# CONVERSIONS OF $\alpha$ -NITROOLEFINS DURING ELECTRON TRANSFER

## IN SOLUTION

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We studied the liquid-phase (in THF) reaction of the electron transfer from cyclooctatetraene dipotassium  $C_8H_8K_2$  to  $\alpha$ -nitroolefins of the general formula (I)  $R^1CH=C(R^2)NO_2$  (I),  $R^1 = R^2 = Ph$  (a);  $R^1 = Ph$ ,  $R^2 = Me$  (b);  $R^1 = C_5H_5FeC_5H_4$ ,  $R^2 = H$  (c).

We previously established [1] that the arylolefins with the nitro group in the aryl fragment undergo cis-trans isomerization without the reduction of the nitro group and without dimerization after the taking up of one or two electrons. It was also shown that the saturation of the olefin bond does not proceed during the interaction of the anionic forms of 4-nitrostilbene with protons; the proton removes the surplus electron with the regeneration of the uncharged nitrostilbene [2].

It was of interest to verify how the position of the nitro group, situated directly on the olefin bond and not on the aromatic nucleus (cf. the structure (I)], influences the result of the electron transfer reaction. On the basis of the data obtained, it can be assumed that the compounds (I) do not form stable anion-radicals or dianions, but dimerize according to the Scheme (1) or (2).

$$\begin{array}{c} \text{R}^{1}\text{CH} = \text{C}(\text{R}^{2})\text{NO}_{2} \xrightarrow{+\frac{1}{2}\text{C}_{8}\text{H}_{8}\text{K}_{2}} [\text{R}^{1}\text{CH} = \text{C}(\text{R}^{2})\text{NO}_{2}]^{-1}} \text{K}^{+} \rightleftharpoons \begin{array}{c} \text{NOOK} \\ \parallel \\ \parallel \\ (\text{II}) \end{array} \xrightarrow{\text{NOOK}} \begin{array}{c} \text{NOOK} \\ \parallel \\ \parallel \\ (\text{III}) \end{array} \xrightarrow{\text{R}^{1}\text{CH} = \text{CR}^{2}} \\ (\text{III}) \end{array} \xrightarrow{\text{NOOK}} \begin{array}{c} \text{NOOK} \\ \parallel \\ R^{1}\text{CH} = \text{CR}^{2} \\ (\text{III}) \end{array} \xrightarrow{\text{NOOK}} \begin{array}{c} (1) \\ \parallel \\ (1) \end{array}$$

$$(II) \xrightarrow{+\frac{1}{2}C_{8}H_{8}K_{2}}_{-\frac{1}{2}C_{8}H_{8}} \xrightarrow{K^{+} \parallel}_{R^{1}CH-CR^{2}} \xrightarrow{(I)}_{(III)} (III)$$

$$(2)$$

$$(III) \xrightarrow{+_{2HC1}}_{-_{2KC1}} \xrightarrow{\text{R}^{1}\text{CH}-\text{CR}^{2}}_{\text{R}^{1}\text{CH}-\text{CR}^{2}} \xrightarrow{\text{R}^{1}\text{CH}-\text{CHR}^{2}}_{\text{R}^{1}\text{CH}-\text{CHR}^{2}} (3)$$

$$(III) \xrightarrow{+_{2HC1}}_{-_{2KC1}} \xrightarrow{\text{R}^{1}\text{CH}-\text{CR}^{2}}_{\text{R}^{1}\text{CH}-\text{CHR}^{2}} \xrightarrow{\text{R}^{1}\text{CH}-\text{CHR}^{2}}_{\text{R}^{1}\text{CH}-\text{CHR}^{2}} (3)$$

After treatment with hydrochloric acid, the dimers of the general formula (III) give the corresponding dinitronic acids (V) which are converted to the hydro-dimers (VI) [Scheme (3)]. The substances obtained were isolated and characterized (Table 1). It should be noted that the formation of the hydro-dimers (VI) proceeds quantitatively during the two-electron transfer. The dimers are formed in 50% yield by the one-electron reduction (0.5 mole of the donor is on 1 mole of the acceptor). A half of the  $\alpha$ -nitroolefin taken reverts without a change of the configuration.

