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SYNTHESIS OF ALKYL AND ARYL 1-PROPENYL ETHER MONOMERS: A NEW APPROACH

J. V. Crivello^a; S. Kong^a; L. Harvilchuck^a

^a Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, U.S.A.

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SYNTHESIS OF ALKYL AND ARYL 1-PROPENYL ETHER MONOMERS: A NEW APPROACH

J. V. Crivello,* S. Kong, and L. Harvilchuck

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180

Key Words: Pentacarbonyliron, Tetracarbonylhydroferrate (1-), Isomerization, Allyl Ethers, 1-Propenyl Ethers, One-Pot Synthesis

ABSTRACT

A new, convenient synthesis of alkyl and aryl 1-propenyl ether monomers in good to excellent yields has been developed. Alkyl and aryl allyl ethers can be smoothly isomerized to the desired 1-propenyl ethers by refluxing in a basic ethanolic solution containing pentacarbonyliron as a catalyst. A simplified two-step, one-pot procedure has also been developed which consists of combining an alcohol with allyl bromide in the presence of base and then adding pentacarbonyliron to isomerize the *in-situ* generated allyl ether to directly give the 1-propenyl ether. Good yields of alkyl 1-propenyl ethers were obtained using this process. Factors affecting the isomerization reaction were investigated and a mechanism was proposed.

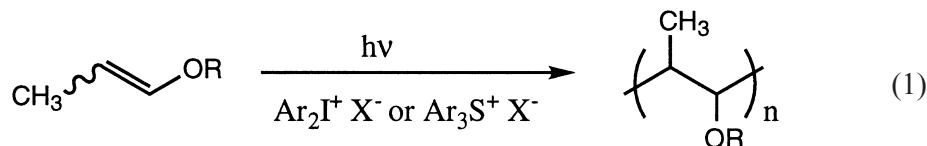
INTRODUCTION

The design and synthesis of reactive monomers and the development of efficient catalysts for cationic polymerization, especially cationic photopoly-

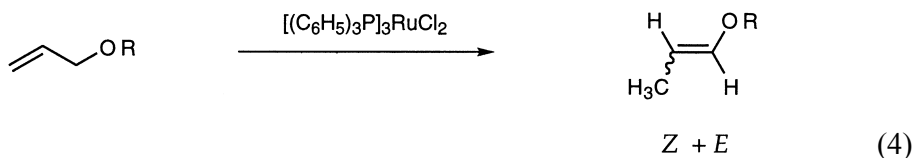
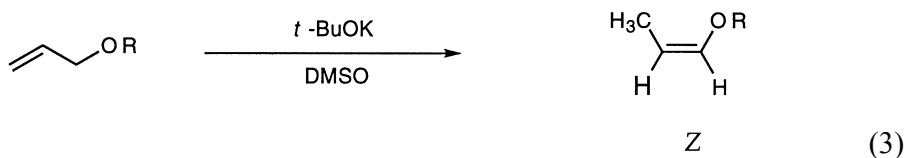
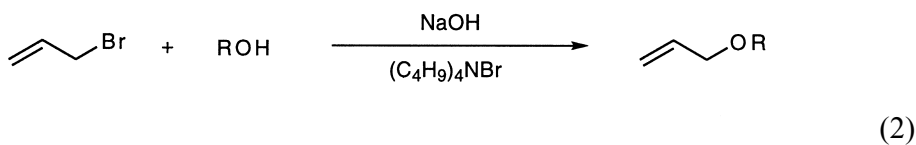
* Author to whom correspondence should be addressed.

merization, has been a topic of central interest in this laboratory for some time.

Alkyl 1-propenyl ethers are a class of highly reactive monomers for photoinitiated cationic polymerization which are currently receiving growing attention in this laboratory and from industry due to their potential applications in coatings, printing inks, and adhesives [1-3] Depicted in Equation 1 is the photopolymerization of these monomers using diaryliodonium or triarylsulfonium salt photoinitiators.



Previously, we have employed a two-step methodology for the preparation of 1-propenyl ethers (Scheme 1). First, an alcohol is condensed with allyl bromide to form the allyl ether (Equation 2), then the resultant allyl ether is isomerized using either a strong base or a ruthenium catalyst (Equations 3 and 4). Compared to their vinyl ether analogues, 1-propenyl ethers display very similar reactivity in cationic polymerization.



Scheme 1.

Although this appeared to be very attractive chemistry, two practical problems remain as obstacles to the use of these new monomers. The base mediated isomerization route depicted in Equation 3 requires stoichiometric amounts of base. On the other hand, ruthenium catalysts are both expensive and are not recovered from the reaction mixtures. For these reasons, it was desirable to develop a simplified, low cost synthesis of 1-propenyl ether monomers which avoids the use of expensive isomerization catalysts.

