

PREPARATION AND *Z-E* ISOMERIZATION OF SUBSTITUTED NITROSTYRENES*IVO BLÁHA^a and Ladislav LEŠETICKÝ^b^a *Institute of Organic Chemistry and Biochemistry,
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This study concerns the synthesis of β -substituted β -nitrostyrenes by two procedures: addition of nitril halogenides to double bonds, connected with the elimination of hydrogen halide, and condensation of aldehydes with substituted nitromethanes, and it compares the utilizability of the two procedures. Two of the substances prepared, methyl (*Z*)-nitro-3-phenylpropenoate and (*Z*)-4-phenyl- β -nitro- β -buten-2-one, were submitted to *Z-E* isomerization at various temperatures, and thermodynamic isomerization parameters were estimated from the dependence of the equilibrium constants on temperature.

Recently, a larger number of papers concerning nitroolefins has been published, especially their rearrangements and isomerizations¹⁻⁵. This study concerns the methods of preparation of β -nitrostyrenes with a negative group in β -position, and *Z-E* isomerization of these compounds.

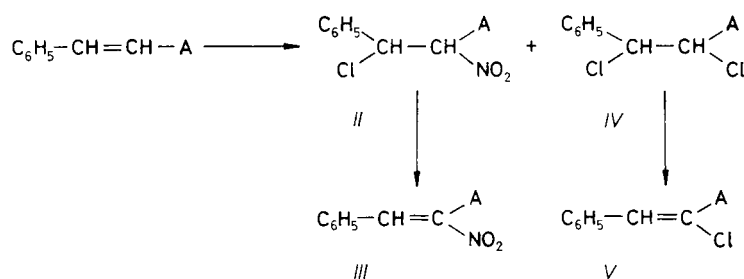
For the preparation of β -nitrostyrenes substituted in the β -position by an electro-negative group we made use of two procedures: addition of nitril halogenides to a double bond⁶⁻¹² (Scheme 1) and condensation of nitro compounds with aldehydes¹³⁻¹⁸.

The first procedure is based on the addition of nitril chloride or nitril iodide to the substituted styrene *I*, with subsequent elimination of hydrogen halide from the halogen-nitro compound *II*, under formation of β -substituted β -nitrostyrene *III* (Scheme 1). In this case the intermediate *II*, in which the halogen atom is in the β -position to the two negative groups, could not be isolated. The products formed by an opposite orientation of the addition are not formed at all, but when nitril chloride is used a side reaction takes place, *i.e.* addition of chlorine to the double bond, under formation of dichloro derivative¹⁹ *IV* which can split off hydrogen chloride under formation of unsaturated chloro derivative *V*.

Both nitril halogenides were added to β -substituted styrenes listed in Table I in which the yields of the products formed are also presented. The use of the more

* Part V in the series Isomerization of Nitroolefins; Part IV: This Journal *41*, 2744 (1976).

reactive nitril chloride is not more advantageous, because nitril chloride is in equilibrium with chlorine and nitrogen dioxide. Therefore, competitive addition of chlorine to the double bond takes place, leading to products *IV* and *V*, which makes the separation of the mixture more difficult. When nitril iodide reacts, the addition of iodine does not take place and substituted nitrostyrene is the only product.



SCHEME I

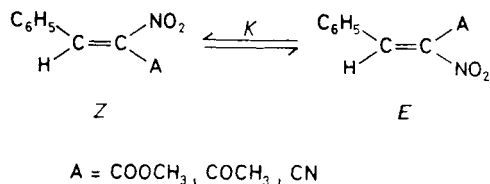
TABLE I

Yields of the addition of nitril halogenides to substituted styrenes

$ \begin{array}{c} \text{C}_6\text{H}_5 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} $	Yield of reaction, wt. %	
	NO ₂ Cl	NO ₂ I
<i>Ia</i> , A = COOCH ₃	<i>IIIa</i> 4 <i>IVa</i> 21	<i>IIIa</i> 18 ^a
<i>Ib</i> , A = COCH ₃	<i>IIIb</i> 22 <i>IVb</i> 20	<i>IIIb</i> 8
<i>Ic</i> , A = CN	<i>IIIc</i> 0 <i>IVc</i> ~30 <i>Vc</i> ~10	<i>IIIc</i> 0
<i>Id</i> , A = CCl ₃	<i>IIIc</i> 0 <i>Vd</i> >50	<i>IIIc</i> 0
<i>Ie</i> , A = SO ₂ CH ₃	<i>IIIe</i> 0 <i>IVe</i> ~40 <i>Ve</i> ~10	<i>IIIe</i> 0
<i>If</i> , A = NO ₂	—	<i>IIIc</i> 0

^a Addition of NO₂I carried out with methyl *cis*-phenylpropenoate gave the same yield.

