_4$), filtered and evaporated to give trans-4,4'-dinitrostilbene(63 mg, 93%) with a m.p. of 302-304°. Reported(43) m.p. 303-304°.

(vi) The Reaction of 2,4-Dinitrophenyl Phenylmethanesulphonate with Triethylamine in DME containing 20% of Deuterium Oxide

Triethylamine(0.313 g, 0.309 mmol, conc^{n}

3.09 x 10^{-3} M) was weighed into a 100 ml volumetric flask. Deuterium oxide(20 ml) was added and the solution was made to the mark with DME at room temperature. The ester(96 mg, 0.284 mmol, conc^{n} 2.84 x 10^{-3} M) was added and the mixture stirred for 1 h. The DME and triethylamine were removed by evaporation under reduced pressure. The remaining liquid was acidified with 3 M hydrochloric acid, washed with ether and the remaining solvent removed by evaporation under reduced pressure. The residue was dried over phosphorus pentoxide in a vacuum dessicator. The white solid obtained was suspended in methylene chloride and converted to the sulphonyl chloride with phosphorus pentachloride in the usual manner(p.96).

The n.m.r. showed complete monodeuteration of the phenylmethanesulphonyl chloride whereas the mass spectrum revealed a trace(~3%) of undeuterated acid chloride was also present.

(vii) <u>The Reaction of 4-Acetyl 2-Nitrophenyl Phenylmethanesulphonate with Triethylamine in DME containing 20% of Deuterium Oxide</u>

The procedure for the reaction was the same as that used for the measurement of the exchange rates(p.114).

Concentration of ester: 6.65 x 10^{-3} M

Concentration of triethylamine: 0.0887 M

The reaction was left for 30 s at 20°. The ester recovered(14.4 mg, 25%) was shown to contain no benzylic deuteriums by nmr spectroscopy. The aqueous layer from the extraction was evaporated to give a white residue. This residue was suspended in methylene chloride and treated with phosphorus pentachloride at room temperature in the normal manner(p.96). The phenylmethanesulphonyl chloride so obtained was found to be monodeuterated at the benzylic position by nmr spectroscopy.

(c) The Exchange Kinetics

(i) The Measurement of the Exchange Rates of the Methylene Protons in Phenyl Phenylmethanesulphonates by Proton Magnetic Resonance Spectroscopy

Triethylamine was weighed into a 25 ml volumetric flask. A little DME was added. Deuterium oxide(5.2 ml) was injected into the flask. The flask was suspended in a constant temperature bath, thermostated to 20±0.1°. The volume of the solution was made to the mark. The contents of the volumetric flask were transferred to a 50 ml flask which was suspended in the bath. The ester(50 mg in 1 ml of DME) was injected into the solution. The flask was swirled and the timer started. After a known period of time the reaction was quenched with 6 ml of 6 M nitric acid. Water(approx. 20 ml) was added to the reaction mixture and the aqueous solution was extracted with ether. The

ether was washed with saturated sodium bicarbonate and water. The ester was dried($MgSO_4$), filtered and evaporated. The ester so obtained was dissolved in deuterated chloroform and the n.m.r. was taken.

Integration of the aromatic region of the n.m.r. spectrum enabled the calculation of the integrand corresponding to one proton. The difference between twice this integrand(i.e. the integrand corresponding to the methylene group) and the measured integrand for the methylene protons gave the amount of deuterium incorporation that had occurred. From the percentage of deuterium incorporated the rate of removal(k) of a methylene proton was calculated(see Appendix I).

For all the measurements the concentration of deuterium oxide was 10 M and the temperature was 20±0.1°.

Data for 4-Chlorophenyl Phenylmethanesulphonate

Concentration of the Ester: 6.80×10^{-3} M

Concentration of Triethylamine: 0.1999 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1} s^{-1}$
40.0	39.5	$2.1\pm0.2 \times 10^{-3}$

Data for 4-Cyanophenyl Phenylmethanesulphonate

Concentration of the ester: 6.52×10^{-3} M

Concentration of triethylamine: 0.197 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1}\ s^{-1}$
10.0	58.3	$1.5 \pm 0.15 \times 10^{-2}$

Data for 4-Nitrophenyl Phenylmethanesulphonate

Concentration of the ester: 6.56×10^{-3} M

Concentration of triethylamine: 0.207 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1}\ s^{-1}$
5.0	43.5	$2.7 \pm 0.3 \times 10^{-2}$

Data for 4-Methoxyphenyl Phenylmethanesulphonate

Concentration of the ester: 6.32×10^{-3} M

Concentration of triethylamine: 0.207 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1}\ s^{-1}$
428.4	61.3	$3.8 \pm 0.5 \times 10^{-3}$

Data for 3-Methoxyphenyl Phenylmethanesulphonate

Concentration of the ester: 6.12×10^{-3} M

Concentration of the triethylamine: 0.206 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1} s^{-1}$
240	61.4	$6.4 \pm 0.7 \times 10^{-4}$

Data for 3-Trifluoromethyl 4-Nitrophenyl Phenylmethanesulphonate

Concentration of the ester: 2.85×10^{-3} M

Concentration of the triethylamine: 0.090 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1} s^{-1}$
0.5	25.6	0.22±0.02

Data for 3-Nitrophenyl Phenylmethanesulphonate

Concentration of the ester: 6.56×10^{-3} M

Concentration of the triethylamine: 0.197 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1} s^{-1}$
5.0	42.0	19±2

Data for 3-Chlorophenyl Phenylmethanesulphonate

Concentration of the ester: 6.56×10^{-3} M

Concentration of the triethylamine: 0.280 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1} s^{-1}$
31	50.9	$2.6 \pm 0.3 \times 10^{-3}$

Concentration of the ester: 6.12×10^{-3} M

Concentration of the triethylamine: 0.207 M

TIME (MIN)	Percentage Deuterium	$k/M^{-1} s^{-1}$
30	40.0	$2.7 \pm 0.3 \times 10^{-3}$

(ii) The Measurement of the Exchange Rates of the Methylene Protons in N-Methyl Phenylmethanesulphonanilides by Proton Magnetic Resonance Spectroscopy

The procedure was the same as that used for the exchange measurements with the sulphonate esters(p.114).

Data for Phenylmethanesulphon-(N-methyl)-anilide

Temperature: $50 \pm 0.1^{\circ}$

Concentration of amide: 0.020 M

Concentration of triethylamine: 1.00 M

TIME (S)	Percentage Deuterium per Methylene	Rate Constant for Exchange/10^{-5} M^{-1} s^{-1}
350	33	2.92
720	40.8	2.42
1725	73.2	2.54

Average rate constant for exchange = $2.6 \pm 0.3 \times 10^{-5}$ M^{-1} s^{-1}

Data for Phenylmethanesulphon-(N-methyl-4-nitro)-anilide

Temperature: $50 \pm 0.1^{\circ}$

Concentration of amide: 0.006 M

Concentration of triethylamine: 1.00 M

TIME (MIN)	Percentage Deuterium per Methylene	Rate Constant for Exchange/10^{-5} M^{-1} s^{-1}
10	19	7.0
30	28.6	7.4

Average rate constant for exchange = $7.2 \pm 0.2 \times 10^{-4}$ M^{-1} s^{-1}

$$\rho \text{ value from these results} = \frac{\log(72/2.6)}{0.78}$$

Thus $\rho = 1.8_5$

(iii) The Technique for the Measurement of the Rate of Exchange of the Methylene Protons in Phenyl Phenylmethanesulphonates by Mass Spectroscopy

Triethylamine(0.53 g, 5.24 mmol) was weighed into a 25 ml volumetric flask. Deuterium oxide(5.2 ml) was added. The flask was suspended in a bath thermostated to 20°. The solution was made to the mark with DME. The solution was transferred to a 50 ml round bottomed flask suspended in the same thermostated bath. A 1 ml aliquot of a solution of the ester(0.161 mmol) in 2 ml of DME was injected into the base solution. Aliquots were removed from the reaction vessel at known times, the reaction being quenched with 10 ml of 6 M nitric acid. The acidic solution was extracted with ether. The ether was washed with saturated sodium bicarbonate, dried($MgSO_4$), filtered and the ether evaporated. The samples of the ester were recrystallised from a few drops of methanol and analysed by mass spectrometry.

