143. *Dismutation Reactions of Di-*p*-methoxyphenylmethanol.*

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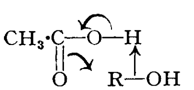
Di-*p*-methoxyphenylmethanol with 0·5 mol. of weak acids yields bisdi-*p*-methoxyphenylmethyl ether; with stronger acids it yields di-*p*-methoxyphenyl ketone and di-*p*-methoxyphenylmethane. The bis-ether and di-*p*-methoxyphenylmethyl ethyl ether, in ethanol–hydrochloric acid, yield di-*p*-methoxyphenylmethane and acetaldehyde; the ethyl ether, in propanol–hydrochloric acid, yields the methane and *n*-propaldehyde. It is suggested that the conjugate acids of di-*p*-methoxyphenylmethyl ethers are intermediates in these dismutations.

WE have already presented evidence (*J.*, 1951, 386) to indicate that di-*p*-methoxyphenylmethanol has very little tendency to react by virtue of its hydroxylic hydrogen atom but readily undergoes reactions which appear to imply carbonium-ion formation. This unusual behaviour of a secondary alcohol has been further examined.

*Action of Acids on Di-*p*-methoxyphenylmethanol.*—(i) Acetic acid in excess either at room temperature or at 100° within a few hours converts the alcohol quantitatively into its acetate. On the other hand, when a half-molecular proportion of acid is heated with the alcohol at 100°, the product is bisdi-*p*-methoxyphenylmethyl ether.

(ii) Formic acid readily dissolves the alcohol, giving a deep red solution from which only polymerised material can be isolated. On the other hand, a mixture of the acid (0·5 mol.) and the alcohol after 4 days at room temperature yielded the bis-ether (60%). It seems probable that the deep colour of the formic acid solution is due to the formation of carbonium ions, a view to which support is given by the ready reaction of this solution with urea and with sodium toluene-*p*-sulphinate to give respectively the disubstituted urea and di-*p*-methoxyphenylmethyl *p*-tolyl sulphone. Neither of these condensations takes place in acetic acid solution but both occur readily when a drop of sulphuric acid has been added, the solution becoming red. This suggests that di-*p*-methoxyphenylmethanol does not give rise to carbonium ions in acetic acid solution in the absence of strong acid and the ready formation of its acetate is therefore not likely to be due to an alkyl–oxygen fission reaction of the unimolecular type. The carbinol is also not prone to react by alkoxyl–hydrogen fission (*loc. cit.*). Possibly its esterification is bimolecular with alkyl-oxygen fission. Xanthhydrol would appear to undergo alkyl–oxygen fission even more readily than does di-*p*-methoxyphenylmethanol since it reacts with amides in acetic acid to yield the corresponding xanthhydryl derivatives (Fosse, *Compt. rend.*, 1907, **145**, 813); it reacts also in this solvent with sodium toluene-*p*-sulphinate to give *p*-tolyl xanthhydryl sulphone. The tolyl sulphones of di-*p*-methoxyphenylmethanol and xanthhydrol undergo reactions which indicate that the C–S bond breaks. Whilst in general they are stable to acids, with alcoholic potassium hydroxide they yield ethyl ethers, presumably by combination of a carbonium ion with ethoxyl:



$$R\text{-}\vdots\text{-}SO_2{\cdot}C_7H_7 + H\text{-}\vdots\text{-}OEt \longrightarrow R{\cdot}OEt + C_7H_7{\cdot}SO_2H.$$

