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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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Base Catalyzed Isomerizations of Allyl Ethers to 1-Propenyl Ethers Using Mixed Alkali Systems

J. V. Crivello[a]; S. Kaur[a]
[a] Department of Chemistry, Rensselaer Polytechnic Institute Troy, New York

To cite this Article Crivello, J. V. and Kaur, S.(1998) 'Base Catalyzed Isomerizations of Allyl Ethers to 1-Propenyl Ethers Using Mixed Alkali Systems', Journal of Macromolecular Science, Part A, 35: 3, 411 — 426

To link to this Article: DOI: 10.1080/10601329808001986

URL: http://dx.doi.org/10.1080/10601329808001986

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J.M.S.—PURE APPL. CHEM., A35(3), pp. 411–426 (1998)

BASE CATALYZED ISOMERIZATIONS OF ALLYL ETHERS TO 1-PROPENYL ETHERS USING MIXED ALKALI SYSTEMS

J. V. Crivello* and Sarjit Kaur †
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

Key Words: 1-Propenyl Ethers, Allyl Ethers, Isomerization, Mixed Alkali Catalysts

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ABSTRACT

Allyl ethers were successfully isomerized to 1-propenyl ethers using the strong inorganic bases CsOH or KOH/CaO as catalysts in the absence of solvents. Both catalyst systems required elevated temperatures and, of the two systems, KOH/CaO is more efficient and cost effective. Using KOH/CaO and conducting reactions at ~200°C for 2-3 hours gave up to 93% isomerization to the 1-propenyl ether. Under similar conditions, no isomerization occurred when either KOH or CaO were used alone. Attempted isomerizations of 2-butenyl ethers to 1-butenyl ethers, were unsuccessful due to a side reaction that results in the elimination of butadiene from the starting material under the basic conditions.

INTRODUCTION

In this laboratory, we have been investigating the development of new, highly reactive monomers which can be employed in photoinitiated cationic

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†Current address: Department of Chemistry, Vassar College, Poughkeepsie, NY 12601.

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polymerizations [1]. The primary motivation for this work derives from the increasing utility of these polymerizations in rapid, high speed industrial processes such as in the application and cure of protective and decorative coatings and in printing inks together with the need to meet the increasing environmental restrictions on these same processes.

Photoinitiated cationic processes can be considered to take place by the generalized four-step mechanism depicted in Scheme 1 [2].

Scheme 1

$$P \xrightarrow{h\nu} H^+X^- \quad (1)$$

$$H^+X^- + M \longrightarrow HM^+X^- \quad (2)$$

$$HM^+X^- + nM \longrightarrow H\text{-}(M)_nM^+X^- \quad (3)$$

$$H\text{-}(M)_nM^+X^- + B^- \longrightarrow H\text{-}(M)_nMB + X^- \quad (4)$$

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In Scheme 1, it is important to note that the first step (Equation 1) is the only step involving the use of light. Photolysis of an onium salt photoinitiator, P, generates a strong Brønsted acid, H^+X-, which in the second step (Equation 2) interacts with the monomer to give the cation $H\text{-}M^+$. In the third step (Equation 3), the polymer undergoes chain growth by the sequential addition of new monomer molecules. In the absence of terminating species, the cationic polymerization, once initiated, will proceed until all the monomer is consumed. However, in practice, adventitious traces of bases, B-, are generally present which eventually terminate the polymerization (Equation 4).

In Scheme 1, the overall rate of the polymerization will be controlled by the slowest step. In contemplating means by which the polymerization can be accelerated it is important to identify the slowest step and to consider ways that it may be optimized. Typical photoinitiators for cationic polymerizations are diaryliodonium and triarylsulfonium salts. These photoinitiators are highly photosensitive ($\Phi \simeq 0.7$) and liberate very strong protonic acids (i.e. superacids) on photolysis [3]. Thus, the only way in which Equation 1 can be further optimized is to increase the quantum yield of the photoinitiator. Given the already high quantum yield of these photoinitiators, further substantial increases are neither straightforward nor likely.

Superacids initiate cationic polymerizations by direct protonation of the monomer (Equation 2) with nearly 100% efficiency. For many photopolymerizations, the propagation reaction shown in Equation 3 is the rate determining process. For any given initiator, the rate of the polymerization is controlled by the reactivity of the monomer with the growing chain end. Hence, it is important to optimize the reactivity of the monomer to achieve the highest rates of photoinitiated cationic polymerization.

