JOURNAL OF CATALYSIS 85, 457–465 (1984)

Double-Bond Migration of 2-Propenyl Ethers to 1-Propenyl Ethers over Solid Base Catalysts

HIROMI MATSUHASHI AND HIDESHI HATTORI

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Received May 3, 1983; revised August 26, 1983

Double-bond migration of ethyl 2-propenyl ether, phenyl 2-propenyl ether, isopropyl 2-propenyl ether, 2,5-dihydrofurane, and 3-methoxycyclohexene was carried out over several kinds of metal oxide catalysts to develop novel heterogeneous catalysts for the reactions and to elucidate the reaction mechanisms. Among the catalysts examined, CaO exhibited the highest activity, and La_2O_3, SrO, and MgO also showed high activities. Thorium oxide, ZrO_2, and Y_2O_3 were slightly active, but ZnO, Al_2O_3, and SiO_2–Al_2O_3 were completely inactive. In the double-bond migration of ethyl 2-propenyl ether and of phenyl 2-propenyl ether over CaO, the *cis* forms of ethyl 1-propenyl ether and phenyl 1-propenyl ether, respectively, were exclusively produced in the initial stage of the reaction. CNDO/2 calculations were done for the total energies of different conformers of ethyl 2-propenyl ether, and of *cis* and *trans* forms of the allylic anions. Based on the experimental results and CNDO/2 calculation, the reaction mechanisms are discussed. It is suggested that the reaction was initiated by an abstraction of an H^+ from allyl ethers by the basic site on catalyst to form *cis*-allylic anion as an intermediate.

INTRODUCTION

Base-catalyzed double-bond migration of alkenes and related compounds has been extensively studied in homogeneous systems (*1, 2*). With heterogeneous catalysts, however, studies has been done mostly on the reactions of alkenes, and only a few papers have reported double-bond migration of unsaturated compounds containing hetero atoms such as N and O.

Although *t*-BuOK (*3–5*), MeONa (*3*), $NaNH_2$ (*5*), NaH (*5*), allyl lithium (*6*), and $PdCl_2(PhCN)_2$ (*7*), were reported as a homogeneous catalyst for double-bond migration of 2-propenyl ethers, only KNH_2/Al_2O_3 (*8*), and Na/Al_2O_3 promoted by iron oxide (*9*) have been presented as heterogeneous catalysts. Thus, development of novel heterogeneous catalysts other than the catalysts mentioned above would be of importance.

In our previous paper (*10*), double-bond migration of 2-propenylamines was studied, and it was found that certain solid base catalysts such as MgO, CaO, and La_2O_3 exhibited high catalytic activities. Similarity of the catalyst system for double-bond migration of 2-propenylamines to that for 2-propenyl ethers in homogeneous system suggests that those heterogeneous catalysts which showed high activities for double-bond migration of 2-propenylamines might be active for double-bond migration of 2-propenyl ethers. In this study, the catalytic activities of several solid base catalysts including MgO, CaO, and La_2O_3 were examined for double-bond migration of 2-propenyl ethers, and the reaction mechanisms are discussed on the basis of selectivity and CNDO/2 calculation for the intermediates.

EXPERIMENTAL METHODS

Reagent. Ethyl 2-propenyl ether was obtained from Eastman Organic Chemicals. 3-Methoxycyclohexene was obtained from Chemical Procurement Laboratories. 2,5-Dihydrofuran and phenyl 2-propenyl ether were purchased from Tokyo Kasei Kogyo Company Ltd. Isopropyl 2-propenyl ether was prepared from 2-propenyl chloride, isopropylalcohol, and sodium metal by the

0021-9517/84 $3.00

Williamson synthesis. All reagents were purified by repeated freeze and thaw technique followed by passage through 3A molecular sieves.

