422. *Mechanism of Elimination Reactions. Part XII. Kinetics of Olefin Eliminations from Ethyl-,* n-*Propyl-,* n-*Butyl,* iso*Butyl-, and 2-Phenylethyl-dimethylsulphonium Salts in Alkaline Alcoholic Media.*

By E. D. Hughes, C. K. Ingold, and G. A. Maw.

Data are recorded to show the effects of certain constitutional changes on the rates of the substitutions and eliminations which primary alkyl-dimethylsulphonium ions undergo in bimolecular reactions with ethoxide ions in anhydrous ethyl alcohol as solvent. The structural effects studied are those of increasing chain length, of successively introduced β-linked methyl substituents, and of a β-phenyl substituent.

The substitutions are composite, since either methyl or the higher alkyl group may be displaced from the sulphonium ion in the bimolecular substitution. In the case of the dimethyl-2-phenylethylsulphonium ion, which shows an outstandingly large rate of total bimolecular substitution, an analysis of products was made which allows the total substitution rate to be divided into its components. It is thus shown that the increase of substitution rate caused by the phenyl substituent is due mainly to the increased rate of displacement of the 2-phenylethyl group itself, and not to any effect of this phenylated group on the rate of displacement of a methyl group. This effect of the phenyl substituent is regarded as essentially polar.

The bimolecular eliminations are simple reactions. Their rates fall with increasing length of the alkyl chain, fall on the introduction of β-linked methyl substituents, and show a striking rise on the introduction of a β-phenyl substituent. These effects, which are considered theoretically in Part XVI, show some marked contrasts with those displayed by the corresponding reactions of primary alkyl bromides.

This paper records the first part of a systematic study by kinetic methods of the effect of chemical constitution on the facility of olefin elimination from alkylsulphonium ions. As with the olefin-forming reactions of alkyl halides, so also with those of alkylsulphonium ions, nucleophilic substitutions usually accompany the eliminations (in the following formulæ the R's need not be identical) :

$$R_2CH\cdot CR_2\cdot\overset{+}{S}R_2 \xrightarrow{\overset{-}{X}} \begin{cases} R_2CH\cdot CR_2X + SR_2 \;.\;.\;.\;.\;.\;.\;.\;. & (S_N) \\ HX + R_2C{:}CR_2 + SR_2 \;.\;.\;.\;.\;.\;.\;. & (E) \end{cases}$$

It is also just as true for the decompositions of alkylsulphonium ions as it is for those of alkyl halides, that the concurrent reactions of substitution and elimination can each pursue either of two mechanisms, *viz.*, the bi- and uni-molecular mechanisms which we label S_N2 and S_N1 for substitution and $E2$ and $E1$ for elimination. Thus, in the general case, four component reactions have to be distinguished and separately considered with respect to the effect of alkyl structure on their rates :

$$R_2CH\cdot CR_2\cdot\overset{+}{S}R_2 \left\{ \begin{array}{l} \xrightarrow{\overset{-}{X}} \begin{cases} R_2CH\cdot CR_2X + SR_2 \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. & (S_N2) \\ HX + R_2C{:}CR_2 + SR_2 \;.\;.\;.\;.\;.\;.\;.\;.\;.\;. & (E2) \end{cases} \\ \xrightarrow[\text{slow}]{} R_2CH\cdot\overset{+}{C}R_2 + SR_2 \xrightarrow[\text{fast}]{\overset{-}{X}} \begin{cases} R_2CH\cdot CR_2X + SR_2 \;.\;.\;. & (S_N1) \\ HX + R_2C{:}CR_2 + SR_2 \;.\;. & (E1) \end{cases} \end{array} \right.$$

Kinetic analyses involving all these reactions will be described in the present group of papers. In this paper we are concerned with a series of sulphonium ions in which the alkyl radical, represented in the above general formulæ by $R_2CH\cdot CR_2\cdot$, is a primary radical of the form $R_2CH\cdot CH_2\cdot$, where either R may be H, Me, Et, or Ph. For such primary alkylsulphonium ions chief importance attaches to the bimolecular mechanisms of substitution and elimination; and by operating with ethoxide ions as the reagent, and in dry ethyl alcohol as the solvent, we can arrange that these reactions, S_N2 and $E2$, shall take exclusive control:

$$R_2CH\cdot CH_2\cdot\overset{+}{S}R_2 + \overset{-}{O}Et \longrightarrow \begin{cases} R_2CH\cdot CH_2\cdot OEt + SR_2 \; . \; . \; . \; . \; . \; . & (S_N2) \\ HO\cdot Et + R_2CH{:}CH_2 + SR_2 \; . \; . \; . & (E2) \end{cases}$$

Each component reaction thus exhibits second-order kinetics, and hence the overall reaction is of this kinetic form.

