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UNUSUAL 1,3-HYDROGEN SHIFT IN THE REACTION OF $Na_2Fe(CO)_4$ WITH METHYL E-3-CHLORO-2-BUTENOATE

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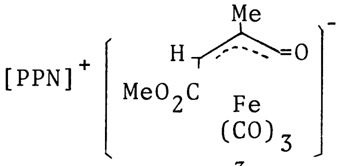
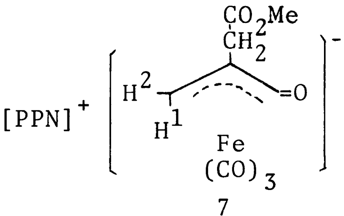
Methyl E-3-chloro-2-butenoate reacts with $Na_2Fe(CO)_4$ in THF at 25°C affording an unexpected [η^3-2-(methoxycarbonylmethyl)-acryloyl]tricarbonylferrate which has been derived by an unusual 1,3-hydrogen shift. The reaction was rationalized by assuming a (η^2-allene)hydridoferrate intermediate.

β-Elimination and readdition of hydridometal complexes are very important factors which determine the structure of organic products in the reaction involving alkyl-1) and alkenyl-2) metal complexes. We now report an unusual 1,3-hydrogen shift in a reaction of a halovinyl compound with $Na_2Fe(CO)_4$, which is reasonably considered to proceed *via* (η^2-allene)hydridocarbonylferrate.

Methyl Z-3-chloro-2-butenoate (3 mmol) reacted with $Na_2Fe(CO)_4$3) (3 mmol) in tetrahydrofuran at 25°C affording the expected {η^3-[Z-2-methyl-3-(methoxycarbonyl)-acryloyl]}tricarbonylferrate, which was isolated as a bis(triphenylphosphine)iminium salt4,5,6) in a 55% yield (Scheme). The reaction may be rationalized by the substitution reaction of the halide with $[Fe(CO)_4]^{2-}$ followed by the insertion of a CO group and the co-ordination of the olefinic group to the iron atom4) (Scheme). The reaction of methyl E-3-chloro-2-butenoate with $Na_2Fe(CO)_4$ also gave yellow micro crystals (yield 59%), however, the following observations and the spectral data of the complex shown in the Table exhibited that the structure is not the expected **6** but [η^3-2-(methoxycarbonylmethyl)acryloyl]tricarbonylferrate **7**6); 1) the ^1H nmr spectrum taken at -30°C7) exhibited the signals due to two metal-coordinated vinylidene protons (δ, 2.15(1H) and 2.51(1H), $J \sim 0$ Hz) instead of the expected terminal methyl protons. Furthermore an AB quartet (δ, 2.29(1H) and 2.92(1H) J=14.0 Hz) due to nonequivalent sp^3 methylene protons was observed which was assigned to the methoxy-carbonylmethyl group. 2) ^{13}C nmr spectrum also showed the presence of a co-ordinated

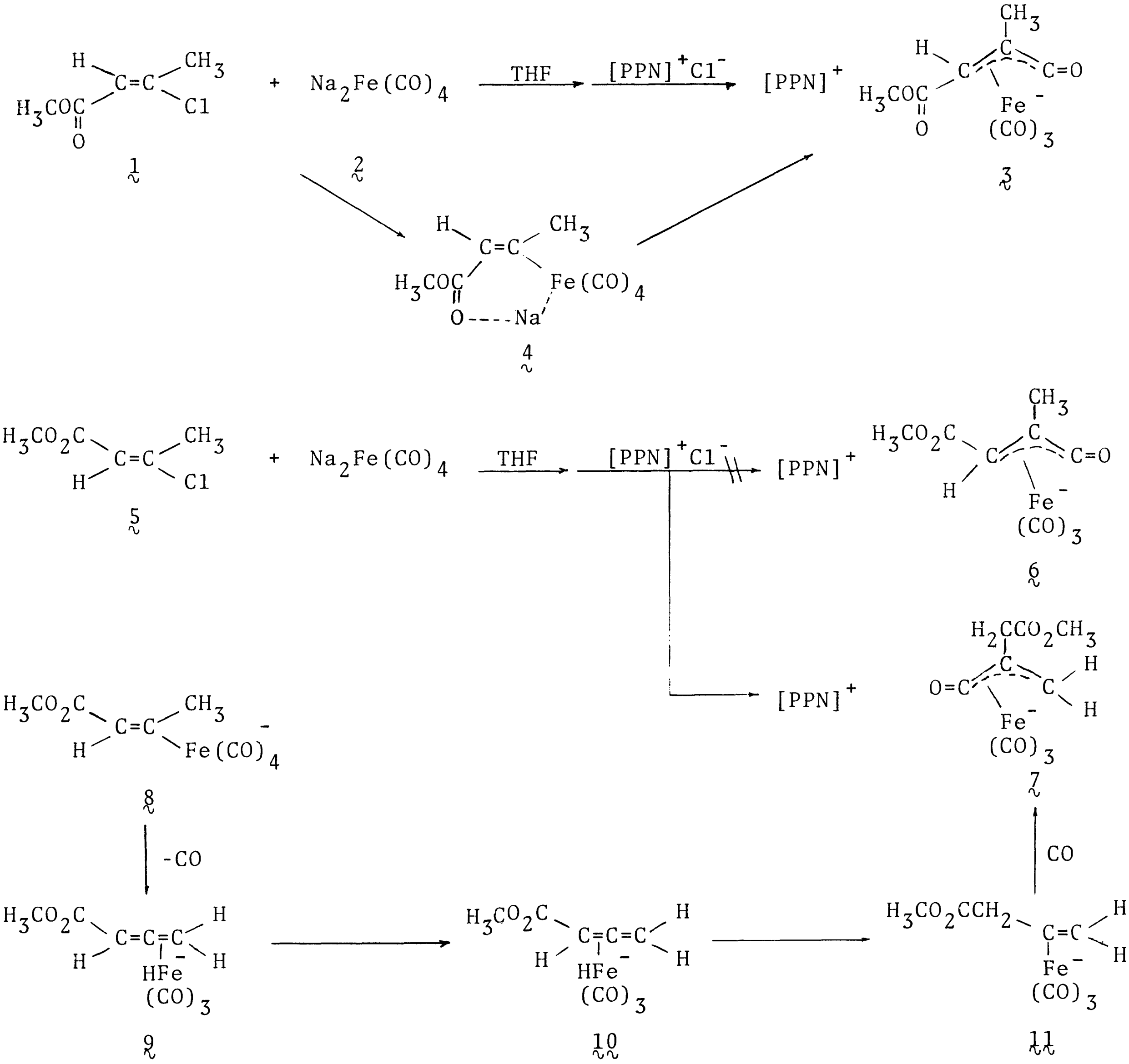
Table. Ir, ^{1}H and ^{13}C nmr Spectral Data of 3 and 7.