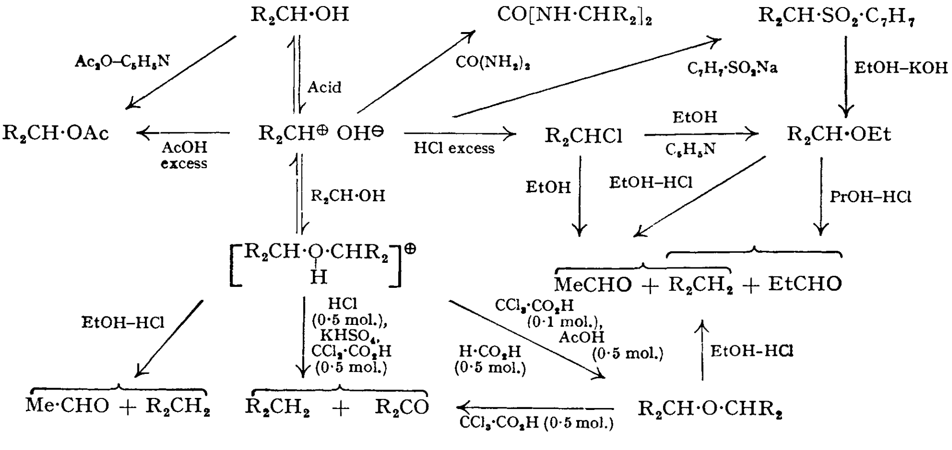
(iii) Trichloroacetic acid in small proportions converts di-*p*-methoxyphenylmethanol into its bis-ether but in higher concentrations effects its dismutation into *pp*′-dimethoxybenzophenone and di-*p*-methoxyphenylmethane, a reaction analogous to that undergone by xanthhydrol (Kny-Jones and Ward, *J.*, 1930, 535).

Dismutation of Di-p-*methoxyphenylmethanol*.—The dismutation of both di-*p*-methoxyphenylmethanol and xanthhydrol is hindered by the use of dioxan as solvent—as is also ether formation—probably owing to solvent–oxonium salt formation. Other strong acids also cause dismutation, *e.g.*, potassium hydrogen sulphate and hydrochloric acid (0·5 mol.).

Kny-Jones and Ward (*loc. cit.*) observed that xanthhydryl chloride reacts with ethyl alcohol, giving xanthen, and although they did not isolate acetaldehyde they found that the reaction solution gave a positive result with Schiff's reagent.

Di-*p*-methoxyphenylmethyl chloride reacts similarly with ethyl alcohol to give di-*p*-methoxyphenylmethane and acetaldehyde (isolated in 75% yield as its 2 : 4-dinitrophenylhydrazone); when pyridine is present di-*p*-methoxyphenylmethyl ethyl ether is produced. This ether also undergoes dismutation in acid solution yielding, when ethyl alcohol is the solvent, the substituted methane and acetaldehyde; when *n*-propyl alcohol is the solvent, propaldehyde and not acetaldehyde is isolated. Similarly bisdi-*p*-methoxyphenylmethyl ether undergoes dismutation in alcoholic solution containing hydrochloric acid, yielding di-*p*-methoxyphenylmethane and acetaldehyde.

Reactions of $R_2CH{\cdot}OH$ ($R = p\text{-}MeO{\cdot}C_6H_4$)

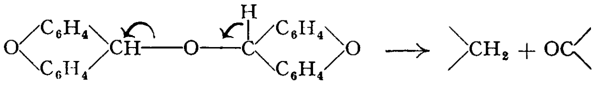


Thermal dismutation of diphenylmethyl derivatives to the corresponding benzophenone and diphenylmethane derivatives has been observed by Nef (*Annalen*, 1897, **298**, 202) and Goldthwaite (*Amer. Chem. J.*, 1905, **33**, 92). Since small amounts of the corresponding *s*-tetraphenylethane derivatives, formed by dimerisation, were also isolated it seems probable that these reactions proceed by a free-radical mechanism.

However, in acid-catalysed dismutation reactions a free-radical mechanism is unlikely because of the polar nature of the solution, and also because of the contrasted behaviour of di-*p*-methoxyphenylmethyl ethyl ether, which by acid-catalysed dismutation yields di-*p*-methoxyphenylmethane but by thermal dismutation yields this compound in only small amounts, the main product being the corresponding ketone, by a reaction more likely to proceed by a free-radical mechanism.

Furthermore no dimerisation products were isolated in the acid-catalysed reactions enumerated above.

