24. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XIII. Decompositions of some Quaternary Ammonium Salts containing the Methyl, Benzyl, and Benzhydryl Groups.*

By E. D. Hughes and C. K. Ingold.

The preconception (Hanhart and Ingold, J., 1927, 997) that the groups named in the title would be eliminated from ammonium hydroxides in the order of preference $CHPh_2 > CH_2Ph > CH_3$ had been verified for the last pair by Collie and Schryver (J., 1890, **57**, 767), who obtained benzyl alcohol as the main product of the decomposition of benzyltrimethylammonium hydroxide; but they also isolated benzyldimethylamine, which proves that the reaction follows both the possible directions. Reinvestigation has confirmed this, and has shown that the ratio in which decomposition follows the two routes is as indicated below :

$$\{C_7H_7{\cdot}\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H \begin{array}{l} \nearrow C_7H_7{\cdot}OH + NMe_3 \;.\;.\;.\;.\; 65\% \\ \searrow MeOH + C_7H_7{\cdot}NMe_2 \;.\;.\; 35\% \end{array}\Big\}\ \text{Total } 100\%.$$

A complication, not mentioned by Collie and Schryver, was encountered in the production of benzaldehyde and benzyl ether, but these are regarded as derived from benzyl alcohol, the one by oxidation at the instance of traces of silver oxide, and the other by dehydration in the presence of electrolytes (Oddo, *Gazzetta*, 1901, **31**, 348).

The decomposition of benzhydryltrimethylammonium hydroxide attained perceptible speed at a temperature noticeably lower than did that of the benzyl compound; nevertheless, the alcohol eliminated in greater proportion was not benzhydrol but methyl alcohol :

$$\{C_{13}H_{11}{\cdot}\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H \begin{array}{l} \nearrow C_{13}H_{11}{\cdot}OH + NMe_3 \;.\;.\;.\;.\; 18\% \\ \searrow MeOH + C_{13}H_{11}{\cdot}NMe_2 \;.\;.\; 51\% \end{array}\Big\}\ \text{Total } 69\%.$$

Two other products were isolated in addition to those represented in these equations. One was benzhydryl ether, which we regard as derived from benzhydrol : its equivalent in terms of benzhydrol has been allowed in deriving the figures given above. The other product (see below) represents a third mode of decomposition of the benzhydrylammonium compound, and accounts for the remaining 31% of material.

We accepted the observations described above as an indication of a possible difference in the orders of the two reactions whereby benzhydryltrimethylammonium hydroxide yields alcohols—a difference such as would cause the proportions of the products to depend fundamentally on the concentration at which decomposition takes place. For reasons given in a later paper, our working hypothesis was that the elimination of benzhydrol is a reaction of the first order, its speed being proportional only to the concentration $[C_{13}H_{11}{\cdot}\overset{\oplus}{N}Me_3]$, whereas that of methyl alcohol is a second-order process, the rate of which is governed by the activity product $f_+f_-[C_{13}H_{11}{\cdot}\overset{\oplus}{N}Me_3][\overset{\ominus}{O}H]$. The decomposition of benzhydryltrimethylammonium hydroxide is not suitable for detailed dynamical study, but we have been able to apply two semiquantitative tests of the working hypothesis outlined.

In the first place the decomposition was carried out in constant volume at different initial concentrations, which are shown in col. 2 of the first table. Col. 3 shows the proportions in which the decompositions pursue jointly the two directions leading to alcohols; the defect of these percentages below 100 represents the extent to which the third side-reaction enters, and this assumes importance only in the case of the more concentrated solutions. Cols. 4 and 5 contain the proportions in which decomposition pursues the paths leading to benzhydrol and methyl alcohol respectively, expressed as percentages of the amount of reaction which follows these two routes jointly.

Expt. No.	Concn. $\{C_{13}H_{11}{\cdot}NMe_3\}{\cdot}OH'$.	Total yield alcohols, %.	Proportions of alcohols, %.	
			$Ph_2CH{\cdot}OH$.	$CH_3{\cdot}OH$.
1	2·95*N*	73	52	48
2	2·40*N*	93	62	38
3	1·26*N*	*ca.* 100	85	15
4	0·69*N*	,, ,,	89	11
5	0·56*N*	,, ,,	91	9

The figures show that the proportions in which benzhydrol and methyl alcohol are eliminated depend fundamentally on the concentration. The sense of the variation is evidently that required by our hypothesis relating to the different orders of the reaction concerned. It can, moreover, easily be shown that, within the limits of uncertainty due to the impossibility of exactly computing the disturbance caused by the third reaction on the dynamics of the other two, the magnitude of the variation found accords with that expected. The whole result is in notable contrast to that recorded by von Braun, Teuffert, and Weissbach for decyltrimethylammonium hydroxide, the two directions of decomposition of which maintain to each other a constant ratio independently of concentration (*Annalen*, 1929, **472**, 121).