The results are tabulated below.

Data for 4-Chlorophenyl Phenylmethanesulphonate

Temperature: 20.0±0.1°

Triethylamine concentration: 0.200 M

Ester concentration: 7.62×10^{-3} M

TIME (S)	% Deuterium	LOG(1/(1-%D/100))
581	12.0	0.055
1200	22.6	0.119
1820	34.1	0.181
2430	42.1	0.238
3021	50.1	0.302
3588	57.1	0.366
4200	62.9	0.431

$k = 2.38 \pm 0.02 \times 10^{-3}$ M^{-1} s^{-1}

Data for 4-Cyanophenyl Phenylmethanesulphonate

Temperature: 20.0±0.1°

Triethylamine concentration: 0.202 M

Ester concentration: 7.18×10^{-3} M

TIME (MIN)	% Deuterium	LOG(1/(1-%D/100))
5.3	36.7	0.199
10.3	59.0	0.397
15.0	70.9	0.537

$k = 1.40 \pm 0.07 \times 10^{-3}$ M^{-1} s^{-1}

Data for 4-Nitrophenyl Phenylmethanesulphonate

Temperature: 20.0±0.1°

Triethylamine concentration: 0.201 M

Ester concentration: 3.10×10^{-3} M

TIME (MIN)	% Deuterium	LOG(1/(1-%D/100))
2.12	30.0	0.155
6.77	70.0	0.481
10.00	79.7	0.692

$k = 2.5 \pm 0.1 \times 10^{-2}\ M^{-1}\ s^{-1}$

Data for 3-Nitrophenyl Phenylmethanesulphonate

Temperature: 20.0±0.1°

Triethylamine concentration: 0.207 M

Ester concentration: 6.85×10^{-3} M

TIME (MIN)	% Deuterium	LOG(1/(1-%D/100))
4.80	48.6	0.289
7.23	63.1	0.433
9.00	69.9	0.522

$k = 2.2 \pm 0.1 \times 10^{-2}\ M^{-1}\ s^{-1}$

Data for Phenyl Phenylmethanesulphonate

Temperature: 20±0.1°

Triethylamine concentration: 0.205 M

Ester concentration: 3.67×10^{-3} M

TIME (MIN)	% Deuterium	LOG(1/(1-%D/100))
122	41.9	0.236
244	64.4	0.448
365	75.8	0.617

$k = 7.5 \pm 0.4 \times 10^{-4}\ M^{-1}\ s^{-1}$

Data for 3-Methoxyphenyl Phenylmethanesulphonate

Temperature: 20.0±0.1°

Triethylamine concentration: 0.199 M

Ester concentration: 2.86×10^{-3} M

TIME (MIN)	% Deuterium	LOG(1/(1-%D/100))
65	27.4	0.139
155	51.4	0.313
246	66.1	0.469

$k = 6.7 \pm 0.3 \times 10^{-4}\ M^{-1}\ s^{-1}$

Data for 4-Methoxyphenyl Phenylmethanesulphonate

Temperature: 20.0±0.1°

Triethylamine concentration: 0.204 M

Ester concentration: 3.03×10^{-3} M

TIME (MIN)	% Deuterium	LOG(1/(1-%D/100)
120	30.3	0.157
252	52.1	0.320
370	66.2	0.471

$k = 4.8 \pm 0.02 \times 10^{-3}\ M^{-1}\ s^{-1}$

(iv) The Measurement of the Rate of Exchange of the Methylene Protons in 2-Chloro 4-Nitrophenyl Phenylmethanesulphonate

Triethylamine was weighed into a 25 ml volumetric flask. Deuterium oxide (5.2 ml) was added, followed by a known amount of triethylammonium chloride. The flask was suspended in a bath thermostated to 20°. The solution was made to the mark with DME. The solution was transferred to a 50 ml round bottomed flask, suspended in the thermostated bath. A 1 ml aliquot of a solution of the ester and 2-chloro 4-nitrophenol was injected into the base solution. After a known amount of time the reaction was quenched with 6 M nitric acid. The acidic solution was extracted with ether. The ether was dried($MgSO_4$), filtered and evaporated. The recovered ester was analysed for exchange by n.m.r. or mass spectroscopy. The results for the four experiments are displayed in table XV.

TABLE XV

The Results of Investigations of the Effect of the Triethylammonium Cation and 2-Chloro 4-Nitrophenoxide on Exchange in 2-Chloro 4-Nitrophenyl Phenylmethanesulphonate

Temperature: 20 ± 0.1°

TIME (MIN)	$[Et_3N]$/M	[Ester]/M	$[Et_3ND^+]$/M	$[ArO^-]$/M	Percentage Exchange
0.50	0.088	0.015	0	0	0†
1.72	0.046	0.006	0.071	0	21.9*
1.72	0.049	0.006	0.071	0.003	23.3*
1.72	0.049	0.006	0.072	0.006	26.6*

†From n.m.r. data

*From mass spectral data

(v) Competition between Phenoxides and Water for Phenylsulphene

Between 4-Methoxyphenoxide and Water

Phenylmethanesulphonyl chloride(102 mg, 0.54 mmol) was dissolved in 50 ml of 20% aqueous DME. To this was added 50 ml of 20% aqueous DME containing 4-methoxyphenol(66.7 mg, 0.54 mmol) and triethylamine(2 g, 20 mmol). The mixture was allowed to stand for 30 m. Most of the DME was removed on a rotovap. The solution was acidified (3 M HCl) and extracted with ether. The ether was washed with 5% sodium hydroxide, dried($MgSO_4$), filtered and evaporated. No ester was detected.

Between 4-Nitrophenoxide and Water

Phenylmethanesulphonyl chloride(133 mg, 0.70 mmol) was dissolved in 2 ml of DME. To this was added a solution of 4-nitrophenol(97.4 mg, 0.70 mmol) and triethylamine(2 g, 20 mmol) in 100 ml of 20% aqueous DME. The solution was stirred at room temperature for 1 m then the reaction was quenched with 3 M hydrochloric acid. The solution was extracted with ether. The extracts were washed with 5% sodium hydroxide(4 times) and water(twice).

The ether was dried($MgSO_4$), filtered and evaporated giving about 4 mg of the crude ester. The ester was identified by comparison with an authentic sample on silica gel T.L.C. (eluent $CHCl_3$/pentane-1:1; Rf=0.25). The aqueous layer was made basic with potassium carbonate and the water removed on a rotovap. The residue was suspended in methylene chloride and treated with excess phosphorus pentachloride. Work-up followed by recrystallisation from carbon tetrachloride gave phenylmethanesulphonyl chloride (133 mg, 85%).

Between 2-Chloro 4-Nitrophenoxide and Water

Phenylmethanesulphonyl chloride(354 mg, 1.85 mmol) was dissolved in a little DME. This was added to 25 ml of a solution of 2-chloro 4-nitrophenol(0.325 g, 1.87 mmol), triethylamine(0.84 ml, 0.61 g, 6.04 mmol) and water(5.2 ml) in DME. After stirring for 10 s at room temperature, excess 3 M hydrochloric acid was added. Water was added to the mixture and the solution was extracted five times with ether. The combined ether extracts were washed with pH 9 buffer(150 ml of 0.1 M NaOH, 50 ml of satd. $NaHCO_3$) until the washes were colourless. The ether was washed once with water, dried($MgSO_4$), filtered and evaporated. This gave 207 mg of the crude ester. The i.r. and m.p. were the same as authentic 2-chloro 4-nitrophenyl

phenylmethanesulphonate. The yield after recrystallisation from methylene chloride-petroleum ether was 201 mg(0.61 mmol, 33%).

Work-up of the aqueous layer followed by treatment with phosphorus pentachloride gave, after recrystallisation from carbon tetrachloride, phenylmethanesulphonyl chloride (188 mg, 53%).

(d) Kinetics of the Elimination Reactions

(i) The General Procedure for the Kinetics of the Triethylamine Promoted Elimination from Phenyl Phenylmethanesulphonates

A known weight of triethylamine was placed in a 100 ml volumetric flask. Deuterium oxide(20 ml) was pipetted into the flask. The solution was made to the mark with DME. Aliquots(3 ml) of the stock solution were pipetted into 1 cm u.v. cells which were inserted into the compartment of the spectrometer. After 10 min, 10 µl portions of a DME solution containing a known amount of the substrate were injected into the cells. The rate of phenoxide release was measured by monitoring the change in the absorbance, with time, at 405 nm. The rate constants for the elimination reactions were determined as described on p.43.

