The Alkaline Fission of 2-Aroyloxyethyldimethylsulphonium Iodides: The Evaluation of Hammett's Substituent Constants for some ortho-*Substituents.*

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It is shown that the ready alkaline fission of 2-aroyloxyethyldimethylsulphonium iodides (Crane and Rydon, *J.*, 1947, 766) proceeds in two stages:

$$\underset{\text{(I)}}{\mathrm{Ar{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}} + \mathrm{NaOH} \rightleftharpoons \mathrm{Ar{\cdot}CO_2Na} + \underset{\text{(II)}}{\mathrm{CH_2{:}CH{\cdot}\overset{+}{S}Me_2\}I^-}} + \mathrm{H_2O} \quad \text{(i)}$$

$$\mathrm{CH_2{:}CH{\cdot}\overset{+}{S}Me_2\}I^-} + \mathrm{NaOH} \longrightarrow \mathrm{CH{\vdots}CH} + \mathrm{SMe_2} + \mathrm{NaI} + \mathrm{H_2O} \quad . \quad \text{(ii)}$$

only the first of which occurs at room temperature, the second requiring heating to 95°.

The rates of alkaline fission at 25° of thirteen sulphonium iodides (I) have been determined. Consideration of the results and of the conditions under which dimethylvinylsulphonium iodide (II), 2-hydroxyethyldimethylsulphonium iodide, and bis-2-methylthioethyl ether bismethiodide are formed from (I) leads to the conclusion that the elimination reaction (i) is reversible, the double bond of (II) being so activated by the adjacent sulphonium pole as readily to undergo additive attack by anions. The mechanisms of the various reactions are discussed.

Hammett substituent constants, σ, are evaluated for *o*-nitro-, *o*-chloro-, *o*-methyl, and *o*-methoxyl groups.

Crane and Rydon (*J.*, 1947, 766) showed that 2-benzoyloxyethyldimethylsulphonium iodide, $\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}$, was remarkably sensitive to alkali, consuming alkali in the cold and breaking down in warm alkali to yield benzoic acid, acetylene, and dimethyl sulphide. The work described in the present paper was undertaken with the object of elucidating the mechanism of this reaction, primarily by studying the influence of substituents in the aroyl group on its rate.

Thirteen 2-aroyloxyethyldimethylsulphonium iodides (I; R = H; *o*-, *m*-, *p*-$\mathrm{NO_2}$; *o*-, *m*-, *p*-Cl; *o*-, *m*-, *p*-Me; *o*-, *m*-, *p*-MeO) were prepared by the action of methyl iodide

$$\text{(I)} \quad \mathrm{R{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}$$

on the corresponding 2-aroyloxyethyl methyl sulphides, obtained by aroylation of 2-hydroxyethyl methyl sulphide in pyridine; some of the iodides were converted into the corresponding chlorides by double decomposition with silver chloride. Some homologues of (I), *viz.*, 3-benzoyloxypropyl-, 3-*p*-nitrobenzoyloxypropyl-, and 4-benzoyloxybutyl-dimethylsulphonium iodides, were prepared similarly; 2-benzoyloxyethyl methyl sulphoxide and sulphone, and 2-*p*-nitrobenzoyloxyethyl methyl sulphone were prepared by oxidation of the corresponding sulphides. The preparations of several other sulphides and derived sulphonium iodides and sulphones are recorded in the Experimental section.

Experiment soon showed that Crane and Rydon (*loc. cit.*) were mistaken in supposing the decomposition of 2-benzoyloxyethyldimethylsulphonium iodide to proceed in one stage in the cold, thus:

$$\mathrm{Ph{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-} + \mathrm{2NaOH} \longrightarrow \mathrm{Ph{\cdot}CO_2Na} + \mathrm{CH{\vdots}CH} + \mathrm{SMe_2} + \mathrm{NaI} + \mathrm{2H_2O}$$

In the cold, at pH *ca.* 10, only one equivalent of alkali is consumed, the major reaction being elimination of benzoic acid, thus:

$$\mathrm{Ph{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-} + \mathrm{NaOH} \longrightarrow \mathrm{Ph{\cdot}CO_2Na} + \underset{\text{(II)}}{\mathrm{CH_2{:}CH{\cdot}\overset{+}{S}Me_2\}I^-}} + \mathrm{H_2O} \quad . \quad . \quad \text{(i)}$$

Acidification at this stage gave an almost theoretical yield of benzoic acid; the formation of dimethylvinylsulphonium iodide (II) in 70% yield was established by addition of sodium picrylsulphonate (Stahmann, Fruton, and Bergmann, *J. Org. Chem.*, 1946, **11**, 518, 704), which resulted in the precipitation of the beautifully crystalline dimethylvinylsulphonium picrylsulphonate. The identity of the latter compound was established by mixed m. p. with a specimen prepared by the action of aqueous sodium hydrogen carbonate on 2-chloroethyldimethylsulphonium iodide, followed by conversion of the resulting dimethylvinylsulphonium iodide (II) into the picrysulphonate. The elimination reaction (i) was accompanied, to a small extent, by substitution :

$$\mathrm{Ph{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^- + NaOH \longrightarrow Ph{\cdot}CO_2Na + \underset{\text{(III)}}{HO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}}$$

the formation of 2-hydroxyethyldimethylsulphonium iodide (III) being established by the isolation of a small amount of the derived picrylsulphonate, identified by mixed m. p. with material prepared from (III) obtained by the action of methyl iodide on 2-hydroxyethyl methyl sulphide. A second equivalent of alkali was consumed by 2-benzoyloxyethyldimethylsulphonium iodide only at 95° ; under these conditions the dimethylvinylsulphonium iodide (II), formed in the first stage, broke down thus :

$$\mathrm{CH_2{:}CH{\cdot}\overset{+}{S}Me_2\}I^- + NaOH \longrightarrow CH{:}CH + SMe_2 + NaI + H_2O} \quad . \; . \; . \quad \text{(ii)}$$

Dimethyl sulphide was identified as its mercurichloride (50% yield), and acetylene by the formation of cuprous acetylide with the cuprous chloride–hydroxylamine reagent. A similar two-stage reaction was established in the same manner for the *m*-nitro- and the *o*-methyl compound (I ; R = *m*-NO_2 and *o*-Me).

The ready elimination reaction (i) was studied kinetically, for the thirteen 2-aroyloxyethyldimethylsulphonium iodides (I) in aqueous solution at 25°, by continuous titration at various pH values, using the very convenient apparatus of Powell and Trendall (*Chem. and Ind.*, 1943, **62**, 368) ; the reactions were followed only up to 50% reaction, at which stage they were becoming inconveniently slow. The reaction is of the second order, being closely of first order with respect to both sulphonium and hydroxyl ions. The results are given in full in Table 3, while the values of the second-order velocity constant, k_2, are collected in Table 1. It will be seen that the reaction is facilitated by electron-attracting substituents, and hindered by electron-releasing substituents, in the phenyl group and that there is no obvious *ortho*-effect.

TABLE 1. *Second-order velocity constants* (*l. mole*$^{-1}$ *min.*$^{-1}$) *for alkaline fission of* $\mathrm{R{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}$ *at* 25°.

R Concn. (M) :	0·002	0·005	0·0075	0·01
H	—	356·5 (321·4 *)	322·1	284·4 (294·4 *)
o-NO_2	—	1242	—	1164 (1148 †)
m-NO_2	—	1285	—	1086
p-NO_2	2061	1611	1607	1358 (1524 †)
o-Cl	—	673·0	—	595·7
m-Cl	—	543·3	—	492·0
p-Cl	512·9	476·4	—	—
o-Me	—	314·1	—	243·8
m-Me	—	322·1	—	272·3
p-Me	—	319·2	—	244·9
o-MeO	—	291·1	—	266·7
m-MeO	—	372·4	—	261·2
p-MeO	—	212·8	—	178·2

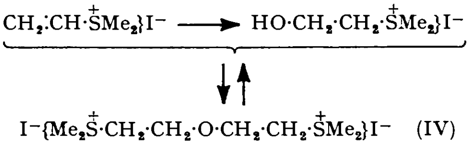
* Chloride. † 0·005M-Sulphonium iodide + 0·005M-KI.

As expected for a reaction between a positive and a negative ion, the reaction shows a negative primary salt effect ; this is demonstrated both by the decrease in k_2 with increasing sulphonium iodide concentration and by the similar retardation of the reaction brought about by the addition of potassium iodide. The slope of the plot of log k_2 against $\sqrt{\mu}$, where μ is the mean ionic strength, is not -1, as required by the simple Brønsted–Bjerrum theory (Brønsted, *Z. physikal. Chem.*, 1922, **102**, 169 ; Bjerrum, *ibid.*, 1924, **108**, 82), but is steeper than this ; this is not unexpected with an ion, such as the cation of (I), which is far from spherical (cf. Olson and Simonson, *J. Chem. Phys.*, 1949, **17**, 1167).

Dimethyl-3-*p*-nitrobenzoyloxypropylsulphonium iodide reacts with alkali more slowly than its lower homologue (I; $R = p\text{-}NO_2$), k_2 being 367·3 for 0·005M initial concentration and 328·1 for 0·01M. 2-Benzoyloxyethyl methyl sulphone was observed to react at about the same rate as the sulphonium iodide (I; R = H), but full kinetic experiments were not carried out; the corresponding sulphoxide reacted immeasurably slowly, as also did 2-benzoyloxyethyltrimethylammonium iodide.

In view of the qualitative observation that, in the unsubstituted case (I; R = H), elimination was accompanied by a small amount of substitution, it seemed necessary to determine the proportions in which the vinyl (II) and hydroxyethyl (III) compounds were formed from the various iodides (I), under the conditions obtaining in the kinetic experiments. Accordingly the thirteen iodies (I) in 0·005M- and 0·01M-solution were titrated with N-sodium hydroxide (1 equivalent); the vinyl- and 2-hydroxyethyl-sulphonium iodides (II) and (III) formed were then estimated by conversion into the picrylsulphonates and fractional crystallisation. The results, for which no great accuracy is claimed, are given in Table 4; it will be seen that there is a correlation with the electronic effect of R, electron-attracting substituents favouring the formation of the hydroxyethyl compound (III), and that there is a marked *ortho*-effect, the proportion of (III) formed from each of the three *o*-compounds being notably smaller than that from the corresponding *m*- and *p*-compounds. Under similar conditions, but in more concentrated solution, dimethyl-3-*p*-nitrobenzoyloxypropylsulphonium iodide gave only 3-hydroxypropyldimethylsulphonium iodide, the homologue of (III). Titration of 2-benzoyloxyethyldimethylsulphonium iodide (I; R = H) in 0·5M-solution in methanol, with sodium methoxide, gave only 2-methoxyethyldimethylsulphonium iodide, $\mathrm{MeO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}$.

