Nucleophilic Displacement Reactions at Carbon, Phosphorus and Sulphur Centres: † Reaction of Aryl Methanesulphonates with Ethoxide; Change in Mechanism with Change in Leaving Group

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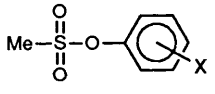
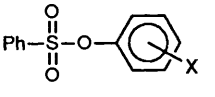
The reactions of ethoxide ion with aryl methanesulphonate esters (**1a–c**) in anhydrous ethanol at 25 °C have been investigated in order to determine the effect of leaving group nucleofugality on the balance between substitution and elimination pathways. The reactions of *p*-nitrophenyl-(**1a**), *m*-nitrophenyl-(**1b**) and *p*-trifluoromethylphenyl-(**1c**) methanesulphonates have been examined by means of kinetic studies, sulphene trapping experiments, and deuterium exchange experiments. It is concluded that the *para*-nitro-substituted ester reacts predominantly by an Elcb-type elimination mechanism *via* a sulphene intermediate, with nucleophilic substitution as a minor concurrent pathway. Conversely, the *meta*-nitro-substituted ester reacts predominantly by substitution, with elimination as a minor concurrent pathway. The evidence available indicates that the *para*-trifluoromethyl-substituted ester reacts solely by substitution. Thus, the mechanism of reaction changes from nucleophilic substitution to elimination–addition as leaving group nucleofugality increases.

As part of a series of studies of the mechanism of reactions of carbon-, phosphorus- and sulphur-based esters, and the effects of alkali metal ions on these reactions, we report here on the mechanism of reaction of ethoxide ion with aryl methanesulphonates **1a–c** in anhydrous ethanol at 25 °C.



	X
1a	*p*-NO_2
1b	*m*-NO_2
1c	*p*-CF_3



	X
2a	*p*-NO_2
2b	*m*-NO_2
2c	*p*-CF_3

Previous reports outlined the observation of alkali metal ion catalysis and inhibition in the reaction of ethoxide with *p*-nitrophenyl benzenesulphonate (**2a**)[1e,g] and further studies showed that the reaction proceeded *via* nucleophilic substitution at the sulphonyl centre.[1h]

It was of interest to investigate how a change in structure, from benzenesulphonate (**2a–c**) to methanesulphonate (**1a–c**), would affect the reaction pathway. Aryl methanesulphonate esters can in principle react by a number of different mechanisms. Nucleophilic substitution at sulphur may occur by either a stepwise (addition–elimination, S_AN) or a concerted [$S_N2(S)$] mechanism. Since acidic protons are present α to the sulphonyl group, elimination–addition mechanisms are also conceivable. These may be stepwise (Elcb), *via* a carbanion intermediate, or concerted (E2). In both cases, a sulphene, $R^1R^2C{=}SO_2$—the sulphonyl analogue of a ketene—is produced and, being a highly reactive electrophile, undergoes reaction with various nucleophiles.[2,3] Finally, aromatic rings activated by nitro groups could in principle react by nucleophilic aromatic substitution (S_NAr), with the methanesulphonate moiety acting as a leaving group. The present work sheds light on these various facets.

Results and Discussion

(a) *Sulphene Trapping Experiments.*—For aryl methanesulphonate esters, an Elcb mechanism, shown in eqns. (1)–(3),

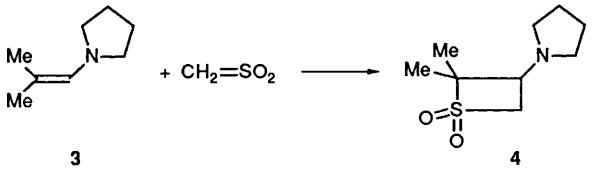
$$CH_3SO_2OAr + EtO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^-CH_2SO_2OAr + EtOH \quad (1)$$

$$^-CH_2SO_2OAr \xrightarrow{k_2} CH_2{=}SO_2 + ArO^- \quad (2)$$

$$CH_2{=}SO_2 + EtOH \xrightarrow{fast} CH_3SO_2OEt \quad (3)$$

involves deprotonation α to the sulphonyl group to form a carbanion, which eliminates aryloxide ion to form a highly reactive sulphene. The sulphene then reacts with ethanol solvent to yield ethyl methanesulphonate, which could also result from direct nucleophilic attack of ethoxide ion on the sulphonyl centre. (Sulphene may also react with ethoxide ion to re-form the carbanion.) However, if another reagent capable of reacting with the sulphene is also present and reacts with sulphene to form a product other than $MeSO_2OEt$, the intermediacy of sulphenes can be inferred.