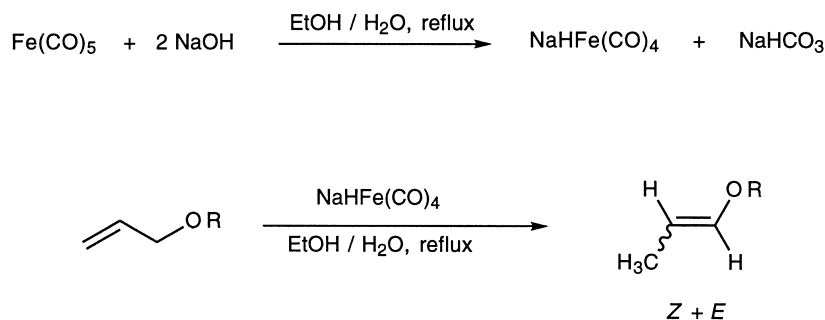
Very recently, we have discovered that the tetracarbonylhydroferrate (1-), $[\text{HFe}(\text{CO})_4]^-$ anion, formed by the reaction of pentacarbonyliron with sodium hydroxide, efficiently catalyzes the isomerization of alkyl allyl ethers and related compounds under mild conditions to their corresponding enol ethers as depicted in Scheme 2 [4].

Noting that sodium hydroxide is used in both the Williamson synthesis of allyl ethers as well as in the catalyst formation, we directed our efforts to synthesize 1-propenyl ethers by a more convenient one-pot approach. In this article, we describe the results of this investigation.

EXPERIMENTAL

General

All reagents were purchased from the Aldrich Chemical Co. and used without additional purification. ^1H NMR spectra were obtained in CDCl_3 on a Varian XL-200 spectrometer. Gas chromatographic (GC) analyses were carried



Scheme 2.

out on a Hewlett-Packard HP-5890 Gas Chromatograph equipped with a high performance capillary HP-1 (crosslinked methyl silicone gum) column and a flame ionization detector. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of Alkyl 1-Propenyl Ethers

The synthetic procedures given below for decyl 1-propenyl ether is typical for the preparation of alkyl 1-propenyl ethers from their allyl ether precursors.

An ethanol-water (15:1 v/v) solution (15 mL) of pentacarbonyliron (0.495 g, 2.53 mmol) and allyl decyl ether (10.0 g, 50.5 mmol) were mixed with solid sodium hydroxide (0.2020 g, 5.05 mmol) under a nitrogen atmosphere. The solution was refluxed for 0.5 hours 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. b.p.¹) to give 9.6 g (96%) product, decyl 1-propenyl ether as a clear, colorless liquid.

¹H NMR (200 MHz, CDCl₃): δ 0.87 (t, CH₃, 3H); 1.45-1.08 (m, (CH₂)₇, 14H); 1.65-1.48 (m, =CH-CH₃; O-CH₂-CH₂, 5H) 3.60 (t, O-CH₂, *E* isomer); 3.70 (t, O-CH₂, *Z* isomer); 4.44-4.28 (m, =CH-CH₃, *Z* isomer); 4.84-4.65 (m, =CH-CH₃, *E* isomer); 5.93 (dd, =CH-OAlk, *Z* isomer); 6.21 (dd, =CH-OAlk, *E* isomer).

Syntheses of Aryl 1-Propenyl Ethers

The synthetic procedures given below are typical for the preparation of substituted aryl 1-propenyl ethers shown in Table 1.

TABLE 1. Aryl 1-Propenyl Ethers Prepared By Isomerization of Allyl Aryl Ethers Using 5.0 mol% Fe(CO)₅ and 10.0 mol% NaOH

Substituents	Isomerization time (h)	Z :E	Purity (%)	Boiling point (mmHg/°C)	Yield (%)
-H	0.5	71:29	99.7	21-22/0.06	64
4 -Me	0.5	73:27	99.4	29/0.05	71
4 -MeO	0.7	69:31	99.9	48/0.007	67
4 -Cl	5	73:27	99.7	44/0.05	73
2,6-difluoro *	~40	59:41	96.0	21-22/0.02	-
2,4,6-trimethyl	~40	63:37	98.0	46/0.012	63

*Using 0.25 mol% Ru(PPh₃)₃Cl₂ at 140°C under nitrogen.

Synthesis of Phenyl 1-Propenyl Ether

Into a 500 mL round bottom three-neck flask equipped with an overhead stirrer, condenser, and nitrogen inlet were placed 9.4 g (0.10 mol) of phenol, 14.5 g (0.12 mol) of allyl bromide, 50 mL of tetrahydrofuran and 4.8 g (0.12 mol) of sodium hydroxide. This mixture was stirred at room temperature for 15 minutes. Then, 1.0 g (3.3 mmol) of tetra-*n*-butylammonium Into a 500 mL round bottom three neck flask equipped with an overhead stirrer, condenser and nitrogen inlet were placed 9.4 g (0.10 mol) of phenol, 14.5 g (0.12 mol) of allyl bromide, 50 mL of tetrahydrofuran and 4.8 g (0.12 mol) of sodium hydroxide. This mixture was stirred at room temperature for 15 minutes. Then, 1.0 g (3.3 mmol) of tetra-*n*-butylammonium bromide was added and the reaction mixture slowly heated to 55°C and maintained at that temperature overnight. The reaction mixture was dried over anhydrous Na₂SO₄ for 30 minutes. After careful removal of the solvent and allyl bromide using a rotary evaporator, the crude allyl phenyl ether was collected and subjected to fractional vacuum distillation.