Owing to the difficulty of controlling pH closely in these large-scale titrations, it was thought desirable to investigate the effect of higher pH; this was done, in the case of the unsubstituted compound (I; R = H), only, by treating the iodide with sodium hydroxide added in one portion, keeping the mixture overnight, and then isolating the sulphonium compounds present as their picrylsulphonates. This reaction was found to be very sensitive to small amounts of alkali in excess of one equivalent; the results of a series of experiments in which 1·00—1·24 equivalents of alkali were used are shown in Table 5. With exactly one equivalent of alkali, the vinyl (II) and hydroxyethyl (III) compounds are the only products but the use of more than one equivalent of alkali leads to the formation of a third sulphonium compound, characterised by a very insoluble picrylsulphonate. This third sulphonium compound proved to be bis-2-methylthioethyl ether bismethiodide (IV); this identity was established by comparison of the bismethiodide itself, as well as the derived chloride, picrate, and picrylsulphonate, with the compound synthesised from bis-2-methylthioethyl ether, prepared by methylation of bis-2-mercaptoethyl ether. The results summarised in Table 5 show that the ether (IV) is formed at the expense of the vinyl compound (II), rather than at the expense of the hydroxyethyl compound (III). Further experiments showed that the vinyl compound (II) was converted into the ether (IV) in weak alkali (*ca.* 0·02N) overnight in the presence of benzoate anions and that both (II) and (IV) were converted into (III) if kept overnight with stronger alkali (*ca.* 0·2N). The relations of the three sulphonium compounds are expressed in the following reaction scheme:



$$\text{(II)}\ \underbrace{\mathrm{CH_2{:}CH{\cdot}\overset{+}{S}Me_2\}I^-} \longrightarrow \mathrm{HO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}}\ \text{(III)}$$

$$\downarrow\uparrow$$

$$\mathrm{I^-\{Me_2\overset{+}{S}{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-}\ \text{(IV)}$$

It is clear from these findings that the hydroxyethyl compound (III) isolated in the large-scale titration experiments cannot have arisen by direct addition of water to the vinyl compound (II), since this reaction has been demonstrated to require much more strongly alkaline conditions.

In other experiments, which were carried out before the sensitivity of the reaction to a slight excess of alkali was realised and in which a slight excess may well have been used, treatment of the *o*-, *m*-, and *p*-nitro- and *p*-chloro-compounds (I; R = *o*-, *m*-, *p*-NO_2, and *p*-Cl) with approximately one equivalent of alkali, added in one portion, gave the ether (IV) in 16%, 32%, 34%, and 67% yield, respectively. The ether (IV) was similarly obtained from dimethyl-2-phenoxyethylsulphonium iodide. 2-Benzoyloxyethyl methyl sulphone afforded the analogous bis-2-methylsulphonylethyl ether, $Me{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}Me$, under similar conditions whereas 2-benzoyloxyethyl methyl sulphoxide was unaffected. Two higher homologues of (I), *viz.*, dimethyl-3-*p*-nitrobenzoyloxypropylsulphonium iodide and 4-benzoyloxybutyldimethylsulphonium iodide, afforded the corresponding hydroxy-compounds, homologues of (III); the choline derivatives, 2-benzoyloxyethyl- and 2-*p*-nitrobenzoyloxyethyl-trimethylammonium iodide, likewise yielded only 2-hydroxyethyltrimethylammonium iodide.

Having thus demonstrated that, under the conditions of the kinetic experiments, the hydroxyethyl compound (III) cannot arise by direct addition of water to the vinyl compound (II), we may return to a consideration of the precise nature of the reaction with alkali under the conditions of the kinetic experiments. Fig. 1 shows log k_2 for the alkaline fission of the sulphonium salts (I) at 0·005M-concentration plotted against Hammett's substituent constants, σ (Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188). The line, drawn by the method of least squares, has the equation log $k_2 = 2{\cdot}543 + 0{\cdot}768\ \sigma$; the correlation between structure and reaction velocity is good, the standard deviation, *s*, being 0·050 and the correlation coefficient, *r*, 0·987 (cf. Jaffé, *Chem. Rev.*, 1953, **53**, 191). No such correlation exists between σ and partial rate constants for elimination and substitution, calculated from the observed values of k_2 and the proportions of (II) and (III) found in the large-scale titration experiments (Table 4). This state of affairs is readily explicable if the system is such that the elimination reaction leading to (II) predominates in the early stages of the reaction, studied in the kinetic experiments, whereas the hydroxyethyl compound (III) is formed only at a late stage in the large-scale titration experiments. Such conditions obtain if the elimination reaction is reversible :

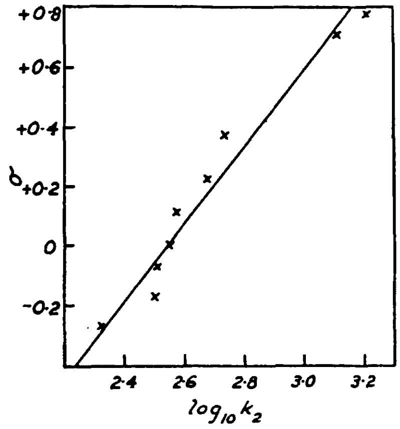


FIG. 1. *Correlation of rate of alkaline fission of* $Ar{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-$ *with substitution in* Ar.

$$R{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2 + OH^- \rightleftharpoons R{\cdot}CO_2^- + CH_2{:}CH{\cdot}\overset{+}{S}Me_2 + H_2O$$

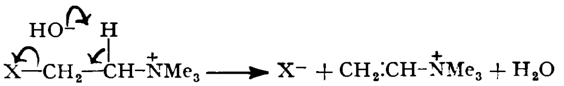
and is accompanied by irreversible direct hydrolysis :

$$R{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2 + OH^- \longrightarrow R{\cdot}CO_2^- + HO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2$$

providing that the rate of the forward elimination reaction is markedly greater than the rates of both the reverse reaction and the hydrolysis.

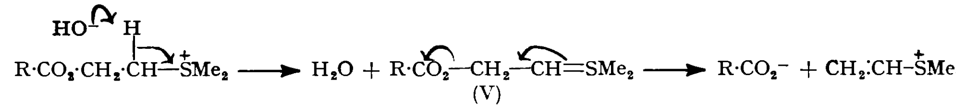
Under the conditions of our kinetic experiments, in which the concentrations of both water and hydroxyl ion were kept constant, the forward elimination reaction is of the first order whereas the reverse reaction is of the second order. In such a system, providing the rate constant for the reverse reaction is relatively small, the observed reaction will closely approximate to first-order kinetics up to half-reaction. Thus, calculation shows that, if the rate constant for the reverse reaction is 10% of that for the forward reaction, the observed rate at half-reaction is 95% of that expected for the forward reaction alone; such a difference would hardly be detectable and would not appreciably upset the calculation of the first-order velocity constant; reference to Fig. 2 will show that some falling off from the first-order velocity was in fact observed. The reasonable correlation of k_2 with σ leads to the conclusion that the concomitant hydrolysis is in all cases slow compared with the elimination; accordingly we regard our k_2 values as reasonable measures of the rate of the forward elimination reaction.

This elimination reaction recalls the formally analogous elimination of hydrogen halides from 2-halogenoethyltrimethylammonium halides (Hofmann, *Jahresber.*, 1858, 339; Baeyer, *Annalen*, 1866, **140**, 311; Bode, *ibid.*, 1892, **267**, 268; Schmidt, *ibid.*, p. 300; *Apoth. Ztg.*, 1912, **27**, 682; Renshaw, *J. Amer. Chem. Soc.*, 1912, **34**, 1618; Renshaw and Ware, *ibid.*, 1925, **47**, 2993), the mechanism of which is clearly :



$$X{-}CH_2{-}\overset{HO^-\ \ H}{CH}{-}\overset{+}{N}Me_3 \longrightarrow X^- + CH_2{:}CH{-}\overset{+}{N}Me_3 + H_2O$$

in which the attack on the α-hydrogen atom is facilitated by withdrawal of electrons under the influence of the ammonium pole. This reaction, however, is restricted to the favourable case in which X = halogen, only hydrolysis to choline being observed when X is an aroyloxy-group, and even then requiring more vigorous conditions than are required for the formation of (II) from (I). The observed enormous difference in alkali-lability between the sulphonium salts (I) and their ammonium analogues, clearly points to a more effective loosening of the α-hydrogen atom under the influence of the adjacent pole in the former case. On the basis of the ionisation potentials (nitrogen, 335 kcal./mole; sulphur, 239 kcal./mole), however, $-\overset{+}{S}R_2$ would be expected to be less powerful in attracting electrons than $-\overset{+}{N}R_3$ and this is borne out by its weaker *m*-orienting effect in aromatic substitution (Baker and Moffitt, *J.*, 1930, 1722; Pollard and Robinson, *ibid.*, p. 1765; Goss, Hanhart, and Ingold, *J.*, 1927, 250). For this reason we regard our elimination reaction as involving the sulphidimine-like intermediate (V), thus :



$$R{\cdot}CO_2{\cdot}CH_2{\cdot}\overset{HO^-\ \ H}{CH}{-}\overset{+}{S}Me_2 \longrightarrow H_2O + R{\cdot}CO_2{-}CH_2{-}\underset{(V)}{CH{=}SMe_2} \longrightarrow R{\cdot}CO_2^- + CH_2{:}CH{-}\overset{+}{S}Me_2$$

This pathway is, of course, not available in the ammonium series owing to the inability of nitrogen, unlike sulphur, to tolerate ten electrons in its outer shell; it is to this fundamental difference in the chemistry of sulphur and nitrogen that we ascribe the alkali-lability of the sulphonium salts (I) as compared with their nitrogen analogues.

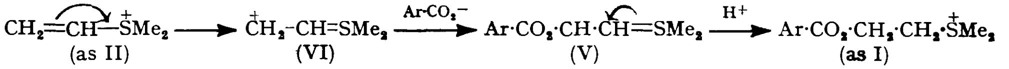
The elimination reaction, as formulated above, calls for facilitation by electron-attracting substituents in R and this is in complete agreement with our experimental findings. Moreover, attack on (I) by hydroxyl ion occurs at a point distant from the benzene ring; this is borne out by the low value of +0·768 observed for the reaction constant, ρ. The reaction thus appears favourable for the evaluation of Hammett substituent constants, σ, for *ortho*-substituents. Calculation by Jaffé's method (*loc. cit.*) from the results in 0·005M-solution leads to the following σ values for the four *o*-substituents studied (the standard derivation is ±0·062) :

Substituent		*o*-NO_2	*o*-Cl	*o*-Me	*o*-MeO
σ		+0·703	+0·366	−0·054	−0·095
E_σ	Present work	+0·757	+0·420	0	−0·041
	Taft, *loc. cit.*	+0·95	+0·37	0	−0·24

Calculation from the less extensive series of results in 0·01M-solution leads to values not significantly different from the above. The sign and magnitude of the σ values for the four *o*-substituents are in full accord with expectation. The Table also gives the E_σ values (Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 3120) obtained from the σ values by equating E_σ for the *o*-methyl group to zero; these may be compared with Taft's values (*loc. cit.*), obtained by a less direct method, which are given in the last line of the Table.