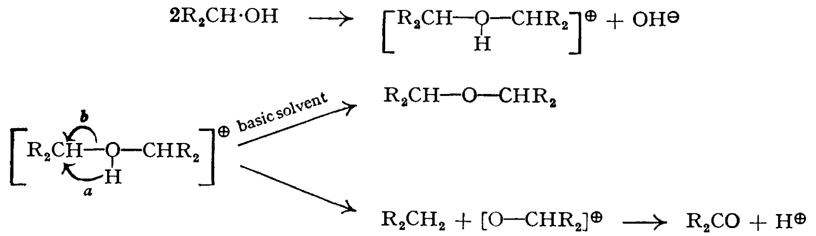
Kny-Jones and Ward (*loc. cit.*) considered that the dismutation of xanthhydrol occurred through the intermediate formation of its ether :



they noted, however, that dixanthhydryl ether undergoes dismutation less readily than does xanthhydrol itself.

A parallel behaviour has not been observed in the relative tendencies of di-*p*-methoxyphenylmethanol and its bis-ether to undergo dismutation by acid catalysis.

Accordingly, it appears more probable that the essential step in the process is the formation, not of an ether, but rather of its precursor, the conjugate acid, by carbonium-ion addition to an alcohol molecule. This conjugate acid may, by proton expulsion, yield the ether—a process likely to be favoured by the presence of pyridine or dioxan—or, alternatively, undergo dismutation.



When the reaction occurs in alcohol the carbonium ion will combine with a molecule of the solvent and the resulting unsymmetrical conjugate acid will undergo dismutation to the methane derivative and acetaldehyde.

It is postulated that during dismutation the proton of the conjugate acid moves over (process *a*) simultaneously with the pair of electrons which previously formed the carbon–oxygen link (process *b*).

In an unsymmetrical conjugate acid, *e.g.*, $\left[Et-\overset{H}{O}-CHR_2\right]^{\oplus}$, the CHR_2 part is reduced to CH_2R_2, and if it is assumed that a proton migrates then the secondary carbon atom, in order to attract it, must possess some slight negative charge.

It is further postulated that this small negative charge is due to the mesomeric effects of the methoxyl groups, since only alcohols with a structure allowing of this mesomeric effect can undergo dismutation. Thus Kny-Jones and Ward (*loc. cit.*) were unable to effect acid-catalysed dismutation of unsubstituted diphenylmethanol. Michler's hydrol undergoes dismutation, although the reaction is complicated by tar formation. *p*-Methoxydiphenylmethanol undergoes dismutation to a slight extent, but di-*p*-*tert.*-butylphenylmethanol not at all.

EXPERIMENTAL

Action of Acetic Acid on Di-p-*methoxyphenylmethanol.*—(a) *Acetic acid in excess.* A solution of the alcohol (0·5 g.) in glacial acetic acid (2 c.c.) was kept at room temperature for 12 hours. Dilution with water precipitated an oil which rapidly solidified (0·5 g.), having m. p. 68—73°; crystallisation from ether–light petroleum (3 c.c.; 1 : 1) yielded di-*p*-methoxyphenylmethyl acetate as needles, m. p. 78—80° undepressed on admixture with a specimen prepared by the action of acetic anhydride as described by Schnackenberg and Scholl (*Ber.*, 1903, **36**, 655). The same result was obtained when the reaction mixture was kept at 100° for 2 hours.

(b) 0·5 *Mol. of acetic acid.* A mixture of the alcohol (0·5 g.) and glacial acetic acid (0·1 g., 0·5 mol.) was kept at 100° for 2 hours and then diluted with water. The precipitated material, after two crystallisations from ethanol, yielded *bisdi*-p-*methoxyphenylmethyl ether* (0·25 g.), needles, m. p. 81—82° (Found : C, 76·2; H, 6·5. $C_{30}H_{30}O_5$ requires C, 76·6; H, 6·4%).

