799. *Mechanism of Elimination Reactions. Part XX.* The Inessentiality of Steric Strain in Bimolecular Olefin Elimination.*

By D. V. BANTHORPE, E. D. HUGHES, and SIR CHRISTOPHER INGOLD.

In order to determine whether polar or (as has been suggested) steric effects are responsible for the Hofmann pattern of structural effects on bimolecular olefin elimination, the kinetics of such reactions of six series of alkyldimethylsulphonium and alkyltrimethylammonium ethoxides and t-butoxides have been investigated. Although the series were chosen in order that they should be critical for the question raised, the results disclosed relations quantitatively recognisable as representative of the Hofmann system of relations, which had been delineated in the earlier extensive literature of 'onium eliminations. The significance of the results with respect to the causal question is therefore considered, jointly with the aid of approximate theoretical calculations, and by analysis of the experimental figures, in the context of eliminations as a whole.

The following conclusions are reached. The inductive and electromeric effects dominate the picture of eliminations down to the simplest examples of Hofmann and Saytzeff. These two polar effects belong to that picture in principle, creating its familiar kinetic and orientational pattern. Steric hindrance is inessential to that pattern. It enters as a complication in certain critical situations above determinable thresholds of molecular complexity, as we should expect from its short-range nature. It cannot be used instead of the inductive effect to explain the kinetic and orientational pattern of eliminations as a whole.

(1) *Theories of the Orientation and Rate of Olefin Elimination.*—A theory of constitutional effects on the elimination reaction,

$$\mathrm{B^- + H{-}C_\beta{-}C_\alpha{-}X \longrightarrow BH + C_\beta{=}C_\alpha + X^-}$$

has been proposed,[1] in which both polar and steric effects are allowed, the former acting universally from the simplest cases upwards, and in ways characteristic of elimination, and the latter constituting, as for most reactions, an incursion with more involved structures. In this theory, polar influences are separated into electrostatic and conjugative components, termed inductive and electromeric, which are made dependent on electronegativity and unsaturation, respectively. The inductive effect is exerted on the acidity of the β-hydrogen atom eventually eliminated as a proton. It leads to a certain pattern of effects on rate and orientation, a pattern which includes and generalises the Hofmann rule. The electromeric effect is exerted on transition-state stability, as affected by

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* Part XIX, *J.*, 1953, 3839.

[1] Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 657; Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093.

conjugation or hyperconjugation involving the developing double bond. It leads to another pattern of constitutional effects, one which generalises the Saytzeff rule. Both effects are always present, each to an extent dependent on mechanism, structure, and solvation.

Two mechanisms are well established, *E*1 (which produces a carbonium ion first), and *E*2 (which is concerted), whilst a third mechanism, *E*1*cB* (which produces a carbanion first), is suspected but is not yet unambiguously established. In the *E*1 eliminations of simple alkyl compounds, whether halides or 'onium ions, a vacant C_α orbital is produced which demands conjugation; and thus the Saytzeff pattern predominates. In the *E*2 eliminations of simple alkyl halides in polar solvents, in which solvation of the escaping anion induces large electron transfers from C_α in the transition state, the Saytzeff pattern again will usually predominate. But in the *E*2 reactions of simple alkyl 'onium ions, including derivatives with bound ionic centres, as in the sulphone group, or, as has more recently been demonstrated, the nitro-group,[2] the polarity induced along the alkyl chain is stronger, and the development, now retarded by solvation, of unsaturation in the transition state is weaker, so that a dominating Hofmann pattern is the usual result.

In analogy with the S_N1 and S_N2 forms of nucleophilic substitution, *E*1 elimination is not uniformly stereospecific, but *E*2 elimination is, an *anti*-conformation of changing bonds corresponding to inversion at C_α. Steric hindrance is assumed to need a certain minimum of ramification in the structures of the reactants and to be less important for elimination than for nucleophilic substitution, because of the more exposed situation of hydrogen than of carbon, and to be still less important for *E*1 than for *E*2 eliminations, because the former depend kinetically on a dissociation.

During the past ten years, these views have been challenged several times by H. C. Brown, who desires a more basic rôle for the steric effect. This was at first to be in substitution for the electromeric effect. It had been suggested that the *E*1 reactions of alkyl halides are controlled mainly by the latter, steric hindrance being unimportant in simple cases. Brown and Fletcher claimed [3] that the *E*1 olefin yields from homologues of t-butyl chloride were out of accord with that idea; however, they were omitting to take account of hyperconjugation at the α- as well as the β-end of the double bond. It was subsequently pointed out [4] that, when that error was overtaken, the polar theory could represent the observations very closely in the nine simpler of the twelve examples then under discussion. The anomaly remained that the three most densely branched structures gave too much olefin, one of them with an irregular isomer ratio, and, as we showed,[4] at an accelerated rate. With those particular structures, it was impossible to establish directly whether the irregularities signalised steric (*i.e.*, non-bonding) interactions, or whether they arose from bonding interactions of kinds which at greater intensity can produce fragmentations and rearrangements of known types. But they were certainly not evidence for the suggested generalisation of steric control.

Brown has disputed these conclusions,* but from an altered position: the electromeric effect is now to be allowed to control the Saytzeff pattern of structural effects, but steric strain is to replace the inductive effect as the cause of the Hofmann pattern. Brown has developed this thesis in eleven papers, and it is in consequence of these that we return to the discussion. He makes it clear that he is claiming, not a steric effect of limited incidence, but one in universal control down to the simplest alkyl groups: the substitution

* His argument [5] that fragmentations and rearrangements are not observed in the reaction conditions is as irrelevant as would be an argument that kinetic effects of hyperconjugation do not exist unless the hydrogen atoms on which hyperconjugation depends are observed to be split off as protons.

[2] Jones, *Science*, 1953, **118**, 387.

[3] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1950, **72**, 1223.

[4] Hughes, Ingold, and Shiner, *J.*, 1953, 3827.

[5] Brown and Berneis, *J. Amer. Chem. Soc.*, 1953, **75**, 10; Brown, Moritani, Nakagawa, and Okamoto, *ibid.*, 1955, **77**, 3607 *et seq.* (5 papers); Brown, Moritani, Nakagawa, Okamoto, and Wheeler, *ibid.*, 1956, **78**, 2190 *et seq.* (5 papers).

of the steric for the inductive effect is to be total: "The Hofmann rule," he says, "is a manifestation of steric effects. . . . There appears to be no need to attribute any portion of the Hofmann-type elimination of 'onium salts to a polar effect resulting from the formal charge carried by the 'onium group."

The field of exemplification is now $E2$ reactions. Our view of these is that both polar effects are present, with a shift of relative importance from the electromeric to the inductive on going from simple alkyl halides to 'onium ions in polar solvents. Steric hindrance is expected only above a certain level of branching density.

The original idea underlying a general steric basis for the Hofmann rule was that, as more space is open to the attacking base at primary than at secondary β-hydrogen, the former reaction-site will be preferred. Schramm [6] first advanced this concept, but its advocacy is due to Brown,[5] whose three arguments, based mainly on orientational data, must now be summarised.

The first is illustrated by the following effects of alkyl structure on the composition of olefins formed from alkyl bromides and ethoxide ions:

R in $R{\cdot}CH_2{\cdot}CMe_2Br$	Me	Et	Pr^i	Bu^t
Alk-2-ene (%) per secondary β-H	35	25	23	7
Alk-1-ene (%) per primary β-H	5	8	9	14

In the "regular shift" from Saytzeff-type to Hofmann-type orientation was seen a reflection of the progressively growing "steric requirements" of R, and hence an argument for the generality of the steric explanation. We question the description "regular shift," and note that the main change of type is with the last example, where, if anywhere, a non-bonding interaction might become important, or else, as we have explained before,[4] the bonding interactions possible in that type of structure. It is not recorded whether the changed orientation is associated with a decreased or increased rate.

The second argument relates to variations in the attacking base. Several substrates and bases were used, but the following results are typical, and as relevant as any to the generalised steric interpretation:

2-Butyl bromide with	EtO^- in EtOH	Bu^tO^- in Bu^tOH
Alk-2-ene (%) per secondary β-H	41	23
Alk-1-ene (%) per primary β-H	6	18

The shift in the attack from secondary in the direction of primary hydrogen, as the reagent is changed from ethoxide ion to t-butoxide ion, was ascribed to the greater space-demands of the latter. However, we think that the change to the t-butyl base–solvent system has made other significant differences. In it, the stronger base will increasingly promote electron-supply to $C_{\beta}C_{\alpha}$ in the transition state, and the less solvating solvent will increasingly inhibit electron-withdrawal from $C_{\beta}C_{\alpha}$ in the transition state, all this reducing its unsaturation and thus diminishing the predominance of the Saytzeff pattern.

Brown's third argument concerned variations in the eliminated group, which, in reactions of 1-methylbutyl (2-pentyl) compounds with ethoxide ions, affected olefin composition as follows:

X in $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHX{\cdot}CH_3$ ...	Br	I	OTs	SO_2Me	SMe_2^+	NMe_3^+
Alk-1-ene (%)	31	30	48	89	87	98

(Ts = p-$C_6H_4Me{\cdot}SO_2$.)

From the halides to the 'onium ions, the orientation changed, as is usual, from Saytzeff-type to Hofmann-type. The proposal was that the larger steric requirements of the

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[6] Schramm, *Science*, 1950, **112**, 367.

'onium groups were responsible. However, the alternative seems to us still open that the responsible factor was their charge, or, more accurately, their electronegativity.*

Because none of these results is critical for the conclusion drawn, we have sought more discriminating methods, but meanwhile considerable success in this has been achieved by others. W. H. Jones showed [2] that $E2$ eliminations involving the nitro-group, like those involving the sulphone group, follow the Hofmann orientational pattern. He noted that, as the nitro-group, like the sulphone group, contains bound ionic centres, it would be expected on the polar view to behave analogously. He noted also that the nitro-group is so small, and his structures so simple, that a steric explanation was scarcely conceivable.

By employing the more intensive method of kinetics, albeit outside the field of simple alkyl structures, several groups of authors have conclusively identified the inductive effect in $E2$ eliminations.[8-10] For example, Saunders and Williams record rates, such as the following, for the $E2$ reactions of ethoxide ions with *para*-substituted phenethyl bromides and dimethylsulphonium ions, reactions in which the steric effect of the *para*-group must be negligible (k_2 in sec.$^{-1}$ mole^{-1} l. at 30°):

R in $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2X$	MeO	Me	H	Cl	COMe	NO_2
10^5k_2, X = Br	16	23	42	191	3720	74,200
10^5k_2, X = SMe_2^+	111	232	500	2440	—	—

It is qualitatively obvious that these rates disclose a polarity series, and the authors proceed to show, by means of linear free-energy comparisons, that they correspond quantitatively to a polar effect of the variable group on acidity at the reaction site in the substrate.

However, any critical investigation of the causal basis of the Hofmann pattern must go back to the simple alkyl structures, in which that pattern was first recognised, and for which the electrostatic interpretation was given, which Brown wishes to replace by a steric interpretation. For the issue is not whether steric hindrance can enter when a molecule is complicated enough, but whether it has basic responsibility for the total Hofmann pattern. We have therefore to start with an ethyl group in an 'onium ion, and build homologues by β-extension. Owing to the steep bank in the non-bonding energy curve, a steric effect, once it starts, should build up very rapidly with increasing material density about the reaction site. On the other hand, an electrostatic effect is subject to the attenuation of relay, and thus should show gentler and more monotonous forms of variation, which can be predicted by empirical comparisons and also very roughly computed. The distinction should be diagnostic below the threshold of structural elaboration at which steric hindrance enters as a complication.

This approach has been successfully applied in an orientational investigation of basic 'onium eliminations by P. A. S. Smith and Frank,[11] who mass-spectrometrically analysed the olefins obtained from quaternary ammonium hydroxides containing different, simultaneously present, olefin-forming alkyl groups. A consistent Hofmann-type orientation was displayed, and, as the authors noted, the pattern of their analytical figures showed clearly that the inductive effect, and not the steric effect, was responsible, though some incursion of the latter in the most complex cases was possible. This important contribution seems in danger of being overlooked, Brown having omitted to mention it

* Illusory support for Brown's thesis has been offered by Cope and others [7] on the basis that the pyrolysis of amine oxides shows an indecisive orientation, *i.e.*, one between the Hofmann and Saytzeff types. This might happen if the transition state were cyclic (*Ei*) and somewhat unsaturated. However, these authors' conclusions that, because effects of polarity and unsaturation cancel, they are individually insignificant, that polarity is therefore insignificant in bimolecular, 'onion decompositions ($E2$), and that accordingly these can owe their Hofmann-type orientation only to steric effects, are obviously inconsequential.

[7] Cope, Lebel, Lee, and Moore, *J. Amer. Chem. Soc.* 1957, **79**, 4720.

[8] Hine and Langford, *J. Amer. Chem. Soc.*, 1956, **78**, 5002.

[9] DePuy and Froemsdorf, *J. Amer. Chem. Soc.*, 1957, **79**, 3710.

[10] Saunders and Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 3712.

[11] Smith and Frank, *J. Amer. Chem. Soc.*, 1952, **74**, 509.

in any of the eleven subsequent papers in which he advocated a general supersession of the inductive by a steric interpretation.

We used the same approach, but with the tool of kinetics, so that we could employ 'onium structures each having only one olefin-forming alkyl group. We shall here describe a main and two supplementary investigations.

(2) *Main Experimental Investigation.*—This was on the kinetics of formation of olefins from primary alkyl groups in *E*2 reactions of 'onium ions. The only prior work in this area is that of Hughes, Ingold, and Maw,[12] which related to series (1) below, and is now extended in that series. We have examined the following four series:

(1) $RR'CH{\cdot}CH_2{\cdot}SMe_2^+ + EtO^-$ in EtOH
(2) $RR'CH{\cdot}CH_2{\cdot}SMe_2^+ + Bu^tO^-$ in Bu^{t}OH
(3) $RR'CH{\cdot}CH_2{\cdot}NMe_3^+ + EtO^-$ in EtOH
(4) $RR'CH{\cdot}CH_2{\cdot}NMe_3^+ + Bu^tO^-$ in Bu^{t}OH

where R = H, Me, Et, Pr^i, Bu^t, and R' = H, Me.

The sulphonium salt decompositions followed three concurrent paths, often to comparable extents:

$$RR'CH{\cdot}CH_2{\cdot}SMe_2^+ + AlkO^- \longrightarrow \left\{\begin{array}{ll} \left.\begin{array}{l} RR'CH{\cdot}CH_2{\cdot}SMe + MeOAlk \\ RR'CH{\cdot}CH_2{\cdot}OAlk + SMe_2 \end{array}\right\} & \dots\dots (S_N2) \\ RR'C{:}CH_2 + HOAlk + SMe_2 & \dots\dots (E2) \end{array}\right.$$

whilst the ammonium salt decompositions pursued nearly exclusively the following two,

$$RR'CH{\cdot}CH_2{\cdot}NMe_3^+ + AlkO^- \longrightarrow \left\{\begin{array}{ll} RR'CH{\cdot}CH_2{\cdot}NMe_2 + MeOAlk & \dots\dots (S_N2) \\ RR'C{:}CH_2 + HOAlk + NMe_3 & \dots\dots (E2) \end{array}\right.$$

In all examples, the overall process, as measured by base consumption, was kinetically of second order, apart from expected salt effects. The second-order rate constants remained steady over large parts of all the runs, and were the same for runs with different initial concentrations of reactants at the same total salt concentration. Rate comparisons were accordingly made at common concentrations of total salt. In the strongly basic conditions of these experiments, solvolytic reactions were completely negligible, as also were reactions involving weakly nucleophilic anions, such as iodide, which in some experiments were present in addition to the alkoxide. Olefin formation was followed as a function of time, and it was found that the proportion in which the total reaction led to olefin did not vary, either during a run, or when initial concentrations were changed from run to run. All this showed that concurrent S_N2 and *E*2 reactions were under observation. Therefore, for each 'onium salt studied, we measured both the second-order rate constant for base consumption, k_2, and the proportion in which the overall reaction led to olefin. This allowed us to compute the separate second-order constants, $k_2(S_N2)$ for substitution, and $k_2(E2)$ for elimination.

Our results for the salts of series (1)—(4) are in Tables 1—4, respectively. We shall comment first on the broader features of these figures, leaving for the moment the detailed forms of the effects of alkyl structure. We shall argue in Section 3 that the general features of the data can be plausibly interpreted on an electrostatic basis, and give no indication of widespread steric effects.

(3) *General Features of the Results.*—In each of the series (1)—(4), the substitution rate is almost independent of alkyl structure. This is no less true when the substituting agent is the larger t-butoxide ion than when it is the smaller ethoxide ion. It is also as true for the sulphonium as for the ammonium salt series, though the two terminating ionic groups are unlikely to have the same steric requirements.

In contrast, the elimination rates depend strongly on alkyl structure, varying in the different series over ranges between 10^2 and $10^{4\cdot5}$. Though the qualitative form of the

[12] Hughes, Ingold, and Maw, *J.*, 1948, 2072.

TABLE 1. *Second-order rate-constants* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *and olefin proportions* (%) *in reactions of* $RR'CH{\cdot}CH_2{\cdot}SMe_2^+$ *with* EtO^- *in* EtOH *at* 64·08°.

$AlkSMe_2^+$	R	R′	10^5k_2	Olefin	$10^5k_2(S_N2)$	$10^5k_2(E2)$
Methyl	—	—	480	—	480	—
Ethyl	H	H	383	20·5	304	79
n-Propyl	Me	H	381	7·6	352	29
n-Butyl	Et	H	406	5·2	385	21
Isopentyl	Pr^i	H	431	3·8	415	16
Neohexyl (3,3-dimethylbutyl)	Bu^t	H	361	0·12	361	0·43
Isobutyl	Me	Me	503	2·0	493	10

TABLE 2. *Second-order rate constants* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *and olefin proportions* (%) *in reactions of* $RR'CH{\cdot}CH_2{\cdot}SMe_2^+$ *with* Bu^tO^- *in* Bu^tOH *at* 34·86°.

