reflexions with F ≥ 3σ (the high value of the divergence factor R was due to decomposition of the crystal during recording, the magnitudes of the standard reflexions decreasing by 50%). The crystals of the adduct (IIb) were rhombic: *a* 9,182 (4), b 25,220 (8), c 12,490 (6) Å, z = 8 (two independent molecules), space group $P2_12_12_1$. The final atom coordinates are given in Table 3. The 6-nitroazolo[1,5-*a*]pyrimidines (Ia-h) were obtained as described in [9].

6-Nitro-7-indolyl-4,7-dihydroazolo[1,5-*a*]pyrimidines (IIa-d, f-h), (IIIa,c,d,f-h), (IVe-g). The nitroazolo[1,5-*a*]pyrimidine (0.01 mole) was boiled with an equimolar amount of the indole in 10 ml of butanol for 15 min. The mixture was cooled, the solid filtered off, washed with 10 ml of ether, dried, and crystallized (Table 1).

LITERATURE CITED

1. V. L. Rusinov, T. L. Pilicheva, O. N. Chupakhin, N. A. Klyuev, and D. T. Allakhverdieva, Khim. Geterotsikl. Soedin., No. 5, 662 (1986).
2. Kh. Ya. Lopatinskaya, A. K. Sheinkman, T. V. Stupnikova, A. N. Krasovskii, and N. A. Klyuev, Khim. Geterotsikl. Soedin., No. 5, 675 (1979).
3. T. Kurihara and K. Nasu, Chem. Pharm. Bull, 29, 2520 (1981).
4. V. L. Rusinov, T. L. Pilicheva, and O. N. Chupakhin, Khim. Geterotsikl. Soedin., No. 9, 1267 (1985).
5. A. K. Sheinkman, Kh. Ya. Lopatinskaya, N. A. Klyuev, and Zh. K. Torosyan, Khim. Geterotsikl. Soedin., No. 2, 234 (1980).
6. V. L. Rusinov, A. Yu. Petrov, O. N. Chupakhin, N. A. Klyuev, and G. G. Aleksandrov, Khim. Geterotsikl. Soedin., No. 5, 682 (1985).
7. V. I. Vysotskii, R. A. Khmel'nitskii, and I. I. Grandberg, Izv. Timiryazevsk. Sk-h. Akad., No. 5, 221 (1970).
8. V. A. Zyryanov, N. A. Klyuev, V. L. Rusinov, A. B. Belikov, I. Ya. Postovskii, and L. F. Gusev, Khim. Geterotsikl. Soedin., No. 4, 558 (1980).
9. V. L. Rusinov, I. Ya. Postovskii, A. Yu. Petrov, E. O. Sidorov, and Yu. A. Azev, Khim. Geterotsikl. Soedin., No. 11, 1554 (1981).

POLAROGRAPHIC EXAMINATION OF 5-ARYL-2-(2-THIENYL)-OXAZOLES AND -1,3,4-OXADIAZOLES

L. D. Patsenker, V. K. Polyakov, A. P. Shkumat,
V. F. Lavrushin, and V. D. Bezuglyi

UDC 547.735'787.3'
793(543.253

The polarographic behavior of 5-aryl-2-(2-thienyl)oxazoles and -1,3,4-oxadiazoles has been studied.

The polarographic behavior of oxazoles and 1,3,4-oxadiazoles containing various aromatic substituents has been studied quite extensively [1-3]. However, no information on the electroreduction of compounds containing heterocyclic instead of aromatic radicals, particularly the thiophene ring, is available. It is known that in thiophene analogs [4] π-electron conjugation similar to that found in aromatic derivatives of oxazole and oxadiazole is present. It has been reported [2, 3] that oxadiazoles with various radicals in the 2- and 5-positions, in contrast to structurally similar oxazoles and oxadiazoles with the same substituents, are reduced with fission of the heterocycle at the —C—O— bond. It was of interest to discover whether this behavior extended to heterocyclically substituted oxadiazoles.

A. M. Gor'kii Khar'kov State University, Khar'kov 310077. Ukrainian Correspondence Polytechnic Institute, Khar'kov 310077. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1550-1552, November, 1986. Original article submitted August 2, 1985.