Catalyst. The MgO, CaO, SrO, and BaO catalysts were prepared from $Mg(OH)_2$ (Kanto Chemical Co.), $Ca(OH)_2$ (Kanto Chemical Co.), $SrCO_3$ (E, Merck Darmstadt), and BaO (E. Merck Darmstadt) by thermal decomposition in a vacuum at proper temperatures. The La_2O_3 catalyst was obtained by thermal decomposition of $La(OH)_3$ at 700°C in a vacuum. Lanthanum hydroxide was prepared by hydrolysis of an aqueous solution of $La(NO_3)_3$ (Nakarai Chemicals Co.) with aqueous ammonia followed by washing with deionized water. The ZrO_2 catalyst was prepared from an aqueous solution of $ZrOCl_2$ by precipitation with aqueous ammonia followed by washing with deionized water, calcining at 500°C in air and outgassing at 500°C. The ThO_2 catalyst was prepared by thermal decomposition of $Th(NO_3)_4$ (Wako Pure Chemicals Industry Co.) at 500°C in air followed by outgassing at 500°C. The ZnO catalyst was prepared from an aqueous solution of $ZnCl_2$ by precipitation with aqueous ammonia followed by washing, calcining at 500°C in air, and outgassing at 500°C. The Y_2O_3 catalyst was prepared from an aqueous solution of $Y(NO_3)_3$ by precipitation with aqueous ammonia followed by washing, drying at 120°C, and outgassing at 700°C. The silica-alumina catalyst (Nikki Chemical Co. Type SA-N) and the alumina catalyst (Nishio Industry, Type AE-11) were commercially available.

Reaction procedures. An all-glass static reactor was employed for carrying out the reaction. Catalysts were placed in a quartz or Pyrex glass reactor, whose volume was ca. 20 ml, and were outgassed at proper temperatures for 3 h. Reactants were introduced through a 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 gas chromatography. A 3-m column packed with VZ-7 was operated at 45°C for analysis of the products of the reaction of ethyl 2-propenyl ether. For separation of *cis*- and *trans*-1-propenyl ethyl ether, a 5-m column packed with benzylcyanide and $AgNO_3$ mounted on Uniport C was used at 40°C. For analysis of the products of the reactions of 2,5-dihydrofuran and 3-methoxycyclohexene, a 10-m column packed with PEG 1500 on Uniport B was used at 80°C. For analysis of the products of the reaction of phenyl 2-propenyl ether, a 3-m column packed with DEGS mounted on Uniport B was operated at 100°C. All columns were of Cu-tubing, 4 mm o.d. and all column packings were purchased from Gasukuro Kogyo Company Ltd. Reaction products were also subjected to ^1H NMR and LGC–mass spectrometric analyses for identification.

CNDO/2 calculation. CNDO/2 calculations with original parameterization were done for the total energies of *s-trans* and *s-cis* forms of ethyl 2-propenyl ether, and of *trans*- and *cis*-allyl ethyl ether anions. In calculation, minimization of the total energy was done by varying the C—H bond lengths on $C^{(1)}$, $C^{(2)}$, and $C^{(3)}$, the C—C bond lengths of $C^{(1)}—C^{(2)}$, and $C^{(2)}—C^{(3)}$, the bond length of $C^{(3)}—O$, and the angle of $O—C_2H_5$ around the $C^{(3)}—O$ axis. In the case of the allylic anions, calculation was done both for a free anion and for the ion-pair in which the Mg^{2+} ion was placed 2.2 Å below the allyl plane and was moved parallel to the plane. The electron densities of carbon atoms 1, 2, and 3 were also calculated for the *trans*- and *cis*-allylic anions.

All calculations were done by use of the HITAC M-200H of Hokkaido University.

RESULTS

The reactions proceeded cleanly; no reactions other than double-bond migration were appreciable over the catalysts examined in this study. The results of the reactions of the various ethers are summarized in Table 1. The MgO, CaO, SrO, and La_2O_3

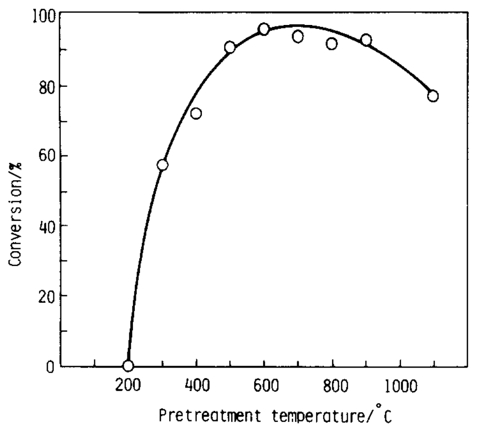


FIG. 1. Variation of the conversion of ethyl 2-propenyl ether over CaO as a function of the outgassing temperature of the catalyst. Reaction temperature, 0°C; reaction time, 1 min; catalyst weight, 16 mg; reactant, 0.1 ml.

catalysts exhibited activities for double-bond migrations of ethyl 2-propenyl ether, phenyl 2-propenyl ether, isopropyl 2-propenyl ether, and 2,5-dihydrofuran. Of these catalysts, CaO exhibited the highest activity. 3-Methoxycyclohexene did not undergo isomerization even at 150°C. The ZrO_2, ZnO, BaO, and Y_2O_3 catalysts gave isomerized products, but these activities were very low as compared with those of the MgO, CaO, SrO, and La_2O_3 catalysts. The silica–alumina and the Al_2O_3 catalysts, which are active for double-bond migration of alkenes, showed no activity.

