BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 841—848 (1970)

Nitroalkenylferrocene. V. New Reactions of α-Halonitroolefins in the Presence of Sodium Alkoxides

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(Received August 4, 1969)

The reactions of 1-iodo-2-ferrocenyl-1-nitroethylene (**1**) and β-bromo-β-nitrostyrene (**5**) with various sodium alkoxides were investigated. The reaction in the presence of an excess of alkoxides gave nitroketones, (**2**) and (**6**), and nitroacetals (**3**) and (**7**). The thermal decomposition of the nitroacetals in a nitrogen atmosphere afforded β-alkoxynitroolefins (**8**), which were found to be useful for obtaining asymmetric nitroacetals (**9**) with different alkoxy groups. The reaction mechanism was discussed by postulating the intervention of a nitrocarbene (**12**) and β-alkoxynitroolefin (**8**). The intermediacy of the nitrocarbene was supported by an experiment using vinylferrocene as a carbene scavenger.

Some information has been given[1,2] on the reactivity of the α-carbon of nitroolefins in preceding papers of this series. With a view to get further information, reactions of 1-iodo-2-ferrocenyl-1-nitroethylene (**1**)[2] and the phenyl analogs, β-bromo-β-nitrostyrene (**5**)[3]in the presence of various sodium alkoxides were investigated. The mechanism of the reaction of β-bromo-β-nitrostyrene with sodium methoxide was discussed by the aid of a reaction in the presence of vinylferrocene. The nitroacetals and β-alkoxynitroolefins which were obtained in these reactions have not yet appeared in the literature. Especially, acetals of an asymmetric structure with different alkoxy groups were first prepared in this investigation.

1) M. Shiga, H. Kono, I. Motoyama and K. Hata, This Bulletin, **42**, 798 (1969).

2) H. Kono, M. Shiga, I. Motoyama and K. Hata, *ibid.*, **42**, 3270 (1969).

3) W. E. Parham and J. L. Bleasdale, *J. Amer. Chem. Soc.*, **73**, 4664 (1951).

Results

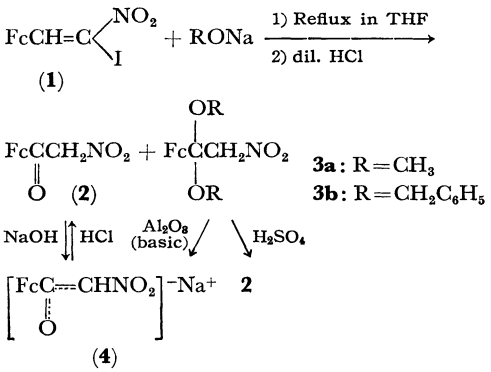
The Reactions of 1-Iodo-2-ferrocenyl-1-nitroethylene with Sodium Alkoxides. The reaction conditions and the products are summarized in Table 1. The structures of the reaction products

TABLE 1. THE REACTIONS OF 1-IODO-2-FERROCENYL-1-NITROETHYLENE IN THE PRESENCE OF SODIUM ALKOXIDES

Reaction temp., reflux in 20 *ml* of THF
Reaction time, 2 hr

FcCH=C(NO$_2$)I (1)		RONa		Products		
(g)	(mol)	(g)	(mol)		(mp°C)	(g) (%)
0.38	0.001	CH_3ONa		**2**	97—98	0.16 54
		0.54	0.01	**3a**	oil	0.04 14
0.38	0.001	$C_6H_5CH_2ONa$		**2**	97—98	0.15 55
		1.30	0.01	**3b**	oil	0.037 8
0.38	0.001	*i*-C_3H_7ONa		**2**	97—98	0.14 51
		0.82	0.01			
0.76	0.002	*t*-C_4H_9ONa		**2**	97—98	0.24 45
		0.96	0.01			

were confirmed by their elemental analyses and by a study of their IR and NMR spectra, which are listed in Tables 4 and 5.



The refluxing of the solution of 1-iodo-2-ferrocenyl-1-nitroethylene (**1**) in tetrahydrofuran with an excess of sodium methoxide gave (nitroacetyl)-ferrocene (**2**) as reddish-orange crystals (mp 97—98°C) and its dimethyl acetal (**3a**) as a dark brown oil, along with a small amount of formylferrocene and an unidentified carbonyl compound.

When an ethereal solution of (nitroacetyl)ferrocene (**2**) was shaken with a dilute solution of sodium hydroxide, the substance easily transferred to the aqueous layer, forming its sodium salt. Because of the strong acidity of **2**, a sodium salt (**4**) was also formed during the chromatographic purification of **2** on basic alumina or on basic Florisil. Especially, the chromatography on basic Florisil using methanol as a solvent gave a pure red solid of the sodium salt, which in turn easily regenerated the original nitroketone by means of dilute hydrochloric acid. The dimethyl acetal (**3a**) was easily converted into nitroketone (**2**) of treating it with sulfuric acid. The chromatography of **3a** on alumina gave sodium salt of the nitroketone (**4**) in a quantitative yield.*1 The results of similar reactions using varying amounts of sodium methoxide are summarized in Table 2, in which the yield of **2** is shown as a total yield of **2** after the coexisting dimethyl acetal has been completely converted into the nitroketone. The maximum yield was attained when ten equivalents of methoxide were used (see also Table 1).