Among the most reactive monomers known in cationic polymerization are vinyl (i.e. enol) ethers [4]. Typically, the polymerizations of such monomers are characterized by a high exothermicity and, for this reason, are commonly conducted at temperatures as low as -100°C in solvents which boil at these temperatures. Vinyl ethers are prepared by the base catalyzed condensation of alcohols with acetylene under high pressure. This synthesis is not well suited for the preparation of multifunctional monomers which are the mainstay of UV cure technology. Consequently, such monomers are expensive and the availability of different types of such multifunctional monomers is severely limited. For these reasons, we have been attempting to find alternative monomers with similar reactivities and properties.

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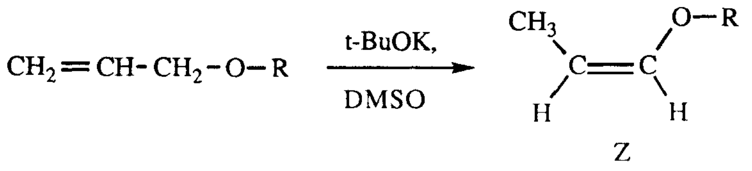
In recent publications, [5, 6, 7, 8] we have reported that 1-propenyl and 1-butenyl ethers are additional classes of reactive enol ether monomers that undergo rapid, efficient cationic photopolymerizations in the presence of diaryliodonium and triarylsulfonium salt photoinitiators. We have also described two novel and convenient routes to the preparation of these monomers by isomerization of the corresponding allyl and crotyl ethers. These methods are depicted in Equations 5 and 6.



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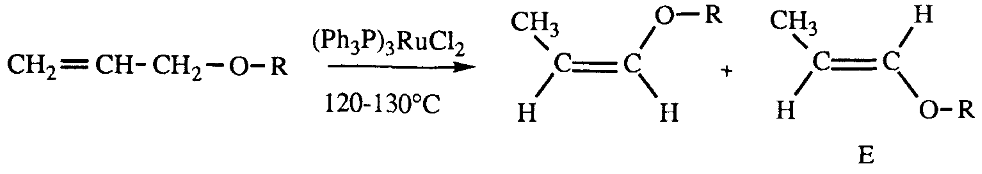

(6)

The high reactivity of these monomers and the fact that they may be obtained from readily available and inexpensive allyl and crotyl ethers make them highly attractive for many potential applications. However, both synthetic methods have certain drawbacks which are outlined below.

Allyl ethers are readily isomerized in quantitative yields to the corresponding *Z* 1-propenyl and 1-butenyl ethers using potassium t-butoxide in dimethylsulfoxide (DMSO) in 15-30 minutes at 110-130°C (Equation 5). However, stoichiometric amounts of potassium t-butoxide must be employed for this reaction and the DMSO used as the solvent in this reaction is difficult to recover for reuse. It is also problematic to remove residual traces of the high boiling DMSO from the products. Allyl ethers may also be isomerized at 120-130°C to a mixture of *Z* and *E* 1-propenyl and 1-butenyl ethers using tris(triphenylphosphine)ruthenium(II) dichloride, $(Ph_3P)_3RuCl_2)$, as a catalyst (Equation 6). Although only catalytic amounts of $(Ph_3P)_3RuCl_2$ are used, this catalyst is expensive and difficult to recover from the monomer for reuse. Neither of the two methods shown above appear to be suitable for large scale or commercial use.

With these difficulties in mind, we have directed our efforts towards an evaluation of alternative catalyst systems, specifically those which do not require the use of solvents.

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EXPERIMENTAL

General

All reagents and solvents used in this work were purchased from Aldrich Co., Milwaukee, WI and used as received. n-Octyl allyl ether, trimethylolpropane di-1-propenyl ether and benzyl 2-butenyl ether were prepared as previously described [6, 8, 9]. Trimethylolpropane diallyl ether was obtained from the Perstorp Co., Perstorp, Sweden.

Gas chromatography analyses were performed on a Hewlett-Packard HP-5890 Gas Chromatograph equipped with a 10 m capillary column (5% phenylmethyl silicone) and a flame ionization detector.

^1H NMR spectra were recorded using a Varian XL-200 MHz or a Varian XL-500 MHz Spectrometer at room temperature in $CDCl_3$. Tetramethylsilane was used as an internal standard.