The Reaction of 3-Trifluoromethyl 4-Nitrophenyl Phenylmethanesulphonate(4.98×10^{-5} M) with Triethylamine(0.0135 M)

Temperature: 20.0 ± 0.1°C

Solutions: 3-Trifluoromethyl 4-nitrophenyl phenylmethanesulphonate: 27 mg in 5 ml of DME

Triethylamine: 0.136 g in 100 ml of solution

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.46	0.042	0.836	16.01	0.497	0.381
0.90	0.065	0.813	18.35	0.539	0.339
1.88	0.107	0.771	20.94	0.577	0.301
3.24	0.161	0.717	23.80	0.615	0.263
5.11	0.226	0.652	25.59	0.637	0.241
8.13	0.316	0.562	27.70	0.658	0.220
9.59	0.357	0.521	32.56	0.702	0.176
12.37	0.424	0.454	40.55	0.757	0.121
13.72	0.453	0.425	49.10	0.796	0.082
			Infinity	0.878	

$$k' = 7.88 \times 10^{-4}\ s^{-1}$$

$$k = 5.80 \times 10^{-2}\ M^{-1}\ s^{-1}$$

A_t = Absorbance at time t A_∞ = Absorbance at t = infinity

The Reaction of 2-Chloro 4-Nitrophenyl Phenylmethanesulphonate(5.29×10^{-5} M) with Triethylamine(0.00270 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2-Chloro 4-nitrophenyl phenylmethanesulphonate

26 mg in 5 ml of DME

Triethylamine: 0.0273 g in 100 ml of solution

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.39	0.011	1.100	26.53	0.504	0.607
0.91	0.025	1.086	29.53	0.546	0.565
1.65	0.046	1.065	33.53	0.591	0.520
3.94	0.105	1.006	40.94	0.669	0.442
8.21	0.197	0. 14	46.45	0.720	0.391
12.42	0.280	0.831	53.44	0.777	.334
15.23	0.329	0.782	60.46	0.827	0.284
16.94	0.359	0.752	64.22	0.850	0.261
20.59	0.418	0.693	67.17	0.867	0.244
23.90	0.469	0.642	Infinity	1.111	

$k' = 3.74 \times 10^{-4}\ s^{-1}$

$k = 0.139\ M^{-1}\ s^{-1}$

The Reaction of 4-Acetyl 2-Nitrophenyl Phenylmethanesulphonate(3.98×10^{-5} M) with Triethylamine(0.00275 M)

Temperature: 20.0 ± 0.1°C

Solutions: 4-Acetyl 2-nitrophenyl phenylmethanesulphonate:

20.0 mg in 5 ml of DME

Triethylamine: 0.0278 g in 100 ml of solution

TIME (MIN)	A_t	$A_\infty - A_t$
0.47	0.011	0.227
1.40	0.029	0.209
3.38	0.063	0.175
5.60	0.092	0.146
8.75	0.126	0.112
13.27	0.160	0.078
17.28	0.182	0.056
20.02	0.194	0.044
24.08	0.205	0.033
28.62	0.216	0.022
Infinity	0.238	

$k' = 1.38 \times 10^{-3}\ s^{-1}$

$k = 0.502\ M^{-1}\ s^{-1}$

The Reaction of 3,4-Dinitrophenyl Phenylmethanesulphonate (6.50×10^{-5} M) with Triethylamine(0.00294 M)

Temperature: 20.0 ± 0.1°C

Solutions: 3,4-Dinitrophenyl phenylmethanesulphonate: 13.2 mg in 2 ml of DME

Triethylamine: 0.0297 g in 100 ml of solution

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.29	0.068	1.197	7.77	0.909	0.356
0.79	0.172	1.093		0.956	0.309
1.35	0.271	0.994	10.12	1.015	0.250
2.14	0.393	0.872	11.98	1.077	0.188
2.79	0.482	0.783	13.15	1.110	0.155
3.44	0.558	0.707	13.88	1.128	0.137
4.41	0.659	0.606	16.01	1.164	0.101
5.06	0.719	0.546	19.32	1.205	0.060
6.26	0.817	0.448	Infinity	1.265	

$k' = 2.63 \times 10^{-3}\ s^{-1}$

$k = 0.895\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl Phenylmethanesulphonate (4.46×10^{-5} M) with Triethylamine (0.00270 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl phenylmethanesulphonate: 22.6 mg in 5 ml of DME

Triethylamine: 0.0273 g in 100 ml of solution

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.33	0.074	0.542	2.49	0.381	0.235
0.52	0.115	0.501	2.73	0.402	0.214
0.67	0.143	0.473	3.10	0.430	0.186
0.91	0.187	0.429	3.44	0.453	0.163
1.20	0.23	0.385	3.73	0.470	0.146
1.43	0.264	0.352	4.07	0.487	0.129
1.59	0.285	0.331	4.31	0.499	0.117
1.91	0.322	0.294	4.65	0.512	0.104
2.23	0.357	0.259	5.15	0.530	0.086
			Infinity	0.616	

$k' = 6.31 \times 10^{-3}\ s^{-1}$

$k = 2.34\ M^{-1}\ s^{-1}$

(ii) <u>The Procedure for the Investigation of the Dependence on Base of the Rate of Release of 4-Nitrophenoxide from 4-Nitrophenyl 4-Nitrophenylmethanesulphonate</u>

Three stock solutions, A, B, and C, were prepared as below, using 20% aqueous DME as the solvent.

A. Triethylamine 4.048 g)
Tetraethylammonium chloride 0.829 g) in 100 ml

B. Triethylammonium chloride 1.721 g in 250 ml

C. Tetraethylammonium chloride 4.143 g in 500 ml

From these three stock solutions, the five solutions for the kinetics having different triethylamine concentrations but the same pH and ionic strength, were prepared as follows:

The desired amount of triethylamine was obtained by pipetting solution A into a 150 ml beaker. For the first kinetic solution 1 ml of B was added to the beaker and the volume was made close to 100 ml with solution C. The pH was measured before transferring the solution to a 100 ml volumetric flask. The solution was made to the mark with a little more of C.

For subsequent solutions for kinetics the desired amount of A was pipetted into the beaker and B was added until the pH was just above that of the first solution. C was now added along with the necessary amount of B to obtain about 100 ml of solution with the same pH as the

first kinetic solution. The pH was also recorded at the end of the kinetic run.

The five solutions so prepared are shown below:

Ionic strength = 0.05 M

Solution	Triethylamine Concentration/M	Initial pH	Final pH
I	0.016	9.41	9.33
II	0.020	9.40	9.38
III	0.040	9.42	9.38
IV	0.060	9.40	9.35
V	0.080	9.41	9.38

A 3 ml portion of the above solutions was pipetted into a 1 cm u.v. cell. 10 µl of a solution of the ester in DME was injected into the cell and the rate of the 4-nitrophenoxide release was followed at 405 nm. The concentration of the 4-nitrophenyl 4-nitrophenylmethane-sulphonate in the cell was about 4×10^{-5} M.

