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DEHYDROGENATION REACTIONS WITH DIPHENOQUINONES

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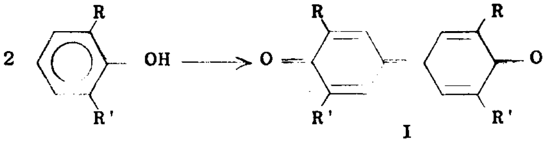
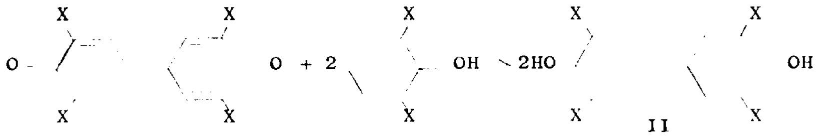
The oxidative coupling with oxygen, of 2,6-disubstituted phenols in which at least one of the substituents is a large, bulky group (such as *t*-butyl) yields diphenoquinones (I) in high yield (1,2). High molecular weight polyethers can be prepared by oxidative coupling of 2,6-disubstituted phenols



I

(1)

if the substituents are small (2), however, under the proper conditions the diphenoquinone is the major product (3). These diphenoquinones are readily reduced to the hydroquinones (4). We have now found that the hydroquinones are produced in high yield by an oxidation-reduction reaction involving a phenol and a diphenoquinone (eqn. 2). The reaction is catalyzed by amines,

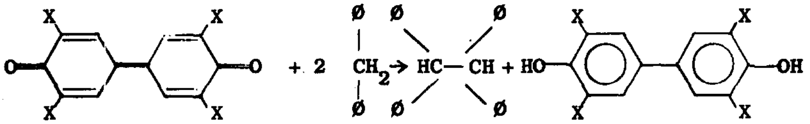


II

(2)

acids and aluminum salts. For example, to a Carius tube was added 1.29 g. (0.0032 moles) of 3,3',5,5'-tetra-t-butyl diphenoquinone, 1.5 g. (0.0073 moles) of 2,6-di-t-butyl phenol and 1 g. of pyridine. The tube was flushed with nitrogen, sealed and placed in a furnace at 250°C. In ten minutes the reaction mixture was pale yellow. The reaction mixture was cooled and diluted with ether and washed with dilute hydrochloric acid to remove pyridine. The ether was evaporated and 10 ml. of hot ethanol was added. On cooling there deposited 2.51 g. (0.0061 moles; 95% yield) of pale yellow crystals, m.p. 186°C. (lit. m.p. 184-185° (4)). This material is identical with an authentic sample of 2,2',6,6'-tetra-t-butyl p,p'-biphenol (II; R=t-butyl). When a more strongly basic amine (e.g., trimethylamine) is used the reaction proceeds readily at 150°C. and reaction of the more powerful oxidant 3,3',5,5'-tetramethyldiphenoquinone with 2,6-dimethylphenol proceeds rapidly at 100°C. to yield principally (80%) the biphenol (I; R=R'=CH_3).

The diphenoquinones also react with hydrocarbons such as diphenylmethane as shown in equation 3.



(3)

To a 100 ml. flask equipped with an air condenser was added 40 ml. of diphenylmethane and 5 g. (0.012 moles) of 3,3',5,5'-tetra-t-butyl diphenoquinone. The solution was refluxed for one hour (260°C.) then cooled and 50 ml. of ethanol was added. The solid that deposited was recrystallized from ethanol-chloroform to yield 2.6 g. (0.0078 moles; 65% yield) of 1,1,2,2-tetraphenylethane, m.p. 208° (lit. 210° (5)).

Further work on the use of these diphenoquinones in dehydrogenation reactions is in progress.

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