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Dodecacarbonyl triiron, an efficient catalyst for photochemical isomerization of unsaturated alcohols, ethers and ester to their corresponding carbonyl compounds, enol ethers and esters

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Abstract

Photochemical isomerization of unsaturated alcohols to their corresponding saturated aldehydes and ketones can be carried out efficiently by irradiation at wavelengths > 560 nm in n-hexane at 25–30 ° C in the presence of catalytic amounts of dodecacarbonyl triiron. Unsaturated ethers and esters are likewise converted into their corresponding enol ethers and esters in moderate to high yields. Results of the reactions of benzylideneacetoneiron tricarbonyl with unsaturated compounds support the previously postulated mechanism in which the $Fe(CO)_3$ moiety is the active species in the catalyses of the carbon-carbon double bond migration.

Introduction

Reactions of unsaturated organic compounds with pentacarbonyliron have been extensively studied [1–9] and many tricarbonyl iron complexes have also been characterized. The reactions indicate carbon–carbon double bond migration in alkenes, unsaturated alcohols, and ethers which is considerable potential in modern organic synthesis. In one such reaction, pentacarbonyliron at high temperatures (120–130 ° C) catalyzes the double bond migration in allylic alcohols to produce their corresponding carbonyl compounds [3]. Conversion of allylic ethers into their corresponding alkenyl ethers have also been reported to occur under ultraviolet irradiation [4]. The reactions with pentacarbonyliron suffer from disadvantages such as the difficulty in handling pentacarbonyliron (a poisonous liquid), a slow rate of reaction, and a low yield of some products [3], and the need for high temperatures and high energy radiation [3,4] which limit its use as a versatile reagent in organic synthesis. We recently reported the use of nonacarbonyl diiron as an efficient catalyst for thermal isomerization of unsaturated alcohols, ethers and esters [10]. We wish now to report that double bond migration in unsaturated alcohols, ethers and esters is efficiently catalyzed by dodecacarbonyl triiron under irradiation at wavelengths > 560 nm in n-hexane or n-pentane at 25–30 ° C [11,12].

The results are tabulated in Table 1. The low temperature at which the reaction occurs, the high rate of the reaction, the high yield of the products, and the fact that it is a solid make dodecacarbonyl triiron a useful catalyst for use by synthetic chemists.

Results and discussion

Photochemical isomerization of unsaturated alcohols was brought about efficiently in deareated, olefin-free n-hexane under nitrogen by irradiation at wavelengths of > 560 nm. As shown in Table 1, primary and secondary allylic alcohols rearranged to the corresponding saturated ketones or aldehydes. *Endo-endo*-tricyclo[5,2,1,$0^{2,6}$]dec-4-en-3-ol [12] and *endo-endo*-tricyclo[5,2,1,$0^{2,6}$]dec-4,8-diene-3-ol (entries 5,7) were converted into their corresponding saturated ketones, while the *exo*-isomer (entry 6) did not undergo isomerization; similar results were reported for the reaction of these alcohols with $Fe_2(CO)_9$ [6,10]. Non-allylic unsaturated alcohols (entries 2,3) were also isomerized to their corresponding saturated carbonyl compounds. The products were separated and identified by comparison with authentic samples.

Isomerization of both allylic and nonallylic ethers to enol ethers also occurred efficiently under irradiation in the presence of catalytic amounts of $Fe_3(CO)_{12}$ (entries 9, 11, 12). In isomerization of allylic esters to the corresponding enol-esters took place much more slowly than those of alcohols and ethers (entries 13,14). The enol ethers and esters were separated and identified spectroscopically and by hydrolysis to the corresponding known carbonyl compounds.

