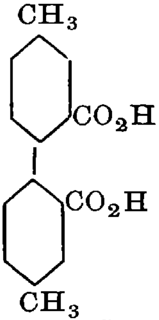
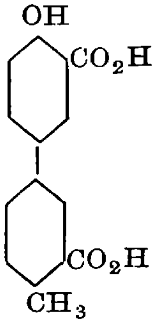
Studies in Diphenyl Series. Part IV. Action of Oxalyl Chloride on Diphenyl Derivatives.

BY NRIPENDRANATH CHATTERJEE.

The action of oxalyl chloride on *pp*′-substituted diphenyl has been studied by Libermann and his co-workers (*Ber.*, 1911, **44**, 1453). They observed that *pp*′-ditolyl gave with oxalyl chloride 4 : 4′-dimethyl-2 : 7-phenanthrenequinone and 4 : 4′-dimethyldiphenic acid (I). However, they observed the formation of only monocarboxylic acid in the case of *pp*′-dianisyl.



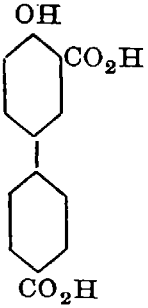
(I)



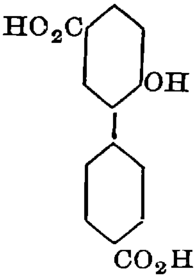
(II)

It has now been found that 4-methoxy-4′-methyldiphenyl (obtained by allowing a *p*-diazonium salt of toluene to react with phenol and afterwards methylating the hydroxydiphenyl obtained with dimethyl sulphate) condenses with oxalyl chloride in presence of aluminium chloride to give 4-methyl-4′-hydroxy-3 : 3′-dicarboxydiphenyl (II) as it gives the ferric chloride reaction for *o*-hydroxy acids and on oxidation 4-methyl-*iso*phthalic acid is obtained.

4-Methoxy and 2-methoxydiphenyl (*Ber.*, 1890, **23**, 2705) gave with oxalyl chloride 4-hydroxy-4′ : 3-dicarboxydiphenyl (III) and 2-hydroxy-4′ : 5-carboxydiphenyl (IV) respectively



(III)



(IV)

The constitution of these products has been proved by the ferric chloride reaction (III positive, IV negative) and by oxidation with alkaline permanganate, both giving terephthalic acid. The diphenyl acids were purified through their acetyl derivatives.

EXPERIMENTAL

4-*Methoxy-4′-methyldiphenyl*.—4-Hydroxy-4′-methyldiphenyl was treated with 15% NaOH solution when the sodium salt was precipitated. After adding an excess of dimethyl sulphate, it was heated on a water-bath for half an hour with frequent shaking. The product was extracted with ether and finally crystallised from ether, m. p. 112°. (Found: C, 84·7; H, 7·0. $C_{14}H_{14}O$ requires C, 84·8; H, 7·0 per cent).

4-*Hydroxy-3:3′-dicarboxy-4′-methyldiphenyl*.—A solution of 4-methoxy-4′-methyldiphenyl (5 g.) in carbon disulphide (50 c.c.) was treated with oxalyl chloride (13 g.) at 0° under stirring and then gradually with anhydrous aluminium chloride (5 g.). After 1½ hours it was further treated with carbon disulphide (25 c.c.) and aluminium chloride (4 g.) and the stirring was continued for 6 hours and the dark green product was treated with sodium carbonate solution and distilled in steam. The residue was filtered off and the filtrate acidified. The precipitate was boiled with calcium carbonate and the resulting solution filtered and acidified. The crude acid precipitated was converted into the corresponding acetyl derivative by boiling with acetic anhydride in presence of a drop of pyridine, m. p. 204°. (Found: C, 64·5; H, 4·1; M. W., 313. $C_{17}H_{14}O_6$ requires C, 64·9; H. 4·4 per cent. M. W., 314). By deacetylation 4-hydroxy-3:3′-dicarboxy-4-methyldiphenyl was obtained, m. p. 280°. (Found: C, 65·9; H, 4·2. $C_{15}H_{12}O_5$ requires C, 66·1; H, 4·4 per cent).

Oxidation of 4-Hydroxy 3:3′-dicarboxy-4′-methyldiphenyl.—A solution of the substance (1 g.) in caustic potash (100 c. c., 1%) was treated gradually below 15° with $KMnO_4$ (500 c. c., 1%) until the colour persisted. MnO_2 was dissolved by treating with SO_2 and 4-methyl*iso*phthalic acid (m. p. 320°) was precipitated by adding the calculated quantity of HCl (*d* 1·19). (Found: C, 59·8; H, 4·4. Calc. for $C_9H_8O_4$: requires C,60·0; H, 4·4 per cent).

By a similar process described above, the following two compounds were also prepared :

4-*Hydroxy-3:4′-dicarboxydiphenyl*, m. p. 304°. (Found: C, 65·3; H, 3·6. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·8 per cent).

The *acetyl* derivative melts at 280°. (Found: C, 63·7; H, 3·8; M. W., 300. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0 per cent. M. W., 298). 4-Hydroxy-3:4′-dicarboxydiphenyl was oxidised as before and terephthalic acid identified as its methyl ester.

2-Hydroxy-5:4′-dicarboxydiphenyl melts above 300°. (Found: C, 64·8; H, 3·5. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·8 per cent).

The *acetyl* derivative melts above 300°. (Found: C, 63·6; H, 3·6; M. W. 299. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0 per cent. M. W., 300).

2-Hydroxy-5:4′-dicarboxydiphenyl was oxidised as before and terephthalic acid identified as its methyl ester.

In conclusion the author desires to express his grateful thanks to Prof. P. C. Mitter for much encouragement and advice during the course of this work.

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Extension of Michael's Reaction. Part V.

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In Part IV (*J. Indian Chem. Soc.*, 1934, **11**, 355) it has been shown that αα′-phenylcarbamylacetone dicarboxylate which contains two active hydrogen atoms in 1:3-position reacts readily with benzaldehyde to yield a compound which, in all probability, possesses a tricyclic structure. A very notable feature of this compound is its remarkable stability towards acid and alkali inspite of its complex molecular structure. In this connection mention should be made of an analogous observation of Knoevenagel (*Annalen*, 1895, **288**, 347) which shows that benzylidenebisacetone dicarboxylic ester, obtained by condensing acetone dicarboxylic ester with benzaldehyde, reacts with another molecule of the aldehyde to yield the following ring-compound