Complex	Ir(KBr, cm^{-1})	^{1}H nmr (δ ppm, TMS, CD_2Cl_2, J Hz)	^{13}C nmr
 3	1990, 1910, 1890 } $\nu_{C\equiv O}$ 1718 $\nu_{\underset{Fe}{C}=O}$ 1678 $\nu_{C=O}$	1.50(s, 3H) $\rangle C-CH_3$ 3.40(s, 1H) CH= 3.42(s, 3H) OMe	20.5(qd, J_{CH}127, J_{CCCH}2.2) Me 32.7(m, J_{CCH_s}5.8) $C\cdots\underline{C}\cdots C$ 47.8(dq, J_{CH}153.7, J_{CCCH} 4.9) H-C= 243.9(s) Fe$\underline{C}$=O
 7	1977, 1905, 1875 } $\nu_{C\equiv O}$ 1725 $\nu_{\underset{Fe}{C}=O}$ 1695 $\nu_{C=O}$	2.15(s, 1H, J≃0) H^1_2 2.51(s, 1H, J≃0) H^2 2.29, 2.92 } (ABq, J=14.0) CH_2 3.48(s, 3H) OMe	31.8(s) $C\cdots\underline{C}\cdots C=O$ 33.4(dd, J_{CH}152, 170) $=CH_2$ 41.4(t, J_{CH}131) CH_2 248.9(s) Fe$\underline{C}$=O

olefinic group (δ, 31.8 (s) and 33.4 (dd, J=152, 170 Hz) ppm), a methylene group (41.4 (t) J=131 Hz) and an acyl-iron group (248.9 ppm (s))$^{4)}$. 3) The ir spectrum showed the terminal $\nu_{C\equiv O}$ of the complex having minus charge on it (1977, 1905 and 1875 cm^{-1}) and a characteristic band of η^3-acryloyl group (1725 cm^{-1}) as well as the $\nu_{C=O}$ of the ester group (1695 cm^{-1}). The complex 7 can be derived by the 1,3-hydrogen shift of the methyl proton in 5.

In order to account for this result we postulate the following reaction route.$^{8)}$ 1) The corresponding alkenyl-iron complex 8 is formed$^{4)}$. 2) Dissociation of a carbon monoxide and the β-elimination of 8 gives (η^2-allene)hydridoferrate 9 which isomerizes to 10. 3) Readdition of the hydride and the migratory insertion of a carbonyl group and the co-ordination of the olefinic group affords 7. The discrepancy of the reaction of 1 and 5 may be partly due to the stabilization effect of a methoxycarbonyl group at *cis* position of $Fe(CO)_4^-$ group in the reaction of 1 which may make a chelate ring such as 4. The β-elimination-readdition reaction of an alkenyl iridium complex *via* a (η^2-allene)hydridoiridium complex was reported$^{2)}$, however, the product was η^3-allyl complex derived by 1,2-hydrogen shift. To our knowledge, this is the first example of a 1,3-hydrogen shift which is reasonably considered to proceed *via* a (η^2-allene)-hydridometal complex.

Scheme



[PPN]$^+$=bis(triphenylphosphine)iminium cation

References and Notes

1) For example, see C. P. Casey and C. R. Cyr, J. Amer. Chem. Soc., 93, 1280(1971) and references cited therein.

2) J. Schwartz, D. W. Hart and B. McGiffert, ibid., 96, 5613(1974).

3) M. P. Cooke, ibid., 92, 6082(1970).

4) The reaction of halovinyl compounds with $Na_2Fe(CO)_4$ giving (η^3-acryloyl)tricarbonylferrate has been reported briefly; T. Mitsudo, H. Nakanishi, T. Inubushi, I. Morishima, Y. Watanabe and Y. Takegami, J. C. S. Chem. Comm., 1976, 416,

J. Chem. Soc. Dalton, 1978, 1298. The further detailed results were presented at the 37 th Annual Meeting of the Chem. Soc. of Japan, Yokohama (1978), J. Chem. Soc. Dalton, in press.

5) X-ray molecular structure of a derivative of **3** was determined, K. Nakatsu, Y. Inai, T. Mitsudo, H. Nakanishi, Y. Watanabe and Y. Takegami, J. Organometal. Chem., 159, 111 (1978).

6) Satisfactory analytical data for **3** and **7** were obtained.

7) ^{1}H and ^{13}C nmr spectra showed the temperature dependence. At 30°C, the signals of the vinylidene group were broadened.

8) 1,3-Sigmatropic reaction in **8** may not be ruled out completely.

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