Allyl phenyl ether was mixed with 5.0 mol% pentacarbonyliron and 10.0 mol% sodium hydroxide dissolved in an ethanol-water solution (15:1 v/v) under nitrogen. The reaction was heated and maintained at reflux Allyl phenyl ether was mixed with 5.0 mol% pentacarbonyliron and 10.0 mol% sodium hydroxide dissolved in an ethanol-water solution (15:1 v/v) under nitrogen. The reaction was heated and maintained at reflux temperature for 0.5 hours until the reaction was complete as determined by GC analysis. The solvents were removed using a rotary evaporator and the dark red solution poured into 200 mL hexane and dried over anhydrous Na₂SO₄. The finely dispersed solid inorganic residues were allowed to settle and the pale red solution was collected. After removal of the solvent, the crude product was vacuum distilled to give 8.6 g (64% yield) of the desired phenyl 1-propenyl ether. Fractional distillation gave 99.7% pure phenyl 1-propenyl ether (29:71 mixture of *E* and *Z* isomers) with a boiling point of 21-22°C/0.06 mm Hg.

¹H NMR (CDCl₃) δ (ppm) 1.65-1.75 (m, 3H, CH₃); 4.82-4.95 (m, =CH-CH₃, *Z* isomer); 5.30-5.46 (m, =CH-CH₃, *E* isomer); 6.36-6.47 (m, 1H, CH-OAr); 6.95-7.36 (m, 5H, ArH).

4-Methylphenyl 1-Propenyl Ether

¹H NMR (CDCl₃) δ (ppm) 1.63-1.74 (m, 3H, CH₃); 2.30 (s, 3H, ArCH₃); 4.77-4.90 (m, =CH-CH₃, *Z* isomer); 5.25-5.41 (m, =CH-CH₃, *E* isomer); 6.32-6.42 (m, 1H, CH-OAr); 6.85-7.12 (m, 4H, ArH).

Elemental Analysis. Calcd. for $C_{10}H_{12}O$: C, 81.04%; H, 8.16%. Found: C, 81.06%; H, 8.12%.

4-Methoxyphenyl 1-Propenyl Ether

1H NMR ($CDCl_3$) δ (ppm) 1.62-1.73 (m, 3H, CH_3); 3.77 (s, 3H, $ArOCH_3$); 4.73-4.86 (m, $=CH-CH_3$, *Z* isomer); 5.23-5.37 (m, $=CH-CH_3$, *E* isomer); 6.28-6.39 (m, 1H, $CH-OAr$); 6.81-6.96 (m, 4H, ArH).

Elemental Analysis. Calcd. for $C_{10}H_{12}O_2$: C, 73.15%; H, 7.37%. Found: C, 72.98%; H, 7.32%.

4-Chlorophenyl 1-Propenyl Ether

1H NMR ($CDCl_3$) δ (ppm) 1.64-1.82 (m, 3H, CH_3); 4.82-5.00 (m, $=CH-CH_3$, *Z* isomer); 5.29-5.46 (m, $=CH-CH_3$, *E* isomer); 6.29-6.38 (m, 1H, $CH-OAr$); 6.87-7.27 (m, 4H, ArH).

Elemental Analysis. Calcd. for C_9H_9ClO : C, 64.11%; H, 5.38%. Found: C, 64.03%; H, 5.36%.

2, 6-Difluorophenyl 1-Propenyl Ether

1H NMR ($CDCl_3$) δ (ppm) 1.56-1.79 (dd, 3H, CH_3); 4.69-4.83 (m, $=CH-CH_3$, *Z* isomer); 5.00-5.17 (m, $=CH-CH_3$, *E* isomer); 6.26-6.30 (m, $CH-OAr$, *Z* isomer); 6.43-6.49 (d, $CH-OAr$, *E* isomer); 6.80-7.13 (m, 3H, ArH).

Elemental Analysis. Calcd. for $C_9H_8F_2O$: C, 63.53%; H, 4.74%. Found: C, 63.28%; H, 4.69%.

2, 4, 6-Trimethylphenyl 1-Propenyl Ether

1H NMR ($CDCl_3$) δ (ppm) 1.51-1.55 (dd, CH_3 , *E* isomer); 1.74-1.79 (dd, CH_3 , *Z* isomer); 2.16-2.25 (t, 9H, $ArCH_3$); 4.49-4.70 (m, 1H, $=CH-CH_3$); 5.92-5.95 (dd, $CH-OAr$, *Z* isomer); 6.29-6.36 (dd, $CH-OAr$, *E* isomer); 6.83 (s, 2H, ArH).

Elemental Analysis. Calcd. for $C_{12}H_{16}O$: C, 81.77%; H, 9.15%. Found: C, 81.75%; H, 9.16%.

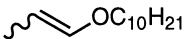
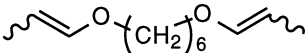
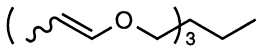
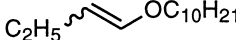
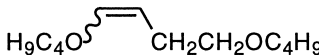
One Pot Synthesis of Alkyl 1-Propenyl Ethers

The synthetic procedures given below are typical for the one-pot preparation of the alkyl 1-propenyl ether monomers shown in Table 2.

