sisted of 63% leaves and 37% branchlets) were gathered from a tree 8 cmϕ.

Sample IV: On October 23, 1967, the material was gathered at Niimi-shi, in Okayama Prefecture (about 600 m above the sea level), the tree was near to the stage of leaf falling. The shoots (the average length of a twig: 25 cm; its weight 6 g, consisted of 67% leaves and 33% branchlets) were gathered from a tree 3 cmϕ.

Isolation of the Essential Oils——The each fresh material cut in small pieces was subjected to steam distillation at the 2nd or 3rd day after gathering. The distilled oil was extracted with ether, and then dried over anhydrous sodium sulfate. After distillation of the ether, the essential oil was obtained.

The weight of fresh materials used, the oils obtained, the yields of oil to the fresh materials, and the physical properties of each oil were shown in Table II.

Analysis of the Oils——The each component of essential oil was identified by the comparison of retention time of gas-liquid chromatography, with that of authentic samples and the oil of methylchavicol, safrole, and methyleugenol type *M. salicifolia*,[2] together with IR spectra of the eluted fractions of column chromatography using activated alumina (300 mesh).

trans-Anethole: Peak 24 (Table I) (IR cm^{-1}: 2960, 2930, 2840, 1605, 1575, 1510, 1470, 1440, 1375, 1305, 1285, 1250, 1175, 1160, 1110, 1035, 965, 840, and 790) was isolated, and determined as *trans*-1-propenyl-4-methoxybenzene by a comparison of the IR spectrum with that of an authentic sample.

Chem. Pharm. Bull.
22(3) 709—711 (1974)

UDC 547.722.2' 313.2' 546.72.057

Organometallic Compounds. XVI.[1] Synthesis of *trans*-1,2-Diferrocenoylethylene

Koji Yamakawa and Michio Moroe

Faculty of Pharmaceutical Sciences, Science University of Tokyo[2]

(Received July 14, 1973)

trans-1,2-Dibenzoylethylene has been synthesized by the Friedel–Crafts reaction of benzene and fumaric chloride.[3] Whereas, the reaction of ferrocene and fumaric chloride in the presence of aluminum chloride catalyst did not gave expected *trans*-1,2-diferrocenoylethylene (I) but saturated compound, 1,2-diferrocenoylethane (III) and β-ferrocenoylpropionic acid (IV) were isolated, which was reported by Sugiyama and Teitei.[4]

trans-1,2-Dibenzoylethylene has also been synthesized by the condensation of ω-bromoacetophenone with alkaline[5] or dehydrogenation of 1,2-dibenzoylethane with selenium dioxide.[6] Therefore, these methods were applied for the corresponding ferrocene derivatives, but I could not be obtained.

However, the Friedel–Crafts reaction of ferrocene and fumaric chloride in presence of large excess amount of sodium chloride using 10—30 times for aluminum chloride catalyst in methylene chloride was carried out carefully protecting from moisture during the reaction. *trans*-1,2-Diferrocenoylethylene (I), mp 220° (decomp.) and *trans*-β-ferrocenoylacrylic acid (II), mp 170—171°, were isolated together with III from the reaction mixture in 18.5% and 5% yield, respectively. The infrared (IR) spectrum of I showed at 1620 cm^{-1} of carbonyl group which shifted ($\Delta\nu$—45 cm^{-1}) over the ketone (III), and equivalent ethylene protons appeared at δ 7.52 in their nuclear magnetic resonance (NMR) spectrum. The structure

---

1) Part XV: K. Yamakawa, R. Sakaguchi, and K. Osumi, *Chem. Pharm. Bull.* 22, 576 (1947).

2) Location: *Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo, 162, Japan.*

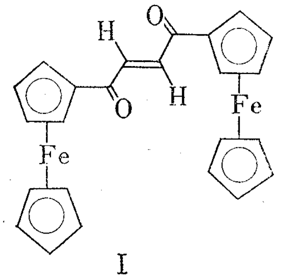
3) R.E. Lutz, *Org. Syntheses, Collective Vol.* **III**, 248.

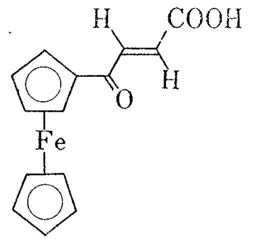
4) N. Sugiyama and T. Teitei, *Bull. Chem. Soc. Japan*, 35, 1423 (1962).