TABLE 2. THE REACTION OF 1-IODO-2-FERROCENYL-1-NITROETHYLENE IN THE PRESENCE OF VARIED AMOUNT OF SODIUM METHOXIDE

Reaction temp., reflux in 20 *ml* of solvent
Reaction time, 2 hr

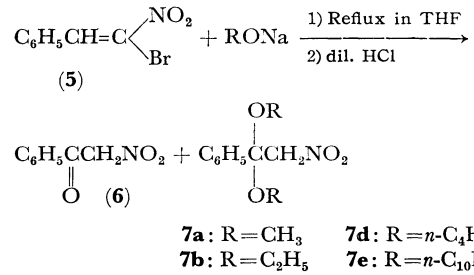
FcCH=C(NO$_2$)I		CH_3ONa		Solvent	Yield* of **2**	
(g)	(mol)	(g)	(mol)		(g)	(%)
0.38	0.001	0.16	0.003	THF	0.05	20
0.38	0.001	0.27	0.005	THF	0.097	36
0.38	0.001	0.54	0.01	THF	0.19	69
0.38	0.001	0.54	0.01	Benzene	0.16	61
0.38	0.001	1.0	0.02	THF	0.18	67

* The yields were expressed as the nitroketones, the nitroacetals being converted to the former by the treatment with alumina.

The reaction of **1** with sodium benzyl oxide gave nitroketone (**2**) and its dibenzyl acetal (**3b**) in 55% and 8% yields respectively. Though the acetal (**3b**) was obtained as a dark brown oil, it was too unstable to be purified; therefore, its yield was estimated by converting it completely into nitroketone (**2**).

A similar reaction with sodium isopropoxide and *t*-butoxide gave nitroketone (**2**) in 51% and 45% yields respectively, but the corresponding acetals could not be found in the products.

The Reactions of β-Bromo-β-nitrostyrene with Sodium Alkoxides. The reaction conditions and the products are summarized in Table 3. The IR and NMR spectra of the reaction products are listed in Tables 4 and 5.



*1 The sodium ion may be supplied from basic alumina for the chromatography.

Table 3. The reactions of β-bromo-β-nitrostyrene in the presence of sodium alkoxides
Reaction temp., reflux in THF, Reaction time, 2 hr.

$C_6H_5CH=C\langle^{NO_2}_{Br}$ (5)		RONa		Product (mp, bp)	Yield	
(g)	(mol)	(g)	(mol)		(g)	(%)
0.57	0.0025	CH_3ONa		**7a** 97.5—98°C/1 mmHg	0.40	76.0
		0.67	0.0125	**6** 108—109°C	trace	
1.14	0.005	CH_3ONa		**7a** 97.5—98°C/1 mmHg	0.82	78.0
		2.7	0.05	**6** 108—109°C	0.10	12.5
1.14	0.005	CH_3ONa		**7a** 97.5—98°C/1 mmHg	0.82	78.0
		5.4	0.1	**6** 108—109°C	0.15	18.0
2.0	8.78×10^{-3}	C_2H_5ONa		**7b** 91.5—92°C/0.6 mmHg	1.49	71.0
		5.9	8.78×10^{-2}	**6** 108—109°C	0.028	2.08
				C_6H_5COOH	0.01	1.4
1.44	6.14×10^{-3}	*n*-C_3H_7ONa		**7c** 104—105°C/0.2 mmHg	1.47	94.4
		5.04	6.14×10^{-2}	**6** 108—109°C	trace	
				C_6H_5COOH	trace	
1.44	6.14×10^{-3}	*n*-C_4H_9ONa		**7d** 120—121°C/0.2 mmHg	1.43	77.4
		6.05	6.14×10^{-2}	**6** 108—109°C	0.06	8.7
				C_6H_5COOH	0.015	1.5
1.13	4.95×10^{-3}	*n*-$C_{10}H_{21}ONa$		**7e** oil	1.82	83.2
		14	4.95×10^{-2}	**6** 108—109°C	trace	
				C_6H_5COOH	trace	
1.14	0.005	$C_6H_5CH_2ONa$		**7f** oil	1.49	82.4
		6.5	0.05	**6** 108—109°C	trace	
				C_6H_5COOH	trace	

Table 4. The IR spectra of nitroacetones, nitroacetals and β-alkoxynitroolefins
(Frequency cm^{-1})

Compound	NO_2 (asym.)	NO_2 (sym.)	C=O	C–O	C=C
2	1553	1317	1673		
3a	1552	1325		1120	
6	1556	1330	1694		
7a	1560	1322		1100	
7b	1562	1326		1100	
7c	1560	1320		1100	
7d	1558	1318		1100	
7e	1550	1342		1100	
7f	1552	1310		1100	
9	1564	1328		1100	
8a	1504	1352			1616
	1488	1322			1600
8c	1518(504)*	1356(671)*			1628
	1498(647)*	1326(647)*			1608
8f	1504(584)*	1356(866)*			1620
	1490(700)*	1320(338)*			1602

* These ε-values were calculated by the usual method on the basis of integrated ratio of *cis* to *trans* isomer obtained from their NMR spectra.