The reactivity of each ether toward double-bond isomerization was in the following order, though there were some exceptions depending on the catalyst:

Ethyl 2-propenyl ether > phenyl 2-propenyl ether > isopropyl 2-propenyl ether > 2,5-dihydrofuran ≫ 3-methoxycyclohexene.

The variation of the conversion in 1 min for the double-bond migration of ethyl 2-propenyl ether over the CaO catalyst as a function of the outgassing temperature of the catalyst is shown in Fig. 1. The catalyst became active when outgassed above 200°C and gave more than 90% conversion when outgassed in the temperature range 500–900°C.

The percentages of the *cis* isomers in the products are plotted against conversion in Fig. 2 for the reactions of ethyl 2-propenyl ether and of phenyl 2-propenyl ether over the CaO outgassed at 600°C. For both reactions, extrapolation to zero conversion gave 100% *cis* isomer. As the reactions proceeded, the value gradually approached to the equilibrium values, which were reported to be 57% *cis* for ethyl 1-propenyl ether (*11*) and about 65% *cis* for phenyl 1-propenyl ether (*4*).

The reaction of ethyl 2-propenyl ether was carried out in the presence of 50 Torr of D_2 or 50 Torr of perdeuterio benzene. In both cases, D atoms were not incorporated either into the reactant or into the product, though the reaction rate was retarded in the presence of perdeuterio benzene.

The CNDO/2 calculation for the total energy of ethyl 2-propenyl ether indicates that the most stable *s-cis* form and *s-trans* form are those shown in Fig. 3, where the molecular structures are drawn in perspective. In both forms, two H atoms on $C^{(1)}$, $C^{(1)}$, H atom on $C^{(2)}$, $C^{(2)}$, $C^{(3)}$, O, and one of the lone pair orbitals on O atom (not shown) are positioned on the same plane (*X*–*Y* plane). The *s-cis* form (I) is more stable

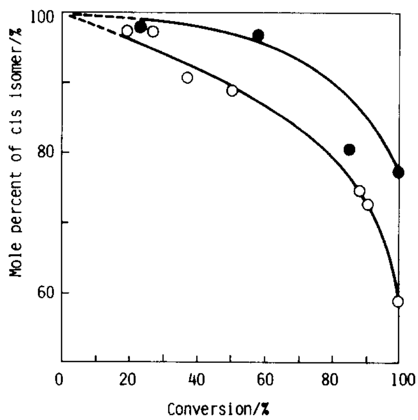
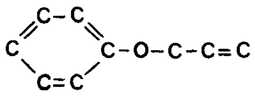
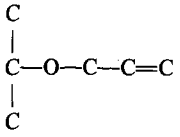
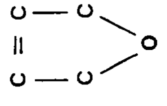
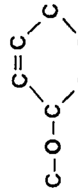


FIG. 2. Variations of the compositions of *cis* isomers in the products for double-bond migration of ethyl 2-propenyl ether (○), and of phenyl 2-propenyl ether (●) at 0°C.