The mechanism of the isomerization reactions described here and those described previously [13,14], is not firmly established, but two routes have been proposed. Because certain mono-olefins give tetracarbonyl-π-olefiniron complexes in reaction with nonacarbonyl diiron [13], it has been suggested that isomerization proceeds through formation of a tetracarbonyl iron-π-complex and subsequent hydride shift. Alternatively, it has been suggested that tricarbonyliron is the active species, giving hydrido-π allyltricarbonyl iron as the intermediate [15]. In order to show light on the mechanism, we used benzylideneacetoneiron tricarbonyl as a source of $Fe(CO)_3$ free from $Fe(CO)_4$. When benzylideneacetoneiron tricarbonyl was treated with allylic alcohols, ethers, or cycloocta-1,5-diene at 95–100 °C in tetralin, a rapid double bond migration occurred and the expected isomerized products were formed. Since $Fe(CO)_3$ is the only reactive species which is present under this condition, this represents good evidence that $Fe(CO)_3$ is the active species responsible for double bond migration in these compounds. The results obtained in the reactions of benzylideneacetoneiron tricarbonyl with the unsaturated substrates are shown in Table 2.

Experimental

General

Products were isolated by chromatography and identified from by their spectral data by comparison with authentic samples. All reactions with $Fe_3(CO)_{12}$ and benzylideneacetone iron tricarbonyl were performed under dry, oxygen-free nitrogen. Nitrogen was purified by passage through alkaline solution of pyrogallol, then

Table 1

Reactions of unsaturated alcohols, ethers, and esters under irradiation at $\lambda > 560$ nm in the presence of $Fe_3(CO)_{12}$

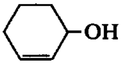
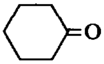
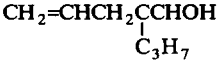
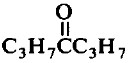
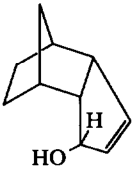
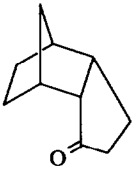
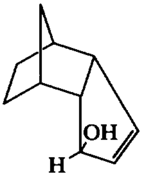
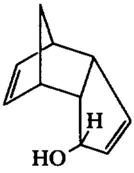
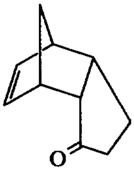
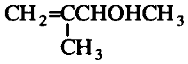
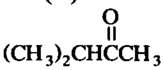
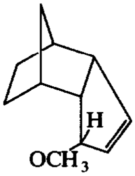
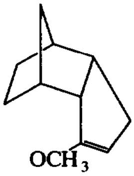
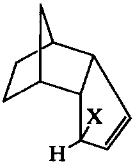
Entries	Substrate	$Fe_3(CO)_{12}$ (mole%)	Time (min)	Isolated yield (%)	Product
1		20	120	90	
2	 $CH_2{=}CHCH_2\underset{C_3H_7}{\underset{\mid}{C}}CHOH$	30	100	88	 $C_3H_7\overset{O}{\overset{\|}{C}}C_3H_7$
3	$CH_2{=}CH(CH_2)_7CH_2OH$	30	120	78	$C_9H_{19}CHO$
4	$CH_2{=}CHCH_2OH$	20	80	90	CH_3CH_2CHO
5		25	60	94	 (I)
6		25	120	No reaction	
7		30	360	60	 (II)
8	 $CH_2{=}\underset{CH_3}{\underset{\mid}{C}}CHOHCH_3$	30	120	88	 $(CH_3)_2CH\overset{O}{\overset{\|}{C}}CH_3$
9		25	60	90	 (III)
10	 (X = OCH_3)	100	120	No reaction	

Table 1 (continued)