The second test consisted in an examination of the effect of carrying out the decomposition of benzhydryltrimethylammonium hydroxide in the presence of a constant concentration of added potassium hydroxide. The method was the same as in the previous series of tests. According to our hypothesis concerning the orders of the reactions, the effect of the added potassium hydroxide should be to favour the formation of methyl alcohol at the expense of the reaction leading to benzhydrol. As the following figures show, this phenomenon was observed, and once again the extent of the effect is, to within the limits of the inevitable uncertainties, of the expected magnitude :

Expt.	Concn. of		Total yield	Proportions of alcohols, %.	
No.	$\{C_{13}H_{11}\cdot NMe_3\}\cdot OH'$.	KOH.	alcohols, %.	$CHPh_2\cdot OH$.	$CH_3\cdot OH$.
4, 5	0·66*N*	nil	*ca.* 100	90	10
6		3·92*N*	85	60	40

It remains to consider the third side-reaction, which we regard as a manifestation of attack by the anion on the α-hydrogen atom of the benzhydryl group, followed by a rearrangement effecting internal neutralisation of the dipole thus formed :

$$\{(C_6H_5)_2CH\cdot\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H \longrightarrow [(C_6H_5)_2\overset{\ominus}{C}\cdot\overset{\oplus}{N}Me_3] \longrightarrow (C_6H_5)_2CMe\cdot NMe_2$$

Stevens has described many migrations of this character, and all the circumstances of reaction which he and his collaborators have elucidated are in excellent agreement with the theory of α-proton attack (J., 1928, 3193, *et seq.*). Ingold and Jessop, who studied α-proton attack in the 9-fluorenyl series, found that solutions of 9-fluorenyltrimethylammonium hydroxide were deeply coloured and presumed the existence in this case of a rather stable intermediate dipole, $(C_6H_4)_2\overset{\ominus}{C}\cdot\overset{\oplus}{N}Me_3$, the sulphonium analogue of which, $(C_6H_4)_2\overset{\ominus}{C}\cdot\overset{\oplus}{S}Me_2$, they subsequently isolated (J., 1929, 2357; 1930, 713). It has since been found that the last substance is readily methylated on its negative carbon atom by an external methylating agent (Kuriyan, *Dissert.*, London, 1932).

Thus the intrinsic probability of the interpretation suggested is very great; but formal proof of the constitution of the basic product is lacking. We hoped to obtain it by methylation and conversion of the methohydroxide into αα-diphenylethylene and trimethylamine, but the neutral product of this decomposition was actually a new crystalline dimeride of diphenylethylene :

$$2\{(C_6H_5)_2CMe\cdot\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H \longrightarrow (C_{14}H_{12})_2 + 2NMe_3 + 2H_2O$$

An indirect confirmation of the assigned structure may, however, be derived from the example next considered.

Benzhydrylbenzyldimethylammonium hydroxide has three possible ways of eliminating an alcohol, and we find that decomposition proceeds along all three routes :

$$\begin{tikzcd}[row sep=tiny] & C_{13}H_{11}\cdot OH + C_7H_7\cdot NMe_2 \\ \{C_{13}H_{11}\cdot\overset{\oplus}{N}(C_7H_7)Me_2\}\overset{\ominus}{O}H \arrow[ur] \arrow[r] \arrow[dr] & C_7H_7\cdot OH + C_{13}H_{11}\cdot NMe_2 \\ & MeOH + C_{13}H_{11}\cdot N(C_7H_7)Me \end{tikzcd}$$

In addition there is a fourth simultaneous reaction which is shown later to involve migration.

As in the example already considered, the extent to which decomposition follows the route leading to benzhydrol depends fundamentally on concentration, this reaction predominating in dilute solution. At an initial concentration of 0·5*N*, the yield of benzhydrol was 80%; at concentration 1·8*N*, it was only 50%; by prior concentration of the solution to a syrup and addition of solid potassium hydroxide before decomposition, the proportion was depressed to under 10%.

