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25. Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XIV. The Action of Tertiary Amines on Triphenylmethyl Halides.

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THIS work is the outcome of attempts to prepare quaternary ammonium salts containing the triphenylmethyl radical.

Nef (Annalen, 1899, 309, 168) found that triphenylmethyl bromide and triethylamine in warm benzene solution gave triethylamine hydrobromide and a gum (not analysed) which he assumed to be a polymerisation product of $CPh_2:C_6H_4$.

Since the formation of quaternary ammonium salts is facilitated by solvents of high cohesion (cf. Richardson and Soper, J., 1929, 1873), the interaction of triphenylmethyl chloride and trimethylamine was studied in the presence of nitromethane and of acetonitrile. The sole crystalline product was, however, a molecular compound, 2CPh₃·OH,NMe₃,HCl, from which water extracted the saline constituent, leaving the carbinol, and benzene removed the carbinol, leaving the salt. The same substance was obtained by crystallising solutions containing the carbinol and the salt. The production of a molecular compound appeared to be peculiar to this example and was not repeated when triphenylmethyl chloride was replaced by the bromide or trimethylamine by triethyl-On the other hand the fundamental reaction, namely, the formation of triphenylamine. carbinol and the appropriate amine hydrohalide, was general within this range of examples, and, in particular, repetition of Nef's experiment led to the isolation of triphenylcarbinol. The accession of a small amount of moisture to the reaction mixtures appears essential for interaction under the conditions used.

Quaternary triphenylmethylammonium salts derived from pyridine have been claimed by Tschitschibabin (J. Russ. Phys. Chem. Soc., 1902, 34, 137), by Hantzsch and Meyer (Ber., 1910, 43, 336), and by Norris and Culver (Amer. Chem. J., 1903, 29, 129). It has been found, however, that the "pyridinium" bromide of Tschitschibabin and of Hantzsch

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and Meyer is a molecular compound, $CPh_3 OH, C_5H_5N, HBr$, and that the "pyridinium" chloride of Norris and Culver is analogously the compound $CPh_3 \cdot OH, C_5H_5N, HCl$. In each case the constituents can be separated and re-associated as in the example described above.

It thus appears that quaternary triphenylmethylammonium salts have not yet been prepared, and are extremely difficult to obtain. The suggested reason for this is that, on account of the greater electron affinity of NR_3^{\oplus} than of Hal, the cation CPh_3^{\oplus} separates more readily from CPh3. NR3[®] than from CPh3. Hal, and that accordingly the stable form of the system

$$\operatorname{CPh}_3 \cdot \overset{\scriptscriptstyle \oplus}{\operatorname{NR}}_3 + \operatorname{Hal}^{\scriptscriptstyle \ominus} \overrightarrow{=} \operatorname{CPh}_3^{\scriptscriptstyle \ominus} + \operatorname{Hal}^{\scriptscriptstyle \ominus} + \operatorname{NR}_3 \overrightarrow{=} \operatorname{CPh}_3 \cdot \operatorname{Hal} + \operatorname{NR}_3$$

is the right-hand member. Until water intervenes, there is no entity present with which CPh_3^{\oplus} can form a more stable co-valent compound than that which it forms with the halide ion, but in the presence of water CPh3[®] is completely removed as the very feebly ionising carbinol.

Two further observations lend confirmation to this suggestion. Treatment of triphenylmethyldimethylamine with excess of methyl iodide led to the isolation of tetramethylammonium iodide, iodine, and triphenylcarbinol. The assumption that the ammonium salt is formed, but decomposes in the sense of the equation $(CPh_3 \cdot \overset{\oplus}{N}Me_3) \overset{\oplus}{\Pi} \longrightarrow CP\overset{\oplus}{h_3} +$

 $NMe_3 + \breve{I}$, explains the formation of these products; for the trimethylamine would naturally be converted into tetramethylammonium iodide, the triphenylmethyl cation and the iodide ion would reversibly unite to give triphenylmethyl iodide, which is known to dissociate reversibly into triphenylmethyl and iodine (Gomberg, J. Amer. Chem. Soc., 1902, 24, 597), and, in so far as water intervenes, the triphenylmethyl cation would be irreversibly removed as carbinol.

Confirmation of the assumption that the cation CPh_3^{\oplus} is liberated from the ammonium complex in the manner suggested was obtained by conducting the reaction in absolute ethyl alcohol; ethyl triphenylmethyl ether was then isolated in addition to tetramethylammonium iodide : $CPh_3^{\oplus} + HOEt \longrightarrow CPh_3 \cdot OEt + H^{\oplus}$.

EXPERIMENTAL.

