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Selective Isomerization of 4-Vinylcyclohexene by Iron Carbonyl Complexes

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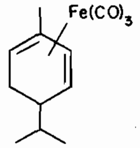
It has been known for some time that reaction of non-conjugated diolefins with pentacarbonyl iron usually leads to the formation of η^4 conjugated Fe-$(CO)_3$ complexes, [1, 2]. There has however been no detailed study of this type of isomerization for reactions with more than one possible product. Both thermal [3] and photochemical [4] methods have been advocated for the preparation of diene $Fe(CO)_3$ systems but there has been no comparative study of these methods. It is now reported that choice of reaction conditions can lead to product selectivity.

Thermal (134 °C, 30 h) reaction of 4-vinylcyclohexene, (1), and $Fe(CO)_5$ gives tricarbonyl(η^4-1-ethylcyclohexa-1,3-dieneiron, (2), and tricarbonyl(η^4-2-ethyl-cyclohexa-1,3-diene) iron, (3)†, in the ratio 5:1. Irradiation of (1) and $Fe(CO)_5$ (hexane solution, pyrex filter, 10 °C, 30 hr) gives (2) and (3) in the ratio 1:5. Neither irradiation of the former mixture nor heating of the latter altered the product ratios. Reaction of (1) with $Ph_3PFe(CO)_3$ is more selective, under photochemical conditions only the Ph_3PFe-$(CO)_2$ complex of 2-ethylcyclohexadiene was produced.

This difference between the photochemical and thermal reactions was unexpected, thus the more simple reaction of α-phellandrene, (4), with $Fe(CO)_5$ was reexamined [5, 6]. α-Phellandrene is an essentially flat ligand with an i-Pr group on one face. Its tricarbonyliron complex (5) can exist in *exo* and *endo* forms [7]. A 1:1 *exo:endo* ratio is obtained from the photochemical procedure and a 4:1 *exo: endo* ratio from thermal reactions. The structure of (5) was determined by reaction of the mixture with trityl fluoroborate, when only the *endo* isomer underwent hydride abstraction to give a cationic salt which was reduced with borohydride to pure *endo* (5). Trifluoroacetic acid isomerized only the *exo* isomer to the *a*-terpinene complex [8]. The reaction of (4) with $Fe(CO)_5$ can be interpreted in terms of the reactivity selectivity principle [9] as follows: the intermediate in the photochemical reaction is more reactive and unable to distinguish the two faces of (4) and the less reactive thermal intermediate reacts faster with the unhindered face of the ligand. This probably means that CO loss in the thermal reaction involves some degree of associative character.



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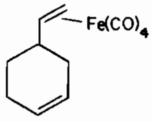

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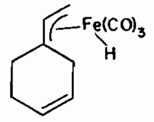

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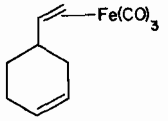

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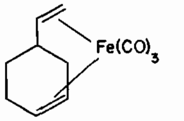

(9)

This idea can be used to rationalize the vinylcyclohexene reactions and to explain the major products in each case, if it is assumed that complex (6) is a common intermediate. Under thermal conditions associative loss of CO from (6), (synchronous loss of CO and C–H addition [10]), gives the η^3-allylFe-$(CO)_3H$ (7). Subsequent isomerization of (7) yields (2), the most accessible η^4 complex. Under photochemical conditions dissociative loss of CO from (6) yields coordinatively unsaturated (8) which rapidly coordinates the other double bond to give (9). Formation of (9) permits isomerization of both double bonds to give (3). Tricarbonyliron complexes similar to (9) have not been isolated but an analogous Rhodium complex has been reported [11].

In an attempt to isolate (6), (1) was reacted with $Fe_2(CO)_9$, under conditions known to produce η^2 olefin $Fe(CO)_4$ complexes [12]. However this low temperature procedure ($T < 60$ °C) gave the same result as thermal reaction with $Fe(CO)_5$ [12], in agreement with the foregoing considerations.

At present the selective isomerization of limonene and of 1,4-dienes obtained from Birch reduction of substituted benzenes is being investigated.

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†Compounds were characterized by elemental analyses, ^1H and ^{13}C n.m.r., and mass spectra.

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