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Rearrangements in the Palladium-Catalyzed Dehydrogenation of Cyclohexylphenols to Phenylphenols

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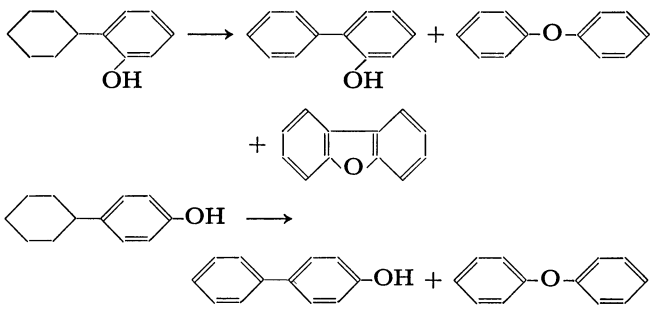
Although allyl phenyl ether is well known to rearrange to *o*-allylphenol upon heating to a high temperature,[2] diphenyl ether does not rearrange to phenylphenols. Photochemically, however, diphenyl ether rearranges not only to *o*- and *p*-phenylphenols[3,4] but also to dibenzofuran.[5]

In the dehydrogeation 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.

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

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

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

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

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

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
o-Cyclohexylphenol	72	23	3
p-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.

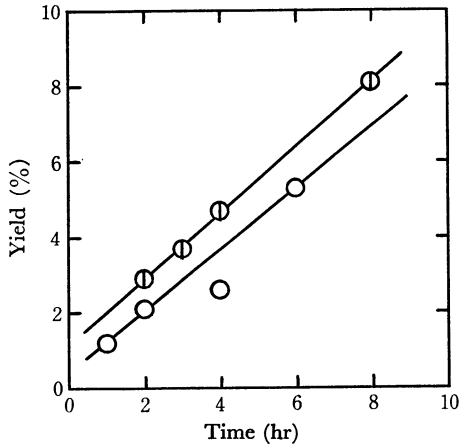

Fig. 1. Dibenzofuran from *o*-cyclohexylphenol(○) and *o*-phenylphenol (①).

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.