TABLE 1. Polarographic Properties of 5-Aryl-2-(2-thienyl)-oxazoles and -1,3,4-oxadiazoles

Comp. No.	Compound	Halfwave potentials, V
I	5-Phenyl-2-(2-thienyl)oxazole	−2,07; −2,27
II	5-(4-Tolyl)-2-(2-thienyl)oxazole	−2,09; −2,31
III	5-(4-Methoxyphenyl)-2-(2-thienyl)oxazole	−2,13; −2,36
IV	5-(4-Chlorophenyl)-2-(2-thienyl)oxazole	−1,73; −2,07; −2,29
V	5-(4-Bromophenyl)-2-(2-thienyl)oxazole	−1,73; −2,08; −2,30
VI	5-(4-Nitrophenyl)-2-(2-thienyl)oxazole	−0,93; −1,60; −1,98; −2,19; −2,47
VII	5-(4-Biphenyl)-2-(2-thienyl)oxazole	−2,00; −2,49
VIII	5-(2-Naphthyl)-2-(2-thienyl)oxazole	−1,58; −1,76; −2,08; −2,29
IX	5-(Phenyl-2-(2-thienyl)oxadiazole	−1,94; −2,20; −2,58
X	5-(4-Tolyl)-2-(2-thienyl)oxadiazole	−1,99; −2,24; −2,59
XI	5-(4-Methoxyphenyl)-2-(2-thienyl)oxadiazole	−2,00; −2,31
XII	5-(4-Aminophenyl)-2-(2-thienyl)oxadiazole	−2,08; −2,36
XIII	5-(4-Bromophenyl)-2-(2-thienyl)oxadiazole	−1,58; −1,94; −2,22; −2,59
XIV	5-(4-Nitrophenyl)-2-(2-thienyl)oxadiazole	−0,82; −1,44; −2,24
XV	2,5-Diphenyloxazole	−2,14; −2,50

With this purpose in mind, we have examined the electroreduction of 5-aryl-2-(2-thienyl)oxazoles and -1,3,4-oxadiazoles (I-XIV) at a dropping mercury electrode with tetramethylammonium iodide in DMF as base electrolyte. It was found that all these compounds are polarographically active, two or three waves being normally seen on the polarograms.

The polarogram of (I), like that of 2,5-diphenyloxazole under the same conditions, shows two one-electron waves. It is known that the reduction of oxazoles and oxadiazoles takes place for the most part at the —C=N— bond, followed by C=C and C—O in the C—O—C grouping [3]. It might be expected that in the case of (I), the first wave would be attributable to reduction of the C=N bond of the oxazole ring, and the second to reduction of the C=C bond in the same ring. Cleavage of the azole heterocycle with fission of the C—O bond and reduction of the thiophene ring were not observed up to −2.6 V.

On acidification of solutions of (I), the first halfwave potential was shifted to more positive values. This is due to the fact that reduction of (I) in acid media is facilitated by protonation of the molecule as a result of the free electron pair on the nitrogen atom.

The polarographic waves for (I) occur at higher potentials than for (XV). The 2-thienyl group normally exerts an electron-donor effect as compared with phenyl [5, pp. 115-116], and consequently should give rise to a reverse shift in the halfwave potentials. However, the deciding factor here is not, apparently, the donor ability of the thiophene ring, but its capacity to render the molecule more polarizable under the influence of the electrostatic field of the dropping mercury electrode. This results in a redistribution of electron density such as to facilitate reduction of the oxazole ring.

In the polarogram of the oxadiazole (IX), three electroreduction waves are seen. The first two one-electron waves are due to the reduction of the two C=N bonds in the azole heterocycle. The third wave is a three-electron wave associated with fission of the C—O bond and opening of the oxadiazole ring, in agreement with earlier reports [2, 3]. This wave is also present in the polarograms of (X) and (XIII). The absence of waves associated with opening of the oxadiazole ring in the case of compounds (XI) and (XII) is most likely due to the fact that they lie behind the reduction wave for the base electrolyte.