Preparation of Di(ethylene glycol) Diallyl Ether [6]

Allyl bromide (60.50 g, 0.500 mol) and di(ethylene glycol) (23.85 g, 0.225 mol) were added to a 250 mL three-neck flask equipped with a mechanical stirrer

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and water-cooled reflux condenser. KOH (32.0 g, 0.57 mol) was added as powdered solid over a period of 1/2 hour. The reaction was stirred at room temperature for 1 hour and then heated at 77-80°C for 3 hours. Gas chromatographic (GC) analysis showed a ratio of 0.22 of monoallyl ether to diallyl ether products. There were added 9.5 g (0.17 mol) KOH and reaction mixture was heated for an additional 12 hours. After this time, GC analysis showed a further increase in the diallyl ether product. The addition of another 4 g (0.033 mol) of allyl bromide and 5 g (0.09 mol) of KOH to the reaction mixture, followed by heating for 3 hours, further increased the conversion of the monoallyl ether to diallyl ether product (ratio: 0.065). The reaction mixture was cooled and the solids were separated by filtration and washed with dichloromethane. The dichloromethane and residual allyl bromide were removed from the combined filtrate fractions using a rotary evaporator. A yellow liquid was obtained which was further stripped under vacuum at 102°C. The remaining product was cooled, filtered and washed three times with water. The organic layer was collected and dried over anhydrous magnesium sulfate. GC analysis showed the purity of the di(ethylene glycol) diallyl ether product was 99% [7], (19 g, 53% yield).

General Procedure for Isomerization Reactions

For small scale reactions, 50-100 mg of the allyl or 2-butenyl ethers were combined with powdered KOH and CaO in an NMR tube. The sample was then immersed in an oil bath and heated at the desired temperature. Upon cooling, $CDCl_3$ was added to the reaction mixture and the ^1H NMR spectrum was recorded. The progress of the isomerization reaction was followed by periodically monitoring changes in the vinylic protons. Specifically, the decrease in the vinyl protons of the allyl group at ~5.2 ppm together with the increase in the methyl resonance of the 1-propenyl group at 1.35 ppm were monitored. Integration of these two resonances provided a means for calculation of the percent conversions. Preparative scale reactions (0.05-0.10 mol) were carried out in 25 mL round bottom flasks equipped with a magnetic stirrer and a reflux condenser fitted with a drying tube.

Calcination of CaO

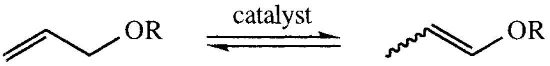
Activated calcium oxide was prepared by calcining calcium hydroxide at 700°C for 3 hours under an atmosphere of helium in an furnace. The CaO thus prepared was sealed in an airtight container and used immediately in subsequent isomerization reactions.

In another experiment, an aqueous solution of KOH was added slowly to a stirred slurry of calcium hydroxide at 85°C, then stirred and heated in an open vessel at 120°C for 12 hours to slowly remove the water. The resulting solid mixture was calcined as described above at 750°C for 12 hours under an atmosphere of nitrogen.

RESULTS AND DISCUSSION

General Considerations

Equation 7 depicts a general reaction for the isomerization of allyl ethers to 1-propenyl ethers.



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The isomerization reaction shown in Equation 7 is driven towards the formation of the 1-propenyl ether product due to the resonance and inductive stabilization provided by the neighboring oxygen atom and the higher thermodynamic stability gained by the conversion of a terminal to an internal double bond. Calculations have given a ΔH value of -4 kcal/mol for this reaction [10]. Based on this thermodynamic driving force, one can predict that in the presence of an efficient catalyst, maximum yields of 1-propenyl ethers in the range of 95-99% should be attainable. Among those catalysts which were considered as candidates for this reaction, basic catalysts appeared to have the most potential. This was based on the following observations. First, the reaction shown in Equation 7 involves proton abstraction followed by a reprotonation. It is difficult to see how this could be achieved using acidic catalysts. More importantly, the 1-propenyl ether product is very reactive and would be immediately polymerized or hydrolyzed by acidic catalysts. Thus, inorganic basic catalysts have the potential of being inexpensive and readily available.

The isomerization of allyl ethers to 1-propenyl ethers using a mixture of DMSO and potassium t-butoxide was first reported by Prosser [11]. Price and Snyder [12] rationalized that the exclusive formation of the *cis* 1-propenyl ether isomer using this reagent was due to the formation of a rigid 1:1 complex of the substrate with potassium t-butoxide in which the potassium atom is simultaneously coordinated to both the end carbon and the oxygen of the allyl ether group in a pseudo five-membered ring. Base catalyzed proton transfer takes place in this complex with the resultant isomerization of the double bond. This mechanism explains the nearly exclusive formation of the *Z* propenyl ether isomer. In the

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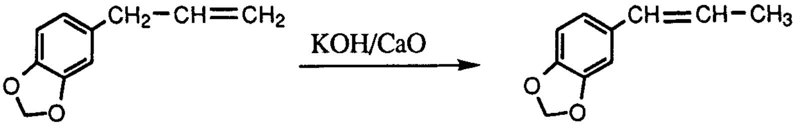
presence of the dipolar aprotic solvent, DMSO, this reaction proceeds homogeneously. Other strong inorganic basic catalysts for this reaction have been described in the literature [13, 14], however, these are less effective, apparently due to the insolubility of those reagents and the heterogeneous nature of the reaction mixtures.

