OXIDATIVE CLEAVAGE OF THE C—C BOND IN PROCESSES INVOLVING THE HETEROAROMATIZATION OF 9R-sym-NONAHYDRO-10-OXA(CHALCOGENA)ANTHRACENES

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The reaction of 9-(2-methoxyphenyl)- and 9-(2-thienyl)-sym-nonahydro-10-selena(thia)anthracenes with trifluoroacetic acid causes their heteroaromatization with the elimination of substituents from the γ *positions of the heterorings. A similar transformation of these compounds, as well as their oxygen and 9-benzyl-substituted analogs, occurs during anode electrochemical oxidation. The stepwise character of the cleavage of the C—C bond, which includes one-electron oxidation of the chalogenapyrans and subsequent fragmentation of the cation-radical intermediates, is substantiated.*

The heteroaromatization of 2H- and 4H-pyrans, as well as their S- and Se-heteroanalogs, may be realized through splitting out of hydrogen (formally a hydride ion) or via elimination of a substituent from the tetragonal carbon atom of the heterocycle. The first pathway (dehydroaromatization), which is realized by the action on pyrans and thio- and selenopyrans of diverse oxidizing agents or in acid-catalyzed disproportionation reactions [1-3], is the most widely accepted and has been most thoroughly investigated. The second pathway has been studied to a lesser extent, since only a small number of reactions of this type are known. Thus, for example, the splitting out of benzyl [4-7], alkyl [8], acetylacetonyl [9], pyranyl [10], and isochromenyl [11] substituents has been detected in the aromatization of pyrans and thiopyrans brought about by chemical and electrochemical oxidation, as well as by the action of strong protic acids. In the little-studied selenopyran series the elimination of a substituent during aromatization has been observed in a single case [3].

In the present research, during a study of the behavior of 4H-selenopyrans in acidic media we observed that 9R-sym-nonahydro-10-selenaanthracenes Ia, d, when dissolved in trifluoroacetic acid, are readily and quantitatively converted to unsubstituted trifluoroacetate IIIa* by eliminating the substituents in the form of anisole (IIa) and thiophene (IIb).

To ascertain the effect of the character of the heteroatom in the heteropyran ring on the ability of chalcogenapyrans to undergo aromatization with the elimination of a substituent we studied the behavior of thiopyrans Ib, e and pyrans Ic, f with respect to trifluoroacetic acid. We found that Ib, e are also capable of splitting out anisyl and thienyl substituents under similar conditions, but the reactions in this case proceed more slowly than for selenides Ia, d, and competing dehydroaromatization was noted in the case of Ib. In the reaction mixture, in addition to unsubstituted trifluoroacetate IIIb and anisole, we detected 9-(4-methoxyphenyl)perhydro-10-thiaanthracene (IV) and trifluoroacetate V, which constitutes evidence for the disproportionation of thiopyran Ib. The inflated (relative to the calculated value for disproportionation) yield of salt V constitutes evidence for a third pathway in the transformation of thiopyran Ib, viz, its oxidative dehydroaromatization with the participation of atmospheric oxygen.

Pyrans Ic, f (c R = $C_6H_4OCH_3$-p, f R = 2-thienyl) were generally incapable of aromatization under similar conditions and underwent processes associated with protolytic cleavage of the heteroring. The character of these transformations will be reported additionally.

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*Oily hygroscopic trifluoroacetates IIIa, b and V were isolated and identified in the form of the known perchlorates by an anion-exchange reaction with perchloric acid.

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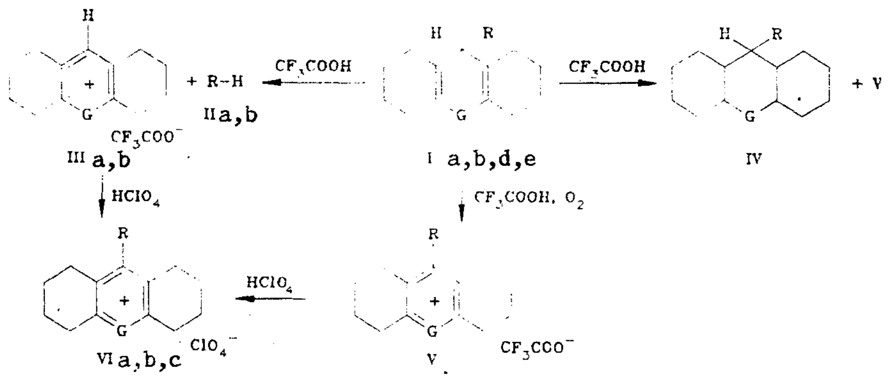
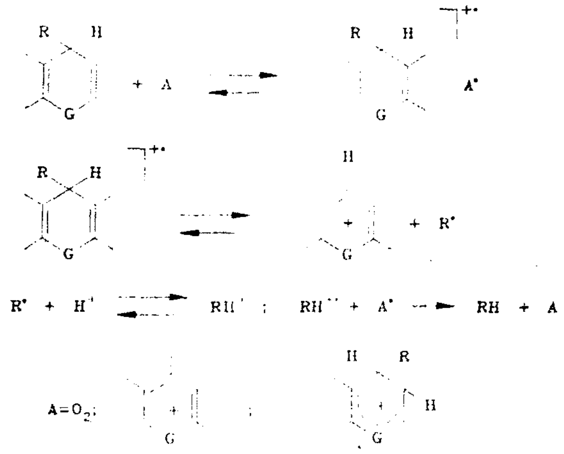


