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Dehydrogenation of 2-(1-Cyclohexenyl)cyclohexanone with Palladium Catalyst

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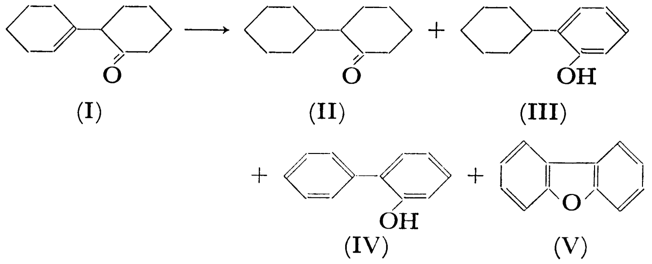
The dehydrogenation reaction of 2-(1-cyclohexenyl)cyclohexanone was carried out in the presence of 5% palladium-on-charcoal at temperatures 280, 300, and 320 °C, the reaction time being 1/2—8 hr. *o*-Cyclohexylphenol and *o*-phenylphenol were obtained as dehydrogenation products, and dibenzofuran as the cyclization product *via* *o*-phenylphenol. In a short reaction time, 2-cyclohexylcyclohexanone was formed together with the dehydrogenation products. The compound disappeared, the amount of two phenols and dibenzofuran increasing with reaction time. The dehydrogenation process is discussed.

Many investigations have been made on the dehydrogenation of alicyclic compounds. In order to obtain *o*-phenylphenol, we carried out the dehydrogenation of *o*-cyclohexylphenol with palladium-on-charcoal and found that various rearranged products were obtained together with the desired *o*-phenylphenol.[1]

The present communication deals with the dehydrogenation of 2-(1-cyclohexenyl)cyclohexanone (I), which was unknown up to now, in the presence of the same catalyst under various conditions. Four products obtained in this procedure were confirmed to be 2-Cyclohexylcyclohexanone (II), *o*-cyclohexylphenol (III), *o*-phenylphenol (IV), and dibenzofuran (V).



(I) (II) (III) (IV) (V)

Experimental

Materials. *5% Palladium-on-charcoal*: The palladium catalyst was prepared by the method of Mozingo.[2]

2-(1-Cyclohexenyl)cyclohexanone (I): 2-(1-Cyclohexenyl)-cyclohexanone (I) was prepared[3] by the self-condensation of cyclohexanone with phosphorus pentoxide, and was purified by distillation: bp 103—104 °C/1 mmHg [bp 114—116 °C/3.5 mmHg[4]]; oxime: mp 157—159 °C [mp 155 °C[5]].

2-Cyclohexylcyclohexanone (II): 2-Cyclohexylcyclohexanone (II) was obtained by catalytic hydrogenation of I in the presence of palladium chloride in methanol,[6] and was distilled; bp 145—147 °C/19 mmHg [bp 135 °C/11 mmHg[6]]; oxime: mp 100—102 °C [mp 102 °C[7]]; semicarbazone: mp 176—178 °C [mp 174—177 °C[8]].

Others: *o*-Cyclohexylphenol (III) and *o*-phenylphenol (IV) were supplied by Sanko Chemical Co. Ltd. Commercial dibenzofuran (V) (Tokyo Kasei Kogyo Co. Ltd.) was used.

Dehydrogenation of 2-(1-Cyclohexenyl)cyclohexanone. A mixture of I (2 g) and 5% palladium catalyst (400 mg) was heated at 280, 300, 320 °C under nitrogen atmosphere. At appropriate intervals of time, aliquots taken from the reaction mixtures were dissolved in benzene, and the catalyst was filtered off. The filtrates were analyzed gas chromatographically for determination of the reaction products.

Determination of Products. Quantitative determination of the products was performed gas chromatographically on a Shimadzu Model GC-1C gas chromatograph (column: 3% XE-60/Chromosorb W, 3 mmφ × 150 cm; temperature 180 °C).

Measurements of Spectra. The IR spectra were recorded on a JASCO Model IRA-1 spectrophotometer in chloroform. The NMR spectra were taken on a Hitachi-Perkin-Elmer Model R-24 (60 MHz) spectrometer, using carbon tetrachloride and tetramethylsilane as the solvent and internal reference, respectively.

Results and Discussion

Dehydrogenation Products. 2-(1-Cyclohexenyl)-cyclohexanone (I) was treated with 5% palladium catalyst at 300 °C for 4 hr under nitrogen atmosphere. The gas chromatogram of the reaction mixture is shown

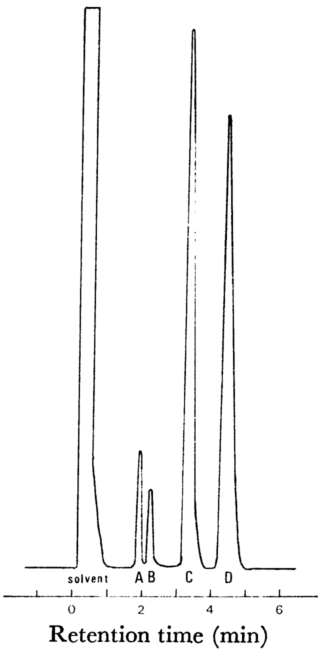


Fig. 1. Gas chromatogram of dehydrogenation products (300 °C, 4 hr).
Column: 3% XE-60/Chromosorb W, 3 mmφ × 150 cm
temperature: 180 °C, carrier: H_2 32.1 ml/min