Synthesis of Decyl 1-Propenyl Ether (I)

Into a 500 mL round bottom three-neck flask equipped with an overhead stirrer, condenser, and nitrogen inlet were placed 15.8 g (0.10 mol) of 1-decanol,

TABLE 2. Alkyl 1-Propenyl Ethers and Related Compounds Prepared by a One-Pot Reaction

Notation	Compound ^a	Z:E ^b	Yield ^c (%)	Boiling Point °C/mmHg
I		53:47	84	65/20
II ^d		52:48	80	53/0.05
III ^e		53:47	78	84.5/0.12
IV ^f		47:53	72	41/0.18
V ^g		46:54	71	51/0.025

^a Identified by comparison with compounds previously synthesized in this laboratory. ^b Det. by GC and ¹H-NMR. ^c Refer to isolated pure compounds; conditions not optimized. ^d From 1,6-hexanedial [3 hours; 5.0 mol% Fe(CO)₅]. ^e From trimethylolpropane diallyl ether [2 hours, 7.0 mol% Fe(CO)₅]. ^f From crotyl chloride (predominantly *trans*) and 1-decanol [5 hours, 5.0 mol% Fe(CO)₅]. ^g From *cis*-2-butene-1,4-diol and 1-bromobutane [0.5 hours, 5.0 mol% Fe(CO)₅].

12.3 g (0.102 mol) of allyl bromide, 50 mL of toluene and 4.4 g (0.11 mol) of sodium hydroxide. The reaction mixture was stirred at room temperature for 15 minutes. Then, 1.0 g (3.3 mmol) of tetra-*n*-butylammonium bromide was added and the reaction mixture slowly heated to 50°C and maintained at that temperature overnight. An ethanol-water mixture (100 mL, 15:1 v/v) was added into the flask and the flask purged with nitrogen for 10 minutes. Pentacarbonyliron 0.98 g (5.0 mmol) was added and the reaction mixture was rapidly heated and held at reflux temperature for 1 hour. Solvents were removed using a rotary evaporator and the resultant dark red solution was poured into 200 mL hexane, the layers separated and the hexane layer dried over anhydrous Na₂SO₄. The inorganic solids were allowed to settle for 30 minutes and the pale red solution was collected. After removing the solvents, the crude liquid product was vacuum distilled. There were obtained 16.6 g (84% yield) of product. Fractional vacuum distillation gave > 99% pure decyl 1-propenyl ether, **I**, with a boiling point of 65°C/20 mm Hg as a 53:47 mixture of *Z* and *E* isomers. **I** prepared by this procedure was identical in all respects to decyl 1-propenyl ether prepared by previously described methods [1-3].

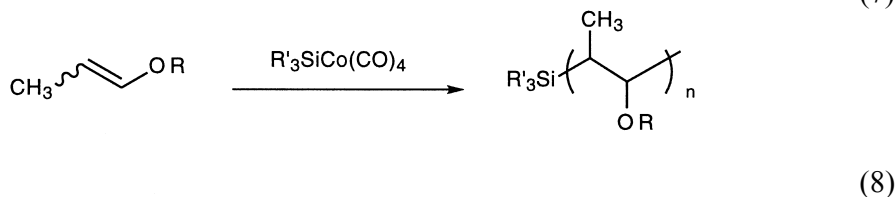
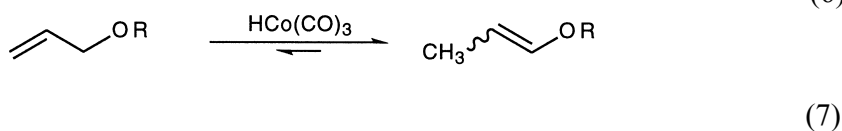
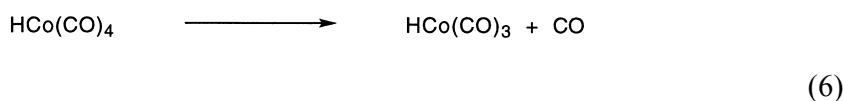
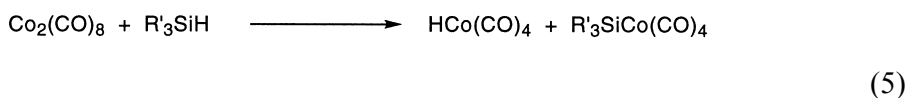
Preparation of Tetraethylammonium Tetracarbonylhydroferrate

Into 40 mL distilled water were placed 7.0 g (0.036 mol) pentacarbonyliron, 6.0 g (0.11 mol) potassium hydroxide and 10.3 g (0.049 mol) tetraethylammonium bromide. The mixture was stirred under nitrogen for 24 hours at which time the tetraethylammonium tetracarbonylferrate salt appeared as a light brown precipitate. The mixture was filtered under nitrogen and the residual solid washed with deaerated water (300 mL) and dried *in vacuo*. A light pink solid was collected by vacuum filtration (4.5 g, 42% yield). The salt is mildly air sensitive and best handled and stored under nitrogen in a dry box. $^1\text{H NMR}$ (CDCl_3) δ (ppm)-8.8 (H-Fe).

RESULTS AND DISCUSSION

Development of Pentacarbonyliron as an Isomerization Catalyst

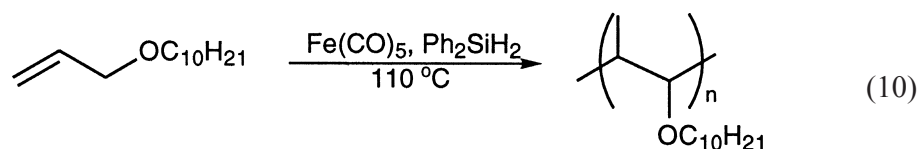
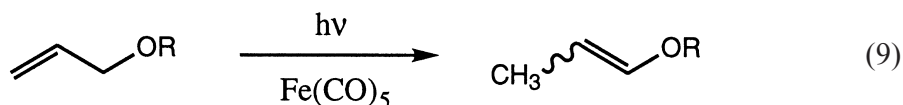
Recent work in this laboratory [5-9] has shown that in the presence of an octacarbonylcobalt/silane catalyst mixture, allyl ethers, undergo exothermic cationic polymerization to form well-defined polymers having silyl end groups. The proposed mechanism is outlined in Equations 5-8 of Scheme 3.



