171. *Acylation and Allied Reactions catalysed by Strong Acids. Part IX.* The Ease of Formation and Reactions of the Diphenylmethyl and Some Triarylmethyl Cations.*

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Diphenylmethanol (benzhydrol) is readily converted by perchloric acid into the diphenylmethyl cation, and some substitution reactions of this ion are studied. Various triarylmethyl cations can be similarly prepared and these are shown to be active entities. A novel reaction of the tri-*p*-methoxyphenylmethyl cation with nitromethane leading to 1 : 1 : 1-tri-*p*-methoxyphenyl-2-nitroethane is discussed.

THE ready formation of ethers from triphenylmethanol and, *e.g.*, methanol in presence of even traces of acid (cf. Hatt, *J.*, 1938, 483) undoubtedly involves the intermediate formation of a triphenylmethyl cation which then reacts with the alcohol (ROH), the overall reactions being as follows :

$$Ph_3C{\cdot}OH + H^+ \rightleftharpoons Ph_3C{\cdot}\overset{+}{O}H_2 \rightleftharpoons Ph_3C^+ + H_2O \quad . \; . \; . \; . \; . \; . \; . \; (1)$$

$$Ph_3C^+ \text{ (or } Ph_3C{\cdot}\overset{+}{O}H_2) + R{\cdot}OH \rightleftharpoons Ph_3C{\cdot}OR + H^+ \text{ (or } H_3\overset{+}{O}) \quad . \; . \; . \; . \; (2)$$

The regeneration of the hydrogen (or hydroxonium) ion thus ensures that the processes are autocatalytic.

Balfe, Kenyon, and Thain (*J.*, 1951, 386; 1952, 790) have suggested, from work on the alkyl–oxygen fission of di-*p*-methoxyphenylmethyl phthalate and on the dismutation reactions of the carbinol, that carbonium-ion formation is a predominant factor in the changes they have investigated. We agree with this view and now present evidence that with a strong acid diphenylmethanol itself also undergoes reactions which indicate that the diphenylmethyl cation can be formed very readily. In view of the fact that 72% perchloric acid was used in most of our experiments, thus introducing some water (2·2 moles per mole of $HClO_4$) into the reaction mixtures, it is not unlikely that the hydrated cation, $Ph_2CH{\cdot}\overset{+}{O}H_2$, is in fact the reactive entity but this does not invalidate the results obtained with highly active components.

We have found that diphenylmethanol, phenol, and 72% perchloric acid in nitromethane at 100° for 4 hours gave 63% of *p*-hydroxytriphenylmethane or 86% of 2 : 4 : 6-trisdiphenylmethylphenol according to the molecular proportions used. The last-named compound has previously been prepared by Schorigin (*Ber.*, 1928, **61**, 2516) using acetic–sulphuric acid as the condensing agent; our procedure is a decided improvement. Similar experiments with anisole gave *p*-methoxytriphenylmethane (89%) which was also converted further into 2 : 4-bisdiphenylmethylanisole (93%): the 2 : 4 : 6-trisubstituted derivative could not be prepared.

Burton and Praill (*Chem. and Ind.*, 1951, 939) have drawn attention to the fact that " benzyl perchlorate " is an active benzylating agent even towards benzene. We now

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* Part VIII, preceding paper.

find that " diphenylmethyl perchlorate," prepared *in situ* from diphenylmethyl chloride and silver perchlorate, will convert benzene during 2 hours at room temperature into triphenylmethane in 65% yield:

$$Ph_2CH^+ClO_4^- + C_6H_6 \longrightarrow Ph_3CH + H^+ClO_4^-$$

The reaction is not so ready as that with the benzyl cation and we have shown (below) that under comparable conditions the triphenylmethyl cation is without action on benzene. The order of activity of the cations towards benzene is thus, benzyl>diphenylmethyl$\gg$ triphenylmethyl, and is in the reverse order of the generally accepted view of their ease of formation.

