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# Photoreaction of Ferrocene with Some Acetylene Derivatives

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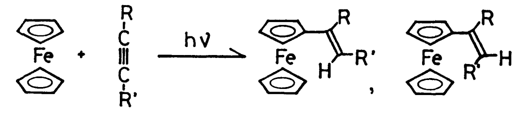
**Synopsis.** The UV-irradiation of ferrocene and dimethyl acetylenedicarboxylate in acetic acid–water solution afforded dimethyl ferrocenylmaleate and dimethyl ferrocenylfumarate in 40 and 5% yield, respectively. Methyl 3-carbamoylpropiolate, dicyanoacetylene, and methyl propiolate were also reactive and the corresponding substituted ferrocenes were obtained. The reaction can be considered to proceed *via* the excitation of the charge transfer complex between ferrocene and acetylene derivatives.

As reported,1) UV-irradiation of the ferrocene-halogenated hydrocarbon–ethanol system gave substituted ferrocene *via* the excitation of the charge transfer complex between ferrocene and halogenated hydrocarbon. We found a similar photo-substitution of ferrocene with some electron defficient acetylene derivatives.

When an acetic acid–water solution of ferrocene (**1**) and dimethyl acetylenedicarboxylate (**2a**) in a quartz vessel was irradiated with 254 nm light for 24 h under nitrogen atmosphere, dimethyl ferrocenylmaleate (**3a**) and dimethyl ferrocenylfumarate (**4a**) were obtained in 40 and 5% yield, respectively. When methyl 3-carbamoylpropiolate (**2b**), dicyanoacetylene (**2c**), and methyl propiolate (**2d**) were used instead of **2a**, photo-products similar to **3a** and **4a** were obtained. However, the yields of the photo-products were lower than those of **3a** and **4a**, and the isomer ratio, **3**/**4**, was different from that obtained in the case of **2a**. The results of the photoreactions are listed in Table 1. Other acetylene derivatives, such as phenylacetylene, diphenylacetylene, methyl 3-phenylpropiolate, phenylpropiolaldehyde, and acetylenedicarboxamide, were unreactive for this photoreaction and gave no substituted ferrocene under the UV-irradiations. The effect of additives and the wavelength of light used were examined for the **1**–**2a**–acetic acid–water systems which showed the highest yields of the photo-products. The results showed that the radical scavenger, cyclohexene, retarded the photo-substitution of ferrocene very little [yield of **3a**: without additive, 21%; with cyclohexene, 14%]. This result indicates that this photo-substitution does not proceed *via* the coupling of free, separate radicals as reported for the reaction of furan with **2a**,2) but proceed *via* the geminate coupling of the radical pair in the solvent cage.3) Benzophenone, a triplet sensitizer, was not effective for the formation of **3a** and **4a**. This result indicates that the contribution of the triplet state of **1** or **2a** for the photo-substitution is very small. In the irradiation with light of wavelength longer than 300 nm(high pressure mercury lamp with a Pyrex filter), only a trace amount of **3a** was obtained and more than 60% of **1** and **2a** were recovered.

The formation of the charge transfer complex between **1** and **2a** in the ground state was supported by the

Table 1. Photo-substitution of ferrocene with some acetylene derivatives1)



**1** **2** **3** **4**

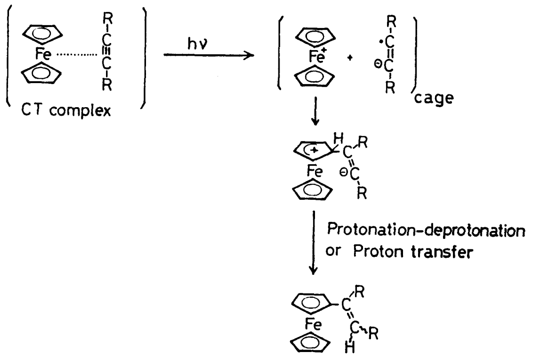
**2a**: $R=R'=\text{-}CO_2Me$
**2b**: $R=\text{-}CO_2Me$, $R'=\text{-}CONH_2$
**2c**: $R=R'=\text{-}CN$
**2d**: $R=\text{-}H$, $R'=\text{-}CO_2Me$

