

ISOMERISATION OF NITROOLEFINES. II.*

ISOMERISATION REACTION OF NITROETHYLENE

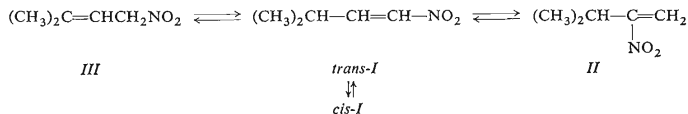
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The reversible rearrangement of the nitro group from the α - to the β -carbon of the double bond in substituted nitroethylenes leads with 1-nitro-1-phenylethylene quantitatively to 1-nitro-2-phenylethylene; 2-nitro-3-methyl-1-butene affords an equilibrium mixture of the starting compound and 1-nitro-3-methyl-1-butene. In the case of the phenylnitroethylenes the back reaction does not proceed, and in the case of the isopropynitroethylenes the back reaction is complicated by isomerisation to the β,γ -unsaturated nitro compound.

The isomerisation of the 3-methylnitrobutenes involves several equilibrium reactions which are shown in Scheme 1. But besides these reactions proceed in this system at least two polyaddition reactions as well.



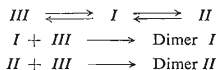
SCHEME 1

Treatment of 2-nitro-3-methyl-1-butene (II) with a solution of triethylamine in tetrahydrofuran gives rise to an equilibrium between the isomers II, *cis-I*, and *trans-I*. From the side of the 1-nitro-3-methyl-1-butene (I) isomerisation proceeds slowly and besides compound II also 1-nitro-3-methyl-2-butene (III) is produced as the result of a three carbon isomerisation of the double bond. The latter compound disappears after some time at 40 and 50°C, whilst at 65°C an equilibrium mixture of the substances I, II, and III is established. This behaviour is evidently due to the steeper temperature dependence of the rate constant for the three carbon isomerisation in comparison with that for the polyaddition reactions. The β,γ -unsaturated

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isomer *III* does not undergo any change on treatment with the base, only its concentration decreases. Actually, three carbon isomerisation takes probably place, but immediately occurs addition of the starting compound to the formed conjugated isomer *I*.

In order to verify the proposed kinetic course, the system of the studied reactions was processed on the analogue computer Meda 80 T. At this some measured rate and equilibrium constants were used as parameters for calculating the others. The kinetic model is shown in Scheme 2*.



SCHEME 2

The maximum deviation of the calculated concentration course from the observed one is 10% when the absolute concentration values were measured with an error of 5%. In Table I are compared the rate constants calculated by the approximation method with those calculated by means of the analogue computer. The numeric values for the thermodynamic and kinetic parameters of the reactions are summarized in Table II.

1-Nitro-1-phenylethylene (*IV*), when treated with the base, is transformed by a rapid unidirectional reaction to 1-nitro-2-phenylethylene (*V*). This reaction we utilized for checking whether approximate calculation of the rate constants is justified. The reaction rate was measured for various concentrations of the starting compound and the catalyst. In all cases, the kinetic course fitted the first-order rate equation. The reaction rate, however, was proportional to the triethylamine concentration and also dependent on the initial concentration of the starting compound (Table III). We may therefore assume the existence of a complex of the starting compound and the catalyst:

TABLE I

Comparison of the Rate Constants Calculated by the Approximation Method (k_a) with those Calculated on the Analogue Computer (k_c)

Reaction	k_c, h^{-1}			k_a, h^{-1}		
	313 K	323 K	338 K	313 K	323 K	338 K
$I \rightarrow II$	0.011	0.018	0.023	0.011	0.02	0.023
$II \rightarrow I$	0.07	0.105	0.12	0.08 ^a	0.12 ^b	0.26
$I \rightarrow III$	0.045	0.08	0.15	0.041	0.056	0.15
$III \rightarrow I$	0.15	0.19	0.30	—	—	—

^aAt 298 K; ^bat 308 K.

* The program scheme for the calculation is available from Dr V. Fidler.



On the assumption of a stationary state we obtain for the reaction rate the relation: $-dc_{IV}/dt = k_1 k_2 c_{IV} c_{\text{amine}} / (k_2 + k_1 c_{IV})$. If $k_2 \gg k_1 c_{IV}$, we obtain for the van't Hoff complex the general expression

$$-dc_{IV}/dt = k_1 c_{IV} c_{\text{amine}}$$

The rate constant k' obtained from the slope of $\log [c_{IV}^0 / (c_{IV}^0 - c_V)]$ versus time involves the triethylamine concentration. On recalculation we obtain for various triethylamine concentrations the single rate constant k_1 (Table III). For evaluation of the activation parameters, the reaction was followed at four different temperatures. The results obtained from two independent measurements were in satisfactory agreement (Table III).

