SYNTHESIS OF TRICYCLIC CYCLOHEXYL

ARYL ETHERS

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In the present paper we studied a method for the preparation of dicyclohexyloxybenzene by the Ullmann reaction from m-dibromobenzene and sodium cyclohexanolate in excess cyclohexanol [1] and established the structures of the secondary products of the reaction.

 $\begin{array}{c} \mathrm{Br}_{2}\mathrm{C}_{6}\mathrm{H}_{4}+\mathrm{C}_{6}\mathrm{H}_{11}\mathrm{ONa} \xrightarrow{\qquad} \mathrm{Br}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{OC}_{6}\mathrm{H}_{11} & (\mathrm{I}) \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$

The highest yields are obtained when a 1:1.25 mole ratio of the reactants is used (Table 1). Together with the ethers, the following secondary reaction products were isolated: 2-hydroxybicyclohexyl (III; from the light fractions) and 1-cyclohexyl-2-(2-oxocyclohexyl)cyclohexane (IV; from the residue). The yield of (III) is proportional to the amount of sodium cyclohexanolate taken for reaction.

The formation of (III) can be explained by the autocondensation of the alcohols [2,3]. Compound (IV) represents the condensation product of (III) and sodium cyclohexanolate, which was confirmed by the counter synthesis of (IV).



It was observed that the use of catalytic amounts of Cu_2I_2 in the Ullmann reaction sharply lowers the yield of the ethers and increases the yield of the secondary products up to 50%. Among the latter was detected phenyl cyclohexyl ether, which is evidently formed as the result of the debromination of the monoether [4].

We also synthesized by the Ullmann reaction, starting with the m- and p-bromophenyl cyclohexyl ethers (I) and sodium phenolate, the unsymmetrical ethers: m-(phenoxyphenoxy)cyclohexane (V) and

Expt . No	Starting m-di bromo- benzene*	substances Na(6 M of cyclo- hexanol	m-Bromo- phenyl cy- clohexyl ether (I)	m-Dicyclo- hexyloxy- benzene (II)	2-Hydroxy- bicyclohexyl (III)
$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \end{array} $	1 1 1	$2,25 \\ 2 \\ 1,25 \\ 1$	$\begin{array}{c} 0,07\\ 0,075\\ 0,375\\ 0,305 \end{array}$	$0,125 \\ 0,184 \\ 0,265 \\ 0,245$	$0,74 \\ 0,61 \\ 0,12 \\ 0,09$

TABLE 1. Yields of Mono- and Diethers as a Function of the Ratios of the Reactants (M)

*The reactivity of p-dibromobenzene is somewhat lower.

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p~(phenoxyphenoxy)cyclohexane (IV). The high nucleophilicity of phenol favors the progress of the Ullmann reaction and leads to the formation of the ethers in high yield.

The structure of the obtained ethers was confirmed by the spectral analysis data.

EXPERIMENTAL SECTION

2-Hydroxybicyclohexyl (III). A mixture of Na cyclohexanolate (from 11.5 g of Na) in 250 ml of cyclohexanol, 59 g of m-dibromobenzene and 1 g of Cu powder was heated, with stirring, at 180-190°C for 5 h, with removal of the excess cyclohexanol by distillation. After cooling, the mixture was treated with water and ether, and then vacuum-distilled. The light fraction was fractionally redistilled to give 28.2 g of a semicrystalline product with bp 105-106° (2 mm) and mp 30° (from petroleum ether). Found: C 78.91; H 12.27%. $C_{12}H_{22}O$. Calculated C 79.06; H 12.16%. From [5,6]: bp 265-270°; 113-114° (3 mm); mp 30-31°.

1-Cyclohexyl-2-(2-oxocyclohexyl)cyclohexane (IV). A mixture of Na cyclohexanolate (from 1.5 g of Na) in 50 ml of cyclohexanol 12 g of (III) and 0.1 g of Cu was heated at 170° for 30 h, with removal of the excess cyclohexanol by distillation. After treatment with water and ether the product was vacuum-distilled to give 1.2 g of a crystalline substance with bp 170-175° (3 mm) and mp 121° (from hexane). Found: C 82.47; H 11.55%; mol. wt. (cryoscopically) 250.22. $C_{18}H_{30}O$. Calculated: C 82.38; H 11.52%; mol. wt. 262.43. Analogous characteristics were found for (IV), which was isolated as a secondary product. In the IR spectrum of (IV) was detected a band at 1710 cm⁻¹ (CO group). From [7]: bp 212-214° (14 mm).

<u>m-(Phenoxyphenoxy) cyclohexane (V)</u>. A mixture of Na phenolate (from 1.15 g of Na and 66 g of phenol), 12.8 g of m-bromophenyl cyclohexyl ether and 0.2 g of Cu powder was heated at 175-180° for 10 h. The mixture was extracted with ether, the excess phenol was distilled off, while the residue was treated in succession with 20% NaOH solution, ether and water, and then distilled. We isolated 10.2 g (76.1%) of m-(phenoxyphenoxy) cyclohexane, bp 158-158.5° (1 mm); mp 32° (from alcohol). Found: C 80.62; H 7.59%. $C_{18}H_{20}O_2$. Calculated: C 80.56; H 7.51%.

<u>p-(Phenoxyphenoxy)cyclohexane (VI)</u>. Similar to the m-ether, from 0.575 g of Na, 47 g of phenol, 6.4 g of p-bromophenyl cyclohexyl ether and 0.2 g of copper powder was isolated 5.3 g of p-(phenoxyphenoxy)cyclohexane, bp 171-172° (2 mm); mp 36.5-37° (from alcohol). Found: C 80.92; H 7.74%. $C_{18}H_{20}O_2$. Calculated: C 80.56; H 7.51%.

CONCLUSIONS

The cyclic ethers, m- and p-(phenoxy)eyclohexanes, were synthesized by the Ullmann reaction.

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