" Triphenylmethyl perchlorate " (Gomberg and Cone, *Annalen*, 1909, **370**, 194), which is very readily obtained from triphenylmethyl chloride and silver perchlorate in nitromethane or from the carbinol and perchloric acid in acetic acid, reacts slowly with anisole at room temperature to give at least 63% of *p*-methoxytetraphenylmethane, which can also be obtained more conveniently in 87% yield from triphenylmethanol, anisole, and 72% perchloric acid in nitromethane at 100° for 6 hours. There is no reaction with benzene under either set of conditions. *p*-Hydroxytetraphenylmethane was also obtained from " triphenylmethyl perchlorate " and phenol in nitromethane at room temperature in 23% (48 hours) and 68% yield (7 days).

The rearrangement of phenyl triphenylmethyl ether to *p*-hydroxytetraphenylmethane has been studied by van Alphen (*Rec. Trav. chim.*, 1927, **46**, 287) who found zinc chloride to be an effective catalyst. We have found that rearrangement also occurred very smoothly with 72% perchloric acid in nitromethane at 100° for 6 hours but only to a slight extent at room temperature during 7 days. It appears that the intermediate cation, $CPh_3{\cdot}\overset{+}{O}HPh$, is relatively stable under the last quoted conditions.

The effect of substituents of opposite type, namely, methoxyl and nitro, on the preparation and activity of " aroyl perchlorates " was studied in Part IV (*J.*, 1951, 529). We have now investigated the ease of formation and reactivity of the tri-*p*-methoxyphenylmethyl cation which is readily obtained from the carbinol and 72% perchloric acid. The combined influence of the three *p*-methoxy-groups should facilitate the separation of the hydroxyl group from the original carbinol and also the perchlorate ion (or other anion) from its salts. When the carbinol was treated with 72% perchloric acid in nitromethane at 100° for 7 days there was obtained a moderately good yield of a nitrogen-containing compound which from its reactions and properties, must be 1 : 1 : 1-tri-*p*-methoxyphenyl-2-nitroethane, $NO_2{\cdot}CH_2{\cdot}C(C_6H_4{\cdot}OMe\text{-}p)_3$. Preferential formation of the nitro-derivative also occurred somewhat unexpectedly when solutions of the carbinol with anisole or phenol in an excess of nitromethane were heated with perchloric acid: no reaction occurred with phenol alone or in nitrobenzene during 7 days at 100°. As far as we are aware this is the first recorded case of a substitution process involving the attack of a purely organic cation on nitromethane.

Tri-*p*-nitrophenylmethanol reacts normally with anisole and phenol in nitromethane under the influence of perchloric acid, yielding 4-methoxy- and 4-hydroxy-4′ : 4″ : 4‴-trinitrotetraphenylmethane, respectively: yields of 31 and 74% were obtained after reaction times of 4 and 3 hours, respectively, at 100°. It is clear that the combined electron-attracting effects of the three nitro-groups in the tri-*p*-nitrophenylmethyl cation do not hinder the reaction with suitably activated molecules.

Our results with the triarylmethyl cations show clearly that, under suitable experimental conditions, they are active entities. Their non-reactivity towards benzene is very similar to the non-reactivity of the acetyl cation towards the same molecule (Burton and Praill, *loc. cit.*), and in our opinion is due to the symmetrical structure of the benzene molecule rather than the size of, or any steric factor connected with, the triarylmethyl cation. The non-reactivity of the tri-*p*-methoxyphenylmethyl cation towards anisole and phenol in nitromethane, and to phenol alone or in nitrobenzene or in methyl cyanide, may appear surprising in view of the results obtained with other triarylmethyl cations. It is however well known that the properties of the perchlorate resemble more nearly those of a " true salt," and we suggest that in nitromethane (or nitrobenzene) there is formation of the solvated salt $[R{\cdot}NO_2{\rightarrow}C^+(C_6H_4{\cdot}OMe)_3]ClO_4^-$, owing to the electron-donating properties of the nitro-group. It would appear that the solvated cation is unreactive towards anisole and phenol, but that that from nitromethane undergoes slow conversion into the tri-*p*-methoxyphenylnitroethane. It is probable that this is an " intramolecular " process. A similar rearrangement does not appear to occur in nitrobenzene or in methyl cyanide.

The above suggestion that nitromethane can act as an electron-donor towards a triarylmethyl cation has been envisaged by Bentley, Evans, and Halpern (*Trans. Faraday Soc.*, 1951, **47**, 711; see also Bentley and Evans, *J.*, 1952, 3468) in their work on the ionisation of triarylmethyl chlorides in nitroalkanes.