**3a**, **4a**: $R=R'=\text{-}CO_2Me$
**3b**, **4b**: $R=\text{-}CO_2Me$ (or $\text{-}CONH_2$), $R'=\text{-}CONH_2$ (or $\text{-}CO_2Me$)
**3c**, **4c**: $R=R'=\text{-}CN$
**4d**: $R=\text{-}CO_2Me$, $R'=\text{-}CH_3$

| **1** (mmol) | **2** (mmol) | Solvent (40 ml) | Light Source3)/Time (h) | Conversion (%) | Products and yields2) (%) | |
|---|---|---|---|---|---|---|
| | | | | | **3** | **4** |
| 0.2 | **2a** 0.4 | $CH_3CO_2H$-$H_2O$ (3 : 1, v/v) | LP / 24 | 64 | **3a** : 40.6(26) | **4a** : 4.7(3) |
| 2.0 | **2b** 2.0 | $CH_3CO_2H$ | LP / 24 | 60 | **3b** : 7.4( 4.4) | **4b** : 7.4(4.4) |
| 4.0 | **2c** 2.0 | $CH_3CO_2H$ | LP / 21 4) | 6.4 | **3c** : 16.1( 1) | **4c** : 6.7(0.4) |
| 1.0 | **2d** 2.0 | $CH_3CO_2H$-$H_2O$ (3 : 1, v/v) | LP / 13 | 15 | — | **4d** : 20.3(3) |

1) These photoreactions were carried out below 25 °C. 2) Yields based on consumed ferrocene. The yields in parentheses are the net yields based on ferrocene used. 3) LP denotes a low pressure mercury lamp. 4) This reaction was carried out above 35 °C.

spectral data. The UV-spectra of **1** and **2a** in acetic acid showed an increment of absorption in the 250—300 nm region and the NMR spectra (measured at 90 MHz) of the mixed solution of **1** and **2a** in acetic acid showed a small downfield shift of the proton signals of **1** and an upperfield shift of those of **2a**, as compared to the corresponding proton signals measured independently. Based on these spectral data and on the effect of additives, the following processes can be considered for the present photo-substitution of ferrocene: i) The excitation of the charge transfer complex of **1** and **2a** to its singlet state. ii) One electron transfer from **1** to **2a**, followed by the formation of ferrocenium cation and anion radical of **2a**. iii) Coupling of the radical anion of **2a** with ferrocenium cation in the solvent cage. iv) Deprotonation and protonation to the anionic center of olefin,[4] or proton transfer.



When acetone, acetonitrile, ethyl acetate, and methanol was used as the solvent, the yields of **3a** were much lower. This solvent effect indicates that the protic solvent with high polarity is necessary for this photo-substitution.

## Experimental

*Materials.* Commercially available ferrocene (Wako Junyaku, GR-grade reagent) was used without further purification. Dimethyl acetylenedicarboxylate (Wako Junyaku, EP-grade reagent) was purified by column chromatography on silica gel (Merck, GF-254, Type 60) before use. Methyl 3-carbamoylpropiolate was prepared by mixing dimethyl acetylenedicarboxylate and ammonia-water for several hours. Dicyanoacetylene was prepared by the method described in the literature.[5] Commercial methyl propiolate (Wako Junyaku, EP-grade reagent) was used without further purification. Acetic acid and other solvents used in this reaction were all purified by distillation under nitrogen atmosphere and dried just before use.

*Irradiation Procedure.* The general execution of the photoreaction is represented by the procedure for the photosubstitution of ferrocene with dimethyl acetylenedicarboxylate.

