206. *Acylation and Allied Reactions catalysed by Strong Acids. Part XI.* The Dismutation of Diphenylmethanol by Perchloric Acid.*

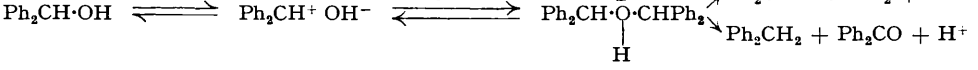
By H. Burton and G. W. H. Cheeseman.

Diphenylmethanol is converted by perchloric acid into benzophenone and diphenylmethane. The reaction mechanism is discussed with particular reference to the intermediate formation of the diphenylmethyl cation.

During an investigation of the reactions of the diphenylmethyl cation (Burton and Cheeseman, *J.*, 1953, 832) two experimental methods were used. The cation was derived from diphenylmethyl perchlorate, prepared either from diphenylmethyl chloride and silver perchlorate, or from diphenylmethanol and 72% perchloric acid. The latter procedure had certain advantages for the preparation of some compounds, *e.g.*, 2 : 4-bisdiphenylmethylanisole; the reactions studied were clearly not unduly influenced by the presence of some water.

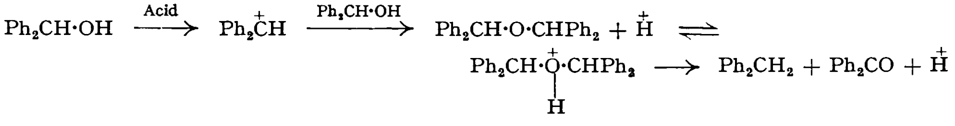
Diphenylmethyl perchlorate was shown to react with benzene under anhydrous conditions at room temperature for 2 hours to give 65% of triphenylmethane. An investigation of the parallel reaction between diphenylmethanol, benzene, and 72% perchloric acid has shown that only traces of triphenylmethane are formed. The reaction mixture was heated under reflux for 6 hours and bisdiphenylmethyl ether, benzophenone, and diphenylmethane were the main products.

Balfe, Kenyon, and Thain (*J.*, 1952, 790) have studied the action of strong acids, such as hydrochloric and trichloroacetic, on di-*p*-methoxyphenylmethanol and have isolated di-*p*-methoxyphenylmethane from their reaction products. The scheme which these authors suggested to explain their results would in the case of diphenylmethanol be as follows :



$$Ph_2CH{\cdot}OH \overset{Acid}{\rightleftharpoons} Ph_2CH^+\,OH^- \overset{Ph_2CH\cdot OH}{\rightleftharpoons} Ph_2CH{\cdot}\underset{H}{\overset{+}{O}}{\cdot}CHPh_2 \left\langle \begin{array}{l} \nearrow Ph_2CH{\cdot}O{\cdot}CHPh_2 + H^+ \\ \searrow Ph_2CH_2 + Ph_2CO + H^+ \end{array}\right.$$

When bisdiphenylmethyl ether was treated with 72% perchloric acid in boiling benzene, it was found to undergo dismutation more readily than diphenylmethanol itself; triphenylmethane was also isolated as a by-product. It therefore seemed possible that dismutation of the alcohol might be occurring *via* the intermediate ether (cf. Kny-Jones and Ward, *J.*, 1930, 535). If this is the case the above reaction sequence would have to be modified as follows :



$$Ph_2CH{\cdot}OH \xrightarrow{Acid} Ph_2\overset{+}{C}H \xrightarrow{Ph_2CH\cdot OH} Ph_2CH{\cdot}O{\cdot}CHPh_2 + \overset{+}{H} \rightleftharpoons$$

$$Ph_2CH{\cdot}\underset{H}{\overset{+}{O}}{\cdot}CHPh_2 \longrightarrow Ph_2CH_2 + Ph_2CO + \overset{+}{H}$$

The conversion of the ether into diphenylmethane and benzophenone probably occurs by weakening of one of the C–O linkings after addition of a proton to the oxygen.