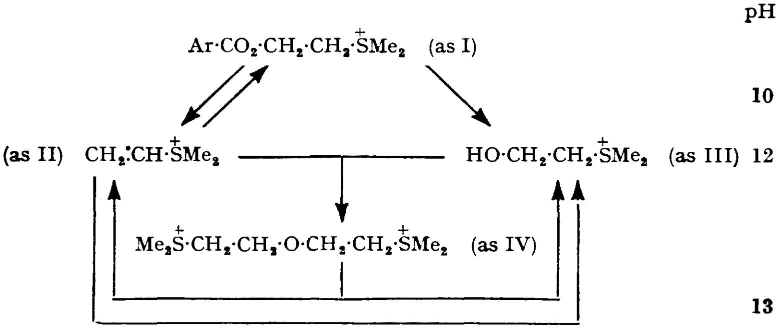
The unreactivity of sulphoxides compared with sulphones in this reaction is in conformity with the formulation of the latter alone as bearing a positive charge on the sulphur atom; such a positive charge is of importance for the necessary initial loosening of the attacked hydrogen atom.

The reverse elimination reaction clearly involves polarisation of the double bond in (II) and attack by a benzoate, or substituted benzoate, anion on the resulting, positively charged terminal carbon atom, followed by eventual recombination with a proton. This type of reaction, reminiscent of the addition reactions of the carbonyl group, is not known in the nitrogen series [the addition reactions of neurine, observed by Bode and Schmidt (*locc. cit.*) and referred to by Wenkert and Hansen (*Chem. and Ind.*, 1954, 1262) require very different experimental conditions] and may well involve the intermediate formation of the cation (VI), structurally similar to the unchanged intermediate (V) postulated in the forward elimination reaction, the whole process being :



Similar addition reactions, involving hydroxyl ion and the anion derived from (III), are clearly responsible for the formation of the hydroxylethyl compound (III) and the ether (IV) from the vinyl compound (II).

It is important to note that the reverse elimination, hydrolysis, and addition must all be involved in the formation of the ether (IV) from the vinyl compound (II) under conditions too weakly alkaline to allow the formation of the necessary hydroxyethyl compound (III) by direct addition of water to (II). The various reactions involved in the interconversion of the four sulphonium compounds are summarised in the annexed scheme, in which the figures at the side are the approximate minimum pH values at which the various reactions become of importance.



The hydrolysis by which (III) is formed directly from (II) seems likely to be of Ingold's $B_{AC}2$ type ("Structure and Mechanism in Organic Chemistry," Bell, Edinburgh, 1953, p. 754), involving attack by hydroxyl ion at the carbonyl carbon atom and, as such, facilitated by electron-attracting groups in R and subject to the *ortho*-effect; the experimental findings as to the effect of structure on the yield of the hydroxyethyl compound (III) in the large-scale titration experiments (Table 4) are in conformity with these requirements. The occurrence of this irreversible hydrolysis simultaneously with the reversible elimination leads to the conclusion that, at pH 10, any of the iodides (I) would eventually be converted entirely into the hydroxyethyl compound (III); although the period of contact with alkali at this pH was much longer in the large-scale titrations than in the kinetic experiments, it was never sufficient to allow complete conversion into (III) although 82% conversion was observed in the favourable case of the *p*-nitro-compound.

EXPERIMENTAL

2-Aroyloxyethyl Methyl Sulphides.—The aroyl chloride (1 mol.) was added in portions to 2-hydroxyethyl methyl sulphide (1 mol.) and pyridine (1·5—2·5 mols.), the temperature being kept below 30° by water cooling. After the addition was complete, the mixture was heated on the steam-bath for 2 hr. The semi-solid cooled reaction mixture was acidified with 2N-hydrochloric acid, and the product extracted with chloroform and distilled. The following were prepared in this way, in the yields indicated: 2-benzoyloxyethyl methyl sulphide (65%), b. p. 132°/2 mm.; methyl 2-*o*- (not purified), 2-*m*- (not purified), and 2-p-*nitrobenzoyloxyethyl sulphide* (83%), cream leaflets (from aqueous ethanol), m. p. 70° (Found: C, 50·2; H, 4·7. $C_{10}H_{11}O_4NS$ requires C, 49·8; H, 4·6%); 2-o- (80%), b. p. 110—111°/0·2 mm., $n_{\rm D}^{20}$ 1·5580 (Found: C, 52·1; H, 4·9. $C_{10}H_{11}O_2ClS$ requires C, 52·0; H, 4·8%), 2-m- (75%), b. p. 110°/0·15 mm., $n_{\rm D}^{20}$ 1·5550 (Found: C, 51·6; H, 5·0%), and 2-p-*chlorobenzoyloxyethyl methyl sulphide* (70%), b. p. 108°/0·1 mm., $n_{\rm D}^{20}$ 1·5594 (Found: C, 52·0; H, 4·9%); *methyl* 2-o- (87%), b. p. 100°/0·1 mm., $n_{\rm D}^{20}$ 1·5433 (Found: C, 62·7; H, 6·5. $C_{11}H_{14}O_2S$ requires C, 62·8; H, 6·7%), 2-m- (81%), b. p. 108°/0·2 mm., $n_{\rm D}^{20}$ 1·5419 (Found: C, 63·2; H, 7·1%), and 2-p-*toluoyloxyethyl sulphide* (79%), b. p. 108°/0·5 mm., $n_{\rm D}^{20}$ 1·5441 (Found: C, 63·3; H, 7·0%); 2-o- (79%), b. p. 132°/0·2 mm., $n_{\rm D}^{20}$ 1·5518 (Found: C, 58·3; H, 6·6. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·2%), 2-m- (81%), b. p. 130°/0·2 mm., $n_{\rm D}^{20}$ 1·5485 (Found: C, 58·3; H, 6·3%), and 2-p-*anisoyloxyethyl methyl sulphide* (88%), b. p. 132°/0·2 mm., $n_{\rm D}^{20}$ 1·5560 (Found: C, 58·6; H, 6·6%).

2-p-*Aminobenzoyloxyethyl methyl sulphide.* Finely powdered methyl 2-*p*-nitrobenzoyloxyethyl sulphide (20 g.) and reduced iron (30 g.) in 80% aqueous ethanol (100 ml.) were boiled under reflux with stirring; addition of concentrated hydrochloric acid (0·5 ml.) resulted in an exothermic reaction which was moderated by water-cooling. After the initial reaction had subsided, heating was continued for 30 min. and the mixture filtered while hot. Concentration under reduced pressure brought about the separation of prismatic needles, m. p. 88—89° (15·9 g.); recrystallisation from ethanol afforded the *sulphide* (14·5 g., 83%) as needles, m. p. 89—90° (Found: C, 56·5; H, 6·2. $C_{10}H_{13}O_2NS$ requires C, 56·8; H, 6·2%). The N-*acetyl derivative*, obtained by heating the sulphide (1 g.) with acetic anhydride (3 ml.) at 100° for a few min., crystallised from aqueous ethanol in prismatic needles, m. p. 119—120° (Found: C, 56·7; H, 5·9. $C_{12}H_{15}O_3NS$ requires C, 56·9; H, 6·0%).

2-Aroyloxyethyldimethylsulphonium Halides.—(a) *Iodides.* The appropriate sulphide (1 mol.) was kept overnight, at room temperature, with methyl iodide (2 mols.), preferably in acetone solution. The iodide which separated was collected and recystallised, heating being kept to a minimum to avoid decomposition; a few iodides were converted into the corresponding picrates or picrylsulphonates by addition of aqueous sodium picrate or sodium picrylsulphonate (Golumbic, Fruton, and Bergmann, *J. Org. Chem.*, 1946, **11**, 518) to an aqueous solution. The following were prepared in this way in the yields indicated: 2-benzoyloxyethyldimethylsulphonium iodide (85%), plates (from ethanol), m. p. 132—133° (decomp.) [Crane and Rydon, *loc. cit.*, record m. p. 128—129° (decomp.)] (Found: C, 39·0; H, 4·5. Calc. for $C_{11}H_{15}O_2IS$: C, 39·1; H, 4·5%), characterised as the *picrylsulphonate*, needles (from methanol), m. p. 193—194° (decomp.) (Found: C, 40·9; H, 3·5. $C_{17}H_{17}O_{11}N_3S_2$ requires C, 40·6; H, 3·4%); *dimethyl*-2-o-*nitrobenzoyloxyethylsulphonium iodide* (37% overall), pale yellow flattened needles (from ethanol), m. p. 118° (decomp.) (Found: C, 34·8; H, 3·6. $C_{11}H_{14}O_4NIS$ requires C, 34·5; H, 3·7%); *dimethyl*-2-m-*nitrobenzoyloxyethylsulphonium iodide* (69% overall), pale yellow needles (from aqueous ethanol), m. p. 139·5° (decomp.) (Found: C, 35·0; H, 3·6%); *dimethyl*-2-p-*nitrobenzoyloxyethylsulphonium iodide* (79%), yellow needles (from aqueous ethanol), m. p. 138° (decomp.) (Found: C, 35·2; H, 3·8%), characterised as the *picrylsulphonate*, cream needles (from methanol), m. p. 181° (Found: C, 37·5; H, 2·9; N, 10·3. $C_{17}H_{16}O_{13}N_4S_2$ requires C, 37·2; H, 2·9; N, 10·2%); 2-o- (54%), stout needles (from ethanol), m. p. 101° (decomp.) (Found: C, 36·0; H, 3·8. $C_{11}H_{14}O_2SClI$ requires C, 35·5; H, 3·8%), 2-m- (55% overall), prismatic needles (from ethanol), m. p. 138° (decomp.) (Found: C, 36·0 H, 3·6%), and 2-p-*chlorobenzoyloxyethyldimethylsulphonium iodide* (51%), needles (from water), m. p. 153° (decomp.) (Found: C, 35·5; H, 3·7%); *dimethyl*-2-o-*toluoyloxyethylsulphonium iodide* (74%), white needles (from ethanol), m. p. 117—118° (decomp.) (Found: C, 41·2; H, 4·8. $C_{12}H_{17}O_2IS$ requires C, 40·9; H, 4·8%), characterised as the *picrate*, small yellow needles (from water), m. p. 170—171° (Found: C, 48·2; H, 4·7; N, 8·3. $C_{18}H_{19}O_9N_3S$ requires C, 48·1; H, 5·0; N, 8·4%), and *picrylsulphonate*, pale yellow needles (from methanol), m. p. 167° (Found: C, 41·7; H, 3·9; N, 8·4. $C_{18}H_{19}O_{11}N_3S_2$ requires C, 41·7; H, 3·7; N, 8·1%); *dimethyl*-2-m-*toluoyloxyethylsulphonium iodide* (64%), needles (from ethanol), m. p. 109—110°

