REDOX PROPERTIES OF 2,4-DIARYL-SUBSTITUTED CYCLOHEXA[b]THIOPYRYLIUM SALTS

N. N. Ivanova, N. T. Berberova,
A. S. Archegova, E. S. Klivov,
A. V. Shpakov, O. Yu. Okhlobystin,
and S. K. Klimenko

A scheme for formation of 6,6′,7,7′-tetrahydro-2,2′,4,4′-tetraaryl-8,8′-bis(5H-1-benzothiopyranyls) through intermediate radicals and cation radicals was substantiated as a result of a study of the electrochemical behavior of 2,4-diarylcyclohexa[b]thiopyrylium tetrafluoroborates and 2,4-diaryl-4H-cyclohexa[b]thiopyrans and comparison with the results of their oxidative dimerization. The formation of 2,4-diaryl-cyclohexa[b]thiopyranyl radicals is also confirmed by EPR spectroscopy.

It has been previously shown [1] that 2-R-4-R′-cyclohexa[b]thiopyrylium tetrafluoroborates Ia-c are readily deprotonated under the influence of bases to give 2-R-4-R′-6,7-dihydro-5H-1-benzothiopyrans IIa-c with subsequent oxidation of the latter to 6,6′,7,7′-tetrahydro-2,2′-di-R-4,4′-di-R′-8,8′-bis(5H-1-benzothiopyranyls) IIIa-c. The oxidation possibly proceeds with the participation of radical and ion-radical particles that develop in intermediate steps [1].

Monocyclic heteroaromatic pyrylium and thiopyrylium cations are electrochemically reduced with the transfer of one electron and the formation of the corresponding radicals, which are capable of dimerization at the $C_{(4)}$ or $C_{(2)}$ and $C_{(6)}$ positions, depending on the degree of substitution [2, 3]. The electrochemical behavior of thiopyrylium salts with a condensed alicycle has not been studied. To ascertain the intermediate radicals and cation radicals in the course of the formation of dimers IIIa-c from tetrafluoroborates Ia-c we used cyclic voltammetry to study their electrochemical behavior on a platinum electrode.

Tetrafluoroborates Ia-c are capable of facile, reversible, one-electron reduction leading to stable cyclohexa[b]thiopyranyl radicals IVa-c (Table 1). A linear dependence of the maximum current on the square root of the potential-scanning rate is observed over the range from 0.5 to 50 V/sec; this constitutes evidence for the diffusion character of the reduction step.

The formation of radicals IVa-c is also evidently the first step in the reaction of salts Ia-c with bases. It is known [4, 5] that pyridine and the hydroxide anion can act as one-electron reducing agents and are capable of inducing the development of pyranyl radicals on reaction with aryl-substituted pyrylium perchlorates.

The preparative electrolysis of cation Ia at its reduction potential leads to anhydro base IIa, which is oxidized reversibly on the anode (E_{ap} = 0.234 V, E_{cp} = 0.157 V). Compound IIa is also formed when pyridine is added to the electrochemical cell containing cation Ia. The formation of anhydro base II in the electrolytic reduction of cation Ia and its subsequent oxidation to dimer IIIa are confirmed by the addition of genuine samples of IIa and IIIa to the electrochemical cell. Since the aryl substituents attached to the $C_{(2)}$ and $C_{(4)}$ atoms hinder the recombination of radicals IVa-c, the latter are stabilized by the ejection of a hydrogen atom from the $C_{(8)}$ position of the condensed alicycle. (See scheme in the middle of the next page.)

The Ia-c cations are capable of one-electron oxidation (see Table 1) leading to unstable dication radicals Va-c. The exhaustive electrolysis of the Ia cation at the oxidation potential in methylene chloride leads to dication VIa and then to dimer IIIa (E_{ap} = 0.21 V, E_{cp} = 0.12 V).

Dimers IIIa-c are readily oxidized on a platinum anode (Table 2). The oxidation process is reversible, and the limiting current corresponds to one electron, which indicates the formation of cation radicals VIIa-c.