The retention of the configuration can be explained on the basis that the excess olefin either did not generally participate in the reaction or was formed as a result of the disproportionation of the anion-radicals (II) to the dianions (IV) and the uncharged molecules (I). Taking  $\alpha,\beta$ -dinitrostilbene as an example, we showed [3] that the isomerization "succeeds" in being accomplished for the investigated series of acceptors in the course of the disproportionation: the olefin recovered from the reaction has a configuration which differs from

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	Product of the conversion of the acceptor							
Acceptor	structure	mp, *C	molecular mass (mass spectro- metric)	elemental composi- tion, %	PMR (CC <sup>1</sup> 4, HMDS, δ, ppm)	yie1d of the product, %		
$\begin{array}{c} PhC=CPh \\   &   \\ H & NO_2 \end{array}$	PhCHCH (NO <sub>2</sub> ) Ph *	129	452 **	Found: C 74,10; H 5,11; N 5,88. C <sub>28</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> . Caculated: C 74,32; H 5,34; N 6,19	7,1 (10H, 2Ph), 7,4 (10H, 2Ph) 6,0 (2H, CH) 6,2 (2H, CH)	98		
iPhC=CNO2     H Me	Me PhCHCHNO <sub>2</sub> * PhCHCHNO <sub>2</sub> Me	100	) 328 **	Found: C 65.73; H 6,00; N 8,31 Ct <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> . Calculated: C 65.85; H 6,10; N 8,54	7,1 (5H, Ph) 7,3 (5H, Ph) 5,5 (2H, CH) 5,7 (2H, CH) 2,23 (3H, Me) 2,0 (3H, Me) -	96		
$\begin{array}{c} H \\ \downarrow \\ c_5H_5FeC_5H_4C = CNO_2 \\ \downarrow \\ H \end{array}$	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CHCH <sub>2</sub> NO <sub>2</sub> *	260	516	Found: C 55.08; H 4.59; N 5.29; Fe 21.62. C $_{24}$ H $_{24}$ Fe $_{2}$ N $_{2}$ O <sub>4</sub> . Catculated: C 55.85; H 4.69; N 5.42: Fe 21.64	_	99		

TABLE 1. Products of the Reaction of  $C_8H_8K_2$  with  $\alpha$ -Nitroolefins

\*The IR spectrum contains the bands corresponding to the  $NO_2$ group in alkanes (1560 and 1375 cm<sup>-1</sup>) and lacks the bands corresponding to  $-C=CNO_2$  (1525 and 1330 cm<sup>-1</sup>). +M<sup>+</sup> is not fixed. The molecular mass is deduced on the basis of the analysis of the fragment ions.

the initial one. Therefore, the first of the explanations considered is the more probable. It should be noted that  $\beta$ -ferrocenyl- $\alpha$ -nitroethylene (Ic) also forms the hydrodimer during the electron transfer. We previously noted [4] that the electron transfer to  $\beta$ -ferrocenyl- $\alpha$ -cyanoethylene does not induce dimerization under the same conditions. Such a difference in the behavior of the nitro and cyano derivatives, which have a similar structure, should be considered in more detail.

It is known that the reduction of cinnamonitrile and related aromatic nitriles proceeds with the formation of hydrodimers. The absence of the hydrodimers in the products of the two- or one-electron liquid-phase reduction of a nitrile - the ferrocenyl analog of cinnamonitrile - may be explained by the particular action of the ferrocenyl substituent [5]. The last possesses a larger volume (able to show shielding action) and is more effective than the phenyl substituent in ensuring the delocalization of the unpaired electron [6], i.e., it is able to induce the redistribution of the spin density according to the Scheme (4).

$$\begin{array}{c} \operatorname{RCH}\overline{C}\operatorname{HX} \to (\operatorname{RCH}=\operatorname{CHX})^{-*} \\ (\operatorname{VII}) & (\operatorname{VIII}) \end{array} \tag{4}$$

 $\mathbf{R} = \mathbf{C}_5 \mathbf{H}_5 \mathbf{F} \mathbf{e} \mathbf{C}_5 \mathbf{H}_4.$ 