TABLE 1

Isomerization of 2-Propenyl Ethers

Reactant	Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Catalyst weight (mg)	Pretreat. temp. (°C)	Reaction temp. (°C)	Reaction time (min)	Conversion (%)	Rate[a] ($mol \cdot min^{-1} \cdot m^{-2}$)
Ethyl 2-propenyl ether	MgO	135	17	600	0	1	72	2.8×10^{-4}
	CaO	72	16	600	0	1	95	7.3×10^{-4}
	SrO	10	29	1000	0	1	85	26×10^{-4}
C—C—O—C—C=C	BaO	0.2	85	800	0	5	1.6	1.7×10^{-4}
	La_2O_3	27	19	700	0	1	92	16×10^{-4}
	ThO_2	42	174	500	100	30	3.2	1.3×10^{-7}
	ZrO_2	65	92	500	100	30	2.3	1.1×10^{-7}
	Y_2O_3	50	20	700	0	5	<0.1	$<1.8 \times 10^{-7}$
	ZnO	3	56	400	117	60	0	0
	Al_2O_3	147	214	500	100	180	0	0
	SiO_2–Al_2O_3	445	29	500	100	120	0	0
Phenyl 2-propenyl ether	MgO	135	17	600	0	1	26	0.8×10^{-4}
	CaO	52	16	700	0	1	23	2.0×10^{-4}
	SrO	10	16	1000	0	1	5	2.3×10^{-4}
	La_2O_3	27	16	700	0	1	17	2.9×10^{-4}
Isopropyl 2-propenyl ether	MgO	117	146	700	110	180	19	4.9×10^{-8}
	CaO	52	437	500	110	180	54	11×10^{-8}
 $\underset{\underset{\displaystyle C}{\vert}}{\overset{\overset{\displaystyle C}{\vert}}{C}}$—O—C—C=C	SrO	10	92	1000	105	180	<0.1	$<0.5 \times 10^{-8}$
	La_2O_3	27	109	700	105	180	4	6.0×10^{-8}

2,5-Dihydrofuran 	MgO	135	157	700	100	30	10	0.2×10^{-6}
	CaO	71	34	500	0	30	29	5.4×10^{-6}
	SrO	10	117	1000	0	30	24	9.2×10^{-6}
	La_2O_3	27	91	700	100	30	91	17×10^{-6}
3-Methoxycyclohexene 	MgO	145	340	500	100	180	0	0
	CaO	71	92	500	150	180	0	0

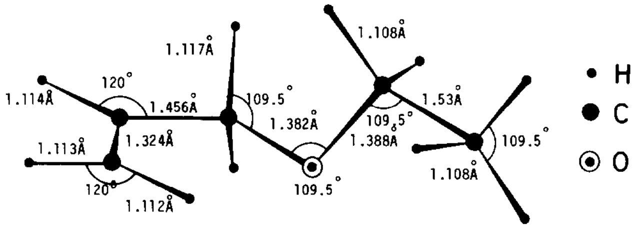
[a] Average rates in the reaction time indicated in this table.

than the *s-trans* form (II) by 2.43 kcal/mol. For a free anion, the most stable *cis*-allylic anion and *trans*-allylic anions are shown in Fig. 4. In both forms, two H atoms on $C^{(1)}$, $C^{(1)}$, the H atom on $C^{(2)}$, $C^{(2)}$, $C^{(3)}$, the H atom on $C^{(3)}$, O and one of the lone pair orbitals on the O atom are on the same plane ($X-Y$ plane). The *trans*-allylic anion (IV) is more stable than the *cis*-allylic anion (III) by 0.74 kcal/mol. When the Mg^{2+} ion is placed 2.2 Å below the allyl plane and moved parallel to the allyl plane ($X-Y$ plane), the total energy of the allylic anions becomes a function of the position of the Mg^{2+} ion. The region in which the Mg^{2+} ion was moved is shown in the shaded area in Fig. 5. The variations of the total energies of *cis*- and *trans*-allyl ethyl ether anions as a function of the position of the Mg^{2+} ion are shown in Figs. 6 and 7, respectively. For both anions, the total energies became minimized when the Mg^{2+} ion was placed at $(x, y, z) = (0.65, 0.25, -2.2)$. In the most stable state, the *cis*-allylic anion was more stable than the *trans*-allylic anion by 2.57 kcal/mol.

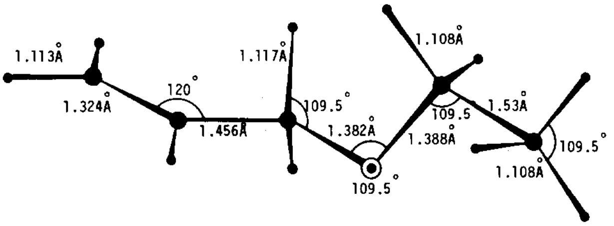
The electron densities of the carbon atoms of *cis*- and *trans*-allylic anions were also calculated. Those of carbon atoms 1, 2, and 3 were 4.1803, 3.9144, and 4.3331, respectively, for the *cis*-allylic anion, and were 4.1872, 3.9111, and 4.3386, respectively, for the *trans*-allylic anion. For both *cis*- and *trans*-allylic anions, the electron density was the highest on the terminal carbon atoms.

