645. *Fission of the Alkyl–Oxygen Bond in Carbinols and of the Alkyl–Sulphur Bond in Sulphides and Sulphones.*

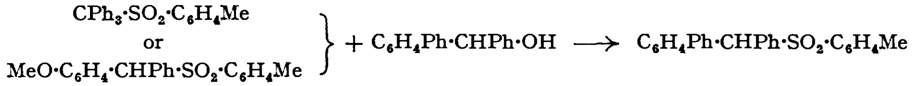
By M. P. Balfe, J. Kenyon, and C. E. Searle.

From *p*-methoxyphenylphenylcarbinol, 4-diphenylylcarbinol, and triphenylcarbinol, sulphones and sulphides are formed by reaction with toluene-*p*-sulphinic acid and *p*-thiocresol in acid solutions, and alkyl interchange occurs when some of these derivatives are warmed with the carbinols in acid solution. Coloured solutions in anhydrous acids are formed by a number of substituted diphenylcarbinols and other carbinols containing electron-releasing substituents; they are analogous to the coloured solutions of triphenylcarbinols in sulphuric acid. From some of these solutions, polymeric and sulphonated derivatives have been isolated.

p-METHOXYPHENYLPHENYLCARBINOL, 4-diphenylylphenylcarbinol, and triphenylcarbinol react with toluene-*p*-sulphinic acid in formic acid solution, or in acetic acid in the presence of a little sulphuric acid, to yield the corresponding sulphones (cf. the preparation of sulphones from

$$\text{CRR'R''}{\cdot}\text{OH} + \text{C}_6\text{H}_4\text{Me}{\cdot}\text{SO}_2\text{H} \longrightarrow \text{CRR'R''}{\cdot}\text{SO}_2{\cdot}\text{C}_6\text{H}_4\text{Me} + \text{H}_2\text{O}$$

di- and tri-phenylcarbinol in acetic–hydrochloric acid solutions; Hinsberg, *Ber.*, 1917, **50**, 468). Triphenylmethanethiol and *p*-tolyl triphenylmethyl sulphide have been obtained by similar reactions of triphenylcarbinol with hydrogen sulphide and with *p*-thiocresol. The reaction of toluene-*p*-sulphinic acid with a mixture of one molecular proportion each of *p*-methoxyphenylphenylcarbinol and triphenylcarbinol yields *p*-methoxyphenylphenylmethyl *p*-tolyl sulphone as the main product. These reactions indicate scission of the alkyl–oxygen bond in the carbinols. Scission of alkyl–sulphur bonds is shown by the formation of triphenylmethane when *p*-tolyl triphenylmethyl sulphide or sulphone is heated in formic acid solution (cf. the reduction of triphenylcarbinol to the hydrocarbon in formic acid solution; Kauffmann and Pannwitz, *Ber.*, 1912, **45**, 766) and by the formation of 4-diphenylylphenylmethyl *p*-tolyl sulphone or sulphide on reaction of 4-diphenylylphenylcarbinol in acid solutions with *p*-tolyl triphenylmethyl sulphone or *p*-methoxyphenylphenylmethyl *p*-tolyl sulphone or with *p*-tolyl triphenylmethyl sulphide.



$$\left.\begin{array}{c}\mathrm{CPh_3{\cdot}SO_2{\cdot}C_6H_4Me}\\ \text{or}\\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CHPh{\cdot}SO_2{\cdot}C_6H_4Me}\end{array}\right\} + \mathrm{C_6H_4Ph{\cdot}CHPh{\cdot}OH} \longrightarrow \mathrm{C_6H_4Ph{\cdot}CHPh{\cdot}SO_2{\cdot}C_6H_4Me}$$

It has long been known that triphenylcarbinol forms coloured solutions in concentrated sulphuric acid, or in formic acid, and this is ascribed to formation of the carbonium cations. Tri-*p*-methoxyphenylcarbinol reacts similarly in dilute sulphuric acid (Baeyer and Villiger, *Ber.*, 1902, **35**, 1194), and coloured solid products can be isolated from solutions of this carbinol in acids. It has now been found that diphenylcarbinol and a number of substituted derivatives yield coloured solutions in concentrated sulphuric acid, and some of the substituted compounds do so in formic acid and in trichloroacetic acid. The colours are discharged on dilution of the solutions with water. In the preparation of 4-diphenylylphenylcarbinol, a by-product is formed which gives a colour on dissolution in formic acid. As Ziegler and Boye (*Annalen*, 1927, **458**, 229) have pointed out, the estimation of the " basicity " of carbinols (*i.e.*, their tendency to ionise to the carbonium cation) by determination of the extent to which the coloured solutions must be diluted with aqueous alcohol, before the colour is discharged, can only be applied to materials which are known to be free from colour-forming impurities.