$AlkSMe_2^+$	R	R′	10^5k_2	Olefin	$10^5k_2(S_N2)$	$10^5k_2(E2)$
Ethyl	H	H	835	32·5	564	271
n-Propyl	Me	H	402	8·2	369	33
n-Butyl	Et	H	350	5·5	331	19
Isopentyl	Pr^i	H	343	2·3	335	7·9
Neohexyl	Bu^t	H	270	1·2	267	3·2

TABLE 3. *Second-order rate constants* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *and olefin proportions* (%) *in reactions of* $RR'CH{\cdot}CH_2{\cdot}NMe_3^+$ *with* EtO^- *in* EtOH *at* 104·22°.

$AlkNMe_3^+$	R	R′	10^5k_2	Olefin	$10^5k_2(S_N2)$	$10^5k_2(E2)$
Methyl	—	—	20·3	—	20·3	—
Ethyl	H	H	101·8	70·1	30·5	71·3
n-Propyl	Me	H	27·6	18·7	22·4	5·16
n-Butyl	Et	H	26·6	10·6	23·8	2·82
n-Decyl	C_8H_{17}	H	17·3	15·0	14·7	2·60
Isopentyl	Pr^i	H	26·4	4·0	25·3	1·06
Neohexyl	Bu^t	H	24·0	0·35	24·0	0·084
Isobutyl	Me	Me	27·1	6·2	25·4	1·68

TABLE 4. *Second-order rate constants* (k_2 *in sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *and olefin proportions* (%) *in reactions of* $RR'CH{\cdot}CH_2{\cdot}NMe_3^+$ *with* Bu^tO^- *in* Bu^tOH *at* 72·85°.

$AlkNMe_3^+$	R	R′	10^5k_2	Olefin	$10^5k_2(S_N2)$	$10^5k_2(\mathrm{E}2)$
Ethyl	H	H	30,200 *	99·8	—	30,100
n-Propyl	Me	H	513	72·8	140	373
n-Butyl	Et	H	274	31·9	186	87·7
Isopentyl	Pr^i	H	211	10·7	188	22·5
Neohexyl	Bu^t	H	181	0·42	180	0·72

* Extrapolated from measurements at lower temperatures.

variation always conforms to the Hofmann pattern, the quantitative spread of rates is markedly greater in the ammonium than in the sulphonium salt series. On an electrostatic view of Hofmann control, the greater spread of rates in the ammonium series would be ascribed to the greater electronegativity of the trimethylammonium than of the dimethylsulphonium pole, as established, for example, by their orienting effects in aromatic substitution.

Olefin proportions are generally larger in the ammonium than in the sulphonium salt series. This also can be ascribed to the greater electronegativity of the ammonium than of the sulphonium pole, because, in elimination, either pole activates the same β-hydrogen, whereas in substitution, the greater electronegativity of the ammonium pole is set against its greater bond stability.

All rates, both of substitution and elimination, in both the sulphonium and the ammonium salt series, are much greater at a common temperature in the t-butoxide–t-butyl alcohol medium than in the ethoxide–ethanol medium. This is to be expected from both the greater basic strength of the t-butoxide ion than of the ethoxide ion, and the smaller ion-solvating power of t-butyl alcohol than of ethyl alcohol.

Apart from one individual result, which is to be specially discussed (Section 11) the spread of elimination rates under alkyl variation, in both the sulphonium and the ammonium salt series, is greater in the t-butoxide–t-butyl alcohol medium than in the ethoxide–ethanol medium. On the theory of electrostatic orientation, this is easily understood, because a considerable part of any inductive effect consists in a " direct effect " transmitted through the medium, and that part becomes strengthened as the dielectric constant of the medium becomes reduced.

The sensitivity to medium of the extent of spread of elimination rates under alkyl variation is greater for the ammonium than for the sulphonium salts. This is a natural consequence of electrostatic orientation, because the greater electronegativity of the ammonium pole will establish the inductive effect, which is medium-dependent, in stronger and more nearly exclusive control in the ammonium than in the sulphonium salt series.

In both the sulphonium and ammonium series, the proportions of olefin are generally greater in the t-butoxide–t-butanol medium than in the ethoxide–ethanol medium. In elimination, unlike substitution, activation arising from the 'onium centre has to be transmitted to β-hydrogen. Accordingly the difference mentioned can be ascribed to the stronger transmission of electrostatic induction in the medium of lower dielectric constant.

The sensitivity of olefin proportions to medium is more marked in the ammonium than in the sulphonium salt series. Once again, this is an expected result of electrostatic orientation, because the greater electronegativity of the ammonium pole will establish the inductive effect, which in elimination has to be transmitted, in part through the medium, in stronger control in the ammonium than in the sulphonium salt series.

We do not see how the eight preceding general relations exhibited by our rate data, which uniformly illustrate Hofmann-type orientation, could be understood on the basis of any self-consistent picture of an exclusive steric control of such orientation.

(4) *The Structural Rate Pattern.*—We shall find it convenient for our discussion of the detailed effects of alkyl structure on elimination rates in series (1)—(4), to consider these rates in the form of free-energies of activation, $G^‡$. This allows us to set down the differences, $\Delta G^‡$, which arise when, in the parent olefin-forming group $RR'CH{\cdot}CH_2$ with $R = R' = H$, either R or R′ is replaced by Me, Et, Pr^i, or Bu^t; and to set down also the second differences, $\Delta\Delta G^‡$, which result from the replacement of any R or R′ by its next higher homologue. These first and second free-energy differences are given in Table 5.

TABLE 5. *Effects of alkyl structure on the free energies of activation (kcal./mole) in olefin elimination.*

		Alkyl·SMe_2^+				Alkyl·NMe_3^+			
		(1) EtO^-		(2) Bu^tO^-		(3) EtO^-		(4) Bu^tO^-	
Alkyl	β-R	$\Delta G^‡$	$\Delta\Delta G^‡$	$\Delta G^‡$	$\Delta\Delta G^‡$	$\Delta G^‡$	$\Delta\Delta G^‡$	$\Delta G^‡$	$\Delta\Delta G^‡$
Ethyl	H	0	0	0	0	0	0	0	0
n-Propyl	Me	0·67	0·67	1·29	1·29	1·96	1·96	3·02	3·02
n-Butyl	Et	0·88	0·21	1·63	0·34	2·44	0·48	4·01	0·99
Isopentyl	Pr^i	1·06	0·18	2·16	0·53	3·17	0·73	4·95	0·94
Neohexyl	Bu^t	3·49	2·43	2·71	0·55	5·07	1·90	7·32	2·36
Isobutyl	Me_2	1·38	—	—	—	2·81	—	—	—

These figures naturally reflect some of the general relations already noted. Thus the first differences, and also the second differences, change from series to series in the order (4) > (3) > (2) > (1). However, one of the alkyl groups, neohexyl (3,3-dimethylbutyl), breaks this regularity between series (2) and (1).

In series (2), to describe that first, the largest second difference accrues when the γ-carbon atom is first introduced into the growing alkyl chain, *i.e.*, the n-propyl group; and, then, three comparable and considerably smaller second differences are successively added as three δ-carbon atoms are successively included, in the n-butyl, isopentyl, and neohexyl groups. Qualitatively, this is a form of variation which is to be expected from control by the inductive effect, but would be difficult to attribute to a steric effect. The same description applies to series (1), (3), and (4), if, in these series, we limit the number of added δ-carbon atoms to two. For convenience in the ensuing discussion, we shall designate this much of the total array of results as the " normal pattern." In series (1), (3), and (4), the neohexyl group is associated with especially large free energies. These constitute what we shall call the " anomaly."

There is internal evidence that quite different causes underlie the normal pattern and the anomaly; for the latter follows its own very different pattern. Thus, whilst all energy differences of the normal pattern are considerably greater in the ammonium than in the sulphonium salt series, the largest second difference within the area of the anomaly is in the sulphonium series. Again, whereas in the normal pattern sensitivity to the change of medium is greater in the ammonium than in the sulphonium series, the effect of that change on the anomaly is much greater in the sulphonium series. Therefore we do not think that the cause of the anomaly has any connexion with that of the Hofmann rule, *i.e.*, with electronegativity. The absence of suitably situated hydrogen excludes its derivation from the Saytzeff-rule cause, *i.e.*, hydrogen-hyperconjugation. Furthermore, our alkyl structures were chosen with a view to avoiding such situations as might bring into play those bonding interactions which at greater intensity produce fragmentations and rearrangements. Not only for these negative reasons, but also for the positive ones mentioned in Section 11, we think that the cause of the anomaly is steric.

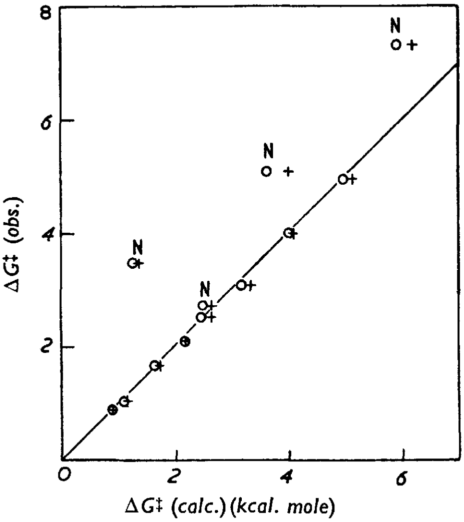

FIG. 1. *Observed and calculated effects of homology on free-energies of activation in E2 reactions.*

○ *Method* (*a*), *with* $i = 0{\cdot}20$, $0{\cdot}40$, $0{\cdot}56$, $0{\cdot}97$ *for series* 1, 2, 3, 4, *respectively.*

+ *Method* (*b*) (*no disposable constants*).

The straight line corresponds to perfect agreement with experiment. Neohexyl points are marked N.

(5) *More Detailed Consideration of the Inductive Effect.*—Let us turn back to the normal pattern, and examine its inductive interpretation more closely. The simplest development of this view would be on the lines of one of the earlier treatments, such as that of Branch and Calvin,[13] of the inductive interpretation of the acid-strengths of carboxylic acids, since our problem is one of the propagation of an acidifying influence. We might assume either (*a*) that $\Delta G^{\ddagger} = I + ni$, where I and i are the free energy increments associated with γ- and δ-carbon atoms respectively, and n is the number of the latter, or (*b*) that the inductive effect is damped uniformly by Branch and Calvin's factor of 2·8 for each carbon atom traversed, *i.e.*, that $\Delta G^{\ddagger} = I(1 + n/2{\cdot}8)$. Values computed by these two methods are compared with the observational data in Fig. 1, where the anomaly of the neohexyl group stands out clearly.

[13] Branch and Calvin, " Theory of Organic Chemistry," Prentice-Hall, New York, 1941, p. 201.

A more fundamental approach is to try to calculate the charge distribution in the alkyl groups from the electric fields in the bonds and the longitudinal bond polarisabilities, as has been done by Remick,[14] and also by Eyring and others.[15] Then, from the calculated β-hydrogen charges, one can compute electrostatic work terms for the proton transfers, and assume these to be contributions to the activation energies of the eliminations.

Bond polarisabilities are better known[16] now than at the times of the former calculations, particularly as regards the C–C bond; but for the C–N and C–S bonds values must be assumed, and our assumed values were obtained by applying to the recorded spherical-average polarisabilities of these bonds.[17] the known principal polarisability ratios of the C–C bond.[16] The fields in the C–C and C–H bonds were computed by assuming coulombic contributions with Slater screening from the separate atoms. A major difficulty presented itself in the computation of fields in the bonds between carbon and the other polyelectronic atoms, because these fields depend on small differences between large quantities, which are not determined accurately enough by these methods. Eyring and his co-workers, who were calculating the dipole moments of the halogenoalkanes, encountered the same difficulty, and avoided it by replacing this particular part of their calculation by an empirical correlation with a known dipole moment. We were dealing with ions of unknown dipole moment, and we wanted to know the amount of charge remaining on the 'onium atoms.* We could see no way to deduce this reliably, and therefore took it as one-half of the formal charge, feeling that at least the uncertainty would be within a factor of 2. We knew that our results could be wrong by such a factor for other reasons, notably, that we neglect the direct effect, *i.e.*, induction transmitted through the solvent, though this must constitute a considerable fraction of the total induction: we neglect the direct effect because of the well-known difficulty of improving the quantitative performance of the Bjerrum theory sufficiently for this type of application. In short, our calculation does not aspire to do more than account for an order of magnitude and a pattern of variation of kinetic results, preferably those applying to a medium of high enough dielectric constant to transmit only a relatively small direct effect.

With the modifications described, we used the data and methods of Eyring.[15] Two general points emerged. One was that, across each carbon atom, the calculated inductive effect became attenuated by a factor of about 5, instead of the factor of about 3 which would have fitted our results much better (cf. Fig. 1). The second feature was that the fading of the effect at the remote ends of the alkyl groups was more rapid than our results require. Qualitatively, both these features would be expected from the neglect of the direct effect, which will always carry an appreciable fraction of the induction, that fraction rising, because of the difference between power-law and exponential fading, as the intramolecular path of induction lengthens.

The calculated reductions, caused by the alkyl residues attached to the β-carbon atom, of the positive charge q residing on the β-hydrogen atom, enabled us to compute work terms, representing the inductive effect of structure variation on the proton-extraction process, from the formula $-\Delta qe/r$, where e is the electronic charge, and r is the charge separation between the attacked hydrogen and the attacking alkoxide ion in the transition state. The uncertainty in r is not critical in this context: the H · · · O *charge*-separation is probably somewhat smaller than the internuclear separation, which however is somewhat larger in the transition state than in the normal bond; and so, in order to have a firm figure, we adopted the normal bond-length as our approximation for r. We took token

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* It could be derived by volume-integration from a sufficiently accurate and detailed electron-density map obtained by determination of the crystal structure of a suitable 'onium salt. No relevant structure determination of the required standard has yet been completed.

[14] Remick, *J. Chem. Phys.*, 1941, **9**, 653.

[15] Smith, Ree, Magee, and Eyring, *J. Amer. Chem. Soc.*, 1951, **73**, 2263; Smith and Eyring, *ibid.*, 1952, **74**, 229.

[16] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

[17] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 531.

account of the entropy term in the free energy, by allowing for the changes, between one alkyl group and another, in the number of β-hydrogen atoms, and thus we obtained the free-energy differences given in Table 6, where they are compared with the activation free-energy differences observed in ethanol, the medium having the higher dielectric constant of the two that we employed.

From these calculations it appears that we ought to expect the inductive effect to produce free-energy differences of the order of magnitude of those observed, and, except for the neohexyl group, according to the pattern of those observed.

TABLE 6. *Calculated alkyl inductive effects in 'onium ions on β-hydrogen charges and thence on free energies of activation of E2 eliminations; and comparison with observed free energies of activation in ethanol.*

	Alkyl·SMe_2^+			Alkyl·NMe_3^+		
	$10^3\Delta q/e$	$\Delta G^{\ddagger}$ (kcal./mole)		$10^3\Delta q/e$	$\Delta G^{\ddagger}$ (kcal./mole)	
Alkyl		Calc.	Obs.		Calc.	Obs.
Ethyl	0	0	0	0	0	0
n-Propyl	1·3	0·72	0·67	3·8	2·0	1·96
Isobutyl	2·5	1·60	1·38	7·4	3·4	2·81
n-Butyl	1·5	0·80	0·88	4·1	1·7	2·44
Isopentyl	1·6	0·83	1·06	4·3	1·8	3·12
Neohexyl	1·7	0·87	3·49	4·5	1·9	5·07

(6) *Application to Recorded Product Compositions.*—Many more 'onium eliminations have been studied with respect to product compositions than with respect to kinetics, and it would be a formidable task to cover kinetically all the significantly different examples for which data on products are recorded. It is therefore of interest to see how far the pattern of structural effects revealed by our limited kinetic study can interpret the existing large body of data on product compositions. To this end, we have surveyed the literature of the basic decompositions, for which product compositions have been recorded, of acyclic tetra-alkylammonium and trialkylsulphonium salts. We did not include cyclic 'onium salts because of the variety of special stereochemical conditions they involve. All the eliminations obey the Hofmann rule, with the generalisations and exceptions predicted by accepted polar theory. All the reactions may be safely assumed to proceed by the bimolecular mechanisms, S_N2 and $E2$. They are nearly all reactions, lacking kinetic control, of 'onium hydroxides, or in a few cases ethoxides (which behave very similarly to hydroxides), in very concentrated solutions, at undetermined temperatures considerably higher, particularly in the ammonium salt series, than would be used in a kinetic investigation; and in these conditions they give, especially in the ammonium series, enhanced proportions of olefin.

For ammonium hydroxides giving only one olefin, we have assumed that substitution occurs only at methyl, and for each methyl at a rate independent of the other alkyl groups. We have also assumed that, relatively to substitution, the rate of elimination is increased by a constant factor on going from our kinetic conditions to pyrolysis conditions. From the yield of propene from trimethyl-n-propylammonium hydroxide, we assess this factor as 24, and use it for all ammonium salts. The olefinic bond is assumed to enter the branches of an unsymmetrical secondary or tertiary alkyl group in the ratio of the rates applying to the comparable primary alkyl groups. The olefin proportions, thus calculated from the rate data of Table 3, are compared in Table 7 with the proportions recorded in the literature. For sulphonium hydroxides yielding a single olefin, the method of calculation was the same, except that the constant factor, assessed from the yield of ethylene from ethyldimethylsulphonium hydroxide, was 1·5, and the now appreciable substitution in the primary alkyl groups was taken as having a rate one-fifth of that of substitution in the methyl group. The olefin proportions, thus calculated from the rates of Table 1, are compared in Table 8 with the values available in the literature.

TABLE 7. *Proportions (%) of olefin from pyrolyses of* $RNMe_3^+OH^-$.

