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Reduction of α,β-Unsaturated Carbonyl Compounds to the Saturated Alcohols Using Hydridocarbonyliron Complexes

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Synopsis. Tetracarbonylhydridoferrate was found to be effective for the selective reduction of α,β-unsaturated carbonyl compounds to the corresponding saturated alcohols. The reactions proceeded stereospecifically and (−)- and (+)-neodihydrocarveol were obtained exclusively from (+)- and (−)-carvone respectively. The reaction mechanism is briefly discussed.

Hydridocarbonyliron complex $[HFe_m(CO)_n^-]$ have been reported to be useful hydrogenating reagents for α,β-unsaturated carbonyl compounds,[1,2] conjugated dienes,[3] and the C=N double bond of *N*-benzylideneaniline,[4] giving saturated carbonyl compounds, monoenes, and *N*-benzylaniline, respectively. But the reduction of a carbonyl group to an alcohol has never been reported.

In the course of our research on the selective reduction of several essential oils with α-enone moiety using tetracarbonylhydridoferrate $[HFe(CO)_4^-]$ (**1**), we found unexpectedly that **1** in tetrahydrofuran was effective for the selective reduction of carbonyl groups to the corresponding alcohols. In this paper, we wish to report about these reactions.

Experimental

Infrared spectra were recorded on a Hitachi 260-10 Infrared Spectrophotometer, NMR spectra were measured on a Hitachi R-600 FT-NMR Spectrophotometer, and mass spectra were measured on a RM-50 Hitachi GC-MS. Gas chromatography was carried out on a Yanagimoto G-180 Model equipped with a glass column packed with polyethyleneglycol 20 M[†] (10%) on Chromosorb (0.3 cmϕ × 1.5 m) and a Yanagimoto G-8 Model equipped with a stainless column packed with Silicone Gum SE-30 (10%) on Chromosorb (0.3 cmϕ × 2 m). Optical rotations were measured on a Union High Sensibility Specific Rotary Meter PM-71.

Materials. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride under argon just before use. Pentacarbonyliron and deuterium oxide (Merck) were used without further purification. The following organic compounds, (+)- and (−)- carvone, α- and β-ionone, diethyl ketone, benzylideneacetone and triethylenediamine, were commercial products of the highest available purity. Piperitenone was supplied from Ogawa and Co., Ltd. All reduction experiments were carried out under argon atmosphere.

Preparation of 1 in THF. To the THF solution (40 ml) of triethylenediamine (3.7 g, 33 mmol), deionized water (0.59 ml, 33 mmol) or D_2O (0.66 ml, 33 mmol) was injected by syringe and the mixture was stirred for 30 min at 60 °C under argon atmosphere. Then, pentacarbonyliron (1.5 ml, 11 mmol) was injected and the reaction mixture was stirred for further 1 h at the same reaction conditions. The solution was used for the next reaction *in situ*.[5]

Representative Reduction of α-Ionone Using 1. To the solution of **1** (22 mmol) in THF, α-ionone (1.13 ml, 5.5 mmol) was injected, and the mixture was stirred at 60 °C under argon atmosphere till the reaction was completed perfectly. After the air oxidation of the solution at room temperature for 1 d, iron oxide was centrifuged. And THF was removed with a rotary evaporator. The residue was purified by column or thin layer chromatography (silica gel, hexane: ethyl acetate= 4 : 1). The product was identified as 4-(2,6,6-trimethyl-2-cyclohexenyl)-2-butanol by means of IR, NMR, MS, and GLC. Yield >98% (GLC).

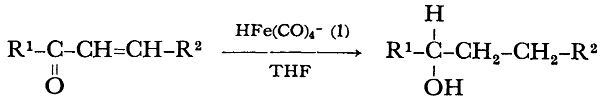
4-(2,6,6,-Trimethyl-2-cyclohexenyl)-2-butanol. IR (cm^{-1}): 3300, 2900, 1440, 1110; MS (*m/e*); 196 (M^+); NMR ($CDCl_3$) (δ): 0.88 (6H, d, $C(CH_3)_2$), 1.24 (3H, s, $=C-CH_3$). 1.44 (3H, s, $O-C-CH_3$), 0.98—2.2 (8H, m), 3.6—4.0 (1H, m), 5.25—5.6 (1H, m).

4-(2,6,6,-Trimethyl-1-cyclohexenyl)-2-butanol. IR (cm^{-1}): 3350, 2900, 1460, 1120; MS (*m/e*): 196 (M^+); NMR ($CDCl_3$) (δ): 0.97 (6H, s, $C(CH_3)_2$), 1.13 (2H, s, $=CH_2-$), 1.23 (2H, s, $-CH_2-$), 1.59 (3H, s, $O-C-CH_3$), 1.1—2.0 (6H, m), 3.4—3.92 (1H, m).

