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Electrochemical synthesis of pentamethylenediazirine*

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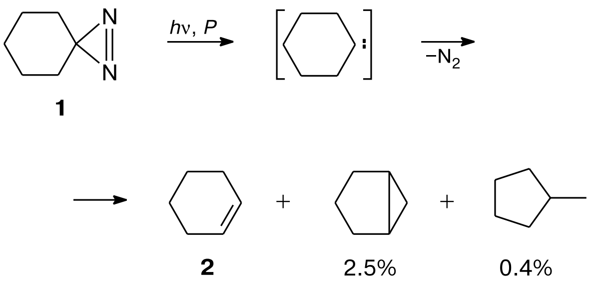
Electrochemical synthesis of pentamethylenediazirine at the Pt/Ti anode was conducted. The reaction is reversible. The rate constants of the direct and reverse processes were estimated. The product and current yields of the target compound approach to 100%.

Key words: pentamethylenediazirine, pentamethylenediaziridine, electrochemical synthesis.

Diazirines are efficient sources of carbenes.[1] For instance, photolysis of pentamethylenediazirine **1** under high pressure affords cyclohexene **2** in high yield (Scheme 1).[2]

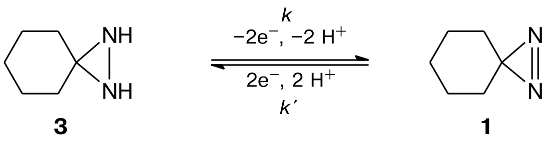
Scheme 1



Usual methods for the synthesis of diazirines are the oxidation of the corresponding diaziridines with mercury oxide, bichromate, silver oxide, and others.

In the present work, compound **1** was synthesized by the electrochemical oxidation of pentamethylenediaziridine **3** (Scheme 2).[3,4]

Scheme 2



The oxidation products of compound **3** in an undivided cell using the Pt/Ti anode were analyzed by ^{1}H, ^{13}C NMR and UV spectroscopy. The analysis showed that the oxidation of compound **3** affords up to 50% of compound **1** without formation of by-products. The UV spectra of the electrolyte containing a mixture of compounds **1** and **3** coincided with the published[5] spectra of compound **1**. The UV spectra of a solution of compound **3** oxidized in an undivided cell upon passing different amounts of electricity are shown in Fig. 1. When the content of compound **1** increases monotonically, the content of compound **3** decreases, correspondingly, to some limiting value (Fig. 2) equal approximately to 50%, which can be due to reversibility of the process in an undivided cell. This conclusion was completely confirmed by the electrolysis of the initial compound in a diaphragm-divided cell loaded with a mixture of equal amounts of compounds **1** and **3**. In the presence of a diaphragm, the initial substrate in this mixture can be oxidized with almost 100% conversion, *i.e.*, until the initial substrate disappeared completely (Fig. 3).

Using the data presented in Fig. 3, we estimated the rate constant of substrate oxidation in the direct pathway (k) by the first-order equation

$$C_t/C_0 = \exp(-kt), \qquad (1)$$

where C_0 and C_t are the initial concentration of compound **3** and its concentration to the moment t. The k value was 0.12 h^{-1}. The curve for the consumption of compound **3** calculated by the first-order equation with $k = 0.12$ h^{-1} is shown in Fig. 3. Since in the absence of a diaphragm and in equilibrium the contents of the initial

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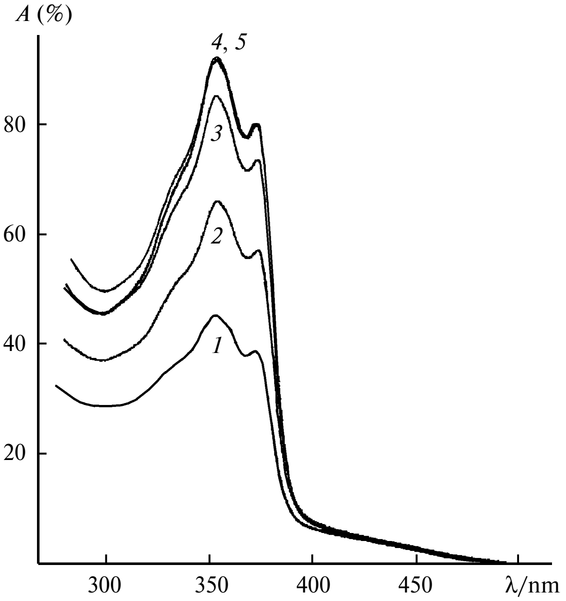

