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Nitroalkenylferrocene. II. The Condensation Reaction of Nitroolefins with Aromatic Carbonyl Compounds

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The condensation reactions of β-ferrocenylnitroethylene (**1**), with various aromatic aldehydes in the presence of an excess of sodium methoxide were investigated. The main products of these reactions were ferrocenylnitroalkenols (**2**), which were obtained from precursory sodium salts by the acidification of the reaction mixture. Sodium nitroalkanolate (**4**) was postulated as an intermediate in these reactions. On the other hand, the reaction of **1** with acetophenone resulted in a different condensation, one giving 1-benzoyl-2-ferrocenyl-3-nitropropane (**11**) and 1-benzoyl-2-ferrocenylethylene (**12**).

Various reactions of nitroolefins have been reported by several authors,[1-5] but most of these reports were concerned with the reaction of β-carbon of nitroolefins. With a view of getting some information on the reactivity of the α-carbon of nitroolefins, the condensation of β-ferrocenylnitroethylene (**1**)[6] with aromatic aldehydes was investigated for this paper.

The sodium salt of the nitroethylene (1) reacted with aldehyde in methanol solution at 0°C. The reaction mixture, after it had been kept stirring for 20 hr, was poured into water and the excess of aldehyde was removed with benzene. The acidification of the aqueous solution with dilute hydrochloric acid gave 3-ferrocenyl-2-nitro-1-aryl-2-propen-1-ol (**2**). The product (**2**) is considered to exist in the original reaction mixture as its sodium salt. It was found that some of the nitroalkenols are apt to decompose to give formylferrocene during the extraction of the alkaline solution with benzene. Hence, the preferred procedure for obtaining the nitroalkenols (**2**) is to pour the reaction mixture directly into dilute hydrochloric acid and then to extract it with benzene. The results of the condensation reaction are summarized in Table 1. The NMR and IR spectra of the nitroalkenols (**2**) are shown in Tables 2 and 3. The condensation reactions usually produced a small

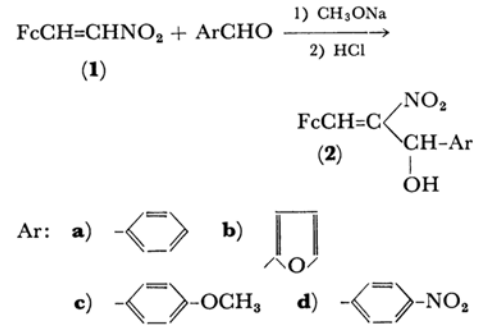


TABLE 1. CONDENSATION REACTION OF β-FERROCENYLNITROETHYLENE WITH AROMATIC ALDEHYDES
(Reaction temp. 0°C. Reaction time 20 hr)

β-Ferrocenylnitroethylene		Aromatic aldehyde			CH_3ONa		Ar in the product (**2**)	Yield	
(g)	(mol)		(g)	(mol)	(g)	(mol)		(g)	(%)
1.28	0.005	Benzaldehyde	2.6	0.025	1.35	0.025	Phenyl (**2a**)	0.93	52
1.28	0.005	Furfural	2.4	0.025	1.35	0.025	2-Furyl (**2b**)	0.62	35
1.28	0.005	*p*-Anisaldehyde	3.4	0.025	1.35	0.025	*p*-Methoxyphenyl (**2c**)	0.83	43
1.28	0.005	*p*-Nitrobenzaldehyde	3.7	0.025	1.35	0.025	*p*-Nitrophenyl (**2d**)	1.17	

1) A. Dornow and F. Boberg, *Ann.*, **578**, 101 (1952).
2) F. Boberg, A. Marei and G. R. Schultze, *ibid.*, **655**, 102 (1962).
3) A. Dornow and F. Borbeg, *Chem. Ber.*, **83**, 261 (1950).
4) D. N. Robertson, *J. Org. Chem.*, **25**, 47 (1960).
5) A. Dornow and A. Frese, *Ann.*, **581**, 211 (1953).
6) M. Shiga, H. Kono, I. Motoyama and K. Hata, This Bulletin, **41**, 1897 (1968).

Table 2. The IR spectra of nitroalkenols (**2**) and its derivatives (**7**), (**8**)

Compound	Frequency (cm^{-1})					
	C=C	NO_2 (asym.)	NO_2 (sym.)	-O-C- ‖ O	C=O	OH
2a	1632	1505	1313			3420
2b	1625	1498	1310			3380
2c	1627	1506	1315			3400
2d	1625	1525	1328			3430
7	1635	1513	1315	1235	1736	
8	1633	1512	1314	1233	1735	

amount of by-products, consisting of formylferrocene and two unidentified ferrocene derivatives, one of which was considered to be a dimer of **1** on the basis of its IR spectrum.

