INVESTIGATION IN THE FIELD OF CYCLOHEXYLPHENYL ETHERS

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UDC 542.91:547.562.4:547.593.12

In searches for new substances for the production of thermostable materials, we began investigations in the field of the synthesis of ethers with cyclohexyl and phenyl radicals. The simplest representative of this series – cyclohexylphenyl ether (I) – was first synthesized by heating potassium cyclohexanolate with iodobenzene to 140-150° in the presence of copper powder [1] and Cu_2I_2 at the temperature 200° [2].

We produced the ether (I) from iodobenzene and sodium cyclohexanolate by heating with copper powder at 175°. In an attempt to produce the ether (I) from potassium phenolate and bromocyclohexane at 190°, o-cyclohexylphenol with mp 48-52° (according to the data of [3]: mp 56-57°) was obtained, with an admixture of p-cyclohexylphenol.

Ethers including three rings in the molecule were synthesized analogously. We produced the dicyclohexyl ether of hydroquinone by the reaction of sodium cyclohexanolate with 1,4-dibromobenzene or with the cyclohexyl ether of 4-bromophenol. The dicyclohexyl ether of resorcinol was produced by heating sodium cyclohexanolate with 1,3-dibromobenzene. Together with 1,3- and 1,4-dicyclohexyloxybenzenes, we isolated cyclohexyl ethers of 3- and 4-bromophenol from the reaction products. The structures of all the ethers were confirmed by the IR spectra.

A comparison of the properties of the ethers obtained with the properties of 1,4- and 1,3-diphenoxybenzenes indicated that replacement of the benzene rings by cyclohexyl rings lowers the solidification point of the ether.

EXPERIMENTAL METHOD

Cyclohexylphenyl Ether (I). A mixture of sodium cyclohexanolate, produced from 11.6 Na and 240 g cyclohexanol, with 120 g C_6H_5I and 1 g of copper powder, was heated fro 12 h at 175°, gradually distilling off the excess cyclohexanol. As the reaction mixture was cooled, it was decomposed with water and extracted with ether. After removal of the ether, the residue was redistilled. We isolated 59.1 g (67.1% on the basis of sodium cyclohexanolate) (I); bp 126° (13 mm); n_D^{20} 1.5272; d_4^{20} 1.0040; solidification point 56°. Found: C 81.92; H 9.15%. $C_{12}H_{16}O$. Calculated: C 81.77; H 9.15%. According to the data of [1, 4]; bp 140° (21.5 mm); n_D^{20} 1.527; d_4^{20} 1.0047 and 0.9795.

o-Cyclohexylphenol. We gradually added 90 g bromocyclohexane (large excess) over a period of 12 h at 190° to potassium phenolate (from 34 g phenol and 12 KOH) in a flask with a reflux condenser and dropping funnel. The yield of o-cyclohexylphenol was 69%; bp 156-157° (12 mm); mp 48-52°. Found: C 81.99; H 9.21%. $C_{12}H_{16}O$. Calculated: C 81.77; H 9.15%.

Cyclohexyl Ether of 4-Bromophenol. A mixture of sodium cyclohexanolate from 4.6 g Na and 120 ml cyclohexanone, 47.2 g p-dibromobenzene, and 0.2 g copper powder was heated to 175° for 5 h. Two products were isolated: 1) the cyclohexyl ether of 4-bromophenol, bp 127-140° (1 mm); yield 21.8 g (42.7% on the basis of p-dibromobenzene); mp 44° (from absolute alcohol) (according to the data of [5] mp 44-45°); 2) dicyclohexyl ether of hydroquinone; bp 180-185° (1 mm); mp 68-69° (from absolute alcohol); yield 6.3 g (11.5% on the basis of p-dibromobenzene).

Dicyclohexyl Ether of Hydroquinone. To sodium cyclohexanolate from 1.7 g Na in 50 ml cyclohexanol we added 17.8 g of the cyclohexyl ether of 4-bromophenol and 0.5 g copper powder. The mixture was heated to 190° for 30 h, distilling off the excess cyclohexanol. After cooling, treatment with water and with ether,

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 524-525, March, 1972. Original article submitted January 29, 1971.

the residue was redistilled. We isolated 8.06 g (42%) of the dicyclohexyl ether of hydroquinone with bp 184-194° (4 mm), mp 68-69° (from absolute alcohol). Found: C 78.85; H 9.45%. $C_{18}H_{26}O_2$. Calculated: C 78.78; H 9.55%.

Cyclohexyl Ether of 3-Bromophenol. A mixture of sodium cyclohexanolate (from 5.75 g Na and 150 ml cyclohexanol) with 43.4 g 1,3-dibromobenzene was heated at 190° for 3 h, distilling off the excess cyclohexanol. After treatment with water and ether, the following products were isolated: 1) cyclohexyl ether of 3-bromophenol, yield 10.2 g (20% on the basis of m-dibromobenzene); bp 125-126° (2 mm); n_D^{20} 1.5565; d_4^{20} 1.3218. [Found: C 56.45; H 6.19; Br 30.76%. $C_{12}H_{15}BrO$. Calculated: C 56.49; H 5.93; Br 31.32%]; 2) dicyclohexyl ether of resorcinol: yield 18.5%; bp 175-176° (1 mm); mp 36-37°. Found: C 78.94; H 9.87%. $C_{18}H_{26}O_2$. Calculated: C 78.78. H 9.55%.

The dicyclohexyl ether of resorcinol was obtained in a 59-60% yield from the cyclohexyl ether of 3-bromophenol formed, in the reaction with sodium cyclohexanolate.

CONCLUSIONS

1. 1,4-Dicyclohexyloxy- and 1,3-dicyclohexyloxybenzene and the cyclohexyl ether of 3-bromophenol were synthesized.

2. In the reaction of potassium phenolate with bromocyclohexane at 190°, o-cyclohexylphenol is obtained instead of the expected cyclohexylphenyl ether.

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