Fig. 1. Change in the UV spectra of pentamethylenediaziridine with the electrolysis time. The amount of electricity passed through an undivided cell: 0.6 (*1*), 0.9 (*2*), 1.2 (*3*), 1.5 (*4*), and 1.8 kC (*5*).

substrate and reaction product are equal, the equilibrium constant should be equal to 1, *i.e.*, the rate constant of the reverse reaction k' should be equal to the rate constant of the direct reaction k.

Using the values of rate constants for the direct and reverse reactions, we calculated the curve of accumulation of compound **1** in the absence of a diaphragm. In this case, the overall process is described by a system of differential equations

$$\begin{cases} dC_1/dt = -kC_1 + k'C_2, \\ dC_2/dt = kC_1 - k'C_2, \end{cases} \qquad (2)$$

where C_1 and C_2 are the concentrations of the initial substrate and reaction products, respectively. The k and k' values for an undivided cell were calculated from the constant values obtained for a divided cell taking into account that the current density in an undivided cell is by 2.5 times higher than that in a divided cell. Therefore, for an undivided cell the k and k' values were accepted to be $2.5k$ or 0.3 h^{-1}. In this case, the calculated data agree with the experimental results.

The current yields (J) of compound **1** for the both types of cells were calculated by the formula

$$J = 2nyF/100\% \cdot It,$$

where y is the conversion of the initial compound, F is the amount of passed electricity, n is the number of moles of the initial substrate, t is the time of achievement of the y conversion, and I is the total current. The current yield

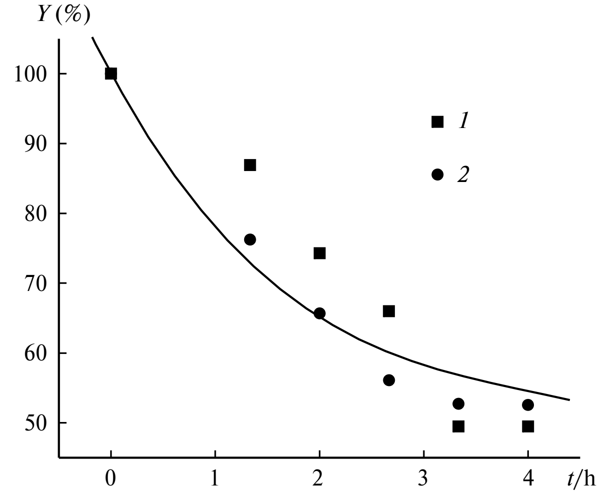

Fig. 2. Dependence of the content of compound **3** on the electrolysis time for an undivided cell according to the data of UV spectroscopy (*1*) and iodometry (*2*). Solid line is theoretical.

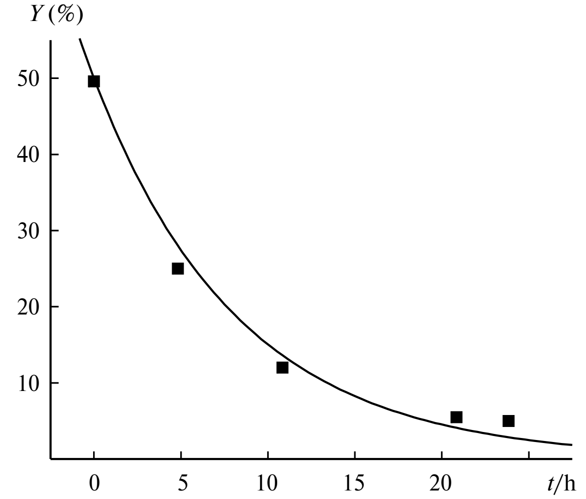

Fig. 3. Dependence of the content of compound **3** on the electrolysis time according to the iodometry data for a divided cell. Solid line is the calculation of the content of compound **3** by the first-order equation.

decreases with an increase in the conversion, although it remains at a rather high level (Fig. 4).