*Photoreaction of Ferrocene (1) with Dimethyl Acetylenedicarboxylate (2a).* The acetic acid-water(3 : 1, v/v, 40 ml) solution of **1** (37 mg, 0.2 mmol) and **2a** (57 mg, 0.4 mmol) was degassed and then filled with nitrogen. This sample solution was irradiated in a quartz vessel with a low pressure lamp(Taika Kogyo, 16 W) for 24 h. After the irradiation, 100 ml of ethyl acetate was added to the reaction mixture and washed with water and then with aqueous sodium hydrogencarbonate solution. The ethyl acetate solution was dried and concentrated under reduced pressure. The residue was subjected to preparative TLC on silica gel (Merck, CF-254). **3a** and **4a** were obtained as a mixture. Further separation with TLC afforded 17.3 mg (40.6%) of **3a** as a red-purple oily solid. **3a**: IR(KBr) 1718, 1725 cm$^{-1}$ (C=O), 1620 cm$^{-1}$ (C=C), 1100, 1000 cm$^{-1}$ (monosubstituted ferrocene); NMR($CCl_4$), δ(ppm from TMS) 3.69 (s, 3H, $-CH_3$), 3.85 (s, 3H, $-CH_3$), 4.15 (s, 5H, $C_5H_5$), 4.32 (4H, $C_5H_4$), 5.86 (s, 1H, olefinic proton); MS(70 eV), *m/e*, 328(M$^+$). Found: C, 57.96; H, 5.00%. Calcd for $C_{16}H_{16}O_4Fe$: C, 58.57; H, 4.88%, M, 328. From another fraction, 2 mg (4.7%) of **4a** was obtained. **4a**: IR(direct) 1720, 1725 cm$^{-1}$ (C=O), 1620 cm$^{-1}$ (C=C), 1100, 1000 cm$^{-1}$ (monosubstituted ferrocene); NMR($CCl_4$), δ(ppm from TMS) 3.65 (s, 3H, $-CH_3$), 3.86 (s, 3H, $-CH_3$), 4.06 (s, 5H, $C_5H_5$), 4.30 (t, 2H, 3-, 4-position of $C_5H_4$–), 4.70 (t, 2H, 2-, 5-position of $C_5H_4$–), 6.37 (s, 1H, olefinic proton); MS(70 eV), *m/e*, 328(M$^+$). Found: C, 58.10; H, 4.95%. Calcd for $C_{16}H_{16}O_4Fe$: C, 58.57; H, 4.88%, M, 328.

**3b** and **4b** were obtained in the photoreaction of **1** with **2b**. **3b** and **4b** were obtained as a mixture and further separation was not possible. NMR(mixture in $CCl_4$), δ(ppm from TMS) 3.71(s, 3H, $-CH_3$ of ester **4b**), 3.87(s, 3H, $-CH_3$ of ester **3b**), 4.13(s, 5H, $C_5H_5$ of **4b**), 4.19(s, 5H, $C_5H_5$ of **3b**), 4.3—4.6(6H, $C_5H_4$– of **3b**, and $H_2$, and $H_5$ of $C_5H_4$– of **4b**), 4.74(t, 2H, $H_3$, $H_4$ of $C_5H_4$– of **4b**), 5.34 (s, 1H, olefinic proton of **3b**), 6.08(s, 1H, olefinic proton of **4b**); IR(mixture, KBr) 3490, 3390, 1630, 1550 cm$^{-1}$ ($NH_2$ of primary amide), 1665 cm$^{-1}$ (C=O of amide), 1715 cm$^{-1}$ (C=O of ester), 3080, 1600, 780 cm$^{-1}$ (C=C), 1100, 1000, 830 cm$^{-1}$ (monosubstituted ferrocene).

**3c** and **4c** were obtained only when the acetic acid solution of **1** and **2c** was irradiated at 35—40 °C. As the isolation of **3c** and **4c** was not possible, the assignment and the quantitative analysis were done based on the NMR spectra of the mixture. NMR(mixture in $CCl_4$), δ(ppm from TMS) 4.24 (s, 5H, $C_5H_5$ of **4c**), 4.26(s, 5H, $C_5H_5$ of **3c**), 4.49 (t, 2H, $H_2$, $H_5$ of $C_5H_4$– of **4c**), 4.60(t, 2H, $H_2$, $H_5$ of $C_5H_4$– of **3c**), 4.94(t, 2H, $H_3$, $H_4$ of $C_5H_4$– of **4c**), 5.05(t, 2H, $H_3$, $H_4$ of $C_5H_4$– of **3c**), 5.72(s, 1H, olefinic proton of **3c**), 6.45(s, 1H, olefinic proton of **4c**); IR(direct) 3080, 1605, 770 cm$^{-1}$ (C=C), 2210 cm$^{-1}$ (–C≡N), 1105, 1030, 990(sh) cm$^{-1}$ (monosubstituted ferrocene).

**4d** was obtained in the photoreaction of **1** with **2d** in acetic acid–water solution. As a main product, **4d** was obtained from TLC. NMR($CCl_4$), δ(ppm from TMS) 2.12 (s, 3H, $-CH_3$), 3.81 (s, 3H, $-CH_3$ of ester), 4.10 (s, 5H, $C_5H_5$), 4.32 (s, 4H, $C_5H_4$–), 6.17 (s, 1H, olefinic proton). IR(KBr), 1725 cm$^{-1}$ (C=O), 1580 cm$^{-1}$ (C=C), 1100, 1000 cm$^{-1}$ (ferrocene).

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