

Reductive cyclization of *o*-nitroazo compounds

M. POTÁČEK and K. PICKA

*Department of Organic Chemistry, Faculty of Natural Sciences,
J. E. Purkyně University, 611 37 Brno*

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It has been confirmed that the intermediates in the reduction of 2,4-dinitroazobenzene with hydrazine to give 6-nitro-2-phenylbenzotriazole are 2,4-dinitrohydrazobenzene and its cyclization product, 6-nitro-2-phenylbenzotriazole-1-oxide. The cyclization reaction follows first-order kinetics with respect to 2,4-dinitrohydrazobenzene. The reaction rate depends on pH, the rate constant being in the range of pH 6.5—9.5 proportional linearly to the concentration of hydroxyl anions.

Было изучено восстановление 2,4-динитроазобензола гидразином до 6-нитро-2-фенилбензотриазола и было доказано, что оно протекает через образование таких промежуточных продуктов, как 2,4-динитрогидразобензол и, образующийся из него закрытием цикла, 6-нитро-2-фенилбензотриазол-1-оксид. Указанная циклизация описывается кинетическим уравнением первого порядка по отношению к 2,4-динитрогидразобензолу, ее скорость зависит от pH среды и в области pH 6,5—9,5 ее константа скорости линейно зависит от концентрации анионов гидроксила.

Several 2-(2-hydroxyphenyl)benzotriazole derivatives have already been prepared in this laboratory [1, 2]. Substances of this class are prepared most frequently by oxidative cyclization of *o*-aminoazo compounds [3, 4] or by reduction of *o*-nitroazo compounds with various reduction agents [5—7].

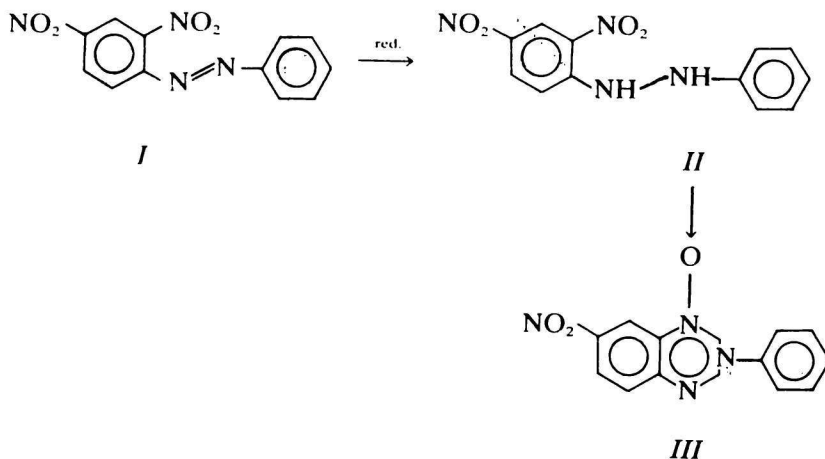
We have been interested mainly in 2-(2-hydroxyphenyl)benzotriazoles which, due to their favourable absorption properties in the u.v. region, are good plastics-stabilizers. The substances can be obtained from readily accessible 2-hydroxy-2'-nitroazobenzenes by reductive cyclization. The course of the reduction has not been fully understood and, thus, the objective of the present work was to clarify and explain the reaction pathway.

Previous studies on the polarographical reduction of 4-X-2-nitro-2'-hydroxy-5'-methylazobenzenes [8] showed that in the pH range 3—12 the reduction of the azo group of the substances was a 2-electron process occurring at a lower negative potential than that at which the reduction of the nitro group occurs.

Our new experiments in the field of electrochemical reduction of 2-hydroxy-5-methyl-2'-nitroazobenzene on a mercury cathode at a potential equal to the half-wave potential of the reduction of the azo group of the molecule have shown that, again, this was a two-electron process. The presence of 2-(2-hydroxy-5-methylphenyl)benzotriazole-1-oxide in the reaction mixture as an inter-

mediate of the process was proved by spectrophotometry. These results indicated that the chemical cyclization may occur in a similar manner, *i.e.* the intermediate of the cyclization may be an *o*-nitrohydrazo compound. It was important now to choose a suitable *o*-nitroazo compound the reduction of which would give a relatively stable *o*-nitrohydrazo compound. The latter substance should then be only slowly converted to 2-phenylbenzotriazole-1-oxide, thus making possible to prove its role as an intermediate in the reaction by spectral methods. The choice of a particular reduction agent was also important as this should be sufficiently stable and should not interfere with the determination of the expected products. 2,4-Dinitroazobenzene (*I*) and 2,4-dinitrohydrazobenzene (*II*) as the substrates and hydrazine as the reduction agent fulfil the above-mentioned requirements.

The reductive cyclization of *I* with hydrazine in ethanol at room temperature was monitored by spectrophotometry. The spectrum showed the presence of a band corresponding to *II* which was subsequently converted to 6-nitro-2-phenylbenzotriazole-1-oxide (*III*) (Scheme 1)



Scheme 1

The reaction of *II* to *III* was pH-dependent, *e.g.* at pH 10 the cyclization was so fast that in monitoring the conversion of *I* to *III* the presence of *II* in the reaction medium could not be detected. The reductive properties of hydrazine are known to be pH-dependent.