TABLE II
Kinetic and Thermodynamic Data for the Isomerisation of the Methylnitrobutenes

Reaction	E_A , kcal/mol	$\log A$	ΔS^\ddagger , cal/deg mol
$I \rightarrow II$	6.3	2.5	-51
$II \rightarrow I$	4.6	2.2	-52.5
$I \rightarrow III$	10.2	6.5	-31
$III \rightarrow I$	6.0	3.3	-47

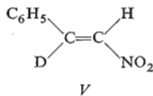
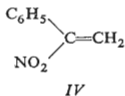
	K_{298}	ΔG_{298} , kcal/mol	ΔH , kcal/mol	ΔS , cal/deg mol
$I \rightleftharpoons II$	0.135	1.18	2.4	4.2

TABLE III
Kinetic Data for the Isomerisation of Substance IV

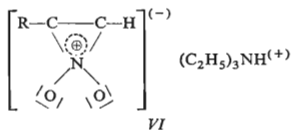
c_{IV}^0 , mol/l	$1 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	$7 \cdot 10^{-2}$	$1 \cdot 10^{-2}$
c_{amine} , mol/l	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$3 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
k' , min^{-1}	0.0145	0.097	0.177	0.252	0.49	0.042	0.025
k_1 , $\text{l} \cdot \text{min}^{-1} \cdot \text{mol}^{-1}$	14.5	19.4	17.7	12.6	16	8.5	2.5

Measurement	E_A , kcal/mol	$\log A$	ΔS^\ddagger , cal/deg mol
1	5.71	4.4	-40.4
2	5.76	3.5	-46.5

The isomerisation of α -nitrostyrene (*IV*) in tetrahydrofuran containing 5% of deuteriumoxide afforded β -nitrostyrene (*V*) in which one hydrogen atom was to 86% replaced by deuterium. The PMR spectrum proved that deuteration had occurred at the β -position to the nitro group. β -Nitrostyrene (*V*) does, under identical conditions,



deuterium not exchange. Besides the findings stated in the previous paper¹ also the following further facts support the proposed mechanism: a) *cis*-configuration of the β -hydrogen atom and the nitro group is essential in order that rearrangement can take place – *cis*-1-nitro-1-propene does not undergo rearrangement, first must proceed its isomerisation to the *trans*-isomer²; b) *cis*- α -nitrostilbene, treated with sodium methoxide, yields the watersoluble carbanion salt, but not the *trans*-isomer³; c) the high negative values for the activation entropy and the low values for the activation energy speak for a higher ordered arrangement of the transition state with respect to the starting compound and for the synchronous formation and breaking of bonds; d) the results of the kinetic studies confirm the existence of a complex of the starting compound and the base for which we assume a structure of type *VI*; e) also the deuterium exchange is in accord with the proposed reaction course.



On the basis of the stated facts we conclude that the rearrangement course proceeds through the stage of the complex which the starting compound forms with the catalyst (rate-determining step), followed by its rapid decomposition to the product and the catalyst. In most cases are both steps reversible and an equilibrium between the isomers is established. In the case of the nitrostyrenes differ the thermodynamic stabilities of the isomers evidently so much that the reaction is irreversible (in α -nitrostyrene the nitro group and the benzene ring will be rotated out of the plane of the double bond, whereas β -nitrostyrene is a planar molecule with an extended delocalisation of the π -electrons)⁴.

EXPERIMENTAL

Synthesis and Identification

1-Nitro-3-methyl-1-butene⁵ (I) was prepared by dehydration of 1-nitro-3-methyl-2-butanol with phthalic anhydride⁶. The product contains besides the *trans*-isomer also 1–2% of the *cis*-isomer. Overall yield 55%, b.p. 79–81°C/18 Torr, n_D^{20} 1.4573. NMR spectrum: 3.26–2.75 τ multiplet (H at double bond); 7.45 τ multiplet (CH); 8.84 τ doublet (CH₃); J_{CH-CH_3} = 6.7 Hz.

