BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3270—3273 (1969)

Nitroalkenylferrocene. IV.[1] Preparation of 1-Ferrocenyl-2-iodo-2-nitroethylene and Configurations of Several Nitroalkenylferrocenes

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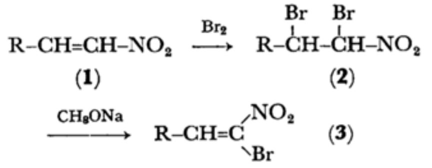
(Received May 19, 1969)

A new method of synthesizing 1-ferrocenyl-2-iodo-2-nitroethylene (**6**) was presented, whereas 1-ferrocenyl-2-halo-2-nitroethylene could not be prepared by the usual method, involving the direct halogenation of the nitroolefin. The iodonitroethylene (**6**) was prepared by the reaction of the sodium salt of 1-ferrocenyl-2-nitroethylene with iodine or with potassium iodide. This procedure proved to be useful for introducing various groups on the α-carbon of the nitroethylene. The stereochemistry of nitroalkenylferrocenes, including some previously reported ones, was discussed on the basis of their spectral data.

In the course of study of the reactions of nitroalkenyl-ferrocenes, it has been found that a sodium salt (**5**) which was obtained when 1-ferrocenyl-2-nitroethylene (**4**) was treated with sodium methoxide reacted directly with iodine to give 1-ferrocenyl-2-iodo-2-nitroethylene (**6**). The usual method[2] for the synthesis of α-halonitroethylene (**3**) from α-nitroethylene (**1**) through dibromide (**2**) was found to be unsuccessful when applied to 1-ferrocenyl-2-nitroethylene (**4**). The reaction of **4** with bromine gave no dibromide, but the ferrocene nuclei was largely decomposed, even at $-65°C$ in the presence of bromine.

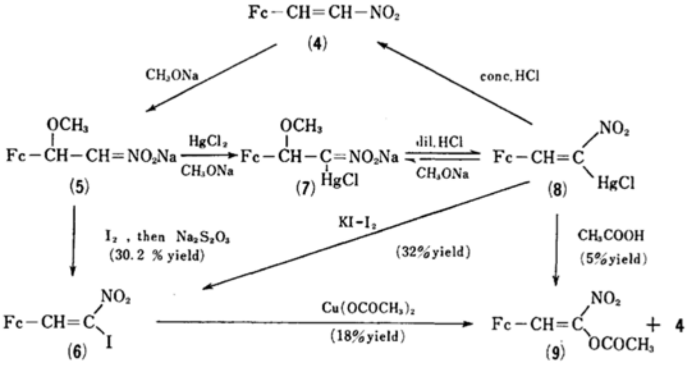


$$\underset{(\mathbf{1})}{\text{R–CH=CH–NO}_2} \xrightarrow{\text{Br}_2} \underset{(\mathbf{2})}{\text{R–}\overset{\text{Br}}{\overset{|}{\text{C}}}\text{H–}\overset{\text{Br}}{\overset{|}{\text{C}}}\text{H–NO}_2}$$

$$\xrightarrow{\text{CH}_3\text{ONa}} \text{R–CH=C}\begin{smallmatrix}\diagup\text{NO}_2\\ \diagdown\text{Br}\end{smallmatrix} \quad (\mathbf{3})$$

On the other hand, 1-ferrocenyl-2-iodo-2-nitroethylene (**6**) was easily obtained in a 30% yield when the sodium salt (**5**) was treated with iodine in dry ether under an atmosphere of nitrogen and then treated with aqueous sodium thiosulfate. The sodium salt (**5**) also reacted with mercury(II) chloride in the presence of excess sodium methoxide to give a brownish sodium salt (**7**). The brownish salt (**7**), on treatment with dilute hydrochloric acid, was easily converted into 1-ferrocenyl-2-chloromercuri-2-nitroethylene (**8**), which separated as a blue solid. The structure of **8** was assumed on the basis of its IR spectrum: an olefinic absorption band at 1588 cm^{-1}, an asymmetrical NO_2 stretching band at 1480 cm^{-1}, and a pair of symmetrical NO_2 stretching bands at 1290 cm^{-1} and 1282 cm^{-1}. The results of elemental analyses also support the structure.

When **8** was stirred with iodine and potassium



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[1] Part III: H. Kono, M. Shiga, I. Motoyama and K. Hata, This Bulletin, **42**, 3267 (1969).

