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

By E. D. Hughes.

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*, $2CPh_3{\cdot}OH,NMe_3,HCl$, 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 triethylamine. On the other hand the fundamental reaction, namely, the formation of triphenylcarbinol 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 and Meyer is a molecular ***compound***, $CPh_3{\cdot}OH,C_5H_5N,HBr$, 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 $CPh_3{\cdot}NR_3^{\oplus}$ than from $CPh_3{\cdot}Hal$, and that accordingly the stable form of the system

$$CPh_3{\cdot}\overset{\oplus}{N}R_3 + \overset{\ominus}{Hal} \rightleftharpoons \overset{\oplus}{CPh_3} + \overset{\ominus}{Hal} + NR_3 \rightleftharpoons CPh_3{\cdot}Hal + NR_3$$

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 $CPh_3^{\oplus}$ 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 $(CPh_3{\cdot}\overset{\oplus}{N}Me_3)\overset{\ominus}{I} \longrightarrow \overset{\oplus}{CPh_3} + NMe_3 + \overset{\ominus}{I}$, 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 $MeCN$–$CHCl_3$, from which the *compound*, $2CPh_3{\cdot}OH,NMe_3,HCl$, 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. $2CPh_3{\cdot}OH,NMe_3,HCl$ requires C, 79·9; H, 6·8; N, 2·3; Cl, 5·8%], forming flat leaflets sol. in $CHCl_3$, acetone, MeCN, EtOAc, and $MeNO_2$ and insol. in Et_2O, ligroin, and CCl_4. Addition of Et_2O 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 $CHCl_3$ alone or $CHCl_3$–$MeNO_2$ were used as solvents.

The molecular compound (5 g.), on washing with cold H_2O, gave $CPh_3{\cdot}OH$ (4 g., m. p. 159—160°, and after crystn., 161°); NMe_3,HCl was identified in the filtrate by conversion into picrate. An attempt to crystallise the molecular compound from EtOH also gave $CPh_3{\cdot}OH$. On washing with C_6H_6 the molecular compound yielded NMe_3,HCl, and the filtrate, on evapn., gave $CPh_3{\cdot}OH$.

Solutions of $CPh_3{\cdot}OH$ (2 mols.) in the min. quantity of $CHCl_3$ and of NMe_3,HCl (1 mol.) in $MeNO_2$ 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 $MeNO_2$ 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 $CHCl_3$ pptd. Et_3N,HCl, which was washed with Et_2O 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 Et_2O, and the solution, on evapn., gave $CPh_3{\cdot}OH$.

Action of Trimethylamine on Triphenylmethyl Bromide.—The bromide (Henderson, J., 1887, **51**, 224), m. p. 150°, reacted with Me_3N much as described above, and Me_3N,HBr and $CPh_3{\cdot}OH$ were isolated.

Action of Pyridine on Triphenylmethyl Chloride.—Interaction in $MeNO_2$–$CHCl_3$ or in EtOAc gave, after a few days, the crystalline *compound* $CPh_3{\cdot}OH,C_5H_5N,HCl$, 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. $CPh_3{\cdot}OH,C_5H_5N,HCl$ requires C, 76·7; H, 5·9; N, 3·7; Cl, 9·45%]. It separated in stout rhombic prisms, sol. in $CHCl_3$, MeCN, and $MeNO_2$ and insol. in Et_2O, CCl_4, and ligroin. The same compound was obtained by crystallising a mixture of $CPh_3{\cdot}OH$ (1 mol.) and C_5H_5N,HCl (1 mol.) from $CHCl_3$.

Action of Pyridine on Triphenylmethyl Bromide.—Interaction in $MeNO_2$–$CHCl_3$ gave the *compound* $CPh_3{\cdot}OH,C_5H_5N,HBr$, which was recrystallised from $MeNO_2$–$CHCl_3$, and washed with $CHCl_3$–acetone, m. p. 155—190° (Tschitschibabin, *loc. cit.*, gives 162°) (Found : C, 68·2; H, 5·0; N, 3·4; Br, 19·1. $CPh_3{\cdot}OH,C_5H_5N,HBr$ 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 Et_2O, and cryst. from H_2O, had m. p. $> 300°$ (Found : I, 62·9. Calc. for NMe_4I : I, 63·2%). The salt was completely pptd. by the addition of Et_2O 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°. It was recrystallised from EtOH; m. p. and mixed m. p. with $CPh_3{\cdot}OEt$, 84°.

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