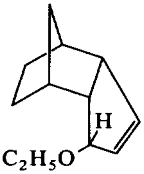
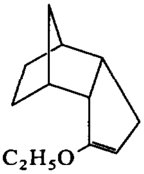
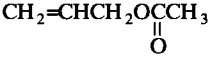
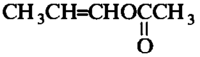
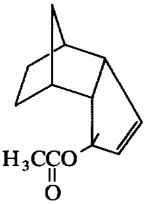
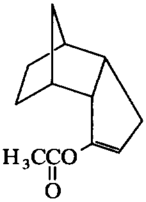
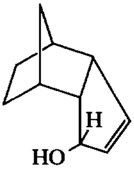
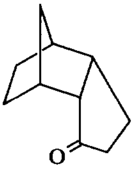
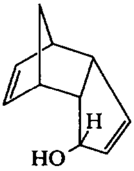
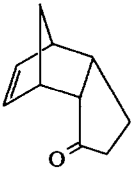
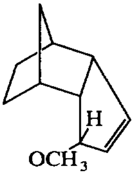
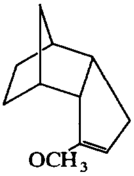
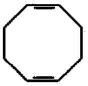
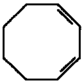
Entries	Substrate	$Fe_3(CO)_{12}$ (mole%)	Time (min)	Isolated yield (%)	Product
11		30	60	80	
12	$C_2{=}CHCH_2OC_2H_5$	20	60	85	$CH_3\text{-}CH{=}CHOC_2H_5$
13	 $CH_2{=}CHCH_2O\underset{\underset{O}{\|}}{C}CH_3$	50	300	75	 $CH_3CH{=}CHO\underset{\underset{O}{\|}}{C}CH_3$
14		80	400	60	 (IV)

Table 2

Reactions of benzylideneacetoneiron tricarbonyl with unsaturated substrates at 95–100°C in tetralin

Substrate	Time (min)	Product	Yield (%)
	5		73
	15		60
	5		85
	30		90

concentrated H_2SO_4, and finally KOH. n-Hexane and n-pentane were stirred with concentrated H_2SO_4 for two weeks, then washed with aqueous sodium bicarbonate and dried over calcium chloride, and then over sodium wire and finally fractional distilled from P_2O_5 and stored over sodium wire. The irradiation source was a 700 W linear tungsten-halogen lamp with an aqueous 1 M solution of CrO_3 as the filter (2 cm path length) to absorb all the light of < 560 nm.

General procedure for the isomerization reactions of unsaturated alcohols, ethers and esters in the presence of dodecacarbonyl triiron

A solution of the substrate (0.01 mol) in degassed solvent (100 cm^3) was stirred with a catalytic amount of $Fe_3(CO)_{12}$ (0.002–0.008 mol) and irradiated for 60–400 min under nitrogen with the temperature of the solution kept at 25–30 °C by passage of water through a coil inserted into the filter solution. The reaction was monitored by gas chromatography. Evaporation of the solvent followed by column chromatography of the residue on silica-gel with a non-polar eluent followed by vaccum distillation gave the isomerized products in 60–94% yield (Table 1). Enol ethers and esters obtained from the reactions of compound (entries 9, 11–14 Table 1) were also hydrolyzed with 4 *N* hydrochloric acid to the corresponding carbonyl compounds.

Reactions of benzylideneacetoneiron tricarbonyl with unsaturated substrates

A solution of the substrate (0.001 mol) and 0.4 molar equivalent of benzylideneacetoneiron tricarbonyl in degassed tetralin (10 ml) was heated at 90–100 °C for 5–30 min under nitrogen (Table 2). The reaction was monitored by gas chromatography. Evaporation of the solvent followed by column chromatography on silica gel and vaccum distillation gave the pure product in 73–90% yield. Some selected IR and ^{1}H-NMR data (in CCl_4) are: (I) ν (cm^{-1}): 2950, 2875, 1730, 1461, 1410, 1328, 1170, 935; δ (ppm): 1.02–2.7 (14 H, complex); (II) ν (cm^{-1}): 3010, 2980, 2940, 2920, 2880, 1710, 1630, 1460, 1440, 1430, 1410, 1170, 1020; δ (ppm): 5.5 (2H, unresolved), 1.1–2.6 (10 H, complex); (III) ν (cm^{-1}): 3070, 2960, 2900, 2870, 2860, 1645, 1465, 1360, 1315, 1040; δ (ppm): 4.25 (1H, unresolved), 3.5 (3H, singlet), 2.05–2.75 (5H, complex), 1.36 (2H, unresolved), 0.9–1.24 (5H, complex); (IV) ν (cm^{-1}): 3060, 2960, 2940, 2880, 1760, 1740, 1620, 1455, 1380, 1280, 1120, 1070, 960, 910; δ (ppm); 5.4 1H, broad, unresolved), 2.05 (3H, singlet), 1.2–2.5 (12H, complex).

Acknowledgment

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