Kinetic Run with Solution I

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.016 M

Initial pH: 9.41

Final pH: 9.33

TIME (MIN)	A_t	LOG(100-%Rxn)
5	0.026	1.982
13	0.059	1.957
31	0.127	1.899
47	0.178	1.848
63	0.222	1.803
81	0.268	1.748
99	0.307	1.695
130	0.362	1.606
161	0.409	1.513
185	0.439	1.441
218	0.472	1.346
245	0.493	1.272
268	0.509	1.206
300	0.526	1.122
370	0.553	0.942

$k = 1.10 \times 10^{-4}\ s^{-1}$

Kinetic Run with Solution II

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.02 M

Initial pH: 9.40

Final pH: 9.32

TIME (MIN)	A_t	LOG(100-%Rxn)
10	0.039	1.970
27	0.099	1.919
53	0.174	1.845
72	0.222	1.790
99	0.279	1.714
120	0.317	1.656
151	0.364	1.570
182	0.402	1.485
220	0.433	1.402
232	0.452	1.341
257	0.470	1.275
298	0.494	1.167

$k = 1.08 \times 10^{-4}\ s^{-1}$

Kinetic Run with Solution III

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.04 M

Initial pH: 9.42

Final pH: 9.38

TIME (MIN)	A_t	LOG(100-%Rxn)
3	0.016	1.988
21	0.097	1.923
37	0.156	1.869
53	0.208	1.814
71	0.260	1.752
90	0.304	1.692
120	0.371	1.579
151	0.422	1.469
175	0.455	1.379
208	0.489	1.261
235	0.512	1.154
258	0.527	1.075
300	0.544	0.956
360	0.570	0.761
Infinity	0.598	

$$k = 1.37 \times 10^{-4}\ s^{-1}$$

Kinetic Run with Solution IV

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.06 M

Initial pH: 9.40

Final pH: 9.35

TIME (MIN)	A_t	LOG(100-%Rxn)
6	0.033	1.977
10	0.051	1.963
19	0.091	1.932
37	0.154	1.879
62	0.235	1.798
82	0.286	1.738
108	0.346	1.655
130	0.387	1.587
160	0.434	1.494
193	0.472	1.401
220	0.501	1.314
242	0.520	1.245
267	0.535	1.182
308	0.558	1.063
Infinity	0.631	

$k = 1.18 \times 10^{-4}\ s^{-1}$

Kinetic Run with Solution V

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.08 M

Initial pH: 9.41

Final pH: 9.38

TIME (MIN)	A_t	LOG(100-%Rxn)
19	0.088	1.930
35	0.148	1.875
52	0.201	1.820
70	0.256	1.754
88	0.302	1.689
118	0.361	1.590
149	0.415	1.474
174	0.446	1.390
206	0.480	1.274
234	0.503	1.173
257	0.517	1.098
289	0.534	0.984
358	0.559	0.734
Infinity	0.591	

$k = 1.35 \times 10^{-4}\ s^{-1}$

The Reaction of 4-Nitrophenyl 4-Nitrophenylmethanesulphonate (3.74×10^{-5} M) with Triethylamine

Procedure: see p 136

Results;

Temperature: $20.0 = 0.1^{\circ}$

Triethylamine concentration: 0.02 M

Triethylammonium chloride concentration: 5×10^{-4} M

Tetraethylammonium chloride concentration: 4.25×10^{-3} M

'pH' = 9.9

TIME (MIN)	A_t	LOG(100-%Rxn)
1.7	0.021	1.987
7.2	0.072	1.953
12.8	0.118	1.989
21.4	0.182	1.888
28.2	0.227	1.828
37.5	0.282	1.774
46.4	0.327	1.724
53.4	0.359	1.684
59.7	0.387	1.647
64.9	0.408	1.616
76.4	0.449	1.549
82.0	0.467	1.516
94.2	0.501	1.446
104.3	0.525	1.389
112.2	0.540	1.348
120.1	0.556	1.301
150.1	0.601	1.131
175.3	0.628	0.984
INF	0.695	

$$k = 3.1 \times 10^{-4}\ s^{-1}$$

(iii) Procedure for the Kinetic Measurements used in the Determination of the Hammett Plot for 4-Nitrophenyl Phenylmethanesulphonates

Two stock solutions were prepared using aqueous DME as the solvent.

A. Triethylammonium chloride: 0.3456 g in 50 ml

B. Tetraethylammonium chloride: 0.4140 g in 50 ml

Triethylamine(0.2025 g) was weighed into a 100 ml beaker and solutions A and B were added to obtain about 50 ml of solution with pH = 9.39. The solution was transferred to a 50 ml volumetric flask and made to the mark with a little 20% aqueous DME. 3 ml of this solution was pipetted into a 1 cm u.v. cell. The substrate, 10 µl of a 1×10^{-2} M solution in DME, was injected into the cell and the rate of phenoxide release was followed at 405 nm. This procedure was followed for the five esters.

The Reaction of 4-Nitrophenyl Phenylmethanesulphonate (6.66×10^{-5} M) with Triethylamine(0.05 M)

Temperature: 20.0 ± 0.1°C

Solutions: 4-Nitrophenyl phenylmethanesulphonate: 11.7 mg in 2 ml of DME

Triethylamine: 0.2025 g in 100 ml. Ionic strength 0.05 M. pH: 9.39

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
8	0.012	0.808	390	0.432	0.388
16	0.024	0.796	444	0.476	0.344
56	0.087	0.733	499	0.512	0.308
76	0.115	0.705	551	0.542	0.278
123	0.174	0.646	610	0.574	0.246
192	0.253	0.567	730	0.628	0.192
279	0.339	0.485	806	0.657	0.156
335	0.392	0.428	870	0.680	0.133
			Infinity	0.820	

$k = 3.31 \times 10^{-5}\ s^{-1}$

The Reaction of 4-Nitrophenyl 4-Chlorophenylmethanesulphonate(6.71×10^{-5} M) with Triethylamine(0.05 M)

Temperature: 20.0 ± 0.1°C

Solutions: 4-Nitrophenyl 4-Chlorophenylmethanesulphonate:

6.6 mg in 1 ml of DME

Triethylamine: 0.2025 g in 100 ml. Ionic strength 0.05 M. pH: 9.39

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
3	0.004	0.609	464	0.408	0.205
22	0.033	0.580	517	0.433	0.180
88	0.120	0.493	549	0.446	0.167
118	0.152	0.461	600	0.468	0.145
157	0.191	0.422	650	0.483	0.130
217	0.247	0.366	696	0.495	0.118
275	0.291	0.322	771	0.517	0.096
300	0.311	0.302	821	0.527	0.086
355	0.343	0.270	836	0.532	0.081
410	0.380	0.233	Infinity	0.613	

$k = 3.92 \times 10^{-5}\ s^{-1}$

The Reaction of 4-Nitrophenyl 3-Chlorophenylmethanesulphonate(5.39×10^{-5} M) with Triethylamine(0.05 M)

Temperature: 20.0 ± 0.1°C

Solutions: 4-Nitrophenyl 3-Chlorophenylmethanesulphonate:

5.3 mg in 1 ml of DME

Triethylamine: 0.2025 g in 100 ml. Ionic strength 0.05 M. pH: 9.39

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
1	0.007	0.664	478	0.467	0.204
58	0.088	0.583	520	0.483	0.188
128	0.174	0.497	547	0.498	0.173
188	0.242	0.429	620	0.529	0.142
215	0.266	0.405	666	0.545	0.126
271	0.319	0.352	742	0.570	0.101
325	0.359	0.312	791	0.584	0.087
380	0.402	0.269	806	0.589	0.082
434	0.438	0.233	Infinity	0.689	

$k = 4.25 \times 10^{-5}\ s^{-1}$

The Reaction of 4-Nitrophenyl 3-Nitrophenylmethane-sulphonate(6.61×10^{-5} M) with Triethylamine(0.05 M)

Temperature: 20.0 ± 0.1°C

Solutions: 4-Nitrophenyl 3-nitrophenylmethanesulphonate:

6.7 mg in 1 ml of DME

Triethylamine: 0.2025 g in 100 ml. Ionic strength 0.05 M. pH: 9.39

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
16	0.051	0.825	226	0.471	0.405
25	0.077	0.799	283	0.541	0.335
37	0.108	0.768	330	0.590	0.286
51	0.140	0.736	391	0.644	0.232
67	0.183	0.693	448	0.684	0.192
75	0.198	0.678	506	0.722	0.154
79	0.208	0.668	549	0.744	0.132
89	0.230	0.646	622	0.775	0.101
127	0.305	0.571	636	0.780	0.096
162	0.370	0.506	Infinity	0.876	

$k = 7.46 \times 10^{-5}\ s^{-1}$

The Reaction of 4-Nitrophenyl 4-Nitrophenylmethanesulphonate(1.03×10^{-4} M) with Triethylamine(0.05 M)

Temperature: 20.0 ± 0.1°C

Solutions: 4-Nitrophenyl 4-nitrophenylmethanesulphonate:

20.9 mg in 2 ml of DME

Triethylamine: 0.2025 g in 100 ml. Ionic strength 0.05 M. pH: 9.39

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
5	0.068	1.560	127	1.025	0.550
18	0.207	1.368	143	1.096	0.479
31	0.347	1.228	171	1.205	0.370
48	0.509	1.066	207	1.307	0.268
55	0.568	1.007	233	1.366	0.209
59	0.596	0.979	263	1.420	0.155
70	0.679	0.896	311	1.479	0.096
85	0.791	0.784	371	1.525	0.050
107	0.926	0.649	406	1.544	0.031
			429	1.552	0.023
			Infinity	1.575	

$k = 1.45 \times 10^{-4}\ s^{-1}$

(iv) The Procedure for the Investigation of the Depression of the Rate of 2-Chloro 4-Nitrophenoxide Release, in the Reaction of 2-Chloro 4-Nitrophenyl Phenylmethanesulphonate with Triethylamine, by Triethylammonium Chloride

Two stock solutions were prepared using 20% aqueous DME as the solvent.

