Acylation and Allied Reactions Catalysed by Strong Acids. Part XIV. Some Reactions of the α-Chlorodiphenylmethyl ($^+CPh_2Cl$) and p-Methoxytriphenylmethyl Cations.*

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Diphenylmethylene dichloride (benzophenone chloride) with silver perchlorate or, more conveniently, aluminium chloride gives products showing the reactions of the α-chlorodiphenylmethyl cation, $^+CPh_2Cl$. Convenient methods of preparation of *p*-hydroxytriphenylmethanol and *p*-methoxytriphenylmethyl chloride are developed and various reactions of the *p*-methoxytriphenylmethyl cation are studied. The " rearrangement " of *p*-methoxytriphenylmethyl phenyl ether by hydrogen chloride gives 4-hydroxy-4′-methoxytetraphenylmethane.

In continuation of work described in Part IX (*J.*, 1953, 832) on the reactions of various di- and tri-arylmethyl cations we have investigated some reactions involving, in the first place, the α-chlorodiphenylmethyl cation. We have found that when silver perchlorate (1 mol.) is treated with diphenylmethylene chloride (1 mol.) in nitromethane there is immediate precipitation of silver chloride, and the resulting product reacts slowly with anisole at room temperature giving a good yield of *p*-methoxytriphenylmethyl chloride :

$$CPh_2Cl_2 + AgClO_4 \longrightarrow AgCl + {}^+CPh_2Cl\}ClO_4^-$$
$$^+CPh_2Cl\}ClO_4^- + PhOMe \longrightarrow p\text{-}OMe\cdot C_6H_4\cdot CPh_2Cl + HClO_4$$

The α-chlorodiphenylmethyl cation is, however, much less reactive than the diphenylmethyl cation (*loc. cit.*); thus it does not react with benzene under the conditions (2 hours at room temperature) which for the latter cation lead to triphenylmethane.

We have also found that aluminium chloride is an excellent catalyst for the " α-chlorodiphenylmethylation " of anisole and phenol. Diphenylmethylene dichloride (1 mol.) and aluminium chloride (1 mol.) in carbon disulphide form an insoluble complex which when treated with anisole (1 mol.) gives a good yield of *p*-methoxytriphenylmethyl chloride. The product similarly obtained from phenol (1 mol.) was hydrolysed directly to the alcohol. The methoxy-chloride can also be prepared conveniently by chromic oxide oxidation of *p*-methoxytriphenylmethane to the alcohol and subsequent treatment with acetyl chloride. Gomberg and Jickling's method (*J. Amer. Chem. Soc.*, 1915, **37**, 2578) of preparation of *p*-hydroxytriphenylmethanol is not suitable for its large-scale production. Ioffe and Khavin (*J. Gen. Chem. U.S.S.R.*, 1949, **19**, 903) have modified Gomberg and Jickling's method so that the formation of relatively large amounts of 4 : 4′-dihydroxytetraphenylmethane is avoided in experiments on a larger scale. We find that the action of phenol (1 mol.) with the diphenylmethylene dichloride–aluminium chloride complex is a much more convenient preparative method.

p-Hydroxy- and *p*-acetoxy-triphenylmethanol and fuchsone when treated with perchloric acid under suitable conditions all give *p*-hydroxytriphenylmethyl perchlorate, which is readily hydrolysed to *p*-hydroxytriphenylmethanol. The alcohol can also be obtained by direct hydration of fuchsone by perchloric acid in aqueous acetone (cf. Ioffe and Khavin, *loc. cit.* : Bistrzycki and Herbst, *Ber.*, 1903, **36**, 2335).

The ready preparation of *p*-methoxytriphenylmethyl chloride has enabled us to investigate various reactions, notably with phenol and *m*-dimethoxybenzene. It was found advantageous to carry out condensations with the chloride in presence of dry hydrogen chloride; reasonable yields of the tetra-arylmethanes were obtained. The use of *p*-methoxytriphenylmethyl perchlorate with phenol led to a mixture since, under the conditions used, extensive demethylation occurred.

We have also found that *p*-methoxytriphenylmethyl phenyl ether is " rearranged " to

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4-hydroxy-4'-methoxytetraphenylmethane by dry hydrogen chloride at 95° (cf. van Alphen, *Rec. Trav. chim.*, 1927, **46**, 287). It is very probable that this so-called rearrangement involves, first, fission of the ether to phenol and *p*-methoxytriphenylmethyl chloride and then the interaction of these to give the tetra-arylmethane (cf. Hart and Cassis, *J. Amer. Chem. Soc.*, 1954, **76**, 1634).