It is impossible to acknowledge that the shielding effect of the ferrocenyl group is substantial, because the reduction of the  $\alpha$ -nitroolefin (Ic) induces the fast dimerization according to the schemes (1) or (2). It can be inferred that the character of the influence of the ferrocenyl substituent in the anion-radicals of the type (VII) or (VIII) depends on the nature of the group X. When X = NO<sub>2</sub>, the ferrocenyl group does not prevent the fixation of the electron density of the type (VII); this is in agreement with the data of [7]. When X = CN, the electronic influence of the ferrocenyl group is compared with the CN group; therefore the anion-radical of the type (VIII), which can exist without dimerization, is formed.

#### EXPERIMENTAL

The following initial compounds were utilized:  $cis-\alpha$ -nitrostilbene (Ia) with the mp 73-74°C (MeOH, cf. [8]),  $cis-\omega$ -methyl- $\omega$ -nitrostyrene (Ib) with the mp 64-66°C (MeOH, cf. [9]), and trans- $\alpha$ -nitro- $\beta$ -ferrocenylethylene (Ic) with the mp 139-140°C (hexane, cf. [10]).

TABLE 2. Main Paths of the Fragmentation of the Hydrodimer of  $\alpha$ -Nitrostilbene

Ion	m/z	Retative in- tensity, %	Ion	z/m	Relative intensity, %
$\begin{array}{c} {\rm M}^+ \\ [{\rm M}-2{\rm H}_2-{\rm Ph}]^+ \\ [{\rm M}-2{\rm NO}_2-{\rm H}_2]^+ \\ [{\rm M}-2{\rm NO}_2-{\rm H}_2-{\rm Ph}]^+ \\ [{\rm M}-{\rm Ph}{\rm CH}{\rm NO}_2-{\rm NO}_2]^+ \\ [{\rm M}-{\rm Ph}{\rm CH}{\rm NO}_2-{\rm Ph}{\rm NO}_2]^+ \end{array}$	452 371 358 281 270 193	$\begin{array}{c c} 0,01\\ 2,0\\ 3,0\\ 3,0\\ 6,0\\ 49,0 \end{array}$	$[Ph-CH=CHPh]^+ \\ [M-PhCH=CHPh-NO_2-H]^+ \\ Ph^+ \\ C_5H_3^+ \\ C_4H_4^+ \\ C_4H_4^+ \\ \end{cases}$	180 179 77 63 55 58	88.0 100.0 78.0 25.0 12,0 29,0

<u>Two-Electron Reduction of  $\alpha$ -Nitroolefins</u>. To the solution of 1.0 mmole of the acceptor in 20 ml of THF was added the solution of 1.0 mmole of  $C_8H_8K_2$  in 20 ml of THF under argon at -40°C. The mixture was stirred for 30 min; the temperature was increased to -5°C prior to the addition of 0.5 ml of water. The yield (100%) of  $C_8H_8$  was determined by GLC. The residue obtained was filtered off, washed with ether, and dried. According to the TLC analysis of the filtrate on Silufol with markers (the eluant was the 3:4 mixture of hexane:ether), the initial isomer and the product of its conversion to the stereoisomeric form are absent.

The dry dipotassium salt of the dimer was dissolved in water; 1 ml of conc. HCl was added at -5-0°C. The precipitated residue was filtered off, washed with water, and dried. The yields and the characteristics of the products are presented in Table 1.

<u>One-Electron Reduction of  $\alpha$ -Nitroolefins</u>. To the solution of 1.0 mmole of the acceptor in 20 ml of THF was added the solution of 0.5 mmole of  $C_8H_8K_2$  in 15 ml of THF under argon at -40°C. The mixture was stirred for 30 min; the temperature was increased to -5°C prior to the addition of 0.5 ml of water. The yield of  $C_8H_8$  was 100% according to the GLC. The residue obtained was filtered off, washed with ether, and dried. According to the TLC analysis of the filtrate on Silufol (the eluant was the 3:4 mixture of hexane:ether), only the initial isomer occurs in all cases. After the removal of the solvent, ~0.50 mmole of the initial acceptor was isolated in all cases.