When kept, the solutions of some carbinols in concentrated acids deposit solids, apparently of a polymeric nature. The solids deposited from solutions of *p*-methoxyphenylphenylcarbinol in concentrated sulphuric acid are soluble in water and contain up to 11·1% of sulphur. By treatment with phosphorus pentachloride followed by aqueous ammonia, the solid of highest sulphur content is converted into a solid which contains 4·4% of sulphur and 2·2% of nitrogen, *i.e.*, in proportions approximately corresponding to the sulphonamido-group, which suggests that in the original material about one-third of the sulphur is present in sulphonic groups; of the rest, part may be present as carbonium sulphate. A colourless polymeric substance also resulted from the action of formic acid on *p*-methoxyphenylphenylcarbinol.

EXPERIMENTAL.

4-Diphenylylphenylcarbinol.—*p*-Phenylbenzophenone (Friedel–Crafts reaction from diphenyl) was reduced with zinc in alcoholic sodium hydroxide to the carbinol, m. p. 94° after recrystallisation. Repeated recrystallisation from light petroleum did not remove impurities which gave a purple colour in formic acid solution. The redistilled material, b. p. 258—260°/17 mm., m. p. 94—95°, was free from these impurities. When heated at 210° for 3 hours the carbinol undergoes some decomposition but no ether is formed.

Derivatives. The ***hydrogen phthalate***, prepared by the usual method, had m. p. 166—167° after recrystallisation from aqueous methyl alcohol (Found: C, 79·1; H, 4·9. $C_{27}H_{20}O_4$ requires C, 79·4; H, 4·9%). Its sodium, potassium, and ammonium salts are sparingly soluble in water. The ***hydrogen succinate***, prepared in the usual way, had m. p. 91—92° after recrystallisation from ether–light petroleum (Found : equiv., 354. $C_{23}H_{20}O_4$ requires equiv., 360). Both acid esters are sparingly soluble in organic solvents, and do not yield crystalline salts with the common alkaloids.

The carbinol (1·3 g.) was warmed for 1 hour in formic acid (25 c.c.) containing sodium formate (1 g.). The ***formate*** (1·3 g.) was precipitated on dilution with water and after recrystallisation from light petroleum, and then from alcohol, had m. p. 65—66° (Found : C,82·9; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

Einhorn's method yielded the ***benzoate*** (2·4 g. from 2·6 g. of carbinol), m. p. 108° after recrystallisation from ethyl alcohol (Found, after heating at 100°/14 mm. for 2 hours : C, 85·9; H, 5·5. $C_{26}H_{20}O_2$ requires C, 85·7; H, 5·5%).

The ***methyl ether*** (2·4 g.) was formed when the carbinol (2·6 g.) was heated under reflux for 1 hour in methyl alcohol (25 c.c.) containing sulphuric acid (0·1 c.c.) and had m. p. 78° after two recrystallisations from light petroleum (Found : C, 87·8; H, 6·6. $C_{20}H_{18}O$ requires C, 87·8; H, 6·6%).

The *chloride* was prepared from the carbinol by (i) thionyl chloride–pyridine, (ii) warm concentrated hydrochloric acid, (iii) acetyl chloride, the mixture being left over solid potassium hydroxide until it solidified, and (iv) passage of dry hydrogen chloride through a solution in benzene, in presence of anhydrous calcium chloride. The chloride was extracted from these various preparations by, and recrystallised from, light petroleum; it had b. p. 252—256°/18 mm., m. p. (after fusion and resolidification) 72—73° (Found : Cl, 12·6. $C_{19}H_{15}Cl$ requires Cl, 12·8%). When the material is kept the m. p. falls to that of the freshly recrystallised material, 60—70°, which is not raised by heating the salt below the m. p. or by keeping it *in vacuo*. The methyl ether (m. p. and mixed m. p. 77—78°) crystallises on cooling a warmed solution of the chloride in methyl alcohol.