Experimental

Diphenylmethylene dichloride (benzophenone chloride) was estimated by Andrews and Kaeding's method (*J. Amer. Chem. Soc.*, 1951, **73**, 1010).

Claisen's solution was prepared by dissolving potassium hydroxide (50 g.) in water (100 c.c.) and methanol (100 c.c.).

Reaction of "α-Chlorodiphenylmethyl Perchlorate" with Anisole.—Benzophenone chloride (11·9 g.; 93% pure) was added dropwise to a solution of silver perchlorate (10·4 g., 0·05 mole) and anisole (21·6 g., 0·20 mole) in nitromethane (50 c.c.); there was immediate precipitation of silver chloride. The dark red mixture was kept at room temperature for 5 days and then filtered. The filtrate was poured on crushed ice and extracted with ether, and the ethereal extracts were washed free from acid and dried (Na_2SO_4). Solvent and excess of anisole were removed by heating to 100°/0·1 mm.; the residue (14·6 g.) was heated under reflux with acetyl chloride (15 c.c.) in dry ether (30 c.c.). *p*-Methoxytriphenylmethyl chloride separated on cooling and was filtered off. Crystallisation from ether containing acetyl chloride gave the methoxychloride (11·1 g., 78%) as colourless prisms, m. p. 121—123°.

p-*Methoxytriphenylmethyl Chloride.*—(*a*) Powdered aluminium chloride (20·3 g., 0·15 mole) was added in portions to an ice-cooled solution of benzophenone chloride (35·8 g.; 93% pure) in anisole (16·2 g., 0·15 mole) and carbon disulphide (60 c.c.). After the initial reaction had moderated, the mixture was heated under reflux for 1 hr., then cooled, and crushed ice was added to decompose the dark red complex which had separated. Ether was added, and the organic layer separated, washed with dilute hydrochloric acid and water, and dried (Na_2SO_4). The residue (47·3 g.) after evaporation was heated under reflux with acetyl chloride (50 c.c.). *p*-Methoxytriphenylmethyl chloride separated on cooling and was filtered off in two crops, m. p. (mainly) 121—123°. The product was washed with ether and light petroleum and dried in a vacuum-desiccator over soda lime. The total yield was 39·3 g. (91%).

(*b*) *p*-Methoxytriphenylmethane (13·0 g., 0·04 mole; Burton and Cheeseman, *J.*, 1953, 832) was dissolved in acetic acid (100 c.c.), and the stirred solution kept at 60° while a solution of chromium trioxide (4·8 g., 0·048 mole) in water (3 c.c.) and acetic acid (30 c.c.) was added dropwise during 30 min. The mixture was kept at 60° for a further hour, then poured into water and extracted with ether. The combined ethereal extracts were washed with 2N-sodium hydroxide, dried (Na_2SO_4), and evaporated. The residue (13·5 g.) was converted into *p*-methoxytriphenylmethyl chloride (9·7 g., 66%), m. p. 117—121°, as described above. The mother-liquor contained benzophenone, isolated as its oxime, m. p. and mixed m. p. 141—142·5°.

p-*Hydroxytriphenylmethanol.*—Benzophenone chloride (47·4 g.; 97% pure) was added rapidly to a suspension of powdered aluminium chloride (26·8 g., 0·20 mole) in carbon disulphide (50 c.c.), whereupon a solid complex separated; a solution of phenol (18·8 g., 0·20 mole) in carbon disulphide (50 c.c.) was then added to the mixture. After the mixture had been heated under reflux for 4 hr., carbon disulphide was removed by distillation and the residual solid decomposed with water. The crude solid was filtered off, washed with water, and dissolved in N-sodium hydroxide (300 c.c.). The solution was shaken with ether to remove benzophenone, a current of air passed through the alkaline phase to remove dissolved ether, and *p*-hydroxytriphenylmethanol (51·5 g., 96%), m. p. (mainly) 156—159°, liberated with carbon dioxide. The alcohol was obtained as pale yellow prisms, m. p. 172°, by crystallisation from benzene (Found: C, 82·45; H, 5·8. Calc. for $C_{19}H_{16}O_2$: C, 82·6; H, 5·8%). It was converted into *p*-acetoxytriphenylmethanol (m. p. 136—139°) when heated under reflux with acetic anhydride and sodium acetate for 1 hr. (Gomberg and Jickling, *J. Amer. Chem. Soc.*, 1915, **37**, 2589). The reaction between benzophenone chloride and excess of phenol (*idem, ibid.*) was found to yield 47% of *p*-hydroxytriphenylmethanol and 31% of 4 : 4'-dihydroxytetraphenylmethane.