5) K.F. Armstrong and R. Robinson, *J. Chem. Soc.*, **1934**, 1650.

6) J.P. Schaefer, *J. Am. Chem. Soc.*, **84**, 713 (1962).

NII-Electronic Library Service

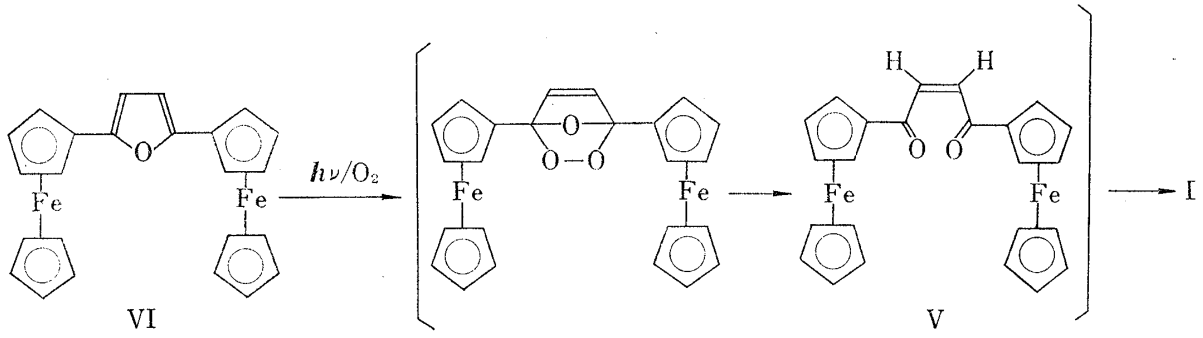

I


II

of I and II were confirmed by the reduction of I and II by ferrocene and hydrochloric acid to give known III and IV, respectively, in quantitative yield.[7]

The authors previously reported[7] that reduction of some enones by ferrocene and hydrochloric acid or aluminum chloride occurrs by the formation of ferricinium ion from ferrocene molecule with loss of one electron. Formation of I and II in the above modified Friedel-Crafts reaction may considered that formation of ferricinium ion is prevented due to interactions between aluminum chloride and sodium chloride.

Synthesis of *cis*-1,2-ferrocenoylethylene (V) was also attempted. Schenck[8] reported that photooxidation of 2,5-diphenylfuran gave *cis*-1,2-dibenzoylethylene. Therefore, photooxidation of 2,5-diferrocenylfuran (VI)[9] was carried out by irradiation with 100 W high-pressure mercury lamp (Ushio UM-102) while oxygen gas was bubbled in the acetone solution at −60——80° for 25 min. Pyrolysis of the ozonide intermediate occurred by being allowed to stand at room temperature. The oxidation product was chromatographed to give a brown needles, mp 220° (decomp.), which was identical with I. *cis*-Isomer (V) could not be isolated in this reaction. It may be considered that the intermediate *cis*-isomer (V) was easily isomerized into *trans*-isomer (I) by thermal condition.



Experimental

All melting points are uncorrected. IR spectra were measured for KBr disk with a Hitachi EPI-2 spectrophotometer. NMR spectra were determined in $CDCl_3$ with a JEOL-JNM-4H-100 spectrometer at 100 MHz, using TMS as internal reference.

Modified Friedel-Crafts Reaction of Ferrocene and Fumaric Chloride——A solution of ferrocene (20 g) in dry methylene chloride was added aluminum chloride (14.5 g) and sodium chloride (31 g) with rapid stirring in an ice bath. And then, to the solution was added, dropwise, fumaryl chloride (7.2 g) in dry methylene chloride (10 ml). The reaction period, the reaction mixture poured into ice-water (100 ml), and separated methylene chloride layer. The organic layer was washed with 5% sodium bicarbonate, water and dried. After evaporation of the solvent, the residue was chromatographed on alumina. Ferrocene (16 g) was recovered from benzene eluent, and two fractions (1) and (2) were eluted with ethyl acetate. Fraction 1 gave 1,2-diferrocenoylethane (III) (0.2 g), mp 186—187°, which was identical with the authentic specimen.[4] Fraction 2 gave *trans*-1,2-diferrocenoylethylene (I) as brown needles, mp 220° (0.9 g; 18.5% yield based on unrecovered ferrocene). *Anal.* Calcd. for $C_{24}H_{20}O_2Fe_2$: C, 62.37; H, 4.37. Found: C, 62.52; H,

---

[7] K. Yamakawa and M. Moroe, *J. Organometal. Chem.*, 50, C 43 (1973).