Second-order kinetics for bimolecular elimination ($E2$) from sulphonium ions has been previously established in the following cases. (1) The overall decomposition of dithian methohydroxide, $\{S{<}[CH_2\cdot CH_2]_2{>}SMe\}^+OH^-$, in water was shown by Green and Sutherland to be a reaction of the second order (*J.*, 1911, **99**, 1174), Mansfield (*Ber.*, 1886, **19**, 696, 2658) and V. Meyer (*ibid.*, p. 3262) having previously proved that the main product of the reaction is the ethylene derivative, $MeS\cdot CH_2\cdot CH_2\cdot S\cdot CH{:}CH_2$. (2) Hughes and Ingold showed that trimethyl-2-phenylethylammonium hydroxide in aqueous solution yielded styrene by a reaction of the second order (*J.*, 1933, 523). (3) The same authors established that, in the aqueous decomposition of dimethyl-*tert.*-butylsulphonium hydroxide, $\{SMe_2Bu^t\}^+OH^-$, *iso*butylene is formed mainly by a reaction of the second order ($E2$), even though the accompanying substitution, which produces *tert.*-butyl alcohol, is a reaction of the first order (S_N1) (*J.*, 1933, 1571). (4) Gleave, Hughes, and Ingold established that formation of ethylene by the decomposition of triethylsulphonium hydroxide in water or aqueous alcohol is a second-order process (*J.*, 1935, 235). (5) Similar kinetics were established for the production of propylene by the decomposition of methyldi*iso*propylsulphonium hydroxide in aqueous alcohol (*idem, ibid.*).

The sulphonium ions now studied were all of the type alkyl-dimethylsulphonium, $Alk\overset{+}{S}Me_2$, the variable group Alk being chosen in order to illustrate the following three types of progressive structural change. (Series 1.) The series Alk = ethyl, *n*-propyl, *n*-butyl illustrates effects due to the progressive lengthening of the alkyl chain. (Series 2.) The series ethyl, *n*-propyl, *iso*butyl illustrates the effect of successively introduced β-linked methyl groups up to the limit set by the necessity of retaining one β-hydrogen atom. (Series 3.) The series ethyl, *n*-propyl, 2-phenylethyl shows the relative magnitude of effects attributable to the capacity for hyperconjugation displayed by the terminal methyl group of *n*-propyl and to the power of ordinary conjugation possessed by the phenyl group in 2-phenylethyl.

The reactions of the iodides of all these sulphonium ions with sodium ethoxide in ethyl alcohol were studied at 63·9°. They show, as they should, a negative salt effect, a detailed investigation of which will be published later. For the purpose of our structural comparisons we have therefore used approximately the same initial concentrations in all cases, *viz.*, 0·05M-sulphonium iodide and 0·095M-sodium ethoxide. We find in each case two second-order reactions, S_N2 and $E2$. The first-order reactions S_N1 and $E1$ do not become appreciable in any of the examples treated. Our procedure was therefore to measure the rate constant, k_2, of the total second-order reaction, $S_N2 + E2$, by following the loss of alkali, and then to divide it into its components, $k(S_N2)$ and $k(E2)$, on the basis of a measurement of the proportion in which olefin is produced. The proportion should, of course, remain constant through the course of the change; and it was in fact shown to do so, such a demonstration being possible in these alkaline conditions, because the olefins, when once formed, do not become destroyed by interaction with the solvent, as they do in acidic solutions. The constancy of the olefin proportion with time having been shown, further measurements of the olefin proportion were usually made towards the end of reaction, for the sake of the greater accuracy thus attainable.

Table I contains the main series of measurements of the total bimolecular rate-constants, and of the proportions in which olefin is formed, in the reactions of the alkyl-dimethylsulphonium ions. In Table II these data are analysed in terms of the rate-constants of the individual bimolecular reactions of substitution and elimination, S_N2 and $E2$.

