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Note

Montmorillonite-catalysed regiospecific rearrangement of benzyl phenyl ether

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o-Benzylphenol has been obtained as the exclusive product in the rearrangement of benzyl phenyl ether in a clay environment.

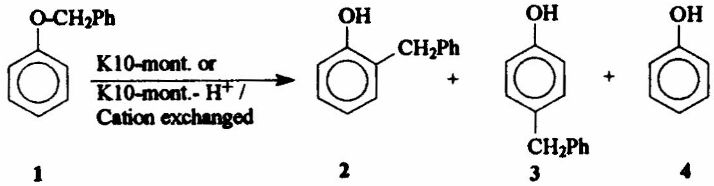
Benzyl phenyl ether has been found to be converted rapidly by aluminium bromide in chlorobenzene solution to a mixture of about 40% phenol, 55% *o*-benzylphenol and dichlorodiphenyl-methane[1]. Mere heating at 250°C of benzyl phenyl ether gives a mixture of *o*- and *p*-benzylphenols[2]. Photorearrangement of benzyl phenyl ether too results in a mixture of *o*- and *p*-benzylphen-ols[3].Contrary to these reports, we report herein the exclusive formation of *o*-benzylphenol **2** in the rearrangement of benzyl phenyl ether **1** (Scheme I) with K10-montmorillonite clay and acidic Al^{3+} cation-exchanged clays. It may be mentioned here that the preparation of *o*-benzylphenol by bezylation of phenol also results in a mixture of products[4].

Recently, clays and clay-based reagents have found extensive applications in organic synthesis. Acidic or cation-exchanged montmorillonite clays have been found to be efficient solid acid catalysts in a number of acid catalysed reactions[5].They enjoy advantages such as: (i) easy handling, (ii) recovery of catalyst, (iii) greater chemo/regioselectivity, etc. Our interest[6,7] in utilising clays for achieving selectivity and catalysts in organic reactions prompted us to study the rearrangement of benzyl phenyl ether. In these reactions, one gram of benzyl phenyl ether was thoroughly mixed with an equal or excess amount of either natural or H^+/cation-exchanged clays. The mixture was taken in a round-bottomed flask and placed in a water-bath for 3 to 12 hr. Thereafter, the mixture was worked-up and analysed using a Shimadzu LC-6A modular HPLC system [reverse phase column (ODS), UV detector] and methanol as the mobile phase. The percentage yield and product distribution of these various reactions are presented in Table I.

It can be seen from the table that when the reaction was carried out in the presence of natural clays, in addition to the *o*-benzylphenol, *p*-benzylphenol **3** and phenol **4** were also formed. Longer reaction periods increased yield of the *ortho*-isomer.

When the reaction was carried out in the presence of acidic or Al^{3+} cation-exchanged clays, *o*-benzylphenol was found to be the exclusive product and this was formed in 3 hr. This may be due to the greater acidity of H^+ or Al^{3+} exchanged clays. We are unable to account for the 2% formation of *para*-product in the case of Fe^{3+} exchanged clay. The lower yield of *o*-benzylphenol in the case of Mn^{2+}, Co^{2+} and Ni^{2+} exchanged clays can probably be due to low Bronsted acidity of Co^{2+}, Mn^{2+} and Ni^{2+} exchanged clays. On the contrary, high yield in the case of Cu^{2+} exchanged clay is due to its high activity and that the reactants are considered to be concentrated within 10 Å volume of the clay surface[8].

Thus, the present study highlights the utility of



Scheme I

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Table I — Percentage conversion and product distribution[a] in the rearrangement of benzyl phenyl ether 1

Catalyst	Reaction period (hr)	Conversion (%)	Yield (%)		
			o-Benzylphenol	*p*-Benzylphenol	Phenol
K10-montmorillonite	3	91	55	36	–
K10-montmorillonite*	3	90	78	2	10
K10-montmorillonite	6	93	61	25	7
K10-montmorillonite	9	95	77	–	18
K10-montmorillonite	12	100	100	–	–
K10-montmorillonite-H^+	3	100	100	–	–
K10-montmorillonite-Al^{3+}	3	100	100	–	–
K10-montmorillonite-Fe^{3+}	3	100	98	2	–
K10-montmorillonite-Co^{2+}	3	52	52	–	–
K10-montmorillonite-Co^{2+}	6	59	59	–	–
K10-montmorillonite-Mn^{2+}	3	60	40	5	15
K10-montmorillonite-Ni^{2+}	3	45	45	–	–
K10-montmorillonite-Ni^{2+}	6	51	51	–	–
K10-montmorillonite-Cu^{2+}	3	90	67	13	10

[a] Analysed by HPLC; error limit ±.

* Catalyst- substrate ratio 2:1.

acidic or cation-exchanged clays as the reagent of choice for the regiosoecific conversion of benzyl phenyl ether to *o*-benzylphenol, the optimum condition being the substrate to catalyst ratio 1:1, the reaction period being 3 hr.

Acknowledgement

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