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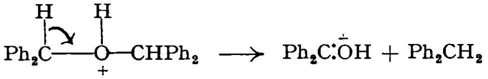
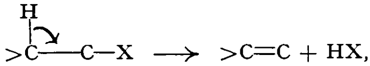
* Part X, *J.*, 1953, 837.

It has been reported by Hauser and Kantor (*J. Amer. Chem. Soc.*, 1951, **73**, 1437) that



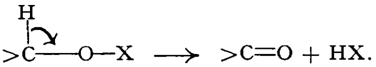
$$Ph_2\overset{H}{C}-\underset{+}{\overset{H}{O}}-CHPh_2 \longrightarrow Ph_2C\overset{-}{:}OH + Ph_2CH_2$$

the same dismutation * can be effected by potassium amide. In this case the mechanism of the reaction is clearly equivalent to the well-known elimination reaction



$$>\overset{H}{C}-C-X \longrightarrow >C{=}C + HX,$$

and can be expressed as follows :



$$>\overset{H}{C}-O-X \longrightarrow >C{=}O + HX.$$

Both these processes are analogous to base-catalysed prototropic changes whereas the dismutation reaction brought about by acid is equivalent to acid-catalysed prototropy.

Reference has already been made to the reaction $Ph_2\overset{+}{C}H + C_6H_6 \longrightarrow Ph_3CH + \overset{+}{H}$, occurring in the system, silver chloride–diphenylmethyl perchlorate–benzene. The isolation of triphenylmethane from the above experiments with diphenylmethanol and bisdiphenylmethyl ether is therefore additional evidence that the intermediate formation of diphenylmethyl cations does take place. This reaction must proceed relatively slowly as only small amounts of triphenylmethane were isolated; the presence of water in the system must also be of paramount importance since it would favour the production of the $Ph_2CH{\cdot}\overset{+}{O}H_2$ ion. When a solution of the bis-ether in anisole was treated with 72% perchloric acid at 100° for 4 hours, *p*-methoxytriphenylmethane and 2 : 4-bisdiphenylmethylanisole were the only products obtained (cf. Part IX). This result was not unexpected in view of the increased ease of substitution of the anisole nucleus compared with that of benzene, and the large excess of anisole present.

Bisdiphenylmethyl ether was recovered unchanged after 6 hours' refluxing with formic acid (0·5 mol.) in benzene. The bis-ether was partly converted into diphenylmethyl trichloroacetate when treated with trichloroacetic acid (0·5 mol.) in boiling benzene for 6 hours, but with 2·5 mol. of the acid under similar conditions the yield of ester was almost quantitative. No trace of a ketonic product could be detected. Bisdi-*p*-methoxyphenylmethyl ether, however, undergoes partial dismutation when treated with trichloroacetic acid (0·35 mol.) in benzene at 40° for 6 hours. The ester was also obtained in 65% yield from diphenylmethanol and trichloroacetic acid (1·2 mol.) in boiling benzene for 6 hours.

Balfe *et al.* (*loc. cit.*) also investigated the action of strong acids on a series of substituted diphenylmethanols. From their results, and the earlier failure of Kny-Jones and Ward (*loc. cit.*) to effect the dismutation of diphenylmethanol with dilute acids or 0·05N-hydrochloric acid, they postulate that only those alcohols, in which mesomeric effects operate to increase the electron density at the secondary carbon atoms of the intermediate $R_2CH{\cdot}\underset{H}{\overset{+}{O}}{\cdot}CHR_2$ ions, are able to undergo dismutation. As diphenylmethanol does undergo dismutation in the presence of perchloric acid this view must now be modified, but clearly the occurrence of such mesomeric effects facilitates the dismutation process.

On the basis of the second reaction sequence, the failure of earlier attempts to effect the dismutation of diphenylmethanol and bisdiphenylmethyl ether must be due to the use of an insufficiently strong acid to form the intermediate $Ph_2CH{\cdot}\underset{H}{\overset{+}{O}}{\cdot}CHPh_2$ ion.