The reaction of β-bromo-β-nitrostyrene (**5**) with an excess of sodium methoxide gave ω-nitroacetophenone (**6**)[4] as white crystals (mp 108—109°C) and its dimethyl acetal (**7a**) as a pale yellow oil (bp 97.5—98°C/1.0 mmHg) in 18% and 78% yields respectively. The increase in the amount of sodium methoxide from five to twenty equivalents to the bromonitroolefin brought about a marked increase in the yield of nitroacetal (**7a**), as is shown in Table 3. The reactions of **5** with sodium ethoxide, *n*-propoxide, and *n*-butoxide gave diethyl, dipropyl, and dibutyl acetal (**7b, c, d**) of ω-nitroacetophenone respectively as the main products, all in good yields. Each reaction also gave small amounts of ω-nitroacetophenone (**6**) and benzoic acid, the latter of which had been found to be formed by the decomposition of the intervening alkoxynitroolefins, as will be described later. The reactions of **5** with sodium decyl oxide and sodium benzyl oxide gave a pale yellow oil consisting of nitroacetals (**7e**) and (**7f**), in 83.2% and 82.4% yields respectively. Besides the oily main product, traces of ω-nitroacetophenone and benzoic acid were obtained as crystalline products in each reaction. Each of the oily products proved to be pure enough, judging from the results of thin-layer chromatography. These nitroacetals are indifferent to aqueous alkali and to dilute acid, and also to heating.

4) A. Lucas, *Ber.*, **32**, 602 (1899).

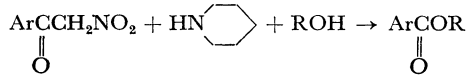
TABLE 5. THE NMR SPECTRA OF NITROKETONES, NITROACETALS AND β-ALKOXYNITROOLEFINS (τ-Value, in $CDCl_3$)

Compound	Benzene ring protons	$-CH_2NO_2$	$-OCH_2R$	$-CH_2-$	$-CH_3$	$=C\langle^{H}_{NO_2}$	Cyclopentadienyl ring protons (unsubst.)	(subst.)
2		4.43(s)					5.66(s)	5.22(t)[a] 5.32(t)[b]
6	2.33(m)	4.07(s)						
7a	2.63(m)	5.28(s)	6.77(s)[c]					
7b	2.62(m)	5.23(s)	6.54(m)		8.76(t)			
7c	2.60(m)	5.20(s)	6.54(m)	8.39(m)	8.98(t)			
7d	2.56(m)	5.16(s)	6.52(m)	8.46(m)	9.06(t)			
9	2.59(m)	5.24(s)	6.57(m) 6.74(s)[c]	8.36(q)	9.04(t)			
8a	2.62(d)		6.25(s)[c] 6.28(s)[c]			3.18(s) 3.05(s)		
8c	2.57(d)		6.03(t) 6.11(t)	8.26(m)	8.99(t)	3.15(s) 3.03(s)		
8f	2.60(d)		5.05(s) 4.95(s)			2.94(s) 3.13(s)		

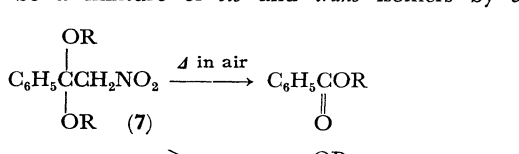
a) 2,5-Protons b) 3,4-Protons c) R=H

Sodium isopropoxide and sodium *t*-butoxide reacted with **5** to give neither nitroacetals nor ω-nitroacetophenone, but it did afford a large amount of benzoic acid.

The Reactions of Nitroketones. The nitroketones (**2** and **6**) were found to act as acids, thus easily forming sodium salts by means of a sodium hydroxide solution or by means of basic alumina during chromatography, as has been described above. When the nitroketones were treated with piperidine and alcohol, they decomposed to give the esters of ferrocenecarboxylic or benzoic acid.



The Reactions of Nitroacetals (7). It was found that the thermal decomposition of nitroacetals (**7**) in air gave alkyl benzoates. On the contrary, the thermal decomposition of nitroacetals (**7**) under an atmosphere of nitrogen afforded quantitatively α-alkoxy-β-nitrostyrene (**8**) and the respective alcohols, the former of which was found to be a mixture of *cis* and *trans* isomers by a



	trans (%)	*cis* (%)
8a: R=CH_3	79	21
8c: R=*n*-C_3H_7	73	27
8f: R=$CH_2C_6H_5$	75	25

study of its IR, UV, and NMR spectra. For example, the IR spectra of α-benzyloxy-β-nitrostyrene (**8f**) (bp 153—154°C/0.005 mmHg) obtained from **7f** showed strong absorption peaks at 1504 cm^{-1} (asym. NO_2) and 1356 cm^{-1} (sym. NO_2) for one isomer, and weak absorption peaks at 1490 cm^{-1} (asym. NO_2) and 1320 cm^{-1} (sym. NO_2) for the other.

The geometric relation between the nitro and phenyl groups in these compounds can be distinguished in the manner described by Watarai *et al.*[5] It is reasonable to consider that the former has a *trans*, and the latter a *cis* configuration with regard to the nitro and phenyl groups, because the absorbance of the asymmetrical NO_2-stretching absorption is weaker than that of the symmetrical one in the case of the former, while the relation is the inverse in the case of the latter.