The formation of the nitroalkenol (**2**) from the nitroolefin (**1**) is interpreted as is shown in the scheme. Sodium methoxide reacts with **1** to generate a carbanion (**3**), which then attacks a carbonyl carbon on the aromatic aldehyde to form a sodium nitroalkanolate (**4**). The intermediate (**4**) is converted into the nitroalkenol (**2**), either by the action of sodium methoxide through sodium nitroalkenolate (**5**) (Course A) or by intramolecular hydrogen transfer through the sodium salt of *aci*-nitroalkenol (**6**) (Course B). Course A seems more favorable than Course B when an excess of sodium methoxide is present in the reaction mixture.

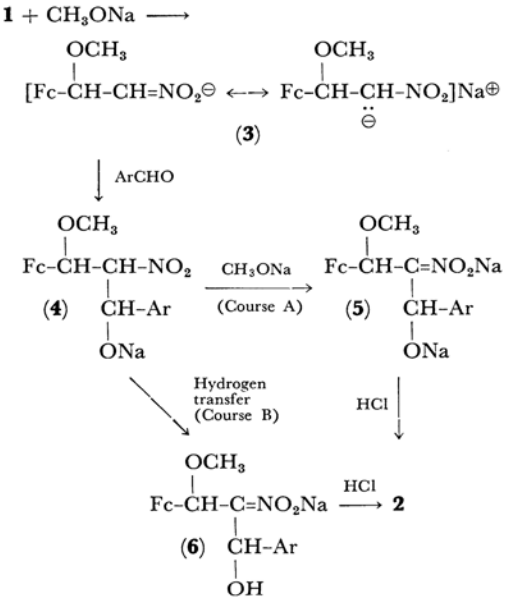
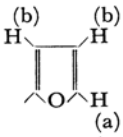


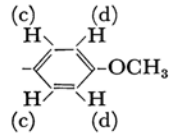
Table 3. The NMR spectra of nitroalkenols (**2**) and its derivatives (**7**) (τ-Value, in $CDCl_3$)

Compound	Cyclopentadienyl ring protons (Subst.)	Cyclopentadienyl ring protons (Unsubst.)	-CH=C(NO2)	=C(NO2)-CH-	OH	Aromatic ring protons	CH_3
2a	5.38(s)	5.76(s)	1.85(s)	5.96(s)	6.14(s)	2.62(s)	
2b	5.40(s)	5.80(s)	1.91(s)	5.95(s)	6.15(s)	2.61(s) [a] 3.62(s) [b]	
2c	5.40(s)	5.73(s)	2.03(s)	5.93(s)	6.11(s)	2.70(d) [c] 3.11(d) [d]	6.21(s) [e]
7	5.36(s)	5.73(s)	1.82(s)	5.86(s)	—	2.60(s)	7.86(s) [f]

a) and b)



c) and d)



e) Methyl protons of methoxy group.
f) Methyl protons of acetoxy group.

Table 4. Condensation of β-ferrocenylnitroethylene with benzaldehyde

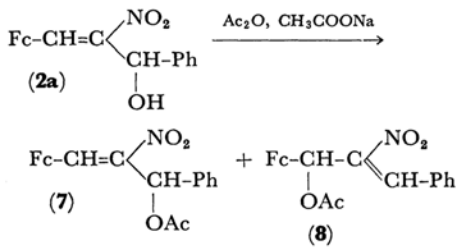
FcCH=CHNO2 (g)	FcCH=CHNO2 (mol)	CH_3ONa (g)	CH_3ONa (mol)	PhCHO (g)	PhCHO (mol)	Solvent	Yield of **2** (%)
1.28	0.005	1.35	0.025	2.6	0.025	Methanol	52
						Pyridine	12
						Tetrahydrofuran	5
						Tetrahydrofuran-Methanol (1:1)	10
1.28	0.005	1.08	0.02	2.0	0.02	Methanol	46
1.28	0.005	0.40	0.0075	0.78	0.0075	Methanol	15

TABLE 5. CONDENSATION OF β-FERROCENYLNITROETHYLENE WITH ACETOPHENONE

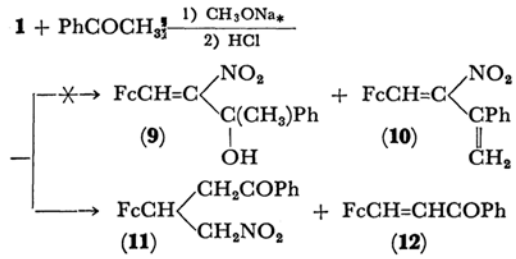
Run	$PhCOCH_3$		$FcCH{=}CHNO_2$		CH_3ONa		Product		
	(g)	(mol)	(g)	(mol)	(g)	(mol)		(g)	(%)
a	3.0	0.025	1.28	0.005	1.35	0.025	**11**	1.57	84
							12	0.07	5
b	9.0	0.075	1.28	0.005	1.35	0.025	**12**	1.35	86
							11	0.05	3

The condensation reactions which were carried out in solvents other than methanol resulted in a low yield of **2** (Table 4). The low yield is probably caused by the insufficient solubilities of the sodium salt (**3**) toward these solvents.