EXPERIMENTAL

p-*Hydroxytriphenylmethane.*—72% Perchloric acid (0·5 c.c.) was added to diphenylmethanol (18·4 g., 0·1 mol.) and phenol (50 g., *ca.* 0·5 mol.) dissolved in nitromethane (50 c.c.). The mixture was kept at 100° for 4 hours, cooled, poured into water, and extracted with chloroform, and the chloroform extract washed with water; volatile products and excess of phenol were then removed in steam. The residual oil was extracted with chloroform, and the extract dried (Na_2SO_4) and evaporated in a vacuum. After two crystallisations from aqueous acetic acid colourless plates (16·3 g., 63%), m. p. 110—112°, were obtained. Pure *p*-hydroxytriphenylmethane, m. p. 112·5—113·5°, was obtained by further crystallisation from aqueous acetic acid and aqueous ethanol. It was readily converted into the dibromo-derivative, m. p. 130—131°. *p*-Hydroxytriphenylmethane is stated to have m. p.s ranging from 110° to 118°; the m. p. of the dibromo-derivative is given as 130° (van Alphen, *Rec. Trav. chim.*, 1927, **46**, 801).

2 : 4 : 6-*Trisdiphenylmethylphenol.*—72% Perchloric acid (5 drops) was added to diphenylmethanol (5·52 g., 0·03 mol.) and phenol (1·0 g., *ca.* 0·01 mol.) dissolved in nitromethane (10 c.c.). The light brown solution was kept at 100° for 4 hours and then cooled to 0°; 2 : 4 : 6-trisdiphenylmethylphenol (5·1 g., 86%), m. p. 162—164°, separated as colourless needles. After two crystallisations from chloroform–methanol (1 : 1; 6 parts; 85% recovery) the m. p. was raised to 166—167°. The phenol was unchanged by treatment with ethereal diazomethane.

p-*Methoxytriphenylmethane.*—72% Perchloric acid (1 c.c.) was added to diphenylmethanol (36·8 g., 0·2 mol.) in nitromethane (120 c.c.) and anisole (120 c.c.). The light brown solution was kept at 100° for 3 hours, then cooled, poured into water, and extracted with ether; the ethereal layer was washed with water (to remove acid) and dried (Na_2SO_4). Solvent and excess of anisole were removed by distillation; the residue after being heated to 140°/20 mm. was distilled at 3 mm. A fraction (49 g., 89%), b. p. 204°/3 mm., solidified to colourless crystals of *p*-methoxytriphenylmethane (m. p. 60—64°). Successive crystallisations from ethanol (5 parts; 77% recovery) and light petroleum (5 parts; 77% recovery) gave the pure ether, m. p. 66—67° (Found : C, 87·15; H, 6·45. Calc. for $C_{20}H_{18}O$: C, 87·55; H, 6·6%).

The residue from the distillation solidified on trituration with light petroleum; the solid (1·8 g.), m. p. 140—145°, was recrystallised from light petroleum (b. p. 80—100°; 40 c.c.), giving colourless needles (1·55 g.), m. p. 146·5—147·5°, of 2 : 4-*bisdiphenylmethylanisole* (Found : C, 89·75; H, 6·25%; *M*, 382. $C_{33}H_{28}O$ requires C, 89·95; H, 6·4%; *M*, 441).

2 : 4-*Bisdiphenylmethylanisole.*—72% Perchloric acid (3 drops) was added to *p*-methoxytriphenylmethane (2·74 g., 0·01 mol.) and diphenylmethanol (1·84, 0·01 mol.) in nitromethane (10 c.c.). 2 : 4-Bisdiphenylmethylanisole crystallised as colourless needles from the reaction mixture, which was kept at 60—70° for 1 hour. After cooling to 0°, the product (4·1 g., 93%) m. p. 146—148°, was filtered off and washed with a little cold nitromethane.