The UV spectrum of **8f** shows two characteristic absorption maxima, at 268 and 290 mμ, the latter of which can be considered to be due to the *trans* configuration because of the more favorable conjugation of nitro group with the phenyl group. The NMR spectrum of **8f** also indicated the presence of stereoisomers (see Fig. 1); one of these exhibits two singlet peaks, at τ 5.05 and 2.94, due to methylene and olefinic protons respectively, while the other exhibits two corresponding singlet peaks, at τ 4.95 and 3.13 respectively. The signal of the *O*-methylene protons of the *trans* isomer is expected to shift toward a higher magnetic field than that of the *cis* isomers by anisotropy of the nitro group. Since the integrated intensity ratio of the methylene and olefinic protons of the former to those of the

5) S. Watarai, K. Yamamura and T. Kinugasa, This Bulletin, **40**, 1448 (1967).

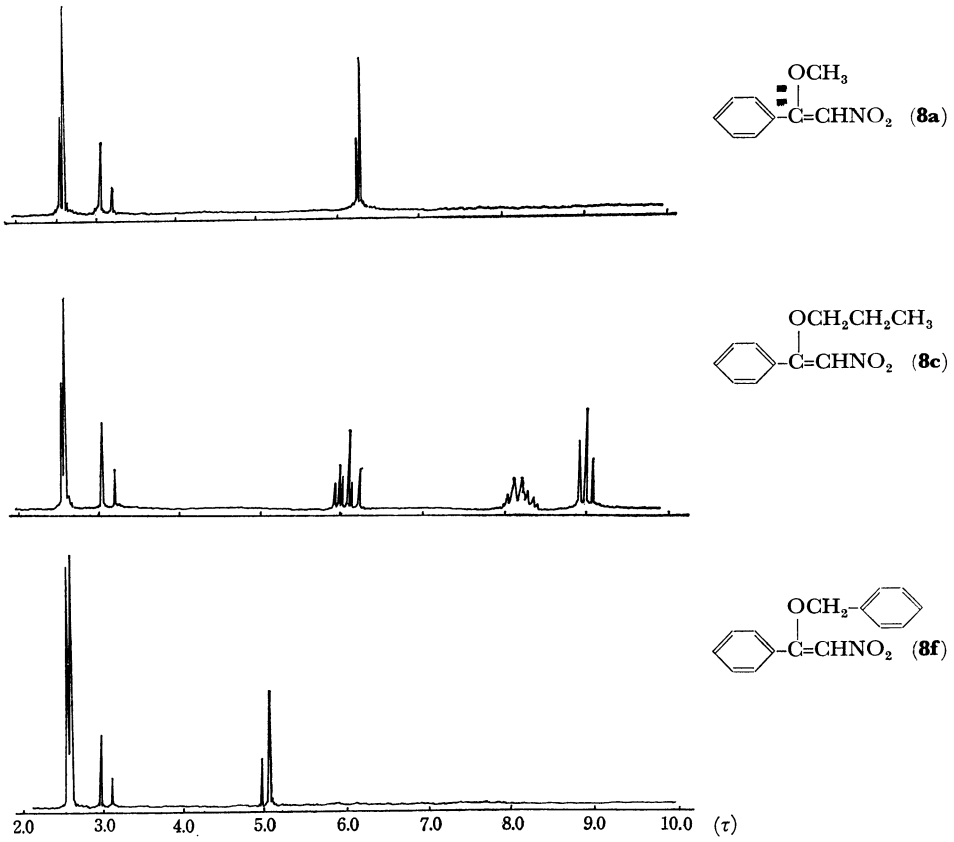
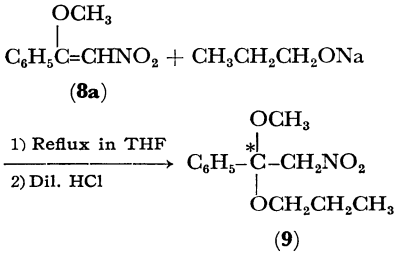


Fig. 1. NMR spectra of α-alkoxy-β-nitrostyrenes.

latter is about 3 : 1, **8f** was considered to be a mixture composed of approximately 75% *trans* and 25% *cis* isomers. The pale yellow viscous oil of **8f** gradually solidified on standing in air. In the IR, UV, and NMR spectra of the solidified product, a decrease in the relative strength of the absorption band to the *cis* isomer was observed. After standing for 5 days, the percentage of the *trans* isomer increased from 75% to 98%, judging from the intensity ratio of the NMR spectra.

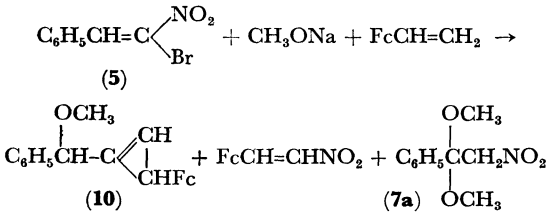
ω-Nitroacetophenone dimethyl acetal (**7a**) and dipropyl acetal (**7c**), on being heated under a nitrogen atmosphere, gave a yellow oil of α-methoxy-β-nitrostyrene (**8a**) (bp 110°C/0.35 mmHg) and an α-propoxy analog (**8c**) (bp 115—116°C/0.2 mmHg) in 96% and 95% yields respectively. The ratios of the *trans* to the *cis* isomers in **8a** and **8c** were similarly calculated to be 3.8 : 1 and 2.7 : 1 respectively from their NMR spectra (Fig. 1).

