BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3463—3464(1971)

The Reduction of Some Quinones and Enones by Ferrocene in the Presence of Aluminum Chloride

Yoshimori OMOTE, Ryuichiro KOBAYASHI, Choji KASHIMA, and Noboru SUGIYAMA
Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo

(Received March 3, 1971)

Ferrocene is known to be easily oxidized in the presence of an acid to give ferricinium ion.[1-4] One of us reported that the reaction of ferrocene with fumaroyl chloride in the presence of aluminum chloride did not give 1,2-di(ferrocenylcarbonyl)ethylene, but afforded 1, 2-di(ferrocenylcarbonyl)ethane and β-(ferrocenylcarbonyl)propionic acid.[5] Schaaf and Lenk[6] reported the oxidation of ferrocene in the Friedel-Crafts reaction of ferrocene with some acyl or aroyl chlorides.

We now wish to report our finding that some quinones and enones are reduced by ferrocene in the presence of aluminum chloride to give phenols and saturated ketones respectively.[7] The limitation of the reaction is also examined.

Reduction of Quinones by Ferrocene. Coan *et al.*[8] found the formation of a charge-transfer complex of ferrocene with *p*-benzoquinone or chloranil, but they failed to isolate the complex. We examined the reaction of *p*-benzoquinone with ferrocene in dichloromethane in the presence of aluminum chloride and found that the products were hydroquinone and ferricinium chloride in the molar ratio 1: 1.8. Chloranil and ferrocene afforded tetrachlorohydroquinone and ferricinium chloride in a molar ratio 1: 1.7 under similar conditions.

Thus it might be concluded that two moles of ferrocene react with one mole of a quinone to give two moles of ferricinium ion and one mole of the corresponding hydroquinone.

Reduction of Enones by Ferrocene. The reduction of a variety of enone compounds and other olefinic compounds by ferrocene in the presence of aluminum chloride has been checked. The results are summarized in Table 1 from which it might be concluded that an enedione structure –COCH=CHCO– is essential for the reduction by ferrocene.

As regards stoichiometry of this reaction, the reduction of 1,2-dibenzoylethylene by ferrocene was examined in detail. When 1,2-dibenzoylethylene was brought into reaction with ferrocene in the presence of aluminum chloride in a molar ratio 1: 1: 2 (substrate: ferrocene: aluminum chloride), about half of the substrate was reduced to 1,2-dibenzoylethane, and ferrocene gave ferricinium ion in the molar ratio 1: 1.9 (product: ferricinium ion). This reveals that one mole of an enone whose structure contains –COCH=CHCO– is reduced by two moles of ferrocene.

TABLE 1. REDUCIBILITY OF SOME ENONES COMPARED WITH THAT OF SOME OLEFINIC COMPOUNDS

$RCH=CR'R''$

R	R′	R″	Reducibility
C_6H_5CO-	C_6H_5CO-	H–	+
C_6H_5CO-	HOOC–	H–	+
CH_3OCO-	CH_3OCO-	H–	+
C_6H_5-	C_6H_5-	H–	–
$-CH_2CH_2CH_2CH_2-$		H–	–
C_6H_5-	HOOC–	H–	–
CH_3-	HOOC–	H–	–
CH_3CO-	CH_3-	CH_3-	–
FcCO–	C_6H_5-	H–	–

Fc: Ferrocenyl

Experimental

Quinones, Enones and Related Compounds. The following compounds were prepared according to literature: bromosuccinic anhydride,[9] bp$_{25}$ 148°C, β-benzoylacrylic acid,[10] mp 94—95.5°C, 1,2-diacetylethylene,[11] mp 76—79°C, *trans*-1, 2-dibenzoylethylene,[12] mp 108°C, *trans*-β-acetylacrylic acid,[13] mp 125—126°C. Other compounds used were commercial products.

Reduction of p-*Benzoquinone by Ferrocene.* Aluminum chloride (0.39 g, 2.94 mmol) and *p*-benzoquinone (0.11 g, 1.02 mmol) were added into 35 m*l* of dry dichlolomethane and stirred for 5 min. Ferrocene (0.186 g, 1.00 mmol) was then added. After stirring for 80 min at room temperature, the reaction mixture was poured into ice water and the dichloromethane layer was washed with water, dried and evaporated to dryness. The residue was purified by silica-gel chromatography with benzene-ethyl acetate (2: 1) to give hydroquinone (0.079 g, 0.72 mmol), which was identified by comparing with an authentic sample by UV and tlc technique. For comparison, *p*-benzoquinone (0.11 g) was treated in the same procedure as described above but without fer-

---

[1] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Amer. Chem. Soc.*, **74**, 2126 (1952).

[2] V. Weinmayr, *ibid.*, **77**, 3009 (1955).