2-Nitro-3-methyl-1-butene (II) prepared from 2-nitro-3-methyl-1-butanol⁷ by the same procedure as above was obtained in 53% yield; b.p. 77°C/67 Torr, n_D^{20} 1.4585. NMR spectrum: 3.74 τ (2 Hz splitting, H at double bond *cis* to NO₂); 4.59 τ (H *trans* to NO₂); 6.87 τ septet (CH); 8.85 τ doublet (CH₃); J_{CH-CH_3} = 7 Hz.

1-Nitro-3-methyl-2-butene⁸ (III) is produced in 47% yield by reaction of 1-chlor-3-methyl-2-butene with silver nitrite in ether. After distilling through a column, the product had b.p. 60–61°C/12 Torr. NMR spectrum: 4.50 τ triplet (CH); 5.15 τ doublet (CH₂); 8.15 τ and 8.22 τ (CH₃); J_{CH-CH_2} = 8 Hz.

1-Nitro-2-phenylethylene (V) prepared according to literature⁹ was purified by repeated crystallisation from hexane, b.p. 58–59°C.

1-Nitro-1-phenylethylene (IV). A methanolic solution of 0.2 mol of 2-nitro-2-phenyl-1,3-propanediol¹⁰ was added dropwise with stirring to an equivalent amount of sodium methoxide in methanol, and immediately started the sodium salt of the acinitro compound to separate out. The reaction mixture was then cooled to 0°C, and after 15–20 minutes was the salt collected with suction, washed with methanol and ether, and at 0°C transferred with stirring into a solution of 2 g of urea in dilute acetic acid covered with half of its volume of ether. After 15 minutes was the ethereal layer separated and the aqueous layer was twice extracted with ether. The combined extracts were washed with sodium hydrogen carbonate solution and water and then dried over magnesium sulphate. Evaporation of the solvent afforded crude 2-nitro-2-phenylethanol in 80% yield; m.p. 75–76°C (ether-light petroleum). A mixture of 2-nitro-2-phenylethanol (5 g; 0.03 mol) and benzoyl chloride (6 ml) in benzene (20 ml) was refluxed for two hours. On cooling crystallised 6 g of the benzoate; m.p. 81–81.5°C (benzene). The mother liquors gave further 1.5 g of the pure substance. For C₁₅H₁₃NO₄ (271.2) calculated: 66.4% C, 4.8% H, 5.15% N; found: 66.15% C, 4.85% H, 5.35% N. 1-Benzoyloxy-2-nitro-2-phenylethane (4.5 g; 0.016 mol) was heated under nitrogen in a vacuum distilling apparatus. At 180–190°C (bath temperature) started the substance to pyrolyse, and from the mixture distilled the olefine IV together with benzoic acid. After the pyrolysis had finished, the apparatus was washed with ether, and the ethereal solution was shaken with sodium hydrogen carbonate solution and dried with magnesium sulphate. Then was the solvent evaporated under reduced pressure and product IV distilled under nitrogen; b.p. 81–82°C/1.5 Torr, yield 2.0 g (85%), n_D^{20} 1.5735. For C₈H₇NO₂ (149.1) calculated: 64.5% C, 4.7% H, 9.4% N; found: 64.2% C, 5.1% H, 9.6% N. NMR spectrum: 3.6 τ (H *cis* to NO₂); 4.22 τ (H *trans* to NO₂); 2.61 τ (H of Ar). 1-Nitro-1-phenylethylene, a yellow liquid which in light turns greenish, becomes on standing a dark brown glassy mass. With hydroquinone stabilised solutions of this compound in tetrahydrofuran, stored in the dark, do not change their concentrations at room temperature over a period of several days and at –20°C over a number of weeks.

Kinetic Measurements

Into a 5–10 ml flask fused-on to a reflux condenser was pipetted a solution (3–5 ml) of the nitro-olefine in tetrahydrofuran. The flask was immersed in a thermostated bath and after 30 minutes the reaction was started by adding a solution of triethylamine in tetrahydrofuran. In certain time intervals were by means of a micropipette withdrawn samples (c. 50 μ l) into small flasks which contained solid oxalic acid corresponding twice to three times the amount required for neutralisation the triethylamine content of the samples. The samples were then analysed by gas chromatography.

Gas chromatography: The analysis of the products as well as the determination of their purity were performed by gas chromatography on a Chrom 2 apparatus (Laboratorní přístroje, Prague) fitted with flame-ionisation detector. As stationary phase for separating the 3-methylnitrobutenes was used 30% diethylene glycol succinate and for separating the nitrostyrenes 20% Apiezon L on Chromosorb W. The other conditions are identical with those in the previous paper¹.

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