[8] G.O. Schenck, *Angew. Chem.*, 69, 579 (1957).

[9] K. Yamakawa and M. Moroe, *Tetrahedron*, 24, 3615 (1968).

NII-Electronic Library Service

3.99.

The alkaline solution was acidified with 10% HCl to give 1,2-diferrocenoylacrylic acid (II) as deep red plates, mp 170—171° (0.3 g; 4.9% yield based on unrecovered ferrocene). *Anal.* Calcd. for $C_{14}H_{12}O_3Fe$: C, 59.19; H, 4.26. Found: C, 59.13; H, 4.31.

Photooxidation of 2,5-Diferrocenylfuran (VI)——A solution of VI[9] (0.1 g) in 100 ml of acetone was irradiated with a Ushio-100 W mercury high pressure lamp, while air was bubbled through the mixture at −60~ −80°. After 25 min the solvent was removed *in vacuo* at room temperature. The residue was chromatographed on alumina to give unreacted VI (50 mg) from benzene elution, and next fraction with ethyl acetate gave *trans*-1,2-diferrocenoylethylene (I) (5 mg), which was identical with I described above.

Chem. Pharm. Bull.
22(3) 711—714 (1974)

UDC 547.743.1'534.1.09 : 615.31.015.4.076.9

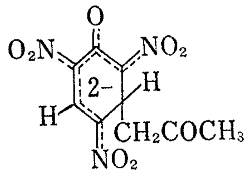
Mechanism of the Color Reaction of Active Methylene Compounds with 1,3,5-Trinitrobenzene Derivatives. VI.[1] A Protonated Species of the Meisenheimer Type Compound derived from Picric Acid and Acetone[2]

TOYOSHIGE KABEYA, KAZUYA KOHASHI, and YOSUKE OHKURA

Faculty of Pharmaceutical Sciences, Kyushu University[3]

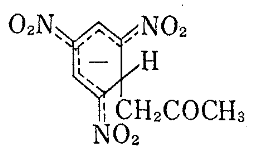
(Received July 26, 1973)

In the previous paper of this series,[4] the color reaction of picric acid and acetone under the Janovsky conditions[5] was elucidated by isolating disodium salt of the Meisenheimer type anion I (I-2Na) shown in Chart 1 and the bicyclic type compound.



I

Chart 1



II

Chart 2

During the course of study on the spectral behavior of aqueous solution of I-2Na, we found that a new species was obtained in crystalline forms when I-2Na was treated with an acid. The new species was stable in an acidic medium, though sodium salt of the Meisenheimer type anion II (Chart 2) derived from 1,3,5-trinitrobenzene (TNB) and acetone was already observed to regenerate the original components on dissolving it in acidic media.[6] This paper describes the isolation of the new species and its absorption spectral behavior.

---

1) Part V: K. Kohashi, T. Kabeya, Y. Ohkura, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **21**, 2187 (1973).
2) This forms "Organic Analysis LXXXIX". Part LXXXVIII: (1).
3) To whom all inquiries should be addressed. Location: *Katakasu, Higashi-ku, Fukuoka.*
4) T. Kabeya, K. Kohashi, Y. Ohkura, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **21**, 2168 (1973).
5) J.V. Janovsky and L. Erb, *Ber.*, **19**, 2155 (1886); J.V. Janovsky, *ibid.*, **24**, 971 (1891). For reviews see T. Nambara, *Bunseki Kagaku*, **13**, 184 (1964); E. Buncel, A.R. Norris, and K.E. Russell, *Quart. Rev.*, **22**, 123 (1968); K. Kohashi and Y. Ohkura, *Kagaku No Ryoiki*, **27**, 303 (1973).
6) M. Kimura, *Yakugaku Zasshi*, **73**, 1219 (1953); *idem*, *Pharm. Bull.* (Japan), **3**, 75 (1955).

NII-Electronic Library Service