(decomp.) (Found : C, 40·7; H, 5·0%); *dimethyl*-2-p-*toluoyloxyethylsulphonium iodide* (89%), rods (from methanol), m. p. 133·5° (decomp.) (Found : C, 40·8; H, 4·6%), characterised as the *picrylsulphonate*, flat needles (from aqueous ethanol), m. p. 151° (Found : C, 41·8; H, 3·9; N, 8·3. $C_{18}H_{19}O_{11}N_3S_2$ requires C, 41·7; H, 3·7; N, 8·1%); 2-o-*anisoyloxyethyldimethylsulphonium iodide* (65%), needles (from ethanol), m. p. 110—111° (decomp.) (Found : C, 39·3; H, 4·6. $C_{12}H_{17}O_3IS$ requires C, 39·1; H, 4·7%), characterised as the *picrylsulphonate*, cream-coloured cubes (from methanol), m. p. 184—185° (Found : C, 40·3; H, 3·6; N, 7·9. $C_{18}H_{19}O_{12}N_3S_2$ requires C, 40·5; H, 3·6; N, 7·9%); 2-m- (74%), needles (from ethanol), m. p. 129° (decomp.) (Found : C, 39·4; H, 4·6%), and 2-p-*anisoyloxyethyldimethylsulphonium iodide* (66%), leaflets (from ethanol), m. p. 126—127·5° (decomp.) (Found : C, 38·8; H, 4·5%).

The solubilities of the iodides in water at 25°, determined by estimating iodide ion in saturated solutions prepared (*a*) by stirring the finely powdered salt with water at 25° and (*b*) by allowing hot saturated solutions to cool to 25° with stirring, are given in Table 2. The great solubility of the *o*-methoxy-compound is surprising.

TABLE 2. *Solubility in water at 25° of 2-aroyloxyethyldimethylsulphonium iodides,*

$R\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot \overset{+}{S}Me_2\}I^-$.

R	H	*o*-NO₂	*m*-NO₂	*p*-NO₂	*o*-Cl	*m*-Cl	*p*-Cl
Solubility (moles/l.) ...	0·194	0·062	0·031	0·023	0·102	0·034	0·011
R	*o*-Me	*m*-Me	*p*-Me	*o*-MeO	*m*-MeO	*p*-MeO	
Solubility (moles/l.) ...	0·076	0·122	0·043	0·537	0·055	0·063	

(b) *Chlorides.* The appropriate sulphonium iodide was stirred or shaken with an excess of freshly precipitated silver chloride. After filtration, the solution was evaporated to dryness under reduced pressure and the residue of sulphonium chloride recrystallised. The following were prepared in this way in the yield indicated : 2-*benzoyloxyethyldimethylsulphonium chloride* (69%), deliquescent prisms (from absolute ethanol and anhydrous ether), m. p. 152° (decomp.) (Found : C, 53·6; H, 6·2. $C_{11}H_{15}O_2ClS$ requires C, 53·8; H, 6·1%); *dimethyl*-2-m-*nitrobenzoyloxyethylsulphonium chloride* (81%), needles (from absolute ethanol), m. p. 136—137° (decomp.) (Found : C, 45·2; H, 4·5. $C_{11}H_{14}O_4NClS$ requires C, 45·3; H, 4·8%); *dimethyl*-2-p-*nitrobenzoyloxyethylsulphonium chloride monohydrate* (87%), needles (from ethanol), m. p. 109° (decomp.) (Found : C, 42·7; H, 5·0. $C_{11}H_{14}O_4NClS,H_2O$ requires C, 42·7; H, 5·2%); *dimethyl*-2-p-*toluoyloxyethylsulphonium chloride* (60%), needles (from ethanol–ether), m. p. 148° (decomp.) (Found : C, 55·0; H, 6·2. $C_{12}H_{17}O_2ClS$ requires C, 55·3; H, 6·5%); 2-p-*chlorobenzoyloxyethyldimethylsulphonium chloride* (68%), prismatic needles (from ethanol), m. p. 166° (decomp.) (Found : C, 46·9; H, 5·0. $C_{11}H_{14}O_2Cl_2S$ requires C, 46·6; H, 4·9%).

2-*Aroyloxyethyl Methyl Sulphones and Sulphoxides.*—2-Benzoyloxyethyl methyl sulphide (10 g.), in acetone (20 ml.), was treated at room temperature with aqueous hydrogen peroxide (5·8 ml. of 30%) in acetone (20 ml.). After being kept overnight, the solution was evaporated under reduced pressure, leaving an oil which crystallised in a vacuum-desiccator. Recrystallisation from ether–light petroleum (b. p. 40—60°) gave 2-*benzoyloxyethyl methyl sulphoxide* (8·1 g., 75%) as prisms, m. p. 62—65°; a second crop (2·0 g., 18%), m. p. 59—62°, was obtained from the mother-liquor. The analytical sample, obtained by further recrystallisation, had m. p. 65—66° (Found : C, 57·0; H, 5·7. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·6%).

This sulphoxide (6 g.), in acetone (20 ml.), was treated at room temperature with a saturated solution of potassium permanganate in acetone until no further oxidation occurred. Filtration, evaporation of the filtrate, and recrystallisation from aqueous ethanol afforded 2-*benzoyloxyethyl methyl sulphone* (6 g., 93%) as prismatic needles, m. p. 62·5—63·5° (Found : C, 52·6; H, 5·3. $C_{10}H_{12}O_4S$ requires C, 52·6; H, 5·1%). Alternatively, 2-benzoyloxyethyl methyl sulphide (11·3 g.), in acetic acid (30 ml.), was heated on the steam-bath while aqueous hydrogen peroxide (25 ml. of 30%) was added in portions. After the initial vigorous reaction had abated, the mixture was heated for a further 1½ hr. and evaporated under reduced pressure. Crystallisation from aqueous ethanol afforded the sulphone (9·8 g., 74%), m. p. 62·5—63·5°.

Methyl 2-*p*-nitrobenzoyloxyethyl sulphide (15 g.), in acetic acid (45 ml.), was gently refluxed while aqueous hydrogen peroxide (32 ml. of 30%) was added in portions. The mixture was then refluxed for a further hour and then evaporated to dryness under reduced pressure. Recrystallisation from ethanol–" Ethyl cellosolve " afforded *methyl* 2-p-*nitrobenzoyloxyethyl sulphone* (12·5 g., 74%) as pale yellow needles, m. p. 137—138° (Found : C, 44·4; H, 4·2. $C_{10}H_{11}O_6NS$ requires C, 43·9; H, 4·1%).

2-*Benzoyloxyethyl Ethyl Sulphide and its Derivatives.*—Ethyl 2-hydroxyethyl sulphide

(20 g.; Demuth and Meyer, *Annalen*, 1887, **240**, 310) in pyridine (25 ml.) was slowly treated with benzoyl chloride (26·5 g.), and the mixture heated on the steam-bath for 2 hr. The *sulphide* (33·8 g., 79%), isolated in the usual manner, had b. p. 86—88°/0·03 mm. (Found: C, 63·1; H, 6·7. $C_{11}H_{14}O_2S$ requires C, 62·9; H, 6·7%); this compound was prepared by Davis and Ross (*J.*, 1950, 3061) who, however, record neither b. p. nor analytical data.

The sulphide (5·0 g.) was kept overnight with methyl iodide (8 g.). Recrystallisation of the deposited solid from ethanol yielded *2-benzoyloxyethylethylmethylsulphonium iodide* (6·6 g., 85%), as needles, m. p. 106—107° (decomp.), raised to 110—111° (decomp.) by further recrystallisation (Found: C, 41·3; H, 4·8. $C_{12}H_{17}O_2IS$ requires C, 40·9; H, 4·9%).

The sulphide (1 g.), in acetic acid (8 ml.), was treated with aqueous hydrogen peroxide (6 ml. of 30%) and the mixture boiled under reflux for 1 hr. Evaporation and recrystallisation from ethanol–light petroleum (b. p. 60—80°) yielded *2-benzoyloxyethyl ethyl sulphone* (0·75 g., 65%) as flat needles, m. p. 38° (Found: C, 54·5; H, 5·8. $C_{11}H_{14}O_4S$ requires C, 54·5; H, 5·8%).

2-Aroyloxyethyl Aryl Sulphides and Sulphones.—2-Hydroxylethyl phenyl sulphide (23·9 g.; Kirner and Richter, *J. Amer. Chem. Soc.*, 1929, **51**, 3413), in pyridine (25 ml.), was slowly treated with benzoyl chloride (22·2 g.), and the mixture heated on the steam-bath for 30 min. Isolation in the usual manner afforded *2-benzoyloxyethyl phenyl sulphide* (30·5 g., 70%), b. p. 134°/0·05 mm. (Found: C, 70·2; H, 6·0. $C_{15}H_{14}O_2S$ requires C, 69·8; H, 5·5%). This sulphide (5·5 g.), in acetic acid (15 ml.), was treated with aqueous hydrogen peroxide (12·5 ml. of 30%), and the mixture boiled under reflux for 30 min. Addition of water and recrystallisation of the precipitate from ethanol afforded *2-benzoyloxyethyl phenyl sulphone* (5·5 g., 89%) as long needles, m. p. 123° (Found: C, 62·3; H, 4·9. $C_{15}H_{14}O_4S$ requires C, 62·1; H, 4·9%).

2-Hydroxyethyl phenyl sulphide (2·4 g.), in pyridine (3·5 ml.), was slowly treated with *p*-nitrobenzoyl chloride (2·9 g.), and the mixture heated on the steam-bath for 1 hr. Working up in the usual manner, followed by recrystallisation from aqueous ethanol, afforded *2-*p*-nitrobenzoyloxyethyl phenyl sulphide* (3·0 g., 64%) as pale yellow prisms, m. p. 52—54° (Found: C, 59·3; H, 4·4. $C_{15}H_{13}O_4NS$ requires C, 59·4; H, 4·4%).

2-Hydroxyethyl *o*-nitrophenyl sulphide (5·0 g.; Bennett and Berry, *J.*, 1927, 1668) was benzoylated as usual with benzoyl chloride (3·6 g.) in pyridine (11 ml.); *2-benzoyloxyethyl* o*-nitrophenyl sulphide* (7·4 g., 97%) cystallised from ethanol in lemon-yellow prismatic needles, m. p. 111—112° (Found: C, 59·3; H, 4·4. $C_{15}H_{13}O_4NS$ requires C, 59·4; H, 4·3%); oxidation of this sulphide (0·5 g.) with 30% aqueous hydrogen peroxide (3 ml.) in acetic acid (5 ml.) yielded *2-benzoyloxyethyl* o*-nitrophenyl sulphone* (0·48 g., 87%), pale yellow needles (from aqueous ethanol), m. p. 99—100° (Found: C, 54·0; H, 4·0. $C_{15}H_{13}O_6NS$ requires C, 53·7; H, 3·9%). *2-Benzoyloxyethyl* p*-nitrophenyl sulphide*, prepared as for the *o*-isomer, crystallised from ethanol in pale yellow prismatic needles, m. p. 60—61° (Found: C, 59·6; H, 4·5%).