Scheme 3.

A key step in this scheme is the isomerization of the allyl ether to the corresponding 1-propenyl ether (Equation 7). Polymerization takes place by a cationic mechanism involving a silyl-cobalt species (Equation 8). Other Group VIII transition metal carbonyls were also found to be effective for this new type of polymerization reaction although in all cases, more vigorous reaction conditions were required [10].

Among the metal carbonyl reagents, which were most effective for the isomerization polymerization of allyl ethers, was pentacarbonyliron. In addition, it had been previously shown by other workers [11] that pentacarbonyliron is capable of isomerizing allyl ethers at elevated temperatures or under UV irradiation (Equation 9). While the polymerization of alkyl allyl ethers at elevated temperatures was successfully carried out as shown in Equation 10, we have failed thus far in our attempts to induce the polymerization of these compounds photochemically. In the presence of 10 mol% pentacarbonyliron and 1.5 mol% of diphenylsilane or triphenylsilane, only isomerization of the allyl ether to the corresponding 1-propenyl ether was observed even after prolonged irradiation. Furthermore, we observed that this catalyst system was also ineffective for the photopolymerization of the corresponding 1-propenyl ethers.



From these experiments it can be concluded that for an isomerization/polymerization to occur, efficient catalysts for both the isomerization of the allyl ethers and the cationic initiation of the polymerization of the 1-propenyl ethers are required. Irreversible consumption of the 1-propenyl ethers by an exothermic polymerization will further drive the isomerization equilibrium. In addition, for efficient cationic polymerization a counteranion with low nucleophilicity is also required. Based on these prerequisites, we believe that the mechanism in the thermally induced isomerization/polymerization (Equation 9) is different from that of the photochemically induced isomerization reaction (Equation 10).

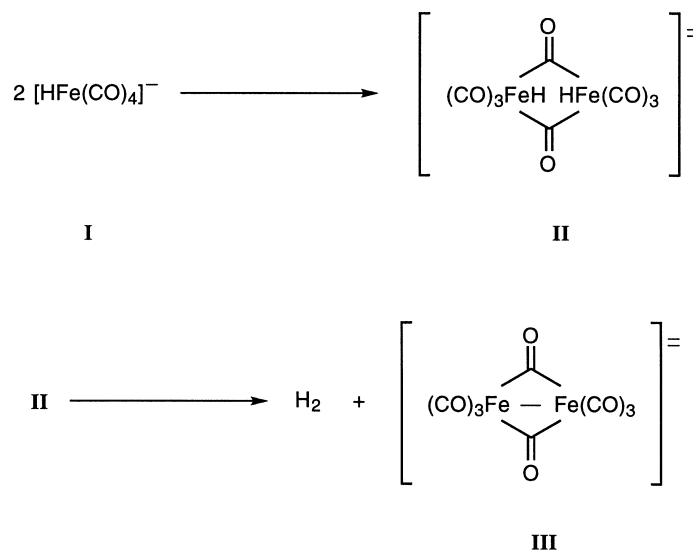
Dekker *et al.* [12] have proposed that the photochemical reaction of pentacarbonyliron with a silane gives the silyl-iron species $R_3Si[HFe(CO)_4]$ as the major product. This species is isoelectronic with the corresponding cobalt species shown in Equation 8 which is responsible for cationic polymerization of the 1-propenyl ether. However, it appears that in the case of the above silyl-iron compound either dissociation to give the silyl cation, R_3Si^+ does not occur or the $HFe(CO)_4^-$ anion which is also generated is too nucleophilic to permit polymerization. There is some evidence to substantiate these conclusions as will be discussed later in this article. The mechanism of the thermally induced cationic polymerization depicted in Equation 10 has not been elucidated. However, we speculate that the reaction may involve the formation of a silyl-iron species with a multinuclear iron carbonyl anion with sufficiently low nucleophilic character which allows cationic polymerization to occur at elevated temperatures.

In the photochemical experiments shown in Equation 9, extensive isomerization of the alkyl allyl ether occurred. Although it is well known [13] that pentacarbonyliron photochemically decomposes to give tricarbonyliron, which catalyzes alkene isomerizations via an $Fe(CO)_3(\eta^3\text{-alkenyl})H$ complex, it was not certain whether or not the $HFe(CO)_4^-$ anion participated in the isomerization. Accordingly, the stable, isolable ammonium salt of this anion, $Et_4N[HFe(CO)_4]$, was prepared according to the procedure described by Cole *et al.* [14]. It was observed that this salt readily catalyzes the isomerization of allyl decyl ether in ethanol at room temperature with a 90% conversion after 24 hours. At 80°C, 80% isomerization to decyl 1-propenyl ether took place in 1 hour using 5% of the catalyst. A similar observation was also made by Sternberg *et al.* [15] in which 1-hexene was isomerized to a mixture of 2- and 3-hexene in an ether solution containing $Et_4N[HFe(CO)_4]$. By analogy, we suggest that $R_3SiHFe(CO)_4$ formed as shown in Equation 13 catalyzes isomerization of allyl ethers.