4-Diphenylylphenylmethyl p-*Tolyl Sulphone*.—Sodium toluene-*p*-sulphinate (1·0 g.) was added to a solution of the carbinol (1·3 g.) in formic acid (10 c.c.), and the mixture boiled for 1 minute and then poured into water. The precipitated *sulphone* (2·1 g.), recrystallised from methyl acetate, had m. p. 197—198° (Found : S, 7·8. $C_{26}H_{22}O_2S$ requires S, 8·0%).

4-Diphenylylphenylmethyl p-*Tolyl Sulphide*.—The carbinol (1·3 g.) was added slowly to a solution of *p*-thiocresol (0·7 g.) in warm formic acid (10 c.c.). The mixture was diluted with water and the precipitate (2·0 g.) filtered off. After two recrystallisations from aqueous acetone it yielded the *sulphide*, m. p. 130—131° (Found : S, 8·7. $C_{26}H_{22}S$ requires S, 8·7%). On oxidation with potassium permanganate in acetic acid solution it yielded the sulphone, m. p. and mixed m. p., 196—197°.

p-*Methoxyphenylphenylmethyl* p-*Tolyl Sulphone*.—Prepared from the carbinol (2·0 g.) and sodium toluene-*p*-sulphinate (2·0 g.) in formic acid (20 c.c.), the sulphone separated on dilution with water; it had m. p. (after recrystallisation from methyl acetate) 161—162° (cf. Part II, *J.*, 1942, 605, and Part V, *J.*, 1946, 810; the m. p. 87—88° recorded on p. 811 of Part V is incorrect). In a similar experiment in which sodium toluene-*p*-sulphinate (1 mol.) was added to a mixture of *p*-methoxyphenylphenylcarbinol (1 mol.) and triphenylcarbinol (1 mol.), this sulphone was the main product.

p-*Tolyl Triphenylmethyl Sulphone*.—The carbinol (1·3 g.) was warmed in 30 c.c. of acetic acid containing 5 drops of sulphuric acid, sodium toluene-*p*-sulphinate (0·8 g.) was added, and after 5 minutes, on addition of 5 c.c. of water, the sulphone was precipitated and was recrystallised from benzene–light petroleum; it had m. p. 172—173° (Found : S, 7·6. Calc. for $C_{26}H_{22}O_2S$; S, 8·0%). Meyer and Fischer (*J. pr. Chem.*, 1910, [ii], **82**, 521) give m. p. 173°; as they observe, the sulphone decomposes in the presence of water.

p-*Tolyl Triphenylmethyl Sulphide*.—The carbinol ((5·2 g.) and *p*-thiocresol (2·6 g.), warmed together in anhydrous formic acid for 30 minutes, gave the sulphide, m. p. and mixed m. p. 149° (cf. Part V, *J.*, 1946, 807).

Triphenylmethanethiol.—Hydrogen sulphide was passed through a solution of the carbinol (2·6 g.) in acetic acid (20 c.c.) and sulphuric acid (2 drops) until the yellow colour was no longer restored on warming. Addition of water (3 c.c.) precipitated the thiol (2·1 g.) which, recrystallised from alcohol, had m. p. 106—107° and yielded a benzoate, m. p. 186—187°. Vorländer and Mittag (*Ber.*, 1913, **46**, 3450) record m. p. 107° and 185° for the thiol and benzoate respectively. 4-Diphenylyl- and *p*-methoxyphenylphenylcarbinol also react with hydrogen sulphide, but the products could not be purified.

