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REDUCTIONS WITH IRON PENTACARBONYL

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Iron carbonyl compounds have recently been shown to effect some unusual and useful transformations.[1] We have found that iron pentacarbonyl selectively reduces enol acetates, vinyl chlorides, and α,β-unsaturated aldehydes to the corresponding olefins. The reagent also reduces α-acetoxy ketones to the respective ketones under similar conditions. As can be seen from the examples in Table I, ketones, esters, and olefins remain unchanged by the reagent. In constrast to other methods, iron pentacarbonyl thus accomplishes in a single step these reductive conversions without recourse to preliminary protection of other reducible functionality.

X = OAc, Cl, CHO

SCHEME I

In the general procedure, the substrate and iron pentacarbonyl[2] (1:5-10 mole ratio) were refluxed in dibutyl ether under nitrogen. Excess iron pentacarbonyl was destroyed by the addition of cupric chloride in acetone or ferric chloride in ethanol. The mixture was diluted with water, acidified to dissolve metal salts, and extracted with ether. After drying and removal of solvent, yields were determined by isolation or glc analysis with an internal standard. Structures were determined by spectral data and comparison with authentic samples. No attempt was made to optimize yields.

Our preliminary investigations indicate that the reduction can proceed through intermediates possessing radical character. The reaction of 17-acetoxy-3-methoxy-1,3-5(10),-16-estratetraene (1) with iron pentacarbonyl was investigated in a variety of solvents

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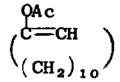
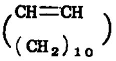
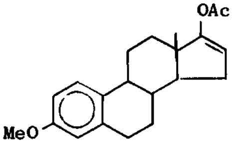
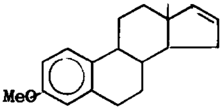
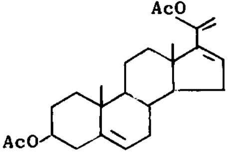
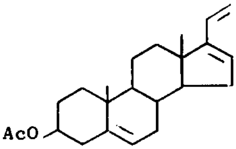
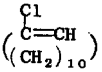
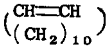
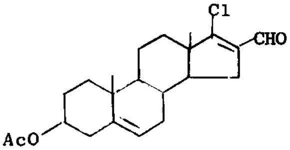
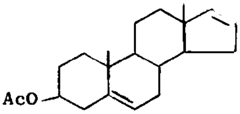
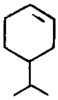
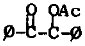
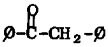
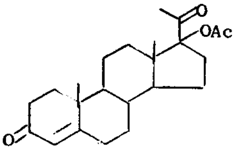
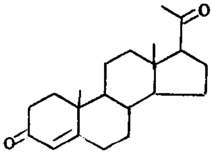
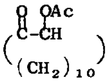
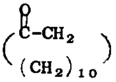
Table I

Substrate	[Eq. Fe(CO)$_5$]	Time (hr)	Product	Yield, %
 $\left(\overset{OAc}{C}{=}CH\ (CH_2)_{10}\right)$	[5]	30	 $\left(CH{=}CH\ (CH_2)_{10}\right)$	40[a]
	[10]	24		35
	[10]	96		40
 $\left(\overset{Cl}{C}{=}CH\ (CH_2)_{10}\right)$	[10]	36	 $\left(CH{=}CH\ (CH_2)_{10}\right)$	30[a]
	[10]	24		36[b]
	[5]	7		36[a]
 $\phi-\overset{O}{\overset{\|}{C}}-\overset{OAc}{C}-\phi$	[6]	24	 $\phi-\overset{O}{\overset{\|}{C}}-CH_2-\phi$	75
	[10]	48		40
 $\left(\overset{O}{\overset{\|}{C}}-\overset{OAc}{CH}\ (CH_2)_{10}\right)$	[6]	26	 $\left(\overset{O}{\overset{\|}{C}}-CH_2\ (CH_2)_{10}\right)$	42

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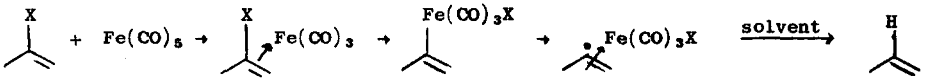
[a] Yield determined by glc. [b] The dechlorinated Δ^{16}-aldehyde was obtained after 5 hours.

the formation of deacetoxylated product being followed by tlc. Best results were obtained using dibutyl ether or cumene, while 2-heptanone proved less satisfactory. No olefinic product was observed in toluene or dimethylformamide. These results suggest that the hydrogen atom-donating ability of the solvent is an important factor. This is further supported by the realization of a 40% isolated yield of olefin obtained by reduction in toluene containing 2 equivalents of tri-n-butyltin hydride, an established source of hydrogen atoms.[3] Reduction of 1 under anhydrous conditions in dibutyl ether followed by work-up with deuterium oxide did not lead to deuterium incorporation into the olefinic moiety, thus precluding hydrolytic cleavage of a metal-carbon bond.

A possible mechanism for reduction of vinyl substituted compounds that accomodates the initial results is given in Scheme II.



Scheme II

Coordination of iron pentacarbonyl with the substituted vinyl compound is followed by insertion of iron into the C-X bond. A similar insertion process has been invoked to explain the formation of tricarbonylbuta-1,3-dieneiron from 2-bromobuta-1,3-diene on reaction with diiron nonacarbonyl.[4] Thermal homolysis of the Fe-C bond leads to a vinyl radical, probably coordinated with an iron species. Abstraction of hydrogen from solvent results in product. Similar mechanistic considerations for the reduction of α-acetoxy ketones requires initial coordination of the ketone to iron pentacarbonyl and insertion of iron into the C-OAc bond, followed by a homolytic pathway to complete the reduction.

Acknowledgement

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2. Iron pentacarbonyl was obtained from Alfa Inorganics and used as received.

3. L. W. Menapace and H. G. Kuivila, J. Am. Chem. Soc., 86, 3047 (1964).

4. R. N. Greene, C. H. DePuy, and T. E. Schroer, J. Chem. Soc. (C), 3116 (1971).