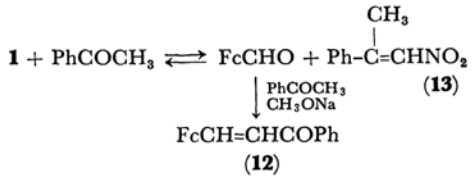
When 3-ferrocenyl-2-nitro-1-phenyl-2-propen-1-ol (**2a**) was treated with acetic anhydride and sodium acetate, two isomeric acetates were obtained. One of them, obtained in a 56% yield, was found by a study of its IR and NMR spectra to be the normal acetylation product (**7**). The other product, obtained in a 6.7% yield, was tentatively identified as the rearrangement product (**8**) from the results of its elemental analysis, but the lack of its NMR data does not permit any conclusive structural assignment.



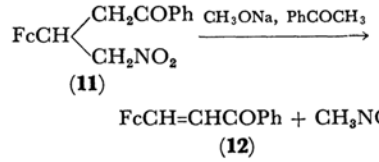
In contrast with the behavior of aldehyde, the similar reaction of the nitroethylene (**1**) with acetophenone gave quite a different result; instead of an analogous nitroalkenol (**9**) or its dehydration product (**10**), 1-benzoyl-2-ferrocenyl-3-nitropropane (**11**) was obtained as the condensation product of a carbanion generated from acetophenone with β-carbon on **1**, together with a small amount of 1-benzoyl-2-ferrocenylethylene (**12**).[7,8]



As is shown in Table 5, when a large excess of acetophenone was used (Run b), **12** was obtained in a good yield. It may be assumed that the formation of **12** is to be ascribed to the condensation of the excess acetophenone with formylferrocene, which is itself produced by the following exchange reaction between acetophenone and β-ferrocenylnitroethylene (**1**):



However, this inference is ruled out by the experimental finding that 2-phenyl-1-nitropropene (**13**) could not be detected in the reaction product. A better explanation seemingly lies in the fact that the primary product (**11**) was easily decomposed into 1-benzoyl-2-ferrocenylethylene (**12**) and nitromethane in the presence of sodium methoxide and an excess of acetophenone.



Experimental

General Procedure of Preparing Nitroalkenol (2). The reaction conditions and the products of the condensation reactions of β-ferrocenylnitroethylene with aromatic aldehydes are summarized in Table 1. A typical reaction procedure was as follows: To 1.28 g (0.005 mol) of finely-powdered β-ferrocenylnitroethylene in 7 m*l* of absolute methanol at 0°C, there were added slowly 1.35 g (0.025 mol) of sodium methoxide, which had been freshly-prepared from absolute methanol and sodium metal. Subsequently, 0.025 mol of aromatic aldehyde was added, drop by drop, into the mixture with stirring. After it had been stirred for 20 hr, the reaction mixture was poured into a mixture of 10% hydrochloric acid (100 m*l*) and benzene (30 m*l*), and then stirred for a few more minutes. The benzene layer which separated from the aqueous 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 under reduced pressure, the residual blue-violet oil was dissolved in 2 m*l* of chloroform and chromatographed on alumina, using chloroform as the solvent, the chromatographic column being covered with aluminum foil in order to prevent the

7) K. Schlögl, *Monatsch. Chem.*, **88**, 601 (1957).
8) J. Boichard, J. P. Monin and J. Tirouflet, *Bull. Soc. Chim. France*, **1963**, 851.

decomposition of unstable nitroalkenol (**2**) by exposure to the light. The first fraction of the chromatography gave the starting material, and the second fraction gave a mixture of **2** and by-products as a blue-violet oil, which was then subjected to further chromatography on Florisil, using benzene as the solvent. Nitroalkenol (**2**) was obtained as a blue-violet oil from the second fraction, whereas the first and the third fraction gave by-products. The nitroalkenol (**2**) thus obtained was purified again by chromatography on Florisil.

3-Ferrocenyl-2-nitro-1-phenyl-2-propen-1-ol (2a). The condensation reaction of β-ferrocenylnitroethylene (**1**) (1.28 g) with benzaldehyde (2.6 g) gave a blue-violet oil of nitroalkenol (**2a**) (0.93 g, 52%).

Found: C, 61.81; H, 4.59; N, 4.11%. Calcd for $C_{19}H_{17}FeNO_3$: C, 62.80; H, 4.68; N, 3.85%.