From the comparison of the yields of the reactions published in literature it follows that the negative substituents attached to the double bond decrease the yields of the addition reactions of nitril halogenides. The data shown in Table I confirm this conclusion. In the series mentioned nitroolefins only afforded both isomeric methyl 3-phenylpropenoates and *trans*-4-phenyl-3-buten-2-one. In both cases both geometric isomers of substituted nitrostyrenes *III* are formed in a ratio corresponding to the thermodynamic equilibrium at the reaction temperature (Scheme 2).



SCHEME 2

The condensation procedure consists in the reaction of benzaldehyde or the Schiff's base derived from it with substituted nitromethane. Among the modifications of this described method we applied three to the group of four substituted nitromethanes (see Table II).

The Knoevenagel-Walter¹⁴ method (Method 1) is suitable for nitroacetonitrile only, for which other methods are not suitable. We found that it is not necessary to add a catalyst and to heat the mixture, because nitroacetonitrile is one of the strongest C-acids¹⁶. The condensation catalysed with titanium tetrachloride¹⁸ (Method 2) is suitable for nitroacetates and nitropropanone. The condensation of

TABLE II
Yields (%) of condensations of substituted nitromethane with benzaldehyde or benzylidene-aniline

O ₂ N—CH ₂ —A	Method ^a		
	1	2	3
<i>a</i> , A = COOCH ₃	13	20	40
<i>b</i> , A = COCH ₃	traces	40	9
<i>c</i> , A = CN	64	2	7
<i>d</i> , A = CCl ₃	0	0	0

^a See the text.

the Schiff's base with substituted nitromethane in acetic anhydride¹⁷ (Method 3) is, of the group of substances used, suitable for nitroacetates only.

The β -nitrostyrenes prepared, substituted in β -position with a negative group, easily undergo thermal *Z-E* isomerization^{2,3,5,20,21} (Scheme 2). In solution of methyl (*Z*)-2-nitro-3-phenylpropenoate (*IIIa*) in nitrobenzene equilibrium of both geometric isomers is attained at room temperature within several hours, while at elevated temperatures a few minutes suffice. The isomerization of (*Z*)-4-phenyl-3-nitro-3-buten-2-one (*IIIb*) should be carried out above 400 K. For the evaluation of the equilibrium constants of isomerization the ratio of the intensities of the methyl group signals in the ¹H NMR spectrum was used. The values of the equilibrium constants and Gibbs's functions at various temperatures for compounds *IIIa* and *IIIb* are given in Table III. The enthalpies and the entropies of the reactions were determined from the dependence of the logarithm of the equilibrium constant on $1/T$ (Table IV).

TABLE III

Values of the equilibrium constants and Gibbs's functions of the isomerization of methyl 2-nitro-3-phenylpropenoate (*IIIa*) and 4-phenyl-3-nitro-3-buten-2-one (*IIIb*) at various temperatures

<i>IIIa</i>			<i>IIIb</i>		
Tempera- ture K	K	$-\Delta G$ kJ mol ⁻¹	Tempera- ture K	K	$-\Delta G$ kJ mol ⁻¹
293	0.562	1.40	411	0.245	4.81
334	0.588	1.47	432	0.361	3.66
375	0.592	1.63	439	0.361	3.72
385	0.588	1.70	455	0.416	3.32
438	0.626	1.71			
455	0.686	1.43			

TABLE IV

Thermodynamic functions of *Z-E* isomerizations

Compound	ΔH , kJ mol ⁻¹	ΔS , J mol ⁻¹ K ⁻¹
<i>IIIa</i>	1.04	-1.38
<i>IIIb</i>	19.9	36.8

From the position of the equilibrium of *Z-E* isomerization (Tables III and IV) the relative values of non-bonding interactions of the groups bound to the double bond can be evaluated. The non-bonding interaction of the methoxycarbonyl or acetyl and phenyl is bigger in this case than the interaction of the nitro group and the phenyl. From a comparison of thermodynamic parameters of compounds *III* and *IIIb* it follows that the acetyl group is sterically more demanding than the methoxycarbonyl group, because in compound *IIIb* the *Z*-isomer is preferred. In 3-phenyl-2-nitropropenenitrile the thermodynamic parameters were not measured. On condensation reaction the more stable *E*-isomer is formed, because the interaction of the nitrile group with the phenyl is smaller than the interaction of the nitro group.

