LXI.—*Substituted Diaryl Ethers. Part III. A New Synthesis of Substituted Xanthhydrols.*

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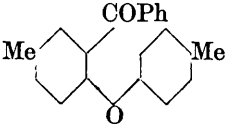
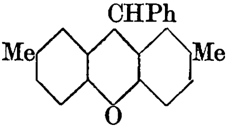
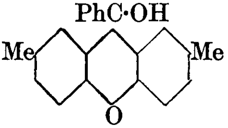
IN a recent communication (J., 1927, 2814) the authors showed that di-*p*-tolyl ether yields only monosubstituted derivatives in the Friedel–Crafts reaction. The product of interaction of benzoyl chloride and di-*p*-tolyl ether was assigned the constitution of an ortho-substituted diaryl ether (I) because it was converted into 9-phenyl-2 : 7-dimethylxanthen (II) and also because its solutions in acetic and sulphuric acids were yellow, indicating xanthhydrol formation through ring closure. The non-formation of a phenylhydrazone was attributed to steric hindrance by the tolyloxy-radical in the ortho-position to the carbonyl group. The supposed ketone (I) has now been found to be the isomeric 9-phenyl-2 : 7-dimethylxanthhydrol (III), which has also been obtained by the action of magnesium phenyl bromide on 2 : 7-dimethylxanthone.



(I.)



(II.)



(III.)

This interaction constitutes a simple method of producing substituted xanthhydrols in good yield from readily accessible materials. Ordinarily, xanthhydrols are prepared from the corresponding xanthones by the Grignard reaction (compare Ullmann and Engi, *Ber.*, 1904, **37**, 2370). This method is unsuitable in the case of the above xanthhydrol, since the preparation of 2 : 7-dimethylxanthone from *p*-cresotic acid is not satisfactory.

9-Phenyl-2 : 7-dimethylxanthhydrol, when boiled with acetic acid, gave 9-phenyl-2 : 7-dimethylxanthen (*loc. cit.*), which was also prepared by Feuerstein and Lipp (*Ber.*, 1902, **35**, 3255) by distillation of 6 : 6′-dihydroxy-3 : 3′-dimethyltriphenylmethane. In Part II (J., 1927, 2815) it was suggested that Feuerstein and Lipp's compound might be a fluorene on the ground that acetic acid is not usually a reducing agent. The xanthen constitution is more in line with the experimental facts, reduction of the xanthhydrol having been brought about by the presence of reducing agents in the acetic acid used : reduction does not take place with specially purified acid. The constitution assigned by Feuerstein and Lipp was confirmed by the re-conversion of their 9-phenyl-2 : 7-dimethylxanthen into the corresponding xanthhydrol by oxidation with lead peroxide.

It has been shown by Schmidlin and Garciá Banús (*Ber.*, 1912, **45**, 3188) that triphenylcarbinol is readily reduced to triphenylmethane by heating with alcoholic sulphuric acid, and Kauffmann and Pannwitz (*ibid.*, p. 766) have shown that a similar reduction takes place by boiling with alcoholic hydrogen chloride. The present authors have obtained similar results with these reagents in the case of 9-phenyl-2 : 7-dimethylxanthhydrol and comparative experiments have shown that the latter is reduced much more readily than triphenylcarbinol. Formic acid also is an effective but less vigorous reducing agent.

By the action of hydrogen chloride on 9-phenylxanthhydrol in chloroform solution, Bünzly and Decker (*Ber.*, 1904, **37**, 2935) obtained a coloured chloride. With hydrogen chloride, 9-phenyl-2 : 7-dimethylxanthhydrol forms a coloured *chloride hydrochloride* which readily loses a molecule of hydrogen chloride, giving the colourless chloride (compare Gomberg and Cone, *Annalen*, 1909, **370**, 142). Work on the application of the above synthesis to the preparation of substituted thioxanthhydrols is in progress.

EXPERIMENTAL.

9-*Phenyl*-2 : 7-*dimethylxanthhydrol*.—Finely powdered 2 : 7-dimethylxanthone (6 g.) was gradually added to a cooled solution prepared from bromobenzene (10 g.), magnesium (1 g.), and anhydrous ether (50 c.c.). A vigorous reaction ensued and a yellow magnesium double compound separated. After addition of benzene (10 c.c.) the mixture was heated on a water-bath for 1 hour. The solvent was removed, and the residue decomposed by careful addition of ice-cold water. Just sufficient dilute sulphuric acid was then added to dissolve basic magnesium salts. On addition of alcohol to the mixture the precipitated oil quickly solidified (yield, 6·2 g.). The product was crystallised from ethyl alcohol–ethyl acetate, 9-phenyl-2 : 7-dimethylxanthhydrol being obtained in colourless rhombohedra which, alone or when mixed with the product of interaction of benzoyl chloride and di-*p*-tolyl ether, melted at 185—186°.