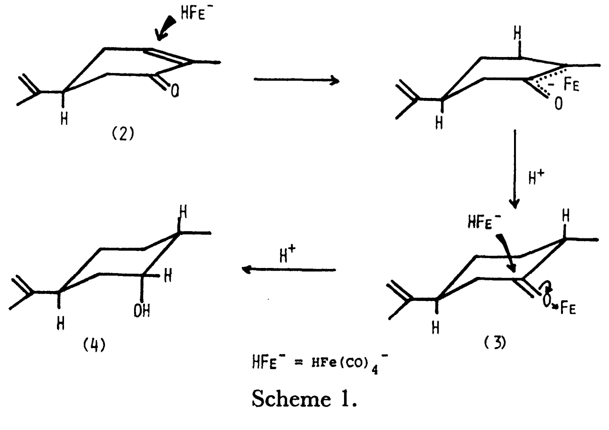
(−)-Neodihydrocarveol. IR (cm^{-1}): 3400, 880; MS (*m/e*): 154 (M^+); NMR ($CDCl_3$) (δ): 0.95 (3H, d, $-CH_3$), 1.05—1.65 (8H, m), 1.72 (3H, s, $=C-CH_3$), 3.2—3.7 (1H, m), 3.58 (1H, s), 4.76 (2H, s).

Results and Discussion

For example, **1** in THF generated *in situ* reacted with (+)-carvone at 60 °C for 9 d under argon atmosphere to give (−)-neodihydrocarveol in almost quantitative yield. This shows that **1** in THF is an efficient reductant of α,β-unsaturated carbonyl compounds to the corresponding saturated alcohols (Eq. 1), although **1** in ethanol gives only (−)-dihydrocarvone from (+)-carvone. Other results are summarized in Table 1. As shown in Table 1, the compounds with α-enone moiety were reduced to the corresponding saturated alcohols in high yields. Piperitenone which has two carbon–carbon double bonds of α-enone moiety was also reduced to the corresponding menthol using 6 equiva-



$$R^1-\underset{\underset{O}{\|}}{C}-CH=CH-R^2 \xrightarrow[\text{THF}]{HFe(CO)_4^-\ (1)} R^1-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CH_2-R^2 \qquad (1)$$



Scheme 1.

[†] 1 M=1 mol dm^{-3}.

TABLE 1. THE REDUCTION OF α,β-UNSATURATED CARBONYL COMPOUNDS USING TETRACARBONYLHYDRIDOFERRATE IN THF

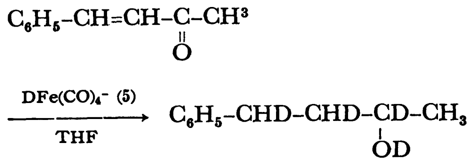
Run	Substrate	Reaction time/d	Product	Yield/%$^{a)}$
1	(+)-Carvone$^{b)}$	9	(−)-Neodihydrocarveol$^{c)}$	>98
2	(−)-Carvone$^{d)}$	9	(+)-Neodihydrocarveol$^{e)}$	>98
3	Piperitenone	26	(±)Menthol	>98
4	α-Ionone	20	4-(2,6,6-Trimethyl-2-cyclohexenyl)-2-butanol	>98
5	β-Ionone	13	4-(2,6,6-Trimethyl-1-cyclohexenyl)-2-butanol	>98
6	Benzylideneacetone	3	4-Phenyl-2-butanol	>98
7	Diethylketone	—	No reaction	—

a) Yields were determined by GLC. b) $[\alpha]_D^{20}+49.8°$ (*c* 9.66, EtOH). c) $[\alpha]_D^{20}-13.5°$ (*c* 1.01, Et OH). d) $[\alpha]_D^{20}-60.1°$ (*c* 9.65, EtOH). e) $[\alpha]_D^{20}+21.4°$ (*c* 1.03, EtOH).

lents of **1**.

As to the stereochemistry, it was found that (+)- and (−)-carvone reacted with **1** to give exclusively (−)- and (+)-neodihydrocarveol respectively, but the corresponding diastereomers such as isodihydrocarveol, dihydrocarveol, and neoisodihydrocarveol were not produced, showing that these reactions proceeded stereospecifically.

The reaction mechanism was assumed as follows (Scheme 1). First, **1** attacked the carbon-carbon double bond of α,β-unsaturated carbonyl moiety of (+)-carvone (**2**) from the sterically less hindered side to form dihydrocarvone (**3**),[6] which was detected in the reaction mixture by means of GLC. Subsequently, **3** is reduced selectively to give (−)-neodihydrocarveol (**4**). However, although it is still uncertain, it seems that **3** exists as a complex with carbonyliron and that the carbonyl group is to some extent activated, because saturated ketones such as diethyl ketone did not react with **1** in THF.



$$C_6H_5\text{-}CH{=}CH\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH^3 \xrightarrow[\text{THF}]{DFe(CO)_4^-\ (5)} C_6H_5\text{-}CHD\text{-}CHD\text{-}\underset{\underset{OD}{|}}{C}D\text{-}CH_3 \qquad (2)$$

Besides, the introduction of deuterium was tried using deuterium oxide (D_2O) instead of water (H_2O) for the preparation of tetracarbonyldeuterioferrate (**5**). The reaction of **5** with benzylideneacetone in THF at 60 °C for 3 d gave the corresponding deuterated alcohol, which was identified by means of IR, NMR, and MS. The similar introduction of deuterium was also noticed in the case of the reaction with (+)- and (−)-carvone.

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5) (**1**) in diethyl ether has been prepared by the similar method; see Ref. 1.

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