Attempted Preparation of Xanthhydryl Acetate.—Acetic anhydride (0·52 g., 1 mol.) was added to a solution of xanthhydrol (1·0 g.) in dry pyridine (1 c.c.). After 2 days at room temperature the mixture was diluted with crushed ice and made just acid to Congo-red. The dried precipitate (1·0 g.), m. p. 175—185° (after crystallisation from benzene), yielded dixanthhydryl ether, m. p. 212—214°, undepressed on admixture with an authentic specimen.

Action of Formic Acid on Di-p-*methoxyphenylmethanol.*—(a) *Formic acid in excess.* The alcohol (0·5 g.) dissolved readily in cold formic acid (2 c.c. of 99%) giving a deep red solution which after 30 minutes had become cloudy. After 4 days the separated solid was removed and dried (0·35 g.). Crystallisation from ethanol yielded a pale yellow powder which sintered at 60—80° [*M* (Rast), 900].

(b) 0·5 *Mol. of formic acid.* After 4 days at room temperature there was isolated bisdi-*p*-methoxyphenylmethyl ether, m. p. and mixed m. p. 76—78°, in 60% yield.

Bisdi-p-*methoxyphenylmethylurea.*—(*a*) A solution of the alcohol (0·2 g.) in formic acid (1 c.c.) was added to urea (0·06 g.) in formic acid (1 c.c.). The brilliant red colour of the alcohol solution faded at once, and a white solid began to separate. After 20 minutes water was added and the solid material (0·2 g.), m. p. 252—254°, crystallised from ethanol or acetone. *Bisdi*-p-*methoxyphenylmethylurea* forms fine needles, m. p. 258—259° (Found : C, 72·1 : H, 6·2 : N, 5·6. $C_{31}H_{32}O_5N_2$ requires C, 72·7 : H, 6·2 : N, 5·5%).

(*b*) In acetic acid only a trace of the urea was formed, the main product being di-*p*-methoxyphenylmethyl acetate (mixed m. p.). When, however, the acid contained a drop of concentrated sulphuric acid the substituted urea was readily obtained [mixed m. p. with product from (*a*)].

Di-p-*methoxyphenylmethyl* p-*Tolyl Sulphone.*—(*a*) Di-*p*-methoxyphenylmethyl chloride (1.0 g.), prepared by the action of cold concentrated hydrochloric acid on the alcohol, was added to a solution of sodium toluene-*p*-sulphinate (1·0 g., 1·5 mols.) in aqueous acetone. After 12 hours at room temperature the yellow solution was diluted with water; the precipitated material, after crystallisation from ether–light petroleum, yielded the sulphone (0·9 g.), m. p. 105—106° alone and when mixed with an authentic specimen (Balfe, Kenyon, and Thain, *J.*, 1951, 386).

(*b*) A solution of di-*p*-methoxyphenylmethanol (1·0 g.) in acetic acid (2 c.c.) containing sulphuric acid (1 drop) was mixed with a solution of sodium toluene-*p*-sulphinate (0·73 g.) in acetic acid (4 c.c.). The brilliant red colour of the alcoholic solution disappeared immediately and after an hour the opalescent solution was diluted and the precipitated sulphone crystallised (m. p. 105—106°). Di-*p*-methoxyphenylmethyl *p*-tolyl sulphone is unaffected by being heated at 100° for 3 hours with glacial acetic acid, or 1 : 1 concentrated hydrochloric acid–dioxan.

Di-p-*methoxyphenylmethyl Ethyl Ether.*—(*a*) Di-*p*-methoxyphenylmethyl chloride (2·4 g.) was added to dry pyridine (1·2 g.), a solid being formed with the liberation of heat; to this was added ethanol (5 c.c.), and the resulting brown solution was heated under reflux for 4·5 hours. After working up in the usual way the *ethyl ether* (2·1 g., 85%) was obtained, having b. p. 153°/0·5 mm., 217—220°/14 mm., n_D^{19} 1·5594 (Found : C, 75·0 : H, 7·4. $C_{17}H_{20}O_3$ requires C, 75·0 : H, 7·35%).