The Reactions of Alkoxynitroolefins. The alkoxynitroolefins (**8**) were easily converted into ω-nitroacetophenone (**6**) or sodium benzoate by treating them with hydrochloric acid or sodium hydroxide solution respectively. The reaction of sodium alkoxide on the alkoxynitroolefins (**8**) leads to the reverse formation of the nitroacetals (**7**). Thus, asymmetric acetals with different alkoxy groups can be prepared by this reaction. For instance, the reaction of sodium propoxide on α-methoxy-β-nitrostyrene (**8a**) afforded ω-nitroacetophenone methyl propyl acetal (**9**) (bp 89—90°C/0.3 mmHg) in an 84% yield. The acetal was obtained as a racemic compound; its resolution into optically active enantiomers has not yet been attempted.



The Reaction of β-Bromo-β-nitrostyrene with Sodium Methoxide in the Presence of Vinylferrocene. Since the reaction of β-bromo-β-nitrostyrene (**5**) with sodium alkoxide to form nitroacetals (**7**) was supposed to proceed through a carbene intermediate, an experiment to capture the

carbene was attempted. When β-bromo-β-nitrostyrene was refluxed with equimolar portions of sodium methoxide and vinylferrocene, 3-ferrocenyl-1-(α-methoxybenzyl)cyclopropene (**10**) was obtained as yellow-brown crystals (mp 88—90°C) in a 6.9% yield, besides small amounts of 1-ferrocenyl-2-nitroethylene,[6] ω-nitroacetophenone dimethyl acetal, and another unidentified nitro compound.

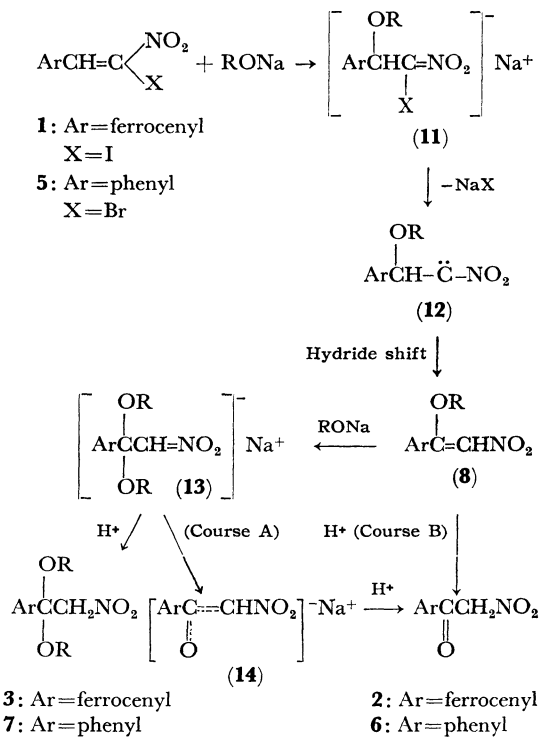


The NMR spectrum of **10** exhibits four singlet peaks, at τ 2.59, 4.79, 5.83, and 6.56, due to phenyl protons, methine in the side chain, ferrocenyl, and methoxy protons respectively, and two doublet peaks, at τ 5.91 and 7.02, corresponding to olefinic and methine protons in the cyclopropene ring. The IR spectrum of **10** shows a strong absorption peak at 1104 cm^{-1} (C–O).

Discussion

As is shown in Scheme 1, sodium alkoxides easily reacted with 1-iodo-2-ferrocenyl-1-nitroethylene (**1**) or β-bromo-β-nitrostyrene (**5**) to give adducts (**11**). The adducts were found to be very stable in organic solvents at room temperature, but they were decomposed into the original halonitroolefins by the action of dilute hydrochloric acid. On the other hand, they were converted into sodium salts of nitroacetals (**13**) or of nitroketones (**14**) when heated above 90°C with an excess of sodium alkoxides. These reactions can be considered to proceed through nitrocarbenes (**12**), which are generated by the α-elimination of sodium halide from the adducts (**11**), followed by an immediate hydride shift to give β-alkoxynitroolefins (**8**). This consideration is based on the fact that alkylcarbenes cause intramolecular insertion into neighboring β- or γ-carbon–hydrogen bonds to give olefins or cyclopropanes respectively.[7]

In order to get evidence of the existence of such a nitrocarbene as a reaction intermediate, the thermal reaction of β-bromo-β-nitrostyrene was attempted in the presence of vinylferrocene. As a result, a small amount of 3-ferrocenyl-1-(α-methoxybenzyl)cyclopropene (**10**) was obtained instead of the expected nitrocyclopropane (**15**), as is shown in Scheme 2. Since Darling and Spanagel have reported that nitrocyclopropane (**19**) was easily converted into cyclopropene (**20**) by the action of sodium methoxide (Scheme 2),[8] the formation of 3-ferrocenyl-1-(α-methoxybenzyl)cyclopropene (**10**) can reasonably be considered to be an indirect evidence of the existence of nitrocyclopropane (**15**) as an intermediate. An alternative cyclopropene derivative (**18**) was not obtained in this reaction. The exclusive formation of **10** may stem from the fact that the intermediate α-ferrocenylcarbanion (**17**) is less stable than the isomeric carbanion (**16**) because of the electron-releasing character of the neighboring ferrocene nucleus.