Cesium Hydroxide Catalyzed Isomerizations

The first strong inogranic base selected for investigation in the isomerization reaction was cesium hydroxide, CsOH, because it was expected to have better solubility in liquid allyl ethers as compared to other inorganic bases. Indeed, when equimolar amounts of CsOH and n-octyl ether were heated in the absence of a solvent for one hour at ~185°C n-octyl 1-propenyl ether was obtained in 72% yield If the amount of CsOH was decreased to 25 mol% that of the allyl ether substrate, the yield of the isomerized product decreased to 15%, even though the reaction mixture was heated for three hours at 200-205°C. These results indicated that as with the DMSO/potassium t-butoxide system, equimolar amounts of CsOH are still required at elevated temperatures to obtain high yields of 1-propenyl ether products. While the isomerization reaction does occur using CsOH in the absence of polar aprotic solvents, the required use of rather expensive CsOH in stoichiometric amounts is an impediment to the use of this isomerization system.

KOH/CaO Catalyzed Isomerizations of Allyl Ethers

It has been reported by Lopuy *et al*. [15] and in a Japanese patent [16] that isosafrole could be obtained in 97% yield when neat safrole and a mixture of KOH and CaO (1:15 ratio) were heated for 20 minutes at 245°C (Equation 8).



(8)

While safrole technically is not an allyl ether, it can be considered an allyl ether analog in which the allyl group and the cyclic ether are electronically linked through the conjugation of the benzene ring. Accordingly, we decided to explore the possibility of using this unusual catalyst system for the isomerization of alkyl allyl ethers.

Our initial results using the KOH/CaO mixed alkali system as the base with neat n-octyl allyl ether as a model compound were very promising and the results

TABLE 1. Investigation of the Isomerization of Allyl n-Octyl Ether

Allyl n-octyl ether (mmol)	KOH* (mol%)	CaO* (mol%)	Time (h)	Temp. (°C)	Isomerization (%)
0.29	10	29	1.3	200-205	77
0.19	50	29	1	230-235	92

*Based on allyl n-octyl ether.

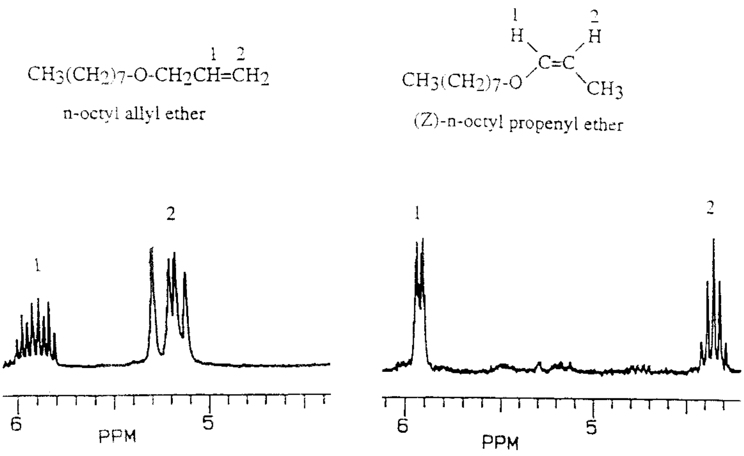


Figure 1. ^{1}H NMR spectra of vinyl region before (left scan) and after (right scan) isomerization of n-octyl allyl ether at 230-235°C for 1 hour.

are given in Table 1. Yields as high as 92% of the desired isomerization product, n-octyl 1-propenyl ether were obtained after heating in the presence of the catalyst system for 1 hour at 230-235°C. As in the case of DMSO/potassium t-butoxide mediated isomerizations, only the *Z*-isomer of the product was obtained. The progress of the isomerization reaction was conveniently monitored by ^{1}H NMR spectroscopy by following the changes in the vinyl region (Figure 1). As isomerization proceeds, the bands at 5.1-5.3 ppm assigned to the terminal CH_2= of the allyl ether double bond decrease and are accompanied by an increase of the bands at 4.25-4.45 ppm assigned to the CH= groups of the 1-propenyl ether double