The migration-reaction was found to be generally more pronounced in this example than in the preceding one, although once again it assumed its chief importance in the experiments with concentrated solutions :

$$\{(C_6H_5)_2CH{\cdot}\overset{\oplus}{N}(CH_2{\cdot}C_6H_5)Me_2\}\overset{\ominus}{O}H \longrightarrow (C_6H_5)_2C(CH_2{\cdot}C_6H_5){\cdot}NMe_2 + H_2O.$$

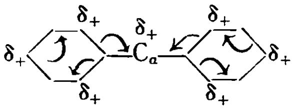
The methohydroxide of the tertiary basic product underwent decomposition in two directions yielding, on the one hand, methyl alcohol and the original tertiary base, and on the other, trimethylamine and triphenylethylene, the definite identification of which establishes the general character of these decompositions of benzhydrylammonium compounds :

$$\{C_6H_5{\cdot}CH_2{\cdot}CPh_2{\cdot}\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H - \begin{array}{l}\nearrow C_6H_5{\cdot}CH{:}CPh_2 + NMe_3 + H_2O \\ \searrow C_6H_5{\cdot}CH_2{\cdot}CPh_2{\cdot}NMe_2 + MeOH\end{array}$$

Finally, it is of interest to compare this decomposition with that of β-phenylethyltrimethylammonium hydroxide, which proceeds at a considerably lower temperature and in one direction only :

$$\{C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\oplus}{N}Me_3\}\overset{\ominus}{O}H \longrightarrow C_6H_5{\cdot}CH{:}CH_2 + NMe_3 + H_2O$$

Evidently the incipient ionisation of the β-hydrogen atom in the β-phenylethyl group is much more pronounced than in the ααβ-triphenylethyl group, and this inference is significant confirmation of the general picture of olefin elimination given by Hanhart and Ingold (Part I, *loc. cit.*). In the system $C_6H_5{\cdot}CH_2{\rightarrow}CH_2{\rightarrow}N\oplus$, the ammonium pole attracts electrons from C_α, the charge on which is relayed to C_β by continued induction; but in the α-phenylated system $C_6H_5{\cdot}\underset{(\beta)}{CH_2}{-}\underset{(\alpha)}{CPh_2}{\rightarrow}N\oplus$ the charge conferred by the pole on Cα will be so largely decentralised by distribution over the attached benzene rings (just as, *e.g.*, in $Ph_3C\oplus$; cf. Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, 421) that little is left for relay to C_β :



EXPERIMENTAL.

Decomposition of Benzyltrimethylammonium Hydroxide.—The corresponding chloride, which gave a picrate, m. p. 170° (Found : C, 50·9; H, 4·8; N, 15·1. Calc. : C, 50·8; H, 4·8; N, 14·8%), was treated with an aq. suspension of CO_3''-free Ag_2O, and the filtered $\{CH_2Ph{\cdot}NMe_3\}^{\cdot}OH'$ solution was standardised acidimetrically and decomposed in the usual way. Reaction commenced at 145° (bath temp.) and was completed at 180° in a current of N. The product collected in dil. HCl was extracted with Et_2O, and the aq. portion partly distilled. In the distillate MeOH was qualitatively identified, and in the residue Me_3N was estimated by basification and passage of the volatile amine into a solution of MeI in MeCN, the Me_4NI thus formed being completely pptd. by the addition of Et_2O (Found : C, 23·9; H, 5·9; I, 63·6. Calc. : C, 23·9; H, 6·0; I, 63·2%). The residual $CH_2Ph{\cdot}NMe_2$, which was extracted with Et_2O, had b. p. 176—178°. The neutral product yielded, in addition to $CH_2Ph{\cdot}OH$, some Ph·CHO, b. p. 175—183° (phenylhydrazone, m. p. and mixed m. p. 156°), and $(CH_2Ph)_2O$, b. p. 290—295° (Found : C, 84·6; H, 7·1. Calc. : C, 84·8; H, 7·1%).

