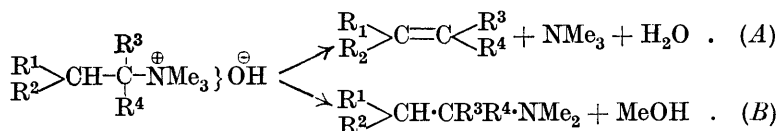# CCCCXI.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part II. Mechanism of Exhaustive Methylation* (continued).

By CHRISTOPHER KELK INGOLD and CHARLES CYRIL NORREY VASS.

IN Part I,* a theory of the mechanism of the decomposition of quaternary ammonium compounds was developed and shown to be in accord with several different types of experimental data. One of the tests applied consisted in tracing the relation between the constitution of an alkyl group (Alk) and the ratio of the olefin formed to the methyl alcohol eliminated in the decomposition of the corresponding trimethylalkylammonium hydroxide ($Alk \cdot NMe_3 \cdot OH$). Expanding Alk to $CHR^1R^2 \cdot CR^3R^4 \cdot$, and naming the simultaneous reactions referred to (A) and (B) for convenience in reference :

$$\begin{array}{c} R^1 \\ R^2 \end{array}\!\!>\!CH\!-\!\overset{R^3}{\underset{R^4}{\overset{\oplus}{C}\!-\!\overset{}{N}Me_3}} \} \overset{\ominus}{OH} \left\langle \begin{array}{l} \nearrow \begin{array}{c} R^1 \\ R^2 \end{array}\!\!>\!C\!\!=\!\!C\!\!<\!\!\begin{array}{c} R^3 \\ R^4 \end{array} + NMe_3 + H_2O \quad . \quad (A) \\ \\ \searrow \begin{array}{c} R^1 \\ R^2 \end{array}\!\!>\!CH \cdot CR^3R^4 \cdot NMe_2 + MeOH \quad . \quad (B) \end{array} \right.$$

theory predicted that the suppression of (A) in favour of (B)

   (i) should be governed by R^1 and R^2 much more than by R^3 and R^4.

   (ii) should increase, tending towards constancy, with increasing R^1 and R^2.

   (iii) should be greater when $R^1R^2CH \cdot$, or any part thereof, is branched than when the corresponding group or part is unbranched but isomeric.

In Part I, prediction (i) was established very fully, (ii) was demonstrated for groups up to and including propyl, and (iii) was confirmed for *n*- and *iso*-propyl. In the present paper, this particular test of the general theory is extended, prediction (ii) is verified up to and including hexyl, and (iii) is further established in the case of *n*- and *iso*-butyl. The results are shown in Table I.

Since the publication of Part I, the technique of these decompositions has been improved in various minor details (*e.g.*, the quantitative collection of the olefin and the more complete exclusion of carbonates and silicates from the hydroxide solution) and we have accordingly to correct the earlier values for propyl and butyl by a

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* The parent paper of this series (Hanhart and Ingold, J., 1927, 997), herein called Part I, was actually published under another (more general) title.

TABLE I.

Decomposition of Trimethylalkylammonium Hydroxides,
$\{Alk \cdot NMe_3\}^{\cdot}OH'$ or $\{CHR^1R^2 \cdot CR^3R^4 \cdot NMe_3\}^{\cdot}OH'$.

| | | | Mols. % olefin (reaction A). | | |
| | | | Previous results. | | This paper |
No.	Alk.	$R^1(R^2=R^3=R^4=H)$.	H. & I.*	v. B.†	(see Table II).
1	Ethyl	H·	—	—	95
2	n-Propyl	CH_3·	81	—	84
3	n-Butyl	$CH_3 \cdot CH_2$·	75	50	79
4	n-Amyl	$CH_3 \cdot CH_2 \cdot CH_2$·	—	40	77
5	n-Hexyl	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2$·	—	27	76
6	n-Heptyl	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2$·	—	25	74
7	n-Octyl	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2$·	—	25	75
8	isoAmyl	$(CH_3)_2CH$·	—	—	72

* Hanhart and Ingold, Part I, *loc. cit.*
† von Braun, *Annalen*, 1911, **382**, 1.

few units per cent.* Although it is necessary to direct attention to the results already on record (Table I), we do not propose here to discuss the cause of the large discrepancies between v. Braun's results and those obtained by us, since this point, which is of considerable interest, will be dealt with in a forthcoming paper by that author. The figures in the last column of the table we regard with confidence. In Nos. 1—7 the suppression of (A) with increasing R^1, and the approach to a constant value (75%) are clearly indicated (prediction ii), and the comparison of Nos. 4 and 8, in which CHR^1R^2· is n- and iso-butyl, respectively, supplies a further confirmation of (iii).

EXPERIMENTAL.

The quaternary compounds were prepared from trimethylamine and the appropriate alkyl bromide or iodide. Benz-n-amylamide (an intermediate in the preparation of n-amyl bromide from piperidine) is described by v. Braun and Sobechi as an oil (*Ber.*, 1910, **43**, 3596). Our specimens were in all cases solid and crystallised from ether–ligroin in needles, m. p. 31—32°, b. p. 205—210°/18 mm.

The method was substantially the same as in Part I, the olefins being weighed as their dibromides (Table II, column 5), and the mixed tertiary bases analysed as their methopicrates. Since the precipitation of these was never complete (Table II, column 7), the compositions deduced from their nitrogen content constitute only an approximate check (Table II, column 8). The hexene, heptene, and octene were collected in chloroform (under hydrochloric acid) and subsequently combined with bromine.

* There is theoretical reason to suspect that the proportion of olefin formed would vary *slightly* with the form of the apparatus used for distillation, so that the 3—4% difference may not all represent experimental error.

TABLE II.

Expt. No.	Alkyl group (Alk).	Salt taken (anion).	Wt. converted into hydroxide.	Olefin formed.		Yield of methopicrates.	Trimethylamine (mols.%).
				Mols. %.	Mean.		
24	Ethyl	Bromide	32·76	94·5		—	—
25	,,	Iodide	39·17	94·8	94·6	93·2	Almost
26	,,	,,	31·14	94·4		92·7	pure *
20	n-Propyl	Iodide	25·89	82·9		—	—
21	,,	,,	40·05	84·1	83·7	91·7	88
22	,,	,,	37·87	84·2		85·0	93
5	n-Butyl	Iodide	38·43	79·6		89·1	80
6	,,	,,	42·46	80·0	79·2	80·0	84
7	,,	,,	41·10	77·9		79·2	82
27	n-Amyl	Bromide	21·72	77·0	76·6	89·4	80
28	,,	,,	25·97	76·1		92·8	80
29	n-Hexyl	Iodide	25·06	75·6	75·6	90·2	78
17	n-Heptyl	Iodide	20·76	74·7		—	—
18	,,	,,	37·43	73·0	73·8	95·4	75
19	,,	,,	40·09	73·6		—	—
12	n-Octyl	Iodide	27·36	73·9		—	—
13	,,	,,	42·55	76·7	75·4	—	—
14	,,	,,	43·85	74·8		94·6	78
15	,,	,,	38·71	76·0		—	—
8	isoAmyl	Bromide	26·23	71·5		—	—
9	,,	,,	37·41	72·2	71·7	94·4	76
10	,,	,,	37·50	71·6		—	—

* The compositions of the constituents are here too close for analysis to be of service.