

## Preliminary communication

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### Organometallic compounds

### XIII★. The reduction of enones by ferrocene and hydrochloric acid

KOJI YAMAKAWA and MICHIO MOROE

*Faculty of Pharmaceutical Sciences, Science University of Tokyo, Shinjuku, Tokyo (Japan)*

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#### SUMMARY

A convenient reduction of enones by ferrocene and HCl is described.

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Sugiyama and Teitei<sup>1</sup> reported an abnormal Friedel–Crafts reaction in which the reaction of ferrocene with fumaroyl chloride in the presence of aluminum chloride did not give 1,2-diferrocenoylethylene as expected, but instead afforded 1,2-diferrocenoylethane and  $\beta$ -ferrocenoylpropionic acid.

It is well known that the ferrocene molecule is easily oxidized by acids to give the ferricinium ion with loss of one electron<sup>2</sup>. We have reinvestigated<sup>3</sup> the above reaction in the presence of excess sodium chloride. 1,2-Diferrocenoylethylene was isolated as the initial product, this was reduced by 2 moles of ferrocene in the presence of hydrochloric acid or aluminum chloride to give 1,2-diferrocenoylethane in quantitative yield. The limitations of the reduction by ferrocene and acid were examined by applying this reduction to several compounds★★. The results are listed in Table 1.



The homogeneous reduction by ferrocene and acid in organic solvents is a useful and convenient method for reduction of the enedione structure  $R-COCH=CHCO-R'$ . After reduction the mixture is easily separated into an organic and an aqueous layer. The ferrocene is quantitatively recovered from the aqueous layer by ascorbic acid and sodium bisulfite.

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★ For Part XII see ref. 5.

★★ After our work had been completed<sup>3</sup> Omote *et al.* reported<sup>4</sup> similar reductions but they did not isolate the enones which are assumed to form during the reactions.

TABLE I

Compound	Product	Yield (%)
Fc-COCH=CHCO-Fc <sup>a</sup>	Fc-COCH <sub>2</sub> CH <sub>2</sub> CO-Fc	99
Fc-COCH=CHCOOH <sup>b</sup>	Fc-COCH <sub>2</sub> CH <sub>2</sub> COOH	99
Ph-COCH=CHCO-Ph( <i>cis</i> )	Ph-COCH <sub>2</sub> CH <sub>2</sub> CO-Ph	99
Ph-COCH=CHCO-Ph( <i>trans</i> )	Ph-COCH <sub>2</sub> CH <sub>2</sub> CO-Ph	99
Ph-COCH=CHCOOH	Ph-COCH <sub>2</sub> CH <sub>2</sub> COOH	90
Ph-COCH=CHCOOCH <sub>3</sub>	Ph-COCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	90
CH <sub>3</sub> COCH=CHCOCH <sub>3</sub> ( <i>trans</i> )	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> COCH <sub>3</sub>	82
Ph-CH=CH-Ph	c	—
Ph-CH=CHCOOH( <i>cis</i> )	c	—
Ph-CH=CHCOOH( <i>trans</i> )	c	—
HOOC-CH=CH-COOH( <i>cis</i> )	c	—
HOOC-CH=CH-COOH( <i>trans</i> )	c	—
EtOOC-CH=CH-COOEt	c	—
ClCOCH=CHCOCl	HOOC-CH=CH-COOH	100
HOH <sub>2</sub> CC=CCH <sub>2</sub> OH	c	—
HOCC=CCOOH	c	—
Fc-COCH=CH-Fc	c	—
Fc-COCH=CH-Ph	c	—
Ph-COCH=CH-Ph	c	—
Fc-CHO	{ FcH Fc-CH <sub>2</sub> OH	{ 60 10
Fc-NO <sub>2</sub>	c	—
Ph-NO <sub>2</sub>	c	—
Santonin	c	—
		100

<sup>a</sup> Lit. <sup>3</sup>, m.p. 220° (dec.). <sup>b</sup> Lit. <sup>3</sup>, m.p. 170–171°. <sup>c</sup> Starting compound recovered unchanged.

#### EXPERIMENTAL

**General procedure** To a mixture of 0.372 g (2 mmol) of ferrocene in 1 ml of conc. HCl was added a solution of 1 mmol of substrate in 10 ml of methylene chloride. The reaction mixture was warmed until the color changed to blue-violet. Then the organic layer was separated, washed with water, and dried. Evaporation of the solvents gave the reduction products or starting materials as listed in Table I. Addition of ascorbic acid to the aqueous layer precipitated crude ferrocene in quantitative yield.

Other solvents used were benzene and ethanol. Other acids used were H<sub>2</sub>SO<sub>4</sub> and dil. HCl.

#### REFERENCES

1. N. Sugiyama and T. Teitei, *Bull. Chem. Soc. Jap.*, **35** (1962) 1423.
2. G. Wilkinson, M. Rosenblum, M.C. Whiting, and R.B. Woodward, *J. Amer. Chem. Soc.*, **74** (1952) 2126; V. Weinmayr, *ibid.*, **77** (1955) 3009.

- 3 K. Yamakawa and M. Moroe, *Second Symposium on the Chemistry of Non-benzenoid Aromatic Compounds, Symposium Papers* p. 68–70, Kyoto, November. 22–23, 1968.
- 4 Y. Omote, R. Kobayashi, C. Kashima and N. Sugiyama, *Bull. Chem. Soc., Jap.* 44 (1971) 3463.
- 5 K. Yamakawa and M. Hisatomo, *J. Chem. Soc., Chem. Commun.*, submitted.