Benzhydryltrimethylammonium Salts.—Benzhydryl bromide was prepared by direct bromination of CH_2Ph_2 (Henderson, J., 1891, **59**, 731), and also by warming an HOAc solution of $CHPh_2{\cdot}OH$ and excess of HBr for a few hr., cooling, collecting the crystals, and washing them with ligroin. Sommelet (*Compt. rend.*, 1925, **180**, 76) prepared $\{CHPh_2{\cdot}NMe_3\}^{\cdot}Br'$ from $CHPh_2Br$ and NMe_3 in C_6H_6, and also from $CHPh_2{\cdot}NMe_2$ and MeBr in C_6H_6, but gives no analysis of the salt. We found the former reaction slow in C_6H_6, and although the reaction in $MeNO_2$ was rapid the yield of salt was impaired owing to the formation of $(CHPh_2)_2O$, m. p. and mixed m. p. 109° (Found : C, 88·5; H, 6·3. Calc. for $C_{26}H_{22}O$: C, 89·1; H, 6·3%); however, smooth and rapid interaction took place in MeCN and the salt, which partly crystallised, was completely pptd. with Et_2O, and the whole washed with Et_2O and crystallised from acetone.

The *bromide* (Found : C, 62·3; H, 6·9; N, 4·7; Br, 25·5. $C_{16}H_{20}NBr$ requires C, 62·7; H, 6·5; N, 4·6; Br, 26·1%), m. p. 145° (decomp., the exact temp. depending on the rate of heating), crystallised from moist solvents with aq. which is removed at 100° or in vac. desiccator. It is very sol. in H_2O, HOAc, HOEt, and $CHCl_3$, moderately sol. in acetone and MeCN, and sparingly sol. in ligroin, Et_2O, C_6H_6, and CCl_4. Treatment of the aq. solution with Br yielded the *tribromide*, as a ppt., which was washed with H_2O and Et_2O and crystallised from $CHCl_3$ as yellow flattened needles, m. p. 138° (Found : C, 41·2; H, 4·4; Br, 51·7. $C_{16}H_{20}NBr_3$ requires C, 41·2; H, 4·3; Br, 51·5%), insol. in H_2O and Et_2O, moderately sol. in $CHCl_3$ and very sol. in acetone. On boiling with H_2O the salt liberates Br. The *picrate* separated from hot H_2O in needles, m. p. 152° (decomp.) (Found : C, 58·2; H, 5·0; N, 12·3. $C_{22}H_{22}O_7N_4$ requires C, 58·2; H, 4·8; N, 12·3%). The iodide had m. p. 170—175° (decomp.) and was very sol. in $CHCl_3$ (see below).