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TABLE 2. Isomerization of Diethylene Glycol Diallyl Ether (DEGBAE)

Reaction	DEGBAE (mmol)	Time, (h)	KOH (mol %)	CaO (mol %)	Isomerization (%)
1	0.27	1	15	30	46
2	0.27	2	15	30	73
3	0.27	2	15	-	0
4	0.27	1.5	15	5	23
5	0.27	1.5	15	10	17
6	0.27	1.5	15	15	25
7	0.27	1.5	15	20	35
8	0.27	1.5	15	25	58
9	0.27	1.5	-	30	0
10	0.27	1.5	15	50	56
11	0.27	1.5	15	66	62
12	0.27	1.5	50	30	83
13	10.8	2	30	40	90
14	10.8	2.5	30	40	94
15	10.8	3.25	30	40	94*
16	91.4	12	40	25	93**

* The isolated yield is 60% ** The isolated yield is 65%.

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bond. The best results were obtained using 50 mol% of KOH and 29 mol% CaO on the basis of the starting allyl ether. When this ratio was decreased (10:29) the yield fell to 77% under the same reaction conditions. Nevertheless, these initial experiments established that the isomerization of alkyl allyl ethers could be conducted using less than stoichiometric amounts of a very inexpensive inorganic base and without the use of solvents.

Following the successful isomerization of n-octyl allyl ether, the KOH/CaO catalyzed isomerization was applied to a second difunctional monomer, di(ethylene glycol) diallyl ether. The results of these isomerizations are shown in Table 2. The isomerization reactions were conveniently monitored and the yields were calculated using ^1H NMR as described above. The results of this isomerization of the diallyl ether monomer clearly show that the isomerization can be carried out to greater than 93% conversions (reactions 13-16) when the reaction mixture is heated for 2-3 hours at 225°C. The product is easily recovered by simply filtering off the

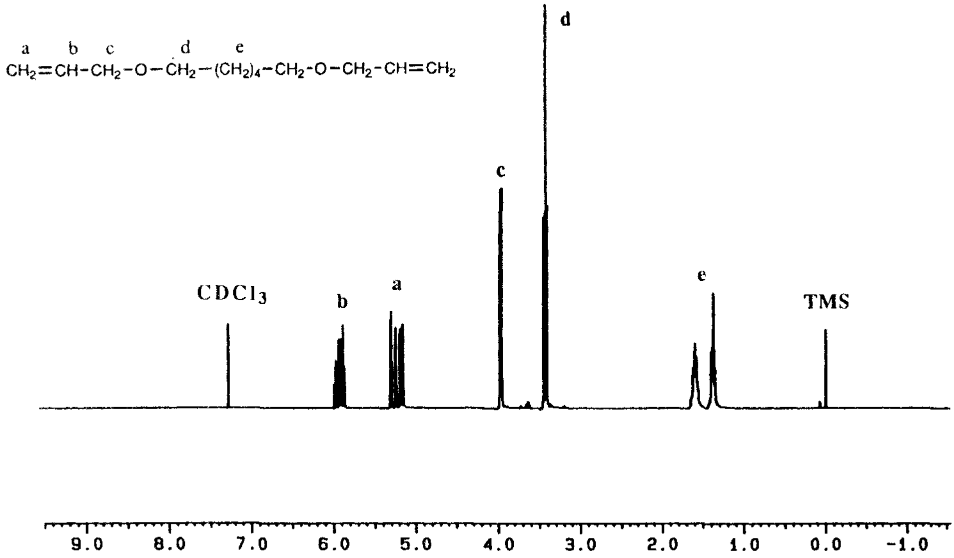

Figure 2. ^{1}H NMR spectrum of 1,6-diallyloxyhexane in $CDCl_3$.

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inorganic solids. The CaO employed in these reactions was used as received from the commercial supplier. The KOH was pulverized to a fine powder and an effort was made to minimize the time of exposure to ambient air and humidity. Reactions 1-12 of Table 2 were conducted in sealed tubes in the presence of air. It appears that traces of water did not perceptibly influence the reaction. Some slight improvements in the yields were observed when the isomerizations were carried out under nitrogen, possibly due to a reduction in the byproducts from oxidation of both the reactant and product. Similarly, the isomerization was successfully applied to other difunctional diallyl ether monomers. For example, Figures 2 and 3, respectively show the ^{1}H NMR of 1,6-diallyloxyhexane and its corresponding isomer, 1,6-di(1-propen-oxy)hexane produced by this isomerization.

