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BRIEF COMMUNICATIONS

Selective O-Adamantylation of Dihydric Phenols by 1,3-Dehydroadamantane

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Abstract—Possibility of synthesis of 1-adamantyl phenyl ethers by one stage without use of a catalyst was researched.

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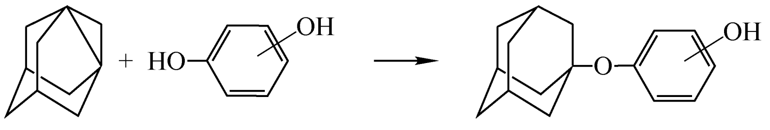
It was shown previously [1] that mono- and dihydric phenols in the presence of catalytic amounts of sulfuric acid are subjected to selective C-adamantylation by 1,3-dehydroadamantane (DHA).

In our study we performed regioselective reactions of O-adamantylation of dihydric phenols by DHA to synthesize 1-adamantyl phenyl ethers:



I **IIa**–**IIc** **IIIa**–**IIIc**

As initial reagents in reaction with DHA (**I**) we used dihydric phenols: catechol (**IIa**), resorcinol (**IIb**) and hydroquinone (**IIc**). Reaction of DHA and **IIa–IIc** occurred in diethyl ether at 1.5–2-fold mole excess of appropriate phenol in a dry argon at 30–35°C for 20–30 min. After the reaction completion the ether was distilled and an obtained residue was washed with hot water to remove unreacted phenol. Then it was analyzed by gas chromatography mass spectrometry

The analysis showed that in the case of lacking of an acidic catalyst a main direction of the DHA reaction was O-adamantylation of dihydric phenols with formation of 1-adamantyl phenyl ethers of 80–88% yield. As side products were also C-adamantylated dihydric phenols (8–10% yield). Formation of fundamentally different products of DHA reaction with dihydric phenols without an acidic catalyst is associated with a change in the reaction mechanism. It was known [2, 3] that in the presence of DHA proton an adamantyl-cation is relatively easily formed and this fact explains formation of products of C-adamantylation of phenols.

Cleaning of the reaction products was conducted by recrystallization from benzene. All produced compounds were solids. Individuality of the obtained 1-adamantyl phenyl ethers was confirmed by TLC, and their composition and structure, by elemental analysis and mass-spectra.

1-Adamantyl 2-phenyl ether (IIIa). To 4.95 g (0.045 mol) of catechol in diethyl ether in a dry argon at a room temperature 4 g (0.0298 mol) of fresh distilled 1,3-dehydroadamantane in 20 ml of absolute diethyl ether was added. The mixture was kept 30 min at 30–35°C. After completion of the reaction the ether was distilled and the residue was washed with hot water. The products was purified after recrystallization from benzene. Yield was 6.3 g (88%), mp 102–103°C. Found (%): C 78.51, H 8.35. $C_{17}H_{22}O$. Calculated (%): C 78.65, H 8.25. Mass spectrum , *m*/*z* (intensity, %): 244 (M^+, 9), 135 (Ad^+, 100), 109 ($[M–Ad]^+$, 7).

1-Adamantyl 3-phenyl ether (IIIb). Similarly to **IIIa** were synthesized 4.95 g (0.045 mol) of resorcinol and 4 g (0.0298 mol) of fresh distilled 1,3-dehydroadamantane . Yield was 6.4 g (92%); mp 41–42°C. Found (%): C 78.69, H 8.24. $C_{17}H_{22}O$. Calculated (%): C 78.65, H 8.25. Mass spectrum , *m*/*z* (intensity, %): 244 (M^+, 11), 135 (Ad^+, 100), 109 ($[M–Ad]^+$, 9).

1-Adamantyl 4-phenyl ether (IIIc). Similarly to **IIIa** were synthesized 4.95 g (0.045 mol) of hydroquinone and 4 g (0.0298 mol) of fresh distilled 1,3-dehydroadamantane. Yield was 5.7 g (80%); mp 130–131°C. Found (%): C 78.74, H 8.20. $C_{17}H_{22}O$. Calculated (%): C 78.65, H 8.25. Mass spectrum , *m*/*z* (intensity, %): 244 (M^+, 15), 135 (Ad^+, 100), 109 ($[M–Ad]^+$, 8).

Mass spectra were recorded by chromatography–mass spectrophotometer “Hewlett Packard” GC 5890 Series II/MSD. Thin layer chromatography was carried out on plates Silufol UV 254, eluent benzene.

CONCLUSIONS

One stage method of 1-adamantyl phenyl ethers production was developed, that enabled synthesis of target products with high yield for small time without use of a catalyst.

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