22. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XI. Decomposition of Quaternary Ammonium Hydroxides containing the* tert.*-Butylcarbinyl Group.*

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It has been suggested (Part I; J., 1927, 997) that in the decomposition of quaternary ammonium hydroxides having hydrocarbon radicals without a β-hydrogen atom the group which is more stable as a cation will be preferentially eliminated; but the examples given were not conclusive because benzyl, for instance, forms not only a more stable cation than methyl but also a more stable anion. A better comparison would be between methyl and primary alphyl groups, and the suggestion indicated would mean that the ethyl group, $CH_3 \rightarrow CH_2$, should *ceteris paribus* be more readily eliminated than the methyl group, $H—CH_2$, because in the former case the inductive effect represented by the arrow should stabilise the cation. Actually, the issue as between methyl and ethyl is confused by the circumstance that the latter has an alternative mode of elimination, but the *tert.*-butylcarbinyl group, the simplest primary alphyl group devoid of a β-hydrogen atom, has not this disadvantage, and the argument illustrated for the ethyl group applies with greater force to this higher homologue, $Me_3C \rightarrow CH_2$. We find that the decomposition of *tert.*-butylcarbinyltrimethylammonium hydroxide proceeds substantially in a single direction and that the alcohol eliminated is methyl alcohol. Thus the order of ease of elimination of the radicals concerned, $CH_3 > CMe_3{\cdot}CH_2$, is the reverse of that anticipated, and the circumstance that primary and secondary paraffin alcohols have never been observed to appear during the decompositions of ammonium hydroxides can, we think, despite the complication of olefin-elimination, be accepted as indicating an intrinsically smaller tendency in primary and secondary alphyl groups than in the methyl group to undergo elimination as an alcohol. On the other hand the case of the *tert.*-butyl group (Part I, *loc. cit.*) will serve as a warning against incautious generalisation. The position of the benzyl group relatively to methyl and primary alkyl groups follows from our observation that benzyl-*tert.*-butylcarbinyldimethylammonium hydroxide decomposes to the extent of at least 90% in the direction leading to benzyl alcohol and the complementary amine, thus indicating the order, $C_6H_5{\cdot}CH_2 > H{\cdot}CH_2 > CMe_3{\cdot}CH_2$.

Experimental.

Preparation.—The most convenient route to *tert.*-butylcarbinylamine and its methyl derivatives was found to be that which proceeds *via* pivalonitrile. Pivalic acid ("Organic Syntheses," VIII, 108) was converted into its chloride, b. p. 103° (Butlerow, *Annalen*, 1874,

173, 373, who used PCl_5, records 105—106°), by treatment on the water-bath with $SOCl_2$, and thence into the amide, m. p. 155°, by means of well-cooled conc. aq. NH_3 and crystn. from H_2O to remove NH_4Cl. From the amide, the nitrile, m. p. 15°, b. p. 106°, was prepared (Butlerow, *loc. cit.*), and this was reduced (Freund and Lenze, *Ber.*, 1890, **23**, 2867; 1891, **24**, 2156; Tissier, *Ann. Chim. Phys.*, 1893, **29**, 373) to the primary amine, b. p. 80—82°, of which the hydrochloride had m. p. 274° (decomp.), the *picrate*, leaflets from alcohol, m. p. 205° (Found: C, 41·9; H, 5·15. $C_{11}H_{16}O_7N_4$ requires C, 41·8; H, 5·06%), and the acetyl derivative, m. p. 75°. Methylation of the primary amine to the tertiary stage was accomplished by Eschweiler's general method (*Ber.*, 1905, **38**, 881), a mixture of the hydrochloride (10 g.) and paraformaldehyde being heated under reflux at 140° (bath temp.) for 3 hr. Treatment with conc. aq. KOH gave an oil consisting of tert.-*butylcarbinyldimethylamine*, which after drying with KOH and with Na had b. p. 96—97° (Found: C, 72·9; H, 14·6. $C_7H_{17}N$ requires C, 73·0; H, 14·8%). The *hydrochloride*, prepared in Et_2O–EtOH and cryst. from EtOH, formed hygroscopic prismatic plates, m. p. 182° (Found: Cl, 23·15. $C_7H_{17}N,HCl$ requires Cl, 23·4%), the *hydrobromide* was obtained as hygroscopic needles, m. p. 170° (Found: Br, 40·8. $C_7H_{17}N,HBr$ requires Br, 40·8%), and the *hydriodide* as small crystals, m. p. 135° (Found: I, 52·8. $C_7H_{17}N,HI$ requires I, 52·3%). The *picrate*, pptd. from Et_2O and cryst. from EtOH, formed stout needles, m. p. 193° (Found: C, 45·6; H, 5·9. $C_{13}H_{20}O_7N_4$ requires C, 45·3; H, 5·8%). A mixture of the tertiary base (5 g.) and MeI (7 g.) was kept for 4 hr. at room temp. and the solid mass formed was ground with Et_2O and crystallised from EtOH, tert.-*butylcarbinyltrimethylammonium iodide* (10 g.) being obtained as a microcryst. mass, m. p. 240° (decomp.) (Found: I, 49·1. $C_8H_{20}NI$ requires I, 49·4%). Similarly the *tert.*-amine (7 g.) and benzyl bromide (12 g.) yielded *benzyl*-tert.-*butylcarbinyldimethylammonium bromide*, which, similarly purified, had m. p. 200° (decomp.) (Found: Br, 27·7. $C_{14}H_{24}NBr$ requires Br, 28·0%).

tert.-Butylcarbinyldimethylamine was also obtained, though in small yield, by the action of *tert.*-butylmagnesium chloride on dimethylaminomethyl *n*-butyl ether (McLeod and Robinson, J., 1921, **119**, 1470).

tert.-Butylcarbinol, prepared by reduction of ethyl pivalate (Richards, *Ann. Chim. Phys.*, 1910, **21**, 337), was converted into the iodide with red P and I, Tissier's method (*loc. cit.*) being unsuccessful in our hands. On treatment with dimethylamine this iodide yielded the hydriodide of the original amine (cf. Noller and Dinsmore, *J. Amer. Chem. Soc.*, 1931, **53**, 1185; 1932, **54**, 1025).

Decomposition of Hydroxides.—A solution of *tert.*-butylcarbinyltrimethylammonium hydroxide was prepared from the iodide (11·9 g.) and a small excess of Ag_2O. Preliminary expts. having shown that the decomp. of the hydroxide yielded no gaseous products (substances which could be collected in dil. acid or Br after condensation of the aq. distillate), the hydroxide solution was distilled (bath temp. 150—200°) in the ordinary way. The distillate yielded 4·95 g. of pure *tert.*-butylcarbinyldimethylamine and the basic residues, when worked up as hydrochlorides, gave 0·82 g. of the salt of the same amine (total yield, 93%). The small loss appeared to be mainly mechanical, a careful search failing to reveal the presence of *tert.*-butylcarbinol or trimethylamine. MeOH was found in quantity and identified as methyl *p*-nitrobenzoate.

The decomposition of benzyl-*tert.*-butylcarbinyldimethylammonium hydroxide was conducted in the same way, and pure *tert.*-butylcarbinyldimethylamine was isolated in 90% yield. Benzyl alcohol was isolated in quantity, but neither MeOH nor *tert.*-butylcarbinol could be obtained.

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