3-Acetoxy-1-ferrocenyl-2-nitro-3-phenylpropene (7) and 3-Acetoxy-3-ferrocenyl-2-nitro-1-phenylpropene (8). To 400 mg of **2a** in 4 m*l* of acetic anhydride, 0.5 g of anhydrous sodium acetate was added. After it had been heated to 95°C for 3 hr, the reaction mixture was poured into 50 m*l* of water. The blue-brown solid (450 mg) which separated as a precipitate was chromatographed on Florisil, using a mixture of benzene-*n*-hexane (5 : 1) as the solvent. The starting material (**2a**) was recovered as the first fraction. After the starting material had then been completely removed, elution with chloroform gave an acetylated product (**7**), (250 mg, 50% yield as a blue-violet oil.

Found: C, 61.80; H, 4.62; N, 3.02%. Calcd for $C_{21}H_{19}FeNO_4$: C, 62.22; H, 4.62; N, 3. 45%.

A third elution, using a mixture of chloroform and a small amount of methanol as the solvent, afforded the isomeric acetate (**8**), (30 mg, 6.7% yield) as a brown solid (mp 62—64°C).

Found: C, 61.02; H, 4.57; N, 3.40%. Calcd for $C_{21}H_{19}FeNO_4$: C, 62.22; H, 4.62; N, 3.45%.

3-Ferrocenyl-2-nitro-1-(2-furyl)-2-propen-1-ol (2b). The condensation reaction of β-ferrocenylnitroethylene (1.28 g) with furfural (2.4 g) gave 0.61 g (35% yield) of nitroalkenol (**2b**).

Found: C, 58.55; H, 4.02; N, 3.35%. Calcd for $C_{17}H_{15}FeNO_3$: C, 57.79; H, 4. 24; N, 3.96%.

3-Ferrocenyl-2-nitro-1-(*p*-methoxyphenyl)-2-propen-1-ol (2c). *p*-Anisaldehyde condensed with β-ferrocenylnitroethylene to give 0.83 g (43% yield) of nitroalkenol (**2c**).

Found: C, 62.64; H, 4.44%. Calcd for $C_{20}H_{19}FeNO_4$, C: 63.61; H, 4.83%.

3-Ferrocenyl-2-nitro-1-(*p*-nitrophenyl)-2-propen-1-ol (2d). The condensation of β-ferrocenylnitroethylene (1.28 g) with *p*-nitrobenzaldehyde (3.7 g) afforded 1.17 g of crude nitroalkenol (**2d**). A small amount of the by-products could not be removed from the crude **2d** by column chromatography, but the IR spectrum of the crude product clearly showed the existence of **2d.**

1-Benzoyl-2-ferrocenyl-3-nitropropane (11). The condensation reaction of β-ferrocenylnitroethylene (1.28 g, 0.005 mol) with acetophenone (3.0 g, 0.025 mol) was carried out much like that with aldehydes. The first fraction of the chromatographic separation of the crude product on alumina gave a small amount of reddish crystals of 1-benzoyl-2-ferrocenylethylene (**12**) (mp 137—140°C, 0.07 g, 5% yield) upon elution with benzene.

The main product (**11**) was obtained as pale yellow crystals (mp 111—113°C, 1.57 g, 84% yield) by elution with chloroform. The IR spectrum of **11** showed absorption bands at 1670 cm^{-1} (C=O) and at 1549 cm^{-1} (NO_2)

Found: C, 63.80; H, 4.86; N, 3.82%. Calcd for $C_{20}H_{19}FeNO_3$: C, 63.66; H, 5.04; N, 3.71%.

1-Benzoyl-2-ferrocenylethylene (12). a) The condensation reaction described above was carried out in the presence of a large excess (9.0 g, 0.075 mol) of acetophenone. A mixture of **12** and formylferrocene was obtained as the first fraction by the chromatography of the crude product on alumina. After the removal of the formylferrocene by sublimation, **12** was obtained as reddish-orange crystals (1.35 g, 86% yield). The IR spectrum of **12** showed absorption bands at 1655 and 1676 cm^{-1} (C=O).

Found: C, 72.58; H, 5.14%. Calcd for $C_{19}H_{16}FeO$: C, 72.15; H, 5.06%.

b) Acetophenone (6.0 g, 0.05 mol) was added to a solution of **11** (0.74 g, 0.0025 mol) and sodium methoxide (0.54 g, 0.01 mol) in absolute methanol (7 m*l*). After being kept standing overnight, the reaction mixture was poured into 100 m*l* of 10% hydrochloric acid and extracted with benzene. The extract was dried over magnesium sulfate and concentrated. The chromatographic separation of the crude product on alumina gave **12** (0.51 g, 65% yield) from the second fraction.