Ref.	R	Found	Calc.	Diff.	Ref.	R	Found	Calc.	Diff.
18, 19	Ethyl	95, 100	98	0	19	Isopentyl	72	62	−10
18, 19	n-Propyl	84, 81	(83)	(0)	11	Neohexyl	20	14	−6
7, 19, 20	n-Butyl	79, 77, 75	80	+3	18	2-Ethylbutyl	43	—†	—
19	n-Pentyl	77, 82	76*	−3	18	3-Propylpentyl	31	—†	—
19	n-Hexyl	76	76*	0	18	Isopropyl	100	100	0
19	n-Heptyl	74, 77	76*	0	18	s-Butyl	100	99	−1
19	n-Octyl	75	76*	+1	18	1-Methylbutyl	100	99	−1
20	n-Decyl	79	80	+1	7	1-Ethylpropyl	98	94	−4
20	n-Docosyl	82	76*	−6	21	1,2,2-Trimethylpropyl	100	100	0
19	Isobutyl	63	70	+7	18	t-Butyl	100	100	0

* Based on k_2 ($E2$) $= 2{\cdot}0 \times 10^{-5}$ sec.$^{-1}$ mol.$^{-1}$ l. for normal homologues higher than butyl under the conditions applying in Table 3.

† The rate data needed for these calculations are not available.

TABLE 8. *Proportions (%) of olefin from pyrolyses of* $RR'R''S^+OH^-$.

Ref.	R	R′	R″	Found	Calc.	Diff.
22	Ethyl	Methyl	Methyl	27	(27)	(0)
22	n-Propyl	Methyl	Methyl	8	10	+2
22	n-Butyl	Methyl	Methyl	4	8	+4
20*	n-Hexyl	Methyl	Methyl	19	~7	?*
20*	n-Decyl	Methyl	Methyl	21, 9*	~7	−2
22	Isobutyl	Methyl	Methyl	2	2	0
22	Isopropyl	Methyl	Methyl	63	81†	+18
22	t-Butyl	Methyl	Methyl	100	100†	0
23	Ethyl	Ethyl	Methyl	55	52	−3
23	Ethyl	Ethyl	Ethyl	86	80	−6
23	n-Propyl	n-Propyl	Methyl	18	27	+9
23	n-Propyl	n-Propyl	n-Propyl	36	57	+21
24	Isopropyl	Isopropyl	Isopropyl	100	100	0

* The second n-decyl figure under " Found " is the result of our revision of this experiment.

† Calculated with rate values already recorded (Hughes *et al.*, *J.*, 1948, 2077, 2084).

Many 'onium eliminations give mixtures, either of non-isomeric or of isomeric olefins, and this affords the opportunity to apply our rate-figures in the calculation, not only of olefin yields, but also of olefin compositions, including isomer ratios. The only additional assumption necessary is that, when different olefin-forming alkyl groups are present together in an ammonium or sulphonium ion, they will become olefinic in the ratio of the rates at which they would do so if each were the only olefin-forming group in its ammonium or sulphonium ion. The available experimental data for two series of ammonium ions, and the corresponding figures calculated from our rates, are given in Tables 9 and 10. A similar comparison for sulphonium ions is in Table 11.

Some of the few misfits in Tables 7—11, which contain all the relevant recorded data, may have experimental causes, as in the one case which, having on hand the material required, we took the opportunity to check (Table 8). Whatever may be the truth about the others, the general reproduction, from our rates by such a " peasant " calculation as this, of the considerable mass of existing observations on product composition, is sufficiently good to leave no doubt that the pattern of structural kinetic effects, which our necessarily limited kinetic investigation discloses, is indeed the pattern to which 'onium decompositions with strong bases as a whole conform.

(7) *First Subsidiary Experimental Investigation.*—Left over for discussion from the results of our main investigation was the " neohexyl anomaly." But before dealing with that, we must report, in order to allow consideration along with it, the results of two

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[18] Hanhart and Ingold, *J.*, 1927, 997.

[19] Ingold and Vass, *J.*, 1928, 3125.

[20] von Braun, Teuffert, and Weissbach, *Annalen*, 1929, **472**, 121.

[21] Stevens and Richmond, *J. Amer. Chem. Soc.*, 1941, **63**, 3132.

[22] Ingold, Jessop, Mandour, and Kuriyan, *J.*, 1933, 533.

[23] Ingold and Kuriyan, *J.*, 1933, 991.

[24] Gleave, Hughes, and Ingold, *J.*, 1935, 236.

TABLE 9. *Yields (%) of olefin, proportions (%) of lower homologues, and proportions (%) of alk-*1*-ene isomers, from pyrolyses of* RR′NMe$_2$$^+OH^-$.

		Yield:	Olefin		Lower homol. or 1-isomer		
Ref.	R	R′	Found	Calc.	Found	Calc.	Diff.
7	Ethyl	n-Propyl	96	99	98	93	−5
7	Ethyl	n-Butyl	98	99	98	96	−2
7	Ethyl	Isopropyl	94	100	41	30	−11
7	Ethyl	Isobutyl	95	98	99	98	−1
7	Ethyl	t-Butyl	91	100	7	4	−3
7	n-Propyl	n-Butyl	94	94	60	64	+4
7	n-Propyl	Isobutyl	94	94	73	75	+2
7	n-Propyl	Isopentyl	96	94	75	82	+7
7	n-Propyl	n-Decyl	95	93	60	65	+5
7	n-Butyl	Isobutyl	92	91	64 *	62 *	−2
11	n-Butyl	Isopentyl	83	89	66	72	+6
11	Isopentyl	Neohexyl	68	71	91	91	0
7	s-Butyl	Methyl	97	100	95	93	−2
25	1-Methylbutyl	Methyl	100	100	98	96	−2
26	t-Pentyl	Methyl	100	100	93	96	+3
26	1,1,3,3-Tetramethylbutyl	Methyl	100	100	100	100	0

* Proportion of but-1-ene.

TABLE 10. *Yields (%) of olefin, and proportions (%) of lower homologue from pyrolyses of* R$_2$R′R″N$^+$OH$^-$ (*ref.* 11).

		Yield:	Olefin		Lower homologue		
R	R′	R″	Found	Calc.	Found	Calc.	Diff.
Ethyl	n-Propyl	n-Propyl	99	100	96	93	−1
n-Propyl	n-Butyl	n-Butyl	95	100	62	64	+2
n-Propyl	Isopentyl	Isopentyl	94	100	96	82	−14
n-Butyl	Isopentyl	Isopentyl	94	100	67	72	+5
n-Propyl	n-Propyl	n-Butyl	93	100	83	84	+1
n-Butyl	n-Butyl	n-Propyl	98	100	64	62	−2

TABLE 11. *Proportions (%) of lower homologues and proportions (%) of alk-*1*-ene isomers from pyrolyses of* RR′R″S$^+$OH$^-$.

Ref.	R	R′	R″	Found	Calc.	Diff.
22	Ethyl	Ethyl	n-Propyl	85	85	0
22	Ethyl	n-Propyl	Methyl	80	73	−7
22	Ethyl	n-Propyl	n-Propyl	63	60	−3
22	Ethyl	Isopropyl	Methyl	25	7	−18
22	Ethyl	Isobutyl	Methyl	93	90	−3
22	Ethyl	Isobutyl	Isobutyl	94	80	−14
22	n-Propyl	n-Propyl	n-Butyl	74	73	−1
22	n-Propyl	n-Butyl	n-Butyl	40	40	0
22	Isopropyl	Isobutyl	Methyl	94	99	+5
27 *	s-Butyl	Methyl	Methyl	73	73	0
25	1-Methylbutyl	Methyl	Methyl	87	80	−7
27 *	t-Pentyl	Methyl	Methyl	86	85	−1

* Kinetically controlled decompositions of ethoxides.

further series of kinetic studies. They were undertaken as a contribution to the general question which the neohexyl anomaly raises, namely, that of at what stage of progressive alkyl ramification should, and does, steric hindrance enter to disturb the normal pattern of control of elimination.

The four series of ’onium salts whose kinetic study comprised our main investigation developed progressive branching and extension from the β-carbon atom of the alkyl chain, the α-carbon remaining secondary throughout. We now wanted to study alkyl branching and extension from the α- and β-atoms, simultaneously and not in quite the simplest cases.

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[25] Brown and Wheeler, *J. Amer. Chem. Soc.*, 1956, **78**, 2199.

[26] Brown and Moritani, *J. Amer. Chem. Soc.*, 1956, **78**, 2203.

[27] Hughes, Ingold, Maw, and Woolf, *J.*, 1948, 2077; Hughes, Ingold, and Woolf, *J.*, 1948, 2084.

With these terms of reference it is less easy to avoid all structures in which the intervention of forces of synartesis, or of hyperconjugation related to fragmentation, might come into question; but it can be done within the prescription of the alkyl series,

$$(5)\quad \mathrm{CHRR'{\cdot}CHR''{\cdot}NMe_3^+ + EtO^-\ in\ EtOH}$$

provided that R and R′ are hydrogen or methyl, R″ being allowed unrestricted homologous development with branching up to t-butyl.

For comparisons we wanted to make with series (3), we imposed on series (5) the further condition that the alkyl groups should each yield only one olefin. Six alkyl groups fulfil these conditions, but, of them, two, the isopropyl and the 1-ethylpropyl group were too simple to be interesting in this part of our enquiry. The remaining groups are those in the ammonium ions listed in Table 12, where we record the overall second-order rate constants, the olefin proportions, and the separated second-order rate constants of substitution and elimination.

TABLE 12. *Second-order rate constants* (k_2 *in* sec.$^{-1}$ mole^{-1} l.) *and olefin proportions* (%) *in reactions of* $\mathrm{CHRR'{\cdot}CHR''{\cdot}NMe_3^+}$ *with* $\mathrm{EtO^-}$ *in* EtOH *at* 100·60° (*series* 5).

Ammonium ion	10^5k_2	Olefin	10^5k_2 (S_N2)	10^5k_2 ($E2$)
$\mathrm{CH_3{\cdot}CHBu^t{\cdot}NMe_3^+}$	227	53·3	105	122
$\mathrm{CH_2Me{\cdot}CHBu^t{\cdot}NMe_3^+}$	127	9·3	116	11·8
$\mathrm{CHMe_2{\cdot}CHBu^t{\cdot}NMe_3^+}$	289	1·9	283	5·5
$\mathrm{CHMe_2{\cdot}CHPr^i{\cdot}NMe_3^+}$	273	20·1	218	54·6

(8) *Second Subsidiary Experimental Investigation.*—The object of this series of experiments was to check the explanation we shall offer of the neohexyl anomaly, by finding out what happens to it in the presence of an α-phenyl substituent, which has a predictable effect on the polar and steric situation, and might have a dramatic effect on the anomaly. The series studied was:

$$(6)\quad \mathrm{CH_2R{\cdot}CHPh{\cdot}SMe_2^+ + EtO^-\ in\ EtOH}$$

where R is allowed homologous development with branching up to t-butyl. The series actually investigated is short of one member, but it is complete enough to provide the background needed to appreciate the result of main interest, *viz.*, that given by the α-phenylneohexyl salt. Our overall rate constants, the olefin proportions, and the dissected rate constants of substitution and elimination, are given in Table 13.

TABLE 13. *Second-order rate constants* (k_2 *in* sec.$^{-1}$ mole^{-1} l.), *proportions of the total reaction which lead to olefin, and proportions of the total substitution which are sited in the α-phenylated alkyl groups of* $\mathrm{CH_2R{\cdot}CHPh{\cdot}SMe_2^+}$ *in its reactions with* $\mathrm{EtO^-}$ *in* EtOH *at* 34·87° (*series* 6).

Alk in $\mathrm{AlkSMe_2^+}$	10^5k_2	Olefin (%)	Subn. in Alk (%)	10^5k_2 (S_N2 in Alk)	10^5k_2 (S_N2 in Me)	10^5k_2 ($E2$)
$\mathrm{CH_3{\cdot}CHPh}$–	248	63·8	84	76	15	158
$\mathrm{CH_2Me{\cdot}CHPh}$–	124	32·2	59	50	35	40
$\mathrm{CH_2Pr^i{\cdot}CHPh}$–	180	28·0	36	47	83	50
$\mathrm{CH_2Bu^t{\cdot}CHPh}$–	559	22·0	13	56	380	123

Substitution in alkyldimethylsulphonium salts usually occurs mainly in the methyl groups, but the α-phenyl substituent in the alkyl groups of series (6) evidently attracts the seat of substitution to the phenyl-bearing position. Substitution predominates in this position in the simpler members of series (6), but sinks again to secondary importance in the higher homologues of the series.

(9) *General Consideration of Steric Effects.*—We consider as steric effects those kinetic effects which are thought to arise from differences of interpenetration pressures, theoretically ascribed to antibonding exchanges of paired electrons, in the transition and initial states of reaction. The major pressures are usually those of bimolecular transition states. We assume that the $E2$ transition state tends to an *anti*-conformation

of the bonds being broken. We do not know how deep is the torsional energy hollow in which the *anti*-conformation lies, but, judging from some figures which concern bimolecular elimination in ring compounds [28] and suggest that a twist of 60° raises the activation energy by 5—8 kcal./mole, we suppose that a twist of 10° would not produce a noticeable energy effect, whereas twists of 20° or more probably would do so.

However, even a strict *anti*-conformation does not define the geometry of all the bonds about the developing double bond in the transition state. One reason for this is that it is not a requirement of any concerted process of reaction that all the bond-changes must at all times keep exactly in pace with one another. We know that, in S_N2 substitutions, electron import and export by the reaction site, even though this is concentrated on one atom, do not exactly balance in the transition state, the lack of balance being the reason why that reaction is subject to inductive polar influences. In *E*2 eliminations, the reaction site spreads over several atoms, and so it is even easier here, as Saunders and others have already noted,[29,30] for one of the correlated bond changes to have run ahead of another by the time that the transition state is reached, though the bond changes are still concerted in the sense that neither could continue without the other, as, indeed, we know from the experimental evidence of second-order kinetics, combined with an absence of prior hydrogen exchange.[30,31] Hence, depending on which bond change makes the more progress initially, the transition state may " lean " from the strictly synchronous form *B* in Fig. 2, either towards an *E*1c*B*-like form *A*, or towards an *E*1-like form *C*, all without losing its *E*2 classification. These variations of form will arise from polar influences. Hofmann-type elimination, implying, as it does, acidic β-hydrogen, will correspond to *A*-type deviation. Saytzeff-type control of elimination implies strong unsaturation, either as in *B*, or with *C*-type deviation. The best double-bond, and the flattest structure, will arise when the concerted bond changes are strictly synchronous, as in *B*.

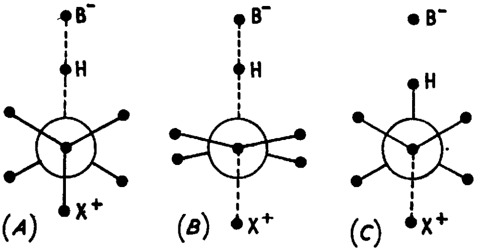

FIG. 2. *Forms of E2 transition state.*
(*A*) *Towards* E1c*B*
(*B*) *Synchronous*
(*C*) *Towards E*1

We can expect the *E*2 transition states of the Hofmann-rule-controlled reactions of 'onium salts to be generally within the range *A*-to-*B*; but there should be differences, according to the type of salt and the solvent. Form *A* should be more closely approached by ammonium than by sulphonium salts, because of the stronger polarity, and hence the stronger acidifying effect of the ammonium than of the sulphonium pole. For a given type of 'onium ion, ammonium or sulphonium, form *B* should be approached more closely in the less polar t-butyl alcohol as solvent than in the more polar ethanol; for it is *lack* of an adequate ion-solvation that promotes separation of the X^+ group. Thus, the reactions in series (3) and (5) of ammonium salts in ethanol should have transition states most like *A*, whilst the reactions of series (2) of sulphonium salts in t-butyl alcohol should have them most like *B*.

Six types of steric compression are conceivable in *E*2 reactions of the system $B^- +$ $H{-}C_{\beta}R_{\beta}R_{\beta}{-}C_{\alpha}R_{\alpha}R_{\alpha}{-}X^+$, supposing that no limit is imposed on constitutional complexity.

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[28] Cristol and Hause, *J. Amer. Chem. Soc.*, 1952, **74**, 2193; cf. Cristol, Hause, and Meek, *ibid.*, 1951, **73**, 674; Hughes, Ingold, and Pasternak, *J.*, 1953, 3832.

[29] Cram, Green, and DePuy, *J. Amer. Chem. Soc.*, 1956, **78**, 790; Saunders and Ašperger, *ibid.*, 1957, **79**, 1612; Saunders and Williams, *ibid.*, p. 3712.

[30] Skell and Hauser, *J. Amer. Chem. Soc.*, 1945, **67**, 1661.

[31] Shiner and Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 4095; Saunders and Edison, *ibid.*, 1960, **82**, 138.

Three of them, (I)—(III) below, involve non-bonding interactions between the base and the cation. The other three, (IV)—(VI), are internal to the cation, and one, (VI), is internal to the alkyl group itself:

(I) $B^- \cdots\cdots R_\beta$ (II) $B^- \cdots\cdots R_\alpha$ (III) $B^- \cdots\cdots X^+$

(IV) $X^+ \cdots\cdots R_\beta$ (V) $X^+ \cdots\cdots R_\alpha$ (VI) $R_\beta \cdots\cdots R_\alpha$

Each of these possible compressions has to be considered, not only in the initial state of the reacting system, but also in its possible transition states within the range *A–B*. We used rigid models in order to make a preliminary study of the various geometrical situations. But we knew, from previous work of this type,[32] that if, thereafter, we would calculate compression energies, without relaxing the condition of rigidity, the results obtained could only be upper limits to the real steric energies, and, where compression is considerable, might well be meaninglessly high upper limits.

