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Efficient Isomerization of Allyl Ethers and Related Compounds Using Pentacarbonyliron

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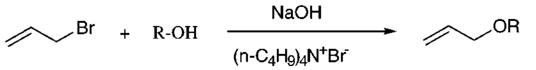
Recent investigations in this laboratory have shown that alkyl 1-propenyl ethers and related compounds having the enol ether structure can be rapidly and efficiently polymerized by onium salt cationic photoinitiators.[1] These compounds are highly attractive for use as monomers in a number of photocurable applications including coatings, inks, and adhesives and in photolithography. Alkyl 1-propenyl ethers can be readily prepared in high yields by first the condensation of alkanols with allyl halides followed by a base[2] or ruthenium complex-catalyzed[3−5] isomerization reaction of the corresponding allyl ethers (eqs 1−4).



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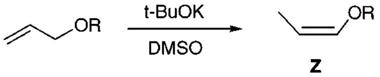

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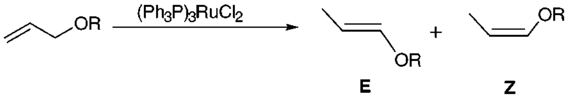

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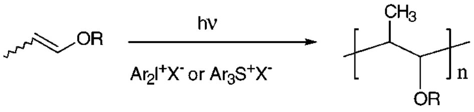

(4)

We wished to extend our polymerization studies to include aryl 1-propenyl ethers. However, the isomerization methods described above for alkyl 1-propenyl ethers were not successful due to the competing Claisen rearrangement. In addition, the high cost of the ruthenium catalyst is also a concern for the large scale and eventual industrial application of these monomers. Examination of the literature revealed that aryl 1-propenyl ethers have been prepared by the base-mediated isomerization of the corresponding allyl aryl ethers with varying degrees of success.[2,6] These methods suffer from the disadvantage that they are not catalytic. The catalytic isomerization of allyl phenyl ether using $PdCl_2(PhCN)_2$ has been reported to be quantitative.[7]

Due to the fact that aryl enol ethers undergo facile hydrolysis and/or polymerization under acidic conditions, the scope of potential catalysts is limited to those which are either neutral or basic. Recent studies carried out in this laboratory have revealed that the tetracarbonylhydroferrate(1−) anion $[HFe(CO)_4]^-$, generated by the reaction of pentacarbonyliron with sodium hydroxide, catalyzes efficient carbon−carbon double bond isomerization under mild conditions. We now wish to report a novel isomerization method based on this inexpensive and readily available catalyst.

Pentacarbonyliron has been used extensively for the isomerization of unsaturated organic substrates.[8] However, as pointed out earlier,[9] these reactions suffer from disadvantages such as the need for high temperatures or UV irradiation, slow reaction rates, low yields of some products, and, in many cases, the use of large, noncatalytic amounts of pentacarbonyliron. Although nonacarbonyldiiron and dodecacarbonyltriiron can effect double bond isomerizations under milder conditions than those employed for pentacarbonyliron, they are considerably more expensive and large mole percentages based on the substrates are also required.[9,10]

It is well-known that pentacarbonyliron can react with sodium hydroxide to form the hydrido species, $Na[HFe(CO)_4]$ (eq 5).[11] This hydride has many known applications[12] in organic chemistry such as effecting the dehalogenation of organic halides, reductive alkylations, aminations, hydroacylations, and carbon−carbon double bond hydrogenations of α,β-unsaturated carbonyl compounds. It was also observed that when 1-hexene was shaken with an ether solution containing preformed $[HFe(CO)_4]^-$ at room temperature for 24 h, 90% isomerization to the corresponding 2- and 3-hexene isomers was obtained.[13] Interestingly, an early patent[14] showed that safrole can be isomerized to isosafrole in very good yield using pentacarbonyliron in the presence of sodium hydroxide at temperatures above 110 °C for several hours. To the best of our knowledge, this is the only case we found which involves the use of pentacarbonyliron in the presence of a base as an isomerization catalyst. On the

$$Fe(CO)_5 + 3NaOH \rightarrow NaHFe(CO)_4 + Na_2CO_3 + H_2O \quad (5)$$

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[11] King, R. B. In *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. I, p 96.

[12] Alper, H. *Tetrahedron Lett.* **1975**, *27*, 2257 and references therein.

[13] Sternberg, H. Z.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 5704.

[14] Radlove, S. B. U.S. Patent 2,575,529, 1951, Maytag & Co.; *Chem. Abstr.* **1952**, *46*, 4812.