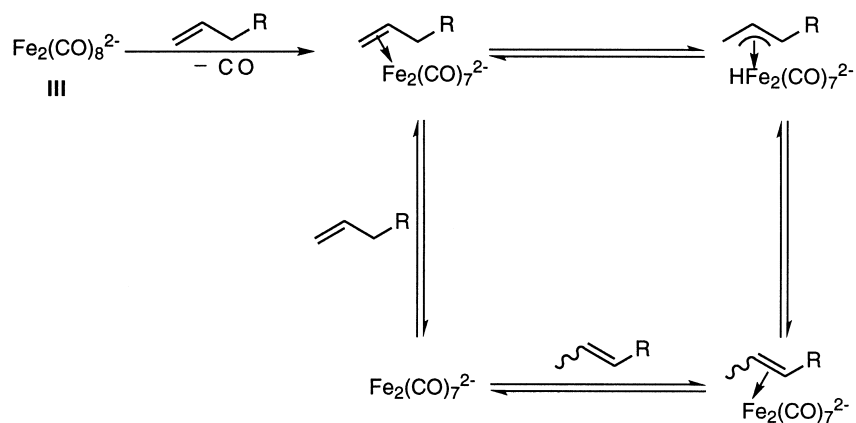
Sternberg *et al.* [14] have proposed the mechanism shown in Schemes 4 and 5 by which $HFe(CO)_4^-$ catalyzes the isomerization of alkenes.

The dimeric anion, **II**, formed by the condensation of two $HFe(CO)_4^-$ (**I**) anions, decomposes with the elimination of hydrogen to afford the binuclear iron complex **III**. The structure of **III** is isoelectronic with that of $Co_2(CO)_8$, which is also known to catalyze alkene isomerizations. Accordingly, a very similar mechanism shown in Scheme 5 is proposed for the basic pentacarbonyliron catalyzed isomerizations [16].

Loss of carbon monoxide generates the coordinatively unsaturated complex, $Fe_2(CO)_7^{2-}$, which can then coordinate with the double bond. Interconversion from the initially formed η^2 complex to an η^3 complex followed

**Scheme 4.**

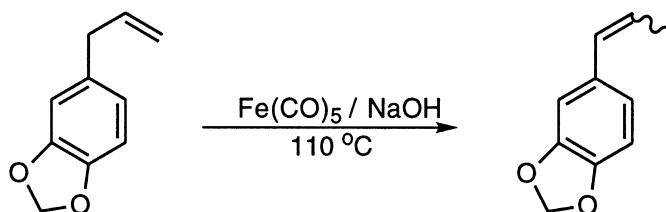
by the shift of a hydrogen atom and reductive elimination results in isomerization of the alkene. Alternatively, since $[\text{HFe}(\text{CO})_4]^-$ is isoelectronic with $\text{HCo}(\text{CO})_4$, which is also an active catalyst for carbon-carbon double bond isomerizations, [15] a very similar mechanistic pathway to that shown in Scheme 5 involving $[\text{HFe}(\text{CO})_4]^-$ may also be written [17].

**Scheme 5.**

On the basis of the above mechanistic considerations it was concluded that the $[\text{HFe}(\text{CO})_4]^-$ anion was a key candidate as an isomerization catalyst for the isomerization of allyl ethers.

Isomerization Under Various Conditions

In an early paper, Radlove [18] described the isomerization of saffrole in the absence of a solvent at 110°C with catalytic amount of pentacarbonyliron and sodium hydroxide.

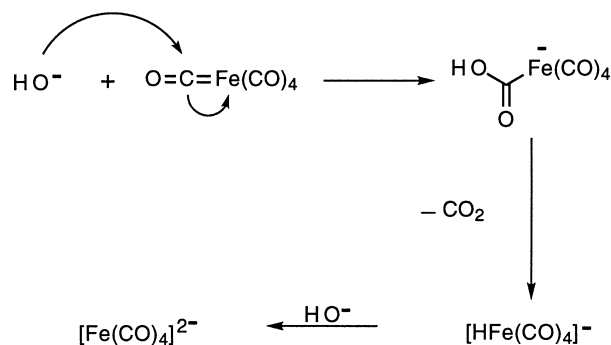


Unfortunately, no mechanistic studies were conducted, although we now suggest that $\text{Na}[\text{HFe}(\text{CO})_4]$ may be involved as a catalyst in this reaction. Similarly, we conducted a series of experiments designed to determine whether $\text{Na}[\text{HFe}(\text{CO})_4]$ produced by an *in-situ* process would catalyze the isomerization of alkyl allyl ethers. The results are shown in Table 3. Using allyl decyl ether as a model compound, our initial attempts to carry out the isomerization of this compound under similar conditions were not successful (Table 3, entry 1) probably because of the insolubility of NaOH in this substrate. In the presence of phase transfer catalysts (entries 2 and 3), significant improvements were observed. However, at high temperatures, it was found that reaction was very inefficient, possibly due to thermal decomposition of the active catalytic species. Using ethanol as a solvent for the reaction, quantitative conversion to decyl 1-propenyl ether was observed at reaction temperatures of $50\text{--}80^\circ\text{C}$, (entries 4 and 5). This method works quite well at low catalyst concentrations (entry 6) but not at room temperature (entry 7). Increasing the concentration of pentacarbonyl iron is beneficial (entry 9) while the presence of oxygen (entry 8) has an adverse effect on the isomerization. The addition of a small amount of water accelerates the reaction and reduces the reaction time (entries 4 and 11). Various $\text{Fe}(\text{CO})_5/\text{NaOH}$ ratios were also investigated entries 9-12). As shown in Scheme 6, insufficient NaOH results in the incomplete conversion of $\text{Fe}(\text{CO})_5$ to the active catalyst because the CO_2 which is formed consumes two equivalents of