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in Fig. 1. The mixture was found to contain four components. It was found that components B, C, and D are identical with dibenzofuran (V), *o*-phenylphenol (IV), and *o*-cyclohexylphenol (III), respectively, in comparison with authentic materials. V was also obtained in the dehydrogenation of III with the same catalyst.[1)]

Component A was separated gas chromatographically (column: 3% XE-60/chromosorb W, 10 mm$\phi \times 75$ cm, 150 °C); semicarbazone: mp 175—177 °C. The spectral data for this compound are given in Table 1, together with those of I and II, which were obtained[6)] by catalytic hydrogenation of I.

TABLE 1. SPECTRAL DATA

Compound	Mp of semicarbazone (°C)	IR (cm^{-1})		NMR δ(ppm)
		$\nu_{C=O}$	δ_{CH_2}	
I	185—187	1734	1450	1.3—3.0 5.28
II	176—178	1730	1450	0.6—2.9
A	175—177	1730	1450	0.6—2.8

Thus, component A was confirmed to be 2-cyclohexylcyclohexanone.

A similar compound, 2,6-dicyclohexylcyclohexanone, was obtained in the dehydrogenation of 2,6-di(1-cyclohexenyl)cyclohexanone.[9),10)]

Effects of Reaction Time and Temperature. The dehydrogenation of I was investigated in detail in the presence of 5% palladium-on-charcoal at temperatures 280, 300, and 320 °C for reaction time 1/2—8 hr. The changes in the amount of products obtained at temperatures 300 and 320 °C are shown in Figs. 2 and 3, respectively.

In all cases, increase in the reaction time caused a decrease in the yield of II and an increase in the amount of the phenols (III and IV). The change was remarkable at higher temperature. In particular, at 320 °C, II disappeared rapidly and V increased (47.3% after 8 hr).

Reaction Process. Since II hydrogenated was produced together with III and IV within 30 min, it is thought that dehydrogenation and hydrogenation take place competitively in an initial stage. Subsequently, II was dehydrogenated into III and IV.* The dehydrogenation occurs more readily in the cyclohexanone ring than in the cyclohexene ring.

III was also dehydrogenated into IV. This process has been reported.[1)] It is thought that V was formed *via* IV, since it was produced in the dehydrogenation of III and in the cyclization of IV in the presence of palladium catalyst.[1)]

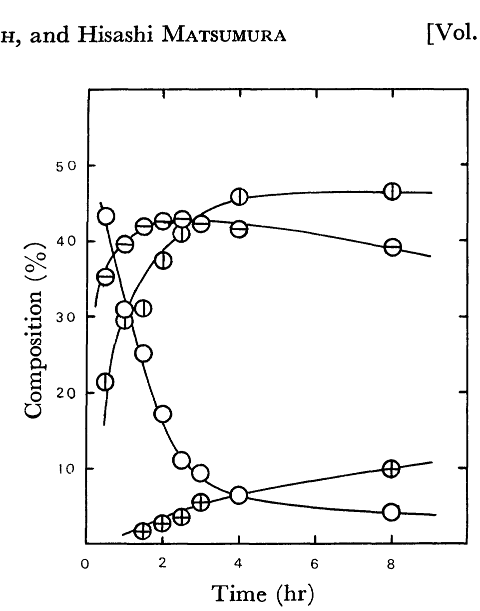

Fig. 2. Dehydrogenation at 300 °C.
○: II, ⊖: III, ⦶: IV, ⊕: V

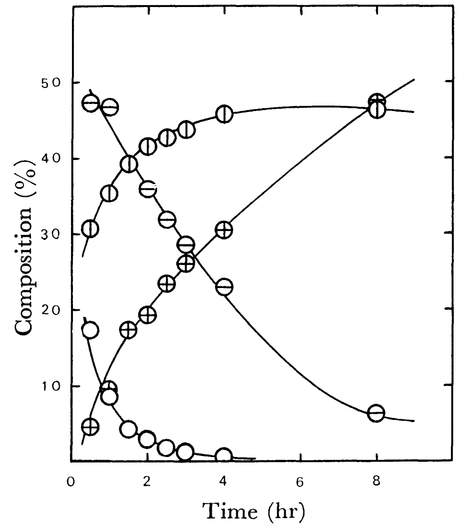

Fig. 3. Dehydrogenation at 320 °C
○: II, ⊖: III, ⦶: IV, ⊕: V

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* The dehydrogenation of 2-cyclohexylcyclohexanone is in progress. The process was found to give *o*-cyclohexylphenol, *o*-phenylphenol, and dibenzofuran.