DISCUSSION

The catalysts which showed activities for double-bond migration of 2-propenyl ethers were MgO, CaO, SrO, and La_2O_3, and it was observed that all these catalysts possessed basic sites on the surfaces. A high *cis*/*trans* ratio in the product, which is usually observed for the homogeneous base-catalyzed reaction, was also observed for the heterogeneous reaction in this study. Therefore, it is concluded that double-bond



(I) s-cis-1-propenyl ethyl ether

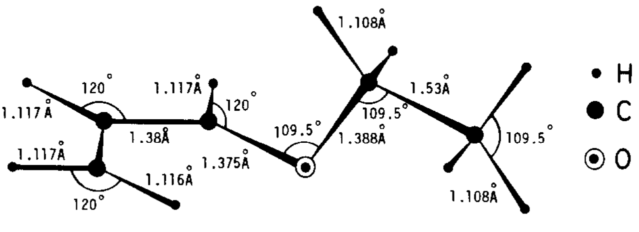


(II) s-trans-2-propenyl ethyl ether

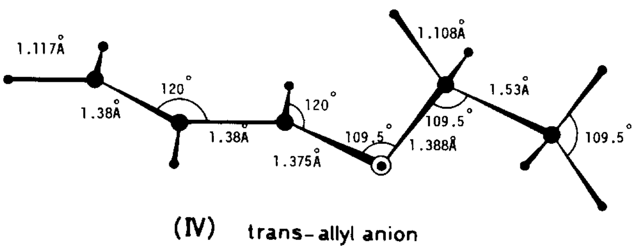
FIG. 3. The structures of the most stable *s-cis* and *s-trans* forms of ethyl 2-propenyl ether.

migration over the MgO, CaO, SrO, and La_2O_3 catalysts is a base-catalyzed reaction and that the active sites on these catalysts are basic sites.

No activities were observed for the SiO_2–Al_2O_3 catalyst, probably because the acidic sites on the surface strongly adsorb the reactant by the lone pair on the O atom. Although it has been suggested that double-bond migration of alkenes over Al_2O_3 is a base-catalyzed reaction (*12*), ethyl 2-propenyl ether did not undergo any reaction over Al_2O_3. Since it is supposed that the basic sites on the alumina surface are adjacent to exposed Al^{3+} ions which act as strong Lewis acid, the Al^{3+}–O^{2-} pair sites



(III) cis-allyl anion



(IV) trans-allyl anion

FIG. 4. The structures of the most stable *cis* and *trans* forms of the allylic anions.

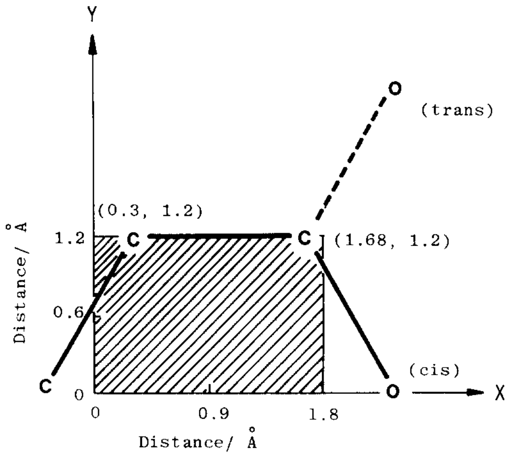


FIG. 5. Region where the Mg^{2+} ion was moved parallel to the allyl plane of *cis* and *trans* forms of allylic anions for CNDO/2 calculation.

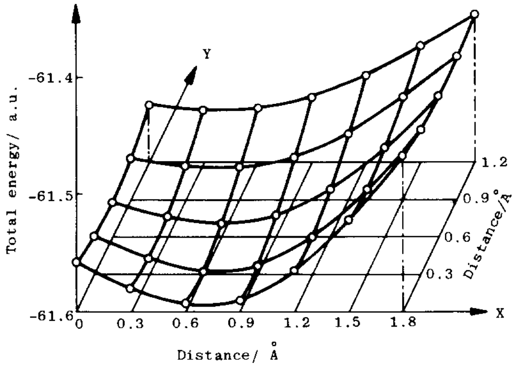


FIG. 6. Variation of total energy of the *trans*-allylic anion as a function of the position of the Mg^{2+} ion. Minimum energy $(X, Y) = (0.65, 0.25)$.