3-Aroyloxypropyl Methyl Sulphides and Derivatives.—Benzoylation of 3-hydroxypropyl methyl sulphide (21·2 g.; Kirner, *J. Amer. Chem. Soc.*, 1928, **50**, 2452) with benzoyl chloride (29 g.) in pyridine (25 ml.) for 6 hr. at 100° afforded *3-benzoyloxypropyl methyl sulphide* (40·7 g., 94%), b. p. 116—118°/0·04 mm. (Found: C, 62·5; H, 6·9. $C_{11}H_{14}O_2S$ requires C, 62·8; H, 6·7%); this sulphide (40 g.), kept overnight with methyl iodide (50 g.), afforded *3-benzoyloxypropyldimethylsulphonium iodide* (53·5 g., 78%), prisms (from ethanol), m. p. 100° (decomp.) (Found: C, 41·4; H, 4·8. $C_{12}H_{17}O_2IS$ requires C, 40·9; H, 4·9%).

Methyl 3-*p*-nitrobenzoyloxypropyl sulphide, prepared from 3-hydroxypropyl methyl sulphide (23 g.) in pyridine (30 ml.) and *p*-nitrobenzoyl chloride (44·5 g.) in benzene (40 ml.) at 100° for 6 hr., could not be induced to crystallise and was kept overnight with methyl iodide (50 g.); *dimethyl-3-*p*-nitrobenzoyloxypropylsulphonium iodide* (53·5 g., 56%), so obtained, crystallised from ethanol in golden-yellow needles, m. p. 116° (decomp.) (Found: C, 36·4; H, 3·8. $C_{12}H_{16}O_4NIS$ requires C, 36·3; H, 4·1%).

4-Benzoyloxybutyl Methyl Sulphide.—4-Chlorobutyl benzoate (30 g.; Synerholm, *Org. Synth.*, 1949, **29**, 30) was slowly added to a solution of sodium methyl sulphide (0·15 mol.) in methanol and the mixture refluxed for 1 hr. Evaporation, addition of water, extraction with ether, and distillation of the dried extract afforded the *sulphide* (12·5 g., 40%), b. p. 100—101°/0·07 mm. (Found: C, 64·4; H, 7·0. $C_{12}H_{16}O_2S$ requires C, 64·2; H, 7·2%); the derived *4-benzoyloxybutyldimethylsulphonium iodide* crystallised from ethanol in needles, m. p. 118—119° (decomp.) (Found: C, 42·8; H, 5·1; I, 34·9. $C_{13}H_{19}O_2IS$ requires C, 42·6; H, 5·2; I, 34·6%).

Neither *4-chlorobutyl* p*-nitrobenzoate*, prepared as usual in 54% yield from tetramethylene chlorohydrin, needles (from ethanol containing a little acetone), m. p. 39° (Found: N, 5·0; Cl, 13·9. $C_{11}H_{12}O_4NCl$ requires N, 5·4; Cl, 13·8%), nor 5-chloropentyl benzoate (Synerholm, *J. Amer. Chem. Soc.*, 1947, **69**, 2581) could be induced to react with sodium methyl sulphide to form the corresponding sulphides.

Choline Derivatives.—Potassium benzoate (58 g.; dried at 130°/20 mm.) was added to a solution of 2-dimethylaminoethyl chloride (from the hydrochloride, 51 g.) in toluene (200 ml.), and the mixture refluxed for 18 hr. The hot mixture was filtered, the solid was washed with hot toluene, and the combined filtrates were distilled, giving 2-dimethylaminoethyl benzoate (40 g.), b. p. 99—105°/1 mm. This was dissolved in acetone (300 ml.), then treated with methyl iodide (37 g.), and the mixture kept overnight. The precipitated leaflets were collected and recrystallised from methanol; 2-benzoyloxyethyltrimethylammonium iodide (64 g., 93%) so obtained had m. p. 246—247° (decomp.) [lit., m. p. 247° (decomp.)] (Found : C, 42·9; H, 5·4. Calc. for $C_{12}H_{18}O_2NI$: C, 43·0; H, 5·4%).

2-Dimethylaminoethyl *p*-nitrobenzoate (40 g.; Einhorn, Fiedler, Ladisch, and Uhlfelder, *Annalen*, 1910, **371**, 142) and methyl iodide (40 g.) were kept in acetone (300 ml.) overnight. The precipitated *trimethyl-*2-p-*nitrobenzoyloxyethylammonium iodide* (61 g., 96%) crystallised from ethanol in yellow needles, m. p. 255—256° (decomp.) (Found : C, 37·9; H, 4·4; N, 7·4. $C_{12}H_{17}O_4N_2I$ requires C, 37·9; H, 4·5; N, 7·4%).

Kinetic experiments.

The action of alkali on the sulphonium salts was followed by continuous titration with sodium hydroxide (0·1 or 0·2N) in the apparatus described by Powell and Trendall (*Chem. and Ind.*, 1943, **62**, 368), the reaction vessel being immersed in a thermostat at 25° ± 0·02°. Successive volumes (0·02 ml.) of standard alkali were added whenever the pH reached the desired minimum value, as determined by matching the colour of the internal indicator with that of a solution of the same indicator in a suitable borate buffer contained in a vessel placed alongside the reaction vessel; the time at which each addition of alkali was made was noted.

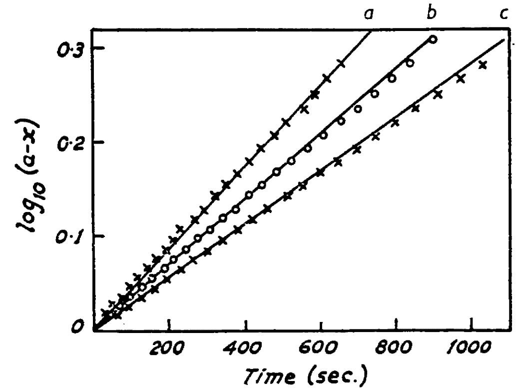


FIG. 2. *Alkaline fission of* p-$NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2$}$I^-$ *in* 0·01M-*solution at* 25°.
a, pH 9·66; *b*, pH 9·55; *c*, pH 9·45.

After numerous trials the following indicator mixtures (Kolthoff and Rosenbloom, " Acid–Base Indicators," MacMillan, London, 1937, p. 173) were found suitable :

	Acid colour	Alkaline colour
A. Phenolphthalein and α-naphtholphthalein; 2 : 1; both 0·1% in 50% aqueous ethanol	Green	Violet-red
B. Alizarin-yellow G and xylene-cyanol FF; 1 : 1·5; both 0·1% in ethanol	Green	Red
C. Thymolphthalein and alizarin-yellow G; 2 : 1; both 0·1% in ethanol	Grey	Rose

The mean pH quoted is the mean of the pH at which each fresh addition of alkali was made and the calculated pH of the solution immediately after each addition of alkali.

At least three runs were carried out at each pH for each concentration of each sulphonium salt. The agreement between runs was good. First-order velocity constants, k_1, were calculated in the usual way from plots of $\log_{10}(a - x)$ against time, the times being the means of those determined in the individual runs; the log plots were satisfactorily linear, the deviation from linearity being such as to make the uncertainty of k_1 only ±3%; Fig. 2 shows the log plots for dimethyl-2-*p*-nitrobenzoyloxyethylsulphonium iodide in 0·01M-solution at three pH values. $\log_{10} k_2$ was obtained by adding the mean pOH to $\log_{10} k_1$. The results are summarised in Table 3; full experimental details are given by Mamalis (Ph.D. Thesis, London, 1953).

TABLE 3. *Rate constants for alkaline fission of aroyloxyalkylsulphonium halides at 25°.*

(1) Concn. (M)	(2) Indicator	(3) pH Min.	(4) pH Mean	(5) 10^4k_1 (min.$^{-1}$)	(6) log k_2	(7) Mean log k_2	(8) Mean k_2 (l. mole^{-1} min.$^{-1}$)
2-Benzoyloxyethyldimethylsulphonium iodide							
0·005	B	9·60	9·87	268	2·558	2·552	356·5
		10·00	10·24	611	2·546		
0·0075	B	9·60	9·99	336	2·536	2·508	322·1
		9·80	10·11	394	2·484		
		10·00	10·24	564	2·511		
0·01	A	9·00	9·66	119	2·415	2·454	284·4
		9·30	9·82	193	2·465		
	C	9·60	9·99	291	2·474		
		9·60	10·12	376	2·455		
	B	10·00	10·35	645	2·459		
2-Benzoyloxyethyldimethylsulphonium chloride							
0·005	A	9·30	9·69	148	2·480	2·507	321·4
	B	9·60	9·87	251	2·530		
		10·00	10·15	458	2·511		
0·01	A	9·00	9·66	130	2·454	2·469	294·4
		9·30	9·82	197	2·475		
	B	9·60	9·99	294·5	2·479		
0·005	A	8·80	9·41	323	3·100	3·094	1242
		9·00	9·52	401	3·083		
		9·30	9·69	617	3·100		
0·005 + 0·005M-KI	A	8·60	9·31	230	3·052	3·060	1148
		8·80	9·41	292	3·055		
		9·00	9·52	392	3·073		
0·01	A	8·60	9·45	334	3·074	3·066	1164
		8·80	9·55	433	3·086		
		9·00	9·66	532	3·066		
		9·30	9·82	717	3·036		
Dimethyl-2-*m*-nitrobenzoyloxyethylsulphonium iodide							
0·005	A	8·80	9·41	320	3·095	3·109	1285
		9·00	9·52	419	3·102		
		9·30	9·69	662	3·131		
0·01	A	8·60	9·45	308	3·039	3·036	1086
		8·80	9·55	392	3·043		
		9·00	9·66	488	3·028		
		9·30	9·82	714	3·034		
Dimethyl-2-*p*-nitrobenzoyloxyethylsulphonium iodide							
0·002	A	8·60	9·23	366	3·333	3·314	2061
		8·80	9·37	463	3·296		
		9·00	9·475	616	3·315		
0·005	A	8·60	9·31	334	3·214	3·207	1611
		8·80	9·41	407	3·200		
		9·00	9·52	534	3·207		
0·0075	A	8·60	9·45	481	3·232	3·206	1607
		8·80	9·55	573	3·208		
		9·00	9·65	671	3·177		
0·005 + 0·005M-KI	A	8·60	9·31	312	3·184	3·183	1524
		8·80	9·41	383	3·173		
		9·00	9·52	484	3·175		
		9·30	9·69	780	3·202		
0·01	A	8·60	9·45	392	3·143	3·133	1358
		8·80	9·55	477	3·127		
		9·00	9·66	600	3·128		
2-*o*-Chlorobenzoyloxyethyldimethylsulphonium iodide							
0·005	A	9·00	9·52	221	2·824	2·828	673·0
		9·30	9·69	331	2·830		
	B	9·60	9·87	500	2·829		