[3] M. F. Hauthorne, *J. Org. Chem.*, **21**, 363 (1956).

[4] O. N. Suvorova, G. A. Domrachev, and G. A. Razuvaey, *Dokl. Akad. Nauk SSSR*, **183** (4), 850 (1968).

[5] N. Sugiyama and T. Teitei, This Bulletin, **35**, 1423 (1962).

[6] R. L. Schaaf and C. T. Lenk, *J. Org. Chem.*, **28**, 3238 (1963).

[7] During the course of our investigation, the reduction of some enones by ferrocene in the Friedel-Crafts reaction was independently presented at the 2nd Meeting of Non-Benzenoid Aromatic Chemistry by K. Yamakawa and M. Moroe, Abstracts of Papers, p. 68—70, Kyoto, Nov. 22—23 (1968).

[8] J.C. Coan, E. Berg, and H.E. Podall, *J. Org. Chem.*, **29**, 975 (1964).

[9] R. Anschütz and L. Kinnkut, *Ber.*, **11**, 1221 (1878).

[10] D. Papa, E. Swenk, F. Uillani, and E. Klingsberg, *J. Amer. Chem. Soc.*, **70**, 3356 (1948).

[11] M. W. Goldberg and P. Müller, *Helv. Chim. Acta*, **21**, 1699 (1938).

[12] Organic Syntheses, Vol. 3, p. 248.

[13] L. Wolff, *Ann.*, **246**, 246 (1891); H. Schinz, G. Gonbani, and V. Theus, *Helv. Chim. Acta*, **38**, 255 (1955).

rocene, and hydroquinone (0.039 g, 0.36 mmol) was obtained. The net amount of hydroquinone, obtained from the reduction of *p*-benzoquinone by ferrocene is 0.36 mmol.

The aqueous layer from the reaction in the presence of ferrocene was treated with tin(II) chloride acidified with hydrochloric acid to afford ferrocene (0.123 g, 0.66 mmol). The amount of ferrocene was assumed to be equal to that of ferricinium ion. The molar ratio of hydroquinone to ferricinium ion is calculated to be about 1: 1.8.

Reduction of Chloranil with Ferrocene. The same procedure as described above was applied to chloranil, which was found to be not reduced by aluminum chloride without ferrocene. The molar ratio of the obtained tetrachlorohydroquinone to ferricinium ion was about 1: 1.7.

Reduction of Enones and Related Compounds. Aluminum chloride (0.14 g, 1.08 mmol) and a substrate (0.54 mmol) were added into 30 m*l* of dry dichloromethane, and stirred for 5 min. Ferrocene (0.54 mmol) was then added. After stirring for 60 to 120 min, an aliquot was taken out from the reaction mixture, poured into ice water and the organic layer was checked for the reduction product by tlc, UV, or glpc (Table 1). In a control experiment, in which each substrate was treated by aluminum chloride without ferrocene under similar conditions, no reduction product was detected.

Stoichiometric Reduction of 1,2-Dibenzoylethylene by Ferrocene. Aluminum chloride (0.12 g), ferrocene (0.1 g), and 1,2-dibenzoylethylene (0.12 g) were added into 30 m*l* of dry dichloromethane and stirred for 90 min at room temperature. After the reaction mixture was poured into ice water, the dichloromethane layer was washed with water, dried and evaporated to dryness, and the residue was purified by silica-gel chromatography with benzene to afford 1,2-dibenzoylethane[14] (0.054 g). The aqueous layer gave ferrocene (0.078 g) when treated with tin(II) chloride.

Reaction of Ferrocene with Bromosuccinic Anhydride. Dabard[15] reported the preparation of β-ferrocenylcarbonylacrylic acid by the Friedel-Crafts reaction of ferrocene with bromosuccinic anhydride. We examined the same reaction in order to confirm the formation of the reduction product. Ferrocene (0.74 g, 4 mmol), bromosuccinic anhydride (0.72 g, 4 mmol), and aluminum chloride (1.16 g, 8.7 mmol) were added into 30 m*l* of dry dichloromethane, and stirred for 5 hr at room temperature. After methylation of the products with diazomethane and purification by silica-gel chromatography with benzene-ethyl acetate (6: 1), methyl β-ferrocenylcarbonylacrylate (84 mg) and methyl β-ferrocenylcarbonylpropionate (150 mg) were obtained. Boron trifluoride, iron(III) chloride, or titanium(IV) chloride instead of aluminum chloride were examined, but no reaction products were detected.

---

[14] J. B. Conant and R. E. Lutz, *J. Amer. Chem. Soc.*, **45**, 1305 (1923).

[15] R. Dabard and B. Gautheron, *Compt. rend., Acad. Sci., Paris*, **254**, 2014 (1962).