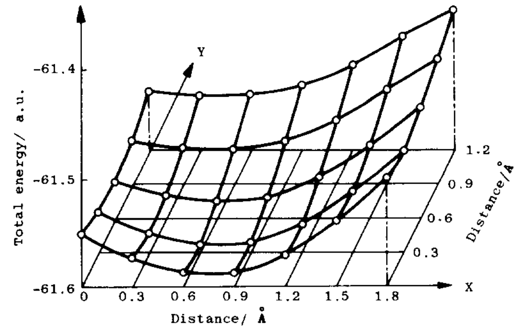


FIG. 7. Variation of total energy of the *cis*-allylic anion as a function of the position of the Mg^{2+} ion. Minimum energy $(X, Y) = (0.65, 0.25)$.

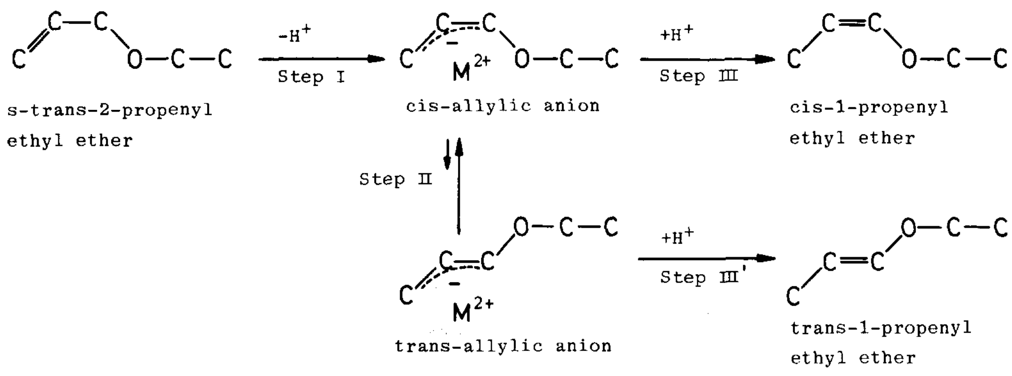
might adsorb the reactant by the O atom rather than abstract an H^+ from the reactant.

The low activities of the ZrO_2, ZnO, and Y_2O_3 catalysts were similar to low activities of these catalysts for butene isomerization as compared with the MgO, CaO, SrO, and La_2O_3 catalysts. Probably the basic sites of the former catalysts are not as strong as those of the latter catalysts.

To draw a reaction scheme, it appears important to take into account the conformation of the reactant. In some cases, the conformation of the reactant is reflected in the geometry of the product (*12, 14*). The CNDO/2 calculation of ethyl 2-propenyl ether suggests that the *s-cis* form is more stable than the *s-trans* form. The energy difference, 2.43 kcal/mol, corresponds to the composition of 98.9% *s-cis* form and 1.1% *s-trans* form at 0°C.

The *s-cis* form and *s-trans* form of ethyl 2-propenyl ether will yield a *cis*-allylic anion and a *trans*-allylic anion, respectively. If the interconversion between the *cis*-allylic anion and the *trans*-allylic anion is slow, the produced ethyl 1-propenyl ether would consist of 98.9% *cis* isomer and 1.1% *trans* isomer. On the other hand, if the interconversion is very fast, the *cis*- and *trans*-allylic anions would reach equilibrium on the surface, and the composition of ethyl 1-propenyl ether would reflect the equilibrated composition of the anions on the surface. Provided that the energy difference between the *cis*-allylic anion and the *trans*-allylic anion on the surface is 2.54 kcal/mol as calculated by the CNDO/2 method, the equilibrated composition at 0°C is 99.1% *cis*-allylic anion and 0.9% *trans*-allylic anion.

In both the reactant and the allylic anion, *cis* forms are thermodynamically more stable. The observed composition was close to 100% *cis*-1-propenyl ethyl ether and *cis*-1-propenyl phenyl ether. It is, however, uncertain as to whether the interconversion between *cis*- and *trans*-allylic anion is fast or slow.



SCHEME I. Reaction scheme for double-bond migration of ethyl 2-propenyl ether.

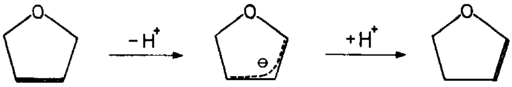
The double-bond migration of ethyl 2-propenyl ether can probably be illustrated by Scheme I.

