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ELECTROCHEMICAL REDUCTION OF N-VINYLAZOLES

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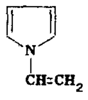
UDC 543.253:547.77'791'792'796

Classical polarography in aprotic solvents was used to study the reduction of N-vinyl derivatives of pyrazole, imidazole, 1,2,3- and 1,2,4-triazoles, and tetrazole. The N-vinylazoles studied were reduced in acetonitrile by a one-electron mechanism with subsequent dimerization of the radical-anions formed. The N-vinyl derivatives of pyrazole, imidazole and tetrazole were reduced analogously in DMF, while N-vinyltriazoles in DMF are reduced by a mixed mechanism with predominant two-electron transfer. Possible schemes for the electrochemical reduction of N-vinylazoles are discussed.

The study of the electrochemical initiation of the polymerization of vinyl monomers requires knowledge of the primary electrochemical steps. The reduction of the vinyl group in styrene and methyl methacrylate in DMF has been shown to occur by different mechanisms [1-3]. Styrene is reduced in a single two-electron step, initiating polymerization by dianions [1, 2], while methyl methacrylate accepts one electron under the same conditions followed by radical-anion recombination [2, 3]. N-Vinylcarbazole under analogous conditions gives one two-electron wave on the polarogram [4]. However, the nature of the solvent plays a role in the reduction of N-vinyl-1,2,4-triazole [5]. The reduction in DMF proceeds in a single two-electron step, while the depolarizer accepts only one electron in acetonitrile [5, 6]. Thus, the electrochemical reduction of even the same type of vinyl monomers may proceed by different pathways.

In order to elucidate the common features and differences in the behavior of N-vinylazoles, we studied the electrochemical reduction of N-vinyl derivatives of pyrazole, imidazole, 1,2,3- and 1,2,4-triazoles and tetrazole (II-IX) in aprotic solvents. For comparison, we investigated N-vinylpyrrole I, tetrazole X and 5-vinyltetrazole XI. In order to exclude the effect of impurities and water, the starting compounds and the solvents were subjected to careful purification.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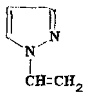
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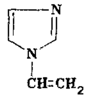
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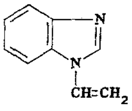
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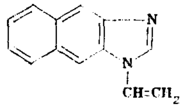
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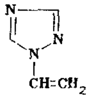
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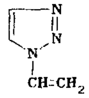
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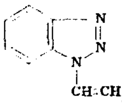
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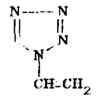
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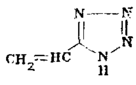
XI

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 315-319, March, 1986. Original article submitted January 16, 1985.

0009-3122/86/2203-0253$12.50

TABLE 1. Polarographic Characteristics and Diffusion Coefficients of N-Vinylazoles

Compound	Solvent[a]	$D\cdot10^6$, cm^2/sec	$E_{1/2}$, V	i, μA	n^b	n^c
I	DMF	8,39	3,(1)	2,6	1,01	0,99
II	DMF	8,31	3,(0)	2,8	1,09	1,07
III	DMF	8,16	3,(0)	2,4	0,93	0,92
IV	DMF	7,51	2,77	3,00	1,17	1,20
	Acetonitrile	17,10	2,89	3,54	0,92	0,94
V	DMF	—	2,35	2,54	0,99	—
	Acetonitrile	—	2,45	3,33	0,93	—
VI	DMF	8,42	2,75	4,40	1,71	1,67
	Acetonitrile	18,90	2,90	3,70	0,96	0,93
VII	DMF	8,40	2,71	4,31	1,68	1,63
VIII	DMF	7,56	2,10	4,40	1,71	1,77
	Acetonitrile	17,20	2,34	4,49	1,16	1,19
IX	DMF	8,66	2,52	3,12	1,21	1,16
X[d]	DMF	—	2,24	—	1,00	—
XI[d]	DMF	—	2,07	—	1,00	—

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[a] 1 mmole/liter vinylazole concentration, 20°C. [b] Calculated relative to the first nitrobenzene wave. [c] Calculated according to the Ilkovic equation. [d] Data from our previous work [8].

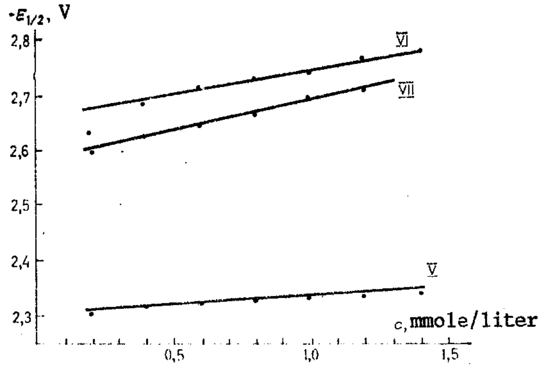


Fig. 1. Dependence of the halfwave potentials of V-VII on the depolarizer concentration (c) in DMF.