(*b*) Di-*p*-methoxyphenylmethyl *p*-tolyl sulphone (0·3 g.) was heated for 10 hours under reflux with ethanolic potassium hydroxide (5 c.c.; N; 80% alcohol). After evaporation of the solvent and working up there was obtained the ethyl ether, b. p. 145—150° (bath-temp.)/0·3 mm., n_D^{19} 1·5610.

p-*Tolyl Xanthhydryl Sulphone.*—Xanthhydrol (2·0 g.) and sodium toluene-*p*-sulphinate (1·8 g., 1 mol.) were each dissolved in warm glacial acetic acid (5 c.c.), and the solutions mixed. Crystals began to separate at once and after 2 hours were removed and washed with alcohol: they (2·4 g.) had m. p. 210—215°. Crystallisation from ethanol yielded p-*tolyl xanthhydryl* *sulphone*, needles, m. p. 215—216° (Found : S, 9·7. $C_{20}H_{16}O_3S$ requires S, 9·55%). This sulphone was unchanged after 3 hours' heating at 100° with acetic or formic acid.

Action of Hydrochloric Acid (0·5 *Mol.*) *on Di*-p-*methoxyphenylmethanol.*—Hydrochloric acid (0·3 c.c.; 6N; 0·5 mol.) was added to a solution of the alcohol (1·0 g.) in acetone (5 c.c.). After evaporation at room temperature a pale pink oil remained which crystallised from ether–light petroleum (15 c.c.; 1 : 1) yielding di-*p*-methoxyphenyl ketone (0·3 g.), m. p. and mixed m. p. 142—143°. The filtrate on evaporation left an oil which crystallised on storage (0·1 g.); after crystallisation from light petroleum this had m. p. 46—48° alone or when mixed with authentic di-*p*-methoxyphenylmethane (see below).

Action of Potassium Hydrogen Sulphate on Di-p-*methoxyphenylmethanol.*—A mixture of finely ground potassium hydrogen sulphate (0·5 g.) and the alcohol (1·0 g.) was heated at 100° for 3 hours. The water-insoluble portion of the reaction product was separated by fractional crystallisation into di-*p*-methoxyphenyl ketone (0·5 g.) and di-*p*-methoxyphenylmethane (0·2 g.), identified by m. p. and mixed m. p. in each case.

Reaction between Di-p-*methoxyphenylmethyl Chloride and Ethyl Alcohol.*—A solution of the chloride (0·5 g.) in ethanol (2 c.c.; 96%) was heated under reflux for 6 hours, a slow stream of carbon dioxide passing through the reaction flask and into two wash-bottles containing 2 : 4-dinitrophenylhydrazine in hydrochloric acid (0·2%; 2N). Acetaldehyde 2 : 4-dinitrophenylhydrazone (0·32 g.; 75%), m. p. 160—161°, was precipitated; after crystallisation from ethanol it had m. p. 165—167° alone and mixed with an authentic specimen.

Ethanol was removed from the non-volatile residue at room temperature, and the residual oil dissolved in ether, washed, and dried (K_2CO_3). The resulting di-*p*-methoxyphenylmethane (0·35 g., 80%) had b. p. 149—151°/0·4 mm., m. p. 49—51° undepressed when mixed with the specimen prepared as described above (Städel and Beck, *Annalen*, 1878, **194**, 323, record m. p. 48—49°).

Formation of Ethyl Xanthhydryl Ether from the Sulphone.—*p*-Tolyl xanthhydryl sulphone (1·0 g.) was heated under reflux with ethanolic potassium hydroxide (20 c.c.; N, 80% alcohol) for 4 hours. The alcohol was evaporated, the residue diluted with water, and the precipitated oil extracted with light petroleum. The insoluble solid had m. p. 120—125° : it (0·1 g.) was separated by crystallisation from ether–light petroleum into dixanthhydryl ether (0·02 g.), m. p. and mixed m. p. 203—205°, and xanthhydrol (0·06 g.), m. p. and mixed m. p. 122—123°. The light petroleum extract yielded *ethyl xanthhydryl ether* (0·5 g., 74%) as an oil which slowly crystallised and then had m. p. 50—60°. Two sublimations at 0·1 mm. yielded the pure material as prisms, m. p. 53—54° (Found : C, 79·7 : H, 6·1. $C_{15}H_{14}O_2$ requires C, 79·7 : H, 6·2%).