A. Triethylammonium chloride 1.377 g)
Triethylamine 0.2024 g) in 100 ml

B. Tetraethylammonium chloride 1.657 g in 100 ml

Four solutions for the kinetics were prepared by mixing A and B in the following proportions;

I	1 ml of A + 9 ml of B	pH = 8.01
III	2 ml of A + 8 ml of B	pH = 8.16
VI	5 ml of A + 5 ml of B	pH = 8.21
VIII	Undiluted A	pH = 8.22

As solution A seemed to deteriorate a new solution of triethylamine was prepared(A').

A'. Triethylammonium chloride 1.377 g)
Triethylamine 0.4036 g) in 100 ml

Four more solutions for kinetics were prepared;

II	1.4 ml of A' + 8.6 ml of B	pH = 8.42
IV	3 ml of A' + 7 ml of B	pH = 8.54
V	4 ml of A' + 6 ml of B	pH = 8.54
VII	7 ml of A' + 3 ml of B	pH = 8.55

3.0 ml of each of these solutions were pipetted into 1 cm u.v. cells which were placed in the compartment of a Gilford spectrophotometer. The compartment was thermostated to 20°. 10 µl of a solution of 24.8 mg of 2-chloro 4-nitrophenyl phenylmethanesulphonate in 5 ml of DME was injected into the cells and the change in absorbance at 405 nm was recorded.

The pH of the solutions was measured on a Radiometer pH meter which had been standardised at pH = 9.00.

Kinetics with Solution I

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.002 M

Triethylammonium chloride concentration: 0.01 M

pH: 8.01

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.081	1.061	31.3	0.740	0.402
0.6	0.107	1.035	35.2	0.785	0.357
1.8	0.148	0.994	39.2	0.828	0.314
2.4	0.168	0.974	43.6	0.867	0.275
4.0	0.212	0.930	45.5	0.883	0.259
8.0	0.320	0.822	48.1	0.903	0.239
12.5	0.429	0.713	52.5	0.931	0.211
16.5	0.511	0.631	57.3	0.959	0.183
20.3	0.580	0.562	61.5	0.981	0.161
24.4	0.645	0.497	66.8	1.005	0.137
27.9	0.695	0.447	90.4	1.073	0.069
			Infinity	1.142	

$k = 4.96 \times 10^{-4}\ s^{-1}$

Kinetics with Solution II

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.00559 M

Triethylammonium chloride concentration: 0.014 M

pH: 8.42

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.036	1.108	12.0	0.758	0.386
0.3	0.074	1.070	13.3	0.799	0.345
0.6	0.098	1.046	14.3	0.830	0.314
1.4	0.173	0.971	15.3	0.856	0.288
1.8	0.205	0.939	16.7	0.887	0.257
2.3	0.248	0.896	17.8	0.910	0.234
2.8	0.285	0.859	19.4	0.941	0.203
3.5	0.336	0.808	20.7	0.961	0.183
4.8	0.419	0.725	22.6	0.988	0.156
5.4	0.461	0.683	23.7	1.001	0.143
6.9	0.541	0.603	24.6	1.013	0.131
7.7	0.582	0.562	26.5	1.031	0.113
8.6	0.628	0.516	28.1	1.045	0.099
9.7	0.672	0.472	30.1	1.061	0.083
10.6	0.709	0.435	48.9	1.127	0.017
11.1	0.724	0.420	Infinity	1.144	

$k = 1.44 \times 10^{-3}\ s^{-1}$

Kinetics with Solution III

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.004 M

Triethylammonium chloride concentration: 0.02 M

pH: 8.16

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.044	1.069	16.9	0.719	0.394
0.4	0.075	1.038	18.6	0.757	0.356
0.9	0.109	1.004	22.8	0.839	0.274
1.5	0.140	0.973	24.8	0.869	0.245
3.7	0.261	0.852	27.8	0.909	0.204
5.2	0.334	0.779	31.6	0.949	0.164
6.9	0.408	0.705	33.1	0.962	0.151
9.2	0.496	0.617	36.1	0.987	0.126
11.4	0.570	0.543	40.7	1.016	0.097
14.5	0.660	0.453	Infinity	1.113	

$k = 9.82 \times 10^{-4}\ s^{-1}$

Kinetics with Solution IV

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.012 M

Triethylammonium chloride concentration: 0.03 M

pH: 8.54

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.039	1.101	4.6	0.647	0.493
0.3	0.100	1.040	5.2	0.696	0.444
0.5	0.132	1.008	6.6	0.796	0.344
0.9	0.198	0.942	7.4	0.841	0.299
1.2	0.252	0.888	8.2	0.879	0.261
1.6	0.306	0.834	9.5	0.933	0.207
1.7	0.332	0.808	10.7	0.971	0.169
2.3	0.402	0.738	11.7	0.998	0.142
2.6	0.441	0.699	12.4	1.012	0.128
2.9	0.487	0.653	13.4	1.034	0.106
3.4	0.537	0.603	25.4	1.127	0.013
3.8	0.580	0.560	Infinity	1.140	

$k = 2.90 \times 10^{-3}\ s^{-1}$

Kinetics with Solution V

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.0160 M

Triethylammonium chloride concentration: 0.04 M

pH: 8.54

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.041	1.089	4.9	0.772	0.358
0.2	0.090	1.040	5.3	0.808	0.322
0.5	0.157	0.973	5.8	0.845	0.285
0.6	0.191	0.939	6.1	0.859	0.271
0.8	0.232	0.898	6.7	0.896	0.234
1.0	0.263	0.867	7.3	0.924	0.206
1.2	0.313	0.817	7.9	0.947	0.183
1.5	0.355	0.775	8.5	0.973	0.157
1.8	0.415	0.715	9.6	1.009	0.121
2.2	0.472	0.658	10.4	1.026	0.104
2.4	0.506	0.624	11.1	1.043	0.087
2.7	0.538	0.592	12.1	1.059	0.071
3.4	0.623	0.507	13.4	1.075	0.055
3.9	0.679	0.451	Infinity	1.130	

$k = 3.76 \times 10^{-3}\ s^{-1}$

Kinetics with Solution VI

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.01 M

Triethylammonium chloride concentration: 0.05 M

pH: 8.21

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.039	1.072	7.8	0.734	0.377
1.0	0.120	0.934	8.8	0.779	0.332
1.1	0.195	0.916	10.5	0.850	0.261
1.8	0.272	0.839	11.9	0.893	0.218
2.6	0.355	0.756	12.8	0.914	0.197
3.9	0.479	0.632	13.9	0.943	0.168
4.4	0.515	0.596	14.6	0.957	0.154
5.1	0.570	0.541	16.3	0.987	0.124
6.1	0.635	0.476	18.2	1.014	0.097
7.1	0.694	0.417	19.3	1.028	0.083
			Infinity	1.111	

$k = 2.21 \times 10^{-3}\ s^{-1}$

Kinetics with Solution VII

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.0279 M

Triethylammonium chloride concentration: 0.107 M

pH: 8.55

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.035	1.062	3.2	0.748	0.349
0.2	0.118	0.979	3.7	0.806	0.291
0.5	0.195	0.902	4.1	0.836	0.261
0.7	0.274	0.823	4.6	0.878	0.219
1.0	0.345	0.752	5.1	0.915	0.182
1.1	0.377	0.720	5.5	0.939	0.158
1.3	0.435	0.662	6.1	0.968	0.129
1.7	0.519	0.578	7.0	1.003	0.094
2.0	0.558	0.539	7.7	1.021	0.076
2.3	0.611	0.486	8.2	1.032	0.065
2.8	0.689	0.408	Infinity	1.097	