Reaction of " Diphenylmethyl Perchlorate " with Benzene.—Freshly distilled diphenylmethyl chloride (19·2 g, 0·095 mole) in benzene (50 c.c.) was added dropwise with shaking to a solution of silver perchlorate (20·7 g., 0·1 mole) in benzene (600 c.c.); there was an immediate precipitation of silver chloride. The mixture was kept at room temperature for 2 hours, the silver chloride filtered off, and the filtrate poured on crushed ice. The yield of silver chloride, after successive washing with benzene, water, and benzene, and drying at 100°, was almost quantitative. The benzene layer was washed free from acid with water and dried (Na_2SO_4). After removal of solvent in a vacuum the residue was distilled at 3 mm. The pale yellow fraction, b. p. mainly 172—175°, crystallised to a mass of slightly coloured needles (15·0 g., 65%). Crystallisation from ethanol (4 parts; 85% recovery) gave colourless needles, m. p. 93—94·5°, of triphenylmethane.

Reactions of the Triphenylmethyl Cation.—(a) *With anisole.* Triphenylmethyl chloride (5·53 g., 0·025 mole) in anisole (12 c.c.) was added dropwise to a solution of silver perchlorate (5·3 g., 0·026 mole) in nitromethane (60 c.c.); there was immediate precipitation of silver chloride. The dark crimson supernatant liquid began to deposit needles after *ca.* 12 hours. The mixture was set aside for 7 days at room temperature and then filtered. The residue was washed with nitromethane and water, dried at 100°, and then extracted with cold chloroform (total 90 c.c.). The residual silver chloride weighed 2·8 g. (98%). The chloroform extracts were treated with charcoal and filtered, and the filtrate was diluted with methanol (45 c.c.). On cooling to 0°, *p*-methoxytetraphenylmethane (3·25 g.), m. p. 197·5—199°, crystallised in colourless needles; a further crop (0·92 g.), m. p. 195—196°, was obtained by concentration of the mother-liquor. The initial filtrate was treated with crushed ice and then extracted with chloroform. The chloroform extracts were washed free from acid with water and dried (Na_2SO_4). Chloroform and excess of anisole were removed at 100°/20 mm.; the residue solidified on trituration with methanol. The impure solid thus obtained gave *p*-methoxytetraphenylmethane (0·2 g.), m. p. 197—199°, after successive crystallisation from 1 : 1 chloroform–methanol and acetic acid : the total yield of ether was thus 63%. When the reaction was carried out in the same solvent mixture for 18 hours, the ether was isolated in 16% yield. When anisole alone was the reaction medium only a trace of the ether was obtained after 24 hours.

The ether was also obtained by addition of 72% perchloric acid (2 drops) to triphenylmethanol (2·0 g.) in anisole (6 g.) and nitromethane (6 g.). The deep red solution was kept at 100° for 6 hours; on cooling to 0°, *p*-methoxytetraphenylmethane (2·35 g., 87%), m. p. 196—198°, crystallised in colourless needles.

(b) *With phenol.* A solution of triphenylmethyl chloride (6·9 g., 0·025 mole) in benzene (10 c.c.) was added dropwise to a solution of silver perchlorate (5·3 g., 0·026 mole) in nitromethane (50 c.c.); there was immediate precipitation of silver chloride. Phenol (10 g.) in nitromethane (30 c.c.) was then added and the mixture kept for 7 days. The solid obtained by filtration was washed with nitromethane and water, dried at 100°, and then extracted with chloroform (Soxhlet). The chloroform extracts yielded *p*-hydroxytetraphenylmethane in two crops (total 5·13 g.), m. p. 282—284°. The residual silver chloride weighed 3·4 g. (96%). The original filtrate was poured on crushed ice and extracted with chloroform. The chloroform extracts were washed free from acid with water and dried (Na_2SO_4). After distillation of the lower-boiling solvents in a vacuum, the excess of phenol was removed by steam-distillation. The residual dark solid was filtered off, dried at 100°, and dissolved in chloroform. The solution was treated with charcoal, filtered, and concentrated to 25 c.c.; cooling to room temperature gave a further 0·53 g. (total yield 68%), m. p. 277—284°.

p-Hydroxytetraphenylmethane was isolated in 23% yield when the reaction was carried out for 48 hours.