Potentiometric studies of a working solution of compound **1** in the background electrolyte at the platinum microelectrodes showed that in the whole potential region (from hydrogen evolution at the cathode to oxygen evolution at the anode) the I,E curves in the initial solution virtually coincide with the curves recorded in the background solution. This implies that the oxidation of compound **3** occurs in a region of higher anodic potentials (simultaneously with oxygen evolution) or it is a secondary process, for instance, chemical oxidation involving oxygen evolved at the anode.

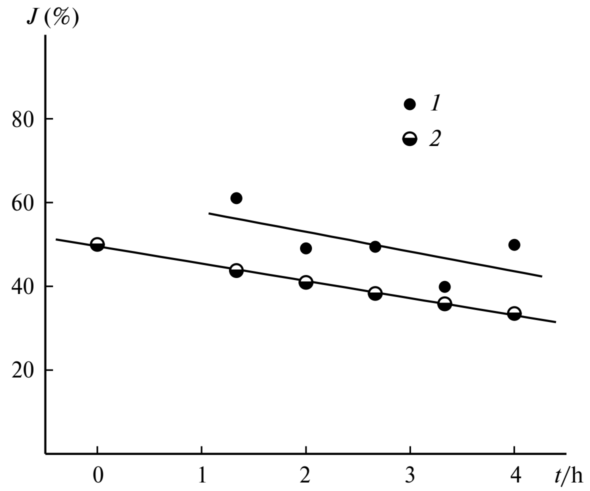

Fig. 4. Change in the current yield (*J*) of compound **1** during electrolysis of compound **3** for an undivided cell according to the data of iodometry (*1*) and UV spectroscopy (*2*).

Thus, the results obtained indicate that the electrochemical synthesis of compound **1** from **3** can be carried out easily and with high current yield using platinated titanium.

Experimental

^{1}H NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker DRX-500 (500 MHz) spectrometers. ^{13}C NMR spectra were obtained on Bruker AM-300 (75.5 MHz) and Bruker DRX-500 (125 MHz) spectrometers relative to the signal of Me_4Si,

The initial pentamethylenediaziridine **3** was synthesized according to a previously described procedure**[6]** and additionally characterized by the ^{1}H and ^{13}C NMR spectra, which coincided with the published[7] spectra. The melting point of compound **3** (103 °C) coincided with that given in Ref. 6. ^{13}C NMR without proton decoupling ($CDCl_3$), δ: 24.4 (t, C(3), C(5), ^1J = 129.4 Hz); 24.6 (t, C(4), ^1J = 129.3 Hz); 35.7 (t, C(2), C(6), ^1J = 128.0 Hz); 56.9 (s, C(1), ^2J = 5.1 Hz).

A 1% solution of compound **3** in a background 0.1 *N* solution of K_2CO_3 in an aqueous-ethanol (1 : 1) mixture was subjected to electrolysis. Electrolysis was carried out in cells with both divided anodic and cathodic spaces and without a diaphragm. In the both cases, perforated platinated titanium with a thickness of the platinum galvanic coating of 5 μm was used as the anode and the cathode was titanium. Electrolysis was performed in the galvanostatic regime using a PI-50 potentiostat. The current density based on the surface of the anodes and electrolyte volume for an undivided cell was 1.25 A dm^{-2} and 1.0 A dm^{-3}, respectively; that for a divided cell was 0.5 A dm^{-2} and 0.35 A dm^{-3}, respectively. The process was conducted at a constant current. The composition of the products was determined by ^{1}H and ^{13}C NMR. The reaction course was monitored using two methods: iodometry and UV spectroscopy. The content of compound **1** in the electrolyte was determined by UV spectroscopy using a Specord-40 instrument from the absorption of the solution at the wavelength 352 nm. Iodometric analysis of the content of compound **3** was the same as in Ref. 5.