TABLE 3. Isomerization of Allyl Decyl Ether under Various Conditions Using $\text{Fe}(\text{CO})_5$

Entry	Solvent	$\text{Fe}(\text{CO})_5$ mol%	NaOH mole %	Reaction Conditions	Conversion (%) / Time (hours) (By $^1\text{H-NMR}$)
1	No	5.0	15.0	130°C	trace / 1
2 ^a	No	5.0	15.0	110 °C, 5% Bu_4NBr	> 80 / 1
3 ^b	No	5.0	No	100 °C, 15% Bu_4NOH (aq.)	30 / 3
4	EtOH	5.0	15.0	reflux	quant. / 2
5	EtOH	5.0	15.0	50°C	quant. / 2
6	EtOH	3.0	9.0	reflux	quant. 3
7	EtOH	10.0	30.0	25°C	90~95 / 30
8	EtOH	3.3	10.0	50°C (in air)	~15 / 3
9 ^c	EtOH/ H_2O	5.0	5.0	reflux	80 / 0.5
10 ^c	EtOH/ H_2O	5.0	10.0	reflux	quant. / 0.5
11 ^c	EtOH/ H_2O	5.0	15.0	reflux	quant. / 0.5
12 ^c	EtOH/ H_2O	5.0	20.0	reflux	54 / 0.5
13 ^c	EtOH/ H_2O	5.0	15.0	$\text{CH}_2\text{CHCH}_2\text{Br}^d$ 1 equiv., reflux	no isomerization
14 ^c	EtOH/ H_2O	5.0	15.0	$\text{CH}_2\text{CHCH}_2\text{Br}^e$ 5%, reflux	no isomerization

^a No increase in conversion at prolonged time. ^b A 55 wt% n- Bu_4NOH aqueous solution was used. ^c A 15/1 (vol.) EtOH/ H_2O was used as solvent. ^d Allyl decyl ether (1 equiv.) added 3 hours after allyl bromide was reacted with the solution. ^e Allyl bromide was added simultaneously with allyl decyl ether at the beginning of the reaction.

**Scheme 6.**

NaOH. On the other hand, excess NaOH will react with the active catalyst, resulting in the formation of $\text{Fe}(\text{CO})_4^{2-}$ which was found to be an inactive catalyst for isomerization. When the NaOH/ $\text{Fe}(\text{CO})_5$ ratio is 2 or 3, CO_2 is converted into HCO_3^- and CO_3^{2-} respectively. In those cases, $[\text{HFe}(\text{CO})_4]^-$ is present in the highest concentration in the solution and optimum isomerization is observed (entries 10 and 11). The presence of allyl bromide (entries 13 and 14) in the reaction mixture inhibits the isomerization reaction.

Comparison with Other Carbonyliron Catalyst Systems

Using optimized conditions (entry 10, Table 3), we carried out the isomerization of several different allylic ethers to investigate the scope of this catalyst system. Thus far, $\text{Fe}(\text{CO})_5/\text{NaOH}$ appears to be among the most efficient and inexpensive catalyst systems for the isomerization of alkyl allyl ethers. Alternative carbonyliron alkyl allyl ether isomerization catalysts were also investigated by other groups and the results are reported in Table 4. Multinuclear iron carbonyl complexes $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ are quite excellent thermal and photocatalysts for alkyl allyl ether isomerizations. However, they are expensive, difficult to prepare and in many cases, large, non-catalytic amounts of these catalysts are required. In addition, the reaction times using these catalysts are generally longer than we have found with the $\text{Fe}(\text{CO})_5/\text{NaOH}$ catalyst system.

A Simplified One-Pot Synthesis of 1-Propenyl Ethers

Our next goal was to combine the Williamson ether synthesis and the pentacarbonyliron catalyzed isomerization to make 1-propenyl ethers directly by

a streamlined two-step, one-pot reaction. In the usual procedure for Williamson ether synthesis, NaOH and allyl bromide are used (Equation 2). Excess NaOH is detrimental to the isomerization reaction as discussed previously. In entry 13 of Table 3, a catalytic quantity of $\text{Fe}(\text{CO})_5/\text{NaOH}$ and allyl bromide were refluxed in EtOH/ H_2O for 3 hours and no isomerization of the allyl bromide was detected. Next, an molar equivalent of allyl decyl ether was added to the reaction mixture and reflux continued. No isomerization of the allyl ether took place. To obtain further insight into the unsuccessful reaction, an equimolar mixture of allyl bromide and $\text{Na}[\text{HFe}(\text{CO})_4]$ (generated *in situ*) in EtOH/ H_2O were combined at 80°C . A highly vigorous reaction took place immediately with the evolution of a gas. The gas was trapped using a Br_2/CCl_4 solution and an oil was isolated. The ^1H NMR spectrum of the oil was identical to that of 1,2-dibromopropane. Based on this observation and the work by H. Alper, [23] we propose that nucleophilic displacement of the allylic bromide took place followed by a reductive elimination, resulting in the formation of propene and $\text{Fe}(\text{CO})_4$ [24]. Clearly, the presence of allyl bromide and similar compounds interferes with the pentacarbonyl catalyzed isomerization.