Decomposition of Benzhydryltrimethylammonium Hydroxide.—The hydroxide solution was prepared and standardised as described above, but the bromide solution required to be shaken with Ag_2O for an unusually long time (times up to 48 hr. were used) in order to ensure complete conversion. Decomposition commenced at (or below) the b. p. of the solution (bath temp. 115°) and was completed at 165° in a current of N. The oil which did not distil at this temp. was divided into neutral and basic portions by means of Et_2O and dil. HCl. The neutral oil yielded cryst. $CHPh_2{\cdot}OH$, which was washed with, and crystallised from, ligroin (m. p. and mixed m. p. 68°), and the residue from the ligroin on warming with NPh:CO gave $NHPh{\cdot}CO{\cdot}O{\cdot}CHPh_2$, which was crystallised from ligroin (m. p. and mixed m. p. 140°) (Found : C, 78·7; H, 5·6; N, 4·7. Calc. : C, 79·2; H, 5·6; N, 4·6%). In another expt. the $CHPh_2{\cdot}OH$ was separated as completely as possible by crystn. from light petroleum in CO_2–Et_2O, and then $(CHPh_2)_2O$ was separated by solution in EtOH and cooling in CO_2–Et_2O, before treatment of the residues with NPh:CO. The $(CHPh_2)_2O$, cryst. from ligroin, had m. p. and mixed m. p. 109°. A solution of the basic oil in ligroin was cooled in CO_2–Et_2O; crystals separated which were identified, m. p. and mixed m. p. 70°, as $CHPh_2{\cdot}NMe_2$ (Found : C, 85·5; H, 8·0; N, 6·7. Calc. : C, 85·3; H, 8·0; N, 6·6%). In another expt. the basic oil (3·0 g.) was treated with picric acid (4·0 g.) in abs. EtOH. The picrate which separated (6·0 g.; theo., assuming oil to be $CHPh_2{\cdot}NMe_2$, 6·2 g.) had m. p. 130—142° (decomp.) (Found : C, 58·2; H, 4·9; N, 12·3%), and after two crystns. from EtOH, m. p. 140—145° (Found : C, 57·7; H, 4·8; N, 12·2%). Benzhydryldimethylamine prepared from $CHPh_2Br$ and Me_2NH by Sommelet's method (*Compt. rend.*, 1922, **175**, 1149) had m. p. 70°, and its *picrate* (large needles), m. p. 196° (Found : C, 57·2; H, 4·4; N, 12·8. $C_{21}H_{20}O_7N_4$ requires C, 57·3; H, 4·5; N, 12·7). In another expt. the basic oil was cooled with CO_2–Et_2O, the cryst. $CHPh_2{\cdot}NMe_2$ filtered under press., and the residual oil converted into picrate (m. p. 130—140°), which was crystallised from EtOH–acetone and aq. acetone to the const. m. p. 151°. Analysis showed this to be *αα-diphenylethyldimethylamine picrate* (Found : C, 58·1; H, 4·9; N, 12·6. $C_{22}H_{22}O_7N_4$ requires C, 58·1; H, 4·8; N, 12·3%). Another portion of the same residual oil was treated for 2 days at room temp. with excess of MeI in MeCN. The crude *αα-diphenylethyltrimethylammonium iodide* was pptd. with Et_2O, washed with $CHCl_3$ and acetone and crystallised from hot H_2O in needles, m. p. 205° (decomp.) (Found : C, 55·5; H, 6·0; N, 3·8; I, 34·9. $C_{17}H_{22}NI$ requires C, 55·6; H, 6·0; N, 3·8; I, 34·6%). This salt is sol. in hot H_2O, but insol. in org. solvents, including $CHCl_3$, and this forms the basis of the separation of $CMePh_2{\cdot}NMe_2$ from $CHPh_2{\cdot}NMe_2$ (the methiodide of which is very sol. in $CHCl_3$—see above) which was used in the quantitative expts. In the distillate from the original decomp. MeOH was diagnosed, and Me_3N estimated, as in the preceding series of expts. In the expts. at const. vol., the solutions were decomposed at their b. p.'s under reflux, and no attention was paid to MeOH and Me_3N; the products separated and estimated by the methods indicated above were $CHPh_2{\cdot}OH$, $(CHPh_2)_2O$ (up to 4%), $CHPh_2{\cdot}NMe_2$, and $CMePh_2{\cdot}NMe_2$; the results are tabulated in the introduction, $(CHPh_2)_2O$ being calculated as $CHPh_2{\cdot}OH$.

Benzhydryldimethylethylammonium Salts.—The iodide was prepared by refluxing a solution of $CHPh_2{\cdot}NMe_2$ and EtI in MeCN for some hrs., pptn. with Et_2O and crystn. from hot H_2O. It was sparingly sol. in cold H_2O, but very sol. in $CHCl_3$. It appears that the solubility of these quaternary ammonium halides in $CHCl_3$ is determined by the presence of the benzhydryl α-hydrogen atom, and association of the anion through that hydrogen atom in anhydrous solvents seems indicated. The corresponding *picrate* separated from aq. acetone in needles, m. p. 141° (Found : C, 59·0; H, 5·1; N, 11·8. $C_{23}H_{24}O_7N_4$ requires C, 59·0; H, 5·1; N, 12·0%).

Decomposition of αα-Diphenylethyltrimethylammonium Hydroxide.—The hydroxide solution, which was pptd. and decomposed as usual, yielded a distillate, which was collected in dil. HCl, and a cryst. residue. The latter was extracted from traces of inorg. salts with C_6H_6 and washed with light petroleum; it crystallised from EtOAc in rosettes of small needles, m. p. 203° [Found: C, 93·2; H, 6·7; *M* (Rast), 381, 375. $C_{28}H_{24}$ requires C, 93·3; H, 6·7%; *M*, 360]. The compound, evidently a dimeride of α-diphenylethylene, is sol. in C_6H_6, $CHCl_3$, and acetone and insol. in Et_2O and ligroin. The amine recovered from the HCl solution was identified as Me_3N by prepn. of the picrate [m. p. and mixed m. p. 216° (decomp.)].