Sulphenes are known to react with enamines by cycloaddition (*via* zwitterionic intermediates).[4] Thus, *N*-(2-methylpropen-1-yl)pyrrolidine (**3**) is known to react with sulphene to form a 3-aminotrimethylene sulphone (**4**) [eqn (4)],[5,6] and may be used as a trapping agent.



3 **4** (4)

In the present work, potassium ethoxide was allowed to react with **1a** in the presence of enamine **3** and the products were partitioned into dichloromethane. The expected sulphone adduct was detected by ^1H NMR spectroscopy, GC and GC/MS in the concentrate of the organic solution. The

† This paper is an extension of our series on Bond Scission in Sulphur Compounds. For previous papers in this series, see ref. 1.

Table 1 Results of sulphene trapping experiments in reactions of methanesulphonate esters **1a–c** with potassium ethoxide

Compound	% Sulphone in extracts of reaction mixture	Overall %sulphone
1a	13	4
1b	<1	<0.06
1c	<0.2	<0.007

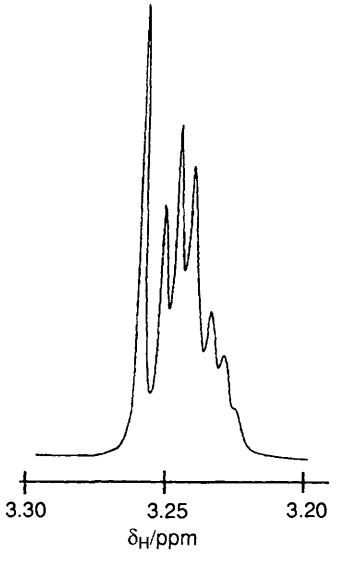


Fig. 1 ^{1}H NMR spectrum of the methyl resonance of **1a** after partial reaction in deuteriated ethanol

concentrate was found to contain 13% sulphone (by mass) and the overall yield of sulphone was 4% based on the starting ester (Table 1). The same experiment was repeated with **1b**, but in this case only trace levels (<1%) of sulphone were detected in extracts of the reaction mixture and the overall yield of sulphone was <0.1%. Lastly, attempts to trap a sulphene intermediate in the reaction of KOEt with **1c** failed to yield detectable amounts of the expected cycloadduct. Therefore, it appears that **1a** and **1b** react by elimination to some extent, with **1a** reacting by elimination to a greater extent than **1b**, and also that **1c** does not react by this pathway to any extent. It must be noted that since the efficiency of the trapping procedure is not known, the extent of reaction by elimination cannot be deduced from these results and the yield of trapped sulphene represents only a minimum value for the extent of reaction by elimination. Clearly, these results do not differentiate between Elcb and E2 elimination mechanisms since both involve sulphene intermediates. This point is addressed in the following section.

(b) *Deuterium Exchange Experiments.*—Aryl methanesulphonates were allowed to react with alkali metal ethoxides in deuteriated ethanol (EtOD) to check for exchange at the methyl position which would indicate that deprotonation and reprotonation of the methyl position, which is the first step in an Elcb mechanism, was occurring.

Significant deuterium uptake from deuteriated ethanol solvent into $MeSO_2OAr$ was observed for **1a–c**. Therefore, a carbanion intermediate is implicated in the reactions of these esters. This conclusion would not be affected by the occurrence of internal return.[7]

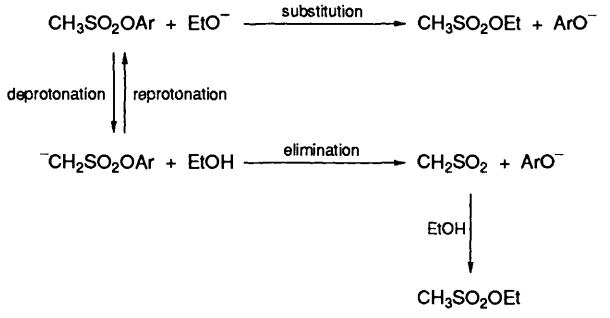
Overlapping spectra of species undeuteriated, monodeuteriated, dideuteriated and trideuteriated at the methyl position were observed by ^{1}H NMR spectroscopy or were inferred when unreacted ester was analysed after partial reaction. Incorporation of a deuteron at the methyl position results in a small