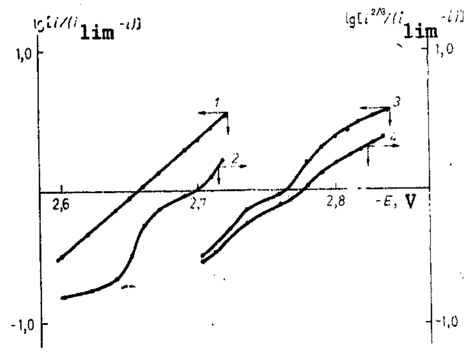


Fig. 2. Graphic analysis of the polarogram of triazole VI in DMF. Concentrations: 1, 2) 0.5 mmole/liter, 3, 4) 3 mmole/liter.

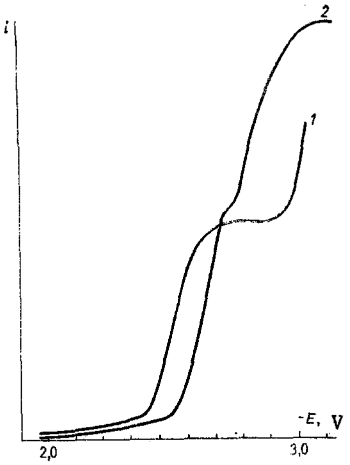


Fig. 3

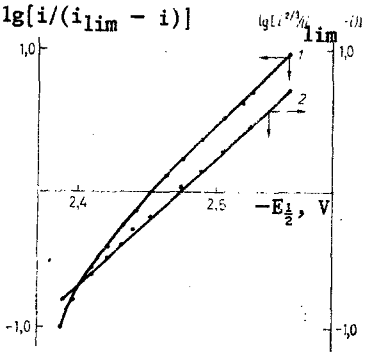


Fig. 4

Fig. 3. Polarograms of imidazole V in acetonitrile: 1) c 0.9 mmole/liter, 2) 5 mmoles/liter. Instrumental sensitivity was 20 and 50 μA, respectively.

Graphic analysis of the polarograms of imidazole V in acetonitrile (c 0.2 mmole/liter).

We should note that pyrazole, imidazole, 1,2,3-triazole and 1,2,4-triazole and polarographically inactive, while tetrazole X, which has four ring nitrogen atoms, is reduced somewhat more readily than its N-vinyl derivative IX (Table 1). All the compounds studied I-IX give one reduction wave in their polarograms at rather large negative potential values (Table 1). The halfwave potentials are shifted toward positive values with increasing number of nitrogen atoms in the five-membered ring. The introduction of phenylene fragments also causes an anodic shift of the potentials on the order of from 0.2 to 0.6 V. The halfwave potentials in acetonitrile are shifted toward cathodic values relative to DMF by an average 0.2 V. Thus, in acetonitrile, only those vinylazoles, in which the number of nitrogen atoms or sum of the nitrogen atoms and phenylene systems is at least three (IV-IX), are polarographically active.

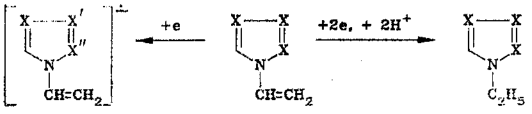
For depolarizer concentrations from 0.2 to 2 mmoles/liter, the wave height is linearly dependent on the concentration. The slope of the logarithmic dependence of the current on the mercury column height is 0.5, while the temperature coefficient is 2.2% per degree, which indicates the diffusional nature of the process. However, the reduction in DMF is irreversible since the slope determined for the dependence of log $[i/(i_{lim} - i)]$ on the potential E is 90-160 mV. The wave irreversibility is also indicated by the cathodic shift in the $E_{1/2}$ values with increasing depolarizer concentration (Fig. 1) [7]. In this case, we should stress that while the halfwave potential shift for 1-vinylnaphtho[2,3-d]imidazole (V) is insignificant, it is 145 mV for 1-vinyl-1,2,4-triazole (VI) and 1-vinyl-1,2,3-triazole (VII). At depolarizer concentrations above 2 mmole/liter, the polarograms do not give linear Heyrovsky-Ilkovic or Koutecki—Hanusch plots (Fig. 2). At even higher concentrations of the depolarizer, a clear doubling of the reduction wave is observed in the polarograms (Fig. 3).

Hence, N-vinylazoles have a tendency to adsorb on the cathode. In particular, at low depolarizer concentrations, the values for the diffusional current activation $[\Delta \log i/\Delta (i/T)]\cdot 19.3$ (on the order of 10 kJ) is in the range between 7.14 and 11.34 kJ, i.e., the limiting currents are determined only by diffusion. On the other hand, in the case of depolarizer concentrations about 2 mmole/liter, the activation energies determined from analogous relationships are approximately 5 kJ, which indicates the superposition of adsorption effects [9]. Thus, all the major measurements were carried out for depolarizer concentrations not exceeding 1 mmole/liter.