The oxadiazoles examined are more easily reduced than the analogous oxazoles. It is known that the first reduction potential is due to transfer of an electron from the cathode to the lower free molecular orbital (LFMO) [5, p. 91]. Quantum chemical calculations which we have carried out by the Pariser—Parr—Pople method (PPP) for 5-aryl-2-(2-thienyl)oxazoles and -1,3,4-oxadiazoles with various substituents in the para-position of the benzene ring have shown that the LFMO in oxadiazoles is lower than in the analogous oxazoles. For instance, in oxadiazoles (IX-XI) the values of the LFMO energies are −2.1150, −2.0167, and −2.0225 eV, whereas in the case of oxadiazoles (I-III) they are −2.0397, −1.9632, and −1.9682 eV. This explains the observation that electroreduction is easier in the first case than in the second.

Electron donor substituents such as methyl, methoxy, and amino [compounds (II), (III), and (X-XII)] result in a shift in the polarographic waves to more negative values, this shift being greater, the greater the electron donor effect of the substituent: $CH_3 < OCH_3 <$

NH_2. This is due to the increased electron density under the influence of these substituents at the electroactive regions of the molecule, which hinders the addition of an electron, and results in the observed shift in the halfwave potentials.

Quantum chemical calculations by the PPP method have shown that the LFMO in compounds containing donor substituents have higher energies than in the unsubstituted molecule, and consequently the reduction of depolarizers with electron density donors will be hindered.

In the polarograms of the halo-compounds (IV), (V), and (XIII), two-electron waves for cleavage of the halogen are seen before reduction of the oxazole or oxadiazole heterocycle, the other potentials having much the same values as in (I) and (IX).

In the case of the depolarizers (VI) and (XIV), a series of waves was obtained, corresponding to the multistage character of the reduction of the nitro-groups, which add electrons in the first instance.

Increasing the length of the conjugated chain as in the biphenylyl (VII) and 2-naphthyl (VIII) compounds results in a shift in the halfwave potentials to more positive values, i.e., it facilitates reduction. This is due both to delocalization of electron density as compared with (I), and to the increased ease of polarization of the molecule under the influence of the electrostatic field of the cathode. The biphenylyl radical causes a smaller shift in potential than the 2-naphthyl group, apparently as a result of slight nonplanarity in biphenyl with consequent interference with π-electron conjugation, whereas the 2-naphthyl group has a rigid structure. Two waves are seen in the polarogram of (VIII) for reduction of the 2-naphthyl group.

Regression analysis of compounds in which the halfwave potential of the first stage of reduction is associated with the electrochemical activity of the azole heterocycle has shown that the values of the potential correlate with the σ_n° constants of the substituents [6, pp. 321-323], conforming to the equations $E_{1/2}^1 = -2.042 + 0.539\sigma_n^\circ$ ($S_0 = 0.202$, $r = 0.910$) for oxazoles (I-III) and (VII), and $E_{1/2}^1 = -1.943 + 0.364\sigma_n^\circ$ ($S^\circ = 0.004$, $r = 0.999$) for oxadiazoles (IX-XII), where $E_{1/2}^1$ is the value of the halfwave potential for the first step in electroreduction, S_0 is the standard deviation of the experimental measurements from the regression line, and r is the correlation coefficient.

EXPERIMENTAL

The 5-aryl-2-(2-thienyl)oxazoles and -1,3,4-oxadiazoles were obtained as described in [4].

Polarography was carried out on an LP-60 automatic polarograph with a sensitivity of 3.57×10^{-11} A/mm. Reduction took place at a dropping mercury electrode in a Heyrovsky electrochemical cell with forced flushing with argon to remove oxygen. The solutions of oxazoles and oxadiazoles used were of concentration 1-3 mmole/liter. The base electrolyte was a solution of tetramethylammonium iodide in DMF (concentration 5×10^{-2} mole/liter). The capillary employed had the following characteristics: with a mercury column of height 50 cm, $m = 0.248$ mg/sec, $\tau = 3.6$ sec (at 2 V).

The number of electrons involved in the reduction of one molecule is given by the Ilkovic equation. The diffusion coefficient required was obtained by calculation from data for styrene in DMF ($D = 7.556 \times 10^{-6}$ cm^2/sec). The halfwave potentials were found with reference to the saturated calomel electrode.

The quantum chemical calculations were carried out as described in [7] using the parameters given in [8].