Both KOH and CaO are required for isomerization to take place. Isomerization did not take place when either only KOH or CaO were used (reactions 3 and 9). In reviewing the results of reactions 1-12, the optimal amount of CaO is observed to be ~25 mol% based on the allyl ether substrate. Using this amount of CaO and keeping the reaction conditions constant, it was observed that increasing the concentration of KOH from 15 to 50 mol% significantly improved the yield of product from ~50% to 83%. It should be noted that reactions 1-12 shown in Table

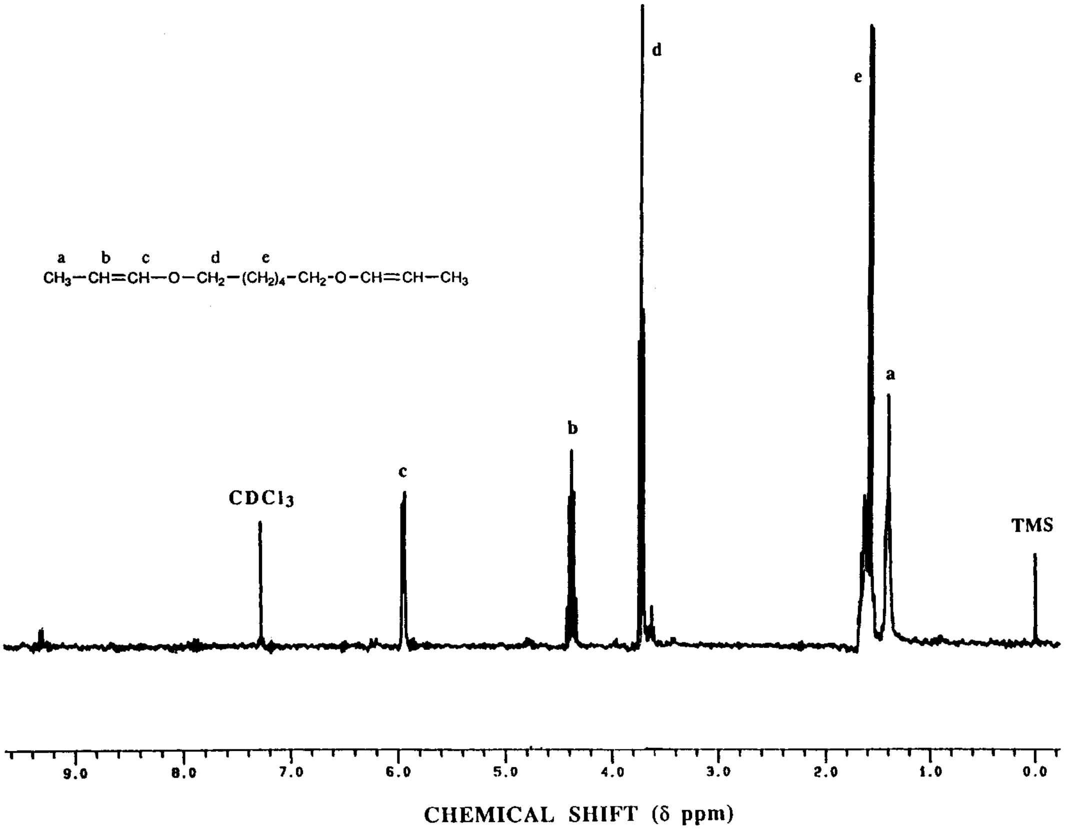

Figure 3. ^1H NMR spectrum of 1,6-di(1-propenoxy)hexane in $CDCl_3$ after isomerization at 220-225°C.

2 are microscale reactions and the yields show a higher degree of variability than larger scale reactions 13-16. All reactions were run in the absence of a solvent as heterogeneous mixtures of the liquid allyl ether substrate in the presence of the solid inorganic bases.