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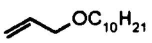
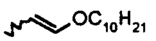
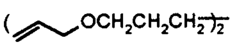
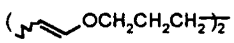
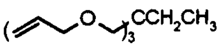
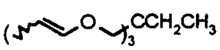
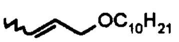
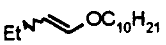
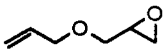
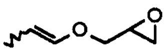
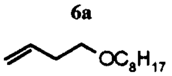
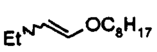
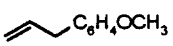
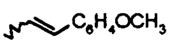
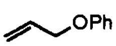
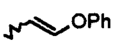
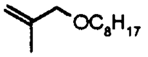
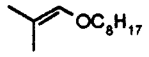
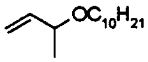
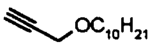
Table 1. Isomerization of Allyl Ethers and Related Compounds with 5 mol % Iron Hydride Catalyst

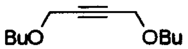
entry	substrate	time, h	product	bp, °C (mmHg)	E:Z[a]	yield,[b] %
1	 **1a**	0.5	 **1b**	55 (0.05)	42:58	96
2[c]	 **2a**	0.5	 **2b**	53 (0.05)	40:60	95
3[c]	 **3a**	1.5	 **3b**	84.5-86 (0.12)	40:60	94
4	 **4a**	0.5	 **4b**	41 (0.18)	58:42	96
5	 **5a**	0.5	 **5b**	52-53 (0.05)	46:54	91
6	 **6a**	0.5	 **6b**	45 (1)	49:51	87
7	 **7a**	3.5	 **7b**	55-56 (0.05)	48:52	87
8	 **8a**	0.5	 **8b**	19.5 (0.06)	96:4	86
9	 **9a**	0.5	 **9b**	43-45 (0.04)	96:4	94
10	 **10a**	0.5	 **10b**	20-22 (0.06)	45:55	84
11[d]	 **11a**	~50	 **11b**	40 (0.03)	_	63



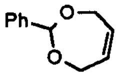
12a



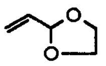
13a



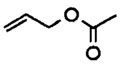
14a



15a



16a



17a

[a] By GC and ^{1}H NMR. [b] Yields refer to purified isolated compounds. [c] 10 mol % ironhydride catalyst used. [d] A second 5 mol % catalyst added after 24 h.

basis of this background, we have recently developed a straightforward, general method for the isomerization of simple alkyl and aryl allyl ethers and several other types of related compounds which is described in this Note.

The method consists of simply combining the substrate with 5 mol % of pentacarbonyliron and 10 mol % of sodium hydroxide in an ethanol–water solution (15:1 by volume) and refluxing the mixture under an atmosphere of nitrogen until the isomerization is complete. The reaction can be conveniently monitored by gas chromatography or ^{1}H NMR. For the isomerization of simple alkyl or aryl allyl ethers, the reaction time is typically 0.5–1.5 h.

As demonstrated in Table 1, this new method is very efficient not only for the isomerization of mono-, di-, and trifunctional allyl ethers (**1a**–**3a**) but also for crotyl ethers (**4a**) and ethers bearing an internal allylic carbon–carbon double bond (**5a**). The successful isomerization of allyl glycidyl ether (2-propenyloxymethyloxirane, **6a**) was surprising to us because we were concerned that the epoxide ring may open in the presence of the iron hydride anion, which is a strong nucleophile. However, no byproducts of this reaction were observed and high yields of the desired isomerized products were obtained. This method can also be used to carry out “zip” reactions which involve multiple step double bond isomerizations (**7a**) in which the double bond migrates over two or three carbon atoms to give the enol ether in good yield. The isomerization reactions are driven toward the formation of the desired 1-propenyl ether products due to the stabilization provided by the oxygen 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.[15]

In each case shown in Table 1, a *Z,E* isomeric mixture was obtained with a small excess of the *Z* isomer except for the isomerizations of **8a** and **9a** which gave predominately the *E* isomer. In addition, we were delighted to observe that 2-propenyloxybenzene (**10a**) can be smoothly isomerized to the corresponding 1-propenyl ether in high

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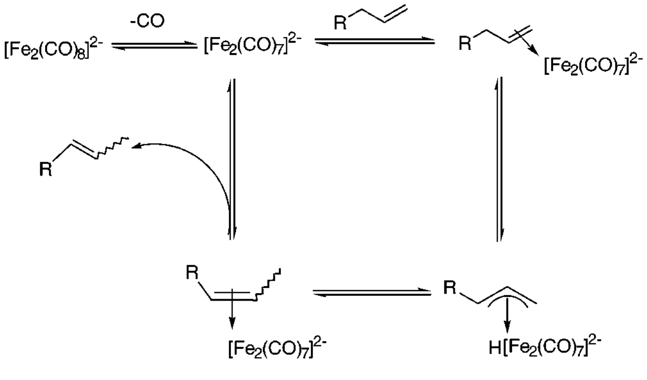
[15] Taskinen, E. *Tetrahedron* **1993**, *48*, 11389.

