

CATALYTIC TRANSFER HYDROGENOLYSIS OF PHENOLS AND AROMATIC AMINES

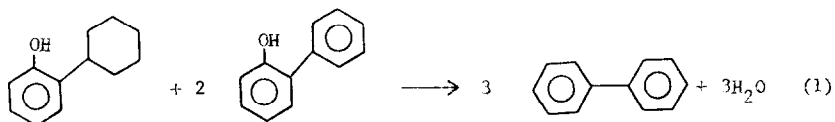
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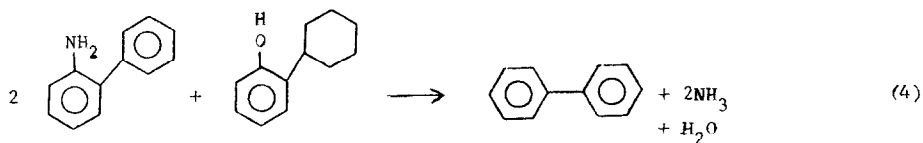
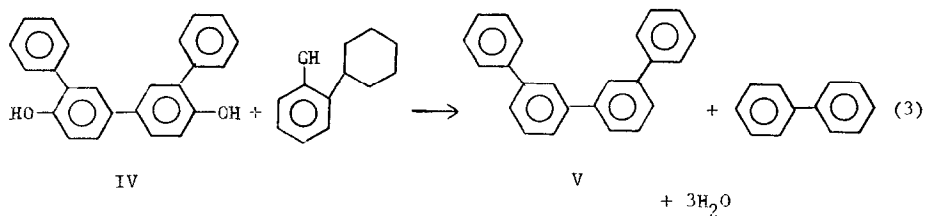
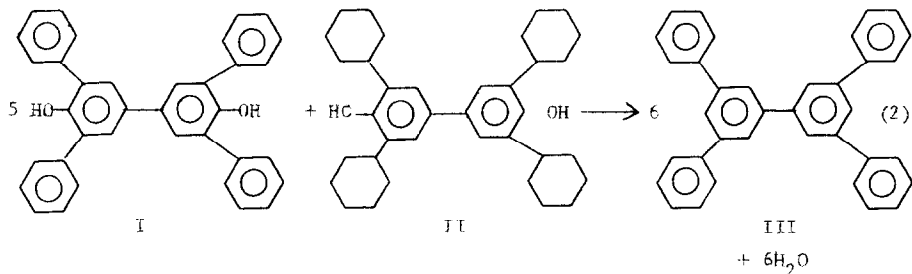
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The hydrogenolysis of phenols and aromatic amines to aromatic hydrocarbons has not been a useful preparative reaction because of concomitant reduction of the aromatic ring.^(1,2) We have found that aromatic hydrocarbons can be obtained in high yield from phenols and amines by catalytic transfer hydrogenolysis over a palladium on alumina catalyst in a Carius tube in the neighborhood of 350°C.

Biphenyl is obtained from *o*-phenylphenol and 2-cyclohexylphenol in 93% yield according to equation (1).



The following reactions have also been performed:

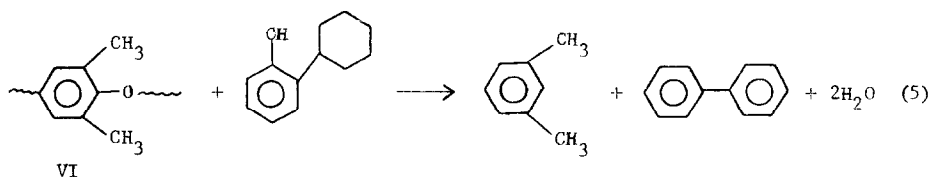


For example: To a Carius tube was added 1.70 g. (0.01 mole) of *o*-phenylphenol, 0.88 g. (0.05 mole) of *o*-cyclohexylphenol and 1 g. of 0.5% palladium on alumina catalyst. The tube was flushed with nitrogen, sealed and heated at 350°C for four hours. On cooling water separated from the colorless solution, ether was added, and the solution washed with dilute sodium hydroxide. The ether layer was evaporated to leave 2.15 g. (0.014 mole; 93% yield) of biphenyl, m.p. 69°C.

The preparation of the more complex hydrocarbon, III, was carried out as follows: To a Carius tube (~ 8 ml. volume) was added 2.45 g. (.005 mole) of 2,2',6,6'-tetraphenyl-*p,p'*-biphenol, 0.514 g. (.001 mole) of 2,2',6,6'-tetracyclohexyl-*p,p'*-biphenol and 2 g. of palladium (0.5%) on alumina pellets. The tube was sealed and heated at 370°C. for 18 hours. On cooling a layer of water separated. The product was extracted with chloroform, the chloroform evaporated and the residue recrystallized 3 times from ethanol to yield 1.85 g. (.0041 mole; 68.3% yield) of 5',5''-diphenyl-1,1':3',1'':3'',1'''-quaterphenyl, m.p. 231-2°C. Anal. Calcd. for C₃₆H₂₆: C, 94.28; H, 5.72. Found: C, 94.1; H, 5.8. The infrared spectrum showed no absorption in the O-H or C-O stretching regions.

In a similar fashion *m*-quaterphenyl, V, m.p. 85.5°C. (lit. 85.5-86°C. ⁽³⁾) was prepared in 52% yield and biphenyl was prepared in an overall yield of 70% from 2-aminobiphenyl according to equation (4). Carbazole remained unchanged under these conditions.

The principal product obtained from hydrogenolysis of poly(2,6-dimethyl-1,4-phenylene oxide), VI, using 2-cyclohexylphenol as a donor was *m*-xylene.



References

1. V. I. Komarewsky, C. H. Riesz and F. L. Morritz in *TECHNIQUE OF ORGANIC CHEMISTRY*, Second Edition, Vol. II, p. 121, Interscience Publishers, New York, 1956.
2. Heuben-Weyl, *Methoden Der Organische Chemie* Band IV, p. 314.
3. G. F. Woods and F. T. Reed, *J. Am. Chem. Soc.*, 71, 1348 (1949).