Tetrahedron Letters No.58, pp. 5085-5087, 1969. Pergamon Press. Printed in Great Britain.

PHOTOLYSIS OF 4-BROMO-2,6-DI-TERT-BUTYLPHENOL IN BENZENE SOLUTION

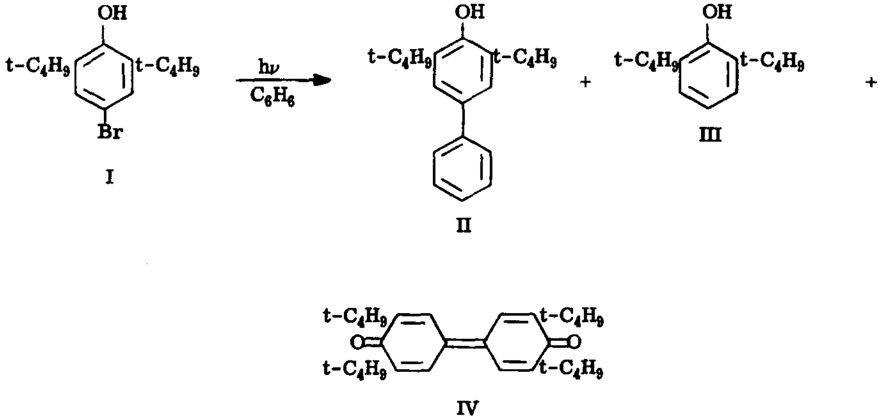
G. R. Lappin and J. S. Zannucci

Research Laboratories, Tennessee Eastman Company,

Division of Eastman Kodak Company, Kingsport, Tennessee 37662

(Received in USA 6 November 1969; received in UK for publication 15 November 1969)

The photolysis of iodoaromatic or bromoaromatic compounds in dilute benzene solution gives fair to good yields of biaryls (1, 2). The aromatic halogen compound is also reductively dehalogenated (ArX → ArH). Hence, photolysis of a 1% solution of 4-bromo-2, 6-di-tert-butylphenol (I) in benzene was expected to produce 2, 6-di-tert-butyl-4-phenylphenol (II) as the major product, along with some 2,6-di-tert-butylphenol (III). However, II and III were produced in only 7.9 and 24.2% yields, respectively. The major product of the reaction (43.2%) was 3, 3', 5, 5'-tetra-tert-butyldiphenoquinone (IV).

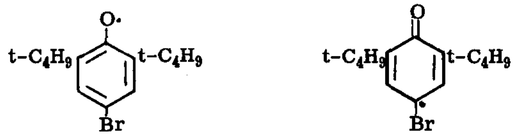


IV was also the major product from the irradiation of a mixture of iodobenzene and 2, 6-di-tert-butylphenol in Freon-113 or from the irradiation of 2, 6-di-tert-butylphenol in benzene to which a few crystals of iodine had been added.

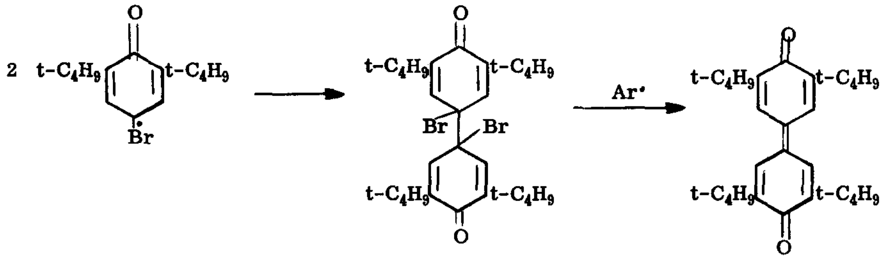
The mechanism for biaryl formation (1, 2) does not account for the production of the diphenoquinone IV; therefore, IV must arise by a competing path.

The photolysis of 4-bromo-2, 6-di-tert-butylanisole (V) produced 2, 6-di-tert-butyl-4-phenylanisole and 2, 6-di-tert-butylanisole in 22.0 and 36.4% yields, respectively. Hence the exceptionally low yield of the biphenyl derivative II is not due to inductive effects or steric inhibition by the two tert-butyl groups, which should exert a similar effect in I and V.

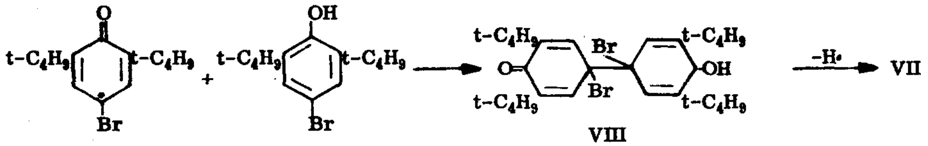
The photolysis of 4-bromo-2, 6-xylenol produced 4-phenyl-2, 6-xylenol in 9.6% yield, virtually the same yield as that obtained in the photolysis of 4-iodo-2, 6-xylenol (3); however, no 3, 3', 5, 5'-tetramethyldiphenoquinone was produced. Thus, production of a diphenoquinone requires an intermediate phenoxy radical stabilized by steric hindrance as well as electron delocalization. A reasonable route to the diphenoquinone IV from 4-bromo-2, 6-di-tert-butylphenol is via the resonance-stabilized phenoxy radical VI. VI is known to dimerize to compound VII, which under radical attack loses bromine atoms to give the diphenoquinone IV (4). Compound VII could not be isolated from our reaction mixture, but this is not surprising because it can lose bromine atoms by both radical attack and photolysis. Compound VII could also arise by attack of radical VI on compound I to give intermediate VIII, which could then lose a hydrogen atom. However, we are not able to distinguish between these two paths.



VI

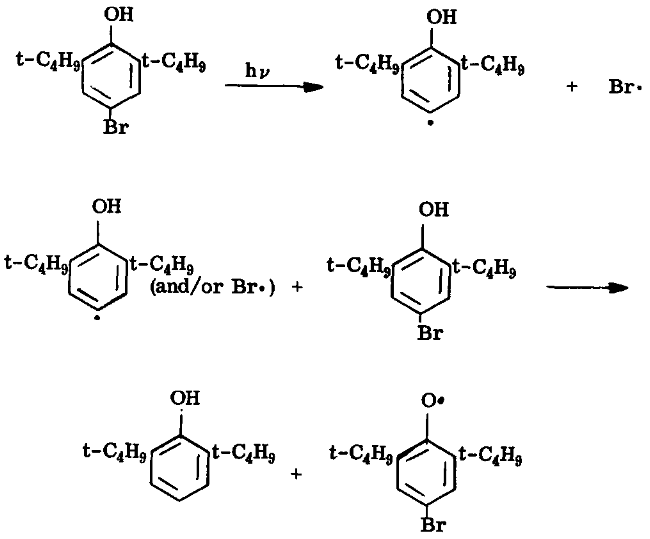


VII



VIII

Radical VI is probably produced as follows:



References

1. W. Wolf and N. Kharash, J. Org. Chem., 30, 2493 (1965).
2. T. Matsuura and K. Omura, Bull. Chem. Soc. Japan, 39, 944 (1966).
3. A. Nickson and B. R. Aaronoff, J. Org. Chem., 29, 3014 (1964).
4. K. Ley, E. Müller, R. Mayer, and K. Scheffler, Chem. Ber., 91, 2640 (1958).