Keeping this restriction in mind, it was possible to successfully develop a two-step, one-pot reaction for the synthesis of a wide variety of alkyl 1-propenyl ethers employing alcohols and allyl bromide as the substrates. First, the Williamson ether reaction is run in the presence of an approximately 15 fold excess of base to fully consume the allylic halide. Then, $\text{Fe}(\text{CO})_5$ is added to induce the isomerization reaction. Some typical alkyl 1-propenyl ether and related monomers prepared by this method are listed in Table 2. We found that this approach works very well: the conversion of the alcohol to allyl ether is generally quantitative as shown by GC analysis. No hydrolysis of the 1-propenyl ether products was observed during the isomerization step. The isolated products were mixtures of *E*, *Z* geometrical isomers with the *Z* isomer being the major product. The purities of these compounds were all higher than 98% by GC analysis. The 1-propenyl ether products could be further purified by distillation over NaH to remove traces of water and/or alcohols.

Allyl aryl ethers tend to undergo Claisen rearrangement at high temperature. For this reason, isomerization catalysts which require a high activation temperature, for example $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$, are not effective. Other catalysts including *t*-BuOK in DMSO [25] or the palladium complex, bis(benzonitrile)dichloropalladium [26] give predominantly *Z* isomers. Using this new method, a mixture of *Z* and *E* isomers are formed. To prepare the aryl 1-propenyl ethers listed in Table 5, the allyl ether precursors were isomerized using 5 mol%

$\text{Fe}(\text{CO})_5$ and 10 mol% NaOH. Although a one-pot reaction is feasible, it was found that the conversion of the phenols to the allyl ethers was not quantitative under the usual reaction conditions. Consequently, excess starting materials may remain in the reaction mixture and affect the isomerization. The reactivity of the allyl aryl ethers towards isomerization is greatly affected by structure. For example, allyl *p*-chlorophenyl ether requires a longer time to isomerize, as also does allyl 2,4,6-trimethylphenyl ether. In the case of allyl 2,6-difluorophenyl ether, only a poor yield of the isomerized compound was obtained. Complete isomerization of this compound was carried out at 140°C using $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$. The cationic photopolymerization of these compounds will be discussed in a future paper.

CONCLUSION

Tetracarbonylhydroferrate (1-), generated *in situ* by the reaction of pentacarbonyliron with sodium hydroxide, catalyzes the efficient isomerization of alkyl and aryl allyl ethers to the corresponding 1-propenyl ethers under mild conditions. A mechanism for the isomerization has been proposed. We have further developed an efficient two-step, one-pot synthesis of alkyl 1-propenyl ethers directly from allyl bromide and alcohols which provides these monomers in good yields.

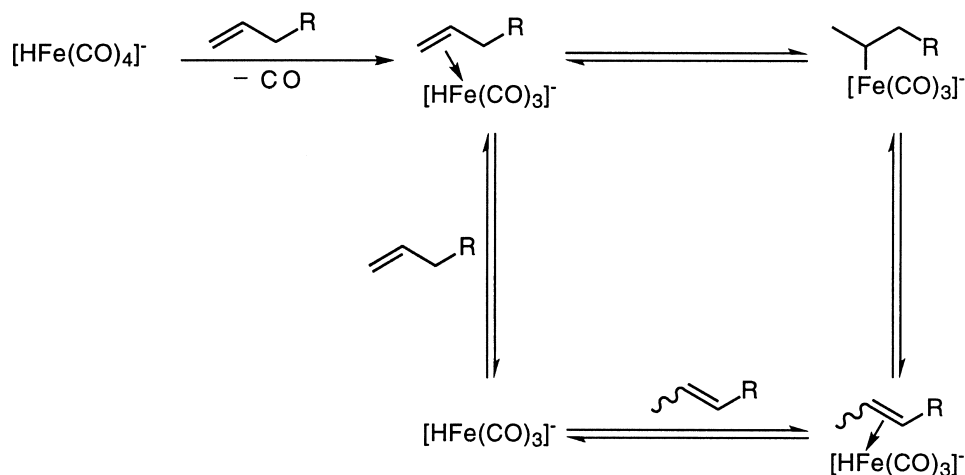
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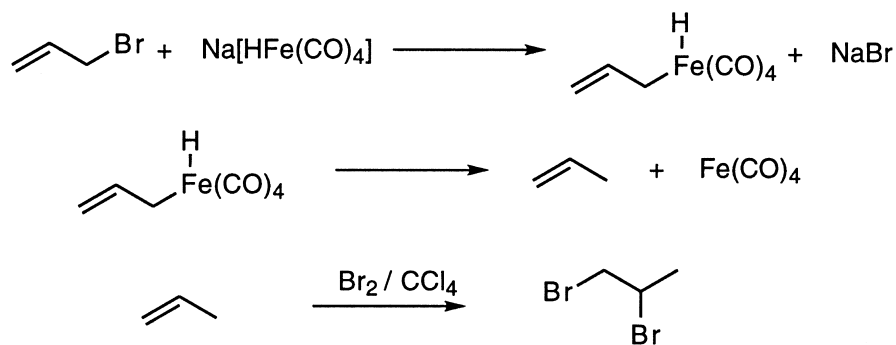
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