$k = 5.75 \times 10^{-3}\ s^{-1}$

Kinetics with Solution VIII

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.02 M

Triethylammonium chloride concentration: 0.1 M

pH: 8.22

TIME (MIN)	A_t	$A_\infty - A_t$	TIME (MIN)	A_t	$A_\infty - A_t$
0.0	0.035	1.040	7.0	0.856	0.219
0.7	0.191	0.884	7.6	0.882	0.193
1.3	0.300	0.775	8.1	0.906	0.169
1.8	0.376	0.699	9.5	0.947	0.128
2.1	0.421	0.654	10.0	0.959	0.116
2.6	0.488	0.587	11.5	0.992	0.083
3.3	0.570	0.506	12.9	1.013	0.062
4.6	0.700	0.375	Infinity	1.075	
5.8	0.786	0.289			

$k = 3.64 \times 10^{-3}\ s^{-1}$

(v) The Procedure for the Investigation of the Dependence on Base of the Rate of Release of 2,4-Dinitrophenoxide from 2,4-Dinitrophenyl 4-Methylphenylmethanesulphonate

Three stock solutions were prepared using 20% aqueous DME as the solvent.

A. Tetraethylammonium chloride	0.5049 g)	) in 100 ml
Triethylamine	0.0328 g)	
B. Triethylammonium chloride	0.0691 g in 250 ml	
C. Tetraethylammonium chloride	0.0829 g in 250 ml	

From these three stock solutions five solutions with different triethylamine concentrations but the same pH and ionic strength were prepared as follows.

The required amount of triethylamine was obtained by pipetting solution A into a 100 ml beaker. This solution was diluted to about 50 ml and adjusted to a pH of 8.64 using solutions B and C. Solution B being used to control the pH and solution C being used to control the volume. The solution for kinetics was transferred to a 50 ml volumetric flask and made to the mark with a little of solution C.

The five solutions so prepared are shown below;

Ionic strength = 0.002 M

Solution	Volume of A/ml	Triethylamine Concentration/M	pH
I	1.0	0.0010	8.65
II	1.5	0.0015	8.64
III	2.0	0.0020	8.64
IV	2.5	0.0025	8.63
V	3.0	0.0030	8.63

3 ml portions of these solutions were pipetted into 1 cm u.v. cells. 10 µl of a solution of 25 mg of 2,4-dinitrophenyl 4-methylphenylmethanesulphonate in 5 ml of DME was injected into the cell and the rate of release of the phenoxide was measured by following the increase in absorbance at 405 nm with time. The cell compartment was thermostated to 20° and the concentration of the ester in the cell was about 4.7×10^{-5} M.

Kinetic Run with Solution I

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.001 M

pH: 8.65

TIME (MIN)	A_t	$A_\infty - A_t$
0.4	0.017	0.598
2.1	0.086	0.529
3.5	0.135	0.480
5.3	0.187	0.428
6.8	0.227	0.388
8.7	0.269	0.346
11.0	0.315	0.300
13.2	0.353	0.262
15.7	0.392	0.223
18.3	0.424	0.195
20.2	0.446	0.169
22.9	0.473	0.142
23.9	0.480	0.135
25.2	0.491	0.124
26.5	0.501	0.114
29.7	0.521	0.094
Infinity	0.615	

$k = 1.05 \times 10^{-3}\ s^{-1}$

Kinetic Run with Solution II

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.0015 M

pH: 8.64

TIME (MIN)	A_t	$A_\infty - A_t$
0.3	0.017	0.602
1.1	0.074	0.545
2.0	0.129	0.490
2.7	0.166	0.453
3.8	0.222	0.397
4.6	0.255	0.364
5.9	0.302	0.317
6.9	0.335	0.284
7.7	0.358	0.261
8.6	0.384	0.235
9.4	0.404	0.215
10.6	0.430	0.189
11.9	0.456	0.163
13.2	0.477	0.142
14.4	0.494	0.125
15.7	0.511	0.108
17.1	0.525	0.094
Infinity	0.619	

$k = 1.82 \times 10^{-3}\ s^{-1}$

Kinetics with Solution III

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.002 M

pH: 8.64

TIME (MIN)	A_t	$A_\infty - A_t$
0.4	0.038	0.578
0.6	0.063	0.553
1.6	0.142	0.474
2.9	0.224	0.392
3.5	0.256	0.360
4.2	0.293	0.323
5.1	0.332	0.284
5.8	0.360	0.256
6.6	0.392	0.224
7.4	0.415	0.201
8.7	0.451	0.165
9.9	0.479	0.137
11.1	0.500	0.116
12.2	0.517	0.099
Infinity	0.616	

$k = 2.50 \times 10^{-3}\ s^{-1}$

Kinetics with Solution IV

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.0025 M

pH: 8.63

TIME (MIN)	A_t	$A_\infty - A_t$
0.24	0.029	0.594
0.79	0.093	0.530
1.55	0.668	0.455
2.28	0.228	0.395
2.88	0.269	0.354
3.67	0.318	0.305
4.45	0.361	0.262
5.49	0.409	0.214
6.59	0.449	0.174
7.49	0.476	0.147
8.59	0.503	0.120
9.39	0.519	0.104
10.08	0.533	0.090
Infinity	0.623	

$k = 3.1^9 \times 10^{-3}\ s^{-1}$

Kinetics with Solution V

Temperature: 20.0 ± 0.1°C

Triethylamine concentration: 0.003 M

pH: 8.63

TIME -(MIN)	A_t	$A_\infty - A_t$
0.25	0.040	0.590
0.59	0.086	0.544
1.31	0.173	0.457
1.84	0.226	0.404
2.24	0.262	0.368
2.84	0.309	0.321
3.17	0.333	0.300
3.68	0.367	0.263
4.21	0.396	0.234
4.96	0.434	0.196
5.28	0.449	0.181
5.62	0.463	0.167
6.10	0.480	0.150
6.69	0.500	0.130
7.22	0.515	0.115
7.88	0.530	0.100
Infinity	0.630	

$k = 3.88 \times 10^{-3}\ s^{-1}$

(vi) Procedure for the Kinetic Measurements Used in the Determination of the Hammett Plots for 2,4-Dinitrophenyl Phenylmethanesulphonate

The pyridine solutions were prepared by dissolving a known weight of pyridine in 100 ml of 20% aqueous DME. 3 ml of this solution was pipetted into a 1 cm u.v. cell contained in the thermostated(20°) compartment of the u.v. spectrometer. 10 µl of a solution of the substrate dissolved in DME(approx. 2×10^{-2} M) was injected into the cell and the rate of 2,4-dinitrophenoxide release was measured by following the change in the absorbance at 405 nm.

The same procedure was used for the reactions with triethylamine.