In the allylic anion, the electron density is the highest on the terminal carbon ($C^{(3)}$). Therefore, the attack of H^+ at the carbon atom 1 would be easier than that of carbon atom 3, and the reverse step of step I should be slower than steps III and III′.

No D atoms were incorporated into the reactant or product when the reaction was carried out in the presence of D_2 or perdeuterated benzene. This suggests that the reaction involves intramolecular H transfer during isomerization.

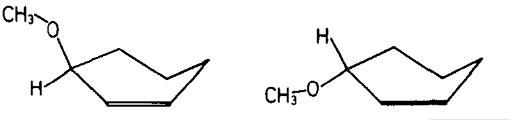
The reaction schemes for the double-bond migration of phenyl 2-propenyl ether and of isopropyl 2-propenyl ether appear to be similar to that of ethyl 2-propenyl ether. For the double-bond migration of 2,5-dihydrofuran, as the geometrical structure is rigid, the reaction proceeds via the *cis*-allylic intermediate as illustrated by Scheme II.

Failure of 3-methoxycyclohexene to undergo double-bond migration was also observed in the reaction with homogeneous



SCHEME II. Reaction scheme for double-bond migration of 2,5-dihydrofurane.

catalysts. In the homogeneous reactions, this has been explained as being due to the fact that the molecule contains only a *trans*-allyl ether group and is incapable of forming a *cis*-allylic anion (*2*). An alternative explanation would be as follows. Since the reaction is to be initiated by an abstraction of an allylic H, 3-methoxycyclohexene should be adsorbed on the surface in such a direction that the allylic H is toward the surface. Consequently, the O atom should be off the surface as illustrated below (**I**).



(I) (II)

The interaction between the O atom and the surface is considered to be strong. The adsorbed state (**II**) may be more stable and most of the adsorbed species may be in a form (**II**), which is unable to undergo double-bond migration.

Finally, importance of the roles of metal cations in base-catalyzed reactions should be noted. As calculated by the CNDO/2 method, the anionic intermediates are stabilized to a great extent and the degrees of the stabilization vary with the position of metal cations to the anionic intermediates. Same situation has been reported for butene isomerization, where the presence of alkali metal cation lower the total energy of the allylic carbanion intermediate (*15*). Therefore, it is suggested that in considering the nature and structure of the active sites for base-catalyzed reactions, relative positions of basic site (O^{2-}) and metal cation should be taken into account.

REFERENCES

1. Pines, H., and Stalick, Y. M., "Base-Catalyzed Reactions of Hydrocarbon and Related Compounds." Academic Press, New York, 1977.
2. Hubert, A. J., and Reimlinger, H., *Synthesis* 97 (1969).
3. Prosser, T. J., *J. Amer. Chem. Soc.* **83,** 1701 (1961).
4. Price, C. C., and Snyder, W. H., *J. Amer. Chem. Soc.* **83,** 1773 (1961).
5. Caubere, P., and Hochy, M. F., *Bull. Soc. Chim. Fr.* 459 (1968).
6. Courtois, G., and Miginiac, L., *Tetrahedron Lett.* 2411 (1972).
7. Galbon, P., and Scheinmann, F., *J. Chem. Soc. Perkin Trans. 2,* **4,** 366 (1972).
8. Hubert, A. J., Georis, A., Warin, R., and Teyssie, P., *J. Chem. Soc. Perkin Trans. 2,* **4,** 366 (1972).
9. O'Grady, T. M., Wennerberg, A. N., U.S. Pat. 3257415 (1966).
10. Hattori, A., Hattori, H., and Tanabe, K., *J. Catal.* **65,** 245 (1980).
11. Okuyama, T., Fueno, T., and Furukawa, J., *Tetrahedron* **25,** 5409 (1969).
12. Lambardo, E. A., Conner, W. C., Jr., Madon, R. J., Hall, W. K., Kharlamov, V. V., and Minachev, Kh. M., *J. Catal.* **53,** 135 (1978).
13. Imizu, Y., Hattori, H., and Tanabe, K., *J. Catal.* **56,** 303 (1979).
14. Tanaka, Y., Imizu, Y., Hattori, H., and Tanabe, K., "Proceedings, 7th International Congress on Catalysis, 1980 Tokyo," p. 1254. 1981.
15. Grabowski, W., Misono, M., and Yoneda, Y., *J. Catal.* **47,** 55 (1977).