To determine the composition of the electrolysis products of compound **3** performed in cells of both types, the reaction mixture was saturated with K_2CO_3 and extracted with Et_2O (3×50 mL). The extract was dried over K_2CO_3, the solvent was distilled off under atmospheric pressure, and the residue was distilled collecting the fraction with b.p. 30—35 °C (30 Torr). The product was obtained in 49.8% yield (0.98 g, 8.9 mmol). (The boiling point, n_d^{20}, and elemental analysis of the obtained sample coincided with the characteristics published**[6]** for compound **1**.) ^{1}H NMR of compound **1** ($CDCl_3$), δ: 1.14 (m, 4 H, 2 HC(2), 2 HC(6)); 1.55 (m, 2 H, 2 HC(4)); 1.68 (m, 4 H, 2 HC(3), 2 HC(5)). ^{13}C NMR ($CDCl_3$), δ: 24.5 (t, C(3), C(5), ^1J = 128.0 Hz); 25.3 (t, C(4), ^1J = 127.0 Hz); 28.2 (s, C(1)); 31.7 (t, C(2), C(6), ^1J = 129.0 Hz). Diazirine **1** was additionally characterized by the HSQC-qs and HMBC-qs methods. Correlation through the bond of the ^{1}H—^{13}C(3), ^{1}H—^{13}C(4), and ^{1}H—^{13}C(2) signals was observed in the 2D HSQC-qs spectrum. The 2D HMBC-qs spectrum exhibited signal correlation through the two bonds ^{1}H—C(2)—^{13}C(3), ^{1}H—C(3)—^{13}C(4), ^{1}H—C(3)—^{13}C(2), and ^{1}H—C(2)—^{13}C(1) and through three bonds ^{1}H—C(2)—C(3)—^{13}C(4), ^{1}H—C(3)—C(2)—^{13}C(1), and ^{1}H—C(4)—C(3)—^{13}C(2).

To elucidate the nature of electrodic processes leading to the oxidation of compound **3**, potentiometric studies at the Pt electrode with a diameter of 0.5 mm were carried out at a potential sweep of 20 and 50 mV s^{-1} using the silver oxide reference electrode.

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References

1. H. M. Frey, *Pure Appl. Chem.*, 1964, **9**, 572.
2. E. Schmitz, D. Habisch, and A. Stark, *Angew. Chem.*, 1963, **75**, 723.
3. E. A. Nizhnikovskiy, V. V. Kuznetsov, and N. N. Makhova, *Book Abstrs "ISE Spring Meeting 2006," Singapore, 17—20 April 2006*, Singapore, 2006, 210.
4. E. A. Nizhnikovskii, V. V. Kuznetsov, M. D. Vedenyapina, E. D. Strel´tsova, N. N. Makhova, and A. A. Vedenyapin, *Materialy Mezhdunarodnoi konf. "Organicheskaya khimiya ot Butlerova i Beil´shteina do sovremennosti"* [*Abstr. International Conf. "Organic Chemistry from Butlerov and Beilstein to the Present*], St. Petersburg, 2006, 208 (in Russian).
5. W. H. Graham, *J. Am. Chem. Soc.*, 1962, **84**, 1063; 1966, **88**, 4677.
6. E. Schmitz and R. Ohme, *Chem. Ber.*, 1961, **94**, 2166.
7. J. Hiroyuki. H. Kiyoto, S. Hiroyasu, J. Yoshio, and K. Tsumoto, *Helv. Chim. Acta*, 2002, **85**, 4272.
8. E. Schmitz, in *Advances in Heterocyclic Chemistry*, Ed. A. Katritzky, Academic Press, New York, 1963, **2**, 114.

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