LITERATURE CITED

1. V. D. Bezuglyi and N. P. Shimanskaya, Zh. Obshch. Khim., 31, No. 10, 3160 (1961).
2. N. P. Shimanskaya and V. D. Bezuglyi, Zh. Obshch. Khim., 33, No. 6, 1726 (1963).
3. V. D. Bezuglyi, N. P. Shimanskaya, and E. M. Peresleni, Zh. Obshch. Khim., 34, 3540 (1964).
4. L. D. Patsenker, A. P. Shkumat, V. K. Polyakov, and V. F. Lavrushin. Dep. in UkrNIINTI, Reg. No. 854 Uk-85.
5. A. F. Pozharskii, Theoretical Fundamentals of Heterocyclic Chemistry [in Russian], Khimiya, Moscow (1985).

6. V. A. Palm, Fundamentals of the Quantitative Theory of Organic Reactions [in Russian], Khimiya, Moscow (1977).
7. G. I. Kagan, I. N. Fundyler, and G. M. Kagan, Teor. Éksp. Khim., 2, No. 5, 589 (1966).
8. R. Phan-Tan-Luu, L. Bouscasse, E. J. Vincent, and J. Metzger, Bull. Soc. Chim. Fr., No. 9, 3283 (1967).

CONVERSION OF 2-AMINO-5-R-PHENYL-1,3,4-OXADIAZOLES INTO 3-R-PHENYL-5-ALKOXY-1,2,4-TRIAZOLES

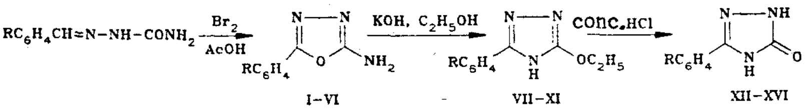
V. Ya. Alekseeva, Yu. A. Boitkov,
I. V. Viktorovskii, and K. A. V'yunov

UDC 547.792.7'793.4.04:
543.51

2-Amino-5-R-phenyl-1,3,4-oxadiazoles have been shown to isomerize in alcoholic potassium hydroxide solution to 3-R-phenyl-5-alkoxy-1,2,4-triazoles. The dissociative ionization of 3-R-phenyl-5-alkoxy-1,2,4-triazoles and 3-R-phenyl-1,2,4-triazolin-5-ones has been examined. The mass spectra of the oxadiazoles have been compared with those of the triazoles.

Some 1,3,4-oxadiazoles have been found to possess valuable biological properties [1]. It has previously been shown that 2-amino-1,3,4-oxadiazoles are converted into 1,2,4-triazoles on treatment with alcoholic potassium hydroxide [2].

The aim of this investigation was to study the isomerization of 2-amino-5-R-phenyl-1,3,4-oxadiazoles to 3-R-phenyl-5-ethoxy-1,2,4-triazoles, and to examine the dissociative ionization of 3-R-phenyl-5-ethoxy-1,2,4-triazoles and 3-R-phenyl-1,2,4-triazolin-5-ones under electron impact.



I, VII, XII R=H; II, VIII, XIII R=4-F; III, IX, XIV R=4-Cl; IV, X, XV R=4-Br, V R=4-NO_2; VI, XI, XVI R=4-CH_3O

Compounds (VII-XI) were obtained by the alcoholysis of 2-amino-5-R-phenyl-1,3,4-oxadiazoles in alcoholic potassium hydroxide at the boil for several hours. Subsequent acid hydrolysis with concentrated hydrochloric acid gave the triazolones (XII-XVI). Crystalline products were obtained (Table 1), the structures of which were confirmed by their elemental analyses, UV, IR, and mass spectra.

The UV spectra of the oxadiazoles (I-VI) were similar to those of known 2-amino-3-R-phenyl-1,3,4-oxadiazoles [3], absorption having a maximum at 270-280 nm and a minimum at 230 nm. In the spectra of the triazoles, the maximum underwent a hypsochromic shift at 250-260 nm.

In the IR spectra of the oxadiazoles, absorption was present corresponding to deformational (970 cm^{-1}) and stretching 1000 cm^{-1} vibrations of the —C—O—C— group. The strong doublet at 3450 cm^{-1} was due to stretching vibrations of the amino-group. The spectrum contained absorption for stretching vibrations of the C=N group at 1650 cm^{-1}. In the IR spectra of the 1,2,4-triazol-5-ones, a typical feature is carbonyl stretching absorption at 1750-1650 cm^{-1}.

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1553-1556, November, 1986. Original article submitted June 17, 1985.