N. G. Chernyshevskii Saratov State University, Saratov 410026. Scientific-Research Institute of the Chemistry of Free Radicals, K. L. Khetagurov North Ossetian State University, Vladikavkaz 362040. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 349-354, March, 1992. Original article submitted June 28, 1990; revision submitted January 29, 1991.

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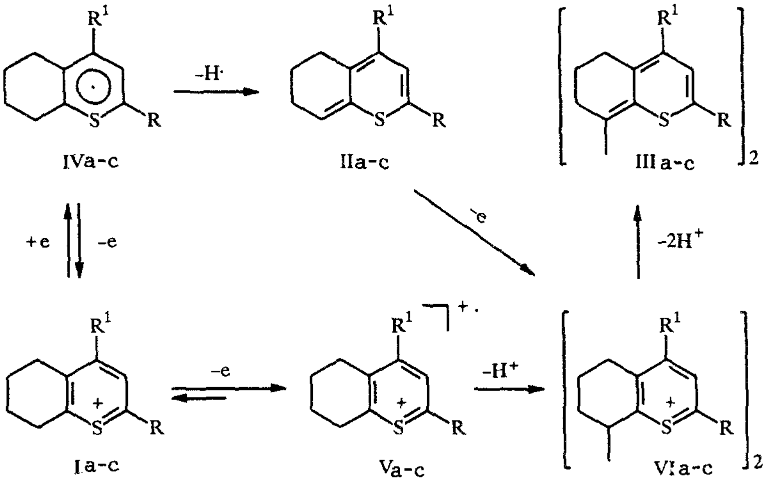
TABLE 1. Electrochemical Behavior of Cyclohexa[b]thiopyrylium Salts Ia-c in Acetonitrile on a Platinum Electrode

Compound	Reduction				Oxidation			
	E_{cp}, V	E_{ap}, V	I_{ap}/I_{cp}	*n*	E_{ap}, V	E_{cp}, V	I_{cp}/I_{av}	*n*
Ia	0,42	0,35	0,89	1	1,20	1,02	0,1	0,8
Ib	0,48	0,41	0,83	1	—	—	—	1
Ic	0.54	0.41	0.73	1	1.20	1.10	0.1	0.7

Notes. E_{ap} and E_{cp} are potential anodic and cathodic peaks, I_{ap}/I_{cp} are corresponding maximal current carrying capacities for oxidation and reduction; for completely reversible processes these ratios equal 1; n – number of electrons.

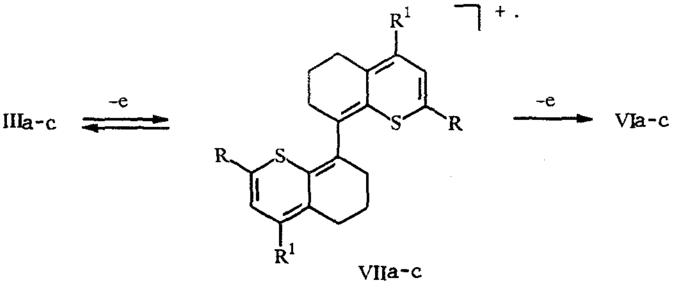
TABLE 2. Electrochemical Oxidation of Dimers IIIa-c and 4H-Thiopyrans VIIIa-c in Methylene Chloride

Compound	E_{ap}, V	E_{cp}, V	I_{cp}/I_{ap}
III a	0,60	0,17	1
III b	0,54	0,12	1
III c	0,59	-0,04	1
VIII a	1,20	0,86	0,40
VIII b	1,31	1,00	0,35
VIII c	1,30	1,00	0,30



I-VI a $R=R^1=Ph$; b $R=C_6H_4OMe$-4, $R^1=Ph$; c $R=R^1=C_6H_4OMe$-4

The exhaustive electrolysis of dimer IIIa leads to the corresponding dication VIa, which was identified by the addition of a genuine sample of VIa diperchlorate.



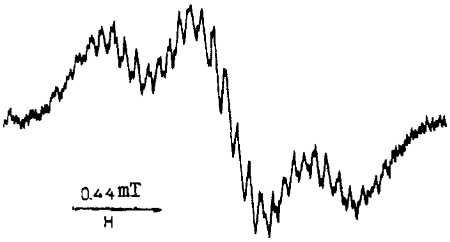


Fig. 1. EPR spectrum of the radical (IVa) obtained in the reduction of 2,4-diphenylcyclohexa[b]thiopyrylium tetrafluoroborate on a zinc mirror.

