Tetrahedron Letters No. 42, pp. 3737-3739, 1965. Pergamon Press Ltd.
Printed in Great Britain.

OXIDATION OF ALKOXYPHENOLS. VII. CYCLICAL TRANSKETALISATION IN THE OXIDATION OF A MIXTURE OF PHENOLS.

F.R. Hewgill and D.G. Hewitt
Department of Organic Chemistry, University of Western Australia,
Nedlands, Western Australia.

(Received 21 August 1965)

We have already shown (1) that the spiro-ketal I can be formed by alkaline ferricyanide or silver oxide oxidation of a mixture of 4-methoxy-2-t-butylphenol and 2,2'-dihydroxy-5,5'-dimethoxy-4,4'-di-t-butylbiphenyl II. From the silver oxide oxidation of a mixture of 4-methoxy-2- and -3-t-butylphenol, which also gave the spiro-ketal I, a small quantity of the hydroxydiphenyl ether* III was isolated, and we now report that this can also be intermediate in the formation of the spiro-ketal I.

---

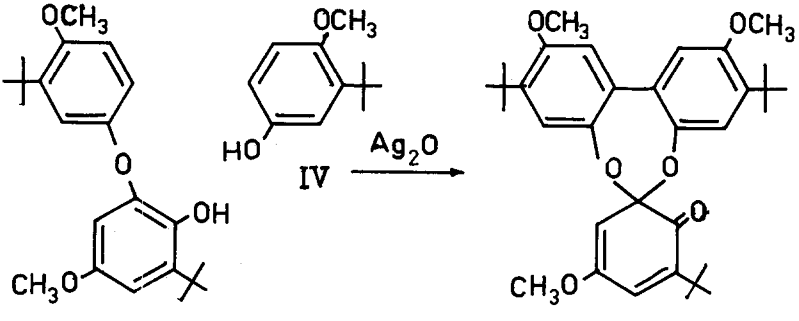
* Larger quantities of the ether III were more conveniently prepared by the method of Bacon and Hill (2), namely by condensation of 2-bromo-4-methoxy-6-t-butylphenol and 4-methoxy-3-t-butylphenol in the presence of cuprous oxide. A modification of this method was previously used to prepare the methyl ether of III.

---

(1) Part V, J. Chem. Soc., 3660 (1965).

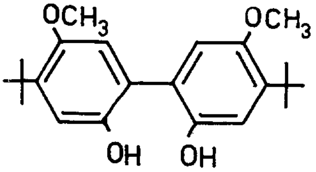
(2) R.G.R. Bacon and H.A.O. Hill, J. Chem. Soc., 1108 (1964).

It will be seen that the hydroxydiphenyl ether III can be considered as two thirds of the spiro-ketal I. We therefore oxidised a mixture of this ether III and the remaining third, namely 4-methoxy-3-t-butylphenol IV in equimolar proportions with silver oxide, thus obtaining the spiro-ketal I, m.p. and mixed m.p. 213-215°, with infrared spectrum identical with that of an authentic sample, in more than 90% yield.

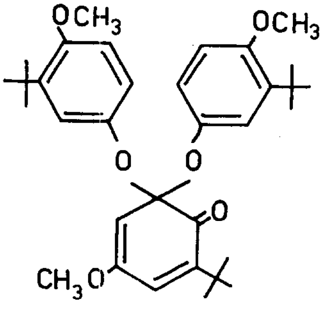


III

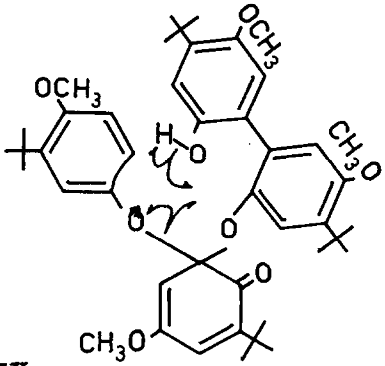
I



II



V



VI

As it seems unlikely that carbon-carbon coupling takes place between III and IV, or between carbon atoms in a possible intermediate V, we conclude that the initial step must be oxidation of the phenol IV to the dimer II; a reaction that is known to occur (3). We suggest that the next step in the reaction is carbon-oxygen coupling between the dimer II and the ether III to give VI. Such compounds are known to dissociate easily to a mixture of two aryloxy radicals (4). The final cyclisation can thus be pictured as oxidation of VI to the corresponding aryloxy radical, and carbon-oxygen coupling to form the spiro-ketal I with simultaneous extrusion of a 4-methoxy-3-t-butylphenoxy radical. The latter can then dimerize to II, which will be incorporated in a further spiro-ketal molecule.

The correctness of this mechanism was shown by either ferricyanide or silver oxide oxidation of a mixture of the ether III and the dimer II in the proportions 2:1, which again gave the spiro-ketal I in $>$90% yield. No spiro-ketal was obtained from the oxidation of ether III alone with either oxidant, nor was any of the symmetrical spiro-ketal, resulting from trimerization of IV, detected in any of these oxidations.

It may be argued that some of compound V should be formed in the first oxidation, but the reversibility of such a process makes this of little consequence.

We are grateful for the award of a C.S.I.R.O. Senior Postgraduate Studentship to D.G.A.

---

(3) Part I, J. Chem. Soc., 4987 (1962).

(4) E. Muller, K. Ley and G. Schlechte, Chem. Ber., **90**, 2660, (1957).