Scheme 1. Reaction mechanism.

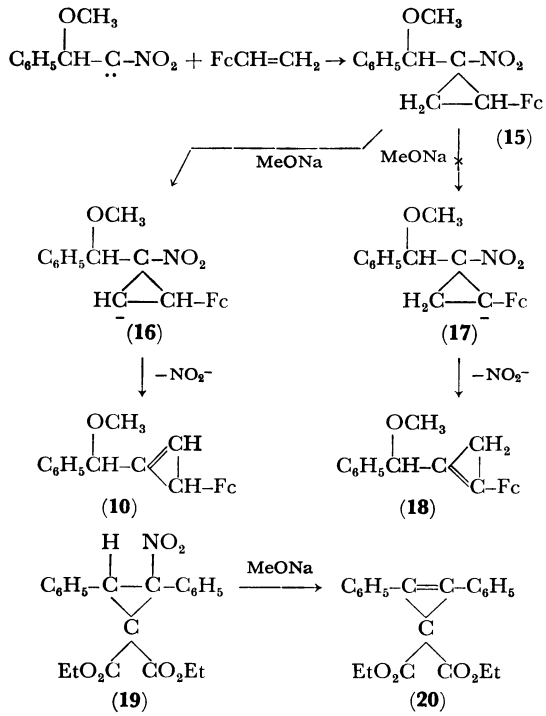
β-Alkoxynitroolefins (**8**), which were expected to be the hydride-shift products from the nitrocarbene (**12**), could not be isolated in these reactions. The further addition of sodium alkoxide to the β-alkoxynitroolefin (**8**) led to the formation of sodium salts of nitroacetals (**13**), which were then easily converted into nitroacetals (**3** or **7**) by dilute hydrochloric acid. Phenylnitroacetals (**7**) were found to be much more stable than ferrocene analogs (**3**). The difference in stability appears to be due to the larger steric hindrance and the larger electron-releasing character of the ferrocene nucleus.

As for the mechanism affording nitroketones (**2** or **6**) two pathways can be considered, as Scheme 1 shows. Course A involves the thermal decomposition of sodium salts of nitroacetals (**13**) into sodium salts of nitroketones (**14**), while Course B involves

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

7) W. Kirmse, "Carbene Chemistry," Academic Press, New York and London (1964), p. 52.

8) S. F. Darling and E. W. Spanagel, *J. Amer. Chem. Soc.*, **53**, 1117 (1931).



Scheme 2. Reaction of nitrocarbene.

the direct attack of hydrochloric acid on β-alkoxynitroolefins (**8**). Course B can be ruled out on the basis of the observation that the reaction of β-bromo-β-nitrostyrene (**5**) with equimolar sodium methoxide gave neither ω-nitroacetophenone, its dimethyl acetal, nor benzoic acid at all; if the reaction followed course B, ω-nitroacetophenone or benzoic acid should be isolated from the reaction mixture when it was treated with dilute hydrochloric acid. Thus, the nitroketone must be produced *via* sodium salts of nitroacetals (**13**) by means of course A.

The effect of the bulk of the alkyl group in sodium alkoxides was not so evident in the reactions with 1-iodo-2-ferrocenyl-1-nitroethylene, but it was striking in those with the phenyl analog. The reaction of β-bromo-β-nitrostyrene with an excess of sodium isopropoxide or *t*-butoxide gave a large amount of benzoic acid, along with a small amount of ω-nitroacetophenone (**6**), while the ferrocene analog (**1**) gave (nitroacetyl)ferrocene (**2**) as the main product. The difference can be interpreted in terms of the stability of the intermediate sodium salts of nitroacetals (**13**). The intermediate sodium salts (**13**) of ferrocenyl series are so unstable because of their much larger steric crowding that they are predominantly converted into the sodium salts of nitroketones (**14**) rather than decomposed to alkyl benzoates. On the other hand, the corresponding intermdiates (**13**) of the phenyl series are considerably stable and give nitroacetals (**3**) preferably; diisopropyl and di-*t*-butyl acetals of ω-nitroacetophenone or their sodium salts can be easily decomposed to isopropyl or *t*-butyl benzoate, followed by hydrolysis to benzoic acid at the reaction temperature (90—95°C), while primary alkyl acetals such as dimethyl acetal are stable at that temperature and are decomposed to benzoate only at a much higher temperature (180—200°C).

