233. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XX. Elimination of Saturated Primary Alcohols by Thermal Decomposition of Sulphonium Hydroxides.*

By C. K. INGOLD and K. I. KURIYAN.

THE production of saturated primary alcohols (the adjective " primary " is held to exclude methyl alcohol) by thermal decomposition of quaternary ammonium hydroxides has been claimed by von Braun (*Annalen*, 1911, **382**, 1), who reported the formation of *n*-heptyl, *n*-octyl, and cetyl alcohols from heptyl-, octyl-, and cetyl-trimethylammonium hydroxides respectively. Our experiments on these compounds do not enable us to confirm either result, and, without wishing to deny that saturated primary alcohols can be produced in this way, we suggest that the claim that they are formed needs further support.

The decomposition of sulphonium hydroxides is in a different case. In a recent study of the degradation of a series of these compounds containing both methyl and ethyl groups (*e.g.*, methylethyl-*n*-propylsulphonium hydroxide), Ingold, Jessop, and Kuriyan found that the aqueous solutions of methyl alcohol obtained from these decompositions contained a significant quantity of ethyl alcohol (this vol., p. 536). We have now studied the decompositions of triethyl- and tri-*n*-propyl-sulphonium hydroxides, and find that the proportion of alcohol elimination (reaction B) in the former case is considerable (14%) and in the latter predominating (64%) :

$$\{(R\cdot CH_2\cdot CH_2)_3S\}\cdot OH' \begin{array}{l} \nearrow R\cdot CH{:}CH_2 + (R\cdot CH_2\cdot CH_2)_2S + H_2O \qquad (A) \\ \searrow R\cdot CH_2\cdot CH_2\cdot OH + (R\cdot CH_2\cdot CH_2)_2S \qquad (B) \end{array}$$

Sulphonium hydroxides containing methyl and ethyl groups were found to undergo decomposition in all three possible directions (methyl and ethyl alcohols and ethylene are formed), and the figures for the proportions of total alcohols are normally distributed between the values appropriate to the trimethyl- and triethyl-compounds :

Alkyl group	Me_3.	Me_2Et.	$MeEt_2$.	Et_3.
Total alcohols (mols. %)	100	73	45	14

A similar statement applies to sulphonium hydroxides containing methyl and *n*-propyl groups :

Alkyl group	Me_3.	Me_2Pr^a.	$MePr_2^a$.	Pr_3^a.
Total alcohols (mols. %)	100	92	82	64

These results may be considered in relation to the hypothesis that the facility of elimination of a given alkyl group in a given way is to a first approximation an intrinsic property of the group rather than an orientation process dependent on the other groups present in the sulphonium complex. In order to test this assumption, we proceed as follows : For a given mode of decomposition of a given sulphonium hydroxide, a quotient is formed by dividing the proportion in which reaction pursues the appropriate direction by the number of those initially present identical groups, one of which thus becomes eliminated. Similar quotients are obtained for the other methods of decomposition of the same sulphonium hydroxide, and the ratios of pairs of these quotients are taken to be representative of the corresponding pairs of eliminated forms—two olefins, two alcohols, or an olefin and an alcohol as the case may be. According to the hypothesis considered, the ratios of quotients obtained in this way from the decompositions of different sulphonium hydroxides should be consistent, and a convenient method of applying the test is to assume consistency, and utilise experimental values for the direction of decomposition of some sulphonium hydroxides to calculate corresponding data for others. For the sulphonium hydroxides already mentioned, this calculation has been carried out and the results are shown in the upper section (Nos. 1—6) of the following table. The asterisks in the column headed "Calc." indicate that the corresponding experimental values are used as part of the basis of the calculation; the figures thus computed for the remaining examples are sufficiently close to those obtained experimentally to indicate that the criterion of consistency is approximately fulfilled. The experimental figures for examples Nos. 3 and 5 are quoted from a previous publication (*idem, ibid.*).

No.	No. of modes of decompn.	Alkyl groups.	Total alcohols, %. Found.	Calc.	No.	No. of modes of decompn.	Alkyl groups.	Total alcohols, %. Found.	Calc.
1	2	Et_3	14	*	4	3	$MeEt_2$	45	*
2	2	Pr_3^a	64	*	5	3	Me_2Pr^a	92	92
3	3	Me_2Et	73	74	6	3	$MePr_2^a$	82	*

No.	No. of modes of decompn.	Alkyl groups.	Compn. of olefin mixture: lower homologue, %. Found.	Calc.	No.	No. of modes of decompn.	Alkyl groups.	Compn. of olefin mixture: lower homologue, %. Found.	Calc.
7	4	Et_2Pr^a	85	89	11	4	Et*iso*Bu_2	94	*
8	4	$EtPr_2^a$	63	68	12	5	$MeEtPr^a$	80	81
9	4	$Pr_2^aBu^a$	74	73	13	5	MeEt*iso*Bu	93	97
10	4	$Pr^aBu_2^a$	40	*					

Opportunity for a further test of the matter is afforded by the study of a series of sulphonium hydroxides containing combinations of the groups ethyl and *n*-propyl, *n*-propyl and *n*-butyl, and ethyl and *iso*butyl. Each of these examples permits of four modes of decomposition, since either radical may appear either as an alcohol or as an olefin. All these sulphonium hydroxides give both alcohols and olefins, and the proportions in which olefins were formed were estimated. The results are shown in the lower portion of the table (Nos. 7—11), and once again a comparison of found and calculated values indicates the absence of any considerable mutual influence between the different alkyl groups.

