Catalysis Letters 10 (1991) 211–214

Zeolite-catalyzed synthesis of 4-phenyl-1,3-dioxolanes from styrene oxide

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Received 17 September 1990; accepted 15 June 1991

Y, US-Y and ZSM-5 zeolites were used as suitable catalysts for the synthesis of 4-phenyl-1-1,3-dioxolanes from styrene oxide and aliphatic ketones. The results suggest that the diffusion factor as well as acidity influence the 1,3-dioxolane yield. The probable mechanism of the reaction is discussed.

Keywords: Acid catalysts; organic synthesis; zeolites; HY; HZSM-5; dioxolane

1. Introduction

So far the application of zeolites in organic synthesis is relatively underdeveloped especially when compared with the use of zeolites in hydrocarbon processing. Their activity associated with the presence of acid centers in the intracrystalline surface makes zeolites especially suitable for application as heterogeneous catalysts in both the liquid and gas phase, especially in the synthesis of many organic intermediates. One example is the rearrangement of epoxides to aldehydes. The use of even very low acidity titanium zeolites [1] is sufficient to isomerize styrene oxide or alkyl- or alkoxy-substituted styrene oxide to phenylacetaldehyde with selectivities higher than 90% at conversions of 90–100%. It is also known that different heterocyclic compounds are formed from epoxides of various structures with specific reagents. Epoxides with ketones form 2,3-dihydrofurans [2] in the presence of base, and dioxolanes [3,4] with anhydrous hydrogen fluoride or a BF_3-etherate complex.

We now report some preliminary observations on the reaction between styrene oxide and aliphatic ketones in the presence of zeolite catalysts which has led to the formation of 2,2-disubstituted-4-phenyl-1,3-dioxolanes.

2. Experimental

HY, HUSY (ultrastabilized) and HZSM-5 zeolites were used as catalysts. The zeolite composition in terms of framework oxide ratio SiO_2/Al_2O_3 was 2.5, 5.0

and 68.0, respectively. The zeolite samples were preheated at 300 °C for 3 h, immediately before use in the reaction. (Styrene oxide, acetone, methyl ethyl ketone, methyl izopropyl ketone and cyclohexanone were supplied by Fluka A.G.) For each experiment a fresh portion of the zeolite (1 g) was placed in a bulb and poured over with a ketone (in the proportion of 0.3 mole of ketone to 0.1 mole of styrene oxide). The zeolite suspension was stirred vigorously under reflux and styrene oxide was added dropwise over a period of an hour. The stirring was continued for 0.5 h and, after cooling, the zeolite catalyst was separated by filtration. The organic solution was distilled to give the desired product(s) as a mixture of isomers. The products were analysed by GLC using 3.5 m (0.04 m i.d.) column with 6% OV101 and 0.2% QF1 on Chromosorb W/HP AW-DMCS (80–100 mesh) and by 300 MHz ^{1}H NMR spectroscopy.

3. Results and discussion

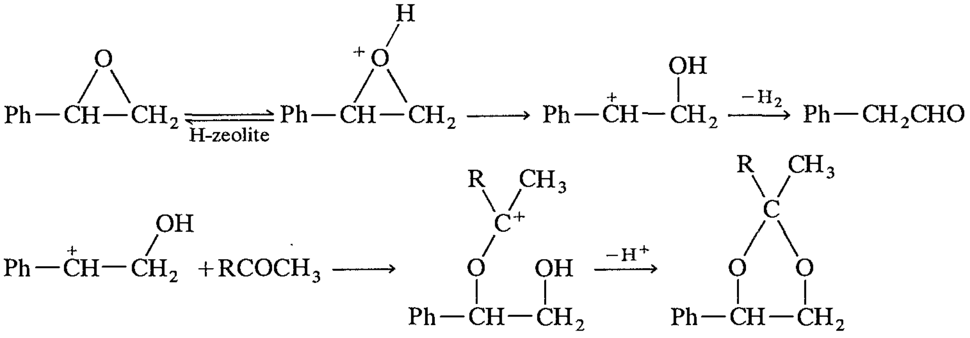
The reaction between styrene oxide and aliphatic ketone in the presence of H-form of zeolites proceeds smoothly, affording almost complete conversion of the epoxide (except for HY zeolite). The results are summarized in table 1. It is clear that 2,2-dialkylsubstituted-4-phenyl-1,3-dioxolanes and 2-phenyl-1,4-dioxaspiro [4,5] decane are synthesized in good yields. The 1,3-dioxolanes having two different alkyl substituents at the position 2, have *cis* and *trans* isomers (the stereochemistry of which was not determined). As shown in table 1, dioxolane yields depend on the type of zeolite used. Both, the structure and acidity of the zeolite seem to influence the yield. Paparatto found (temperature-programmed desorption data) [5] that styrene oxide was capable of entering into the straight channels of the pentasil zeolite (0.52–0.58 nm in diameter) and that the liquid phase isomerization of styrene oxide could be catalyzed by both external and internal acidic sites of the microporous solid. However, no correlation was found between the conversion of the styrene oxide and the zeolite acidity. Y zeolite containing internal cages (1.3 nm in diameter), the volume of which is higher than that of ZSM-5 channel, ought to facilitate the formation of dioxolane

Table 1
The styrene oxide conversion and dioxolane yield

Ketone	Zeolite	Styrene oxide conversion (%)	Dioxolane yield (%)
CH_3COCH_3	H-ZSM-5	> 99	11
CH_3COCH_3	H-Y	52	45
CH_3COCH_3	H-USY	> 99	56
$CH_3COCH_2CH_3$	H-USY	> 99	30
$CH_3COCH(CH_3)_2$	H-USY	> 99	15
Cyclohexanon	H-USY	> 99	44

product. It seems resonable to suggest that both the diffusion factors (efficiencies of diffusions from external to internal surfaces and within internal surfaces) as well as the total number of external sites influence the product yield. In contrast to acidic forms of Y and ZSM-5 zeolites neither NaX, NaY nor KX were active in the condensation reaction of aliphatic ketones with styrene oxide. Mineral acids (HCl and H_3PO_4) have not also catalyzed this reaction. No traces of dioxolane derivatives were observed. The main product was phenylacetaldehyde formed by the rearrangement of styrene oxide.

The mechanism suggested for phenyldioxolane formation is depicted below:



In acid catalyzed reaction preequilibrium between epoxide and its conjugated acid takes place [6]. Epoxide-ring opening can be performed under basic or acid conditions. Ring opening of an unsymmetrical epoxide with nucleophile occurs at either a less or more substituted site of the epoxy carbons (referred to as "normal" and "abnormal" opening, respectively). In the presence of acid zeolite catalysts the epoxy-ring opening reaction resulting in the benzylic carbocation formation [5] which can stabilize to phenylacetaldehyde. This "abnormal" ring opening reaction of epoxides is facilitated by a phenyl group (electron-withdrawing group) attached to the epoxide. We have found that benzylic carbocation can also react with aliphatic ketone closing the dioxolane ring. The dioxolane selectivity is strongly influenced by a structure of zeolite and ketone molecule and less by zeolite acidity.

References

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