4′-*Diethylamino*-9 : 9-*diphenyl*-2 : 7-*dimethylxanthen*.—Diethylaniline (1 g.) and 9-phenyl-2 : 7-dimethylxanthhydrol (1 g.) were heated under reflux in acetic acid solution for 30 minutes. The product, which separated on cooling, was obtained from alcohol–ethyl acetate in colourless needles, m. p. 183—184° (Found by the micro-method : C, 85·5; H, 7·0. $C_{31}H_{31}ON$ requires C, 85·9; H, 7·1%). 4′-*Diethylamino*-9 : 9-*diphenyl*-2 : 7-*dimethylxanthen* is readily soluble in chloroform and ethyl acetate and slightly soluble in ethyl alcohol.

9-*Phenyl*-2 : 7-*dimethylxanthhydrol chloride hydrochloride* was obtained on saturating a solution of 9-phenyl-2 : 7-dimethylxanthhydrol in anhydrous ether (containing a few drops of acetyl chloride) with dry hydrogen chloride. It separated slowly in well-defined, reddish-orange prisms, m. p. 147—149° (Found : Cl, 20·3. $C_{21}H_{17}OCl,HCl$ requires Cl, 19·9%). The chloride hydrochloride is readily soluble in chloroform and acetic acid and insoluble in benzene and ether. It is very susceptible to traces of moisture, being decomposed immediately by water. Heated in a vacuum over quicklime at 130°, it loses a molecule of hydrogen chloride, giving the colourless chloride (Found : HCl, 10·8. Calc. for $C_{21}H_{17}OCl$: HCl, 10·2%). The latter is very unstable, turning red on exposure to air. Its double salt with ferric chloride is identical in all respects with the *ferrichloride* prepared from 9-phenyl-2 : 7-dimethylxanthhydrol by addition of anhydrous ferric chloride to a solution of the xanthhydrol in glacial acetic acid previously saturated with hydrogen chloride, which crystallised from glacial acetic acid, containing hydrogen chloride, in reddish-orange rectangular plates, m. p. 181° (Found : Cl, 30·0. $C_{21}H_{17}OCl,FeCl_3$ requires Cl, 29·4%). It is stable in the air (not showing any signs of decomposition after 2 days), but is slowly decomposed by cold, and more readily by hot water. It dissolves readily in chloroform, nitrobenzene and acetone, but is sparingly soluble in cold acetic acid and insoluble in benzene and ether. The mercuric chloride and gold chloride double salts were prepared in a similar manner, the former consisting of reddish prisms soluble in chloroform and the latter of golden-yellow needles.

Addition of a solution of bromine in acetic acid to a solution of the xanthhydrol in the same solvent saturated with dry hydrogen bromide gave a precipitate of the *tribromide*, which formed short reddish-orange prisms, m. p. 145—146° (decomp.) (Found : Br, 46·1. $C_{21}H_{17}OBr_3$ requires Br, 45·7%). The tribromide is readily soluble in chloroform, nitrobenzene and acetone, but is sparingly soluble in benzene and ether. Water slowly decomposes it with regeneration of the carbinol base.

9-*Phenyl*-2 : 7-*dimethylxanthen*.—Zinc dust was gradually added to a boiling solution of 9-phenyl-2 : 7-dimethylxanthhydrol (1 g.) in 80% acetic acid (50 c.c.). At first a reddish-orange solution was obtained, the colour of which was completely discharged after 10 minutes' boiling. The solid which separated from the hot filtrate was obtained from glacial acetic acid in colourless needles, which melted, alone or when mixed with the 9-phenyl-2 : 7-dimethylxanthen of Feuerstein and Lipp (*loc. cit.*), at 195—196°. Contrary to the statement of these authors, sulphuric acid in contact with the above xanthen does not develop a yellow colour. On heating, however, a yellow solution with a green fluorescence is obtained, owing probably to partial oxidation of the xanthen to the xanthhydrol by the acid.

Oxidation of 9-*Phenyl*-2 : 7-*dimethylxanthen*.—To a hot solution of the xanthen (3 g.) in 80% acetic acid (100 c.c.) was added, during 1 hour, with stirring, freshly prepared lead peroxide (1 mol.) made into a paste with acetic acid. The solution, at first colourless, gradually assumed a deep orange colour. The solid obtained on dilution of the filtrate with water was collected, washed with hot water, dried, and redissolved in glacial acetic acid. The ferrichloride was identical with that from 9-phenyl-2 : 7-dimethylxanthhydrol.

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