

## Anil Formation by Oxidative Depolymerization

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**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-xyleneol by one-electron oxidants has been shown to proceed through the intermediacy of quinone acetals.<sup>1</sup> 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).<sup>2</sup> 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.

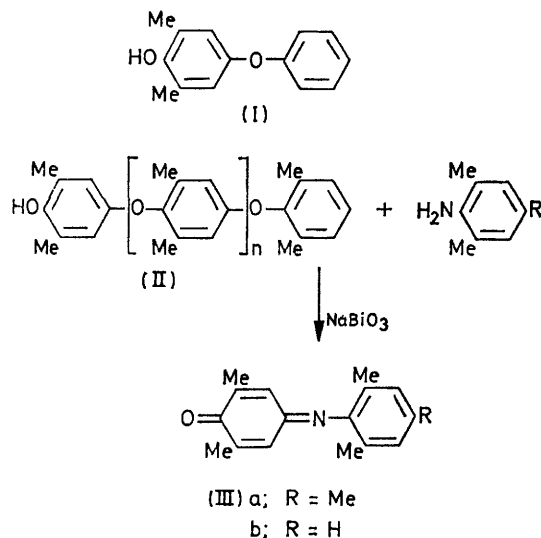
When sodium bismuthate (33 g) was stirred for 3 days at

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%).<sup>3</sup> 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-xyleneol (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<sup>1b</sup> and had a molecular weight range of 500—2000.



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*-butyldiphenylquinone (88%) and azomesitylene (5%).

The depolymerization reaction was applicable also to 2,6-xylydine (2,6-dimethylaniline). In this case, xylydine (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 azoxylydine (1%). The corresponding anil and azo-compound yields for the control reaction without oligomer were 2 and 14%. Dry column chromatography<sup>4</sup> on alumina was used to separate the pink azoxylydine (m.p. 49.5—50.5)<sup>5</sup> from the anil (IIIb): m.p. 77—79°; *m/e* (%) 239 (100, *M*<sup>+</sup>), 224 (30), 210 (65); δ (CDCl<sub>3</sub>) 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.

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<sup>2</sup> D. M. White, *J. Org. Chem.*, 1969, **34**, 297.

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

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<sup>5</sup> E. Haselback, *Helv. Chim. Acta*, 1970, **54**, 1526.