Action of Trimethylamine on Triphenylmethyl Chloride.-Interaction was effected at room temp. in MeCN-CHCl₃, from which the compound, 2CPh₃-OH,NMe₃,HCl, m. p. 190-195° (decomp.), separated, which was crystallised from MeCN and from acetone [Found : C, 79.8; H, 6.8; N, 2.4; Cl, 5.7; Cl (ionisable), 5.7. 2CPh₃·OH,NMe₃,HCl requires C, 79.9; H, 6.8; N, 2.3; Cl, 5.8%], forming flat leaflets sol. in CHCl₃, acetone, MeCN, EtOAc, and MeNO₂ and insol. in Et₂O, ligroin, and CCl₄. Addition of Et₂O to the ultimate mother-liquor pptd. a hygroscopic solid which on treatment with sodium picrate gave trimethylamine picrate, m. p. 216°. The same products were obtained when CHCl₃ alone or CHCl₃-MeNO₂ were used as solvents.

The molecular compound (5 g.), on washing with cold H₂O, gave CPh₃·OH (4 g., m. p. 159-160°, and after crystn., 161°); NMe₃,HCl was identified in the filtrate by conversion into picrate. An attempt to crystallise the molecular compound from EtOH also gave CPh₃·OH. On washing with C₆H₆ the molecular compound yielded NMe₃,HCl, and the filtrate, on evapn., gave CPh₃·OH.

Solutions of CPh₃ OH (2 mols.) in the min. quantity of CHCl₃ and of NMe₃,HCl (1 mol.) in MeNO₂ were mixed. A solid separated : the mixture was heated until this dissolved, and was then filtered and allowed to cool. The crystals, washed with a little MeNO₂ and acetone, proved to be the molecular compound, m. p. and mixed m. p. 190-195° (decomp.).

Action of Triethylamine on Triphenylmethyl Chloride.—Interaction in CHCl₃ pptd. Et₃N,HCl, which was washed with Et₂O and acetone; m. p. 253° (decomp.): picrate, m. p. and mixed m. p. with an authentic specimen 174°. The hydrochloride was completely removed by the addition of Et₂O, and the solution, on evapn., gave CPh₃·OH.

Action of Trimethylamine on Triphenylmethyl Bromide.-The bromide (Henderson, J., 1887, 51, 224), m. p. 150°, reacted with Me₃N much as described above, and Me₃N,HBr and CPh₃·OH were isolated.

Action of Pyridine on Triphenylmethyl Chloride.--Interaction in MeNO2-CHCl3 or in EtOAc

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gave, after a few days, the crystalline compound CPh₃·OH,C₅H₅N,HCl, which was recrystallised from acetone; m. p. 170–175° (Norris and Culver, *loc. cit.*, give 167–167·5°) [Found : C, 77·0; H, 6·0; N, 3·5; Cl, 9·8; Cl (ionisable), 9·4. CPh₃·OH,C₅H₅N,HCl requires C, 76·7; H, 5·9; N, 3·7; Cl, 9·45%]. It separated in stout rhombic prisms, sol. in CHCl₃, MeCN, and MeNO₂ and insol. in Et₂O, CCl₄, and ligroin. The same compound was obtained by crystallising a mixture of CPh₃·OH (1 mol.) and C₅H₅N,HCl (1 mol.) from CHCl₃.

Action of Pyridine on Triphenylmethyl Bromide.—Interaction in $MeNO_2$ -CHCl₃ gave the compound CPh₃·OH,C₅H₅N,HBr, which was recrystallised from $MeNO_2$ -CHCl₃, and washed with CHCl₃-acetone, m. p. 155—190° (Tschitschibabin, *loc. cit.*, gives 162°) (Found : C, 68·2; H, 5·0; N, 3·4; Br, 19·1. CPh₃·OH,C₅H₅N,HBr requires C, 68·6; H, 5·2; N, 3·3; Br, 19·0%).

Action of Methyl Iodide on Triphenylmethyldimethylamine.—(a) In acetonitrile. The amine (Hemilian and Silberstein, Ber., 1884, 17, 746), m. p. 96°, and excess of MeI, in MeCN, left for a few days at room temp., developed a deep red coloration, and a solid separated, which, washed with Et₂O, and cryst. from H₂O, had m. p. > 300° (Found : I, 62.9. Calc. for NMe₄I : I, 63.2%). The salt was completely pptd. by the addition of Et₂O and the solution, on evapn., gave a black solid, partly sol. in hot ligroin. The insol. portion was sol. in KI aq. and had all the properties of iodine. The sol. portion crystallised, on cooling, and was recryst. from ligroin; m. p. and mixed m. p. with triphenylcarbinol, 161°.

(b) In absolute ethyl alcohol. The amine, dissolved in a small vol. of abs. EtOH, and excess of MeI were refluxed for 3 hr. on the water-bath. The unreacted MeI was then removed and the solution, on standing, deposited two kinds of crystal. These were collected, and treated with Et_2O , which effected a complete separation. The insol. portion was recrystallised from H_2O and identified as NMe_4I . The solution, on slow evapn., deposited a solid which, after washing with a little EtOH, had m. p. $80-82^\circ$. It was recrystallised from EtOH; m. p. and mixed m. p. with CPh₃·OEt, 84° .

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