When a solution of diphenylmethanol in nitromethane was treated at room temperature with a little 72% perchloric acid, bisdiphenylmethyl ether crystallised from the reaction mixture in 95% yield. The bis-ether was also similarly obtained in 78% yield in acetic acid as solvent. The formation of the bis-ether in these experiments is clearly facilitated

* The reaction mixture was treated with carbon dioxide and diphenylacetic acid isolated.

by the relative insolubility of this compound in the reaction media. These results indicate clearly that the following reactions are taking place :

$$\mathrm{Ph_2CH{\cdot}OH} + \overset{+}{\mathrm{H}} \rightleftharpoons \mathrm{Ph_2CH{\cdot}\overset{+}{O}H_2} \rightleftharpoons \mathrm{Ph_2\overset{+}{C}H} + \mathrm{H_2O}$$

$$\mathrm{Ph_2\overset{+}{C}H}\ (\text{or } \mathrm{Ph_2CH{\cdot}\overset{+}{O}H_2}) + \mathrm{Ph_2CH{\cdot}OH} \longrightarrow \mathrm{Ph_2CH{\cdot}O{\cdot}CHPh_2} + \overset{+}{\mathrm{H}}\ (\text{or } \mathrm{H_3\overset{+}{O}})$$

The regeneration of the hydrogen (or hydroxonium) ion ensures that the reactions are self-perpetuating.

EXPERIMENTAL

Dismutation of Diphenylmethanol.—A mixture of 72% perchloric acid (0·5 c.c.), diphenylmethanol (18·4 g., 0·1 mol.), and benzene (50 c.c.) was heated under reflux for 5 hours and then poured into water; the benzene layer was separated, washed free from acid, and dried (Na_2SO_4). The residue after removal of solvent was dissolved in ethanol (50 c.c.); on cooling, the solution deposited prisms of bisdiphenylmethyl ether (5·0 g.), m. p. (mainly) 104—107°, which were filtered off. The filtrate was heated under reflux with potassium hydroxide (10 g. in 10 c.c. of water) and hydroxylamine hydrochloride (6 g. in 6 c.c. of water) for 2 hours, then poured into water, and extracted with light petroleum (2 × 30 c.c.). The petroleum extracts were washed with alkali, and the combined aqueous layers made slightly acid by the addition of dilute sulphuric acid. The benzophenone oxime which separated from the acidified solution was filtered off, freed from inorganic contaminants by trituration with water, and dried (yield 4·4 g.; m. p. 141—142·5°). It was hydrolysed by boiling sulphuric acid (30% w/v) to benzophenone (m. p. 49—50°), which was further identified as its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 236—238°). The dried petroleum extract was evaporated in a vacuum and the residue distilled through a short Vigreux column, giving fractions (i) diphenylmethane, b. p. 96—100°/3 mm. (3·6 g.), and (ii) b. p. 166—170°/2·8 mm. (1·1 g.). The syrupy residue from the distillation slowly crystallised from ethanol, yielding impure bisdiphenylmethyl ether. The diphenylmethane rapidly crystallised on cooling in needles (m. p. 24—25°), and was characterised as the tetranitro-derivative, m. p. and mixed m. p. 171—172°. Fraction (ii) was separated into bisdiphenylmethyl ether (m. p. and mixed m. p. 109—110°) and triphenylmethane (m. p. 91·5—93°; mixed m. p. 92—94·5°) by fractional crystallisation from light petroleum. The presence of triphenylmethane in this fraction was confirmed by oxidation with hot nitric acid (*d* 1·33) and the isolation of triphenylmethanol, m. p. 158·5—160° (undepressed when mixed with a pure specimen), from the reaction products.

Dismutation of Bisdiphenylmethyl Ether.—A mixture of 72% perchloric acid (0·5 c.c.), the ether (17·5 g., 0·05 mole), and benzene (50 c.c.) was heated under reflux for 5 hours and then poured into water. The organic layer was separated, washed free from acid, and dried (Na_2SO_4). The residue after removal of solvent was dissolved in ethanol (50 c.c.), and the solution cooled and seeded with starting material. A small quantity of dark oil separated; the alcoholic mother-liquor was decanted and treated with potassium hydroxide (10 g. in 10 c.c. of water) and hydroxylamine hydrochloride (6 g. in 6 c.c. of water) as described for the previous experiment. An identical isolation procedure yielded benzophenone oxime (6·7 g.; m. p. 139—141°), diphenylmethane (4·0 g.; b. p. 98—101°/3 mm.), and a higher-boiling fraction (1·2 g.) consisting mainly of triphenylmethane. There was a resinous residue (4·0 g.) from the distillation.