4 : 4'-Diacetoxytetraphenylmethane prepared by Mackenzie's method (*J.*, 1901, **79**, 1209) had m. p. 189—190° (Found: C, 79·6; H, 5·55. Calc. for $C_{29}H_{24}O_4$: C, 79·8; H, 5·55%) (Mackenzie gives m. p. 171°).

4 : 4′-*Dimethoxytetraphenylmethane*.—4 : 4′-Dihydroxytetraphenylmethane (7·0 g., 0·02 mole) in a solution of sodium hydroxide (2·5 g., 0·063 mole) in water (40 c.c.) and methanol (40 c.c.) was treated dropwise at 60° with stirring with methyl sulphate (6·3 g., 0·05 mole). The solid (5·8 g.), m. p. 156—163°, was collected after 3 hr. Successive crystallisations from acetic acid gave the pure *dimethoxy-compound*, m. p. 176—177° (Found : C, 85·2; H, 6·25. $C_{27}H_{24}O_2$ requires C, 85·2; H, 6·35%).

p-*Hydroxytriphenylmethyl Perchlorate*.—(*a*) 70% Perchloric acid (1·73 c.c.) was added to a solution of *p*-hydroxytriphenylmethanol (2·76 g.) in acetic acid (10 c.c.). Crimson needles of the perchlorate soon separated; these were filtered off, washed with acetic acid, and dried in a vacuum-desiccator (KOH). The salt (2·85 g., 80%) decomposed with bubbling at *ca.* 209—210° : the decomposition point was not strictly reproducible.

(*b*) The perchlorate was obtained in quantitative yield by the addition of an excess of 70% perchloric acid to a solution of fuchsone in acetic acid.

(*c*) Excess of a solution of perchloric acid in acetic acid (prepared from 70% perchloric acid and acetic anhydride) was added to *p*-acetoxytriphenylmethanol dissolved in acetic anhydride and acetic acid. Crimson needles of *p*-hydroxytriphenylmethyl perchlorate separated in 89% yield, decomposing at *ca.* 209—210° (undepressed when mixed with the perchlorate obtained by the methods described above) (Found : C, 63·3; H, 4·2. Calc. for $C_{19}H_{15}O_5Cl$: C, 63·6; H, 4·2%). The perchlorate was also obtained by adding 70% perchloric acid to a solution of *p*-acetoxytriphenylmethanol in acetic acid.

Hydrolysis of p-*Hydroxytriphenylmethyl Perchlorate*.—When water (10 c.c.) was added to a suspension of the perchlorate (1·0 g.) in acetone (10 c.c.), the undissolved solid went into solution and the mixture became much paler. Water and ether were added, the organic layer was separated and *p*-hydroxytriphenylmethanol (0·7 g., 90%), m. p. 156—158°, isolated *via* its sodium salt as described above.

Hydrolysis of Fuchsone.—Dilute perchloric acid (≡ 0·004 mole of $HClO_4$) was added to a solution of fuchsone (1·0 g., 0·004 mole) in acetone (20 c.c.). The mixture became pale yellow : water and ether were then added, the organic layer was separated, and *p*-hydroxytriphenylmethanol (1·0 g., 93%), m. p. 163—169°, isolated *via* its sodium salt as described above.

Fuchsone was recovered unchanged from a solution in acetone and ether which was shaken repeatedly with 2N-sodium hydroxide.

p-*Methoxytriphenylmethyl Perchlorate*.—70% Perchloric acid (4·5 c.c.) was added cautiously to a cooled solution of *p*-methoxytriphenylmethanol (6·8 g.) in acetic anhydride (20 c.c.). Crimson needles of the perchlorate soon separated; these were filtered off, washed with acetic acid, and dried in a vacuum-desiccator (KOH). The salt (7·9 g., 90%) had m. p. 192—193°.

