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CHEMISTRY

Alkylation of Aluminum Phenolate with Unsaturated Monoterpenes

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Useful properties of natural phenolic compounds with terpene substituents (their physiological and antioxidant activity) promote the development of strategies for the synthesis of their analogues and novel derivatives.

Terpenoids are prone to different skeleton rearrangements; therefore, the selectivity of alkylation of aromatic compounds with terpenes is the main condition of the process [1–4].

The use of aluminum alkoxides as catalysts is known to ensure the selective alkylation of phenols. In particular, the alkylation of different phenols with camphene leads to *o*-isobornylphenols in 85% and higher yields [5, 6]. Regio- and stereoselectivity of this process is explained by the fact that the alkylation proceeds intramolecularly within coordination sphere of aluminum [7].

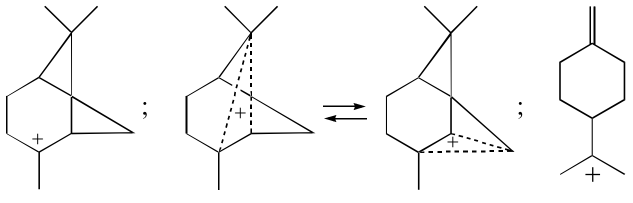
The methods of preparation of aluminum acylates and alkoxides derived from higher fatty acids and aluminum alkoxides of terpene alcohols by the reaction of corresponding acids or alcohols with aluminum or aluminum isopropoxide are known [8–10].

We have found recently that the high reactivity of aluminum phenoxide favors its alkylation with terpene alcohols with high selectivity to give terpenophenols of different structural types [11].

In this work, we have studied the alkylation of aluminum phenoxide with bicyclic unsaturated terpenes (camphene, β-pinene) as a development of concept of reaction realization in organized medium.

We found that the reaction of aluminum phenoxide with camphene at 100°C leads to phenyl isobornyl ether (**I**) (77%, Scheme 1) as a main product. The yield of *o*-alkylated phenol with isobornyl structure of terpene substituent (**IIa**) was 23%. When temperature was increased to 160°C, the reaction lasted for 2 h to form mainly C-alkylation products (95%) with predominance of phenol **IIa** (73%). The yield of O-alkylation product **I** was only 5%.

A specific feature of alkylation of aluminum phenoxide with β-pinene under the same conditions (160°C, 2 h) is a high yield of chroman-like products **III** and **IV** (37%). Moreover, the reaction also leads to *o*-isobornylphenol **IIa** (34%) and *o*-isocamphylphenol **IIb** (10%). *p*-Alkylated phenol (16%), which is not typical for the reactions of $(PhO)_3Al$, was also isolated from the mixture of products. The composition of the alkylation product mixture did not change when the reaction time increased to 6 h. In the reaction of aluminum phenoxide with β-pinene, the structure of the products is determined by carbocations **A**, **B**, and **C** resulting from β-pinene by the Wagner–Meerwein rearrangement and carbocation **D** of the *p*-menthane structure resulting from the opening of the strained four-membered ring of β-pinene. Initially formed carbocations **A**, **B**, and **C** have identical sterical possibilities for addition to aluminum phenoxide [13].



A **B** **C** **D**

All products were isolated by preparative column chromatography on silica gel (70/230μ, petroleum

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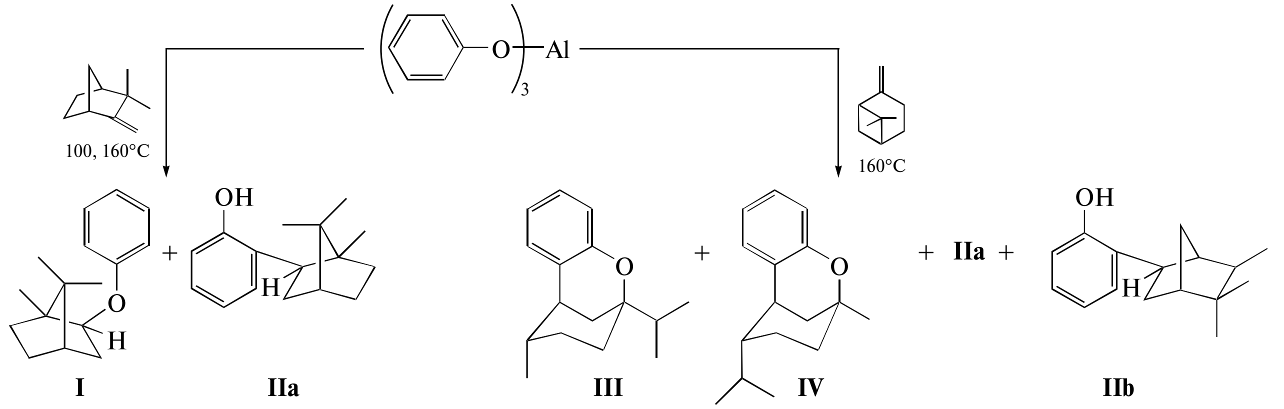

Scheme 1.

ether–Et_2O as an eluent). The structures of obtained compounds were established on the basis of ^1H and ^{13}C NMR data. Physicochemical constants and spectral characteristics of compounds **I–IV** agree well with those described earlier [7, 14].

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