Dismutation of Di-p-*methoxyphenylmethanol and of Bisdi*-p-*methoxyphenylmethyl Ether by Trichloroacetic Acid in Benzene or Dioxan.*—The alcohol (or ether) (1·0 g.) was heated at 40° in benzene or dioxan (1 c.c.) containing varying amounts of trichloroacetic acid, air above the reaction mixture being displaced by nitrogen. Both pure dioxan and a specimen containing peroxides were used but no difference was noted between the reaction products. After the heating, ether (5 c.c.) was added and the solution was washed with alkali and dried (Na_2SO_4). The residue after evaporation of the solvent was triturated with light petroleum (3 × 2 c.c.) in which di-*p*-methoxyphenylmethane is readily soluble : the combined petroleum extracts on evaporation yielded crystalline di-*p*-methoxyphenylmethane. The undissolved residue was triturated with cold ether–light petroleum (10 c.c.; 1 : 4) in which di-*p*-methoxyphenyl ketone is practically insoluble and can be removed therefrom by filtration. The ether–light petroleum extract was evaporated and the residue crystallised—from ether–light petroleum if consisting mainly of di-*p*-methoxyphenylmethanol, or from ethanol if consisting mainly of bisdi-*p*-methoxyphenylmethyl ether. Results are in the following Table.

Di-p-*methoxyphenylmethanol* (2 hours)

$CCl_3{\cdot}CO_2H$ (g.)	Solvent	Products isolated
0·07 (0·1 mol.)	Benzene	Ether 80%
0·07 ,,	Dioxan	Ether 40, unchanged alcohol 50%
0·35 (0·5 mol.)	Benzene	Ether 25, ketone 10, methane 5%
0·35 ,,	Dioxan	Ether 84%
0·35 ,,	None	Ketone 43, methane 32%.

Bisdi-p-*methoxyphenylmethyl ether* (*6 hours*).

0·35	Benzene	Ether 35, ketone 14, methane 3%
0·35	Dioxan	Ether 84%

Decomposition of Di-p-*methoxyphenylmethyl Ethyl Ether with Acids.*—(*a*) A solution of the ethyl ether (1·0 g.) and trichloroacetic acid (0·35 g.) in benzene (1 c.c.) was heated under reflux, a stream of carbon dioxide carrying any volatile products into 2 : 4-dinitrophenylhydrazine solution (also in other experiments recorded below). No volatile aldehydes or ketones were formed; di-*p*-methoxyphenyl ketone (0·11 g.), m. p. 139—141°, and di-*p*-methoxyphenylmethane (0·15 g.), b.p. 148°/0·3 mm., m. p. and mixed m. p. 48—50°, were isolated but the main product was an intractable tar.

(*b*) A solution of the ethyl ether (0·5 g.) in aldehyde-free ethanol (2 c.c.) containing hydrochloric acid (0·18 c.c., 1 mol.) was heated under reflux for 8 hours. Acetaldehyde 2 : 4-dinitrophenylhydrazone was precipitated in the wash-bottles; it (0·25 g., 60%) had m. p. 160°, and after crystallisation 165—167° alone or mixed with authentic material. The residue in the reaction flask yielded di-*p*-methoxyphenylmethane (0·28 g., 67%), m. p. and mixed m. p. 48—50°, and di-*p*-methoxyphenyl ketone (0·02 g.), m. p. 138—140° (mixed with a pure specimen, m. p. 140—142°).