[2] B. Priebs, *Ann.*, **225**, 342 (1884); W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **73**, 4664 (1951).

iodide in dioxane containing a trace of water, 1-ferrocenyl-2-iodo-2-nitroethylene (**6**) was obtained in a 32% yield after the treatment of the crude product with aqueous sodium thiosulfate. The reaction of **8** with iodine was carried out in several kinds of solvents; the results are summarized in Table 1. The chloromercuri compound (**8**) was easily decomposed to the nitroolefin (**4**) and mercury(II) chloride by the action of concentrated hydrochloric acid. The identity of the decomposition product with the starting nitroolefin (**4**), which has been prepared by the condensation of formylferrocene with nitromethane using a base catalyst,[3] was proved by the coincidence of their IR spectra.

TABLE 1. IODINATION OF 1-FERROCENYL-2-CHLOROMERCURI-2-NITROETHYLENE (**8**) (at 0°C)

8		Iodinating reagent	Solvent	Reaction time	Yield of **6**
(g)	(mol)	(g)		(hr)	(%)
15	0.03	I_2 11.1	THF (200 m*l*)	20	19
15	0.03	I_2 11.1	CH_2Cl_2 (200 m*l*)	20	24
15	0.03	I_2 11.1	CCl_4 (200 m*l*)	20	26
15	0.03	I_2 11.1 KI 5	Dioxane (200 m*l*) H_2O (2 drops)	20	32

When **8** was stirred in acetic acid, a small amount of violet oil was obtained, together with the nitroolefin (**4**) as the main product. The minor product was too unstable to be thoroughly purified, and it easily decomposed into formylferrocene. The IR spectrum indicated the presence of acetoxy group (1758 cm^{-1} and 1200 cm^{-1}), as well as nitro group (1502 cm^{-1} (asym. NO_2) and 1325 cm^{-1} (sym. NO_2)). Accordingly, 1-ferrocenyl-2-acetoxy-2-nitroethylene (**9**) was tentatively proposed as the structure of this compound. The same compound (**9**) was also obtained by the reaction of **6** with copper(II) acetate.

Infrared Spectra and Configuration of Nitroalkenylferrocenes. Although various nitroalkenylferrocenes have been synthesized in our laboratory,[1,3,4] no discussion of the geometric relationship between nitro and ferrocenyl groups has yet been undertaken becasue of the difficulty of isolating their geometric counterparts. Recently, however, Watarai *et al.*[5] have shown that the geometric relationship between nitro and phenyl groups in nitrostyrene and the related compounds could be determined by means of their IR spectra. According to their rule, the absorbance of the symmetrical NO_2 stretching absorption band is smaller than that of the asymmetrical one in the case of the cis isomer, while the former is equal to or larger than the latter in the case of the trans isomer. Because of the close structural resemblance of 1-ferrocenyl-2-nitroethylene to β-nitrostyrene, it is quite reasonable to assume that this empirical rule would be applicable to the system of 1-ferrocenyl-2-nitroethylene and would give a strong suggestion regarding its stereochemistry. Thus, the IR spectra of several 1-ferrocenyl-2-nitroalkenes were measured in CCl_4. All the results are summarized in Table 2. By comparing the absorbances of the symmetrical and asymmetrical NO_2 stretching absorption bands with each other, it is evident that the absorbance of the former band considerably exceeds that of the latter in all the compounds listed in Table 2. Therefore, the configuration of these nitroalkenes can be concluded to be trans, according to the Watarai rule.

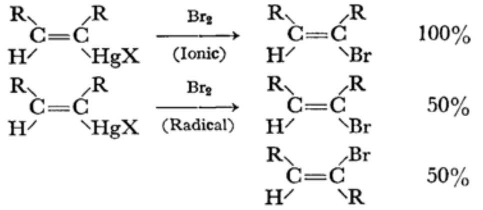
TABLE 2. IR SPECTRA OF NITROALKENYLFERROCENES (cm^{-1}, in CCl_4)

Compound	C=C (ε)	Asym. NO_2 (ε)	Sym. NO_2 (ε)
Fc–CH=CH–NO_2*1 (**4**)	1628 (388)	1518 (285)	1343 (350) 1331 (649)
Fc–CH=C(CH_3)NO_2*1	1652 (283)	1512 (496)	1324 (386) 1313 (1038)
Fc–CH=C(C_2H_5)NO_2*1	1645 (331)	1512 (457)	1323 (512) 1303 (328)
Fc–CH=CINO_2 (**6**)	1596 (492)	1523 (371)	1302 (1294) 1287 (552)
Fc–C(CH_3)=CH–NO_2*2	1606 (332)	1508 (476)	1344 (291) 1320 (980)