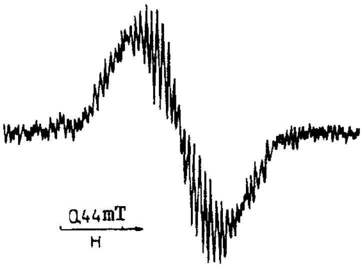
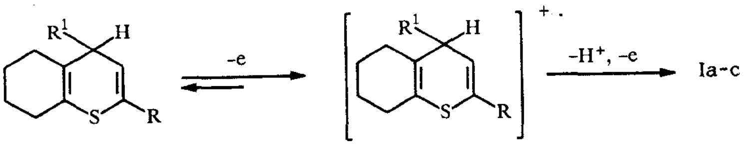


Fig. 2. EPR spectrum of the radical obtained in the reduction of dication VIa on a zinc mirror.

The formation of dimers of the III type is possible in the oxidation of 2-R-4-R′-4H-cyclohexa[b]thiopyrans VIIIa-c. Thus prolonged heating in air of 4H-thiopyrans VIIIa, b in absolute acetone leads to IIIa, b in 3% and 5% yields, respectively. Thiopyrans VIIIa, b remain unchanged in the absence of oxygen under the same conditions.

In the case of electrochemical oxidation in methylene chloride thiopyrans VIIIa-c give a one-electron wave, i.e., oxidation leads to cation radicals IXa-c (see Table 2). The small value of the I_{cp}/I_{ap} ratio provides evidence for the instability of the resulting cation radicals. Fragmentation of cation radicals IXa-c is observed on the secondary cathode branch of cyclic voltammetry: one observes the development of a wave involving the reduction of a proton (E_{cp} = −0.12 V) and a wave involving the reduction of cations Ia-c (E_{cp} = −0.53, −0.31, and −0.49 V, respectively), which were identified by the addition of genuine samples of tetrafluoroborates Ia-c and perchloric acid.



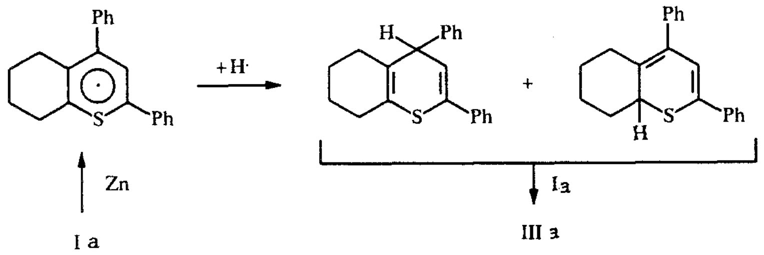
VIIIa-c IXa-c

A wave of oxidation of dimers IIIa-c is formed when the corresponding tetrafluoroborates Ia-c (for identification) are added to the electrochemical cell containing 4H-thiopyrans VIIIa-c. The production of dimers of the III type in the reaction of 4H-thiopyrans and thiopyrylium cations is confirmed chemically. Thus dimer IIIb is isolated in 34% yield when equimolar amounts of 4H-thiopyran VIIIb and tetrafluoroborate Ib are heated in acetonitrile. It is evident that when solutions of 4H-thiopyrans VIIIa-c are heated in the presence of air oxygen, they undergo oxidation to cation radicals IXa-c, as was observed in the oxidative dehydrogenation of 2,4,6-triphenyl-4H-pyran [6]. The presence of Ia-c cations in the reaction mixture leads to further oxidation of cation radicals IXa-c and the production of dimers IIIa-c. The presence of a methoxyphenyl group in the molecules of starting compounds Ia-c and VIIIa-c hinders their electrochemical oxidation.

The formation of stable 2,4-diarylcyclohexa[b]thiopyranyl radicals is confirmed by the chemical reduction of the Ia cation and dication VIa on a zinc mirror in the resonator of the EPR spectrometer in solution in tetrahydrofuran.