Reactions of p-*Tolyl Triphenylmethyl Sulphide and Sulphone*.—(i) *With acid*. The sulphide (0·5 g.) in formic acid (25 c.c.) was heated under reflux for 15 hours, then diluted with water, and extracted with ether, which was washed with aqueous sodium hydroxide. From the ethereal solution, triphenylmethane (0·25 g.; m. p. and mixed m. p. 92—93°) was isolated. From the sodium hydroxide extract *p*-thiocresol was obtained, yielding (Schotten–Baumann) the benzoate, m. p. and mixed m. p. 75°. Triphenylmethane was obtained in a similar experiment with *p*-tolyl triphenylmethyl sulphone.

(ii) *With 4-diphenylylphenylcarbinol*. A solution of the carbinol (1·0 g.) and the sulphide (1·5 g.) in acetic acid (25 c.c.) and sulphuric acid (0·5 c.c.) was warmed on the steam-bath, then diluted with a little water, which discharged the purple colour. 4-Diphenylylphenylmethyl *p*-tolyl sulphide (1·0 g.) separated ; after recrystallisation it had m. p. and mixed m. p. 130—131°. In a similar experiment, using *p*-tolyl triphenylmethyl sulphone, 4-diphenylylphenylmethyl *p*-tolyl sulphone, m. p. and mixed m. p. 196—197°, was obtained.

Reaction of p-*Methoxyphenylphenylmethyl* p-*Tolyl Sulphone with 4-Diphenylylphenylcarbinol*.—The carbinol (0·5 g.) was added to a mixture of the sulphone (0·7 g.), acetic acid (20 c.c.), and sulphuric acid (4 c.c.). After 10 minutes on the steam-bath, the mixture was diluted with water to 50 c.c. 4-Diphenylylphenylmethyl *p*-tolyl sulphone was precipitated; it had m. p., after recrystallisation, and mixed m. p., 195—197°.

Dissolution of the Carbinols in Acids.—Yellow or orange solutions were formed in concentrated sulphuric acid by diphenylcarbinol (I), *p*-methoxyphenylphenylcarbinol (II), 2 : 4- (III) and 3 : 4-dimethoxyphenylphenylcarbinol (IV), *o*-methoxyphenyl-*p*-methoxyphenylcarbinol (V), di-*p*-methoxyphenylcarbinol (VI), xanthhydrol (VII), and triphenylcarbinol (VIII). Purple or violet solutions were formed by 4-diphenylylphenylcarbinol (IX), *p*-phenoxyphenylphenylcarbinol (X), *p*-methoxyphenyl-4-diphenylylcarbinol (XI), *p*-methylthiophenylphenylcarbinol (XII), α-naphthylphenylcarbinol (XIII), and 2-methoxy-1-naphthylphenylcarbinol (XIV). In 98% formic acid, similarly coloured solutions were obtained from (II), (VI), (VII), (VIII), and (XI); colourless solutions were given by (I), (IV), (IX), (X), (XII), (XIII), and (XIV); (X) gave a coloured solution in trichloroacetic acid. All the solutions were decolorised on dilution with water, and after long storage, or on heating, the solutions in sulphuric acid gave water-soluble products.

The reactions with *p*-methoxyphenylphenylcarbinol were examined. A solution of the carbinol (3·0 g.) in concentrated sulphuric acid, after 2 weeks at room temperature, was diluted slowly to 150 c.c. with water, with cooling. The yellow colour was discharged after addition of part of the water, and a dark red solid was finally precipitated. It was dried over quicklime. It softened slowly when heated above 150°, and contained 11·1% of sulphur. When this material was triturated with phosphorus pentachloride and the mixture warmed, it was converted into a brilliant red solid, which was converted by concentrated aqueous ammonia into a brown solid, softening at about 180° [Found: S, 4·4; N, 2·2%; *M* (Rast), 2300]. *p*-Methoxyphenylphenylcarbinol (1·0 g.) dissolved in 98% formic acid (15 c.c.) to give a yellow solution, from which a solid began to separate after 10 minutes. After 2 days the solution was diluted with water and the solid (0·9 g.) separated, crushed, dried, and recrystallised twice from ethyl alcohol, in which it was sparingly soluble; its m. p. (indefinite) was >110°, and its mol. wt. (Rast) 840. Bisdi-(*p*-methoxyphenyl)methyl ether reacted similarly, yielding a solid, m. p. (indefinite) >110° [Found: *M* (Rast), 785].

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BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, August 4th*, 1950.]