Decomposition of Bisdiphenylmethyl Ether by Perchloric Acid in Anisole.—A mixture of 72% perchloric acid (0·3 c.c.), the ether (10·5 g., 0·03 mole), and anisole (25 c.c.) was kept at 100° for 4 hours and then poured into water. The organic material was extracted with ether and the extract washed free from acid and dried (Na_2SO_4). After removal of solvent and excess of anisole through a short Vigreux column, the residue was distilled in nitrogen at 3 mm. The distillate (13·5 g.), obtained by heating to 300°, rapidly solidified to give colourless crystals of *p*-methoxytriphenylmethane. Successive crystallisations from light petroleum and ethanol gave the pure ether (10·1 g.; m. p. 66—67°, undepressed on admixture with an authentic specimen). The mother-liquor from these crystallisations gave no reaction with Brady's reagent. The residue in the flask (2·2 g.) solidified on trituration with light petroleum. It yielded 2 : 4-bisdiphenylmethylanisole (m. p. and mixed m. p. 147—148°) on crystallisation from light petroleum (b. p. 80—100°).

Diphenylmethyl Trichloroacetate.—(a) *Decomposition of bisdiphenylmethyl ether by trichloroacetic acid in benzene.* A solution of the ether (7·0 g., 0·02 mole) and trichloroacetic acid (8·2 g., 0·05 mole) in benzene (20 c.c.) was heated under reflux for 6 hours. The mixture was then poured into water, and the organic layer washed free from acid and dried (Na_2SO_4). The oil left after evaporation of the solvent gradually crystallised, to give impure diphenylmethyl trichloroacetate (12·8 g., 97%), m. p. 46—51°, which after two crystallisations from light petroleum (b. p. 40—60°; 3 parts) formed large colourless prisms, m. p. 53—54° (Found: Cl, 32·8. Calc. for $C_{15}H_{11}O_2Cl_3$: Cl, 32·3%). Hardegger *et al.* (*Helv. Chim. Acta*, 1948, **31**, 438) give m. p. 47—48°. The ester was converted into diphenylmethanol (m. p. and mixed m. p. 67—68°) by boiling 0·5N-alcoholic potassium hydroxide.

(b) A solution of diphenylmethanol (9·2 g., 0·05 mole) and trichloroacetic acid (9·8 g., 0·06 mole) in benzene (25 c.c.) was refluxed for 6 hours. The mixture was then poured into water, and the organic layer washed free from acid and dried (Na_2SO_4). After removal of solvent in a vacuum, the residue was distilled and one main fraction, b. p. 180—183°/4 mm. (10·8 g.), collected. This rapidly solidified, and crystallisation from light petroleum (b. p. 40—60°; 25 c.c.) gave diphenylmethyl trichloroacetate (7·3 g.; m. p. 53—54°) as large colourless prisms.

Bisdiphenylmethyl Ether.—(*a*) 72% Perchloric acid (0·5 c.c.) was added to a solution of diphenylmethanol (55·2 g., 0·3 mole) in nitromethane (75 c.c.). Colourless prisms of the ether (50 g., 95%), m. p. 108—110°, soon crystallised; these were collected after 18 hours.

(*b*) 72% Perchloric acid (2 drops) was added to a solution of diphenylmethanol (2 g.) in acetic acid (5 c.c.). The reaction mixture soon began to deposit colourless prisms of the ether and an emerald-green colour developed in the solution. After 3 days at room temperature the ether (1·15 g.), m. p. 108—109°, was filtered off; a further crop (0·33 g.; same m. p.) separated slowly from the mother-liquor. The total yield was 78%. A somewhat poorer yield was obtained when an equivalent amount of concentrated sulphuric acid was used instead of perchloric acid.

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