Attempts to prepare the above dimeride of α-diphenylethylene by the action of HBr on αα-diphenylethyl alcohol led to the known dimeride, αγ-diphenyl-Δ^{γ}-butene, m. p. 112° [Found: C, 93·2; H, 6·7; *M* (Rast), 356, 352. Calc.: C, 93·3; H, 6·7%; *M*, 360] (cf. Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021).

Benzhydrylbenzyldimethylammonium Salts.—The *bromide* was prepared by interaction of $C_7H_7{\cdot}NMe_2$ with the theo. quantity of $CHPh_2Br$ previously dissolved in the minimal amount of cold MeCN. The salt, which partly crystallised, was completely pptd. with Et_2O and crystallised from acetone or hot H_2O. From the latter it separated with $1H_2O$ and then had m. p. *ca.* 125° (decomp.). The salt is slightly sol. in cold H_2O, very sol. in $CHCl_3$, moderately sol. in acetone, MeCN, and $MeNO_2$, and insol. in C_6H_6, CCl_4, Et_2O, and light petroleum (Found for the dried salt: C, 68·9; H, 6·3; N, 3·6; Br, 20·2. $C_{22}H_{24}NBr$ requires C, 69·1; H, 6·3; N, 3·6; Br, 20·9%. Found for hydrated salt: H_2O, 3·9. $C_{22}H_{24}NBr,H_2O$ requires H_2O, 4·5%). The *picrate*, prepared from the bromide and sodium picrate, separated from dil. EtOH in needles, m. p. 149° (decomp.) (Found: C, 63·4; H, 4·9; N, 10·2. $C_{28}H_{26}O_7N_4$ requires C, 63·4; H, 4 9; N, 10·5%).

Decomposition of Benzhydrylbenzyldimethylammonium Hydroxide.—In this case also the bromide required prolonged shaking with Ag_2O (times up to 2 days) to ensure complete conversion into the hydroxide. The hydroxide solution, although sufficiently stable for standardisation in the cold, underwent rapid and complete decomp. below 90°. It was partly distilled into dil. HCl, and the residue was taken up in Et_2O and the distillate extracted with this solvent. The Et_2O-sol. material was divided into basic and neutral fractions. The latter consisted of cryst. $CHPh_2{\cdot}OH$, accompanied by a small amount of oil which was shown to contain $CH_2Ph{\cdot}OH$ by the recognition of Ph·CHO after oxidation. From the basic fraction, solid separated, which after crystn. from dil. EtOH formed needles, m. p. 128°; it is shown later to be *ααβ-triphenylethyldimethylamine* (Found: C, 87·8; H, 7·5; N, 4·7. $C_{22}H_{23}N$ requires C, 87·7; H, 7·6; N, 4·7%). The *hydrochloride*, cryst. from EtOAc, partly sublimed at 260—280° and when heated quickly had m. p. 280° (Found: Cl, 10·0. $C_{22}H_{23}N,HCl$ requires Cl, 10·5%), and the *picrate* separated from aq. EtOH in needles, m. p. 218° (decomp.) (Found: C, 63·2; H, 5·0; N, 10·8. $C_{28}H_{26}O_7N_4$ requires C, 63·4; H, 4·9; N, 10·6%). The oily portion of the basic fraction, on distillation, yielded benzyldimethylamine, b. p. 178°, and a residue which partly solidified, yielding thus a further quantity of triphenylethyldimethylamine. MeOH was identified as usual in the dil. HCl solution. Decomp. were carried out at different initial concns. of the ammonium hydroxide, and also in very conc. solution after addition of KOH, with the results recorded in the introduction. In the last-mentioned expt. an additional substance, m. p. 205—210° (Found: C, 93·1; H, 6·7%), was obtained in $<1\%$ yield, but was not fully purified and was not identified. It appeared in company with the $CHPh_2{\cdot}OH$ and was separated therefrom by taking advantage of the slight solubility of the hydrocarbon in Et_2O.

ααβ-Triphenylethyltrimethylammonium Salts.—A solution of triphenylethyldimethylamine in MeCN was allowed to react in the cold with MeI (small excess) over-night. Et_2O was added and the pptd. salt was washed with Et_2O and crystallised from H_2O. It had m. p. 238°, and was moderately sol. in hot H_2O, and insol. in $CHCl_3$ and other org. solvents (Found: C, 62·4; H, 6·0; N, 2·9; I, 28·9. $C_{23}H_{26}NI$ requires C, 62·3; H, 5·8; N, 3·2; I, 28·7%). The *picrate* separated from dil. acetone in small needles, m. p. 214° (Found: C, 64·1; H, 5·2; N, 10·4. $C_{29}H_{28}O_7N_4$ requires C, 64·0; H, 5·1; N, 10·3%).