A dried ethereal solution of diazomethane (0·019 mol. in 20 c.c.) was added to a suspension of the phenol (1·0 g., 0·003 mol.) in methanol (10 c.c.); the mixture was kept at 0° for 3 days. Ether and excess of diazomethane were evaporated and the crystalline product (1·0 g.), m. p. 199—200·5°, was collected. The ether was obtained as colourless needles (m. p. and mixed m. p. 200·5—202°) by crystallisation from acetic acid (20 parts; 80% recovery).

Rearrangement of Phenyl Triphenylmethyl Ether.—Phenyl triphenylmethyl ether (0·5 g.) was dissolved in nitromethane (2·0 c.c.) containing one drop of 72% perchloric acid, and the mixture kept at 100° for 6 hours. On cooling to 0°, crystals of *p*-hydroxytetraphenylmethane (0·38 g.), m. p. 279—281° (not depressed on admixture with an authentic sample), separated. The rearrangement occurred only to a slight extent when carried out at room temperature for 7 days.

*Tri-*p*-methoxyphenylmethanol.*—The methoxy-alcohol was prepared from tri-*p*-methoxyphenylmethane according to the methods of Baeyer and Villiger (*Ber.*, 1902, **35**, 1198) and of Lifschitz and Girbes (*Ber.*, 1928, **61**, 1485). The oxidation procedure was modified as follows. Tri-*p*-methoxyphenylmethane (16·7 g., 0·05 mol.) was dissolved in boiling acetic acid (335 c.c.), and lead dioxide (≡ 0·075 g.-atom of oxygen) added in portions during 10 minutes. The mixture was heated under reflux for a further 5 minutes, then cooled and filtered, and the filtrate poured into water. The product was isolated by extraction with ether, the ethereal extracts were washed with dilute aqueous sodium hydroxide and then water and dried (Na_2SO_4). After evaporation, the residue was dissolved in hot ethanol (10 c.c.); on cooling to 0°, the red solution deposited the carbinol as pale orange needles (9·4 g.), m. p. 80—82°. The mother-liquor was treated at the b. p. with picric acid (8·0 g.) dissolved in boiling ethanol (40 c.c.). The crimson picrate (7·5 g.), m. p. 229—230°, which separated was filtered off and was decomposed to the methoxy-alcohol by shaking its suspension in chloroform (20 parts) with 0·05N-sodium hydroxide (1·25 equivs.). The dried (Na_2SO_4) chloroform layer was evaporated in a vacuum and the residual oil crystallised from aqueous acetic acid. The total yield of carbinol was 75—80%. The carbinol was conveniently crystallised from ethanol (2 parts; 82% recovery) or from benzene–light petroleum (1 : 1; 3 parts; 80% recovery).

*Tri-*p*-methoxyphenylmethyl Perchlorate.*—70% Perchloric acid (1·8 c.c.) was added cautiously to a cooled solution of tri-*p*-methoxyphenylmethanol (5·25 g.) in acetic anhydride (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 (5·8 g., 89%) had m. p. 193—195°.

*Reaction of Tri-*p*-methoxyphenylmethanol with Nitromethane.*—The methoxy-alcohol (5·0 g.), nitromethane (20 c.c.), and 72% perchloric acid (0·5 c.c.) were heated together at 100° for 7 days, then poured into water, the product was extracted with chloroform, and the chloroform extracts were washed with water (to remove acid) and dried (Na_2SO_4). The residue obtained after removal of the solvent in a vacuum solidified on trituration with alcohol. The crude solid (3·5 g.), m. p. 101—104°, thus obtained separated from ethanol (35 c.c.) in needles (2·9 g.), m. p. 109·5—111·5°. Repeated crystallisation from ethanol gave colourless needles of 1 : 1 : 1-*tri-*p*-methoxyphenyl-2-nitroethane,* m. p. 113·5—114° (Found: C, 70·55; H, 5·8: N, 3·7. $C_{23}H_{23}O_5N$ requires C, 70·2; H, 5·85; N, 3·6%).

The combined ethanolic mother-liquors when treated at the b. p. with an excess of picric acid yielded 2·2 g. of tri-*p*-methoxyphenylmethyl picrate, m. p. 229—230° (≡ 1·4 g. of unchanged carbinol).