*1 Ref. 3 *2 Ref. 1

A similar conclusion can be derived from the results of the NMR spectra of these compounds. The $J_{\alpha\beta}$-value of the olefinic protons in **4** (12.5 cps) corresponds to that of *trans*-olefin, and the chemical shifts of the olefinic β-protons in the other nitroolefins[3,4] were almost the same as that of 1-ferrocenyl-2-nitroethylene (**4**).

Jensen *et al.*[6,7] have reported that mercuri-



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3) M. Shiga, H. Kono, I. Motoyama and K. Hata, This Bulletin, **41**, 1897 (1968).

4) M. Shiga, H. Kono, I. Motoyama and K. Hata, *ibid.*, **42**, 798 (1969).

5) S. Watarai, K. Yamaura and T. Kinugasa, *ibid.*, **40**, 1448 (1967).

6) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **78**, 2597 (1956); *ibid.*, **82**, 148 (1960).

7) S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956).

olefins are replaced by a cationoid reagent with the retention of the configuration, but not by a radical reagent.

1-Ferrocenyl-2-chloromercuri-2-nitroethylene (**8**) was easily converted to *trans*-1-ferrocenyl-2-nitroethylene (**4**) by the action of hydrochloric acid. According to Jensen's observation, the compound **8** is considered to have a trans configuration with respect to ferrocenyl and nitro groups. A similar consideration can be applied to the compound **6**, which was prepared by the reaction of **8** with iodine and potassium iodide.

Careful examination of the stereochemistry using a molecular structure model reveals that the cis form may bring about a considerable steric strain in the molecule because of a steric interaction between nitro and ferrocenyl groups.

As was expected from this consideration, *cis*-1-ferrocenyl-2-iodo-2-nitroethylene could be obtained neither from the reaction of 1-ferrocenyl-2-chloromercuri-2-nitroethylene with iodine under radical conditions nor from the attempted isomerization of the trans isomer by UV irradiation in CCl_4.

Some interesting phenomena have been observed in the symmetrical NO_2 stretching absorption bands of the nitroalkenylferrocenes. All the nitroolefins studied here have doubly-split absorption bands in the range of 1287—1343 cm^{-1}. The positions and the relative intensities of the split bands depend on the substituents on the double bond of nitroolefin, as well as on the state in which the IR spectra were observed, as is shown in Fig. 1 and Table 2. Such splitting in the symmetrical NO_2 stretching absorption band has never been observed in the benzene analogs. Therefore, it seems to be attributable to a certain influence of the ferrocenyl group on the nitro group. However, no simple explanation of the splitting is possible at present.

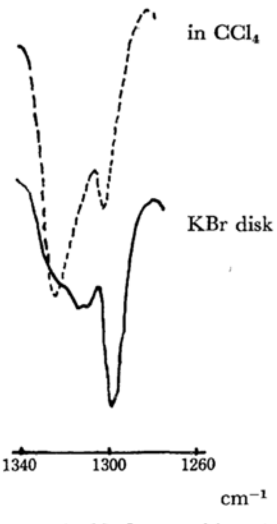

Fig. 1. The symmetrical NO_2 stretching absorption bands of $FcCH{=}C(C_2H_5)NO_2$.

Experimental

1-Ferrocenyl-2-chloromercuri-2-nitroethylene (8). To 10.8 g (0.041 mol) of finely-powdered 1-ferrocenyl-2-nitroethylene in 20 m*l* of absolute methanol, there were slowly added, at 0°C, 10.8 g (0.2 mol) of sodium methoxide which had been freshly prepared from absolute methanol and sodium metal. Subsequently, 20.2 g (0.075 mol) of finely-powdered mercury(II) chloride were added to the mixture with stirring. In a little while, the sodium salt of the chloromercuri compound (**7**) precipitated as a brown solid. An additional 5.4-g portion (0.1 mol) of sodium methoxide was added, and the reaction mixture was stirred for a while. Then, the mixture was poured into 500 m*l* of 20% hydrochloric acid and stirred for half an hour. A blue solid was collected on a filter, washed three times with methanol, and dried in a desiccator under reduced pressure. The finely-powdered material was then stirred in 100 m*l* of chloroform for half an hour in order to remove the unreacted starting material. After filtration, 19.5 g (96% yield) of **8** were obtained as a pale blue solid.