Decomposition of ααβ-Triphenylethyltrimethylammonium Hydroxide.—The hydroxide solution was prepared and decomposed in the usual way. Reaction commenced at 150° (bath temp.) and was completed at 180°. In the distillate, which was received in dil. HCl, MeOH and Me_3N were diagnosed as usual. The product which did not distil was dissolved in C_6H_6 and extracted with dil. HCl. The residue from the C_6H_6 solution had m. p. 68—69°, and after crystn. from EtOH was identified as triphenylethylene, m. p. 70—71° (Found: C, 93·7; H, 6·3. Calc.: C, 93·7; H, 6·3%). A portion of the product was treated with Br (1 mol.) in $CHCl_3$; the solution was evaporated and the residue, presumably *β-bromo-ααβ-triphenylethylene* formed by loss of HBr from $CPh_2Br{\cdot}CHPhBr$, was crystallised from light petroleum, in needles,

m. p. 115° (Found : C, 71·5; H, 4·5; Br, 23·4. $C_{20}H_{15}Br$ requires C, 71·6; H, 4·5; Br, 23·9%). The acid extract on basification and extraction with Et_2O gave ααβ-triphenylethyldimethylamine (m. p. and mixed m. p. 125—126°).

Miscellaneous Observations.—$CHPh_2Br$ (12·5 g.) and $(CH_2Ph)_2NH$ (20 g.) were heated together in a closed tube at 100° for 8 hr. The product, which was washed with Et_2O, was treated (27 g.) with cold $CHCl_3$, in which it partly dissolved. The insol. salt (13 g.) was $(CH_2Ph)_2NH,HBr$. The residue from the $CHCl_3$ was boiled with H_2O and crystallised from light petroleum and from dil. acetone, from which *benzhydryldibenzylamine* separated in long needles, m. p. 129° (Found : C, 88·8; H, 7·0; N, 4·0. $C_{27}H_{25}N$ requires C, 89·2; H, 6·9; N, 3·9%). The *hydrochloride*, for the prepn. of which conc. HCl was required because the base is very weak, had m. p. 180—182° (Found : Cl, 8·2. $C_{27}H_{26}NCl$ requires Cl, 8·9%). The *picrate*, prepared from the base and alc. picric acid, separated from EtOH in silky needles, m. p. 145° (decomp.) (Found : C, 67·5; H, 4·9; N, 9·7. $C_{33}H_{28}O_7N_4$ requires C, 66·9; H, 4·7; N, 9·5%). $CHPh_2Br$ on treatment with $(CH_2Ph)_2NMe$ in MeCN gave *dibenzylmethylammonium bromide*, which separated from EtOAc in rhombs, m. p. 157°, sol. in acetone, $CHCl_3$, EtOAc, and EtOH, and insol. in Et_2O, C_6H_6, CCl_4, and light petroleum (Found : C, 61·8; H, 6·2; N, 4·5; Br, 27·7. $C_{15}H_{18}NBr$ requires C, 61·6; H, 6·2; N, 4·8; Br, 27·4%). The *picrate*, prepared from the bromide and aq. sodium picrate, and cryst. from dil. EtOH, had m. p. 107° (Found : C, 57·2; H, 4·7; N, 12·5. $C_{21}H_{20}O_7N_4$ requires C, 57·3; H, 4·5; N, 12·7%). $CHPh_2Br$, on treatment with $CHPh_2{\cdot}NMe_2$ in MeCN for several days in the cold, yielded *benzhydryldimethylammonium bromide*, which separated from hot H_2O in rhombs, m. p. 206°, containing $1H_2O$ (Found : H_2O, 5·1. $C_{15}H_{18}NBr,H_2O$ requires H_2O, 5·8%). The salt was dried in a good vac. at 50° for analysis (Found : C, 61·2; H, 6·2; Br, 26·9. $C_{15}H_{18}NBr$ requires C, 61·6; H, 6·2; Br, 27·4%).

UNIVERSITY COLLEGE, LONDON.

[*Received, December 8th*, 1932.]