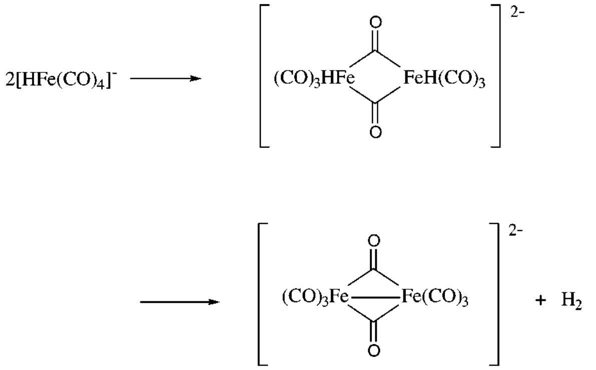
yield. This allows the facile synthesis of 1-propenyl aryl ethers from the corresponding easily prepared allyl ethers avoiding the usual complication of competing Claisen rearrangements. Previous attempts in our group to isomerize this class of compounds using either strong base or ruthenium catalysis were not successful due to this side reaction. Investigations of the polymerization of 1-propenyl aryl ethers are currently in progress in this laboratory.

Our brief investigation of the scope of this new isomerization method showed that the activity of this catalyst system is highly dependent on the structure of the substrate. For example, the isomerization of 2-methyl-4-oxadodec-1-ene (**11a**) requires a longer reaction time than a simple alkyl allyl ether. In addition, the catalyst is deactivated over the long reaction time and the addition of a second portion of catalyst was required to give satisfactory yields of the corresponding enol ether (**11b**). In our attempts to isomerize but-3-en-2-yl ether **12a**, an unidentified byproduct was observed according to GC and ^{1}H NMR analysis which could not be attributed to one of the isomers of the expected products, i.e., *E*,*Z* 3-methyl-4-oxatetradec-2-ene or 2-ethyl-3-oxatridec-1-ene. Separation and isolation of this byproduct from the *Z* and *E* isomers of the product was difficult because of the similarity of the boiling points. We also observed that all the isomerized products rapidly decomposed by hydrolysis on silica gel or alumina chromatography columns. Consequently, chromatographic methods were not successful means of separation for the reaction products, although different solvent systems and chromatographic supports were tried. In a recent paper, Boons et al.[16] reported that the reaction of the Wilkinson's catalyst [$(PPh_3)_3RhCl$] with *n*-butyllithium results in a rhodium hydride catalyst which can isomerize a wide range of unsubstituted and substituted allyl ethers. We conducted the isomerization of **12a** with this catalyst under similar reaction conditions and observed the same byproduct. It should be noted that isomerization of **12a** using $(PPh_3)_3RuCl_2$ at 130 °C led to the formation of many byproducts. Our catalyst was also ineffective in converting propargyl ether **13a** into its 1-decyloxyallene isomer. In this case, only a trace of *n*-decyl alcohol, which appears to be derived from the hydrolysis of the starting material, was observed. Surprisingly, the reaction of 1,4-dibutoxy-2-butyne (**14a**) in the presence of the iron catalyst was very complicated. We have previously reported[17] that the corresponding 1,4-dibutoxy-1,2-butadiene was not formed using ruthenium catalysis. Isomerization of 2-phenyl-4,7-dihydro-1,3-dioxepin (**15a**) was accompanied by decomposition to benzaldehyde. Other screening experiments also ruled out substrates such as 2-ethenyl-1,3-dioxolane (**16a**) and allyl acetate (**17a**) as candidates for isomerization by this method due to unknown reasons.

To confirm that the iron hydride anion is involved in the isomerization reaction, tetraethylammonium tetracarbonylhydroferrate was prepared by an established procedure.[18] The compound thus obtained was used successfully to catalytically isomerize alkyl allyl ethers to 1-propenyl ethers under the same reaction conditions used here. In an early paper, Sternberg[13] proposed that a dimeric ion is formed by condensation of two $[HFe(CO)_4]^-$ ions, which subsequently decomposes into $[Fe_2(CO)_8]^{2-}$ and hydrogen (eq 6).

Scheme 1

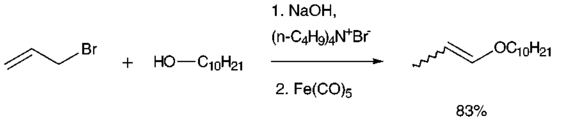




(6)

The structure of the divalent $[Fe_2(CO)_8]^{2-}$ ion is isoelectronic with that of $Co_2(CO)_8$, which also catalyzes olefin isomerizations.[8c] By analogy with this latter cobalt complex, we would like to propose the mechanism in Scheme 1 for the isomerization of allylic ethers by pentacarbonyliron in the presence of base.