TABLE 3. (*Continued.*)

(1) Concn. (M)	(2) Indicator	(3) pH Min.	(4) pH Mean	(5) 10^4k_1 (min.$^{-1}$)	(6) log k_2	(7) Mean log k_2	(8) Mean k_2 (l. mole^{-1} min.$^{-1}$)
2-*o*-Chlorobenzoyloxyethyldimethylsulphonium iodide (*cont.*)							
0·01	A	9·00	9·66	286	2·796	2·775	595·7
		9·30	9·82	413	2·796		
	B	9·60	9·99	564	2·761		
		9·80	10·11	720	2·747		
2-*m*-Chlorobenzoyloxyethyldimethylsulphonium iodide							
0·005	A	9·00	9·52	175	2·733	2·735	543·3
		9·30	9·69	276	2·751		
	B	9·60	9·87	392	2·722		
0·01	A	8·80	9·55	168	2·675	2·692	492·0
		9·00	9·66	212	2·666		
		9·30	9·82	357	2·733		
2-*p*-Chlorobenzoyloxyethyldimethylsulphonium iodide							
0·002	A	9·00	9·475	143	2·679	2·710	512·9
		9·30	9·65	242	2·734		
	B	9·60	9·84	360	2·717		
0·005	A	9·00	9·52	144	2·638	2·678	476·4
		9·30	9·69	230	2·672		
		9·30	9·82	332	2·701		
	B	9·60	9·99	474	2·686		
		10·00	10·24	859	2·694		
Dimethyl-2-*o*-toluoyloxyethylsulphonium iodide							
0·005	B	9·60	9·87	251	2·530	2·497	314·1
		9·80	10·00	326	2·513		
		10·00	10·15	396	2·448		
0·01	B	9·60	9·99	246	2·401	2·387	243·8
		9·80	10·11	314	2·387		
		10·00	10·24	411	2·374		
Dimethyl-2-*m*-toluoyloxyethylsulphonium iodide							
0·005	B	9·60	9·87	242	2·514	2·508	322·1
		9·80	10·00	331	2·520		
		10·00	10·15	435	2·489		
0·01	A	9·30	9·82	182	2·440	2·435	272·3
	B	9·60	9·99	258	2·422		
		9·80	10·11	357	2·443		
Dimethyl-2-*p*-toluoyloxyethylsulphonium iodide							
0·005	B	9·60	9·99	322	2·518	2·504	319·2
		9·80	10·11	401	2·493		
		10·00	10·24	550	2·500		
0·01	A	9·30	9·82	158	2·379	2·389	244·9
	C	9·60	9·99	246	2·401		
	B	9·60	10·12	333	2·402		
		10·00	10·35	534	2·378		
		10·40	10·60	964	2·384		
2-*o*-Anisoyloxyethyldimethylsulphonium iodide							
0·005	A	9·30	9·69	149	2·483	2·464	291·1
	B	9·60	9·87	220	2·472		
		9·80	10·00	273	2·436		
0·01	A	9·00	9·66	127	2·442	2·426	266·7
		9·30	9·82	180	2·435		
	B	9·60	9·99	246	2·401		
2-*m*-Anisoyloxyethyldimethylsulphonium iodide							
0·005	A	9·30	9·60	181	2·568	2·571	372·4
	B	9·60	9·87	246	2·521		
		10·00	10·15	376	2·625		
0·01	A	9·30	9·82	199	2·379	2·417	261·2
	B	9·60	9·99	256	2·418		
		10·00	10·24	495	2·455		

TABLE 3. (*Continued.*)

(1) Concn. (M)	(2) Indicator	(3) pH Min.	(4) pH Mean	(5) 10^4k_1 (min.$^{-1}$)	(6) log k_2	(7) Mean log k_2	(8) Mean k_2 (l. mole^{-1} min.$^{-1}$)
2-*p*-Anisoyloxyethyldimethylsulphonium iodide							
0·005	B	9·60	9·99	221	2·354	2·328	212·8
		9·80	10·11	259	2·303		
		10·00	10·24	360	2·316		
0·01	B	9·80	10·23	300	2·247	2·251	178·2
		10·00	10·35	378	2·227		
		10·40	10·60	756	2·278		
Dimethyl-3-*p*-nitrobenzoyloxypropylsulphonium iodide							
0·005	A	9·00	9·52	117	2·548	2·565	367·3
		9·30	9·69	181	2·567		
	B	9·60	9·87	282	2·580		
0·01	A	9·00	9·66	147	2·507	2·516	328·1
		9·30	9·82	216	2·514		
	B	9·60	9·99	328	2·526		

Isolation of fission products.

Synthesis of Reference Compounds.—*Dimethylvinylsulphonium picrysulphonate.* A mixture of 2-chloroethyl methyl sulphide (11·0 g.; Kirner and Windus, *Org. Synth.*, 1943, Coll. Vol. 2, 136) and methyl iodide (16 g.) was kept at room temperature overnight; the precipitate was collected, washed with ether, and recrystallised from ethanol–ether, affording 2-*chloroethyldimethylsulphonium iodide*, (9·5 g., 38%), white needles, m. p. 90—91° (Found : C, 18·5; H, 3·8. $C_4H_{10}SClI$ requires C, 19·0; H, 4·0%), characterised as its *picrylsulphonate*, needles (from methanol), m. p. 218° (Found : C, 28·5; H, 2·5. $C_{10}H_{12}O_9N_3S_2Cl$ requires C, 28·7; H, 2·9%). The above methiodide (3·78 g.), in water (280 ml.) containing sodium hydrogen carbonate (6·3 g.), was treated with sodium hydroxide (0·6 g.), and the mixture kept at 20° for 2 days. After the pH had been adjusted to 5 with 2N-hydrochloric acid, sodium picrylsulphonate (4 g.) was added and the solution concentrated under reduced pressure to 50 ml. The solid which separated on cooling [4·2 g., 90%; m. p. 199—200° (decomp.)] was recrystallised from methanol; *dimethylvinylsulphonium picrylsulphonate* forms flat cream-coloured needles, m. p. 199—200° (decomp.) (Found : C, 31·7; H, 2·9; N, 11·4; S, 16·9. $C_{10}H_{11}O_9N_3S_2$ requires C, 31·5; H, 2·9; N, 11·0; S, 16·8%).

2-*Hydroxyethyldimethylsulphonium picrylsulphonate.* 2-Hydroxyethyl methyl sulphide (9·2 g.), in acetone (20 ml.), was treated, with cooling, with methyl iodide (16 g.), and the mixture kept overnight. The precipitate [12 g., 51%; m. p. 55—57° (decomp.)] was collected, washed with acetone, and recrystallised from ethanol, yielding 2-*hydroxyethyldimethylsulphonium iodide*, as large deliquescent plates, m. p. 56—57° (decomp.) (Found : I, 53·7. $C_4H_{11}OIS$ requires I, 54·3%). Challenger and Simpson (*J.*, 1948, 1591) record m. p. 56—57° (decomp.), but give no analysis. The *picrylsulphonate* crystallised from methanol in needles, m. p. 169—170° (Found : C, 30·1; H, 3·2. $C_{10}H_{13}O_{10}N_3S_2$ requires C, 30·1; H, 3·3%).

Dithian monomethopicrylsulphonate. 1 : 4-Dithian (1·0 g.; Fuson, Lipscomb, McKusick, and Reed, *J. Org. Chem.*, 1946, **11**, 516) and methyl iodide (1 ml.) were refluxed in ethanol (10 ml.) for 12 hr. The precipitated methiodide was collected and converted in the usual manner into the *picrylsulphonate*, long yellow needles (from water), m. p. 240—242° (decomp.) (Found : C, 31·1; H, 3·1; N, 10·3. $C_{11}H_{13}O_9N_3S_3$ requires C, 30·9; H, 3·1; N, 9·8%).

Dimethyl-2-methylthioethylsulphonium picrylsulphonate. The iodide (Crane and Rydon, *loc. cit.*) was treated with sodium picrylsulphonate in the usual manner; two recrystallisations from water yielded the *picrylsulphonate* as needles (cubes by slow cooling), m. p. 160° (re-solidifying and decomp. above 200°) (Found : C, 30·9; H, 3·5; N, 10·0. $C_{11}H_{15}O_9N_3S_3$ requires C, 30·8; H, 3·5; N, 9·8%).

Derivatives of bis-2-methylthioethyl ether. Bis-2-mercaptoethyl ether (5 g.) (Hull, Weinland, Olsen, and France, *Ind. Eng. Chem.*, 1948, **40**, 513) was dissolved in aqueous sodium hydroxide (3 g. in 20 ml. of water) and treated with methyl sulphate (7 ml.) in one portion. After 2 hr. the mixture was extracted with ether; distillation of the dried extract afforded *bis-2-methylthioethyl ether*, b. p. 110°/11 mm. (Found : C, 43·6; H, 8·2; S, 37·6. $C_6H_{14}OS_2$ requires C, 43·4; H, 8·5; S, 38·6%).

This ether (1 g.) was kept overnight with methyl iodide (2 ml.). Trituration of the product with dry ether, followed by crystallisation from ethanol containing a little water, afforded the *bismethiodide*, prismatic needles, m. p. 142—143° (decomp.) (Found: C, 21·6; H, 4·2; I, 56·0. $C_8H_{20}OS_2I_2$ requires C, 21·3; H, 4·3; I, 56·4%); stirring an aqueous solution with freshly precipitated silver chloride, followed by filtration, evaporation, repeated evaporation with dry ethanol, and recrystallisation from anhydrous ethanol–ether, gave the *bismethochloride*, prisms, m. p. 196—197° (decomp.) (Found: Cl, 25·4. $C_8H_{20}OS_2Cl_2$ requires Cl, 25·1%). The *bismethopicrylsulphonate*, prepared from the iodide in the usual manner, crystallised from water in cream-coloured leaflets, m. p. 215—216° (Found: C, 30·8; H, 3·1; N, 10·6. $C_{20}H_{24}O_{19}N_6S_4$ requires C, 30·8; H, 3·1; N, 10·8%).

