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Isomerization of 1-alkenes using the $Na_2Fe(CO)_4/CuCl$ and $Na_2Fe(CO)_4/BrCH_2CH_2Br$ reagent systems

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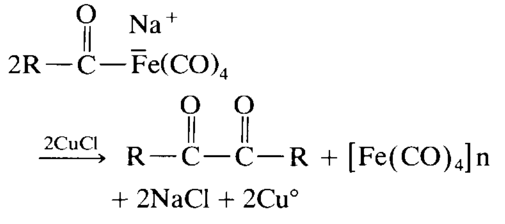
Abstract

The reagent $Na_2Fe(CO)_4$ prepared in situ in THF by the reduction of $Fe(CO)_5$ with sodium naphthalenide reacts with certain alkenes in the presence of CuCl to bring about isomerization of the alkenes. Thus the 1-alkenes (1-dodecene, 1-decene, safrole and allyl benzene) are isomerized to *trans*-2-alkenes, and β-pinene is isomerized to α-pinene. Reactions involving $BrCH_2CH_2Br$ in place of CuCl give similar results.

Keywords: Isomerization; Supernucleophile; Iron tetracarbonyl; Iron–copper bonds; Iron pentacarbonyl; Copper(I) chloride

1. Introduction

It has recently observed in this laboratory that the $NaRCOFe(CO)_4$ species formed by the reaction of $Na_2Fe(CO)_4$ with alkyl halides give α-diketones when treated with CuCl [1]. Similar results were obtained for the reaction of $NaRCOFe(CO)_4$ with I_2 [2].



$$2R-\overset{\overset{O}{\|}}{C}-\overline{Fe}(CO)_4\ Na^+ \xrightarrow{2CuCl} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R + [Fe(CO)_4]n + 2NaCl + 2Cu^\circ$$

It seemed likely that these transformations would involve initial oxidation of the $RCO\overline{Fe}(CO)_4$ to $RCOFe\cdot(CO)_4$ species. We have thus examined the reactions of the coordinatively unsaturated species formed in the oxidation of $^{2-}Fe(CO)_4$ by CuCl and related reagents. We show below that the species produced in this way isomerize certain alkenes.

2. Results and discussion

We have observed that the reagent generated from $Na_2Fe(CO)_4$ (10 mmol) and CuCl (20 mmol) in THF (60 ml) isomerizes 1-decene (10 mmol) to *trans*-2-decene in 12 h at room temperature. The ^{13}C NMR spectrum of the product reveals the absence of 1-decene and other isomers of decene. It is noteworthy that the isomerization of 1-alkenes using the $Fe(CO)_5$ and $NaHFe(CO)_4$ gives a mixture of 2-alkenes and 3-alkenes [3,4]. The selectivity of the $^{2-}Fe(CO)_4/CuCl$ reagent system is further illustrated by the isomerization of certain other alkenes (Table 1).

In the course of efforts to optimize the conditions for this transformation, we observed that when more than 10 mmol of the olefinic substrate was used as equivalent amount of starting material remained unchanged; that is, the isomerization is stoichiometric. Isomerization of $(-)\beta$-pinene to $(-)\alpha$-pinene reveals that there is no skeletal rearrangement in this case. 1,5-Cycloctadiene and 4-vinylcyclohexene failed to undergo isomerization under the reaction conditions used. Furthermore, no isomerization of 1-decene occurs in the absence of CuCl.