We include in the table two previously published examples (Nos. 12 and 13) of sulphonium hydroxides capable of decomposing in five ways (*idem, ibid.*). The actual and theoretical results present an agreement resembling that obtained in the simpler cases.

EXPERIMENTAL.

As the general method of decomposing the sulphonium hydroxides is the same as that described in a previous part (*idem, ibid.*), this record is limited to the preparation of the required sulphonium salts. (1) Triethylsulphonium iodide (Offele, *Annalen*, 1864, **132**, 82), m. p. 150—152° (decomp.), prepared in nitromethane, yielded a *picrate*, long needles, m. p. 152—153°, from water (Found: C, 41·5; H, 4·9. $C_{12}H_{17}O_7N_3S$ requires C, 41·5; H, 4·9%). The value given above for the percentage of olefin elimination is the result of consistent (± 2%) gas analyses confirmed by estimates of ethyl alcohol content of sulphide-free aqueous solutions, from which iodoform was prepared. (2) Tri-*n*-propylsulphonium iodide, prepared by heating the components in nitromethane at 50—55° for several days, precipitation by ether, and reprecipitation from alcohol by ether, yielded a *picrate*, long needles, m. p. 75—76°, from water (Found: C, 46·3; H, 6·0. $C_{15}H_{23}O_7N_3S$ requires C, 46·3; H, 5·9%). Regarding the analytical data the remarks in section (1) apply.

(4) Methyldiethylsulphonium iodide (Klinger and Maassen, *Annalen*, 1888, **243**, 212) yielded a *picrate*, needles, m. p. *ca.* 170°, from water (Found: C, 39·9; H, 4·5. $C_{11}H_{15}O_7N_3S$ requires C, 39·6; H, 4·5%). Iodoform was made from the alcoholic fraction after decomposition. (6) Methyldi-*n*-propyl iodide, prepared in nitromethane, gave a *picrate*, crystallising from water, m. p. 68° (Found: C, 43·0; H, 5·4. $C_{13}H_{19}O_7N_3S$ requires C, 43·3; H, 5·3%). (7) Diethyl-*n*-propylsulphonium iodide, m. p. 162° (decomp.), prepared by heating ethyl sulphide and *n*-propyl iodide in nitromethane at 50—55° for four days, and purified as in (2),

yielded a *picrate*, m. p. 72—73° (Found : C, 43·3; H, 5·3; N, 11·4; S, 9·0. $C_{13}H_{19}O_7N_3S$ requires C, 43·2; H, 5·3; N, 11·6; S, 8·9%). (8) Ethyldi-*n*-propylsulphonium iodide, prepared similarly from ethyl iodide and *n*-propyl sulphide, gave a *picrate* crystallising from water in long needles, m. p. 73·5—74° (Found : C, 45·0; H, 6·0; N, 11·2; S, 8·5. $C_{14}H_{21}O_7N_3S$ requires C, 44·8; H, 5·6; N, 10·6; S, 8·4%).

(9) Di-*n*-propyl-*n*-butylsulphonium sulphate, prepared by heating butyl iodide, propyl sulphide, and excess of suspended silver sulphate in nitromethane at 80° for 20 hours and precipitated by ether, gave a *picrate*, forming needles, m. p. 73°, from water (Found : C, 47·9; H, 6·3. $C_{16}H_{25}O_7N_3S$ requires C, 47·6; H, 6·2%). (10) *n*-Propyl-di-*n*-butylsulphonium iodide, prepared by heating propyl iodide and butyl sulphide in nitromethane at 50—52° for 18 days and precipitation with ether, had m. p. 155—160° (decomp.) and gave a *picrate*, forming long needles, m. p. 67—68°, from water (Found : C, 49·3; H, 6·6; N, 9·8; S, 7·7. $C_{17}H_{27}O_7N_3S$ requires C, 49·5; H, 6·4; N, 10·0; S, 7·6%). (11) Ethyldi*iso*butylsulphonium iodide, prepared by heating ethyl iodide with *iso*butyl sulphide (Grabowsky and Saizew, *Annalen*, 1874, **171**, 254) in nitromethane at 50—55° for 10 days and precipitated with ether, gave a *picrate*, separating in needles, m. p. 75—76°, from water (Found : C, 47·7; H, 6·7. $C_{16}H_{25}O_7N_3S$ requires C, 47·6; H, 6·2%).

UNIVERSITY COLLEGE, LONDON.

[*Received, June* 16*th*, 1933.]