The hydrocracking reaction was conducted in 50 cm<sup>3</sup> steel autoclaves. All operations on loading the reagents and removing the catalysts were conducted in Ar. The amounts of catalyst were 0.2-0.3 mg-atom for ruthenium.

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# $\alpha$ -IODO- $\beta$ -NITROSTILBENE IN THE REACTION WITH MORPHOLINE AND PIPERIDINE

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The reaction of  $\alpha$ -iodo- $\beta$ -nitrostilbene with morpholine or piperidine yields  $\alpha$ -nitro- $\beta$ -morpholino- or  $\alpha$ -nitro- $\beta$ -piperidinostilbene. The reaction is regioselective and stereospecific: only the iodine, and not the nitro group, is substituted; the product obtained has a cis structure regardless of whether the initial substrate had a cis- or a trans-configuration. The prereaction stage probably includes the formation of a charge-transfer complex between substrate and reagent.

Keywords: iodonitrostilbene, morpholino-, piperidinonitrostilbene; nucleophilic vinylic substitution – its regioselectivity and stereospecificity; charge transfer complexes, prereaction formations.

Nitroenamines containing donor and acceptor groups in the conjugated chain are interesting both as biologically active substances and as bearers of properties useful for optronics and magnetoelectronics. There are many studies of their synthesis, and we particularly cite [1, 2].

The reaction of  $\alpha$ -iodo- $\beta$ -nitrostilbene (1) with amines (2a, b), which yields  $\alpha$ -nitro- $\beta$ -aminostilbenes (3a, b) and ammonium salts (4a, b) (scheme 1), is examined in the present communication.



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Reagent	Solvent (abs), E* <sub>T</sub> , kJ/mole	T., °C	Yield of 3 a,b, % †
2a 2a 2a 2a 2b 2b 2b 2b 2b 2b 2b 2b	THF, 37.4 CCl <sub>4</sub> , 32.5 THF CCl <sub>4</sub> THF EtOH, 51.9 CCL THF EtOH THF EtOH THF CCl <sub>4</sub>	25 25 65 25 25 25 25 25 -25 65 76	90 82 95 80 71 87 93 80 94 100 76 71

TABLE 1. Reaction of Substrate 1 with Reagents 2a, b (1:2 Molar Ratio, 24 h Duration)

\* $E_{\rm T}$ : Reichardt degree of polarity of the solvent [3].

<sup>+</sup> Yields for *cis* and *trans* forms of substrate

1 are the same and are averaged for 3-5 experiments.

The stereochemistry of reaction (1) and the yield of the final product 3a, b as a function of the nature of the solvent and temperature were investigated.

It was found that both *cis*- and *trans*-1 only yield *cis*-product 3 (the evidence is reported in the Experimental). The effect of the nature of the solvent and temperature is illustrated in Table 1. The yields are relatively high in all experiments, 100% in some. A product of substitution of iodine with no iodoaminostilbene impurity is obtained in all cases. The product has a *cis*-configuration, i.e., reaction (1) takes place regioselectively and stereospecifically.

The yield is higher the higher the polarity of the solvent, which indicates the appearance of polar transition states during the reaction, compare [3].

The effect of the temperature is weak but distinct: the yields are higher the lower (but not the higher) the temperature. The appearance of a charge-transfer complex between substrate and reagent is probably required for the formation of the final product, compare [4].

Based on the above conclusions, we can hypothesize that the reaction takes place according to scheme (2).

Scheme (2) is in agreement with the mechanism of the reaction between  $\alpha$ ,  $\beta$ -dinitrostilbene and morpholine, kinetically substantiated in [5]. The reactions compared, whose stereospecificity was explained in [5], probably belong to the same class. The regioselectivity observed for reaction (1) becomes understandable when intermediate form 5 is considered, see scheme (2): the negative charge is on the whole localized on the nitro group. This group is converted into a nitronate group, and the iodine anion is the only fragment that can be eliminated. Displacement of iodine instead of the nitro group by morpholine in substrate 1 was also observed in [1], but without any discussion of the mechanism of this reaction.

Prod-	Mp, °C (sol-	Found/Calculated,		Empirical formula	$\frac{\text{IR spectrum}}{v_{s}NO_{2}}   v_{as}NO_{2}$		PMR spectrum (δ, ppm, J, Hz)	
uct	⊘ent)	С	Η	N		Cn	-1	
<b>3</b> a	197-198 (hexane)	73.30 73.44	<u>6.08</u> 6.12	<u>8.99</u> 9.03	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	1330	1552	3.02 t(4H, J=6); 3.75 t(4H, J=6); 7.18 br.s(5H); 7.40 s(5H)
3b	164.5-165 (hexane)	74.31 74.31	$\frac{6.42}{6.46}$	<u>8.89</u> 8.85	C19H20N2O2	1320	1540	$\begin{vmatrix} 3.02 & \text{s} & (4\text{H}, J=6); \\ 1.72 & \text{d} & (6\text{H}, J=6); \\ 7.25 & \text{m} & (10\text{H}) \end{vmatrix}$

TABLE 2. Properties of Products 3a, b

## **EXPERIMENTAL**

The IR spectra were made on a UR-20 in pellets with KBr. The PMR spectra of the prepared compounds in CDCl<sub>3</sub> (at 25°C) were recorded on a Bruker WP-200 with a working frequency of 200 mHz; TMS was the internal standard.

The starting substances were synthesized by the method in [6]:  $cis-\alpha$ -iodo- $\beta$ -nitrostilbene, mp 113-114°C (lit. mp 115-117°C [6]), trans- $\alpha$ -iodo- $\beta$ -nitrostilbene, mp 178.5-179°C (lit. mp 175-176°C [6]).

Preparation of  $cis-\alpha$ -nitro- $\beta$ -morpholino- (3a) and  $cis-\alpha$ -nitro- $\beta$ -piperidinostilbenes (3b). Here 1 mmole of substrate and 1-2 mmole of the corresponding amine were dissolved separately in one of the solvents in Table 1. The solutions were mixed and the mixture turned orange. The precipitated sediment of the product of substitution was washed with hexane to eliminate the amine. The residue was dissolved in hexane, applied on a thin layer of silica gel L 40/100 (Czechoslovakia), and eluted with a hexane-benzene mixture, 2:1. The yields of products are reported in Table 1, and their physical properties are presented in Table 2. A 1:1 mixture of product 3a and the authentic sample prepared according to [2] did not exhibit depression of the mp. We note that the structure of product 3a synthesized in [2] was established by XSA in [7, 8]. The configuration of product 3b was determined by PMR based on the chemical shifts (CS) of methylene group protons in the piperidine ring next to nitrogen. If product 3b had a *trans*-structure, these protons should have fallen in the cone of positive shielding by the phenyl ring located next to and on the same side of the ethylene bond. This would have shifted the signals examined to the strong field. As Table 2 suggests, the CS of the protons of methylene groups in heterocycles next to nitrogens are identical for products 3a, b ( $\delta$  3.02 ppm). This means that product 3b, like product 3a, has a *cis*-configuration.

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