Reactions of Salicylaldehyde: a Novel Oxidative Cyclisation giving Xanthones in Low Yields

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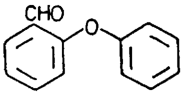
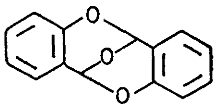
Summary Xanthones are side products of the reaction between salicylaldehyde–copper complexes and aryl halides; they are formed directly from *o*-phenoxybenzaldehydes with copper(II) halides.

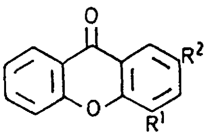
SALICYLALDEHYDE–COPPER[1] complexes react with aromatic or aliphatic halides to form ethers. We now report the co-formation of xanthones in their reaction with aromatic halides as well as the direct transformation with copper(II) halides of *o*-phenoxybenzaldehydes into xanthones.



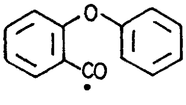
(I)



(II)



(III) R^1 = R^2 = H
(IV) R^1 = H, R^2 = Me
(V) R^1 = H, R^2 = OMe
(VI) R^1 = H, R^2 = NO$_2$
(VII) R^1 = OMe, R^2 = H



(VIII)

Reaction[2] of the copper(II)–salicylaldehyde complex and iodobenzene gave the expected aldehyde (I) (46%) and disalicylaldehyde(II) (9%), together with a mixture of phenols and a solid, m.p. 173—176, which was shown to be identical to the xanthone (III) (8%). The same distribution of products was obtained from the reactions between substituted bromobenzenes and the copper(II)–salicylaldehyde complex. *p*-Bromotoluene gave 2-methylxanthone (IV), m.p. 119—122° (1%), *p*-bromoanisole gave (V), m.p. 129—131° (2%), *p*-bromonitrobenzene gave (VI), m.p. 204—205° (4%), and *o*-bromoanisole gave (VII), m.p. 174—175° (*ca.* 0·1%). No xanthone was isolated from the reaction with *o*-bromotoluene though traces were detected by t.l.c.

Xanthones are formed by heating a phenol and an aromatic carboxylic acid in Ac$_2$O or by a Friedel–Crafts reaction with *o*-phenoxy-aromatic carboxylic acids. Xanthones could have been formed in the reaction between copper(II)–salicylaldehyde complex and aromatic halides through radical oxidation of the phenoxybenzaldehydes. *o*-Phenoxybenzaldehyde was therefore heated in nitrobenzene with copper(II) bromide or chloride; xanthone (50%) was formed (no attempt at optimisation).

The formation of xanthones from aldehydes with copper(II) halides probably involves a radical attack on the formyl group by the halide to give the free radical (VIII) which cyclises with loss of hydrogen to yield the xanthone; the overall reaction involves 2 mol of copper(II) halide per mol of aldehyde as well as the formation of 2 mol each of copper(I) halide and hydrogen halide. Acyl free-radical intermediates analogous to (VIII) have been proposed[3] in cyclisations of this type, which may be regarded as free radical versions[4] of the Friedel–Crafts reaction.

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