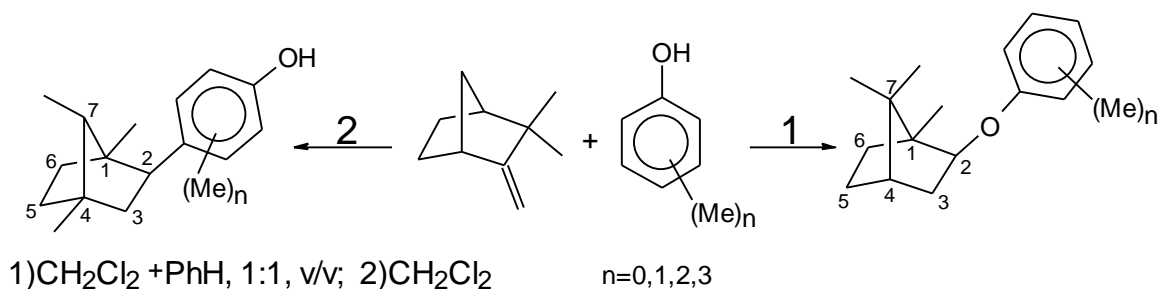


Alkylation of Phenol and its Methyl-Substituted Derivatives by Camphene on Wide-Pore Beta-Zeolite

V. V. Fomenko, D. V. Korchagina, N. F. Salakhutdinov and V. A. Barkhash

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences. 9, Lavrentiev ave., 630090 Novosibirsk 90; fomenko@nioch.nsc.ru

It is shown that alkylation of phenol, anisole, and their methyl-substituted derivatives by camphene on wide-pore beta-zeolite proceeds either as O-alkylation predominantly forming terpenylphenyl ethers with an isobornyl structure of the alicyclic residue (reaction 1, CH_2Cl_2 as a solvent) or as C-alkylation forming the corresponding terpenyl phenols and anisoles (reaction 2, 1:1 v/v mixture of benzene and CH_2Cl_2 as a solvent); the predominant route depends on the structure of substrate and the solvent used. In the latter products, the terpene fragment has an unusual structure: the methyl groups occupy the 1,4,7-positions of the alicyclic framework. In this case, high para-selectivity of alkylation of an aromatic reagent is observed.



It is noteworthy that the products with the 1,4,7-position of methyl groups in the terpene fragment are major products of this phenol alkylation reaction but were previously reported to be by-products in alkylation of alkyl-substituted benzenes and fatty aromatic alcohols by camphene.

The solvent effect on the reaction route is considered for the case of 2,6-dimethylphenol. We performed reactions in a methylene chloride medium, methylene chloride--benzene system, benzene, cyclohexane, and n-hexane. It was found that the dielectric permittivity of the solvent does not markedly affect the reaction route: the reactions in methylene chloride, cyclohexane, and n-hexane occur similarly, whereas in benzene no reaction takes place at all. The "form" of solvent molecules is not critical either: in benzene and cyclohexane the reactions proceed absolutely differently, whereas the results of reactions in cyclohexane and n-hexane are virtually identical. We can assume that the major route-determining factor is a competition between the pi-systems of the solvent and reagent molecules for the active centers of the catalyst, which are responsible for camphene protonation.

Alkylation of 2,3-dimethylphenol by camphene gave a new compound - diterpenylphenol, in which the alicyclic substituents have an unusual structure with the methyl groups occupying the 1,4,7-positions.