It is interesting to speculate why CaO is required together with KOH for the isomerization of allyl ethers. There are several possible roles that CaO may play, namely as a base, dehydrating agent or a catalyst support system which somehow modifies the solubility properties of the reactants. A review of the literature revealed that CaO and MgO have been used as basic catalysts for the isomerization of carbon-carbon double bonds in 5-vinylbicyclo[2.2.1]hept-2-ene, [17] Δ^3-1-alkyl-1-oxophospholenes [18] and other olefins (e.g. 1-hexene, 2-methyl-1-pentene and 3-

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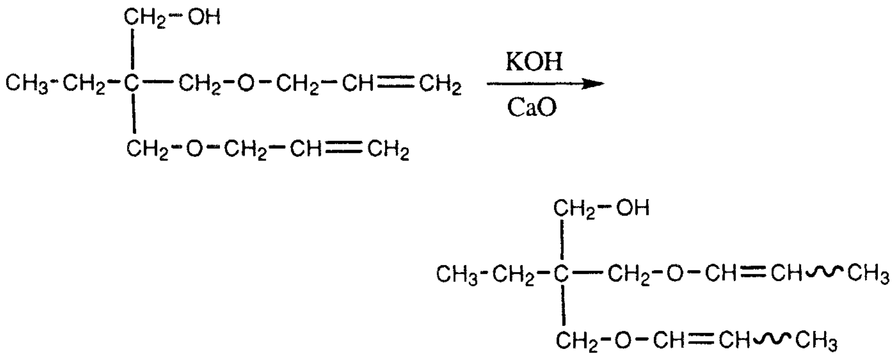
methyl-1-pentene) [19]. Synergistic behavior of CaO or MgO with KOH or NaOH has also been reported for the oxidative methylation of toluene with methane [20], the oxidative coupling of methane [21] and the synthesis of acrylonitrile via the oxidative methylation of acetonitrile [22]. The catalytic activity in the above reactions has been attributed as being due to a synergistic increase in the surface basicity (i.e. "superbasicity") caused by enrichment of the surface layer of a metal oxide with the bialkali ions [19]. Typically, the metal oxide is CaO or MgO and an hat no example of a bialkali is KOH/CsOH. Consideration of this concept of superbasicity suggested that CaO or, alternatively, MgO are possibly sufficiently basic to be involved directly in the isomerization step. Although reaction 9 in Table 2 showed that isomerization took place when only CaO was used, it has been reported that the catalytically active basic O2- sites of alkaline earth metal oxides are easily poisoned by acidic molecules such as carbon dioxide present in ambient air [19b]. Accordingly, a CaO catalyst was freshly prepared by calcining $Ca(OH)_2$ at ~750°C for 2.5 hours under helium. However, no isomerization of the diallyl monomer occurred when this freshly prepared active CaO was used in the absence of KOH and the reaction conducted under an atmosphere of dry nitrogen. In contrast, isomerization was observed when the activated CaO catalyst was used together with KOH and the yields were comparable to those obtained when commercially obtained CaO was used. Although the former result appears to suggest that the isomerization does not depend on the basicity of CaO, further work is warranted to fully understand the synergistic behavior of KOH and CaO.

The KOH/CaO catalyzed isomerization reaction was applied to another monomer, trimethylolpropane diallyl ether (TMPDAE), as shown in Equation 9.



$$CH_3\text{-}CH_2\text{-}\overset{\displaystyle CH_2\text{-}OH}{\underset{\displaystyle CH_2\text{-}O\text{-}CH_2\text{-}CH{=}CH_2}{C}}\text{—}CH_2\text{-}O\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow[CaO]{KOH} CH_3\text{-}CH_2\text{-}\overset{\displaystyle CH_2\text{-}OH}{\underset{\displaystyle CH_2\text{-}O\text{-}CH{=}CH\sim CH_3}{C}}\text{—}CH_2\text{-}O\text{-}CH{=}CH\sim CH_3 \qquad (9)$$

TMPDAE is an interesting substrate which contains a hydroxyl group in addition to the two isomerizable allyl groups. Isomerization of the allyl ether moieties to 1-propenyl ether groups took place with a 50% conversion to give the expected trimethylolpropane di-1-propenyl ether when a mixture of 0.234 mmol of TMPDAE, 40 mol% KOH and 25 mol% CaO were heated at 220-225°C for 3 hours. These results indicated that the weakly acidic hydroxyl proton did not inhibit the isomerization reaction, but that additional KOH is required to compensate for the KOH that abstracts the acidic proton. This was confirmed when the isomerization was repeated with a higher concentration (110 mol%) of KOH and a 90% conversion to 1-propenyl ether groups was obtained by heating the reaction mixture at 220-225°C for 1 hour. The isomerization reactions were followed by ^{1}H NMR spectroscopy·

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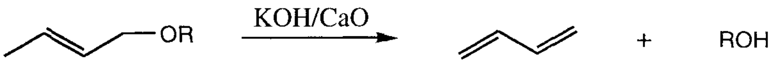
In addition to allyl ethers, the base catalyzed isomerization of 2-butenyl ethers (crotyl ethers) was reevaluated. Previous results have shown that base catalyzed isomerizations of 2-butenyl ethers did not take place using potassium t-butoxide in DMSO but could be carried out successfully (~97% yield) using the ruthenium catalyst, (Ph3P)3RuCl2, at temperatures between 200-220°C for an hour [8]. The base catalyzed isomerization of 2-butenyl benzyl ether to 1-butenyl benzyl ether was attempted using KOH/CaO. No isomerization products were obtained. Instead, ^{1}H NMR spectroscopy and GC results revealed the presence of another product in addition to the unreacted substrate, which was identified as benzyl alcohol. This result suggested that the butenyl group is cleaved during the reaction and eliminated, as 1,4-butadiene. This reaction is depicted in Equation 10.