The two rate-constants $k(S_N2)$ and $k(E2)$ collectively represent three simultaneous reactions, because there are two possible directions of substitution:

$$Alk\cdot\overset{+}{S}Me_2 + \overset{-}{O}Et \longrightarrow \begin{cases} \left.\begin{matrix} Me\cdot OEt + Alk\cdot SMe \\ Alk\cdot OEt + SMe_2 \end{matrix}\right\} \; . \; . \; . \; . \; . \; . \; . & (S_N2) \\ HOEt + Olefin + SMe_2 \; . \; . \; . \; . \; . & (E2) \end{cases}$$

TABLE I.

Second-order rate-constants (k_2 *in* $sec.^{-1}$ $g.\text{-}mol.^{-1}$ *l.*) *and percentages of olefin formed in the reactions of primary alkyl-dimethylsulphonium iodides with sodium ethoxide in dry ethyl alcohol at* 63·95°.

(Initially $[\text{AlkSMe}_2\text{I}]$ ~0·05 and [NaOEt] ~0·095 in all cases.)

Alk in $(\text{Alk}\overset{+}{\text{S}}\text{Me}_2)\overset{-}{\text{I}}$.	10^5k_2.		% Olefin.	
	Individual values.	Mean.	Individual values.	Mean.
Ethyl	400, 386, 380	389	{14·8, 15·6, 15·1 15·8, 15·2, 15·6}	15·4
n-Propyl	371, 392, 380	381	6·8, 7·1, 7·4	7·1
n-Butyl	391, 396	394	4·3, 3·8, 4·6, 4·5	4·3
*iso*Butyl	593, 593	593	2·6, 2·4, 2·3	2·4
2-Phenylethyl	—	28,800 *	{88·8, 89·4, 90·0 88·6, 90·2}	89·4

* Extrapolated from the following results at lower temperatures, *viz.*,

10^5k_2 = 1050, 1050 (Mean, 1050) at 35·05° (T = 308·20°)
,, = 3960, 3990 (,, , 3985) ,, 45·92° (T = 319·07°)

by means of the derived equation

$$\log_{10}k_2 = 14{\cdot}98 - 23{,}900/(2{\cdot}303 \times 1{\cdot}986 \times T).$$

TABLE II.

Analyses of kinetic data for the reactions of alkyl-dimethylsulphonium iodides with sodium ethoxide in ethyl alcohol at 64°, *showing the variation in the rates of bimolecular substitution and elimination with progressive changes in the structure of the alkyl group.*

Series.	Alkyl group.	10^5k_2.	% Olefin.	$10^5k(S_N2)$.	$10^5k(E2)$.
1	$CH_3{\cdot}CH_2{\cdot}$	389	15·4	329	60
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}$	381	7·1	354	27
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}$	394	4·3	377	17
2	$CH_3{\cdot}CH_2{\cdot}$	389	15·4	329	60
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}$	381	7·1	354	27
	$(CH_3)_2CH{\cdot}CH_2{\cdot}$	593	2·4	579	14
3	$CH_3{\cdot}CH_2{\cdot}$	389	15·4	329	60
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}$	381	7·1	354	27
	$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}$	28,800	89·4	3050	25,750