(10) *Absence of Non-bonding Compressions Involving the Base.*—A study, on the lines indicated, of the geometrical situations relevant to the three possible steric interactions (I)—(III) involving the base B^-, showed immediately that no interpenetrations of any kind involving B^- can occur in any initial or transition state, for any base B^- up to at least the size and degree of branching of the t-butoxide ion, for any R_β or R_α group up to at least the size and degree of branching of the t-butyl group, and for either of the X^+ groups used, trimethylammonium and dimethylsulphonium. The calculated clearances were wide, and we formed the impression that it would require " gargoyle " molecules to produce compressions of any of the types (I)—(III).

Compressions of type (I) correspond to Brown's *F*-strain, which he regards as an important orienting influence. Contrary to him, we conclude that *F*-strain does not exist, and indeed, that no steric strains at all involving the base B^- exist, up to, and for some way beyond, the level of constitutional complexity specified in the preceding paragraph.

(11) *The Neohexyl Anomaly.*—It is from steric interactions of type (IV), *i.e.*, between X^+ and R_β, that we expect the lowest threshold of structural complication at which steric effects may enter. In our experiments of series (1)—(4), the pole X^+ was either trimethylammonium or dimethylsulphonium, while the residue R_β ran through the branching homologous series from hydrogen to t-butyl. On examining the geometry of the initial and the two types of transition states of the *E*2 reactions of the ten cations involved, we found that none of them should exhibit any energetic effect due to compressions of type (IV), excepting certain transition states in which R_β has reached its limit in t-butyl, the whole alkyl group then being neohexyl. We can accordingly restrict further discussion of compressions of type (IV) to *E*2 reactions of the neohexyl cations.

Both trimethylneohexylammonium and dimethylneohexylsulphonium ions have compression-free conformations, and thus the initial states of their *E*2 reactions involve no compression. However, their type-*A* transition states involve substantial type-(IV) compressions. By methods elsewhere illustrated,[32] we calculated for the transition state of the trimethylneohexylammonium ion a rigid-model compression energy of 4·5 kcal./mole, and for that of the dimethylneohexylsulphonium ion one of 6·5 kcal./mole, with the assumption, in the latter case, that the sulphur-bound methyl groups, rather than the unshared valency electrons of the sulphonium group, are turned towards the β-t-butyl residue. However, these rigid-model figures can be regarded only as unrealistically high upper limits to the actual steric energy, because the transition states have several degrees of freedom sensitive enough to yield before such potentials. If, as an approximation, we suppose all the yielding to be done by the most sensitive of such degrees of freedom, conformational rotation about the C_α–C_β bond, we can calculate the angles of rotation that would eliminate the calculated compressions, so replacing the compression energies by considerably smaller torsional energies. We cannot do what we should do, minimise

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[32] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

the compressional-plus-torsional energy, and so the calculated angles will again be upper limits, but considerably closer ones, if the torsional energy function is, as we suppose, substantially less steep than the compressional one. The calculated angles are 24° for the ammonium ion, and 30° for the sulphonium ion.

Our experimental results for the *E*2 reactions of these two neohexyl ions suggest (cf. Table 5, and Fig. 1) steric energies of about 1·4 kcal./mole for the ammonium ion in either the ethoxide–ethanol or the t-butoxide–t-butyl alcohol base–solvent system (series 3 and 4), and about 2·2 kcal./mole for the sulphonium ion in the ethoxide–ethanol system (series 1). These two energies are about in proportion to the squares of the calculated angles. If we assume that this quadratic relation is the limit for low angles of a versed-sine function applicable up to 60°, the energy for that angle would be 8 kcal./mole, consistently with the rough estimate of that quantity mentioned in Section 9.

We have still to consider what would be the position if the neohexyl transition states conformed to model *B*. If we start from model *A*, at first retain the R groups where that model puts them, and lengthen the C–X^+ bond by 17% as a first step in changing over to model *B*, then the twists required to eliminate compression become reduced to 10° for the ammonium ion, and 14° for the sulphonium ion. According to the energy relations just mentioned, these angles would correspond to steric energies of 0·3 kcal./mole for the ammonium ion, and 0·5 kcal./mole for the sulphonium ion. And even these small energies disappear, if, in model B, we reduce the angle between those planes of C–R bonds which meet along the C_α–C_β line from 60° to 40° and 32° in the respective cases. Obviously a transition-state model similar to *A* is needed in order to rationalise the experimental results mentioned.

This conclusion leads to one of two possible reasons we can suggest for the striking result that the neohexyl anomaly disappears uniquely in the sulphonium t-butoxide of series (2). For in that series we have, in conjunction, the less electronegative sulphonium pole, and the less solvating t-butyl alcohol as solvent: in that series, more than in any other, the transition state should approach model *B*.

Our other suggestion is based on the idea that, because of its unshared valency electrons, the dimethylsulphonium pole becomes solvated predominantly in their locality. In a strongly solvating solvent, such as the ethanol, of the reactions of series (1), the local solvation may force together, somewhat as in the formation of an oil-drop in water, the more weakly solvated hydrocarbon residues, and may thus secure that the methyl groups, rather than the unshared electrons of the sulphonium pole, are presented to the β-t-butyl residue of the neohexyl group, even though, if our interpretations are correct, the cost in steric energy may be 2·2 kcal./mole. But in a weakly solvating solvent, such as the t-butyl alcohol of the reaction of series (2), desolvation may be easy enough to allow the dimethylsulphonium group to turn its unshared electrons to the β-t-butyl residue, where, on any reasonable estimate of their van der Waals extension, there would be plenty of room for them.

(12) *Search for the Next Higher Thresholds for Steric Hindrance.*—We proceed next to consider possible steric interactions, of type (V), between X^+ and R_α. It is immediately obvious that the geometrical problem is similar for initial states, and for transition states of type *A*, and so it is convenient to deal with these first. Our series 5, the work on which is summarised in Section 7, comprised α-branched alkyltrimethylammonium ethoxides, and is concerned with this problem; and it will suffice to consider the most involved structural situation that that series presents, namely, the one with X^+ as the trimethylammonium group and R_α as the t-butyl residue. Both in the initial state, and in the type-*A* transition state, we find small compressions; but the corresponding upper-limiting compression energies, calculated as before on the rigid model, amount only to about 0·1 kcal./mole. This in itself is negligible, and the smaller but uncertain value of the real energy is in any case irrelevant, because it is the same in both states and so contributes nothing to the activation energy. In order to make a corresponding calculation

for a transition state of type *B*, we assumed that the C–X$^+$ bond is there stretched by 17%, and that the angle between those planes of C–R bonds which intersect along the C_α–C_β line is reduced to 20°. The rigid-model compression energy again came to 0·1 kcal./mole, and so, once more, no contribution to the activation energy is furnished. We might be tempted here to conclude that the threshold for steric interactions of type (V) lies above the limits of structural complexity with which we have been concerned. However, some uncertainty would affect such a conclusion. For we have made no allowance for a solvation volume around X$^+$: if we should have done so, and if also either the C–X$^+$ bond-length or the X$^+$CR$_\alpha$ bond-angle is changed on going from the initial to the transition state, then, depending on the balance of these geometrical changes, an energetic effect, *in either direction*, due to X$^+$ · · · R$_\alpha$ interaction, would be possible, and we could observe either an acceleration or a retardation. This was one of two reasons which led us to investigate series (5), as recorded in Section 7.

Steric pressures of type (V) in the transition state are classified by Brown as *B*-strain. This he regards as a general cause of Hofmann-type orientation in 'onium eliminations. As has been mentioned, we have designed an experimental test of *B*-strain, between the X$^+$ group trimethylammonium, which Brown regards as the most space-demanding of all that he considered, and a much more space-demanding R$_\alpha$ group, t-butyl, than any that he examined in conjunction with it. But before reviewing our experimental results, we must refer to one more item of theory.

This concerns possible steric interactions of type (VI), *i.e.*, within the alkyl group, between residues R$_\alpha$ and R$_\beta$ destined for *cis*-positions in the olefin. To get evidence on this point was our second reason for investigating series (5). Again it will suffice theoretically to discuss only the most involved structural situation in that series, that in which the R groups are t-butyl and methyl. Our study of the geometry of this case revealed no type (VI) compressions, either in the initial state or in a transition state of type *A*. In some transition states of type *B*, depending on their precise geometry, we found compressions, leading to small rigid-model compression energies, but only well towards the limit in which the angle between the C–R planes intersecting along C_α–C_β is reduced to zero, and the C_α–C_β bond is shortened to its double-bond value. These calculations made it clear that in no transition state plausibly applicable to our case would any appreciable steric energy arise owing to compressions of type (VI) between the R groups t-butyl and methyl.

Our steric energy of type (VI) is Brown's *I*-strain. He has invoked it in five of the eleven papers already cited,[5] notably for R$_\alpha$ · · · R$_\beta$ interaction between t-butyl and methyl, which represents equally the limit of alkyl complexity to which he went. In view of this emphasis, we thought we should check experimentally our theoretical conclusion that such strain does not exist within the range of our work. This has been done in the experiments summarised in Section 7, the results of which we can now review.

The experiments dealt with the alkyltrimethylammonium ethoxides of series (5), which parallel some of those of series (3), with the difference that, in series (5), an α-t-butyl or an α-isopropyl group replaces α-hydrogen. The *E*2 rates of corresponding members of the two series are compared in Table 14. At the top of the Table, rates in the two series are linked through the measured rate-constants of the parents of the series. Below that, relative rates are given for each series, with its parent as the rate-standard, so that the effects of homology in the two series can easily be compared.

The ratio of the reaction rates of the parents would be about 3 at a common temperature. The smallness of this difference is remarkable, considering the great structural contrast between the simple C$_2$ alkyl group and the maximally branched C$_6$ alkyl group. This general similarity of rates in the two series persists over comparisons 1—3, which make it clear that the t-butyl α-branch has only a small kinetic effect. Any α-branch should have only a small inductive effect on the β-proton. Any α-alkyl branch possessing suitably situated hydrogen atoms could have a considerable hyperconjugative effect on

TABLE 14. *Elimination rate-constants (k_{E2} in sec.$^{-1}$ mole^{-1} l.) and relative rates for alkyltrimethylammonium ethoxides in ethanol: kinetic effects of α-branches, and of β-homology in the presence and absence of α-branches in the alkyl group.*

	Alkyl	10^5k_{E2} (100·6°)	Alkyl	10^5k_{E2} (104·2°)
	$CH_3{\cdot}CHBu^t$–	122	$CH_3{\cdot}CH_2$–	71
		Rel. rate		Rel. rate
1	$CH_3{\cdot}CHBu^t$–	100	$CH_3{\cdot}CH_2$–	100
2	$CH_3{\cdot}CH_2{\cdot}CHBu^t$–	9·7	$CH_3{\cdot}CH_2{\cdot}CH_2$–	7·2
3	$(CH_3)_2CH{\cdot}CHBu^t$–	4·5	$(CH_3)_2CH{\cdot}CH_2$–	2·4
4	$(CH_3)_2CH{\cdot}CHPr^i$–	22·4 *	$(CH_3)_2CH{\cdot}CH_2$–	2·4

* Half of the observed rate, because the structure provides two equivalent positions for the olefinic double bond.

the developing αβ-unsaturation; but the t-butyl group has no such hydrogen atom. However, when we drop back from a t-butyl to an isopropyl α-branch, so admitting one such hydrogen atom, as in comparison 4, then the rate is raised by a power of ten.

The small kinetic effect of the t-butyl α-branch is accelerating. The small inductive effect allowed to any α-alkyl branch should be retarding. Hence, either the effect is due to some hitherto unrecognised interaction, or it is a steric acceleration of our type (V), arising, as discussed above, from the relaxation of a restriction, caused by the t-butyl α-branch on solvation of the ammonium pole, as the system changes shape on approaching the transition state. If the effect on solvation of a stretching of the $C{-}X^+$ bond dominated that of any contraction of the $R_\alpha C_\alpha X^+$ bond-angle, then the kinetic effect would be an acceleration.

It would be the negative of Brown's *B*-strain. He requires steric retardation in order that *B*-strain shall explain why 'onium eliminations favour the Hofmann rule. He requires such retardation quite generally, down to much simpler structures than our α-t-butyl substituted ones. Our experiments show that the required steric retardations do not exist, because in the structurally extreme cases in which we have looked for them, we find only a small kinetic effect in the wrong direction.

Finally, we have evidence in Table 14 on the question of steric interactions of type (VI) internal to the alkyl group. For comparisons 1—3 show that variations of rate with β-homology follow the same pattern, whether the t-butyl α-branch is there or not. And this is still true in comparison 3, in which, in series (5), one of the β-bound methyl groups must take a *cis*-position relatively to the α-bound t-butyl group: in spite of that, the α-branched salt of series (5) exhibits a rate at least as good as that of its non-α-branched counterpart of series (3). Therefore, as we deduced theoretically, steric inhibition of type (VI) does not exist in 'onium eliminations, up to the limits of branching density to which our investigation extends.

The conclusion is involved that Brown's *I*-strain does not exist in this form either in his examples or ours; for by using a trimethylammonium ion, we have carried into our limiting example a greater overall concentration of space-demands belonging to one side of the developing double bond, than any present in his examples. Our former diagnosis [4] of his constitutional condition that evoked *I*-strain, *viz.*, hyperconjugation related to a known pattern of fragmentation, is thus indirectly supported.

(13) *Suppression of the Neohexyl Anomaly.*—Since the anomalous rate repression in reactions of neohexyl 'onium salts, if we have explained it correctly, constitutes our most authentic steric effect, it seemed desirable to apply a further check to the explanation. A means to do so was found as follows.

The steric explanation assumes an $R_\beta \cdots X^+$ interpenetration of type (IV) (p. 4068) in a transition state of type *A* (Fig. 2, p. 4067). Therefore, the anomalous rate repression should be reduced, and might be eliminated, if we can set up a flatter transition state, one more of type *B*, so increasing the $R_\beta \cdots X^+$ clearance and releasing compression energy from the transition state. We can indeed arrange for such flatter transition states by introducing at the α-position an unsaturated substituent, such as α-phenyl, to conjugate strongly with the developing $C_\alpha=C_\beta$ double bond. This is the significance of our series (6), and of the experiments thereon summarised in Section 8. Our task was to seek the neohexyl anomaly in a series of α-phenyl-substituted ethyl, n-propyl (n-butyl was omitted), isopentyl, and neohexyl 'onium salts of a kind for which the neohexyl anomaly is prominent in the absence of the phenyl substituent.

As routine, the effect of the α-phenyl substituent in the initial state had also to be thought about; and that was more than a formality in this case. For whereas, in a non-α-substituted alkyl 'onium ion, β-bound residue in the complete alkyl group is free in the initial state to take up an *anti*-conformation relatively to the 'onium group, in an α-phenylated ion, a β-bound residue, especially a large one such as the β-t-butyl residue of an α-phenylneohexyl group, will have to " choose " whether to assume an *anti*-conformation relatively to the 'onium group and hence a *syn*- with respect to the phenyl residue, or to take an *anti*-conformation to the phenyl residue and hence a *syn*- to the 'onium group. A study of models suggests that an *anti*-conformation relatively to phenyl will be preferred. But (as can be followed from diagram *A* of Fig. 2, because much of a type-*A* transition state is geometrically similar to an initial state) this conformation will involve an interpenetration $R_\beta \cdots X^+$ of type (IV). Except that it is now in an initial state, this compression is similar to that which was calculated (Section 11) for type-*A* transition states involving simple neohexyl 'onium salts, *i.e.*, without an α-phenyl substituent, as, *e.g.*, in series (1). The compression in the α-phenylated 'onium salt, being in an initial state, should be accelerating. The rigid-model compression energy will, of course, be largely replaced by a smaller energy of torsional deformation in the real initial state. Probably resistance to torsion is smaller in an initial than in a transition state; and thus the resulting kinetic effect might be quite mild.

A glance at Table **13** (p. 4067) will show that our results fulfil all these expectations. The α-phenylated series (6) exhibits elimination rates, which, as β-homology develops, start by showing the usual Hofmann-type retardation. But this does not persist, and the last member of the series, instead of showing an excessive retardation compared to the preceding member, as by the factor of 37 displayed by its counterpart of series (1), exhibits a mild acceleration, actually by a factor of 2·5. Thus, the original neohexyl anomaly is not only cancelled, but is mildly reversed by the α-phenyl substituent. We ascribe the cancellation to the effect of the substituent in flattening the transition state, and the reversal to its effect on the initial state. Consistently with this second proposal, the α-phenylneohexyl example uniquely exhibits (Table 13) a rise of rate in *all three* of its concurrent reactions: a factor of instability in their common initial state is thus indicated, for their transition states are all quite different.

One general conclusion emerges from these results. They confirm the view that steric hindrance is inessential to the general picture of olefin eliminations. When, by good organisation or chance, one gets it, one can, as has been illustrated, very easily lose it, as by a change of solvent, or by an elaboration of structure, or, of course, by a simplification of structure.

(14) *Summary of Main Conclusions.*—It is an unsatisfactory feature of most analyses of structural causes of kinetic effects that, besides the generally strong forces of electropolarity and unsaturation, and the occasionally strong forces of steric repulsion at short range, there must exist between the parts of a reacting system, weaker, but longer-range, and hence more or less general forces, of which it seems very difficult to take account, *e.g.*. quadrupole, and various forms of electron-correlation forces. One knows, in particular, that intervalency forces exist in ethane, which can have nothing to do with group interpenetration and must be general to alkane structures. Some of the irregularities noticeable in most systematic kinetic data may have such causes, but, because every comparison one makes is a second-difference involving four states, minor effects are very difficult to identify

convincingly in the presence of major ones. It is for that reason, not because we have overlooked expected minor effects, that we have confined our interpretations in this paper to the main factors recognised.

Our general conclusions are as follows. The inductive and electromeric effects dominate the picture of eliminations down to the simplest examples of Hofmann and Saytzeff. These two polar effects belong to that picture in principle, creating its familiar kinetic and orientational pattern. Steric hindrance is inessential to that pattern. It enters as a complication, in certain critical situations above determinable thresholds of molecular complexity, as we should expect from its short-range nature. It is not a viable idea to replace the inductive effect by the steric effect in explanation of the kinetic and orientational pattern of eliminations as a whole.

