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BRIEF COMMUNICATIONS

Method of Synthesizing Adamantyl-Substituted Phenols Based on 1,3-Dehydroadamantane

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Abstract—The possibility of obtaining adamantyl-substituted phenols by the reaction of 1,3-dehydroadamantane with phenols in the presence of catalytic amounts of sulfuric acid was studied.

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Sterically hindered phenols and their derivatives are of practical interest as antioxidants possessing high efficiency, thermal stability, and hypotoxicity [1, 2]. The presence of an adamantyl fragment in the structure of such compounds makes it possible to strengthen essentially or to impart to them useful properties [3].

Existing methods of synthesizing such compounds are based on the reactions of appropriate phenols with hydroxy- [4–6] or haloadamantanes [7, 8]. These reactions are carried out at elevated temperatures (up to 200°C) within a long time (up to 16 h) in the presence of catalysts that complicates their application in preparative or industrial syntheses. In this connection the development of new effective methods for the synthesis of adamantyl-substituted phenols is of interest.

The present work is devoted to the development of a new method of synthesizing such compounds, which is based on the reaction of 1,3-dehydroadamantane (1,3-DHA) with phenols in the presence of catalytic amounts of sulfuric acid.

It was found by chromato-mass-spectrometry methods that 1,3-dehydroadamantane (**I**) in the presence of catalytic amounts of sulfuric acid readily reacts with phenol (**II**), pyrocatechol (**III**), resorcine (**IV**), and hydroquinone (**V**) with an appreciable exothermic effect according to the Scheme.

The reactions of 1,3-DHA (**I**) with compounds (**II**–**V**) were carried out in an inert solvent at a 1,5-2-fold molar excess of a corresponding phenol in the atmosphere of dry nitrogen at 30–35°C within 20–30 min.

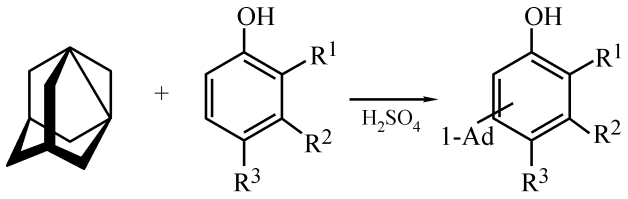
Products of reactions (**VI**)–(**IX**) were isolated by a recrystallization from alcohol. The composition, structure, and individuality of the compounds were proved by the methods of chromato-mass-spectrometry, thin-layer chromatography, and elemental analysis.

In the absence of a catalyst the main products of the reaction are not adamantly-substituted phenols, but phenyladamantyl ethers. Similar facts were observed in the case of 1,3-DHA reactions with phenol [9].

EXPERIMENTAL

Mass spectra were recorded on a Hewlett Packard GC 5890 Series, II/MSD 5972 Series chromato-mass-spectrophotometer. The thin-layer chromatography experiments were carried out on Silufol UV 254 plates with benzene as an eluent.

Scheme.



I **II–V** **VI–IX**

Here $R^1 = R^2 = R^3 = H$ (**II**), (**VI**); $R^1 = OH$, $R^2 = R^3 = H$ (**III**), (**VII**); $R^1 = R^3 = H$, $R^2 = OH$ (**IV**), (**VIII**); $R^1 = R^2 = H$, $R^3 = OH$ (**V**), (**IX**).

4-(Adamant-1-yl)phenol (VI). To 4.20 g (0.045 mol) of phenol in 10 ml of diethyl ether a solution of 4 g (0.0298 mol) of freshly distilled 1,3-dehydroadamantane in 20 ml of diethyl ether was added dropwise in the presence of 0.03 g (0.0003 mol) of sulfuric acid in the atmosphere of dry nitrogen at room temperature. The mixture was exposed for 20 min at 30–35°C, the solvent was evaporated, the precipitate was washed out with hot water, and recrystallized from alcohol. Yield 6.45 g (94%) of a solid product, mp 185–187°C (published 186–187°C [8]). Found (%): C 83.94, H 9.06. $C_{16}H_{20}O$. Calculated (%): C 84.76, H 8.83. Mass spectrum, I_{rel}, %: 228 (M^+ 100%), 171 ($[M\text{-}C_4H_9]^+$, 94%), 134 (Ad^+, 30%).

4-(Adamant-1-yl)pyrocatechol (VII). It was synthesized analogously to compound **VI** from 4.95 g (0.045 mol) of 2-hydroxyphenol (pyrocatechol) and 4 g (0.0298 mol) of 1,3-dehydroadamantane. Yield 5.9 g (81%) of a solid product, mp 143–144°C (published 143–144°C [5]). Found (%): C 78.51, H 8.19. $C_{16}H_{20}O_2$. Calculated (%): C 78.65, H 8.25. Mass spectrum, I_{rel}, %: 244 (M^+ 83%), 187 ($[M\text{-}C_4H_9]^+$, 100%), 150 ($[M\text{-}94]^+$, 26%).

4-(Adamant-1-yl)resorcin (VIII). It was synthesized analogously to compound **VI** from 4.95 g (0.045 mol) of 3-hydroxyphenol (resorcin) and 4 g (0.0298 mol) of 1,3-dehydroadamantane. Yield 6.40 g (88%) of a solid product, mp 234–235°C (published 235–236°C [10]). Found (%): C 78.78, H 8.14. $C_{16}H_{20}O_2$. Calculated (%): C 78.65, H 8.25. Mass spectrum, I_{rel}, %: 244 (M^+ 83%), 187 ($[M\text{-}C_4H_9]^+$, 100%), 150 ($[M\text{-}94]^+$, 23,7%).

4-(Adamant-1-yl)hydroquinone (IX). It was synthesized analogously to compound (**VI**) from 2 4.95 g (0.045 mol) of 4-hydroxyphenol (hydroquinone) and 4 g (0.0298 mol) of 1,3-dehydroadamantane. Yield 6.14 g (84%) of a solid product, mp 212°C (published 210–212°C [7]). Found (%): C 78.59, H 8.11. $C_{16}H_{20}O_2$. Calculated (%): C 78.65, H 8.25. Mass spectrum, I_{rel}, %: 244 (M^+ 83%), 187 ($[M\text{-}C_4H_9]^+$, 100%), 150 ($[M\text{-}94]^+$, 24%).

CONCLUSION

A convenient preparative method of synthesizing adamantylated phenols was developed, which allows these compounds to be obtained at low temperatures (30–35°C) within a short time.

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