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## SHORT COMMUNICATIONS

**Rearrangement of Bornyl Phenyl Ether** 

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We previously studied rearrangement of isobornyl phenyl ether under catalysis by acids and aluminum phenoxide [1]. Comparison of the experimental data obtained in the reaction catalyzed by acids and in the presence of aluminum phenoxide led us to presume that in the first case the rearrangement follows mainly intermolecular mechanism, and in the second, intramolecular. As a result, high regio- and stereoselectivity of the process were rationalized by tandem Claisen and Wagner–Meerwein rearrangements occurring intramolecularly in the initially formed aluminum complex with isobornyl phenyl ether [1].

The alkylation of phenol with excess  $\beta$ -pinene in the presence of aluminum phenoxide afforded mainly optically active bornyl phenyl ether (**I**) and 2-bornylphenol (**IIc**) in approximately equal amounts (35–46 and 22–49%, respectively, depending on the reaction temperature) [2]. Our attempt to promote rearrangement of bornyl phenyl ether with the use of Al(OPh)<sub>3</sub> as catalyst, as in the rearrangement of isobornyl phenyl ether, was unsuccessful. We also failed to obtain phenol **IIc** by heating ether **I** in boiling methylene chloride in the presence of KSF montmorillonite.

Bornyl phenyl ether underwent rearrangement only in the presence of AlCl<sub>3</sub> or boron trifluoride-ether complex on heating to 100 and 160°C, respectively (see table). However, the rearrangement was accompanied by isomerization of the bornyl fragment. The reaction in the presence of AlCl<sub>3</sub> (100°C) afforded 2-isocamphylphenol (IIa) in 65% yield and a difficultly separable mixture of ortho- and para-substituted phenols IIa-IId and IIIa-IIId (30%) with different structures of the terpene substituent. When the reaction temperature was raised to 160°C, the yield of 2-isocamphylphenol (IIa) increased to 75%. The rearrangement in the presence of  $BF_3 \cdot Et_2O$  was less selective. In this case, 30% of 2-isocamphylphenol (IIa) and a mixture of 2- and 4-substituted phenols IIa-IId and IIIa-IIId were formed.

Our experimental data confirm intermolecular character of the rearrangement of ether **I**. The fact that no rearrangement occurred in the presence of  $Al(OPh)_3$ may be rationalized by steric factor. Coordination of bornyl phenyl ether to the aluminum atom in the catalyst leads to such orientation of the phenoxy group that the rearrangement becomes impossible.



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Realizangement of t	only pheny ener (1)				
Catalyst	Reaction time, h	Temperature, °C	Conversion, %	Yield, %	
				IIa	II + I
Al(OPh) <sub>3</sub>	49	160–180	0	_	-
KSF clay	56	CH <sub>2</sub> Cl <sub>2</sub> , reflux	0	_	-
AlCl <sub>3</sub>	2	160	95	78	22

100

160

Dearron company of horney linhany lithar (I)

To conclude, we have studied the rearrangement of phenvl bornvl ether in the presence of Al(OPh)<sub>3</sub>, AlCl<sub>3</sub>,  $BF_3 \cdot Et_2O$ , and KSF clay. No reaction occurs in the presence of Al(OPh)<sub>3</sub> and KSF clay, whereas the rearrangement in the presence of AlCl<sub>3</sub> and BF<sub>3</sub>·Et<sub>2</sub>O occurs intermolecularly, and it yields mainly 2-isocamphylphenol.

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General procedure. A mixture of 0.20 g of bornyl phenyl ether (I) and 0.02 g of  $BF_3 \cdot Et_2O$  or AlCl<sub>3</sub> was heated to 160 or 100°C, respectively, under argon in the absence of a solvent. When the reaction was complete, the mixture was cooled and dissolved in chloroform, the solution was passed through a thin layer of Al<sub>2</sub>O<sub>3</sub>, the solvent was removed under reduced pressure, and the residue was separated by column chromatography. The yields of compounds IIa-IId and IIIa-IIId thus isolated are given in table. Their structure was confirmed by NMR spectroscopy and by comparing with published data [1, 3].

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance II 300 spectrometer at 300.17 and 75.5 MHz, respectively, using CDCl<sub>3</sub> as solvent and reference (CHCl<sub>3</sub>,  $\delta$  7.26 ppm; CDCl<sub>3</sub>,  $\delta_{\rm C}$  76.90 ppm). The products were analyzed by GLC on a Shimadzu GC-2010AF chromatograph equipped with a flame ionization detector (HP-1 capillary column, 60 m× 0.25 mm, film thickness 0.25 µm; oven temperature programming from 100 to 240°C at a rate of 6 deg× min<sup>-1</sup>; carrier gas helium). The progress of reactions was monitored by TLC using Sorbfil plates; spots were

detected by treatment with a solution of vanillin in alcohol, followed by heating to 100-150°C, or by treatment with a solution of potassium permanganate (15 g of KMnO<sub>4</sub> in 300 ml H<sub>2</sub>O containing 0.5 ml of concentrated sulfuric acid). The products were isolated by column chromatography on silica gel (70-230 µm, Alfa Aesar); gradient elution with petroleum etherdiethyl ether with increasing fraction of the latter.

70

35

+ III

30

65

Commercial KSF montmorillonite (Acros Organics), AlCl<sub>3</sub> (Alfa Aesar), and phenol (Alfa Aesar) were used without additional purification; Al(OPh)<sub>3</sub> was generated in situ.

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AlCl<sub>3</sub>

 $BF_3 \cdot Et_2O$