Table 2 Comparison of the extent of deuteriation and the extent of reaction in deuterium exchange studies of **1a** and **1b** in EtOD with a tenfold excess of KOEt + 18-crown-6 over ester

Compound	Extent of deuteriation (%)	Extent of reaction (%)
1a	44	29
1b	33	33

upfield shift (*ca.* 0.015 ppm), as well as splitting due to H-D coupling (*J ca.* 2.4 Hz).[8] In practice, overlapping spectra of CH_3 (singlet), CH_2D (triplet) and CHD_2 (quintet) species are observed (Fig. 1). The presence of the CD_3 species may be inferred from integration. The extent of deuteriation and the extent of reaction for reactions of **1a** and **1b** with 10 equiv. of KOEt and 18-crown-6 were determined and are compared in Table 2.

The observation of uptake of deuterium into unreacted ester removes several possible mechanisms from consideration. In an E2 mechanism and in an $Elcb_{irrev}$ mechanism, the anion $^-CH_2SO_2OAr$ is not in equilibrium with the unreacted ester, so deuterium uptake into unreacted ester cannot occur.[9] In the case of an $Elcb_{rev}$ mechanism, the anion and unreacted ester are in equilibrium and reprotonation of the anion by deuteriated solvent can result in incorporation of one, two and three deuterons (successively). Deuterium uptake into unreacted ester can also occur in a nucleophilic substitution mechanism if deprotonation/reprotonation occurs as a side reaction. Lastly, the Elcb and nucleophilic substitution processes may be concurrent, as outlined in Scheme 1.



Scheme 1

Analysis of the $MeSO_2OEt$ product for deuterium in reactions in EtOD can also be informative. Deprotonation and elimination, followed by reaction of sulphene with labelled solvent always involves uptake of one deuteron into the product. Thus, CH_2DSO_2OEt, CHD_2SO_2OEt and CD_3SO_2OEt may result from deprotonation/reprotonation, followed by either substitution or elimination, but CH_3SO_2OEt can only result from substitution of unexchanged ester. Therefore, the presence of CH_3SO_2OEt as a product would indicate that substitution is occurring to some extent.

When **1a–c** were allowed to react with 1.1 equiv. of KOEt in EtOD and the products analysed by ^{1}H NMR spectroscopy, the methyl signal of ethyl methanesulphonate contained a singlet (due to CH_3SO_2OEt) for reactions of **1a** and **1b**. Therefore, substitution occurs to some extent for these esters. However, the present results do not allow a quantitative assessment of the degree of reaction by substitution because ethyl methanesulphonate could not be recovered quantitatively from the reaction mixture. Ethyl methanesulphonate could not be isolated in the reaction of **1c**, presumably because it was consumed by a subsequent fast reaction with ethoxide to form diethyl ether and methanesulphonate ion. Ethyl methane-

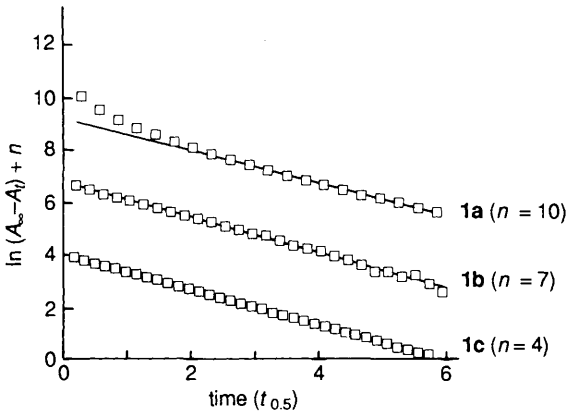


Fig. 2 Plots of $\ln(A_\infty - A_t)$ *vs.* time in half-lives for reactions of **1a–c** and with KOEt in EtOD

Table 3 Comparison of rate constants for the reaction of ethoxide ion with methanesulphonate **1a–c** and benzenesulphonate **2a–c** esters having identical leaving group substituents (X)

	k_{EtO^-}/dm^3 mol^{-1} s^{-1}	
X	**1**	**2**
p-NO_2	1.08	0.0287[a]
m-NO_2	0.0167	0.0140[a]
p-CF_3	0.0030	0.002 69[a]

[a] From ref. 1(*g*).

sulphonate was shown not to undergo deuterium exchange under the conditions of these experiments.