The Reaction of 2,4-Dinitrophenyl 4-Chlorophenylmethane-sulphonate with Pyridine(0.208 M)

Temperature: 20.0 ± 0.1°C

Solution: Pyridine: 1.648 g in a 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)	TIME (MIN)	A_t	LOG(100-%Rxn)
5.0	0.031	1.980	238.0	0.404	1.627
12.77	0.056	1.964	269.5	0.443	1.582
31.22	0.106	1.929	336.0	0.483	1.493
75.00	0.193	1.860	384.5	0.514	1.426
127.0	0.275	1.784	441.5	0.544	1.350
147.0	0.301	1.756	460.5	0.551	1.330
183.5	0.347	1.703	1041.0	0.669	0.659
			Infinity	0.701	

$k' = 5.22 \times 10^{-5}\ s^{-1}$

$k = 2.51 \times 10^{-4}\ \underline{M}^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl 3-Nitrophenylmethanesulphonate(4.53×10^{-5} M) with Pyridine(0.208 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl 3-nitrophenylmethanesulphonate:

26 mg in 5 ml of DME

Pyridine: 1.648 g in 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)
1.12	0.037	1.971
2.34	0.070	1.943
6.99	0.159	1.857
14.35	0.263	1.728
20.96	0.327	1.625
28.24	0.384	1.506
33.46	0.417	1.418
43.09	0.462	1.261
49.05	0.483	1.162
57.60	0.504	1.033
Infinity	0.566	

$k' = 6.44 \times 10^{-4}\ s^{-1}$

$k = 3.10 \times 10^{-3}\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl 4-Nitrophenylmethanesulphonate(4.53×10^{-5} M) with Pyridine(0.200 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl 4-nitrophenylmethanesulphonate:

41.2 mg in 5 ml of DME

Pyridine: 1.582 g in 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)	TIME	A_t	LOG(100-%Rxn)
0.36	0.158	1.834	2.23	0.478	1.132
0.56	0.226	1.772	2.49	0.494	1.067
0.71	0.266	1.715	2.74	0.505	0.939
0.88	0.308	1.646	3.08	0.518	0.801
1.14	0.359	1.545	3.35	0.524	0.720
1.34	0.391	1.467	3.69	0.532	0.580
1.59	0.423	1.371	4.17	0.539	0.403
1.77	0.442	1.303	4.72	0.545	0.160
1.97	0.460	1.226	Infinity	0.553	

$k' = 1.47 \times 10^{-2}\ s^{-1}$

$k = 7.34 \times 10^{-2}\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl Phenylmethanesulphonate (6.03×10^{-5} M) with Pyridine(0.201 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl phenylmethanesulphonate: 25.6 mg in 5 ml of DME

Pyridine: 1.528 g in 100 ml of solution

TIME (MIN)	A_t	A_t (computer adjusted)
192.5	0.182	0.185
226 0	0.202	0.203
289.5	0.237	0.235
445.0	0.307	0.303
575.0	0.354	0.351
728.0	0.398	0.398
1311.0	0.481	0.485
1341.0	0.510	0.515
1550.0	0.531	0.538
1765.0	0.564	0.553
Infinity	0.665	

$k' = 2.13 \pm 0.15 \times 10^{-5}\ s^{-1}$

$k = 1.06 \pm 0.07 \times 10^{-4}\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl 3-Chlorophenylmethanesulphonate (4.29×10^{-5} M) with Pyridine (0.200 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl 3-chlorophenylmethanesulphonate:
24 mg in 5 ml of DME

Pyridine: 1.582 g in 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)	TIME (MIN)	A_t	LOG(100-%Rxn)
1	0.008	1.993	88	0.245	1.713
6	0.028	1.975	93	0.254	1.700
16	0.065	1.940	114	0.288	1.634
22	0.088	1.917	138	0.321	1.563
32	0.118	1.885	168	0.357	1.469
39	0.137	1.863	201	0.388	1.368
48	0.159	1.836	223	0.406	1.296
69	0.208	1.770	232	0.412	1.269
81	0.230	1.737	243	0.418	1.240
			260	0.430	1.177
			Infinity	0.506	

$k' = 1.19 \times 10^{-4}\ s^{-1}$

$k = 5.93 \times 10^{-4}\ M^{-1}\ s^{-1}$

The Reaction 2,4-Dinitrophenyl 4-Cyanophenylmethanesulphonate(7.56×10^{-5} M) with Pyridine(0.208 M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl 4-cyanophenylmethanesulphonate:

41.2 mg in 5 ml of DME

Pyridine: 1.648 g in 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)	TIME MIN)	A_t	LOG(100-%Rxn)
0.44	0.095	1.953	6.59	0.670	1.440
0.74	0.151	1.923	7.37	0.704	1.378
1.01	0.194	1.898	8.55	0.747	1.284
1.49	0.260	1.857	9.40	0.773	1.216
2.11	0.338	1.803	10.25	0.795	1.148
2.64	0.397	1.757	11.52	0.820	1.055
3.25	0.455	1.706	12.87	0.844	0.942
3.93	0.512	1.650	14.86	0.868	0.790
4.64	0.562	1.594	17.59	0.889	0.590
5.30	0.603	1.542	Infinity	0.925	

$k' = 2.97 \times 10^{-3}\ s^{-1}$

$k = 1.43 \times 10^{-2}\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl 4-Methylphenylmethanesulphonate(4.58×10^{-5} M) with Triethylamine(2.28×10^{-3} M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl 4-methylphenylmethanesulphonate:

24.2 mg in 5 ml of DME

Triethylamine: 23.1 mg in 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)
0.27	0.030	1.978
1.10	0.118	1.908
2.00	0.193	1.837
2.93	0.256	1.768
4.10	0.322	1.673
5.46	0.385	1.576
8.35	0.476	1.361
11.35	0.530	1.154
13.52	0.558	0.987
14.89	0.571	0.881
16.88	0.585	0.728
Infinity	0.618	

$k' = 2.90 \times 10^{-3}\ s^{-1}$

$k = 1.27\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl Phenylmethanesulphonate (4.89×10^{-5} M) with Triethylamine (2.39×10^{-3} M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl phenylmethanesulphonate: 24.8 mg in 5 ml of DME

Triethylamine: 24.2 mg in 100 ml

TIME (MIN)	A_t	LOG(100-%Rxn)
0.38	0.110	1.923
0.61	0.166	1.878
0.83	0.214	1.836
1.35	0.309	1.736
2.00	0.400	1.614
2.77	0.479	1.469
3.43	0.528	1.347
3.96	0.558	1.251
4.68	0.589	1.122
5.49	0.616	0.968
6.83	0.644	0.712
Infinity	0.679	

$k' = 7.24 \times 10^{-3}\ s^{-1}$

$k = 3.03\ M^{-1}\ s^{-1}$

The Reaction of 2,4-Dinitrophenyl 4-Chlorophenylmethanesulphonate(9.48×10^{-6} M) with Triethylamine(7.91×10^{-4} M)

Temperature: 20.0 ± 0.1°C

Solutions: 2,4-Dinitrophenyl 4-chlorophenylmethanesulphonate:

5.3 mg in 5 ml of DME

Triethylamine: 8.0 mg in 100 ml

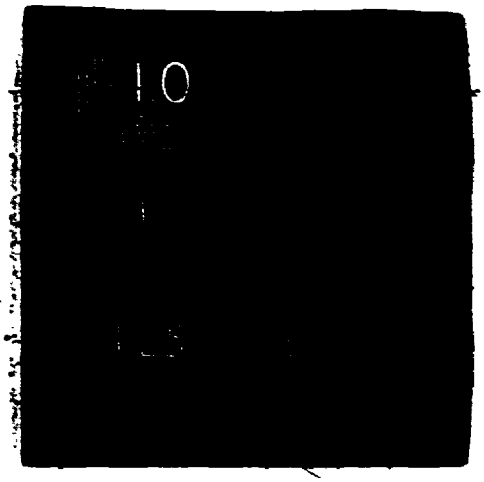
TIME (MIN)	A_t	LOG(100-%Rxn)
0.56	0.044	1.832
0.77	0.058	1.761
0.96	0.068	1.702
1.12	0.076	1.649
1.30	0.083	1.596
1.52	0.091	1.526
1.78	0.098	1.454
1.94	0.103	1.395
2.16	0.107	1.340
2.35	0.111	1.278
2.77	0.118	1.142
3.07	0.122	1.039
3.44	0.124	0.977
3.92	0.128	0.818
4.61	0.131	0.641
Infinity	0.137	

$k' = 1.20 \times 10^{-2}\ s^{-1}$

$k = 15.2\ M^{-1}\ s^{-1}$

3 3

OF/DE



(vii) The Determination of the Proportions of the Base Catalysed Hydrolysis of 2,4-Dinitrophenyl Phenylmethanesulphonates Occurring by Sulphene and Non-sulphene Mechanisms

2,4-Dinitrophenyl 4-nitrophenylmethanesulphonate (200 mg, 0.52 mmol) was dissolved in a mixed solvent of 120 ml of DME plus 30 ml of deuterium oxide. Pyridine (10.4 g, 0.87 mol) was added to the solution. The reaction mixture was stirred at room temperature for 25 min. The majority of the solvent was removed on a Büchi Rotovap. The remaining solution was extracted with ether. The ether was evaporated to give the 2,4-dinitrophenol.