Reaction of p-*Methoxytriphenylmethyl Perchlorate with Phenol*.—A solution of the perchlorate (3·73 g.) in phenol (10 g.) was kept at 100—110° for 6 days. The mixture was poured into sodium carbonate solution, excess of phenol removed by steam-distillation, and the residual oil extracted with ether. Evaporation of the dried ethereal extracts gave a crude solid (2·2 g.) which was partitioned between light petroleum (b. p. 60—80°) and Claisen's solution. *p*-Hydroxytriphenylmethanol (2·05 g., 74%) was liberated by carbon dioxide from the alkaline phase. The alcohol was converted into *p*-acetoxytriphenylmethanol, m. p. and mixed m. p. 136—139°, in 97% yield.

4-*Hydroxy*-4′-*methoxytetraphenylmethane*.—Dry hydrogen chloride was bubbled through a solution of *p*-methoxytriphenylmethyl chloride (3·08 g.) in phenol (10 g.) at 95° for 7 hr. The mixture was then poured into water, and excess of phenol removed by steam-distillation. The residual oil was partitioned between light petroleum (b. p. 60—80°) and Claisen's solution (20 c.c.). Evaporation of the petroleum layer gave an oil (0·5 g.), which yielded *p*-methoxytriphenylmethyl chloride, m. p. and mixed m. p. 121—123°, when heated under reflux with acetyl chloride. The alkaline layer was warmed to prevent crystallisation, and the crude product (2·8 g.) liberated with carbon dioxide. Crystallisation from ethanol (10 c.c.) gave 4-*hydroxy*-4′-*methoxytetraphenylmethane* (1·7 g., 46%), m. p. 189—192°, raised to 197—198° by crystallisation from ethanol and acetic acid (Found : C, 84·8; H, 5·9. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·05%). 4 : 4′-Dihydroxytetraphenylmethane and a smaller amount of the methoxyphenol were obtained from an experiment in which the reaction time was increased to 12 hr. Condensation occurred between *p*-methoxytriphenylmethanol and phenol in nitromethane in the presence of 70% perchloric acid. The yield of 4-hydroxy-4′-methoxytetraphenylmethane was 30% after 4 days at 110—120°.

2 : 4 : 4′-*Trimethoxytetraphenylmethane*.—Dry hydrogen chloride was bubbled through a solution of *p*-methoxytriphenylmethyl chloride (3·08 g.) in *m*-dimethoxybenzene (10 c.c.) at

95° for 12 hr. The mixture was then poured into water, and excess of dimethoxybenzene removed by steam-distillation. An ethereal solution of the non-volatile oil gave the *trimethoxy-compound* in two crops (total 0·63 g., 15%), m. p. 164—166°. The m. p. was raised to 168—169° by crystallisation from benzene–light petroleum (1 : 2) (Found : C, 82·2; H, 6·6. $C_{28}H_{26}O_3$ requires C, 81·9; H, 6·4%). The mother-liquor from the ether crystallisation gave *p*-methoxytriphenylmethyl chloride, m. p. and mixed m. p. 121—123°, when heated under reflux with acetyl chloride. No condensation occurred when *p*-methoxytriphenylmethyl chloride and *m*-dimethoxybenzene were heated alone at 95° for 12 hr.

"*Rearrangement*" *of* p-*Methoxytriphenylmethyl Phenyl Ether*.—Powdered *p*-methoxytriphenylmethyl chloride (6·17 g., 0·02 mole) was added to an ethereal solution of sodium phenoxide [from sodium (0·5 g.), phenol (10 g.) and ether (50 c.c.)] and the mixture heated under reflux for 2 hr. Water was added, the ethereal layer separated, and chloride precipitated as silver chloride from the aqueous layer (yield 2·85 g., 99%). The ethereal layer was washed repeatedly with 2N-sodium hydroxide, dried (Na_2SO_4), and evaporated. Dry hydrogen chloride was passed through the residual oil kept at 95°. The mixture became more and more viscous and solidified after *ca.* 4 hr. The solid dissolved when heated with Claisen's solution (20 c.c.); the crystals which separated on cooling were filtered off and redissolved in methanol–water (1 : 1). The crude phenol, m. p. 166—176°, was liberated with carbon dioxide. Crystallisation from ethanol (4 parts) gave 4-hydroxy-4′-methoxytetraphenylmethane (4·5 g.), m. p. 191—194° (yield 61%). Rearrangement of the ether in nitromethane solution, in the presence of 70% perchloric acid, gave the methoxy-phenol in 24% yield after 6 days at 110—120°.

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