It used to be assumed that, in the alkaline aqueous decompositions of sulphonium ions of the type $\text{Alk}\overset{+}{\text{S}}\text{Me}_2$, the group Alk is eliminated exclusively as olefin, whilst any alcohol simultaneously produced is methyl alcohol. However, Ingold and Kuriyan showed (*J.*, 1933, 991) that, when Alk is ethyl or *n*-propyl, appreciable amounts of ethyl or *n*-propyl alcohol are formed, along with the ethylene or propylene, and the methyl alcohol. Accordingly, we may surely expect that, in alkaline ethyl-alcoholic solutions, ethyl alkyl ethers will be produced, as well methyl ethyl ether, and, of course, the olefins. Thus the observed variations in the, rate-constant $k(S_N2)$ as the group Alk is changed will be due in part to differences in the rate at which this group itself is displaced in bimolecular substitution, and in part to the effect of different alkyl groups on the rate at which a methyl group is displaced in substitution. Owing to experimental difficulties, we have not yet secured any systematic data which would enable these two effects to be distinguished; but an approximate analysis of the matter has been made in one case. This is that of the 2-phenylethyl compound, for which the substitution rate is notably greater than for any of the purely aliphatic compounds. Most of this increase is found to be due to an increased rate of displacement in substitution of the 2-phenylethyl group itself. Direct analysis of the reaction product has given the proportion of styrene as 89·4%, and the proportion of dimethyl sulphide as 98·5%. It follows that ethyl 2-phenylethyl ether must be produced to the extent of 9%. The production of methyl ethyl ether is estimated either as 1·5% by difference, or as 3% on the basis of a difficult determination of the methyl 2-phenylethyl sulphide. On either figure, the 2-phenylethyl group is displaced by substitution several times more rapidly than is the methyl group from the same compound, and several times more rapidly than is methyl or any of the higher alkyl groups from the purely aliphatic sulphonium compounds. We interpret this as a polar effect within the 2-phenylethyl group, in which the phenyl group, as usual, accommodates itself to the electrical requirements of the reaction.

Concerning the elimination rates, we restrict ourselves here to pointing out the facts. They are that the bimolecular rate falls with increasing length of the alkyl chain, and falls on the introduction of β-linked methyl substituents, but rises strikingly on the introduction of a β-phenyl substituent. The first two of these effects present marked contrasts with those exhibited by the bimolecular elimination rates of the primary alkyl halides (Part IX). With these compounds the rate at first rises sharply, and then falls slowly, with increasing length of the alkyl chain; and it rises with the successive introduction of β-linked methyl substituents. It rises strikingly on the introduction of a β-phenyl substituent; in this the alkyl halides and sulphonium ions resemble each other. A theoretical discussion of all these relations will be given in Part XVI.

EXPERIMENTAL.

Materials.—The required sulphonium iodides were not prepared by the apparently easy method of direct addition of alkyl iodides to dimethyl sulphide, because this method often leads to the formation in appreciable quantities of trimethylsulphonium iodide, an impurity difficult to remove. The preparations therefore started from the alkylthiols, and proceeded by way of the methyl alkyl sulphides, to which methyl iodide was finally added. The crude salts, which were often sticky and yellow at first, were washed with dry ether, dissolved in warm absolute ethyl alcohol, and cooled in solution to −80° until crystals began to be formed. Crystallisation was furthered by the slow addition of pre-cooled, dry ether, the solvent being then poured off, and the whole process was repeated until all visible colour had disappeared. The crystals were collected out of contact with moist air, and kept over phosphoric oxide. All the salts, except dimethyl-2-phenylethylsulphonium iodide, were extremely deliquescent, and vacuum weighing bottles were therefore used for their analysis. The iodide-ion content was determined as an indication of purity: Dimethylethylsulphonium iodide gave I = 58·16% (Calc., 58·20%); dimethyl-*n*-propylsulphonium iodide gave I = 54·49% (Calc., 54·69%); dimethyl-*n*-butylsulphonium iodide gave I = 51·58% (Calc., 51·58%); dimethyl*iso*butylsulphonium iodide gave I = 51·69% (Calc., 51·58%); dimethyl-2-phenylethylsulphonium iodide, m. p. 129°, gave I = 43·00% (Calc., 43·17%).

The ethyl alcohol required for the kinetic measurements was prepared by drying commercial "absolute" alcohol with the aid of sodium and ethyl phthalate (Smith, *J.*, 1927, 1288; Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1106).

Method of Kinetic Measurements.—Portions, usually 5 c.c., of the reaction mixture, taken from a standard measuring flask, were enclosed in the cold in sealed tubes, which were placed in the thermostat for known times and then treated by one of the following methods. The tubes after being chilled were either broken under 100 c.c. of cold acetone, the alkali being then determined by means of 0·02N-sulphuric acid, with lacmoid as the indicator; or they were broken under 100 c.c. of ice-cold water, and titrated as before, but with a mixture of equal parts of cresol-red and thymol-blue as indicator. The original solution was made up only approximately by weighing: its exact composition was deduced from readings made on two tubes which were left in the thermostat for ten times the period of half-change of the reaction. All other tubes were shaken for two minutes when first put into the thermostat, the end of the two-minute period being treated as the time-zero of the reaction being investigated. Second-order rate-constants were calculated from the formula $k_2 = \{1/t(a - b)\}\log_e\{b(a - x)/a(b - x)\}$, when t is the time in seconds, and a and b are the initial concentrations of sodium ethoxide and alkyldimethylsulphonium iodide respectively, and x is the concentration of alkali destroyed at time t. The constants thus obtained were corrected for the change in volume of the solvent between the temperature at which the solutions were made up and the temperature of the thermostat.