EXPERIMENTAL

Preparation of Materials

(a) *Alkyldimethylsulphonium Salts.—General.* Previous work having shown that the reaction between dimethyl sulphide and alkyl iodides gives largely trimethylsulphonium iodide, the salts we required were prepared through the appropriate thiol by methylation in two stages. All the salts were white, insoluble in ether, but very soluble in water, and often deliquescent or hygroscopic. They became yellow on exposure to light if not absolutely dry, but were stable in a vacuum over phosphoric oxide, excepting the 1-phenyl-substituted salts, which decomposed during some months even in these conditions.

Ethyldimethylsulphonium iodide. Ethyl methyl sulphide (53 g.) and methyl iodide (100 g.) were mixed in nitromethane (90 ml.) at room temperature. After 1 hr. the crystalline salt was collected under dry nitrogen, washed with ether, and repeatedly precipitated from solution in ethanol with ether; it had m. p. 108° (decomp.; sealed tube) (Found: I, 58·3. Calc. for $C_4H_{11}SI$: I, 58·3%).

Dimethyl-n-propylsulphonium iodide. Propane-1-thiol (50 g.) was converted with ethanolic sodium ethoxide [from sodium (15 g.) and ethanol (280 ml.)] followed by methyl iodide (94 g.) into methyl n-propyl sulphide, which, extracted with ether, had b. p. 94—95° (38 g., 65%). It was mixed with methyl iodide (63 g.) in nitromethane (80 ml.). The next day, precipitation of the sulphonium salt was completed by adding ether, and salt was collected and purified as described above (m. p. 58—59°; sealed evacuated tube) (Found: I, 54·7. Calc. for $C_5H_{13}IS$: I, 54·7%).

n-Butyldimethylsulphonium salts. n-Butyl bromide (102 g.) was refluxed with a solution of thiourea (76 g.) in water (50 ml.) for 5 hr., and the thiouronium salt formed was boiled with 10% aqueous sodium hydroxide (600 ml.) for 2 hr. The thiol, extracted with ether after acidification and dried therein, had b. p. 97—98° (39 g., 59%), and was methylated with methyl iodide (56 g.) in ethanolic sodium ethoxide (10 g. of sodium) to give n-butyl methyl sulphide, b. p. 124—125° (27 g., 65%), which in turn was methylated with methyl iodide (40 g.) in nitromethane (60 ml.) to give the sulphonium iodide (60%), which, isolated and purified as described above, had m. p. 81° (Found: I, 51·7. Calc. for $C_6H_{15}IS$: I, 51·6%). The *picrate*, crystallised from water, had m. p. 51° (Found: C, 41·9; H, 5·3. $C_{12}H_{17}N_3O_7S$ requires C, 41·5; H, 5·2%).

Isobutyldimethylsulphonium iodide. 2-Methylpropane-1-thiol (b. p. 88—90°) was prepared (32 g., 70%) from isobutyl bromide (62 g.) and thiourea (38 g.), and then isobutyl methyl sulphide (b. p. 116°) was prepared (28 g., 83%) from it with the aid of sodium (7 g.), ethanol (100 ml.) and methyl iodide (47 g.). From this, by reaction for 2 days at room temperature with methyl iodide (35 g.) in nitromethane (40 ml.), the sulphonium iodide was formed (70%), and then was isolated and purified as described above (m. p. 91°, decomp.) (Found: I, 51·5. Calc. for $C_6H_{15}IS$: I, 51·6%).

Isopentyldimethylsulphonium salts. Isopentyl bromide (170 g.), which was shown by vapour-phase chromatography to contain less than 2% of the tertiary isomer, was converted, with thiourea (95 g.) in water (55 ml.), into a thiouronium salt, which, on alkaline hydrolysis gave 3-methylbutane-1-thiol (63 g., 56%), b. p. 116—118°, n_D^{25} 1·4412. This was methylated, with the aid of sodium (15 g.), ethanol (200 ml.), and methyl iodide (90 g.), to the methyl sulphide (51 g., 71%), b. p. 136—137°, which was further methylated, as described in the preceding paragraph, to give *dimethyl-3-methylbutylsulphonium iodide* (60%), m. p. 106° (Found:

I, 48·8. $C_7H_{17}IS$ requires I, 48·8%), from which the *picrate*, m. p. 96°, was prepared (Found: C, 43·4; H, 5·7. $C_{13}H_{19}N_3O_7S$ requires C, 43·1; H, 5·5%).

3,3-*Dimethylbutyldimethylsulphonium salts*. 1-Bromo-3,3-dimethylbutane (neohexyl bromide) was prepared [33] by passing ethylene into a stirred mixture of t-butyl bromide (200 g.), powdered aluminium chloride (60 g.), and pentane (80 ml.) at −45°. Fractionation of the washed and dried product gave a head fraction (5 g.) of 1-chloro-3,3-dimethylbutane, and a main fraction (198 g., 85%) of 1-bromo-3,3-dimethylbutane, b. p. 64·3—65·0°/70 mm., n_D^{25} 1·4413 (Found: C, 44·1; H, 8·1; Br, 48·5. Calc. for $C_6H_{13}Br$: C, 43·7; H, 7·9; Br, 48·5%). 3,3-*Dimethylbutane*-1-*thiol*, prepared by refluxing this bromide (93 g.) with thiourea (65 g.) in water (100 ml.) and hydrolysis of the formed thiouronium salt in boiling 10% aqueous sodium hydroxide, underwent cracking on attempted distillation at 20 mm., and was distilled at room temperature under 2 mm., as a clear liquid (48 g., 70%), n_D^{25} 1·3347 (Found: S, 26·8. $C_6H_{14}S$ requires S, 27·1%). This thiol (45 g.), on treatment with sodium ethoxide (8 g. sodium) and methyl iodide (48 g.) in ethanol, gave the 3,3-*dimethylbutylmethyl sulphide* (36 g., 67%), b. p. 154—156°, n_D^{25} 1·4488 (Found: S, 24·3. $C_7H_{16}S$ requires S, 24·2%). A solution of this sulphide (36 g.) and methyl iodide (40 g.) in nitromethane (50 ml.) at room temperature gave within 1 hr. a crystalline mass of 3,3-*dimethylbutyldimethylsulphonium iodide*, which, crystallised from ethanol–ether, had m. p. 165—166° (decomp.) (Found: I, 46·4. $C_8H_{19}IS$ requires I, 46·3%). The *picrate* had m. p. 130° (Found: C, 44·9; H, 5·8. $C_{14}H_{21}N_3O_7S$ requires C, 44·8; H, 5·6%). The low olefin yields obtained in reactions of this cation made it important to be sure that the iodide was pure. Thorough purification was practised, and, to test purity, the salt was chromatographed on Amberlite IR-120 resin, and on paper. No impurities were found.

Dimethyl-1-*phenylethylsulphonium iodide*. 1-Phenylethanol, prepared from bromobenzene and acetaldehyde by the Grignard method, b. p. 104—105°/21 mm., was converted by means of concentrated hydrochloric acid into 1-phenylethyl chloride, b. p. 79—80°/20 mm. (Found: Cl, 25·0. Calc. for C_8H_9Cl: Cl, 25·2%), and through this (200 g.), by the thiourea method, into the thiol (162 g., 76%), b. p. 90—91°/17 mm., which, on treatment (50 g.) with ethanolic sodium ethoxide (9 g. of sodium) and methyl iodide (50 g.) gave the methyl sulphide (45 g., 82%), b. p. 100—102°/18 mm. When this was left with an equivalent of methyl iodide in nitromethane at room temperature for 3 hr. the formed salt was precipitated by ether as a yellow oil (30%). When longer reaction was allowed in an effort to improve the yield, much crystalline trimethylsulphonium iodide was produced. The oil was purified, by dissolution in methanol, from small amounts of trimethylsulphonium iodide which is insoluble in that solvent. The oil did not crystallise and, after it had been washed and triturated with a variety of solvents, and extensively held in a vacuum line, was used for rate measurements (Found: I, 43·2. Calc. for $C_{10}H_{15}IS$: I, 43·2%).

Dimethyl-1-*phenylpropylsulphonium iodide*. 1-Phenylpropan-1-ol, prepared (173 g., 80%) from bromobenzene (270 g.), magnesium (40 g.), and propionaldehyde (100 g.), had b. p. 92—94°/7 mm., n_D^{25} 1·5203 (α-naphthylurethane, m. p. 102°), and was converted (100 g.) with concentrated hydrochloric acid (1·5 l.) into the chloride (92 g., 80%), b. p. 80—82°/8 mm., n_D^{25} 1·5200 (Found: Cl, 23·0. Calc. for $C_9H_{11}Cl$: Cl, 22·9%). It was important to be sure that no appreciable rearrangement had occurred in this reaction, and therefore some of the chloride was hydrolysed back to the alcohol, which was compared with the original alcohol through infrared spectra, and the m. p.s and mixed m. p.s of the α-naphthylurethanes. The chloride has previously been converted into the thiol by the hydrogen sulphide method,[34] which, however, gave a low yield of impure material in our hands. We preferred to reflux the chloride (90 g.) with thiourea (46 g.) in water (70 ml.), so obtaining, after basic hydrolysis, the thiol as a clear liquid (61 g., 70%), b. p. 100—102°/13 mm. (Found: S, 20·8. Calc. for $C_9H_{12}S$: S, 21·1%). The thiol (61 g.), on treatment with ethanolic sodium ethoxide (10 g. of sodium) and methyl iodide (60 g.), gave the methyl sulphide (57 g., 90%), b. p. 107—108°/10 mm. This, when left for 2 hr. at room temperature with an equivalent of methyl iodide in nitromethane, gave the *dimethylsulphonium iodide*, which was precipitated as an oil with ether, but finally obtained, after purification with ethanol–ether, as a white powder, m. p. 106° (decomp.) (Found: I, 41·2. $C_{11}H_{17}IS$ requires I, 41·2%).

Dimethyl-3-*methyl*-1-*phenylbutylsulphonium iodide*. 3-Methyl-1-phenylbutan-1-ol, prepared from bromobenzene (282 g.), magnesium (42 g.), and isovaleraldehyde (150 g.), had (174 g., 60%) b. p. 105—106°/4 mm., n_D^{25} 1·5039, and was converted (144 g.) by means of concentrated

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[33] Schmerling and West, *J. Amer. Chem. Soc.*, 1952, **74**, 3592.

hydrochloric acid (1 l.) into the chloride (137 g., 86%), b. p. 87—88°/3 mm. (Found: Cl, 19·0. Calc. for $C_{11}H_{15}Cl$: Cl, 19·4%). This (90 g.) was refluxed for 2 hr. in water (70 ml.) with thiourea (40 g.), and the thiouronium salt, which was precipitated, was decomposed as usual with sodium hydroxide to give the thiol (40 g., 38%), b. p. 100°/5 mm. This (40 g.) with ethanolic sodium ethoxide (6 g. of sodium) and methyl iodide (35 g.) gave the methyl sulphide (30 g.), b. p. 104—105°/3 mm., n_D^{25} 1·5252. This in turn was left with an equivalent of methyl iodide in nitromethane for 4 hr. at room temperature, before the formed *dimethylsulphonium iodide* was precipitated by means of ether as an oil, which, after purification with ether–ethanol, solidified and had m. p. 95° (Found: I, 37·6. $C_{13}H_{21}IS$ requires I, 37·8%).

3,3-*Dimethyl*-1-*phenylbutyldimethylsulphonium iodide*. We were unable either to add t-butyl chloride to styrene with the aid of Friedel–Crafts catalysts (which polymerised the styrene), or to make, in reasonable yield, 3,3-dimethylbutan-1-ol by a previously described [35] Grignard reaction between t-butyl chloride and ethylene oxide, reactions that might have initiated shorter syntheses than the one by which we eventually obtained this sulphonium salt. Our starting point was 1-bromo-3,3-dimethylbutane, prepared as described above. It was difficult to hydrolyse this to the alcohol by means of aqueous potassium hydroxide, and treatment with ethanolic potassium hydroxide gave a material, b. p. 56—57°/70 mm., n_D^{25} 1·4080, which we presume to be the ethyl ether. Boiling the bromide in water with silver oxide gave alcohols, one, b. p. 37—38°/70 mm., 130°/760 mm., n_D^{25} 1·4330, and the other, b. p. 42—43°/70 mm., 135—136°/760 mm., n_D^{25} 1·4382, which are probably isomers of the required alcohol. Reaction of the bromide with a 3-fold excess of sodium acetate at 250° for 10 hr. in a sealed tube, and hydrolysis of the resulting material with ethanolic potassium hydroxide, gave the required alcohol, but in a yield (30%) insufficient to support the subsequent synthetic steps. Satisfactory conversion was effected by a less often used method, *viz.*, autoxidation of the Grignard reagent.[36] Over the surface of the reagent made from 1-bromo-3,3-dimethylbutane (250 g.) and magnesium (48 g.) in ether, oxygen was blown for 5 hr., with the addition of ether from time to time to replace that lost by evaporation, and with careful maintenance of the temperature at −5° during this highly exothermic reaction. The alcohol (yields 78—86%) had b. p. 80—81°/67 mm.,143—144°/760 mm., n_D^{25} 1·4131. Oxidation of 3,3-dimethylbutan-1-ol to the aldehyde has been accomplished [37] by means of chromic acid, but in yields too low to suit our plans. We dehydrogenated the alcohol by boiling it into a vertical tube 30 cm. long, containing pumice-supported copper chromite [38] and surmounted by a reflux condenser, arranged to return some unchanged alcohol but to allow dehydrogenation products to pass on. By means of a carefully regulated furnace, the catalyst was maintained at 335° ± 10° during this strongly endothermic reaction. After use for 40 min. the catalyst became reduced to a red substance, and was regenerated at 320° with a stream of air for 2 hr.; but after several such treatments the catalysts became inactive. Yields were variable, depending on the condition of the catalyst, the best being 80%. The 3,3-dimethylbutyraldehyde had b. p. 52—54°/106 mm., 102—105°/760 mm., n_D^{25} 1·3940. Its 2,4-*dinitrophenylhydrazone hydrochloride*, crystallised from ethanol, had m. p. 139° (Found: C, 45·2; H, 5·4. $C_{12}H_{17}ClN_4O_4$ requires C, 45·6; H, 5·4%). 3,3-*Dimethyl*-1-*phenylbutan*-1-*ol* was now prepared from the aldehyde by reaction with the Grignard compound from bromobenzene. About 700 g. of this alcohol in all were obtained from several experiments (yields 85—90%). It had b. p. 105—107°/5 mm., m. p. 17°, n_D^{25} 1·5035 (Found: C, 80·2; H, 9·8. $C_{12}H_{18}O$ requires C, 80·8; H, 10·2%). Its α-*naphthylurethane*, crystallised from ligroin, had m. p. 109° (Found: N, 3·8. $C_{23}H_{25}NO_2$ requires N, 4·0%). Conversion of the alcohol into its chloride was not straightforward. Treated with thionyl chloride in pyridine, a method which works smoothly with so many alcohols, this alcohol gave only tar, as may be the general result of the method in application to 1-phenylalkanols.[39] Treatment with aqueous hydrochloric acid, a method generally applicable to 1-phenylalkanols, converted this alcohol into its dehydration product, 3,3-*dimethyl*-1-*phenylbut*-1-*ene*, b. p. 93—96°/10 mm., n_D^{25} 1·5190 (Found: C, 89·2; H, 10·0. $C_{12}H_{16}$ requires C, 89·9; H, 10·1%), which was later obtained in other ways and was shown by its infrared spectrum to

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[34] Levene and Mikeska, *J. Biol. Chem.*, 1926, **70**, 379.
[35] Strating and Backur, *Rec. Trav. chim.*, 1936, **55**, 910.
[36] Whitmore and Lux, *J. Amer. Chem. Soc.*, 1932, **54**, 3448.
[37] Delacre, *Bull. Acad. roy. Belg.*, 1906, 8.
[38] Adkins, Kommes, Struss, and Dasler, *J. Amer. Chem. Soc.*, 1933, **55**, 2992.
[39] Sleight and Clark, *Trans. Roy. Soc. Canada*, 1929, III, **23**, 77.

have been formed in the present reaction without rearrangement. The required 1-*chloro*-3,3-*dimethyl*-1-*phenylbutane* was eventually prepared by dropwise addition of the alcohol to a 5-fold excess of thionyl chloride. After 0·5 hr. on the steam-bath, the excess of thionyl chloride was distilled off, and the residue was fractionated. In several experiments a total of about 600 g. of the chlorohydrocarbon were made in an overall yield of 86%; it had b. p. 98—100°/6 mm., n_D^{25} 1·5110 (Found: Cl, 17·9. $C_{12}H_{17}Cl$ requires Cl, 18·1%). It was important to be sure that this preparation involved no rearrangement of the carbon skeleton. To check this the chloride was converted back into the alcohol (*a*) by solvolysis in 50% aqueous acetone, and (*b*) by oxidation of the derived Grignard reagent with oxygen: the recovered specimens of alcohol were identified with the original alcohol by their infrared spectra, and by the m. p.s and mixed m. p.s of α-naphthylurethanes. Conversion of the chloro-compound into 3,3-*dimethyl*-1-*phenylbutane*-1-*thiol* was effected in poor yield by the hydrogen sulphide method, and in much better yield by the thiourea method. It had b. p. 86—88°/4 mm., n_D^{25} 1·5073 (Found: S, 16·8. $C_{12}H_{18}S$ requires S, 16·5%). A by-product of the hydrogen sulphide method was identified as *bis*-3,3-*dimethyl*-1-*phenylbutyl disulphide,* m. p. 129° (Found: C, 74·2; H, 9·1. $C_{24}H_{34}S_2$ requires C, 74·5; H, 9·1%). The thiol, on methylation with methyl iodide in ethanolic sodium ethoxide, gave the *methyl sulphide,* b. p. 98—100°/6 mm., n_D^{25} 1·5069 (Found: S, 15·1. $C_{13}H_{20}S$ requires S, 15·4%). The reaction of this material with methyl iodide in nitromethane was slow, and, if allowed to proceed beyond low conversions, gave the required sulphonium salt admixed with so much trimethylsulphonium iodide that purification of the former became too difficult. However, we could afford a low yield in this last step and ran the reactions for 7 days at room temperature before precipitating the crude salt (10%) by addition of ether. From the crude salt, by repeated solution and fractional precipitation, by means of ethanol and ether, to constant iodine-content, we obtained chromatographically pure 3,3-*dimethyl*-1-*phenylbutyl-dimethylsulphonium iodide* (28 g., 6%), m. p. 100° (decomp.) (Found: I, 36·2. $C_{14}H_{23}IS$ requires I, 36·2%). The *picrate* had m. p. 109—110° (Found: C, 52·4; H, 5·7. $C_{20}H_{25}N_3O_7S$ requires C, 53·1; H, 5·7%).