(*c*) A solution of the ethyl ether in aldehyde-free *n*-propanol (2 c.c.) containing hydrochloric acid (0·18 c.c.), after being heated under reflux for 9 hours, yielded *n*-propaldehyde 2 : 4-dinitrophenylhydrazone (0·15 g., 35%), m. p. 140—145°; recrystallisation from ethanol gave the pure compound, m. p. 154—155°, undepressed when mixed with an authentic specimen but depressed to <140° when mixed with acetaldehyde 2 : 4-dinitrophenylhydrazone. Di-*p*-methoxyphenylmethane (0·37 g., 88%), m. p. 46—48°, was isolated from the non-volatile reaction mixture.

Decomposition of Bisdi-p-*methoxyphenylmethyl Ether in Acidified Ethanol.*—A solution of the bis-ether (0·5 g.) in aldehyde-free ethanol (4 c.c.) containing hydrochloric acid (0·36 c.c.) was heated under reflux. A precipitate was rapidly formed in the wash-bottles and after 8 hours' heating acetaldehyde 2 : 4-dinitrophenylhydrazone (0·27 g., 57%) was collected and characterised. The non-volatile residue yielded di-*p*-methoxyphenylmethane (0·40 g., 83%), m. p. 48—50°, and di-*p*-methoxyphenyl ketone (0·08 g.), m. p. 135—140°.

Thermal Decomposition of Di-p-*methoxyphenylmethyl Ethyl Ether.*—The ethyl ether (1·27 g.) was heated in an oil-bath, carbon dioxide being passed through the flask and into wash-bottles as before. When the temperature reached 300° a precipitate began to form in the wash-bottles and after 7 hours' heating amounted to 0·10 g. (10%); it had m. p. 160—162° alone and when mixed with an authentic specimen of acetaldehyde 2 : 4-dinitrophenylhydrazone. The non-volatile material yielded di-*p*-methoxyphenyl ketone (0·63 g.; 56%), m. p. and mixed m. p. 138—140°, resin (0·1 g.) and di-*p*-methoxyphenylmethane (0·25 g., 25%), m. p and mixed m p. 45—48°.

Action of Trichloroacetic Acid on Xanthhydrol.—(a) 3·5% *Acid.* A solution of xanthhydrol (1·0 g.) and trichloroacetic acid (0·07 g.) in dry benzene (2 c.c.), in an atmosphere of nitrogen, was kept at 40° for 2 hours. After cooling, crystals of xanthone separated (0·3 g.), m. p. 160—165° (after recrystallisation, 168—170°). The benzene mother-liquor was diluted with ether and washed with sodium hydroxide: after partial evaporation xanthone (0·09 g.), m. p. 167—170°, and xanthen (0·39 g.), m. p. 95—97°, both identified by mixed m. p.s, were collected.

A similar experiment in dioxan yielded xanthone (0·39 g.), m. p. 167—170°, and xanthen (0·35 g.), m. p. 96—98°.

(b) 0·1% *Acid.* To a solution of xanthhydrol (1·0 g.) in dry benzene (10 c.c.), trichloroacetic acid (0·01 g.) was added; subsequent procedure was as described above. Xanthone (0·35 g.), m. p. 168—172°, and xanthen (0·35 g.), m. p. 93—96°, were obtained.

In peroxide-free dioxan the products were unchanged xanthhydrol (0·55 g.) and dixanthyl ether (0·1 g.), m. p. and mixed m. p. 205—210° (after one recrystallisation).

Action of Acids on p-*Methoxydiphenylmethanol.*—(*a*) A solution of the alcohol (2·0 g.) inacetone (6 c.c.) containing hydrochloric acid (0·23 c.c., 0·5 mol.) was heated for 5 hours under gentle reflux, the air having been displaced by nitrogen. After the acetone had evaporated the residue was dissolved in ether, washed, and dried, and the solvent evaporated. Trituration of the residue with ether–light petroleum left di-(*p*-methoxydiphenylmethyl) ether (1·5 g.) which, after crystallisation, had m. p. and mixed m. p. 120—121°. The filtrate yielded *p*-methoxydiphenylmethane (0·15 g.), b. p. 125—130°/0·4 mm., and *p*-methoxybenzophenone (0·1 g.), b. p. 140—160°/0·4 mm., which crystallised on cooling; its 2 : 4-dinitrophenylhydrazone had m. p. and mixed m. p. 205°.