(10)

There are several examples in the literature which also report the elimination of butadiene from 2-butenyl ethers under basic conditions [23, 24]. Further, 2-butenyl ethers have been used as a hydroxyl protecting groups in carbohydrate chemistry because it can be readily eliminated as 1,4-butadiene by the action of potassium t-butoxide in DMSO. For this reason, we have concluded that isomerization of 2- or 3-butenyl groups cannot be achieved using KOH/CaO.

Other Alkaline Earth Oxide Catalysts

In addition to CaO, other alkaline earth metal oxides, MgO and anhydrous BaO, were also evaluated as isomerization catalysts together with KOH. Results of the isomerization reactions with di(ethylene glycol) diallyl ether are reported in Table 3. In both cases when KOH was absent, no isomerization of the monomer took

TABLE 3. Isomerization of DEGBAE Using MgO and BaO

Reaction	DEGBAE (mmol)	Time, (h)	MgO (mol%)	BaO (mol%)	KOH (mol%)	Isomerization (%)
1	0.27	2	30	-	-	0
2	0.27	2	30	-	15	trace
3	0.27	2	-	30	-	0
4	0.27	1.5	-	30	15	50

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place using only these two metal oxides. However, isomerization was observed with BaO when KOH was present; the yields of isomerized products are similar to those obtained for CaO/KOH for comparable concentrations of reactants and under the same reaction conditions. A possible role of the alkaline earth metal oxides in combination with KOH is that they are dehydrating agents [25]. The BaO used in the isomerization reactions was anhydrous. This suggested that if dehydration of the potassium hydroxide is important for the success of the isomerization step, then substitution of CaO with a basic dehydrating agent such as anhydrous potassium carbonate should also be possible. However, when the diallyl ether was heated with K_2CO_3/KOH at 225°C for 2 hours, no isomerization could be detected using ^1H NMR spectroscopy. Although the isomerization of allyl ethers to 1-propenyl ethers does not take place when KOH was used alone in the absence of solvents, the reaction does take place if a dipolar aprotic solvent, such as DMSO, is used [11]. This establishes that the basicity of KOH alone is sufficient for the isomerization but that the poor solubility or low surface area of the KOH in the allyl ether substrates may be the major limiting factor for the reaction. This leads to the speculation that CaO may behave as a supporting medium that brings the allyl ether and KOH together for the isomerization reaction. In an attempt to confirm this possibility, $Ca(OH)_2$ was impregnated with an aqueous solution of KOH and then calcined at 700°C. However, this catalyst was inactive for the isomerization of allyl ethers. At the present time, the role of BaO and CaO in combination with KOH in promoting the isomerization reaction is not clear, but it is evident that these two alkaline earth metal oxides in combination with KOH are highly attractive catalyst systems for these isomerization reactions.

1-Propenyl ether monomers prepared through the use of the above catalyst systems display excellent activity in photoinitiated cationic polymerization. This indicates the absence of residual trace amounts of these highly basic catalysts in the monomers after isomerization.

CONCLUSIONS

The base catalyzed isomerization of liquid allyl ethers to 1-propenyl ethers were successfully carried out with KOH/CaO in the absence of solvents. High yields of isomerized products were obtained in 1-3 hours reaction at temperatures of 200-220°C. The isomerization can be applied to various mono- and difunctional allyl ether substrates and is not inhibited by the presence of hydroxyl groups. It appears that the reaction may be suitable for the large scale preparation of 1-propenyl ether monomers. The results also suggest that this reaction may be adaptable to a flow reactor in which the solid support is KOH/CaO. The isomerization of 2-butenyl ethers failed with KOH/CaO due to the presence of a side reaction that resulted in the elimination of 1,4-butadiene. Investigation into the role of CaO indicated that its basicity or the possibility as a dehydrating agent are not likely to be major factors in this base catalyzed isomerization reaction.

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Received September 5, 1997

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