Trimethylsulphonium salts. These were obtained as unintended products or by-products in experiments on the preparation of 1-phenylalkyldimethylsulphonium salts. The iodide, m. p. 212° (decomp.) (Found: I, 62·4. Calc. for C_3H_9IS: I, 62·3%), and nitrate (Found: NO_3, 44·5. Calc. for $C_3H_9NO_3S$: NO_3, 44·6%) were prepared.

Paper-chromatography of sulphonium salts. We habitually used this method of checking their purity, employing Whatman's No. 1 paper, and the following two solvents: (*a*) butan-1-ol–acetic acid–water (5 : 1 : 4 v/v); (*b*) propan-1-ol–ammonia–water (6 : 3 : 1 v/v). The salts were run as iodides or hydroxides, and detected by sprays of potassium chloroplatinate and Bromophenol Blue respectively. The R_F values increased with homology from 0·43 to 0·88. Control experiment showed that impurities, isomeric ones, or close homologues, in 3% concentrations could be detected by these methods.

(b) *Alkyltrimethylammonium Salts.—General.* Many of the halides were prepared from the alkyl halide and a 2-fold excess of trimethylamine in an equal volume of nitromethane or ethanol. Nitrates, which are more soluble than the halides in ethanol and t-butyl alcohol, the solvents used in the kinetic studies, were prepared from the halides with the aid of silver nitrate. The filtered aqueous solutions, free from halide and silver ions, were evaporated at 60—80° under reduced pressure, and the residual nitrate was crystallised several times from ethanol–ether or methyl acetate.

Ethyltrimethylammonium salts. The bromide had m. p. 338° (sealed, evacuated tube) (Found: Br, 47·6. Calc. for $C_5H_{14}BrN$: Br, 47·7%), the iodide m. p. >300° (Found: I, 59·2. Calc. for $C_5H_{14}IN$: I, 59·1%), and the *nitrate* m. p. 265° (decomp.) (Found: NO_3, 41·3. $C_5H_{14}N_2O_3$ requires NO_3, 41·4%).

Trimethyl-n-propylammonium salts. The bromide had m. p. 238° (decomp.) (Found: Br, 44·1. Calc. for $C_6H_{16}BrN$: Br, 44·0%), and the *nitrate* m. p. 133—134° (Found: NO_3, 37·8. $C_6H_{16}N_2O_3$ requires NO_3, 38·0%).

Isopropyltrimethylammonium salts. The bromide had m. p. 308° (decomp.) (Found: Br, 44·2. Calc. for $C_6H_{16}BrN$: Br, 44·0%), and the *nitrate* m. p. 290° (Found: NO_3, 37·7. $C_6H_{16}N_2O_3$ requires NO_3, 38·0%).

n-Butyltrimethylammonium salts. The bromide had m. p. 195° (Found: Br, 41·0. Calc. for $C_7H_{18}BrN$: Br, 41·0%), and the *nitrate* m. p. 168° (sealed tube) (Found: NO_3, 34·7. $C_7H_{18}N_2O_3$ requires NO_3, 34·8%).

Isobutyltrimethylammonium salts. The bromide had m. p. 240° (Found: Br, 40·8. Calc. for $C_7H_{18}BrN$: Br, 41·0%), and the *nitrate* m. p. 110° (Found: NO_3, 34·6. $C_7H_{18}N_2O_3$ requires NO_3, 34·8%).

Trimethyl-t-butylammonium iodide. t-Butyl bromide, on reaction with trimethylamine in nitromethane, gave trimethylamine hydrobromide. Accordingly, t-butylamine (20 g.) was treated with methyl iodide (40 g.) in the presence of sodium hydroxide, and the solution was saturated with ammonium sulphate and extracted with ethanol. The extract on treatment with methyl iodide yielded the quaternary salt (Found: I, 52·0. Calc. for $C_7H_{18}IN$: I, 52·3%).

Isopentyltrimethylammonium salts. The *bromide* decomposed above 215° (Found: Br, 37·8. $C_8H_{20}BrN$ requires Br, 38·1%), and the *nitrate* had m. p. 113° (sealed, evacuated tube) (Found: NO_3, 32·2. $C_8H_{20}N_2O_3$ requires NO_3, 32·3%).

3,3-*Dimethylbutyltrimethylammonium salts.* 1-Bromo-3,3-dimethylbutane and trimethylamine in nitromethane had to be heated in sealed tubes for 5 hr. at 60° in order to effect extensive reaction. The *bromide* had m. p. 287° (decomp. in sealed tube) (Found: Br, 35·9. $C_9H_{22}BrN$ requires Br, 35·9%), and the *nitrate* m. p. 219° (sealed tube) (Found: NO_3, 30. $C_9H_{22}N_2O_3$ requires NO_3, 30·1%).

n-Decyltrimethylammonium bromide. This salt decomposed above 205° (Found: Br, 28·4. Calc. for $C_{13}H_{30}BrN$: Br, 28·5%). Solutions of the nitrate were inconveniently surface-active, and the kinetic study was therefore made on the bromide.

NNN-*Trimethyl*-1,2,2-*trimethylpropylammonium salts.* Salts of this cation could not be made from trimethylamine and the complementary alkyl halide, and had to be prepared by methylation of the primary alkylamine, which was obtained by reduction of a ketoxime. Pinacolone (77 g.) was converted into its oxime (71 g.), m. p. 79°, and this was then reduced in ethanol (1·2 l.) by sodium (90 g.). The solution was acidified and evaporated, and the residue, dissolved in the minimum of water, was basified and extracted with pentane, to give pinacolylamine (40 g.), b. p. 103—104°. This amine (100 g.) was refluxed for 4 hr. with methyl iodide (284 g.) and a saturated aqueous solution of sodium carbonate (75 g.), to give dimethylpinacolylamine (40 g.), b. p. 130°, n_D^{25} 1·4160. Then this tertiary amine was left for 2 days with excess of methyl iodide in nitromethane, before ether was added to precipitate the quaternary *iodide*, which, after purification, had m. p. 208° (Found: I, 47·0. $C_9H_{22}IN$ requires I, 46·9%). The *nitrate* decomposed above 215° (Found: NO_3, 29·7. $C_9H_{22}N_2O_3$ requires NO_3, 30·0%). It was confirmed by the infrared, and by proton-magnetic-resonance spectra that no skeletal rearrangements had occurred during these syntheses.

1-*Ethyl*-2,2-*dimethylpropyltrimethylammonium salts.* The method of synthesis was as in the preceding example, except that we started further back. A reaction between t-butyl chloride (250 g.), magnesium (62 g.), and propionaldehyde (130 g.) gave 2,2-dimethylpentan-3-ol (196 g.), b. p. 132—135°, n_D^{25} 1·4175. To a stirred solution of this (190 g.) in acetic acid (120 g.), a solution of chromic oxide (67 g.) in acetic acid (50 ml.) and water (20 ml.) was slowly added below 30°, to yield, by extraction with pentane, 2,2-dimethylpentan-3-one (120 g.), b. p. 124—126°, n_D^{25} 1·4020. This (114 g.) was converted into its oxime (90 g.), m. p. 85°, which was reduced with sodium and ethanol as before, to give the amine (50 g.), b. p. 126°, n_D^{25} 1·4253. This (47 g.) was treated with methyl iodide and sodium carbonate to give the *NN*-dimethyl derivative (30 g.), b. p. 135—138°, which was converted, as in the lower-homologous example, into the *trimethylammonium iodide*, m. p. 168° (Found: I, 44·6. $C_{10}H_{24}IN$ requires I, 44·7%), and *nitrate*, m. p. 173° (Found: NO_3, 27·9. $C_{10}H_{24}N_2O_3$ requires NO_3, 28·2%).

1-*Isopropyl*-2-*methylpropyltrimethylammonium salts.* 3-Bromo-2,4-dimethylpentane was obtained from Grignard-synthesised 2,4-dimethylbutan-3-ol and hydrogen bromide, as described by Jamison, Lesslie, and Turner,[40] who, in spite of a previous statement that this reaction yielded only rearranged products,[41] claimed that theirs was unrearranged. We confirmed their conclusion, by back-conversion of the bromide, though its Grignard derivative by reaction with oxygen, into an alcohol which was identified with the original alcohol by comparison of their infrared spectra. Our objective was a quick method of getting the salts named in the side-heading by reaction of the bromide with trimethylamine, but the only solid product we thus obtained was trimethylamine hydrobromide, and we therefore fell back on the oxime method. Di-isopropyl ketone was converted into its oxime, b. p. 180°, m. p. 34°, which was reduced with sodium and ethanol to 3-*amino*-2,4-*dimethylpentane*, b. p. 150—153°,

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[40] Jamison, Lesslie, and Turner, *J. Inst. Petroleum*, 1949, **35**, 592.

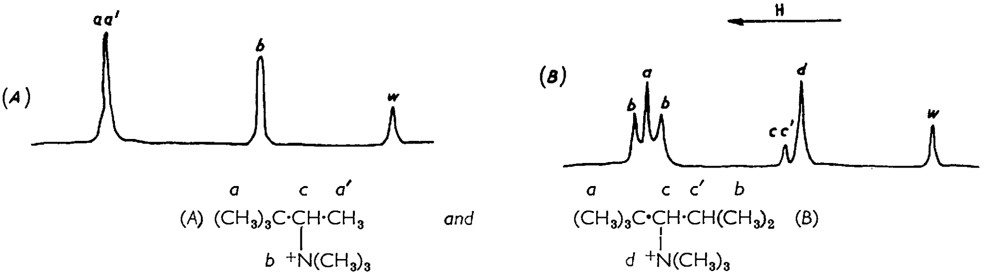
[41] Whitmore and Johnson, *J. Amer. Chem. Soc.*, 1938, **60**, 2265.

which was converted into the *alkyltrimethylammonium iodide*, m. p. 196° (Found: I, 44·7. $C_{10}H_{24}IN$ requires I, 44·7%), by two steps of methylation as described in the preceding paragraph. The *nitrate* had m. p. 172° (Found: NO_3, 28·0. $C_{10}H_{24}N_2O_3$ requires NO_3, 28·2%).

1-*Isopropyl*-2,2-*dimethylpropyltrimethylammonium salts.* Prepared from t-butyl chloride (250 g.), magnesium (62 g.) and isobutyraldehyde (95 g.), 2,2,4-trimethylpentan-3-ol (97 g.), b. p. 150—151°, n_D^{25} 1·4220, was oxidised (66 g.), as described in the preceding paragraph but one, to 2,2,4-trimethylpentan-3-one (37 g.), b. p. 136—140°, n_D^{25} 1·4013, the oxime, m. p. 140°, of which was reduced (45 g.) as usual to the amine (39 g.), b. p. 120°. An attempt to convert this (45 g.) with methyl iodide and sodium carbonate solution in one step into the tertiary amine led to 3-*methylamino*-2,2,4-*trimethylpentane hydriodide* (Found: I, 44·6. $C_9H_{22}IN$ requires I, 44·5%), from which the secondary amine was liberated, and, by repetition of the treatment, converted into the dimethylamino-compound (30 g.), b. p. 142°. The same compound was made from the primary amine in 50% yield by treatment at 135° with a 2-fold excess of paraformaldehyde. It was converted by methyl iodide in nitromethane at 60° for 5 days into the *trimethylammonium iodide* (15%), which decomposed above 150° (Found: I, 42·4. $C_{11}H_{26}IN$ requires I, 42·5%). The *nitrate* had m. p. 147° (Found: NO_3, 26·4. $C_{11}H_{26}N_2O_3$ requires NO_3, 26·5%).

Proton magnetic resonance spectra of ammonium salts. Dr. B. Figgis very kindly checked for us by this method, using 10% solutions of nitrates in deuterium oxide, the constitutions of some of the more highly branched cations, particularly those with a t-butyl residue in the alkyl group, in order that no unwanted rearrangement during synthesis should pass undetected. Tracings of two records are in Fig. 3. Measurements of the line areas showed the different sets of equivalent hydrogen atoms to be present in the correct proportions.

FIG. 3. *Structure-determination by proton magentic resonance of*:



Interpretation of A: Duplicate letters show the assignments; line *w* belongs to light water, an impurity in the solvent. The area-ratio, *aa'*/*b* = 1·34 (theor. 1·33). The atom marked *c* should give a quartet of weak lines, and a quartet which might be thus assigned can be seen between the strong lines at higher resolution than is suitable for line-intensity measurements. Also at higher resolution, the lines of *a* and *a'* are partly resolved, the latter, which are the weaker, lying towards higher sweep-fields.

Interpretation of B: Duplicate letters show the assignments; line *w* is the light-water line. The area-ratios are: $(a + b)/d = 1{\cdot}61$ (theor. 1·67); $cc'/d = 0{\cdot}21$ (theor. 0·22); $a/b = 1{\cdot}55$ (theor. 1·50). The doublet *b* owes its separation to an interaction involving the proton *c'*.

(c) *Olefins*.—These were required as reference substances to aid identification by b. p., n_D^{25}, gas chromatography, and particularly infrared spectra. Most of them were made from an alcohol, by conversion in boiling acetic anhydride into the acetate, and pyrolysis of the latter at 420—430°. Other methods were used occasionally.

3,3-*Dimethylbut*-1-*ene*. Prepared from pinacolyl acetate, b. p. 80—82°/100 mm., this had b. p. 41°, n_D^{25} 1·5712. Attempts to prepare it directly from the alcohol and phosphoric acid gave about equal amounts of two rearrangement products, 2,3-dimethylbut-1- and -2-ene, b. p. 61—63° and 72—74°, respectively.

4,4-*Dimethylpent*-2-*ene*. Prepared from 2,2-dimethylpentan-1-ol by way of the acetate, b. p. 155°, this had b. p. 75° (Br no., 162. Calc.: 163).

2,4-*Dimethylpent*-2-*ene*. 2,4-Dimethylpentan-3-ol (50 g.), slowly distilled with concentrated sulphuric acid (2·5 ml.), yielded the olefin (14 g.), b. p. 82—83° (Br no., 163. Calc.: 163).

2,4,4-*Trimethylpent*-2-*ene*. 2,2,4-Trimethylpentan-3-ol gave the acetate, b. p. 55—56°/9 mm., n_D^{25} 1·4116, and thence the olefin, b. p. 104—105° (Br no., 143. Calc.: 143).

3-*Methyl*-1-*phenylbut*-1-*ene*. 3-Methyl-1-phenylbutan-1-ol was converted into its acetate, b. p. 105—108°/4 mm., n_D^{25} 1·4843, which was pyrolysed in a stream of nitrogen on glass-wool at 430° to give the olefin, b. p. 80—81°/8 mm., n_D^{25} 1·5266.

3,3-*Dimethyl*-1-*phenylbut*-1-*ene*. This was prepared from 3,3-dimethyl-1-phenylbutan-1-ol, both through the acetate, b. p. 106—108°/3 mm., n_D^{25} 1·4837, as described in the preceding example, and also directly by boiling the alcohol (10 g.) with acetic anhydride (40 ml.) in the presence of zinc chloride (0·2 g.). It had b. p. 90—92°/8 mm., n_D^{25} 1·5193.

Kinetics

(a) *Procedures*.—Rates of reaction at temperatures regulated to ±0·02° between alkyldimethylsulphonium iodide or nitrate, or alkyltrimethylammonium nitrate, bromide, or iodide, and either sodium or potassium ethoxide in ethanol, or potassium or sodium t-butoxide in t-butyl alcohol were measured by disappearance of base. Procedures for the four main types of runs follow.

Sulphonium ethoxides. A solution in dry ethanol of dried (Abderhalden) and weighed sulphonium iodide, or in the case of trimethylsulphonium, the nitrate, was mixed with the required volume of stock ethanolic sodium ethoxide at 0° or 20°, and transferred in 5 ml. lots, by a jacketed automatic pipette, to nitrogen-filled constricted tubes which were cooled to −78° and sealed. Batches of 12—16 tubes were placed in the thermostat, and two were taken therefrom for analysis at the time-zero 7—8 min. later, as well as two after 10 half-lives. These gave the initial concentrations, and the remaining tubes were taken one by one at suitably spaced times after the zero. For analysis, the tubes, quenched at −78° and broken under water containing enough ethanol to keep the sulphides in solution, were either titrated directly with standard acid in nitrogen, or acidified with hydrochloric acid and back-titrated with standard sodium hydroxide, Bromocresol Blue–Methyl Red being the indicator.

Sulphonium t-butoxides. A solution in dry t-butyl alcohol of the dried sulphonium iodide was delivered by a jacketed automatic pipette at 30°, or, in the cases of the ethyl and 3,3-dimethylbutyl salts, at 65°, directly into the constricted tubes which were then cooled to −78°, then stock t-butyl alcoholic potassium t-butoxide, or in some cases sodium t-butoxide, was added by means of an automatic pipette at 30°, whereafter the tubes were sealed. The concentration of 3,3-dimethylbutyl salt being limited by solubility, sodium perchlorate was added to make the total salt the same as in the other cases. The analytical procedures were as before.