Experimental

(Nitroacetyl)ferrocene (2) and Its Dimethyl Acetal (3a). To 0.001 mol (0.38 g) of 1-iodo-2-ferrocenyl-1-nitroethylene in 20 m*l* of dry THF, 0.01 mol (0.54 g) of sodium methoxide was added. After it had been refluxed for 2 hr on a water bath, the reaction mixture was poured into a mixture of 100 m*l* of a 5% sodium hydroxide solution and 20 m*l* of benzene. The benzene layer was then separated off, and the aqueous layer was washed three times with benzene. After the aqueous solution had been acidified with 5% hydrochloric acid, it was extracted with 30 m*l* of benzene. When the benzene solution was shaken with 100 m*l* of a 5% NaOH solution, the nitroketone moved to the aqueous layer, forming its sodium salt, while the nitroacetal remained in benzene unchanged. The benzene layer was washed three times with 100-m*l* portions of water and dried over anhydrous magnesium sulfate. Then, the benzene was removed by distillation to give 0.04 g (14% yield) of a dark brown oil of **3a**.

Found: C, 51.00; H, 4.83; N, 4.07%. Calcd for $C_{14}H_{17}FeNO_4$: C, 52.66; H, 5.32; N, 4.38%.

The aqueous alkaline layer, on the other hand, was acidified with 5% hydrochloric acid and extracted three times with 20-m*l* portions of benzene, after which the benzene solution was dried over anhydrous magnesium sulfate. After the removal of the solvent, 0.199 g of crude (nitroacetyl)ferrocene (**2**) was obtained. Recrystallization from a mixture of *n*-hexane and methylene dichloride (3 : 1) gave 0.16 g (54% yield) of orange crystals (mp 97—98°C).

Found: C, 53.04; H, 3.77; N, 5.04%. Calcd for $C_{12}H_{11}FeNO_3$: C, 52.74; H, 4.02; N, 5.12%.

(Nitroacetyl)ferrocene Dibenzyl Acetal (3b). Following the procedure described above, (nitroacetyl)-ferrocene dibenzyl acetal was prepared from 1-iodo-2-ferrocenyl-1-nitroethylene and sodium benzyl oxide in an 8% yield. The dark brown oil thus obtained is unstable and is apt to decompose to (nitroacetyl)-ferrocene even on standing in the air.

ω-Nitroacetophenone Dimethyl Acetal (7a). To 0.005 mol (1.14 g) of β-bromo-β-nitrostyrene in 60 m*l* of dry THF, 0.05 mol (2.7 g) of sodium methoxide was added. After having been refluxed for 2 hr on a water bath, the reaction mixture was poured into a mixture of 200 m*l* of 10% hydrochloric acid and 30 m*l* of benzene. The aqueous layer was separated off, and the benzene layer was shaken three times with 100-m*l* portions of water and then with 100 m*l* of a 5% sodium hydroxide solution. Thus, ω-nitroacetophenone was separated as its sodium salt. The benzene layer, which contained the acetal **7a**, was washed three times with 100-m*l* portions of water and then dried over anhydrous magnesium sulfate. The benzene solution, after the removal of the solvent, gave 1.1 g of crude ω-nitroacetophenone dimethyl acetal, which was distilled under reduced

pressure to give 0.82 g (78.0% yield) of **7a** as a pale yellow oil (bp 97.5—98°C/1.0 mmHg).

Found: C, 57.11; H, 6.53; N, 6.76%. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.16; N, 6.63%.

The aqueous alkaline layer, which contained the nitroketone, was acidified with 5% hydrochloric acid and then extracted three times with 20-m*l* portions of benzene. The benzene solution thus obtained was dried over anhydrous magnesium sulfate. After the removal of the solvent, the residual pale yellow crystals were dissolved in 3 m*l* of benzene and chromatographed on basic alumina, using methanol as the eluent. The first yellow fraction gave the sodium salt of ω-nitroacetophenone,*2 which was treated with 5% hydrochloric acid and then extracted with 30 m*l* of benzene. The benzene extract gave 0.1 g (12.5% yield) of white crystals of ω-nitroacetophenone (**6**) (mp 108—109°C). ω-Nitroacetophenone was also easily obtained by the chromatography of the acetal (**7**) on basic alumina, using methanol as the eluent.

ω-Nitroacetophenone Diethyl Acetal (7b), Dipropyl Acetal (7c) and Dibutyl Acetal (7d). Following the procedure described above, pale yellow oils of ω-nitroacetophenone diethyl acetal (bp 91.5—92°C/0.6 mmHg), dipropyl acetal (bp 104—105°C/0.2 mmHg) and dibutyl acetal (bp 120—121°C/0.2 mmHg) were obtained by reactions with sodium ethoxide, *n*-propoxide, *n*-butoxide respectively in 71%, 94.4%, and 77.4% yileds.

Found: C, 60.44; H, 6.95; N, 5.84%. Calcd for $C_{12}H_{17}NO_4$ (**7b**): C, 60.25; H, 7.11; N, 5.85%.

Found: C, 63.30; H, 8.10; N, 5.30%. Calcd for $C_{14}H_{21}NO_4$ (**7c**) C, 62.92; H, 7.86; N, 5.24%.

Found: C, 64.74; H, 7.94; N, 4.86%. Calcd for $C_{16}H_{25}NO_4$ (**7d**): C, 65.08; H, 8.47; N, 4.74%.