Reactions of aryl methanesulphonates with KOEt in deuteriated ethanol were also monitored by UV-VIS spectrophotometry. With the base in pseudo-first-order excess over ester, nonlinear plots of $\ln(A_\infty - A_t)$ *vs.* time were obtained for reactions of **1a**, but not **1b** or **1c**, as shown in Fig. 2. Deviation from first-order reaction kinetics for **1a** may be explained by the gradual incorporation of deuterium into unreacted ester as the reaction progresses. Reaction by an Elcb-type elimination mechanism would involve a substantial primary kinetic isotope effect for reaction of ester deuteriated at the methyl position if deprotonation/reprotonation is at least partially rate limiting, and hence the observed rate of reaction would steadily decrease during the experiment as increasing amounts of deuterium are incorporated into the methyl position of the unreacted ester, giving rise to the observed non-first-order kinetics. In contrast, reaction by nucleophilic substitution would be subject to a much smaller secondary isotope effect for reaction of esters deuteriated at the methyl position, so it is not surprising that **1b** and **1c** give rise to first-order kinetics. Therefore, these results are consistent with the premise that **1a** reacts by an Elcb mechanism to a significant extent with the deprotonation/reprotonation step being at least partially rate limiting, while **1b** and **1c** react predominantly or totally by substitution at sulphur (S_AN).

(c) *Reaction Pathways.*—The results of sulphene trapping experiments described above show that **1a** and **1b** react by elimination to some extent, with the extent of reaction by elimination greater for **1a** than for **1b**. Analysis of product for deuterium uptake for reactions in labelled solvent is consistent with a substitution mechanism also operating to some extent for both of these esters. Deviations from first-order kinetic behaviour in the reaction of **1a** with KOEt in EtOD imply that **1a** reacts by elimination to a significant extent. The absence of such deviations for reactions of **1b** and **1c** may be taken as evidence that these esters react by substitution to a significant extent.

Useful information can be derived on comparing the reactivities of methanesulphonate and benzenesulphonate esters having the same leaving groups (Table 3). In each case, the second order rate constant for the reaction of ethoxide (k_{EtO^-}) is derived from data for the reaction of KOEt in the presence of excess 18-crown-6 in order to remove possible complications from metal ion effects.[1c–e] The rate constants corresponding to esters with *meta*-nitro and *para*-trifluoromethyl substituents are similar in magnitude, but the rate constant for *p*-nitrophenyl methanesulphonate is *ca.* 37 times greater than that of the corresponding benzenesulphonate. Also, the ratio of rate constants for **1a**/**1b** is 63, while for **2a**/**2b** the ratio is 2.1 (the **1b**/**1c** ratio is 5.6, similar to the **2b**/**2c** ratio of 5.2). The similarity of the rate constants and the **1b**/**1c** and **2b**/**2c** rate ratios suggests that a common mechanism is operating for **1b**, **1c**, **2b** and **2c**. Since the aryl benzenesulphonates (**2a–c**) are known to react by nucleophilic substitution,[1e,g] the same mechanism may be inferred for **1b** and **1c**. Conversely, the large difference in rates and in the **1a**/**1b** and **2a**/**2b** rate ratios implies that a mechanism other than substitution is operating for **1a**.

On the basis of the arguments and evidence presented above, the *para*-nitro-substituted ester **1a** is considered to react predominantly by an Elcb-type elimination mechanism with nucleophilic substitution as a minor concurrent pathway. Conversely, the *meta*-nitro-substituted ester **1b** is considered to react predominantly by substitution with elimination as a minor concurrent pathway. The available evidence indicates that the *para*-trifluoromethyl-substituted ester **1c** reacts solely by substitution. Apparently, as the leaving ability of the nucleofuge is increased along the series **1c**(*p*-CF_3) ⟶ **1b**(*m*-NO_2) ⟶ **1a**(*p*-NO_2), the rate of elimination is steadily increased relative to the rate of substitution until, in the case of **1a**, elimination becomes the dominant pathway.

