Anil Formation by Oxidative Depolymerization

By EMIL KON and EDWARD MCNELIS*
(*Chemistry Department, New York University, New York, N.Y.* 10003)

Summary Mixtures of substituted anilines and oligomers of poly-(2,6-dimethyl-1,4-phenylene) ether in benzene were oxidized by sodium bismuthate to give anils such as 2,6-dimethyl-*p*-benzoquinone-4-(2′,4′,6′-trimethyl)anil, a product of oxidative depolymerization.

THE oxidative polymerization of 2,6-xylenol by one-electron oxidants has been shown to proceed through the intermediacy of quinone acetals.[1] Since these acetals have the property of reverting to free radicals, attempts to depolymerize polymers in the presence of other phenols have been successful. For example, poly-(2,6-dimethyl-1,4-phenylene) ether was oxidized in the presence of excess of phenol to give the mixed dimer (I).[2] We report the novel oxidative depolymerization of an oligomer of poly-(2,6-dimethyl-1,4-phenylene) ether (II) with substituted anilines to give anils.

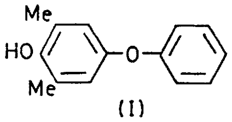
When sodium bismuthate (33 g) was stirred for 3 days at room temperature with benzene (100 ml) containing the oligomer (II)† (4·1 g) freed of monomer and mesidine (13·5 g) (2,4,6-trimethylaniline), no oligomer was recovered. The products were the anil (IIIa) (87%) and the azo-derivative of mesidine (7%).[3] Without the presence of the oligomer the yields of the anil and the azo-compound under the same conditions were 0·5 and 10%, respectively. If the oligomer were replaced with monomer, the yield of anil was 14%.

The relatively slow rate of oxidation of mesidine was demonstrated by a competitive oxidation wherein mesidine (4·5 g) and 2,6-xylenol (4·1 g) in benzene (100 ml) were oxidized for 24 h with sodium bismuthate (33 g) to afford the phenolic polymer (66%), (IIIa) (20%), and the azo-compound (2%).

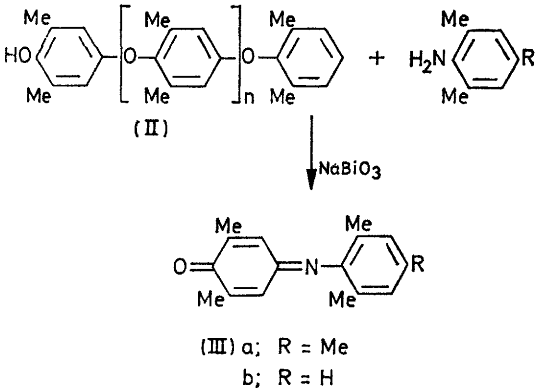
Products were isolated and purified by alumina column chromatography after removal of polymer by methanolic coagulation.

---

† The oligomer was prepared by the activated manganese dioxide method[1b] and had a molecular weight range of 500—2000.



(I)



(II)

(III) a; R = Me

b; R = H

When no quinone–acetal equilibrium is possible, as in the case of the oxidation of 2,6-di-t-butylphenol, no anil was formed. The phenol (6·8 g) and mesidine (13·5 g) in benzene (100 ml) were oxidized by sodium bismuthate (33 g) overnight at room temperature to yield, 3,3′,5,5′-tetra-t-butyldiphenoquinone (88%) and azomesitylene (5%).

The depolymerization reaction was applicable also to 2,6-xylidine (2,6-dimethylaniline). In this case, xylidine (12·1 g) and (II)† (4·1 g) were treated with excess of bismuthate for 3 days to give the anil (IIIb) (50%), xylenol polymer (24%), and azoxylidine (1%). The corresponding anil and azo-compound yields for the control reaction without oligomer were 2 and 14%. Dry column chromatography[4] on alumina was used to separate the pink azoxylidine (m.p. 49·5—50·5)[5] from the anil (IIIb): m.p. 77—79°; *m/e* (%) 239 (100, M^+), 224 (30), 210 (65); δ (CDCl$_3$) 1·94 (3H, d, J 3 Hz), 1·98 (6H, s), 2·12 (3H, d, J 3 Hz), 6·40 (1H, q, J 3 Hz), 7·02 (3H, m), 7·16 (1H, q, J 3 Hz). A correct elemental analysis was obtained.

(*Received*, 14*th May* 1973; *Com.* 683.)

---

[1] (a) G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. Finkbeiner, *J. Amer. Chem. Soc.*, 1965, **87**, 3996; E. McNelis, *J. Org. Chem.*, 1966, **31**, 1255; (c) W. J. Mijs, O. E. Van Lohuizen, J. Bussink, and L. Vollbracht, *Tetrahedron*, 1967, **23**, 2253.

[2] D. M. White, *J. Org. Chem.*, 1969, **34**, 297.

[3] The physical and spectral properties of these compounds were identical to literature values: B. C. Saunders and J. Wodak, *Tetrahedron*, 1967, **23**, 473.

[4] B. Loew and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

[5] E. Haselback, *Helv. Chim. Acta*, 1970, **54**, 1526.