ω-Nitroacetophenone Didecyl Acetal (7e). A similar procedure using sodium decyl oxide gave the didecyl acetal (**7e**). It was obtained as a yellow oil after 1-decanol had been removed under reduced pressure from the alkali-insoluble fraction of the reaction product. Though an attempt to purify it by vacuum distillation resulted in failure, it was proved to be almost pure nitroacetal (**7e**) by means of thin-layer chromatography and IR spectrum. The yield of **7e** was calculated to be 83.2% after converting it completely into ω-nitroacetophenone by chromatography on alumina.

ω-Nitroacetophenone Dibenzyl Acetal (7f). The dibenzyl acetal was obtained similarly using sodium benzyl oxide; its yield was calculated to be 82.4% in the manner described for **7e**.

α-Methoxy-β-nitrostyrene (8a). ω-Nitroacetophenone dimethyl acetal (**7a**) (1 g) was heated for 2 hr at 180—200°C under an atmosphere of nitrogen. The yellow oil of **8a**, obtained by thermal decomposition, was purified by distillation under reduced pressure (bp 110°C/0.35 mmHg, 0.81 g, 96% yield).

Found: C, 60.41; H, 5.38; N, 7.71%. Calcd for $C_9H_9NO_3$: C, 60.32; H, 5.02; N, 7.82%.

α-Propoxyl-β-nitrostyrene (8c). On heating 1 g of ω-nitroacetophenone dipropyl acetal (**7c**) at 200°C for 2 hr under an atmosphere of nitrogen, a yellow oil of **8c** was obtained. It was purified by distillation under reduced pressure (bp 115—116°C/0.2 mmHg, 0.73 g, 95% yield).

Found: C, 64.51; H, 6.21; N, 6.54%. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.28; N, 6.76%.

α-Benzyloxy-β-nitrostyrene (8f). A similar procedure using 1 g of ω-nitroacetophenone dibenzyl acetal (**7f**) (180°C, 1 hr) afforded an orange-yellow oil of **8f** (bp 153—154°C/0.005 mmHg, 0.42 g).

Found: C, 70.97; H, 5.34; N, 5.03%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.09; N, 5.49%.

ω-Nitroacetophenone Methyl Propyl Acetal (9). To 0.005 mol (0.89 g) of α-methoxy-β-nitrostyrene (**8a**) in 50 m*l* of dry THF, 0.02 mol (1.64 g) of sodium *n*-propoxide was added. After having been refluxed for 1 hr on a water bath, the reaction mixture was treated in the manner described for the preparation of **7a**. A pale yellow oil of **9** was then isolated by distillation under reduced pressure (bp 89—90°C/0.3 mmHg, 0.99 g, 84% yield).

Found: C, 60.58; H, 7.31; N, 6.41%. Calcd for $C_{12}H_{17}NO_4$: C, 60.25; H, 7.11; N, 5.85%.

3-Ferrocenyl-1-(α-methoxybenzyl)cyclopropene (10). To 0.005 mol (1.14 g) of β-bromo-β-nitrostyrene in 50 m*l* of dry THF, 0.005 mol (0.27 g) of sodium methoxide and 0.005 mol (1.06 g) of vinylferrocene were added. After having been refluxed for 20 min on a water bath, the reaction mixture was poured into a mixture of 200 m*l* of water and 30 m*l* of benzene. The benzene layer was separated, washed three times with 100-m*l* portions of water, and dried over magnesium sulfate. After the removal of the solvent, the residue was dissolved in 5 m*l* of a mixture of benzene and *n*-hexane (1 : 1) and chromatographed on Florisil, using a mixture of benzene and *n*-hexane (1 : 1) as the eluent. The second blue fraction gave 0.14 g of 1-ferrocenyl-2-nitroethylene. The third fraction gave yellow-brown crystals of 3-ferrocenyl-1-(α-methoxybenzyl)cyclopropene (**10**) (mp 88—90°C, 0.12 g, 6.9% yield).

Found: C, 72.66; H, 5.61%. Calcd for $C_{21}H_{20}FeO$: C, 73.25; H, 5.81%.

The first fraction consisted of recovered vinylferrocene. The fourth fraction gave pale yellow crystals of the sodium salt of ω-nitroacetophenone, which was found to be produced from its dimethyl acetal during the chromatography, because ω-nitroacetophenone was not detected in the original reaction mixture.

Decomposition of Nitroketones in the Presence of Piperidine and Alcohol. A mixture of 1.3 g (0.005 mol) of (nitroacetyl)ferrocene (**2**), 30 m*l* of absolute methanol, and 4 g of piperidine was stirred at 0°C for 20 hr. Then the reaction mixture was poured into a mixture of 10% hydrochloric acid (100 m*l*) and benzene (30 m*l*), followed by stirring for a few more minutes. The benzene layer was washed three times with 50-m*l* portions of water and then dried over magnesium sulfate. After the benzene had been removed by distillation, the residue was dissolved in 3 m*l* of benzene and chromatographed on alumina, using benzene as the solvent. The first fraction of the chromatography gave 0.92 g (76% yield) of methyl ferrocenecarboxylate.

A similar procedure using ethanol instead of methanol afforded ethyl ferrocenecarboxylate (8% yield). Similarly, the reaction of ω-nitroacetophenone with methanol and ethanol in the presence of piperidine gave methyl benzoate and ethyl benzoate respectively in 54 and 9% yields.

*2 ω-Nitroacetophenone was found to be converted into its sodium salt during chromatography on basic alumina.