The results of the present work, indicating a change in mechanism from S_AN to Elcb as the leaving ability of the nucleofuge increases, are consistent with previous findings. Sulphene-forming eliminations are known to be highly sensitive to leaving group structure.[10] A case in point is the alkaline hydrolysis of aryl 1- and 2-butanesulphonates, which has been found to proceed by a stepwise elimination–addition (Elcb) mechanism *via* a sulphene intermediate. The effect of variation of aryl substituents on the rate at 70 °C was investigated, giving a ρ value of 4.6 and a correlation with σ substituent constants (a σ^- correlation is expected, but substituents which are strongly electron withdrawing by resonance were not used).[11] This value may be compared to ρ = 2.8 (σ°) for the alkaline hydrolysis of aryl benzenesulphonates at 50 °C, which proceeds by nucleophilic displacement at sulphur.[11] The large difference in ρ values implies that the butanesulphonates do not react by nucleophilic substitution. The elimination reaction shows a much greater sensitivity to leaving group nucleofugality than the substitution reaction.

In the present work, where the two mechanisms have similar rates, the same pattern as above appears to hold. Thus, as nucleofugality is increased, elimination is favoured over substitution and eventually (**1a**) the rate of elimination exceeds the rate of substitution and elimination becomes the dominant pathway. Thus, if one considers Hammett plots of log rate *vs.* substituent constant for elimination and substitution pathways, with the plot for elimination having the greater slope, a crossover occurs as the leaving ability of the nucleofuge increases, resulting in elimination being the dominant pathway for esters with good leaving groups.

Conclusions

The results presented here allow a number of conclusions to be drawn regarding the mechanisms involved in reaction of ethoxide with various aryl methanesulphonates.

(*a*) Uptake of deuterium into the methyl position of unreacted ester from EtOD solvent is observed for **1a–c**, indicating that deprotonation of the methyl group to form a carbanion intermediate occurs in all three cases.

(*b*) Sulphene intermediate is trapped to a significant extent by cycloaddition to an enamine in the reaction of KOEt with **1a**, while only traces of cycloadduct are observed for **1b**, and none is detected in the reaction of **1c**. Consequently, **1a** and **1b** must react by elimination to some extent.

(*c*) Analysis of the ethyl methanesulphonate product in the reactions of **1a** and **1b** reveals undeuteriated product, CH_3SO_2OEt, which can only result from a substitution mechanism. Consequently, **1a** and **1b** must also react by substitution to some extent.

(*d*) The non-first-order kinetic behaviour of **1a** in its reaction with KOEt in EtOD is interpreted as resulting from gradual uptake of deuterium into unreacted ester, with an Elcb mechanism as a major reaction pathway. Results for **1b** and **1c** are consistent with substitution being the major pathway for these esters.

(*e*) The rate constants for the reaction of **1a–c** with ethoxide ion, when compared to the analogous results for **2a–c**, suggest that **1b** and **1c** react predominantly or entirely by nucleophilic substitution, while **1a** reacts by a different mechanism.

(*f*) To summarise: the *para*-nitro-substituted ester is considered to react predominantly by an Elcb-type elimination mechanism *via* a sulphene intermediate, with nucleophilic substitution as a minor concurrent pathway. Conversely, the *meta*-nitro-substituted ester is considered to react predominantly by substitution, with elimination as a minor concurrent pathway and deprotonation/reprotonation as a side reaction. The available evidence suggests that the *para*-trifluoromethyl-substituted ester reacts solely by substitution.

Experimental

Materials.—The general procedure of Crossland and Servis was followed for the synthesis of the methanesulphonate esters,[12] with modifications as described below. The substituted phenol (0.02 mol) was dissolved in dry diethyl ether (dichloromethane for **1a**) (100 cm^3), and redistilled Et_3N (4.2 cm^3; 0.03 mol) was added. Methanesulphonyl chloride (1.8 cm^3; 0.022 mol) was added dropwise from a syringe with stirring. The reaction mixture was stirred under nitrogen for *ca.* 1 h, and completion of the reaction was confirmed by TLC. After reaction was complete, the reaction mixture was transferred to a separating funnel and extracted with distilled water (3 × 30 cm^3), 10% aq. HCl (3 × 30 cm^3), saturated aq. $NaHCO_3$ (3 × 30 cm^3), and saturated aq. NaCl (30 cm^3). The organic solution was dried (anhydrous Na_2SO_4), filtered, concentrated under reduced pressure, and the crude product was repeatedly recrystallised from ethanol to constant m.p. Purified esters gave satisfactory ^1H and ^{13}C NMR spectra and IR spectra, as well as elemental analyses.