The nitro-compound was readily soluble in boiling 2N-sodium hydroxide but insoluble in boiling 2N-sodium carbonate. It gave crystalline sodium, potassium, and barium salts, from which it was regenerated * by acidification. The compound gave no colour with aqueous or alcoholic ferric chloride solutions, and did not react with bromine-water or toluene-*p*-sulphonyl chloride in pyridine at 100°.

When bromine (1 c.c.) was added dropwise to a solution of the compound (0·55 g.) in acetic acid (10 c.c.), heat was evolved. The mixture deposited crystalline solid which was collected after 30 minutes, washed with acetic acid and water, and dried. The *tribromo*-derivative, crystallised in colourless needles from aqueous acetic acid, had m. p. 173—176° (Found: C, 43·4; H, 3·55. $C_{23}H_{20}O_5NBr_3$ requires C, 43·8; H, 3·2%).

*Reaction of Tri-*p*-methoxyphenylmethyl Perchlorate with Ethanol.*—A suspension of the perchlorate (1·3 g.) in ethanol (5 c.c.) was refluxed for 3 hours during which time dissolution occurred and the mixture lightened in colour. The solution on cooling to 0° deposited tri-*p*-methoxytriphenylmethane (0·7 g., 70%), m. p. 53—55° (Found: C, 78·5; H, 6·9. Calc. for $C_{22}H_{22}O_3$: C, 79·0; H, 6·65%). Oxidation of the product with lead dioxide gave the alcohol, which was isolated (see above) as the picrate, m. p. and mixed m. p. 229—230°.

*Tri-*p*-nitrophenylmethanol.*—Tri-*p*-nitrophenylmethane (Hantzsch, *Ber.*, 1919, **52**, 495) was converted into the alcohol by chromium trioxide oxidation as described by Fisher and Fisher (*Ber.*, 1904, **37**, 3357). Small quantities of 4 : 4′-dinitrobenzophenone were isolated as a by-product.

*Reaction of Tri-*p*-nitrophenylmethanol with Anisole.*—72% Perchloric acid (2 drops) was added to tri-*p*-nitrophenylmethanol (0·79 g., 0·002 mol.) dissolved in anisole (1·3 g., 0·012 mol.) and nitromethane (1·3 g.). The mixture was kept at 100° for 4 hours and then poured into water. The product was extracted with chloroform, and the chloroform extracts were washed with water (to remove acid) and dried (Na_2SO_4). The residual oil obtained after removal of volatile products in a vacuum solidified on trituration with benzene. Successive crystallisation from benzene (15 parts) and ethanol (350 parts) gave *4-methoxy-4′ : 4″ - 4‴-trinitrotetraphenylmethane* (0·30 g., 31%), m. p. 211—213°. The m. p. was raised to 213·5—215° by further crystallisation from ethanol (Found: C, 64·2; H, 3·85; N, 8·3. $C_{26}H_{17}O_7N_3$ requires C, 64·3; H, 3·95; N, 8·65%).

*Reaction of Tri-*p*-nitrophenylmethanol with Phenol*—Perchloric acid (72% w/w; 6 drops) was added to a solution of the nitro-alcohol (2·4 g., 0·006 mol.) and phenol (2·8 g., 0·03 mol.) in nitromethane (3·6 c.c.). The mixture was kept at 100° for 3 hours and then poured into water. The product was extracted with chloroform and the chloroform extracts were washed free from acid with water. Solvent and excess of phenol were removed in steam. The crude solid collected by filtration was dissolved in boiling ethanol (100 parts). The cooled solution deposited

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* The regenerated or freshly prepared nitro-compound was obtained crystalline with difficulty, presumably because of its existence in normal and *aci*-forms.

4-*hydroxy*-4′ : 4″ - 4‴-*trinitrotetraphenylmethane* (2·13 g., 74%), m. p. 281—282°, as a yellow crystalline powder. The phenol crystallised from acetic acid (20 parts) in pale yellow prisms, m. p. 282—283° (Found : C, 63·7; H, 3·85; N, 9·05. $C_{25}H_{17}O_7N_3$ requires C, 63·7; H, 3·65; N, 8·9%).

We thank Imperial Chemical Industries Limited for a grant towards the cost of this investigation.

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[*Received, November* 18*th*, 1952.]