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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 (−)β-pinene to (−)α-pinene reveals that there is no skeletal rearrangement in this case. 1,5-Cyclooctadiene 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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