p-Nitrophenyl methanesulphonate (**1a**), m.p. 87–88 °C (lit., 82–83;[13] 88–89;[14] 93–93.5;[15] and 94 °C[16]). *m*-Nitrophenyl methanesulphonate (**1b**), m.p. 64–65 °C (lit.,[17] 77–79 °C). *p*-Trifluoromethylphenyl methanesulphonate (**1c**), m.p. 43–44 °C.

Anhydrous ethanol, 18-crown-6, cryptands, and alkali metal ethoxides were prepared and/or purified as described previously.[1g] Deuteriated ethanol (Aldrich 99.5 + atom% D) was dried twice with 3 Å molecular sieves.

Kinetic Methods.—Reaction rates were measured by following absorbance changes in the UV-visible region of the reacting solutions, due to the release of aryloxide ion, using a Perkin-Elmer Lambda 5 spectrophotometer. All reactions were carried out under pseudo-first-order conditions with the base in excess. The base concentration was at least 10 times greater than the substrate concentration and usually more than 20 times greater. The solutions were equilibrated in the thermostatted cell block of the spectrophotometer and maintained at 25.0 ± 0.1 °C during reaction.

Rate constants were calculated from at least 30 absorbance readings spanning three half-lives. An infinity absorbance reading was taken after at least 10 half-lives. Rate constants were calculated as the slope of a plot of $\ln(A_\infty - A_t)$ *vs.* time. It is estimated from replicate runs that the error in any particular measured rate constant is not greater than *ca.* ±3%.

Deuterium Exchange Experiments.—The following is a representative procedure used to evaluate the extent of deuterium exchange at the methyl position and simultaneously the extent of reaction of a methanesulphonate ester.

m-Nitrophenyl methanesulphonate (**1a**) (0.0560 g, 0.260 mmol) was weighed out into a flask equipped with a nitrogen inlet and magnetic stirrer and dissolved in magnesium-dried deuteriated ethanol (EtOD, 15.0 cm^3) under a stream of nitrogen. A stock solution of base was prepared by mixing potassium ethoxide (2.00 cm^3 of 1.68 mol dm^{-3} KOEt in EtOD) and crown ether (6.00 cm^3 of 0.980 mol dm^{-3} 18-crown-6 in EtOD) solutions in a sealed vial. A portion (6.00 cm^3, 2.52 mmol KOEt, 4.41 mmol 18-crown-6) of the resulting solution was added to the rapidly stirred ester solution. After being stirred for 3.0 min under nitrogen, the reaction was stopped by addition of saturated aq. $NaHCO_3$ (10 cm^3). The precipitated salts were filtered off, the filtrate was extracted with diethyl ether (6 × 20 cm^3), and the aqueous solution was saved. The ether extracts were concentrated on a rotary evaporator to 30 cm^3, then extracted with 5% aq. Na_2CO_3 (6 × 30 cm^3), and saturated aq. KCl (4 × 30 cm^3) before being dried (anhydrous Na_2SO_4), filtered and concentrated. (The aqueous carbonate extracts were also saved.)

The extent of deuterium incorporation into the methyl position of the unreacted ester was determined using ^1H NMR spectroscopy by integration of the residual methyl resonance against the aromatic resonances. The methyl signal showed small upfield shifts (*ca.* 0.015 ppm) and splittings due to H-D coupling (J_{CH_2D} *ca.* 2.4 Hz)[8] which are characteristic of partial deuteriation of methyl groups. Overlapping spectra of all three species having protons at the methyl position were observed.

The combined aqueous extracts were adjusted to pH > 10 with aq. NaOH, made up to the mark in a 250 cm^3 volumetric flask, and the absorbance of the resulting solution at 400 nm was measured. This value was used to calculate the extent of reaction (amount of *m*-nitrophenoxide released) using the measured extinction coefficient of *m*-nitrophenoxide under identical conditions (1417 dm^3 mol^{-1} cm^{-1}).