(*b*) A solution of the alcohol (1·0 g.) and toluene-*p*-sulphonic acid (0·4 g.) in benzene (10 c.c.) was heated under reflux (under nitrogen) for 5 hours. The isolated products were di-(*p*-methoxydiphenylmethyl) ether (0·5 g.), m. p. 120—121°, *p*-methoxydiphenylmethane (0·1 g.), and *p*-

methoxybenzophenone (0·12 g.), m. p. and mixed m. p. 59—61°. The identity of *p*-methoxydiphenylmethane was confirmed by its demethylation followed by benzoylation; the m. p. of the resulting *p*-benzylphenyl benzoate was not depressed on admixture with an authentic specimen, m. p. 86—87°.

Action of Acids on Di-p-*dimethylaminophenylmethanol* (*Michler's Hydrol*).—(a) *Trichloroacetic acid.* A solution of the alcohol (1·0 g.) and trichloroacetic acid (0·6 g.; 1 mol.) in acetone (5 c.c.), in an atmosphere of nitrogen, was kept at 40° for 4 hours. After 30 minutes the colour of the solution changed from blue to claret-red and crystals began to separate. The crystals (0·3 g.) consisted of the di-ether of Michler's hydrol and, after crystallisation had m. p. 195—197° alone or admixed with an authentic specimen prepared as described by Möhlau and Heinze (*Ber.*, 1902, **35**, 361). The decanted acetone solution yielded a further 0·05 g. of the di-ether, together with Michler's ketone (0·33 g.) and some tar.

(b) *Hydrochloric acid.* A solution of the alcohol (2·7 g.) in 2N-hydrochloric acid (10 c.c.) after 5 hours at 100° yielded Michler's ketone (0·73 g.) and the di-ether of Michler's hydrol (0·35 g.).

pp'-*Di*-tert.-*butylbenzophenone.*—Prepared by a Friedel–Crafts reaction from *tert.*-butylbenzene and carbonyl chloride in carbon disulphide, in 64% yield, this had m. p. 134—135° (Found : C, 85·8; H, 8·9. Calc. for $C_{16}H_{18}O$: C, 85·7; H, 8·85%). Cristal, Hayes, and Haller (*J. Amer. Chem. Soc.*, 1946, **68**, 913) record m. p. 134·5—135°.

Di-p-tert.-*butylphenylmethanol.*—A mixture of the foregoing ketone (10 g.), potassium hydroxide (6 g.), zinc dust (5 g.), and ethanol (100 c.c.) was heated under vigorous reflux for 6 hours and worked up as usual. The resulting *di*-p-tert.-*butylphenylmethanol* (9·7 g.) had m. p. 98—100°; it separated from ether–light petroleum in fine, silky needles, m. p. 103—104° (Found : C, 85·2; H, 9·4. $C_{21}H_{28}O$ requires C, 85·1; H, 9·4%).

Action of acids. A mixture of the alcohol (1·0 g.) and trichloroacetic acid (0·27 g., 0·5 mol.) was heated at 100°, the clear solution becoming semi-solid after a few minutes. After 30 minutes the product was washed with water and crystallised from ethanol–acetone : it consisted of *bisdi*-p-tert.-*butylphenylmethyl ether*, fine needles, m. p. 218—219° (Found : C, 88·2; H, 9·35. $C_{42}H_{54}O$ requires C, 87·8; H, 9·4%).

A solution of the alcohol (1·0 g.) in acetone (2 c.c.) containing hydrochloric acid (0·17 c.c., 0·5 mol.) was heated under reflux for 8 hours. The bis-ether (0·8 g.), m. p 216—218°, was readily isolated, but of a substituted benzophenone there was no trace

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