We have found that the hydrazine-induced reductive cyclization of *I* proceeds through the intermediate *II*. The conversion of the latter compound to *III* follows first-order kinetics with respect to the starting substance, the rate constant of the process being, in the pH range 6.5–9.5, a linear function of the concentration of hydroxyl anions (the dependence of the logarithm of the rate constant on pH is a straight line with the slope equal to 1 (Fig. 1)). At pH > 10 the reaction is very fast, almost instantaneous; above pH 12 a different, not identified product is formed.

Experimental

Compounds I—IV were prepared as described (Table 1) and their purity was checked by thin-layer chromatography on silica gel.

The electronic spectra (Table 1) were measured at 25°C in aqueous 40% propanol. The cyclization was monitored at the same temperature using a Unicam SP 1800 spectrophotometer equipped with an SP 874 cell thermostat. The concentration of the hydrazo compound was 7×10^{-5} M. The pH in the range 2—12 was adjusted using a universal buffer according to Davies [9] and measured with a Radelkis OP-205 pH-meter.

The monitoring of the cyclization of compound II was based on the increase of the absorbancy at 294 nm corresponding to III (Fig. 2).

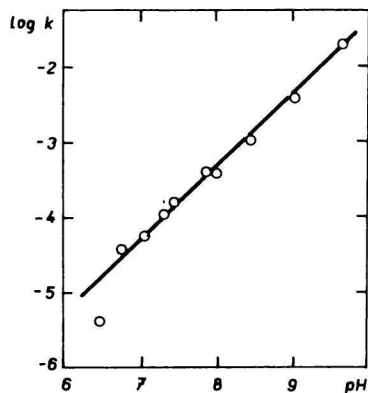


Fig. 1. Rate constant vs. pH in the cyclization of 2,4-dinitrohydrazobenzene.

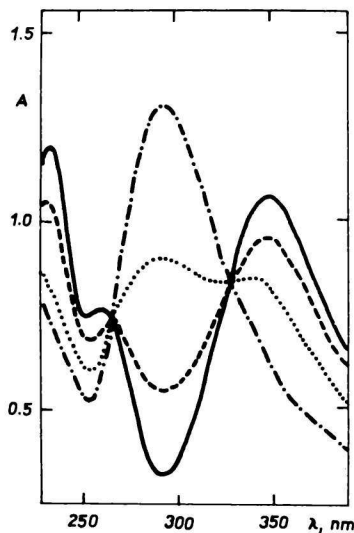


Fig. Cyclization of 2,4-dinitrohydrazobenzene at pH 7.40, $t = 25^\circ\text{C}$, $c_{01} = 6.88 \times 10^{-5}$ M. — $t = 2$ min; - - - $t = 30$ min; ···· $t = 90$ min; - · - · $t = 360$ min.

From

$$A = A_1 + A_2 = \epsilon_1 c_1 + \epsilon_2 c_2,$$

$$c_1 + c_2 = c_{01},$$

where A is the absorbancy, c_1 and c_2 are the instantaneous concentrations of the hydrazo compound and of the oxide, respectively, c_{01} is the starting concentration of the hydrazo compound and ϵ is the molar extinction coefficient, it follows

$$c_1 = \frac{c_{01} \epsilon_2 - A}{\epsilon_2 - \epsilon_1}$$

The rate constants were calculated from the first-order kinetic equation

Table 1

Physicochemical characteristics of the compounds under investigation

Compound	Ref.	Melting point		Crystal- lized from	Ultraviolet data					
		Ref.	Found		λ_{\max} nm	$\epsilon \cdot 10^{-3}$	λ_{\max} nm	$\epsilon \cdot 10^{-3}$	λ_{\max} nm	10^{-3}
<i>I</i> 2,4-Dinitroazobenzene	[10]	116—117	118—119	ethanol	336	1.76				
<i>II</i> 2,4-Dinitrohydrazobenzene	[10]	120	119—120	ethanol	231	1.82	262	1.05	349	1.46
<i>III</i> 6-Nitro-2-phenylbenzo- triazole-1-oxide	[11, 12]	175	178—180	ethyl acetate	294	1.92	370	0.60		
<i>IV</i> 6-Nitro-2-phenylbenzotriazole	[13]	178	176—177	ethyl acetate	207	1.64	268	1.62	327	2.11

$$\log \frac{\varepsilon_2 c_{01} - A}{(\varepsilon_2 - \varepsilon_1) c_{01}} = -\frac{k}{2.303} t$$

by the least square method (Table 2).

Table 2

Kinetic data of cyclization of 2,4-dinitrohydrazobenzene at different pH

pH	k s ⁻¹	τ s
6.43	3.90×10^{-6}	1.78×10^5
6.72	3.45×10^{-7}	2.00×10^4
7.05	5.42×10^{-5}	1.28×10^4
7.28	1.10×10^{-4}	6.30×10^3
7.40	1.63×10^{-4}	4.25×10^3
7.84	3.99×10^{-4}	1.74×10^3
7.96	3.96×10^{-4}	1.75×10^3
8.41	1.09×10^{-3}	6.36×10^2
9.00	3.88×10^{-3}	1.79×10^2
9.64	1.99×10^{-2}	3.48×10

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