Last, by combining this new isomerization method with the Williamson ether synthesis, it is now possible to prepare 1-propenyl ethers using a streamlined, two-step one-pot reaction. First, the alcohol and allyl bromide are combined with base in the presence of a phase transfer catalyst. When the etherification reaction is complete, pentacarbonyliron is added to isomerize the allyl ether. Using this method, 1-propenyl ether **1b** was conveniently prepared in 83% yield (eq 7).



(7)

In conclusion, we have developed a novel method of carrying out the efficient isomerization of allyl ethers and several related classes of compounds. This method has several advantages such as high reaction rate, mild conditions, and low cost which make it attractive for both academic and industrial uses. It is also worth noting that the difference in the reactivity and reaction rates of different substrates toward isomerization could be used to carry out selective isomerizations. This new method should also find use in the deblocking of allyl ethers used as hydroxyl protecting groups since the 1-propenyl ether group can be readily removed by acid-catalyzed hydroly-

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[16] Boons, G.; Burton, A.; Isles, S. *J. Chem. Soc., Chem. Commun.* **1996**, 141.

[17] Crivello, J. V.; Yoo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 2493.

[18] Cole, T. E.; Pettit, R. *Tetrahedron Lett.* **1977**, *9*, 781.

sis under mild conditions. We briefly examined the scope of this method and confirmed the role of the iron hydride as the catalytically active species in this reaction. This catalyst system, which has high activity even in the presence of water and other impurities, allows us to prepare 1-propenyl ethers simply and directly by a one-pot reaction.

Experimental Section

General. All the organic reagents employed in this investigation as well as substrates **6a**, **8a**, **9a**, **10a**, **16a**, and **17a** were used as purchased from the Aldrich Chemical Co. without additional purification. General procedures for the preparation of allyl ethers were described in previous publications.[1a−c]

Gas chromatographic analyses were performed using a high-performance capillary HP-1 (cross-linked silicone gum) column and a flame ionization detector. ^{1}H NMR spectra were obtained at 200 MHz at room temperature in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. The enol ethers prepared during this work were fully characterized by ^{1}H NMR spectroscopic and elemental analysis and compared with authentic compounds prepared as described previously.[1a−f]

Isomerization of Allyl Ethers and Related Compounds. A typical experimental procedure for the isomerization of the compounds shown in Table 1 is given below.

Isomerization of Allyl Ether 1a. An ethanol−water (15:1 v/v) solution (15 mL) of pentacarbonyliron (0.495 g, 2.53 mmol) and allyl ether **1a** (10.0 g, 50.5 mmol) was mixed with solid sodium hydroxide (0.2020 g, 5.05 mmol) under a nitrogen atmosphere. The solution was refluxed for 0.5 h, and the solvent was evaporated under reduced pressure. The remaining solution was mixed with 100 mL of hexane and filtered, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and distilled (bp 55 °C/0.05 mmHg; lit. bp) to give 9.6 g (96%) product, 1-propenyl ether **1b** as clear, colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.21 (dd, *E* isomer), 5.93 (dd, *Z* isomer), 4.84−4.65 (m, *E* isomer), 4.44−4.28 (m, *Z* isomer), 3.70 (t, *Z* isomer), 3.60 (t, *E* isomer), 1.65−1.48 (m, 5H), 1.45−1.08 (m, 14H), 0.87 (t, 3H).

One-Pot Synthesis of 1-Propenyl Ether 1b. Into a 500 mL round-bottom three-necked flask equipped with an overhead stirrer, thermometer, condenser, and nitrogen inlet were placed 31.6 g (0.2 mol) of 1-decanol, 24.2 g (0.2 mol) of allyl bromide, 75 mL of toluene, and 8.8 g (0.22 mol) of sodium hydroxide. The reaction mixture was stirred at room temperature for 15 min. Then, 0.9 g (3.0 mmol) of tetra-*n*-butylammonium bromide was added and the reaction mixture slowly heated to 50 °C and maintained at that temperature overnight. The reaction mixture was sparged with a flow of nitrogen for 10 min and 100 mL of an ethanol−water solution (15:1 v/v) of 1.96 g (0.01 mol) of pentacarbonyliron was added. The reaction mixture was brought to reflux temperature and maintained at that temperature for 1 h. The solvent was evaporated under reduced pressure. The same workup as described above gave 32.9 g (83%) 1-propenyl ether **1b** as a clear, colorless liquid.

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Supporting Information Available: ^{1}H NMR spectra of all compounds listed in Table 1 with the exception of purchased substrates **16a** and **17a** and elemental analyses of new compounds **10b and 11b** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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