The number of electrons determining the limiting current were calculated using the Ilkovic equation and the diffusion coefficients and by comparison with freshly purified nitrobenzene as a standard. The results obtained are given in Table 1. In DMF, I-V and IX are reduced by a one-electron mechanism. Upon the addition of a proton donor (phenol), a virtual doubling of the limiting current is noted. The wave height for VI-VIII in DMF corresponds to the transfer of more than one electron and falls short of the two-electron level by only 20-30% (Table 1). A two-electron wave is found upon the addition of phenol.

In acetonitrile, IV-VI and VIII accept one electron upon reduction (Table 1) while the reduction in the presence of phenol proceeds by a two-electron mechanism.

These results indicate the following conclusions. N-Vinylazoles are reduced under classical polarography conditions by a one-electron mechanism to radical-anions. Linearization of the curve in a plot of $\log[i^{2/3}/(i_{lim} - i)]$ vs E for the one-electron waves obtained in acetonitrile at low depolarizer concentrations (Fig. 4) indicates possible fast bimolecular reactions of the primary radical-anions, which accounts for the irreversibility of the reduction process and the absence of a radical-anion signal in the ESR spectra. The reduction in the presence of proton donors proceeds by a two-electron mechanism related to protonation of the radical-anions and subsequent reduction of the vinyl group to give saturation of the double bond by analogy to the reduction in aqueous media [6].



X=C or N

In DMF, the compounds studied are reduced either by a one-electron mechanism (I-V, IX) or by a mixed mechanism (VI-VIII), when some of the molecules accept one electron, while the remainder are reduced to dianions without intermediate protonation of the radical-anions. This may be used to explain the finding that the number of electrons transferred to the molecule upon the reduction of the compounds is 1.7-1.8. Since the reduction of all the N-vinylpyrazoles was carried out under identical conditions, these data may serve to indicate that the electrochemical reduction in DMF proceeds without the participation of protons. Furthermore, tetrazole X and C-Vinyltetrazole XI are reduced by a one-electron mechanism under the same conditions in DMF.

The proposed mixed reduction mechanism is apparently characteristic only for N-vinyltriazoles in DMF. A simple calculation shows that, in this case, 7-8 of 10 depolarizer molecules are reduced to dianions and only 2-3 are reduced to radical-anions which undergo subsequent chemical reactions. However, a shift in the reduction mechanism is also characteristic for N-vinyltriazoles in the presence of phenol.

EXPERIMENTAL

All the compounds studied were obtained by reported procedures and their physical indices corresponded to literature values [10-16]. A sample of 1-vinylpyrrole (I) was kindly supplied by Dr. A. I. Mikhaleva. These samples were purified immediately before use. The solvents were purified by modifications of the methods reported by Mann [17].

The polarograms were taken on an OH-105 polarograph manufactured in Hungary and by an LP-7 polarograph manufactured in Czechoslovakia using 0.1 mole/liter tetrabutylammonium perchlorate as the base electrolyte relative to the saturated calomel electrode. The reduction was carried out on a dropping mercury electrode with an ordinary capillary (m = 1.47 mg/sec, t = 4.47 sec) and with induced dropping (m = 2.6 mg/sec, t = 0.25 sec). The working depolarizer concentrations were in the range from 0.2 to 1.4 mmole/liter. The temperature measurements were carried out in the range from 12 to 35°C. Freshly-distilled nitrobenzene was used as the standard.

The diffusion coefficients were calculated using the Stokes—Einstein equation:

$$D = \frac{2.96 \cdot 10^{-7} \rho^{1/3}}{\eta \cdot M^{1/3}}.$$

The value $\rho^{20} = 1.0857$ for 1-vinyl-1,2,4-triazole was determined pycnometrically. The ρ values for the other compounds were taken from the literature [10, 11, 14, 15, 18-20].

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STUDIES OF 1-AZABICYCLICS.

23.* NITRATION OF 1,2-DIHYDROPYRROLIZINE AND ITS HOMOLOGS

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UDC 547.759:542.958.1:541.621:543.422

Nitration of 1,2-dihydropyrrolizine and its homologs with a mixture of nitric acid and acetic anhydride has been shown to give a mixture of 5-, 6-, and 7-nitro-1,2-dihydropyrrolizines. The distribution of isomers with respect to the position of alkyl substituents in the nonaromatic portion of the bicyclic is discussed.

Within the pyrrole series, the nitration of pyrrole, its homologs, and various derivatives has been extensively studied [2-7]. 1,2-Dihydropyrrolizines are cyclic analogs of 1,2-dialkylpyrroles, and, in this regard, it would be interesting to study the behavior of compounds I-V in nitration reactions. We therefore decided, first of all, to determine the isomeric distribution of mononitro-substituted 1,2-dihydropyrrolizines and homologs among the nitration products; this knowledge is a prerequisite for a more general investigation of the effects of structural factors on the positional selectivity of the reaction.

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*For Communication 22, see [1].

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 320-324, March, 1986. Original article submitted Feburary 18, 1985.

0009-3122/86/2203-0257$12.50