The EPR spectrum of radical IVa (Fig. 1) is a triplet (1:2:1) due to coupling of the energy levels of the unpaired electron with the magnetic nuclei of the two protons in the 8 position of the hydrogenated ring (a_H^8 = 0.69 mT). Each component of the triplet is split into a complex multiplet that is a triplet (1:2:1 with a_H^5 = 0.23 mT) of septets [1:6:15:20:15:6:1 with $a_H^{o,p}$(Ph) = 0.08 mT]. Splitting from the remaining protons of the heterocyclic system is not observed and does not contribute to the width of the individual line of the spectrum.

Under the influence of excess zinc in acetonitrile tetrafluoroborate Ia is converted to a mixture of 2,4-diphenyl-4H- and 2,4-diphenyl-6H-cyclohexa[b]thiopyran with substantial preponderance of the former. Taking into account the EPR data, this can be explained by stabilization of intermediate radical IVa due to the detachment of a hydrogen atom from the solvent [7]. Dimer IIIa, which is apparently formed as a result of oxidation of the mixture of 4H- and 6H-thiopyrans by the unchanged Ia cation, was isolated from the reaction mixture in 16% yield when the ratio of starting salt Ia to zinc was 2:1.



The EPR signal obtained by the reduction of dication VIa on a zinc mirror (Fig. 2) provides evidence for delocalization of the unpaired electrons over the entire framework of the heterocyclic biradical and the substituent without an appreciable (under the experimental conditions) exchange interaction between the electrons.

The overall form of the EPR spectrum is a quartet [a triplet (1:2:1) of doublets]. The maximum spin density is related to the 5 and 8 positions of the saturated fragment: a_H^5 = 0.40 mT, a_H^8 = 0.29 mT. The weaker splitting of the hyperfine structure (hfs) belongs to the ortho, para, and meta protons of two phenyl substituents: $a_H^{o,p}$ = 0.07 mT, a_H^m = 0.04 mT.

An unresolved EPR spectrum was observed in the oxidation of dimer IIIa with aluminum chloride in methylene chloride.

Thus the scheme for obtaining dimers of the III type from salts I proposed in [1] actually includes a step involving the formation of radicals and cation radicals in which the formation of thiopyranyl radicals IV precedes the development of anhydro bases II, i.e., the reaction proceeds primarily via pathway 1. However, considering the ability of the Ia-c cations to undergo electrochemical oxidation, one cannot completely exclude the possibility that the reaction also takes place via pathway 2, i.e., through the formation of dication radicals.

EXPERIMENTAL

The ^{13}C NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Varian FT-80A spectrometer. Tetrafluoroborates Ia-c were obtained by the methods in [8-10], anhydro base IIa, dimers IIIa-c, and diperchlorate VIa were obtained by the methods in [1, 11], and 4H-thiopyrans VIIIa-c were obtained by the methods in [10, 12, 13].

The electrochemical measurements were made using an automated system consisting of a PI-50 pulse potentiostat, a PR-8 programmer, and an Iskra-226 personal-professional computer. The reference points (E_{peaks} and I_{peaks}) were obtained by construction and processing of the Fourier representation of the experimental curve. The functional dependence (of I_{max} on the square root of the potential-scanning rate) was constructed by approximation of the values by an exponential series of the 16th degree.

The number of electrons was determined as compared with a standard of the same concentration (with ferrocene for oxidation and with 2,4,6-triphenylpyrylium perchlorate for reduction). The working electrode was a platinum needle electrode with an area of 1.3 by 10^{-2} cm^2, the reference electrode was a silver chloride electrode with a water-impermeable membrane, and the auxiliary electrode was a platinum coil.

The acetonitrile was purified by fractional distillation over phosphorus pentoxide and then twice over calcium hydride. The methylene chloride was fractionally distilled over calcium hydride. The inert electrolyte was a 0.1 M solution of tetrabutylammonium perchlorate, and the depolarizer concentration was $5 \cdot 10^{-3}$ mole/liter.

The EPR spectra were recorded with a Radiopan SE/X-2543 radiospectrometer in tetrahydrofuran at 25°C. The samples were evacuated to a pressure of $4.5 \cdot 10^{-3}$ mm.