Ammonium ethoxides. The ammonium nitrates, which are very deliquescent, were dried at 40—50°/0·15 mm., and all subsequent transfers were conducted in a dry-box. Stock ethanolic potassium ethoxide was added to an ethanolic solution of the ammonium nitrate, the potassium nitrate was filtered off under dry nitrogen, and the filtrate was made up to the required volume. When ammonium bromides were used, the precipitated potassium bromide was similarly filtered off. The sealed tubes were of Pyrex, but, as this became appreciably attacked at 100° after about 8 hr., the analytical results for infinite time were calculated from the initial concentrations of ammonium salts. These were determined by weighing, and also by ion-exchange with Amberlite IRA–120 (H^+), which converted the ammonium nitrates into nitric acid that could be titrated as such. The analytical procedure for following the progress of the reaction was complicated by the formation of tertiary amines, which had to be removed before the measurement of alkalinity. More volatile amines were removed from the water-diluted analytical sample in a stream of nitrogen during 20—30 min. at 70°. Less volatile or residual amines were thereafter extracted. For this purpose, sodium chloride was added to a mixture of the analytical sample (5 ml.) and water (60 ml.), and the solution was extracted with carbon tetrachloride (6 × 10 ml.) and ether (1 × 30 ml.).

Ammonium t-butoxides. The procedure was the same, except for two points. First, because the filtration of potassium nitrate was mechanically troublesome, we went through with it only in a few experiments, and in most left the salt in suspension, having shown that that made no difference to the results. Secondly, because the reaction temperature was lower, the alkali did not attack the glass, and we were therefore able to determine initial reactant concentrations with the aid of ten-half-life analytical values in the usual way.

(b) *General Kinetic Phenomena*.—Runs were made on several of the salts in the absence or an alkoxide, in order to check the occurrence of solvolyses, and of any attack by iodide of nitrate ion. All such reactions were negligibly slow in comparison with the reactions with alkoxide ions.

The reactions with alkoxides are subject to (generally negative) salt effects, stronger in t-butyl alcohol than in ethanol, and runs whose rates were to be compared were therefore set up at common (±0·002M) concentrations of total salt. In the Tables that follow, these concentrations may be taken as the sum of the reagent concentrations in runs on iodides, and the larger individual reagent concentration in those on nitrates or bromides. In a few cases, which are indicated, the salt concentration was made up by the addition of sodium perchlorate.

Because of salt effects, the second-order constants should not remain constant during a run, but they usually did so within the error of observation over most of it, with a drift towards the end. These drifts were not all upwards, as would be expected from the nature of the reactions: with sulphonium ethoxides and some sulphonium t-butoxides they were downwards. In these sulphonium ion reactions, much inert salt is present in solution, and we suppose that the growing relative excess of this increasingly protects the reactive ions. A suspected cause of tail-drift arose in the reactions of sulphonium t-butoxides, *viz.*, that, usually at a late stage in these runs, potassium iodide began to be precipitated from the t-butyl alcohol.

Rates decrease in the order: potassium, sodium, and lithium ethoxide in ethanol; t-butoxide in t-butyl alcohol (largest decrease in the last series); addition of lithium perchlorate in a

TABLE 15. *Illustrative runs.*

Run 14: 3,3-*Dimethylbutyldimethylsulphonium iodide and sodium ethoxide in ethanol at* 64·08°. {At the time-zero, $[\mathrm{R_3S^+}] = 0{\cdot}0498$, $[\mathrm{EtO^-}] = 0{\cdot}0983$M at 20°. Samples (6·28 ml.) were mixed with 0·1017N-hydrochloric acid (8·0 ml.), excess of which was titrated with 0·01603N-sodium hydroxide.}

Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2
0	11·51	—	25	18·90	345	65	24·46	339	∞	31·39	—
0	11·51	—	35	20·81	347	75	25·36	342	∞	31·37	—
10	15·08	343	45	22·12	336	85	26·20	347			
21	17·89	336	55	23·41	338	90	26·37	338			

Mean 10^5k_2 (uncorr.) 342, (corr.) 366 ± 5.

Run 64: *n-Butyldimethylsulphonium iodide and potassium t-butoxide in t-butyl alcohol at* 34·92°. {At the time-zero, $[\mathrm{R_3S^+}] = 0{\cdot}0295$, $[\mathrm{Bu^tO^-}] = 0{\cdot}0823$M at 35°. Samples (7·27 ml.) were titrated with 0·0142N-hydrochloric acid.}

Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2
0	42·13	—	16	38·55	353	38	35·35	346	∞	26·96	—
0	42·07	—	22	37·73	333	49	32·80	455	∞	27·04	—
5	40·97	331	28	36·52	360	57	31·79	482			
10	39·77	350	33	36·14	335	72	30·02	558			

Mean 10^5k_2 (no correction required) 344 ± 11.

Run 106: *Trimethyl*-1,2,2-*Trimethylpropylammonium nitrate and potassium ethoxide in ethanol at* 100·60°. {At the time-zero, $[\mathrm{R_4N^+}] = 0{\cdot}0783$, $[\mathrm{EtO^-}] = 0{\cdot}1518$M at 20°. Samples (5·00 ml.) were titrated with 0·0334N-hydrochloric acid.}

Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2
0	22·70	—	10	20·82	200	20	19·16	215	30	17·94	215
0	22·70	—	12	20·47	202	22	19·00	207	35	17·40	217
5	21·72	196	15	19·76	225	25	18·50	216	40	16·52	244

Mean 10^5k_2 (uncorr.) 210, (corr.) 225 ± 10.

Run 124: *Isopentyltrimethylammonium nitrate and potassium t-butoxide in t-butyl alcohol at* 72·85°. {At the time-zero, $[\mathrm{R_4N^+}] = 0{\cdot}0787$, $[\mathrm{t\text{-}BuO^-}] = 0{\cdot}1547$M at 35°. Samples (7·00 ml.) were titrated with 0·0617N-hydrochloric acid.}

Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2	Time (min.)	Titre (ml.)	10^5k_2
0	17·57	—	15	15·50	199	31	13·95	203	60	12·12	207
0	17·53	—	20	14·92	205	40	13·40	195	∞	8·62	—
10	16·05	208	25	14·36	207	50	12·85	192	∞	8·62	—

Mean 10^5k_2 uncorr. 203, corr. 214 ± 5.

TABLE 16. *Second-order rate constants of reactions of alkyldimethylsulphonium iodides with sodium ethoxide in ethanol.*

Run	Alkyl	Temp.	$[R_3S^+]_0$	$[EtO^-]_0$	10^5k_2	
1	Ethyl	64·08°	0·0486	0·0997	383	$\pm$ 6
2	,,	,,	0·0471	0·0993	383	5
3	n-Propyl	,,	0·0494	0·0999	385	7
4	,,	,,	0·0494	0·1001	379	7
5	n-Butyl	,,	0·0495	0·0989	412	8
6	,,	,,	0·0499	0·1000	404	6
7	,,	,,	0·0521	0·0974	402	10
8	Isobutyl	,,	0·0489	0·1000	509	7
9	,,	,,	0·0491	0·0989	497	8
10	Isopentyl	,,	0·0498	0·0997	430	5
11	,,	,,	0·0494	0·0990	428	6
12	,,	,,	0·0497	0·0996	436	8
13	3,3-Dimethylbutyl	,,	0·0490	0·0995	353	12
14	,,	,,	0·0498	0·0983	366	5
15	,,	,,	0·0494	0·0990	365	5
16	Methyl *	,,	0·0493	0·1494	480	5
17	,, *	,,	0·0489	0·1490	479	5
18	Ethyl	,,	0·0982	0·0500	372	8
19	,,	,,	0·1191	0·0302	380	3
23	1-Phenylethyl	34·87	0·0474	0·0996	249	16
24	,,	,,	0·0468	0·0995	246	11
27	1-Phenylpropyl	,,	0·0504	0·0972	130	11
28	,,	,,	0·0505	0·0948	120	5
29	,,	,,	0·0498	0·1001	127	6
30	3-Methyl-1-phenylbutyl	,,	0·0483	0·0998	181	3
31	,,	,,	0·0493	0·0996	180	7
32	3,3-Dimethyl-1-phenylbutyl	,,	0·0496	0·0993	558	22
33	,,	,,	0·0475	0·0985	557	12
34	,,	,,	0·0481	0·0996	563	16
36	Ethyl	34·73	0·0528	0·1030	6·23	0·04
37	,,	,,	0·0503	0·0997	6·28	0·07
38	n-Propyl	,,	0·0512	0·1020	6·55	0·07
39	,,	,,	0·0512	0·1020	6·56	0·03
40	3,3-Dimethylbutyl	,,	0·0519	0·1001	5·54	0·03
41	,,	,,	0·0519	0·1001	5·54	0·05
42	Ethyl	44·68	0·0514	0·1007	34·7	0·7
43	,,	,,	0·0507	0·1003	34·7	0·4
44	n-Propyl	,,	0·0514	0·0958	34·5	0·4
45	,,	,,	0·0517	0·1004	35·4	0·7
46	3,3,-Dimethylbutyl	,,	0·0504	0·1020	29·0	0·4
47	,,	,,	0·0501	0·1000	28·8	0·6
48	Ethyl	72·79	0·0532	0·1005	1081	10
49	,,	,,	0·0495	0·0999	1070	15
50	n-Propyl	,,	0·0513	0·1021	1087	13
51	,,	,,	0·0469	0·1021	1080	25
52	3,3-Dimethylbutyl	,,	0·0515	0·0989	1097	13
53	,,	,,	0·0515	0·0994	1089	10

* The sulphonium nitrate was used.

TABLE 17. *Second-order rate constants of reactions of alkyldimethylsulphonium iodides with potassium t-butoxide in t-butyl alcohol at* 34·92°.

Run	Alkyl	$[R_3S^+]_0$	$[Bu^tO^-]_0$	10^5k_2		Run	Alkyl	$[R_3S^+]_0$	$[Bu^tO^-]_0$	10^5k_2	
54	Ethyl	0·0267	0·0860	835	$\pm$ 29	64	n-Butyl	0·0295	0·0823	344	$\pm$ 11
55	,,	0·0372	0·0745	835	48	65	Isopentyl	0·0334	0·0824	348	28
56	,, *	0·0273	0·0650	217	15	66	,,	0·0366	0·0820	348	14
57	,, *	0·0230	0·0643	226	20	67	,,	0·0355	0·0857	336	14
58	n-Propyl	0·0315	0·0804	406	27	70	3,3-Dimethyl-butyl *	0·0120	0·0783	80	15
59	,,	0·0333	0·0855	394	10						
60	,,	0·0316	0·0821	396	36	71	,, *	0·0215	0·0647	69	12
61	,,	0·0334	0·0818	409	13	72	,, *	0·0274	0·0688	74	14
62	n-Butyl	0·0310	0·0819	349	11	73	,, *	0·0247	0·0767	75	10
63	,,	0·0309	0·0828	357	18						

* With sodium t-butoxide, and added sodium perchlorate to make total salt up to 0·113M.

TABLE 18. *Second-order rate constants of reactions of alkyltrimethylammonium nitrates with potassium ethoxide in ethanol.*

Run	Alkyl	Temp.	$[R_4N^+]_0$	$[EtO^-]_0$	10^5k_2	
80	Ethyl	104·22°	0·0779	0·1523	101·6 ±	1·6
81	,,	,,	0·0778	0·1522	102·0	1·6
82	,,	,,	0·1540	0·0782	99·0	1·5
83	,, *	,,	0·0988	0·1302	100·3	1·3
85	n-Propyl	,,	0·0763	0·1508	27·8	0·6
	,,	,,	0·0779	0·1521	27·4	0·6
87	Isopropyl	,,	0·0756	0·1490	164	6
88	,,	,,	0·0732	0·1500	168	5
89	n-Butyl	,,	0·0795	0·1525	27·1	1·0
90	,,	,,	0·0788	0·1520	26·1	1·1
91	Isobutyl	,,	0·0732	0·1463	27·3	0·8
92	,,	,,	0·0736	0·1490	26·9	1·5
93	t-Butyl †	,,	0·0588	0·0932	947	92
94	Isopentyl	,,	0·0776	0·1516	26·3	0·7
95	,,	,,	0·0777	0·1518	26·6	1·2
96	3,3-Dimethylbutyl	,,	0·0756	0·1532	23·6	0·7
97	,,	,,	0·0731	0·1510	24·3	0·6
98	n-Decyl ‡	,,	0·0823	0·1606	17·3	0·7
99	,, ‡	,,	0·0829	0·1557	17·3	0·9
100	Phenethyl	44·60	0·0736	0·1512	170	17
101	,,	,,	0·0834	0·1530	168	15
102	,,	25·06	0·0833	0·1536	5·61	0·07
103	,,	,,	0·0800	0·1521	5·61	0·05
104	Methyl	104·22	0·0732	0·1521	20·3	0·5
105	1,2,2-Trimethylpropyl	100·60	0·0714	0·1482	229	13
106	,, ,,	,,	0·0783	0·1518	225	10
108	1-Ethyl-2,2-dimethylpropyl	,,	0·0810	0·1493	127	7
109	,, ,, ,,	,,	0·0765	0·1534	126	9
110	1-Isopropyl-2,2-dimethylpropyl	,,	0·0817	0·1480	282	17
111	,, ,, ,,	,,	0·0617	0·1492	296	20
112	1-Isopropyl-2-methylpropyl	,,	0·0774	0·1535	278	10
113	,, ,, ,,	,,	0·0793	0·1502	268	12

* With sodium ethoxide, and added sodium perchlorate to make total salt 0·1533M.
† The ammonium iodide was used. All salts remained in solution.
‡ The ammonium bromide was used.

TABLE 19. *Second-order rate constants of reaction of alkyltrimethylammonium nitrates with potassium t-butoxide in t-butyl alcohol.*

Run	Alkyl	Temp.	$[R_4N^+]_0$	$[Bu^tO^-]_0$	10^5k_2	
114	Ethyl	34·92°	0·0690	0·1553	97 ±	8
115	,,	,,	0·0732	0·1489	91	7
116	,, *	,,	0·0660	0·1501	95	8
117	,,	44·60	0·0725	0·1498	468	25
118	,,	,,	0·0725	0·1527	469	30
119	n-Propyl	72·85	0·0784	0·1480	520	21,
120	,,	,,	0·0710	0·1501	507	20
121	,, *	,,	0·0719	0·1509	510	17
122	n-Butyl	,,	0·0750	0·1468	274	10
123	,,	,,	0·0830	0·1481	274	12
124	Isopentyl	,,	0·0787	0·1547	214	5
125	,,	,,	0·0770	0·1520	208	6
126	3,3-Dimethylbutyl	,,	0·0761	0·1508	184	8
127	,, ,,	,,	0·0830	0·1513	178	5

* Potassium nitrate removed by filtration.

reaction with a potassium or sodium alkoxide reduced the rate. Therefore the same base had to be used in runs whose rates were to be compared. In Table 2 (p. 4059) the rate for 3,3-dimethylbutyldimethylsulphonium t-butoxide, which was measured with sodium t-butoxide because a difficulty of solubility required the total salt concentration to be made up with sodium perchlorate, is given as for the potassium salt, by comparison with the rates for ethyldimethylsulphonium t-butoxide, which was measured with both sodium and potassium salts.

Water was a dangerous impurity and some trouble was taken to get it out, and keep it out, in preparing and handling solvents and salts. Much use was made of the dry-box, and routine Karl Fischer determinations were made. Some runs on sulphonium iodides and potassium t-butoxide in t-butyl alcohol with added water showed that proportions of water, 0·03—0·08M, *i.e.*, comparable to those of the intended reagents, would cut down the rate of reaction to between one-half and one-quarter of its proper value.

(c) *Results.*—Rate constants were calculated from the formula $k_2 = [2{\cdot}303/\{t(b - a)\}] \log\{a(b - x)/b(a - x)\}$, and in the Tables all are expressed in $\text{sec.}^{-1}\ \text{mole}^{-1}\ \text{l}$. The ± error values are formal standard deviations. Mean constants for the runs were corrected for the change of volume of the solvent between the temperature at which initial concentrations were set and the temperature of reaction. Table 15 reports one run of each of the four types in order to show the degree of significance attaching to the second-order rate-constants. The corrected mean rate-constants of the principal series of runs are assembled in Tables 16—19.

Olefin Determinations

(a) *Methods.*—Several were used. The aspiration and the extraction method have been described before,[42] but modifications were introduced which improved their accuracy. In a few cases the determinations were made as a run progressed, but usually they were made after the reaction had run nearly to completion. In either case, pairs of tubes were taken from the thermostat together, one for measurement of the total reaction by alkali disappearance, and the other for the olefin determination.

Aspiration. This was used for ethylene and propene, and in a few experiments for higher olefins. The tube containing the sample (5—80 ml., depending on how much olefin was expected) was broken in a bottle under just enough acid to neutralise the alkali, the olefin then being drawn at 40°, in a stream of nitrogen for 2—3 hr., into the absorption system. This system consisted of two traps of saturated aqueous mercuric chloride (40 ml. each), or 3N-hydrochloric acid, according as a sulphonium or an ammonium salt was being decomposed (in the former case a precipitate appeared only in the first trap), a small condensing spiral at 0°, to retain ethanol and water, the absorption coil into which the gases entered by a rose at the bottom, and a final potassium iodide trap. The absorption coil, which contained 130 ml. of a solution in carbon tetrachloride of 3—4 times the required amount of bromine, was kept at 0° in the dark, and tilted slightly so that the gas collected in the turns of the coil, thus providing a contact time of 1·5 min. The final titration of the mixed potassium iodide and bromine solutions was with thiosulphate, and the bromine solution was standardised with the aid of a blank experiment with a zero-time sample. This method was checked, and shown to be accurate, by application to a tetraethylammonium salt, which was assumed to give 100% of ethylene. Acid could not be used to stop the reactions in t-butyl alcohol, because it seemed to dehydrate this alcohol slightly. These reactions were therefore run to completion, and the olefin was aspirated from the non-acidified solutions.