Found: C, 25.26; H, 2.31; N, 2.56%. Calcd for $C_{12}H_{10}FeNO_2HgCl$: C, 29.26; H, 2.03; N, 2.84%.

Repeated elemental analyses failed to give good results owing to the difficulty of purification.

1-Ferrocenyl-2-iodo-2-nitroethylene (6). (a) Into 15 g (0.03 mol) of 1-ferrocenyl-2-chloromercuri-2-nitroethylene (**8**) in 200 m*l* of dioxane, a solution of iodine (11.1 g) and potassium iodide (5 g) in 200 m*l* of dioxane containing two drops of water was slowly added with stirring at 0°C. After having been stirred for 20 hr, the reaction mixture was poured into a solution of 30 g of sodium thiosulfate in 200 m*l* of water; then the mixture was stirred for another hour. Subsequently, the mixture was extracted with ether, and the solution was washed with aqueous sodium thiosulfate and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on Florisil using a mixture of benzene and *n*-hexane (1 : 3) as the solvent. The first fraction gave blue needles of 1-ferrocenyl-2-iodo-2-nitroethylene (**6**) (3.7 g, 32% yield), mp 139—141°C, after recrystallization from methanol. NMR spectra (in $CDCl_3$): τ 5.70 (5H, unsubstituted ring H, singlet), 5.28 (2H, substituted ring H, triplet), 4.91 (2H, substituted ring H, triplet), and 1.22 (1H, vinyl H, singlet).

Found: C, 37.02; H, 2.49; N, 3.62%. Calcd for $C_{12}H_{10}FeNO_2I$: C, 37.59; H, 2.61; N, 3.65%.

(b) To a solution of 5.14 g (0.02 mol) of 1-ferrocenyl-2-nitroethylene in 100 m*l* of dry ether, 3 g (0.05 mol) of sodium methoxide were added at 0°C under an atmosphere of nitrogen. After the reaction mixture had been decolored, a solution of 13 g (0.05 mol) of iodine in 200 m*l* of dry ether was added, drop by drop, to the stirred mixture within an hour. After it had then been stirred for 2 hr, the solution was let stand overnight. Then the reaction mixture was treated in the way described for the procedure (a). After the removal of the solvent from the dried ethereal solution thus obtained, the residue was repeatedly extracted with a mixture of benzene and *n*-hexane (1 : 1). The residue, obtained from the extracts by the removal of the solvent, was chromatographed on Florisil using a mixture of benzene and *n*-hexane (1 : 3). The first fraction gave 2.3 g (30.2% yield) of **6**.

1-Ferrocenyl-2-acetoxy-2-nitroethylene (9). (a) 1-Ferrocenyl-2-iodo-2-nitroethylene (**6**) (0.5 g, 0.002 mol) dissolved in 3 m*l* of dioxane was added to a mixture of 20 m*l* of ethanol and 20 m*l* of water containing 1.5 g of copper(II) acetate, and then the mixture was heated at 90°C for 4 hr. At the end of the reaction, the hot reaction mixture was poured into 100 g of ice water and the product was extracted with ether. The extracts were shaken with 5% hydrochloric acid, and then washed with water and dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was chromatographed on Florisil with benzene to afford 1-ferrocenyl-2-nitroethylene (**4**). Further elution with chloroform afforded crude **9** (90.1 mg, 18% yield) as a blue violet oil which contained a small amount of formylferrocene. Formylferrocene is considered to be produced by the decomposition of the unstable product (**9**) during elution, although the chromatographic column was covered with aluminum foil in order to prevent the decomposition of the product by light.

(b) 1-Ferrocenyl-2-chloromercuri-2-nitroethylene (**8**) (10 g) was added to 20 m*l* glacial acetic acid, and the mixture was heated at 95°C for 3 hr. At the end of the reaction, the reaction mixture was poured into 200 m*l* of water. The precipitate was collected by filtration and washed with water. The product was then dissolved in 30 m*l* of benzene and dried over anhydrous magnesium sulfate. The benzene solution, treated much as in the procedure (a), afforded 0.3 g (5% yield) of **9**.

Spectral Measurements. The infrared spectra were measured in carbon tetrachloride using a 0.52-mm rock salt cell on a Hitachi EPI-G2 grating infrared spectrometer.