Oxidative Dimerization of 2,4-Diphenyl-4H-cyclohexa[b]thiopyran (VIIIa, $C_{21}H_{20}S$) and 2-(4-Methoxyphenyl)-4-phenyl-4H-cyclohexa[b]thiopyran (VIIIb, $C_{22}H_{22}OS$). A. A solution of 0.9 g (3 mmole) of 4H-thiopyran VIIIa or 1 g (3 mmole) of 4H-thiopyran VIIIb in 7 ml of absolute acetone was boiled in a sealed ampul for 370 h. This procedure gave 0.02 g (3%) of 6,6′,7,7′-tetrahydro-2,2′,4,4′-tetraphenyl-8,8′-bis(5H-1-benzothiopyranyl) (IIIa) and 0.5 g (5%) of 6,6′,7,7′-tetrahydro-2,2′-bis(4-methoxyphenyl)-4,4′-diphenyl-8,8′-bis(5H-1-benzothiopyranyl) (IIIb). Dimers IIIa and IIIb were identical to the compounds previously obtained [11] with respect to the results of elementary analysis, the IR spectra, and the melting points.

B. A solution of 0.9 g (3 mmole) of 4H-thiopyran VIIIa or 1 g (3 mmole) of 4H-thiopyran VIIIb in 7 ml of absolute acetone was boiled in a sealed ampul filled with helium (with prior evacuation with threefold freezing in liquid nitrogen and thawing). The solvent was evaporated to give 0.85 g of 4H-thiopyran VIIIa, with mp 89-91°C (mp 89-91°C [12]), or 0.9 g of 4H-thiopyran VIIIb with mp 107-108°C (mp 107-108°C [13]). The thiopyrans were identical to the compounds previously obtained with respect to the results of elementary analysis and IR spectroscopy.

C. A mixture of 1 g (3 mmole) of 2-(4-methoxyphenyl)-4-phenyl-4H-cyclohexa[b]thiopyran (VIIIb) and 1.21 g (3 mmole) of 2-(4-methoxyphenyl)-4-phenylcyclohexa[b]thiopyrylium tetrafluoroborate (Ib) in 60 ml of acetonitrile was heated for 6 h at 50°C in a stream of argon and then maintained for 16 h at 20°C. This procedure gave 0.5 g (34%) of 6,6′,7,7′-tetrahydro-2,2′-bis(4-methoxyphenyl)-4,4′-diphenyl-8,8′-bis(5H-1-benzothiopyranyl) (IIIb) with mp 204-206°C. Dimer IIIb was identical to the previously obtained compound [11] with respect to its melting point and IR spectrum.

Reduction of 2,4-Diphenylcyclohexa[b]thiopyrylium Tetrafluoroborate (Ia, $C_{21}H_{19}BF_4S$) with Zinc in Acetonitrile. A. A 1.56-g (24 mmole) sample of zinc dust was added in portions in a stream of argon to a solution of 2.34 g (6 mmole) of tetrafluoroborate Ia in 16 ml of dry acetonitrile. After 72 h, the solution was separated by decantation, and the solvent was evaporated at reduced pressure in a stream of argon to give a mixture of 2,4-diphenyl-4H-cyclohexa[b]thiopyran (VIIIa) and 2,4-diphenyl-6H-cyclohexa[b]thiopyran in the form of an oil. ^{13}C NMR spectrum of the alicyclic fragment of the 4H-thiopyran: 22.61 (CH_2), 22.75 (CH_2), 29.52 (CH_2), 29.45 (CH_2), 49.41 ppm (CH); of the 6H-thiopyran: 23.00 (CH_2), 23.12 (CH_2), 28.33 (CH_2), 30.90 (CH_2), 42.78 ppm (CH). The yield was 90%.

B. A 0.19-g (3 mmole) sample of zinc dust was added in a stream of argon to a solution of 2.34 g (6 mmole) of tetrafluoroborate Ia in 16 ml of dry acetonitrile. After 240 h, the precipitated dimer IIIa, with mp 217-219°C, was separated. The yield was 0.3 g (17%).

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