It has been reported that $Na_2Fe(CO)_4$ reacts with

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CuBr to give clusters containing Fe–Cu bonds [5]. The IR spectrum of the mixture prepared by use of $Na_2Fe(CO)_4$ (10 mmol) and CuCl (20 mmol) exhibits two strong broad bands at 1970 cm^{-1} and 1870 cm^{-1} similar to those reported for the cluster anions. It was thus of interest to determine whether the reaction of $Na_2Fe(CO)_4$ with two equivalents of CuCl would give a $Fe(CO)_4$ unit that could be used for complexation with α,β-unsaturated carbonyl compounds. For example, it has been reported that the $Fe(CO)_4$ complex of methyl acrylate on reaction with PhLi at −78°C gives $PhCOCH_2CH_2COOCH_3$ in 67% yield [6]. The $Na_2Fe(CO)_4/2CuCl$ combination failed to cause a similar transformation on treatment with methyl acrylate followed by the addition of PhLi at −78°C. However, addition of CuCl (20 mmol) to $Na_2Fe(CO)_4$ (10 mmol) in the presence of 1,3-cyclooctadiene and stirring of the mixture for 12h at room temperature gave a small amount (10%) of the corresponding diene-$Fe(CO)_3$ complex.

We also found that the use of $BrCH_2CH_2Br$ in place of CuCl also results in isomerization of alkenes (Table 2). Whereas the results obtained with allylbenzenes, β-pinene are the same as that observed with $Na_2Fe(CO)_4/CuCl$, the reaction with 1-decene and 1-dodecene leads to a mixture of *cis* and *trans* 2-decenes. Although both the $Na_2Fe(CO)_4/CuCl$ and $Na_2Fe(CO)_4/BrCH_2CH_2Br$ reagent systems give coordinatively unsaturated species that can isomerize certain alkenes, the detailed outcome can be different for the two systems.

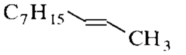
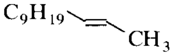
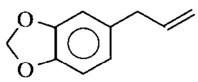
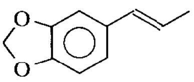
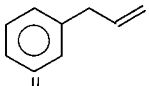
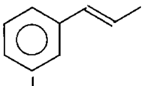
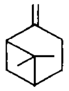
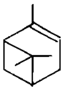
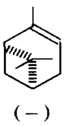
Several transition metal complexes isomerize olefins [7,8]. However, in many cases the process is not a useful one because a mixture of products is formed, and severe reaction conditions are needed. The procedures reported here involving $Na_2Fe(CO)_4/CuCl$ and $Na_2Fe(CO)_4/BrCH_2CH_2Br$ combinations should be useful for isomerizations under mild conditions. The results also indicate that the reaction of $Na_2Fe(CO)_4$ with CuCl or 1,2-dibromoethane provides access to organometallic reagents with interesting reactivities. The nature of the intermediates and the mechanism of the observed transformations and the possibilities of further utilization of the reagent systems will be the subject of future studies.

3. Experimental details

3.1. General

All reactions were carried out under dry nitrogen atmosphere. The THF was freshly distilled over sodium-benzophenone ketyl. $Fe(CO)_5$ was supplied by Fluka. Commercially supplied alkenes and 1,2-dibromoethane were distilled before use. CuCl (Fluka)

Table 1
Isomerization of olefins by use of the $Na_2Fe(CO)_4/CuCl$ reagent system

Entry No	1-Alkene [a]	2-Alkene	Yield (%) [b]
1	C_8H_{17}-CH=CH_2		83
2	$C_{10}H_{21}$-CH=CH_2		80
3			87
4			76
5	 (±)	 (±)	79
6	 (−)	 (−)	78

[a] Reactions were carried out for 12 h at 25°C under N_2 atmosphere with $Na_2Fe(CO)_4$ (10 mmol), 1-alkene (10 mmol) and CuCl (20 mmol) in THF (60 ml). [b] Yields are of products isolated by column chromatography on silica gel. The products were identified from spectral data (IR, ^1H and ^{13}C NMR) and by comparison with data for authentic samples.

was purified by treatment with distilled water containing SO_2. After decantation of the water the chloride was washed with dry ether and then ethanol, and dried under vaccum at 100°C for 3 h. IR spectra were recorded on a Perkin-Elmer model 1310 and Jasco FT-5300 with polystyrene as reference. The ^1H and ^{13}C NMR spectra were recorded on JEOL-FX-100 or Brucker-AC-200 spectrometers with $CDCl_3$ as solvent and TMS as reference. Column chromatography was carried out on silica gel (100–200 mesh).