Extraction. This was used for most of the olefins higher than propene, but the details varied from case to case. For example, a tube containing a sample (25 ml.) from the reaction of a sulphonium salt, cooled to −78°, was broken under carbon tetrachloride (150 ml.) at its f. p., and the solution was washed in cold-jacketed separating funnels with 0·5N-hydrochloric acid (10 ml.), with water (20 ml.), and twice with saturated aqueous mercuric chloride (40 ml., with shaking for 5 min., and storage for 10 min. at −20°, each time). The precipitate was removed by filtration into an evacuated flask, and the olefin was then determined by uptake of bromine, from added standard bromine, in the dark at 0° during 30—180 min. depending on the type and concentration of the olefin. In experiments with ammonium salts, the washings with mercuric chloride were replaced by washings with 3N-hydrochloric acid (20 ml. each), and no filtration was necessary. Quantities of sample and reagents, and times, were varied in order to detect systematic errors, and blank experiments were conducted at all stages. It is a feature of the method that olefin losses are corrected by factors based on blank determinations, which for but-1-ene gave 1·13, 3-methylbut-1-ene, 1·04, 3,3-dimethylbut-1-ene 1·02, and styrene and its homologues 1·00. Some difficulties arose. Thus the small proportions in which 3,3-dimethylbut-1-ene was formed necessitated large samples: for sulphonium reactions in ethanol, 75 ml. was about optimal; but for sulphonium reactions in t-butyl alcohol, kinetic control was abandoned, and runs were made with 2—4 g. of salt in 125 ml. of 0·25N-potassium t-butoxide. The aromatic sulphides, R·CHPh·SMe, were not completely removed by washing with aqueous mercuric chloride, and contact for 12 hr. with alcoholic mercuric chloride was

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[42] Hughes, Ingold, and Shapiro, *J.*, 1936, 225; Hughes, Ingold, Masterman, and MacNulty, *J.*, 1940, 899.

found to be more effective, though slightly low olefin values resulted. Aromatic olefins and ethers were liable to be substituted by bromine, as shown by the development of hydrogen bromide, determined by iodate, unless the excess of bromine was kept low in the analysis of olefins of this type.

Optical absorption. The aromatic olefins, $\mathrm{R{\cdot}CH{:}CHPh}$, were also determined spectrophotometrically, by absorption at 248 mμ, with a Unicam S.P. 500 spectrophotometer. The results agreed well with the bromometric values. It was necessary to allow for the absorption of sulphides, $\mathrm{RCH_2{\cdot}CHPh{\cdot}SMe}$, the concentrations of which were obtained by difference after determination of the methyl sulphide (p. 4086). The following extinction coefficients at 248 mμ were determined:

$\mathrm{CH_3{\cdot}CHPh{\cdot}S{\cdot}CH_3}$	$1{\cdot}07 \times 10^3$;	$\mathrm{CH_2{:}CHPh}$	$1{\cdot}35 \times 10^4$
$\mathrm{(CH_3)_2CH{\cdot}CH_2{\cdot}CHPh{\cdot}S{\cdot}CH_3}$	1·10 ,, ;	$\mathrm{(CH_3)_2CH{\cdot}CH{:}CHPh}$	1·30 ,,
$\mathrm{(CH_3)_3C{\cdot}CH_2{\cdot}CHPh{\cdot}S{\cdot}CH_3}$	1·01 ,, ;	$\mathrm{(CH_3)_3C{\cdot}CH{:}CHPh}$	1·49 ,,

Colorimetry. The small yields of 3,3-dimethylbut-1-ene obtained from the sulphonium salt were re-measured by a modification of MacPhee's method, which depends on the blue colour given by olefins (and many other compounds) with acid solutions of complex molybdates containing a palladous salt. The reagent was prepared as he describes,[43] but, although it is stable, its properties were found to vary from batch to batch, and therefore the same batch had to be used for analysis and calibration. The olefin was extracted as described above, but with tetrachloroethane (200 ml.) instead of carbon tetrachloride, and then the olefin was aspirated from that solvent by a stream of nitrogen at 45° and collected in a trap cooled by liquid nitrogen.

TABLE 20. *Proportion of olefin formed in reactions of alkyldimethylsulphonium iodides and sodium ethoxide in ethanol.*

Run	Alkyl	Temp.	Method	[Total salt]$_0$ *	Sample (ml.)	No. of points	Olefin (%)	
128	Ethyl	34·73°	Asp.	0·1502	25—50	8	14·5	± 0·7
129	,,	45·68	,,	0·1513	,,	7	16·2	0·8
130	,,	64·08	,,	0·1498	,,	10	20·5	0·5
131	,,	72·79	,,	0·1500	,,	7	21·2	0·7
132	n-Propyl	34·73	,,	0·1501	,,	10	5·0	0·5
133	,,	45·68	,,	0·1496	,,	8	6·4	0·3
134	,,	64·08	,,	0·1480	,,	12	7·6	0·5
135	,,	72·79	,,	0·1532	,,	11	8·3	0·4
136	n-Butyl	64·08	Ext.	0·1532	,,	7	5·4	0·8
137	,, †	,,	,,	0·1623	,,	7	5·4	0·8
138	,,	,,	,,	0·1520	10	6	5·0	0·8
139	,,	,,	,,	0·1520	25—50	4	5·9	0·5
140	Isobutyl	,,	,,	0·1623	50	4	2·0	0·6
141	Isopentyl	,,	,,	0·1520	25	5	3·7	0·5
142	,,	,,	,,	0·1670	10	5	3·6	0·7
143	,,	,,	,,	0·1530	50	5	3·9	0·4
144	3,3-Dimethylbutyl	,,	,,	0·1501	25	5	0·21	0·10
145	,,	,,	,,	0·1500	75	5	0·35	0·15
146	,,	,,	,,	0·1523	,,	3	0·12	0·06
147	,,	,,	,,	0·1529	,,	7	0·36	0·10
148	,,	,,	,,	0·3521	,,	3	0·15	0·08
149	,,	,,	,,	0·3513	,,	5	0·10	0·07
150	,,	,,	,,	0·3800	,,	5	0·15	0·08
151	,,	,,	,,	0·3581	25	3	0·08	0·04
152	,,	,,	Col.	0·1500	75	8	0·12	0·06
154	1-Phenylethyl	34·87	Ext.	0·1523	5—15	5	63·2	2·0
155	,,	,,	,,	0·1500	,,	8	64·1	1·5
156	,,	,,	UV	0·1408	5	3	63·8	0·6
157	,,	64·08	,,	0·1531	,,	3	69·1	0·8
158	1-Phenylpropyl	34·87	Ext.	0·1501	5—15	11	32·2	1·4
159	,,	,,	,,	0·1562	,,	2	32·6	1·0
160	3-Methyl-1-phenylbutyl	,,	,,	0·1530	20	7	27·1	1·2
161	,, ,,	,,	UV	0·1523	5	3	28·2	0·3
162	3,3-Dimethyl-1-phenylbutyl	,,	Ext.	0·1518	5—15	8	22·3	1·1
163	,, ,,	,,	UV	0·1600	5	3	22·0	0·3

* In nearly all runs the initial molar ratio of sodium ethoxide to sulphonium iodide was about 2 : 1.
† The proportion of olefin produced remained constant at 25, 30, 50, 60, and 75% of reaction.

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[43] MacPhee, *Analyt. Chem.*, 1954, **26**, 221.

TABLE 21. *Proportions of olefin formed in reactions of alkyldimethylsulphonium iodides with potassium t-butoxide in t-butyl alcohol at* 34·86°.

Run	Alkyl	Method	[Total salt]$_0$ *	Sample (ml.)	No. of points	Olefin (%)	
164	3,3-Dimethyl-1-phenylbutyl	UV	0·1503	5	3	46·0 ±	0·5
165	Ethyl	Asp.	0·1103	56	3	32·4	1·0
166	,,	,,	0·1135	56	3	32·3	1·1
167	n-Propyl	,,	0·1237	28—140	4	7·7	0·2
168	,,	,,	0·1213	28	3	8·2	1·5
169	,,	,,	0·1103	56	2	9·0	0·1
170	n-Butyl	Asp., Ext.	0·1203	20—40	5	5·5	0·7
171	Isopentyl	Ext.	0·1125	,,	5	2·9	0·9
172	,,	,,	0·1131	,,	4	1·6	0·5
173	,,	Asp.	0·1201	,,	3	2·4	0·4
174	3,3-Dimethylbutyl †	Ext.	>0·25	120	8	1·1	0·4
175	,, ‡	,,	0·1120	60	3	1·4	0·6
176	,, ‡	Col.	0·1032	75	2	1·2	0·3

* In runs 164—173, the initial molar ratio of potassium t-butoxide to sulphonium iodide was about 5 : 2.

† Not kinetically controlled: more sulphonium iodide was added than would dissolve in 0·25N-potassium t-butoxide in t-butyl alcohol.

‡ The initial solutions were approximately 0·025M in the sulphonium iodide, 0·065M in sodium t-butoxide, and such a concentration in sodium perchlorate as to bring the total salt up to the figures given.

TABLE 22. *Proportions of olefin formed in reactions of alkyltrimethylammonium nitrates with potassium ethoxide in ethanol.*

Run	Alkyl	Temp.	Method	[Total salt]$_0$ *	Sample (ml.)	No. of points	Olefin (%)	
177	Ethyl	104·2°	Asp.	0·9030	10	5	72·5 ±	1·5
178	,,	,,	,,	0·6130	22	7	69·5	1·3
179	,,	,,	,,	0·1523	20	3	70·3	1·0
180	n-Propyl	,,	,,	0·1532	75	3	18·0	0·7
181	,,	,,	,,	0·6230	10	3	19·5	0·9
182	Isopropyl	,,	,,	0·6234	10	6	97·2	1·6
183	n-Butyl	,,	Ext.	0·1531	80	2	10·7	0·5
184	,,	,,	,,	0·7032	50	4	10·5	0·2
186	Isobutyl	,,	,,	0·1493	25—30	6	6·2	1·0
187	t-Butyl	,,	,,	0·1523	25	5	98·0	1·9
188	Phenethyl	,,	UV	0·1612	5	5	100·3	0·6
189	n-Decyl	,,	Ext.	0·1523	20	4	15·0	0·9
190	Isopentyl	,,	,,	0·1547	50	3	4·5	0·1
191	,,	,,	,,	0·1555	80	2	3·8	0·3
192	,,	,,	,,	0·8032	50	2	3·5	0·1
193	3,3-Dimethylbutyl	,,	,,	0·1521	50—75	4	0·27	0·06
194	,,	,,	,,	0·5320	50	2	0·53	0·04
195	,,	,,	,,	0·7240	80	2	0·33	0·01
196	,,	,,	Col.	0·1520	25	4	0·36	0·05
197	1,2,2-Trimethylpropyl	100·6	Ext.	0·1583	20	4	53·0	0·7
198	,, ,,	,,	,,	0·8732	10	4	53·7	0·8
199	1-Ethyl-2,2-dimethylpropyl-	,,	,,	0·1864	10	3	9·3	0·2
200	,, ,,	,,	,,	0·6490	10	3	9·4	0·3
201	1-Isopropyl-2,2-dimethylpropyl-	,,	,,	0·6130	10	3	2·8	1·0
202	,, ,, ,,	,,	Hyd.	0·6130	4	4	1·9	0·4
203	1-Isopropyl-2-methylpropyl-	,,	Ext.	0·1623	25	3	20·0	0·5
204	,, ,, ,,	,,	,,	0·7023	10	3	20·2	0·5

* The initial total salt is given as the concentration of the supplied potassium ethoxide, because the potassium precipitates almost all the nitrate from the smaller supply of the ammonium nitrate. This supply was about 55% of that of the ethoxide in all experiments except those at 104·2° having total salt concentrations in the range 0·5—0·9M, when it was about 65%.

Very little of the solvent was thus carried over, as is important, because the aspirate has to be totally miscible with the medium (aqueous acetic acid) of the reagent. Acetic acid (10 ml.) and the reagent (30 ml.) were added to the aspirate, and the solution was left at room temperature in the dark for 3 hr. to allow the development of colour. The colour intensity, as read on a Spekker absorptiometer, with an Ilford red filter No. 608, was compared with a calibration curve, constructed from similar measurements on artificially prepared solutions in acetic acid of 3,3-dimethylbut-1-ene. It was shown that sulphides and alcohols were not present in the

Table 23. *Proportions of olefin formed in reactions of alkyltrimethylammonium nitrates and potassium t-butoxide in t-butyl alcohol at* 72·85°.

Run	Alkyl	Method	[Total salt]$_0$ *	Sample (ml.)	No. of points	Olefin (%)	
205	Ethyl	Asp.	0·1500	12	3	99·5	± 1·3
206	,,	,,	0·3201	7	3	100·1	1·5
207	n-Propyl	,,	0·1530	7	4	72·3	1·0
208	,,	,,	0·1562	12	3	73·3	1·2
209	n-Butyl	Ext.	0·2712	56	3	31·9	1·3
210	,,	,,	0·3623	56	3	31·9	0·9
211	Isopentyl	,,	0·1542	56—85	3	10·6	0·5
212	,,	,,	0·4420	75	3	11·3	0·7
213	3,3-Dimethylbutyl	,,	0·2613	56—75	6	0·41	0·13
214	,,	,,	0·8031	28	2	0·49	0·05
215	,,	,,	0·8320	28	3	0·37	0·05

* Potassium t-butoxide and the ammonium nitrate was supplied in the ratio of about 15 : 8 in all these experiments. The total initial salt concentration is taken as that of the supplied t-butoxide, because almost all the nitrate is precipitated as potassium nitrate.

samples analysed, that ethers gave no colour, and that the whole sample gave no colour if previously treated with bromine.

Hydrogenation. Bromometric determination of the small yield of olefin from 1-isopropyl-2,2-dimethylpropyltrimethylammonium ethoxide was rendered inaccurate by concurrent substitution, as checked by iodate titration of the hydrogen bromide formed, and recourse was therefore had to catalytic hydrogenation by Warburg's micromanometric technique. The experiments were done at 25°, with mercury as the manometric fluid, effects of temperature and pressure fluctuations being annulled by a compensating thermobarometer. The sample (4·0 ml.) and acetic acid (3·0 ml.) were placed in the Warburg flask, and platinum oxide (0·005 g.) and acetic acid (0·5 ml.) in the side-arm. Nitrogen was passed through the apparatus for 1 min. and then hydrogen for 4 min. Then the system was sealed, and brought to equilibrium by shaking for 5 min., whereafter the catalyst was tipped into the inner flask. Absorption of gas was rapid, and, at constant volume, reductions of pressure of about 30 mm. were recorded. The method was calibrated by use of artifically prepared olefin solutions.

Gas-chromatography. Most of the olefins were identified, along with the other volatile products of the sulphonium and ammonium salt decompositions, by gas-chromatography, and the same method served to confirm in an approximate way the lower yields of olefin as given by chemical or optical analysis.

(b) *Results.*—Typical runs are not presented here, because so many methods, and variations of method, were used. In Tables 20—23, the determined mean percentages of olefin are assembled, along with indications of the experimental method, the number of points for which the analysis was performed in each reaction, and the formal deviation. The key to the indications of method is as follows: Asp. = aspiration; Ext. = extraction; UV = optical absorption; Col. = colorimetry; Hyd. = hydrogenation.

Miscellaneous Analyses

(a) *Dimethyl Sulphide.*—This was aspirated from the reaction products with traps of aqueous mercuric chloride as described on p. 4083, and the precipitate was weighed [44] as $2Me_2S,3HgCl_2$. We required to know the proportions of methyl sulphide formed in the decompositions of the dimethyl-1-phenylalkylsulphonium ethoxides, in order to complete the determination of olefin by ultraviolet absorption spectrophotometry (p. 4083), and also in order to understand the rate changes generally in that series (p. 4066), in which our results for product composition are summarised in Table 24.

(b) *Other Products.*—Most of the products formed in the reactions studied in this paper had been identified in previous work, which we supplemented only in a few particular points. The decomposition of ethyldimethylsulphonium ethoxide, which gives 20% of ethylene, was shown, nevertheless, to yield dimethyl sulphide and ethyl methyl sulphide in the molecular ratio 4 : 1, by aspirating the sulphides, trapping them at a low temperature, methylating them with methyl iodide in nitromethane, and chromatographing the sulphonium iodides comparatively

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[44] Faraghar, Merrell, and Comay, *J. Amer. Chem. Soc.*, 1929, **51**, 2774.

TABLE 24. *Proportions of products formed in reactions of dimethyl-*1*-phenylalkylsulphonium iodide with sodium ethoxide in ethanol at* 34·87°.

Run	1-Phenylalky	Me_2S * %	Olefin %	Substitution (%) to give Me_2S	RSMe
216	1-Phenylethyl	94	63·8	30·2	6
217	1-Phenylpropyl	72	32·2	39·8	28
218	3-Methyl-1-phenylbutyl	54	28·0	26·0	46
219	3,3-Dimethyl-1-phenylbutyl	32	22·0	10·0	68

* All figures in this column are means of 5 readings.

with authentic specimens of the components of the mixtures. On the other hand, the decomposition of ethyltrimethylammonium ethoxide gave trimethylamine hydrochloride in proportion corresponding to the ethylene, whilst the obtained ethyldimethylamine hydrochloride accounted for all the rest of the decomposition. The products from 3,3-dimethylbutyl-dimethylsulphonium and -trimethylammonium ethoxide were identified by gas-chromatography, authentic specimens of the separate products being used for identification of the peaks. Incidentally, from the latter decomposition, the new amine, 3,3-dimethylbutyldimethylamine, b. p. 125—127°, the *hydrochloride* of which decomposed above 130° (Found: Cl, 21·3. $C_8H_{20}NCl$ requires Cl, 21·5%), was isolated in 90% yield. The products from the much-branched quaternary ammonium ethoxides of Series (5) (cf. Section 7) were similarly identified by gas-chromatography, and those from the 1-phenylalkylsulphonium ethoxides of Series (6) (cf. Section 8) were separated chemically and by chromatography on alumina or kieselguhr, the olefins bring identified mainly by infrared analysis.

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

[*Received, March* 21*st*, 1960.]