The dried residue - the dipotassium salt of the dimer - was dissolved in water prior to the dropwise addition of 1 ml of conc. HCl at 0°C. The precipitated residue was filtered off, washed with water, and dried. The same hydrodimers were obtained in the H-form; they are characterized by the data in Table 1. The yields were ~50%.

The control experiment was performed by the methods described above, but without the addition of cyclooctatetraene dipotassium. The initial  $\alpha$ -nitroolefins were isolated without change (quantitative recovery).

Mass Spectrometric Investigation. The mass spectra were obtained on an MS-30 instrument with the DS-50 system for the treatment of the data, and the ionizing voltage of 70 V. The temperature conditions were as follows: the ionization chamber at 250°C and the source of the direct sample input at 100-130°C.

The  $M^+$  with m/z 516 was fixed for the hydrodimer of  $\beta$ -ferrocenyl- $\alpha$ -nitroethylene. The  $M^+$  characteristics of the hydrodimers of  $\alpha$ -nitrostilbene and  $\omega$ -methyl- $\omega$ -nitrostyrene were not fixed, but the fragment ions correspond with the structure of the hydrodimer, e.g., for the hydrodimer of  $\alpha$ -nitrostilbene (Table 2).

The molecular mass of the dipotassium salt of the dimer of  $\beta$ -ferrocenyl- $\alpha$ -nitroethylene was determined by the method of equilibrium sedimentation in water. Found: molecular mass 598.  $C_{24}H_{22}Fe_2N_2O_4K_2$ . Calculated: molecular mass 592.

#### CONCLUSIONS

1. The reaction of  $\alpha$ -nitroolefins, containing the aryl or the ferrocenyl substituent at the double bond, with cyclooctatetraene dipotassium in THF gives dimers - derivatives of propane- $\omega$ , $\omega$ -dinitronic acids.

2. The distribution of the spin density in the anion-radicals of  $\alpha$ -nitro- and  $\alpha$ -cyano- $\beta$ -ferrocenylethylenes is characterized as follows: the NO<sub>2</sub> group surpasses the ferrocenyl group

in the competition for the unpaired electron, and the CN group appears to be comparable with, or even weaker than, the ferrocenyl group.

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GEMINAL SYSTEMS.

33.\* REACTIONS OF 1,1-DIALKOXYUREAS WITH ELECTROPHILES AND NUCLEOPHILES. SYNTHESIS OF CYCLIC 1,1-DIALKOXYUREAS AND NH-DIALKOXYAMINES

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We were the first to synthesize 1,1-dialkoxyureas (DAU) [2, 3] in order to convert them subsequently into NH-dialkoxyamines [2, 4]. In the present work, we studied certain chemical properties of this new class of organic compounds. It was shown that the presence of an ONO fragment determines the most characteristic property of DAU, namely, the tendency to react with electrophiles and the similarity in this respect with related geminal systems acyclic [5, 6], cyclic [7], and bicyclic N,N-dialkoxyamines (see [7]).

Thus, similarly to N,N-dialkoxy-N-tert-alkylamines [6], 2-alkoxyisoxazalidines [8], and their carbon analogs, the acetals [9], DAU (I) is readily split by acetyl chloride with substitution of the alkoxy group by chlorine

 $Me_2NCON(OMe)_2 \xrightarrow{MeCOCl} \begin{bmatrix} Me \\ i \\ Me_2NCON - O^+ - COMeCl^- \\ i \\ OMe \end{bmatrix} \rightarrow Me_2NCON(Cl)OMe$ (II)

Similarity is also observed in the nature of the acid-catalyzed substitution of the N-alkoxyl group (cf. [5, 8])

 $\begin{array}{c} Me_{2}NCON(OMe)OCH_{2}Ph \xrightarrow{MeOH} (I) \\ (III) \gamma - collidine \cdot HC1 \end{array}$ 

This reaction was used to synthesize, starting from (I) and (IV), the previously unknown 2-dimethylcarbamoyl derivatives of 1,3,2-dioxazolidine (V) and perhydro-1,3,2-dioxazine (VI)+ \*For communication 32, see [1].

+For the preliminary communication, see [10]. The N-tert-alkyl derivatives of these heterocycles have been described in [5].

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