EXPERIMENTAL

The checking of the purity of the compounds, the analyses of the reaction mixtures and the determination of the yields of non-isolated products were carried out by gas chromatography on a Chrom 2 instrument (Laboratory Instruments, Prague), using silicone elastomer SE-30 as stationary phase. Quantitative analysis was carried out by measuring the peak heights after previous calibration of the detector response at a known concentration. Preparative column chromatography was carried out on a column (3 × 120 cm) packed with silica gel of 100–160 mesh particle size. For the identification of compounds spectral methods were used (UV, IR, ¹H NMR), and in some cases also mass spectra. The configuration assignment of nitroolefins was carried out by means of the symmetrical vibration of the nitro group in the IR spectrum²².

The addition of nitril chloride was carried out according to an adjusted procedure⁸. The adjustment consisted in the immediate introduction of the nitril chloride formed into a flask with the olefin. Only 4-phenyl-3-nitro-3-buten-2-one (*IIIb*) was formed in a reasonable yield, and it was separated by column chromatography on silica gel, using heptane–benzene 3 : 1 mixture as eluent. After double crystallization from tetrachloromethane, the yellow *Z*-4-phenyl-3-nitro-3-buten-2-one was obtained, m.p. 98–99°C. For C₉N₉NO₃ (179.2) calculated: 60.33% C, 5.06% H, 7.82% N; found: 60.64% C, 5.02% H, 7.53% N. NMR spectrum: 7.62 τ (CH₃), 2.65 τ (H *trans* to NO₂), 2.55 τ centre of a multiplet (C₆H₆). IR spectrum: 1 391 cm⁻¹ (NO₂ sym), 1 550 cm⁻¹ (NO₂ as), 1 630 cm⁻¹, 1 648 cm⁻¹ (C=C), 1 710 cm⁻¹ (C=O).

The addition of nitril iodide was carried out according to literature¹¹. When added to compounds *Ia* and *Ib* two substances were detected in the reaction mixture — the starting compound and a nitroolefin which was isolated by column chromatography. Ester *IIIa* was eluted with a benzene–chloroform mixture (9 : 1), ketone *IIIb* with heptane–benzene (3 : 1). *IIIa* was obtained as a yellow oil which solidified on drying in a vacuum (oil pump, 100 Pa). After crystallization from a mixture of chloroform and light petroleum it melted at 57°C (ref.¹⁷ 57.5–58°C). NMR spectrum: 6.13 τ (CH₃), 2.59 τ (H *trans* to NO₂), 2.60 τ (centre of a multiplet, C₆H₅). IR spectrum: 1 382 cm⁻¹ (NO₂ sym), 1 540 cm⁻¹ (NO₂ as), 1 650 cm⁻¹ (C=C), 1 740 cm⁻¹ (C=O).

Condensation according to Knoevenagel and Walter was carried out according to literature¹⁶, the yields of compounds *IIIa* and *IIIb* were low. For the preparation of (*E*)-3-phenyl-2-nitropropenenitrile (*IIIc*) the following procedure was the most convenient: 2.1 g (20 mmol) of benzaldehyde and 1.7 g (20 mmol) of nitroacetonitrile¹⁶ was dissolved in 10 ml abs. ethanol. After 30–60 min crystals of *IIIc* started to settle. After 12 h standing, suction-drying and recrystallization from tetrachloromethane, ochre coloured needles were obtained, with m.p. 99–100°C

ref.¹⁶ 100–101°C). Yield, 2.2 g (64%). NMR spectrum: 1.36 τ (H *cis* to NO₂), 1.91–2.45, multiplet (C₆H₅). IR spectrum: 1 327 cm⁻¹ (NO₂ sym), 1 550 cm⁻¹ (NO₂ as), 1 600 cm⁻¹, 1 628 cm⁻¹ (C=C), 2 247 cm⁻¹ (C≡N).

Condensation of benzaldehyde with substituted nitromethane under catalysis with titanium tetrachloride was carried out according to a published procedure¹⁸. Compounds *IIIa* and *IIIb* crystallized out from the evaporated reaction mixture by standing at 0°C. The pure products were obtained by recrystallization.

Condensation of the Schiff's base with substituted nitromethane was carried out according to literature¹⁷. *IIIa* was separated on a silica gel column, in other instances the substances were not isolated.

Z-E Isomerization. 1 ml of a 0.5 mol l⁻¹ solution of compounds *IIIa* and *IIIb* in nitrobenzene was poured into a cell for the measurement of the NMR spectra followed by hexamethyldisiloxane. The closed cell was heated at a selected temperature for 30 min. After cooling the ¹H NMR spectrum was measured in the region of the methyl group. This procedure was repeated 4–5 times at each temperature and the equilibrium constant was determined from the mean values of the measurements.

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