The ether (1 g.), dissolved in warm acetic acid (10 ml.), was treated in portions with 30% aqueous hydrogen peroxide (3 ml.). After the initial vigorous reaction had abated, the mixture was heated on the steam-bath for an hour and then evaporated under reduced pressure. Two crystallisations of the residue from chloroform–light petroleum (b. p. 40—60°) yielded *bis-2-methylsulphonylethyl ether* as prismatic needles, m. p. 78° (Found: C, 31·4; H, 6·3. $C_6H_{14}O_5S_2$ requires C, 31·3; H, 6·1%).

Allyldimethylsulphonium picrylsulphonate. Allyl iodide (2·1 g.) and dimethyl sulphide (0·8 g.) were kept overnight in ether (10 ml.). The oily methiodide remaining after decantation of the ether was dissolved in water (20 ml.) and treated with sodium picrylsulphonate (1·5 g.) in a little water. Two recrystallisations of the precipitate from methanol afforded the *picrylsulphonate* as needles, m. p. 175—176° (Found: C, 33·8; H, 3·4; N, 10·7. $C_{11}H_{13}O_9N_3S_2$ requires C, 33·4; H, 3·3; N, 10·6%).

3-*Hydroxypropyldimethylsulphonium picrylsulphonate.* 3-Hydroxypropyl methyl sulphide (1 g.) and methyl iodide (2 ml.) were mixed and kept at room temperature overnight. The oily product was washed with ether, dissolved in water (15 ml.), and treated with sodium picrylsulphonate (1·5 g.) in a little water. Two crystallisations from methanol yielded the *picrylsulphonate* as pale yellow needles, m. p. 155° (Found: C, 32·2; H, 3·8; N, 10·6. $C_{11}H_{15}O_{10}N_3S_2$ requires C, 32·0; H, 3·6; N, 10·2%).

2-*Hydroxyethyltrimethylammonium picrylsulphonate*, prepared in the usual way from choline chloride and sodium picrylsulphonate, crystallised from methanol in needles, m. p. 245° (decomp.) (Found: C, 33·4; H, 4·1; N, 14·2. $C_{11}H_{16}O_{10}N_4S$ requires C, 33·3; H, 4·1; N, 14·1%).

Reactions under Titration Conditions.—(a) 2-*Aroyloxyethyldimethylsulphonium iodides.* A solution of the sulphonium iodide (0·01 mole) in water (1 l.) containing a few drops of indicator was stirred mechanically at 25° while N-sodium hydroxide was added dropwise; fresh alkali was added when the pH reached 9·3 (indicator A) or 10·0 (indicator B). pH control was necessarily less precise in these experiments than in the kinetic runs; the mean pH was about 9·8 with indicator A and 10·2 with B. When 1 equiv. (10 ml.) of alkali had been added, the solution was acidified by addition of N-hydrochloric acid (10 ml.), and the benzoic acid (theoretical yield) removed by extraction with ether (3 × 100 ml.). Sodium picrylsulphonate (3·15 g., 0·01 mole) was added to the residual aqueous solution which was then concentrated under reduced pressure at below 35°. Crops of crystals were collected at various stages during the concentration and their compositions determined from a mixed m. p. curve constructed by using mixtures of authentic dimethylvinyl- and dimethyl-2-hydroxyethyl-sulphonium picrylsulphonates; mixtures containing 60% or more of the hydroxy-compound were recrystallised before having recourse to the m. p. curve; the m. p. bath was preheated to 165° for mixtures containing less than 50% of the hydroxy-compound and to 160° for mixtures containing more than 50%. Correction for solubility was made on the basis of separations of known mixtures of the two picrylsulphonates in the presence of the equivalent of sodium iodide; the correction factor for the vinyl compound was 1·11 and for the hydroxy-compound, 1·33.

In a typical experiment, 2-benzoyloxyethyldimethylsulphonium iodide (3·38 g.) in water (1 ml.), titrated with N-sodium hydroxide (10 ml.) and indicator B, gave the following crops: (*a*) At 200 ml., pale yellow needles, m. p. 198—199°, 0·95 g., 99% vinyl; (*b*) at 100 ml., flat yellow needles, m. p. 198—199°, 0·90 g., 99% vinyl; (*c*) at 70 ml., small yellow needles, m. p. 197—198°, 0·40 g., 97% vinyl; (*d*) at 30 ml., felted pale yellow needles, m. p. 166—169° (not depressed by authentic 2-hydroxyethyl), 0·64 g., 2-hydroxyethyl. Yields: vinyl 2·22 g., hydroxy-ethyl 0·67 g. Corrected yields: vinyl 64·7%, hydroxyethyl 22·3%. Two duplicate experiments gave vinyl 70·0% and 68·7%, hydroxyethyl 20·0% and 10·0%. Average yields: vinyl 68%, hydroxyethyl 18%.

At least two experiments were carried out with each iodide at each concentration; the results are collected in Table 4.

In one experiment, 2-benzoyloxyethyldimethylsulphonium iodide (2·5 g.), partially dissolved in water (30 ml.), was titrated at 25° with 0·5N-sodium hydroxide (14·8 ml.) at pH *ca.* 10·0. N-Hydrochloric acid (7·4 ml.) was added and the benzoic acid removed with ether; the aqueous layer was freed from dissolved ether and divided into two equal portions. To the first, sodium picrylsulphonate (1·57 g.) in a little water was added; there was immediate deposition of dimethylvinylsulphonium picrylsulphonate (0·93 g., 66%), cream-coloured needles, m. p. 196—198° (decomp.), and a further crop (0·12 g., 9%), m. p. 196—198° (decomp.), was obtained by concentration of the mother-liquor; neither crop showed a depression of m. p. on admixture with authentic material. The second portion was treated with N-sodium hydroxide (5·0 ml.; 1·35 equiv.) and kept overnight at room temperature. N-Hydrochloric acid (5·0 ml.) was added, followed by sodium picrylsulphonate (1·57 g.); concentration yielded 2-hydroxyethyldimethylsulphonium picrylsulphonate (0·80 g., 55%), needles, m. p. and mixed m. p. 167—169°.

TABLE 4. *Fission products of* $R{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-$ *under titration conditions* (% *yields*).

	0·01M		0·005M			0·01M		0·005M	
R	(II) (%)	(III) (%)	(II) (%)	(III) (%)	R	(II) (%)	(III) (%)	(II) (%)	(III) (%)
H	68	18	72	18	*o*-Me ...	93	0	97	0
o-NO_2 ...	77	12	75	10	*m*-Me ...	73	15	74	10
m-NO_2 ...	8	74	15	82	*p*-Me ...	70	15	87	2
p-NO_2 ...	6	69	8	73	*o*-MeO ...	82	0	82	0
o-Cl	66	3	62	5	*m*-MeO	80	11	82	0
m-Cl	38	52	41	47	*p*-MeO ...	83	0	84	0
p-Cl	—	—	60	20					

(b) *Dimethyl-*3-p-*nitrobenzoyloxypropylsulphonium iodide.* The iodide (4·0 g., 0·01 mole), partially dissolved in water (60 ml.), was titrated, with stirring, at pH *ca.* 10 with 0·5N-sodium hydroxide (20 ml.); N-hydrochloric acid (10 ml.) was added and the mixture kept overnight. The precipitated solid was identified by mixed m. p. as *p*-nitrobenzoic acid (1·60 g., 96%), m. p. 238—240°; the filtrate was treated with sodium picrylsulphonate (3·15 g.) in a little water. Concentration under reduced pressure yielded two crops of 3-*hydroxypropyldimethylsulphonium picrylsulphonate* (2·45 g., 59%), m. p. 155—156° and 153—155°; recrystallisation from methanol gave the pure salt, pale yellow needles, m. p. 155—156°, not depressed on admixture with an authentic specimen (Found: C, 32·3; H, 3·7; N, 10·6. $C_{11}H_{15}O_{10}N_3S_2$ requires C, 32·0; H, 3·6; N, 10·2%). No allyldimethylsulphonium picrylsulphonate could be detected.

(c) 2-*Benzoyloxyethyldimethylsulphonium iodide and sodium methoxide.* The iodide (3·4 g.) in methanol was treated, in portions, with sodium methoxide, from sodium (0·23 g.) and methanol (20 ml.). After the mixture had been kept for 30 min., then acidified and filtered, a solution of sodium picrylsulphonate (3·15 g.) in water (25 ml.) was added. The precipitate (2·1 g., 51%) was collected and recrystallised from methanol; 2-*methoxyethyldimethylsulphonium picrylsulphonate* forms needles, m. p. 177° (Found: C, 32·8; H, 3·7. $C_{11}H_{15}O_{10}N_3S_2$ requires C, 32·0; H, 3·6%).

Reactions with Alkali added in One Portion.—(a) 2-*Benzoyloxyethyldimethylsulphonium iodides.* The iodide (0·01 mole), suspended in water (25 ml.), was treated with N-sodium hydroxide (10·0 ml.), stirred until dissolution was complete, and kept at room temperature for 6 hr. A further quantity (*x* ml.) of N-sodium hydroxide was then added and the mixture kept overnight at room temperature. The solution was then treated with N-hydrochloric acid (10·0 + *x* ml.), and the benzoic acid removed by filtration; sodium picrylsulphonate (3·2 g.), in a little water, was added and any immediate precipitate of bis-2-methylthioethyl ether bismethopicrylsulphonate collected after 5 min.; the filtrate from this was worked up as usual for dimethylvinyl- and 2-hydroxyethyldimethyl-sulphonium picrylsulphonate. The uncorrected yields of the various picrylsulphonates obtained in this way from 2-benzoyloxyethyldimethylsulphonium iodide are recorded in Table 5.

TABLE 5. *Products from* $C_6H_5{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{S}Me_2\}I^-$ *and* NaOH.

Extra NaOH added (*x* ml.)	0·0 *	0·4	0·8	1·2	1·6	2·4 †
(II) (%)	70	21	0	0	0	0
(III) (%)	7	7	11	10	8	9
(IV) (%)	0	54	72	74	73	73

* Mean of 4 experiments. † Mean of 2 experiments.