A special method of making up solutions had to be employed in the case of dimethyl-2-phenylethylsulphonium iodide, owing to its low solubility in ethyl alcohol at 0°. The iodide was dissolved in half the total amount of alcohol at 46°, and portions of 2·5 c.c. of this solution were run into portions of 2·5 c.c. of alcohol containing the requisite amount of sodium ethoxide cooled to 0°. (Allowance was made for thermal expansion when measuring volumes at 46°.) The sulphonium iodide crystallised while the tubes were being sealed, but it redissolved completely while they were being shaken for the initial two minutes in the thermostat. The kinetics of the reaction could then be followed as usual.

Methods for Olefin Estimation.—Ethylene and propylene were estimated by the aspiration method (Hughes, Ingold, and Shapiro, *J.*, 1936, 225), and *n*-butylene, *iso*butylene, and styrene by the extraction method (Hughes Ingold, Masterman, and MacNulty, *J.*, 1940, 899), organic sulphides being removed, in either case, with the aid of saturated aqueous mercuric chloride (cf. Part VI, this vol., p. 2042), before the olefin was determined by uptake of bromine.

Results of Measurements.—The results of the main series are summarised in Table I. Their experimental basis is illustrated in Tables III, IV, and V. Table III records the first of the three rate measurements at 63·95° on dimethylethylsulphonium iodide, and Tables IV and V the first two of the six olefin estimations made with this substance. The first of the olefin estimations shows that the proportion in which olefin is formed remains constant during the reaction. The second olefin experiment is of the same type as all the subsequent ones, and is concerned with the amount of olefin in the product of the completed reaction.

The reaction with the dimethyl-2-phenylethylsulphonium salt went too quickly at 63·95° to be measured with accuracy. The proportion of olefin in the completed reaction at this temperature was determined, but it was not directly proved in this case that the proportion remained constant throughout reaction. The rate of the overall reaction at 63·95° was obtained by extrapolation from measurements at lower temperatures, the particulars of which are given in the footnote beneath Table I.

Some further measurements have been made, which are not included in Table I, because they relate to conditions other than those to which the data of Table I apply. One group of these additional results has already been partly quoted in Part VIII (this vol., p. 2049), and the main particulars of the experiments are therefore now recorded. They are in Table VI. Some further measurements of a generally similar kind will be included in a later paper dealing with salt effects on sulphonium salt decompositions.

TABLE III.

Illustrating determinations of total second-order rate-constants (k$_2$ *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) : *dimethylethylsulphonium iodide* (*Expt. A*).

(Solvent : EtOH. Temp. 63·95°. Initially [SMe$_2$EtI] = 0·0494M and [NaOEt] = 0·0966N. In the Table [SMe$_2$EtI] and [NaOEt] are each expressed in c.c. of 0·02134N-acid per 5 c.c. sample.)

t (min.).	[NaOEt].	[SMe$_2$EtI].	10^3k_2.	t (min.).	[NaOEt].	[SMe$_2$EtI].	10^3k_2.
0	22·55	11·53	—	42	16·37	5·35	3·76
4	21·29	10·27	—	46	16·03	5·01	3·78
12	20·10	9·08	3·64	51	15·72	4·70	3·71
20	18·85	7·83	3·67	55	15·46	4·44	3·70
24	18·29	7·27	3·70	59	15·14	4·12	3·77
30	17·54	6·52	3·75	63	14·96	3·94	3·72
34	17·13	6·11	3·74	67	14·68	3·66	3·74
38	16·72	5·70	3·76	∞	11·02	—	—

(Mean k_2 = 3·73 × 10^{-3} sec.$^{-1}$ g.-mol.$^{-1}$ l.; corrected for solvent expansion, k_2 = 4·00 × 10^{-3} sec.$^{-1}$ g.-mol.$^{-1}$ l.)