The deuterium oxide was removed, on a Büchi Rotovap, from the aqueous layer. The residue was suspended in methylene chloride (approx. 100 ml) and excess phosphorus pentachloride was slowly added. The methylene chloride was decanted onto ice and this mixture was stirred for 1 hour. The water layer was removed. The methylene chloride was washed (3 times) with water, dried ($MgSO_4$), filtered and the solvent evaporated.

The crude 4-nitrophenylmethanesulphonyl chloride so obtained was recrystallised from methylene chloride-petroleum ether and the n.m.r. and mass spectra were taken. From the mass spectrum the ratio of the monodeuterated 4-nitrophenylmethanesulphonyl chloride to the undeuterated 4-nitrophenylmethanesulphonyl chloride was determined. From

TABLE XVI

The Proportions of the Hydrolysis of 2,4-Dinitrophenyl Phenylmethane-sulphonates Occurring via Sulphene and Non-sulphene Mechanisms

ESTER	Yield of sulphonyl chloride	The ratio of hydrolysis occuring via	
		Non-sulphene route	Sulphene Route
$C_6H_5CH_2SO_3C_6H_3(NO_2)_2$-2,4	86 %	1	1.65
4-$ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	85 %	1	4.7
3-$ClC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	96 %	1	9.4
3-$NO_2C_6H_2CH_2SO_3C_6H_3(NO_2)_2$-2,4	92 %	1	32.0
4-$CNC_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	88 %		∞
4-$NO_2C_6H_4CH_2SO_3C_6H_3(NO_2)_2$-2,4	35 %		∞

this ratio the proportions of the reaction occurring by the two mechanisms was deduced. This procedure was repeated for the five other 2,4-dinitrophenyl phenylmethanesulphonates with the results shown in table XVI.

The same method was used to determine the amount of deuterium incorporated when 2,4-dinitrophenyl phenylmethanesulphonate was reacted with triethylamine. The n.m.r. showed that only monodeuterated product had been formed in this case and hence all the hydrolysis occurred by the sulphene route.

Appendix I

The steps involved in the exchange of the benzylic hydrogens of the esters are depicted in the following equation;

$$\underset{A}{PhCH_2SO_2OAr} \xrightarrow{k_1} \underset{B}{PhCHDSO_2OAr} \xrightarrow{k_1/2} \underset{C}{PhCD_2SO_2OAr}$$

secondary isotope effects have been ignored.

Thus

$$\frac{\delta[A]}{\delta t} = -k_1[A] \qquad \frac{\delta[B]}{\delta t} = k_1[A] - \frac{k_1}{2}[B]$$

$$\frac{\delta[C]}{\delta t} = \frac{k_1}{2}[B]$$

At $t = 0$; $[A] = [A]_o$, $[B] = 0$ and $[C] = 0$

Thus at time t

$$[A] = [A]_o e^{-k_1 t}$$

Hence

$$\frac{\delta[B]}{\delta t} = k_1[A]_o e^{-k_1 t} - \frac{k_1}{2}[B]$$

and thus

$$[B] = \frac{k_1[A]_o}{(k_1/2) - k_1}(e^{-k_1 t} - e^{-k_1 t/2})$$

Rate of incorporation of deuterium $\frac{\delta D}{\delta t} = k_1[A] + \frac{k_1}{2}[B]$

Substituting for [A] and [B]

$$\frac{\delta D}{\delta t} = k_1[A]_o e^{-k_1 t/2}$$

Integrating one obtains the amount of deuterium incorporated at time t($[D]_t$).

$$[D]_t = -2[A]_o e^{-k_1 t/2} + \text{const.}$$

at time t = 0, [D] = 0.

Thus const. = $2[A]_o$

Hence

$$[D]_t = 2[A]_o(1 - e^{-k_1 t/2})$$

or $$\text{In}[D]_t = \frac{k_1 t}{2}$$

Appendix II

Equilibria in 20% aqueous DME

i) Measurement of the 'pKa' of Triethylamine

Procedure

Triethylamine(0.5 ml, 0.36 g, 3.5 mmol) was dissolved in 250 ml of 20% aqueous DME. A column of Rexyn 203(OH) ion exchange resin was prepared. The column was washed with sodium hydroxide(2M), distilled water and finally with 20% aqueous DME. The triethylamine solution was passed through the column and the last 100 ml was collected in a flask, protected from carbon dioxide. 63 ml of this purified solution was poured into a beaker and titrated, potentiometrically in an atmosphere of nitrogen, with hydrochloric acid(0.24 M, solvent 20% aqueous DME) which had been purged with nitrogen. The potentiometer was standardised at pH = 9.00 and pH = 8.00 with aqueous buffers.

Results

Titre/ml	pH	Titre/ml	pH
0.00	9.58	2.80	7.82
0.20	9.32	2.90	7.71
0.30	9.23	3.00	7.57
0.40	9.15	3.10	7.39
0.60	9.02	3.20	7.14
0.80	8.90	3.30	6.76
1.00	8.80	3.40	6.38
1.20	8.71	3.50	6.01
1.40	8.62	3.55	5.83
1.60	8.54	3.60	5.61
1.70	8.49	3.65	5.27
1.80	8.45	3.70	4.83
1.90	8.40	3.75	3.77
2.00	8.36	3.80	3.25
2.20	8.26	3.85	3.01
2.40	8.14	3.90	2.83
2.50	8.07	4.00	2.63
2.60	7.99	4.10	2.48
2.70	7.91	4.20	2.38

End point = 3.73 ml

'pH' at half neutralization equals 'pKa' = 8.43

ii) Calculation of Accurate Triethylamine and Triethylammonium Ion Concentrations using 'pKa' = 8.43

The equilibrium can be written

$$Et_3N + H_3O^+ \underset{Ka}{\rightleftharpoons} Et_3\overset{+}{N}H + H_2O$$

Initial Concentrations	a	b
Concentrations at Equilibrium	a-α	b+α

$$Ka = \frac{[Et_3N][H^+]}{[Et_3\overset{+}{N}H]} = \frac{(a-\alpha)[H^+]}{(b+\alpha)}$$

Assuming the meter reading of 'pH' in 20% aqueous DME is directly proportioned to $[H^+](44)$ the values of 'Ka' and '$[H^+]$' obtained from the meter readings may be substituted for Ka and $[H^+]$ in the above equation and α can be determined. Hence a-α and b+α may be calculated.

These concentrations of triethylamine(a-α) and triethylammonium ion(b+α) are the ones tabulated in the results and discussion.

iii) Measurement of the Equilibrium Constant Between 4-Nitrophenol and Triethylamine

The general procedure was similar to the method outlined by Bayles and Chetwyn(45). 4-Nitrophenol(0.138 g, 0.988 mmol) was dissolved in 100 ml of 20% aqueous DME. 2 ml of this solution were pipetted into a 100 ml volumetric flask and the solution was made to the mark with 20% aqueous DME(conc^{n} 1.98×10^{-4} M). Triethylamine(0.201 g, 1.99 mmol) was dissolved in 100 ml of 20% aqueous DME(conc^{n} 1.99×10^{-2} M).

5 ml of the phenol solution were pipetted into a 10 ml volumetric flask. A known volume of the triethylamine solution was added from a 5 ml burette, and the solution was made to the mark with 20% aqueous DME. The u.v. absorbance spectrum was taken and the results are shown in the table.

$[Et_3N]_a$ (10^{-3} M)	A_{404nm}	$[ArO^-]_e$ (10^{-5} M)	$[BH^+]$ (10^{-3} M)	$[ArOH]_e$ (10^{-5} M)	K_{eq} (10^{-2} M)
1.00	0.425	3.94	0.96	5.97	2.72
1.99	0.543	5.03	1.94	4.85	2.68
3.98	0.705	6.53	3.91	3.35	3.26
9.95	0.840	7.78	9.87	2.10	2.92

a = added e = equilibrium $K_{eq} = \dfrac{[ArO^-][Et_3NH^+]}{[ArOH]}$

The value of the extinction coefficient of 4-nitrophenoxide ion at 404 nm was found to be 10,800 by measuring the absorbance of 404 nm of a solution of known concentration of the phenoxide. The phenol did not absorb significantly at 404 nm and an isobestic point was observed at 347 nm.

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