The degree of deuterium uptake into both the unreacted ester and ethyl methanesulphonate product were evaluated by means of the procedure outlined below.

m-Nitrophenyl methanesulphonate (0.0217 g, 1 × 10^{-4} mol) was weighed into a round bottom flask equipped with a nitrogen inlet and magnetic stirrer and dissolved in dry EtOD (7 cm^3). Potassium ethoxide (95 mm^3 of a 1.116 mol dm^3 solution of KOEt in EtOD, 1.1 equiv.) was added and the rapidly stirred solution was allowed to react under nitrogen for 5 min. The reaction was stopped by the addition of saturated aq. $NaHCO_3$ (4 cm^3) and water (5 cm^3) and the mixture was extracted with diethyl ether (5 × 20 cm^3). The extracts were dried (anhydrous $CaSO_4$), filtered and concentrated, traces of solvent were removed under water aspirator pressure, and the resulting concentrate was analysed by ^1H NMR spectroscopy.

Synthesis of Enamine and Sulphone.—*N*-(2-Methylpropen-1-yl)pyrrolidine was prepared by established procedures.[6,18,19] An authentic sample of the sulphone resulting from reaction of sulphene with the enamine was prepared as follows.

2,2-Dimethyl-3-pyrrolidinotrimethylenesulphone. Following the procedure of Singh [6] and Opitz,[5] methanesulphonyl chloride (0.780 cm^3; 0.010 mol) was dissolved in dry diethyl ether (10 cm^3) and the solution was added dropwise with stirring to a cooled solution of *N*-(2-methylpropen-1-yl)pyrrolidine (1.25 g, 0.010 mol) and triethylamine (4.2 cm^3, 0.030 mol) in dry diethyl ether (10 cm^3). The reaction mixture was stirred for 30 min, the precipitated Et_3NHCl was filtered off, and the solution was concentrated. The residue was dissolved in 2 mol dm^{-3} HCl (30 cm^3) and allowed to stand for 2 h in order to hydrolyse unreacted enamine. The solution was neutralized ($NaHCO_3$) and extracted with dichloromethane. The organic solution was dried (anhydrous Na_2SO_4) and concentrated to yield the crude product (1.607 g, 79%). The solid was recrystallised twice from aqueous methanol to give 2,2-dimethyl-3-pyrrolidinotrimethylenesulphone, m.p. 64 °C (lit.,[5] 68 °C). $\delta_H(CDCl_3)$ 1.49 (s, 3 H, Me), 1.54 (s, 3 H, Me), 1.77 (m, 4 H, CH_2 × 2), 2.41 (m, 4 H, CH_2N × 2), 2.76 (dd, 1 H, CH), 3.86 [s, 1 H, CH_a (one of the geminal pair)] and 3.88 [d, 1 H, CH_b (one of the geminal pair)].

Trapping Experiments.—The following is a representative procedure used to trap sulphene intermediates by cycloaddition to an enamine in the reactions of the methanesulphonate esters.

p-Nitrophenyl methanesulphonate (1.47 g, 5.00 mmol) and *N*-(2-methylpropen-1-yl)pyrrolidine (6.35 g, 0.051 mol; 10 equiv.) were weighed into a flask and potassium ethoxide (8.0 cm^3 of a 1.28 mol dm^{-3} solution in ethanol, 0.010 mol; 2 equiv.) was added dropwise with stirring over 15 min. Dichloromethane (50 cm^3) was added, the mixture was filtered, and washed with water (3 × 50 cm^3) and saturated brine (50 cm^3) before being dried (anhydrous Na_2SO_4) and concentrated under reduced pressure. The crude product (0.67 g) was purified by flash chromatography (1 × 10 cm column), eluting with 1:1 ethyl acetate–light petroleum (b.p. 60–110 °C). The initial fractions were collected and concentrated (0.3824 g) and analysed for sulphone by TLC, ^1H NMR spectroscopy, GC and GC/MS.

The concentrate was analysed for sulphone by GC using a DB5 capillary volumn under the following conditions: F.I.D. detector temperature, 250 °C; injector temperature, 225 °C; oven temperature, 40 °C for 6 min then 10° min^{-1} to 250 °C for 13 min. Values for percentage sulphone were obtained by comparing the area of the sulphone peak (retention time 23.5 min) to the peak area of a standard solution of sulphone.

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