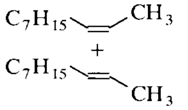
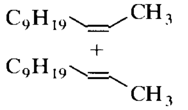
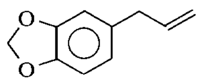
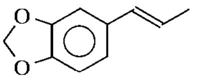
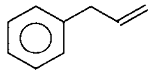
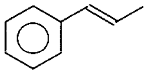
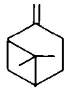
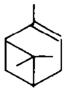
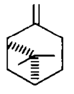
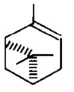
3.2. Representative procedure for isomerization using $Na_2Fe(CO)_4$ / CuCl system

To a suspension of $Na_2Fe(CO)_4$ [prepared from $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol), naphthalene (1.28 g, 10 mmol)] in THF (60 ml) was added 1-decene (1.4 g, 10 mmol). The mixture was stirred for 2 h under nitrogen, and CuCl (2 g, 20 mmol) was then added with stirring during 30 min using a solid addition flask. The mixture was stirred for 10 h at room temperature and then added to water (30 ml) containing ceric ammoniumnitrate (5.48 g, 10 mmol) to decompose the metal carbonyl. The organic phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (2 × 30 ml). The combined organic extract was washed with water (20 ml), and then brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography with hexane as eluent to give *trans* 2-decene (83%). IR(neat)ν_{max} 2960, 2850, 950 cm^{-1}. ^{13}C NMR ($CDCl_3$): 131.7, 124.5, 32.5, 31.8, 29.6, 29.2, 22.6, 17.7, 13.9.

3.3. Representative prodcedure for isomerization using $Na_2Fe(CO)_4$ / $BrCH_2CH_2Br$

To a suspension of $Na_2Fe(CO)_4$ [prepared from $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol), naphthalene (1.28 g, 10 mmol)] in THF (60 ml) was added 1-decene (1.4 g, 10 mmol). The mixture was stirred for 2 h under nitrogen, and then 1,2-dibromoethane (1.87 g, 10 mmol) was added slowly with stirring. The mixture was stirred for 10 h at room temperature. The resulting mixture was poured in to water (30 ml) containing ceric ammoniumnitrate (5.48 g, 10 mmol) to decompose the metal carbonyl. The organic phase was separated, and the aqueous phase was saturated with NaCl and shaken with ether (2 × 30 ml). The combined organic extract was washed with

Table 2
Isomerization of alkenes using $Na_2Fe(CO)_4/BrCH_2CH_2Br$ system.

Entry No	1-Alkene [a]	2-Alkene	Yield (%) [b]
1	$C_8H_{17}-CH=CH_2$		80
2	$C_{10}H_{21}-CH=CH_2$		76
3			81
4			75
5	 (±)	 (±)	78
6	 (−)	 (−)	79

[a] Reactions were carried out for 12 h at 25°C under N_2 atmosphere with $Na_2Fe(CO)_4$ (10 mmol), 1-alkene (10 mmol) and $BrCH_2CH_2Br$ (10 mmol) in THF (60 ml). [b] Yields are of products isolated by column chromatography on silica gel. The products were identified from spectral data (IR, ^1H and ^{13}C NMR) by comparison with data for authentic samples.

water (20 ml), then brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography with hexane as eluent to give a mixture of *cis* and *trans* 2-decene (80%). The NMR data of the mixture indicate that the *trans*-2-decene is the major product (greater than 80%). IR (neat)ν_{max}: 2960, 2850, 980, 900 cm^{-1}. ^{13}C NMR ($CDCl_3$): 131.7, 130.4, 129.6, 124.5, 32.9, 32.5, 32.1, 31.6, 29.6, 29.2, 22.6, 22.2, 17.7, 14.2, 13.9.

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