

DOUBLE BOND MIGRATION OF ALLYL ETHERS OVER SOLID BASE CATALYSTS

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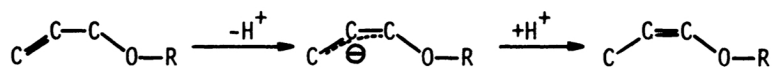
Double bond migrations of allyl ethers were carried out over various solid base catalysts. Magnesium oxide, CaO, SrO, and La₂O₃ exhibited high activities. High cis/trans ratios in the products suggest that the reaction proceed via cis- π -allylic anions as intermediates.

In contrast to extensive studies of catalytic double bond migration of alkenes over heterogeneous catalysts, little attentions were paid to those of unsaturated compounds containing hetero atoms. Although a number of works on double bond migrations of allyl ethers in homogeneous systems were studied,¹⁻⁴⁾ only KNH₂ supported on Al₂O₃ has been reported as heterogeneous catalyst for the reactions.⁵⁾ We wish to report high catalytic activities of certain solid base catalysts for double bond migration of allyl ethers to propenyl ethers.

An all glass static reactor was employed for carrying out the reaction. The starting material, which is included in Table 1, was placed in a quartz or Pyrex glass reactor, and pretreated in a vacuum at proper temperature. After pretreatment, reactor was sealed. Reactant was introduced through breakable seal by distillation into the reactor thermostated at liquid nitrogen temperature. The reaction was started by rapid melting of the reactant at reaction temperature. Products were analyzed by g. l. c. and NMR.

Results are summarized in Table 1. Magnesium oxide, CaO, SrO, and La₂O₃ exhibited activities for double bond migration of allyl ethyl ether, allyl isopropyl ether, allyl phenyl ether, and 2,5-dihydrofuran. 3-Methoxycyclohexene could not undergo isomerization even at 150°C. Besides the catalysts listed in Table 1, ZrO₂, ZnO, BaO and YO₂ showed low activities. Silica-alumina and Al₂O₃ which are active catalysts for double bond migration of alkenes were completely inactive. Acidic sites on these catalysts may strongly adsorb the reactant at a lone pair of oxygen atom, and become inactive. The reactivities of allyl ethers are in the order: allyl ethyl ether > allyl phenyl ether > 2,5-dihydrofuran > allyl isopropyl ether \gg 3-methoxycyclohexene.

The initial percentage of cis isomer in the produced propenyl ether was 100% in the case of allyl ethyl ether and allyl phenyl ether over CaO. This, combined with the result that active catalysts possess basic sites on the surfaces,⁶⁻⁹⁾ suggests that the reaction proceeds via cis- π -allylic anion which is formed by abstraction of an H⁺ from the reactant as shown below.



The anions may be stabilized in the form of cis by the presence of the counter cations of basic sites.

3-Methoxycyclohexene can not produce cis allylic anion as intermediate but trans allylic anion, which is supposed to be unstable on the surface. This interprets no reactivity of 3-methoxycyclohexene.

Table 1 Isomerization of Allyl Ethers ^{a)}

Reactant	Catalyst	Starting material	Pretreat. temp.(°C)	Weight of catalyst(mg)	Reaction temp.(°C)	Reaction time(min)	Conv. (%)
Allyl ethyl ether	MgO	Mg(OH) ₂	600	17	0	1	72
	CaO	Ca(OH) ₂	600	16	0	1	95
	La ₂ O ₃	La(OH) ₃	700	19	0	1	92
	SrO	SrCO ₃	1000	29	0	1	85
	Al ₂ O ₃	Al(OH) ₃	500	214	100	180	0
	SiO ₂ -Al ₂ O ₃		500	26	100	120	0
	Allyl phenyl ether	MgO	Mg(OH) ₂	600	17	0	1
CaO		Ca(OH) ₂	700	16	0	1	23
La ₂ O ₃		La(OH) ₃	700	16	0	1	17
SrO		SrCO ₃	1000	16	0	1	5
Allyl isopropyl ether	MgO	Mg(OH) ₂	700	146	110	180	19
	CaO	Ca(OH) ₂	500	437	110	180	54
	La ₂ O ₃	La(OH) ₃	700	109	105	180	4
	SrO	SrCO ₃	1000	92	105	180	trace
2,5-Dihydrofuran	MgO	Mg(OH) ₂	700	157	100	30	10
	CaO	Ca(OH) ₃	500	34	0	30	29
	La ₂ O ₃	La(OH) ₃	700	91	105	30	91
	SrO	SrCO ₃	1000	117	0	30	24
3-Methoxy-cyclohexene	MgO	Mg(OH) ₂	500	340	100	180	0
	CaO	Ca(OH) ₂	500	92	150	180	0

a) 0.1 ml of reactant was allowed to react

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