Bis-2-methylthioethyl ether bismethopicrylsulphonate so obtained crystallised from hot water in pale yellow leaflets, m. p. 215—216° not depressed on admixture with an authentic specimen (p. 1062) (Found: C, 30·6; H, 3·3; N, 11·1. Calc. for $C_{20}H_{24}O_{19}N_6S_4$: C, 30·8; H, 3·1; N, 10·8%). Replacement of sodium picrylsulphonate by sodium picrate in the above experiment yielded *bis-2-methylthioethyl ether bismethopicrate*, yellow needles (from water containing a little ethanol), m. p. 175—176° (Found: N, 12·5. $C_{20}H_{24}O_{15}N_6S_2$ reuires N, 12·9%), while the use of calcium picrate yielded a *calcium picrate compound* of the bismethopicrate, orange needles (from water–ethanol), m. p. 232° (decomp.) (Found: C, 34·6, 34·1; H, 2·1, 2·8; N, 14·0, 13·9. $C_{20}H_{24}O_{15}N_6S_2,C_6H_2O_7N_3Ca_{\frac{1}{2}}$ requires C, 34·6; H, 2·9; N, 14·0%). Either picrate, when shaken with 4N-hydrochloric acid under nitrobenzene, followed by washing of the aqueous layer with ether and evaporation, yielded bis-2-methylthioethyl ether bismethochloride, deliquescent prisms (from anhydrous ethanol–ether), m. p. 196° (decomp.) not depressed on admixture with an authentic specimen (Found: C, 36·0; H, 7·4. Calc. for $C_8H_{10}OS_2Cl_2$: C, 36·0; H, 7·5%). This methochloride (2·65 g.) was refluxed for 3 hr. with sodium iodide (3·5 g.) in acetone (25 ml.). The mixture was concentrated to 15 ml. and the solid rejected; further concentration, followed by several recrystallisations from ethanol, yielded the bismethiodide, m. p. and mixed m. p. 142—143° (decomp.).

In another experiment, the iodide (3·38 g.), in water (50 ml.), was treated with 2N-sodium hydroxide (10·0 ml.). Solution of the iodide was complete after shaking for 2 min. Next morning sodium picrylsulphonate (3·2 g.), in water (40 ml.), was added: dimethylvinylsulphonium picrylsulphonate (2·30 g., 61%) separated in leaflets, m. p. 192° raised by recrystallisation from water to 199°, not depressed on admixture with authentic material.

The following experiments were carried out to demonstrate the interconversions of the various sulphonium compounds in alkali:

(i) *Vinyl into ether.* 2-Benzoyloxyethyldimethylsulphonium iodide (3·38 g.) was stirred for 2½ hr. with water (25 ml.) containing N-sodium hydroxide (10·0 ml.); the solution was divided into two equal portions. The first portion was acidified with N-hydrochloric acid (5·0 ml.), and the precipitated benzoic acid removed by filtration; addition of sodium picrylsulphonate (1·6 g.) to the filtrate yielded dimethylvinylsulphonium picrylsulphonate (1·2 g., 63%), m. p. 193—195° (decomp.) raised to 196—197° (decomp.), not depressed on admixture with authentic material, by recrystallisation from methanol. The second portion was treated with more N-sodium hydroxide (0·4 ml.) and kept overnight; acidification with N-hydrochloric acid (5·4 ml.), removal of benzoic acid by filtration, and addition of sodium picrylsulphonate (1·6 g.) afforded bis-2-methylthioethyl ether bismethopicrylsulphonate (1·4 g., 72%), m. p. and mixed m. p. 208—210°.

(ii) *Vinyl into hydroxyethyl.* The iodide (3·38 g.) was stirred for 2½ hr. with water (25 ml.) and N-sodium hydroxide (10·0 ml.); the solution was acidified with N-hydrochloric acid (10·0 ml.), the benzoic acid removed by filtration, and the filtrate divided into two equal parts. From the first, addition of sodium picrylsulphonate (1·6 g.) precipitated dimethylvinylsulphonium picrylsulphonate (1·1 g., 58%), m. p. 193—195° (decomp.) raised by one recrystallisation from methanol to 196—197° (decomp.), not depressed on admixture with authentic material. N-Sodium hydroxide (5·4 ml.) was added to the second portion which was then kept at room temperature overnight; neutralisation (5·4 ml. of 2N-hydrochloric acid), and addition of sodium picrylsulphonate (1·6 g.), precipitated 2-hydroxyethyldimethylsulphonium picrylsulphonate (1·0 g., 50%), m. p. and mixed m. p. 156—158°.

(iii) *Ether into hydroxyethyl.* The iodide (3·38 g.), in water (25 ml.), was treated with N-sodium hydroxide solution (10·8 ml.), stirred until dissolution was complete (5 min.), and then kept at room temperature overnight; N-hydrochloric acid (10·8 ml.) was then added and benzoic acid removed by filtration. A portion (0·5 ml.) of the filtrate was treated with sodium picrylsulphonate, giving bis-2-methylthioethyl ether bismethopicrylsulphonate, m. p. and mixed m. p. 211—213°. The rest of the filtrate was treated with N-sodium hydroxide (10·8 ml.) and kept for 48 hr. at room temperature. Addition of N-hydrochloric acid (10·8 ml.), followed by sodium picrylsulphonate (3·2 g.), yielded 2-hydroxyethyldimethylsulphonium picrylsulphonate (2·5 g., 63%), m. p. and mixed m. p. 157—158°.

(b) *Dimethyl-*3-p-*nitrobenzoyloxypropylsulphonium iodide.* The iodide (3·97 g., 0·01 mole), water (70 ml.,) and N-sodium hydroxide (10·0 ml.) were kept at room temperature overnight. Addition of N-hydrochloric acid (10·0 ml.) precipitated *p*-nitrobenzoic acid (1·65 g., 99%; m. p. 238—239°) which was removed by filtration. The filtrate was treated with sodium picrylsulphonate (3·15 g.) and kept at 5° overnight. The golden yellow needles (1·8 g.), m. p. 154°, were collected and a second crop (1·7 g.; total yield, 89%) was obtained by concentration of the mother-liquor; recrystallisation from methanol yielded 3-hydroxypropyldimethylsulphonium picrylsulphonate, yellow needles, m. p. and mixed m. p. 155°.

(c) 4-*Benzoyloxybutyldimethylsulphonium iodide.* The iodide (1·85 g.) in water (15 ml.) and N-sodium hydroxide (5·0 ml.) was kept for 3 days at 20°. Acidification (5·0 ml. of 2N-hydrochloric acid), removal of benzoic acid by filtration, and addition of sodium picrylsulphonate (1·6 g.) afforded 4-*hydroxybutyldimethylsulphonium picrylsulphonate* (1·5 g., 70%), m. p. 139—141°, which crystallised from methanol in prismatic needles, m. p. 141° (Found: C, 34·0; H, 4·2; N, 9·6. $C_{12}H_{17}O_{10}N_3S_2$ requires C, 33·7; H, 4·0; N, 9·9%).

(d) 2-*Benzoyloxyethyl methyl sulphone.* The sulphone (0·56 g.), suspended in water (10 ml.), was treated with N-sodium hydroxide (2·5 ml.; 1 equiv.), kept overnight at room temperature, and acidified with N-hydrochloric acid (2·5 ml.). After removal of the benzoic acid by ether-extraction, the aqueous layer was evaporated to dryness and the residue extracted with hot chloroform. Concentration of the extract and addition of light petroleum (b. p. 40—60°) yielded bis-2-methylsulphonylethyl ether (0·33 g.) as needles, m. p. 75—77° raised to 78°, not depressed on admixture with authentic material, by recrystallisation from the same solvents (Found: C, 31·5; H, 6·3. Calc. for $C_6H_{14}O_5S_2$: C, 31·3; H, 6·1%).

(e) 2-Benzoyloxyethyl methyl sulphoxide was recovered unchanged after treatment with sodium hydroxide in the manner described for the sulphone.

(f) *Dimethyl*-2-*phenoxyethylsulphonium iodide.* The iodide (3·1 g.; Crane and Rydon, *loc. cit.*) was suspended in water (50 ml.) and treated with N-sodium hydroxide (10 ml.). Next morning N-hydrochloic acid (10·0 ml.) was added and phenol extracted with ether. Addition of sodium picrylsulphonate to the aqueous layer afforded an immediate precipitate of bis-2-methylthioethyl ether bismethopicrylsulphonate (2·7 g., 69%), orange needles, m. p. and mixed m. p. 213—214°. Concentration of the mother-liquor yielded dimethylvinylsulphonium picrylsulphonate (0·25 g., 7%), m. p. 192—194° raised to m. p. and mixed m. p. 199—200° by recrystallisation from water.

(g) 2-*Benzoyloxyethyltrimethylammonium iodide.* The iodide (3·35 g.), N-sodium hydroxide (10·0 ml.), and water (30 ml.) were kept at room temperature for 3 days. Addition of N-hydrochloric acid (10·0 ml.) precipitated benzoic acid (1·05 g., 86%), which was removed by filtration. Addition of sodium picrylsulphonate (3·1 g.) to the filtrate precipitated *choline picrylsulphonate* (2·8 g., 71%), m. p. 234—244° (decomp.), raised to m. p. and mixed m. p. 244° (decomp.) by recrystallisation from methanol (Found: N, 14·1. $C_{11}H_{16}O_{10}N_4S$ requires N, 14·1%).

(h) *Dimethyl*-2-p-*nitrobenzoyloxyethylammonium iodide.* The iodide (1·9 g.), N-sodium hydroxide (5·0 ml.), and water (30 ml.) were kept at room temperature for 3 days. Unchanged starting material (0·07 g.) was removed by filtration; acidification of the filtrate with N-hydrochloric acid (5·0 ml.) precipitated *p*-nitrobenzoic acid (0·75 g., 94%), which was removed by filtration. Addition of sodium picrylsulphonate (1·4 g.) then precipitated choline picrylsulphonate (1·1 g., 55%), m. p. 235—240° (decomp.).

Action of more than One Equivalent of Alkali.—(a) 2-*Aroyloxyethyldimethylsulphonium iodides.* The iodide (0·01 mole), in water (10—40 ml.) containing N-sodium hydroxide (20 ml.), was heated to 95—100° in a slow stream of nitrogen. The effluent gases were led up a short column and passed through a trap cooled to −30° into a tube containing cuprous chloride–hydroxylamine. The contents of the cold trap were treated with a solution of mercuric chloride (2·5 g.) in ethanol (25 ml.); colourless prisms of dimethyl sulphide–mercuric chloride complex, m. p. and mixed m. p. 150—152°, were deposited. Acidification of the alkaline reaction mixture precipitated the benzoic acid which was collected and weighed. 2-Benzoyloxy-, 2-*m*-nitrobenzoyloxy-, and 2-*o*-toluoyloxy-ethyldimethylsulphonium iodides all gave acetylene, dimethyl sulphide (50, 49, and 64% yield), and the benzoic acid (87, 71, and 82% yield); similar results were obtained when the first equivalent of alkali was added slowly in the cold.

(b) 2-*Benzoyloxyethyltrimethylammonium iodide.* Under the above conditions no acetylene was produced and there was only a faint smell of trimethylamine; acidification of the residue afforded a theoretical yield of benzoic acid and treatment with sodium picrylsulphonate gave choline picrylsulphonate, m. p. and mixed m. p. 244° (decomp.).

(c) *Picrylsulphonates.* Under the same conditions, the following picrylsulphonates afforded dimethyl sulphide, isolated and identified as the mercuric chloride complex and as the sulphidimine, in the yields indicated: dimethylvinylsulphonium (80%); 2-hydroxyethyldimethylsulphonium (84%); bis-2-methylthioethyl ether (70%).

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