

Rearrangements in the Palladium-Catalyzed Dehydrogenation of Cyclohexylphenols to Phenylphenols

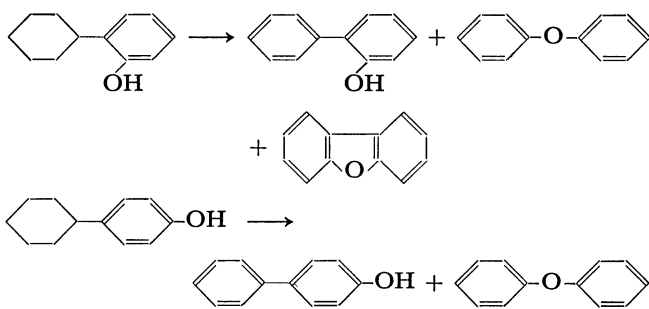
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Although allyl phenyl ether is well known to rearrange to *o*-allylphenol upon heating to a high temperature,²⁾ diphenyl ether does not rearrange to phenylphenols. Photochemically, however, diphenyl ether rearranges not only to *o*- and *p*-phenylphenols^{3,4)} but also to dibenzofuran.⁵⁾

In the dehydrogenation of cyclohexylphenols to phenylphenols, we found the formation of diphenyl ether as a rearrangement product and dibenzofuran as a cyclization product.



Experimental

Materials. Cyclohexylphenols: *o*- and *p*-Cyclohexylphenols were prepared by Friedel-Crafts type condensation of phenol with cyclohexyl chloride in the presence of ferric chloride hexahydrate,⁶⁾ and were purified by fractional recrystallization. The purity of each cyclohexylphenol was checked by gas-chromatography.

Palladium Catalyst: Five per cent palladium-charcoal catalyst, manufactured by Kawaken Fine Chemical Co. Ltd., Tokyo, was used without purification.

Dehydrogenation of Cyclohexylphenols. A mixture of 1 g of *o*- or *p*-cyclohexylphenol and 200 mg of palladium catalyst was heated at 300°C (bath temperature) for 4 hr under nitrogen atmosphere. The reaction mixture was dissolved in benzene, and the catalyst was filtered off. The filtrate was analyzed gas-chromatographically for the determination of reaction products.

Identification and Determination of the Products. Identification and quantitative determination of each product were performed gas-chromatographically on a Shimadzu Model GC-1C (column packing: XE-60) with authentic materials.

Results and Discussion

Gas-chromatographical analysis of the dehydrogenation products gave results given in Table 1.

TABLE 1. DEHYDROGENATION PRODUCTS FROM CYCLOHEXYLPHENOLS (in %)

Starting material	Phenylphenol	Diphenyl ether	Dibenzofuran
<i>o</i> -Cyclohexylphenol	72	23	3
<i>p</i> -Cyclohexylphenol	79	17	—

Although the main products are *o*- and *p*-phenylphenols, respectively, a considerable amount of diphenyl ether is found in both cases. Formation of diphenyl ether on dehydrogenation of cyclohexylphenols involves a novel rearrangement, containing C-C bond fission between the two benzene nuclei and the new C-O bond formation. It is not clear, however, whether the formation of diphenyl ether results by intramolecular or intermolecular rearrangement.

Cyclization to dibenzofuran also occurred in the dehydrogenation of *o*-cyclohexylphenol. Under the same condition, *o*-phenylphenol also cyclizes to give dibenzofuran (5%) and diphenyl ether (trace), but *p*-phenylphenol and diphenyl ether do not give dibenzofuran. Changes in the yields of dibenzofuran from *o*-cyclohexylphenol and *o*-phenylphenol with the reaction time were very similar to those shown in Fig. 1.

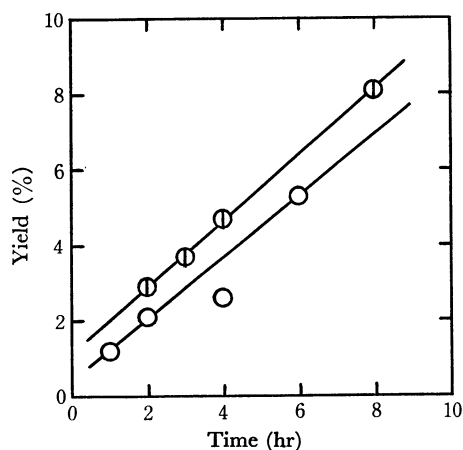


Fig. 1. Dibenzofuran from *o*-cyclohexylphenol (○) and *o*-phenylphenol (⊙).

From these results, it is concluded that diphenyl ether is directly formed in the dehydrogenation of the *o*- and *p*-cyclohexylphenols, and dibenzofuran is produced *via* *o*-phenylphenol.

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2) A. A. Shamshurin and R. A. Ibadulin, *Zh. Obshch. Khim.*, **19**, 1669 (1949); *Chem. Abstr.*, **44**, 1443^r (1950).

3) M. S. Kharasch, *Science*, **116**, 309 (1952).

4) D. P. Kelley, J. T. Pinky, and R. D. Rigby, *Tetrahedron Lett.*, **1966**, 5953.

5) H. Stegemeyer, *Naturwissenschaften*, **53**, 582 (1966).

6) A. R. Abdurasuleva and K. N. Akhmedov, *Uzb. Khim. Zh.*, **1964** (5), 31.