TABLE IV.

Illustrating determinations of olefin designed to show that the proportion is constant throughout reaction : ethylene from dimethylethylsulphonium iodide by the aspiration method (*Expt. A*).

(Solvent : EtOH. Temp. 63·95°. Initially [SMe$_2$EtI] = 0·0520M and [NaOEt] = 0·0965N. Pairs of tubes were withdrawn from the thermostat at the zero of time, after one-third, after two-thirds, and after the completion, of the reaction. One tube of each pair was used to estimate loss of alkali, and the other the formation of ethylene. In the Table [SMe$_2$EtI] and [NaOEt] are each expressed in c.c. of 0·02284N-acid per 5 c.c. sample, whilst the bromine surviving out of a standard quantity supplied, and the bromine absorbed, are each expressed in c.c. of 0·01133N-thiosulphate per 5 c.c. sample.)

[NaOEt].	[SMe$_2$EtI].	% Reaction.	Br$_2$ present.	Br$_2$ used.	% C$_2$H$_4$.
21·03	11·34	0·0	21·20	—	—
17·31	7·62	32·8	18·90	2·30	15·3
13·11	3·42	69·8	16·53	4·67	14·7
9·69	—	100·0	14·60	6·60	14·4

(The mean of the figures in the last column, 14·8%, is entered, as the main result of this experiment, in Table I.)

TABLE V.

Illustrating the normal method of determining olefin proportion : ethylene from dimethylethylsulphonium iodide by the aspiration method.

(Solvent : EtOH. Temp. 63·95°. Initially [SMe$_2$EtI] = 0·0511M and [NaOEt] = 0·0977N. In the Table the alkali is expressed in c.c. of 0·02134N-acid per 5 c.c. sample, whilst the olefin is given by the amount of bromine, measured in c.c. of 0·01228N-thiosulphate, which survives, out of a standard amount supplied, in a 10 c.c. sample of the reaction mixture.)

Initial readings.		Final readings.	
Alkali.	Bromine.	Alkali.	Bromine.
22·78	25·30	10·90	13·43, 11·98, 11·50
22·84	25·20	10·86	12·47, 12·02
22·81 (mean)	25·25 (mean)	10·88 (mean)	12·28 (mean)

(Alkali consumed : 11·93 c.c. Olefin formed : 12·97 c.c. Proportion of olefin = 15·6%.)

TABLE VI.

Some additional second-order rate-constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*), *and percentages of formed olefin, for the reaction of dimethylethylsulphonium iodide with sodium ethoxide* (*cf. Part VIII*).

(Solvent : EtOH. Temp. 45·08°.)

Initial concentrations.			
[SMe_2EtI].	[NaOEt].	10^5k_2.	% Olefin.
0·0207	0·0951	41·9	—
0·0213	0·0945	41·3	—
0·0208	0·0938	—	12·0
0·0213	0·0963	—	11·9

Estimation of Sulphides formed from Dimethyl-2-phenylethylsulphonium Ethoxide.—The apparatus usually employed for the estimation of ethylene or propylene by aspiration was used with slight modifications for the estimation of dimethyl sulphide in the product of the completed reaction between dimethyl-2-phenylethylsulphonium iodide and sodium ethoxide in ethyl alcohol at 64°. The conditions of reaction were the same as those under which the production of styrene was estimated. The usual bromine traps were omitted from the aspiration apparatus, and three traps containing saturated aqueous mercuric chloride were provided. The formed dimethyl sulphide was aspirated into these from the reaction mixture at 40° in a stream of nitrogen. The precipitated complex was collected and weighed. The assumption was made that it has the composition $3HgCl_2,2(CH_3)_2S$ (Phillips, *J. Amer. Chem. Soc.*, 1901, **23**, 253; Hughes and Ingold, *J.*, 1933, 1571; MacNulty, Thesis, London, 1938). The residual reaction mixtures from a number of such aspirations were combined, and worked up for methyl 2-phenylethyl sulphide. They were shaken with aqueous mercuric chloride, and the precipitated complex, assumed to have the composition $3HgCl_2,2C_8H_9{\cdot}S{\cdot}CH_3$, was collected and weighed. The result of these analyses have already been given (p. 2074).

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

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