Ia,b IIa, IV, V, VIc R=$C_6H_4OCH_3$-*n*; Id,e IIb R=2-thienyl VIa,b R=H; Ia,d IIIa, VIa G=Se; Ib,e IV, VIb,c G=S

The more pronounced (as compared with thiopyrans) ability of selenopyrans to undergo aromatization with the elimination of a substituent, which correlates with their lower one-electron oxidation potentials [12] (literature analogs [7-12]), makes it possible to propose an oxidative stepwise mechanism for cleavage of the C—C bond of the heteroring with substituents:



Atmospheric oxygen [7], the chalcogenoniapyrylium salts that develop in the reaction mixture, and the protonated forms of the chalcogenopyrans may act as one-electron oxidizing agents of the chalcogenopyrans. The competitive participation of the enumerated electron-acceptors in the one-electron oxidation of the chalcogenopyrans cannot be excluded.

TABLE 1. Results of the Electrochemical Oxidation of Ia-i*

Compound	E_{pa}, V	E_{pc}, V	I_{pc}/I_{pa}	*n*	$-E_{pc}$, V
Ia	0,90	0,83	0,37	1.05	0,52
Ib	0,97	0,84	0.16	0,80	0,64
Ic	1,08	0,95	0,35	0,97	0,79
Id	0,98	0,84	0,47	0,82	0,56
Ie	0,99	0,83	0,38	0,80	0,63
If	1,14	0,98	0,28	0,84	0,75
Ig	0,95	0,86	0,43	0,85	0,51
Ih	1,04	0,80	—	0,83	0,64
Ii	0,87	0,78	0,10	0,84	0,79

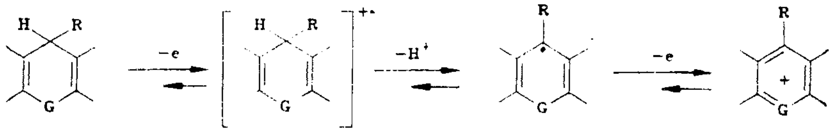
*E_{pa} and E_{pc}, respectively, are the potentials of the anode and cathode peaks in volts, I_{pc}/I_{pa} is the ratio of the reduction and oxidation peaks (for completeness of the reversible process this ratio is equal to unity), and n is the number of electrons determined as compared with a standard (ferrocene).

The data that we obtained on the fragmentation of the cation radicals of Ia-f generated by their electrochemical oxidation in aprotic media serve as a confirmation of the proposed mechanism.

The anode oxidation of Ia-f, as well as 9-benzyl-substituted 10-chalcogenohydroanthracenes Ig-i (I g G = Se, h G = S and G = O) on a platinum electrode in methylene chloride showed that all of these compounds are oxidized in a one-electron, slightly reversible step leading to the formation of cation radicals (Table 1).

It is apparent from Table 1 that the I_{pc}/I_{pa} ratio ranges from 0.10 to 0.40; the difference in the anode and cathode peaks ranges from 70 to 200 mV, which constitutes evidence for the instability of the particles formed during oxidation.

Not only waves of reduction of the corresponding cation radicals (E_{pc}) but also the product of their fragmentation, which are reduced in the negative-potential region ($-E_{pc}$), are observed on the cathode branch of the cyclical voltamperograms. These waves correspond to reduction of the mixture of the substituted and unsubstituted cations, which was demonstrated in an independent experiment. An independent peak corresponding to reduction of a proton was also observed in a number of cases. It is evident that partial fragmentation of the resulting cation radicals via a $-H^+$, $-e$ reaction scheme occurs in the electrochemical oxidation of Ia-f:



The exhaustive electrolysis of Ia-f at the oxidation potential in acetonitrile and methylene chloride also leads to mixtures of substituted and unsubstituted cations — anisole for Ia-c (E_{pa} of anisole = −1.56 V in CH_2Cl_2) and thiophene for Id-f (E_{pa} of thiophene = −1.84 V in CH_2Cl_2), which were identified by the addition of the pure substances. The anisyl and thienyl radicals formed in the fragmentation apparently react with the solvent or unoxidized chalcogenopyran. In the case of Ig-i a substance that is reduced at E_{pc} = −1.29 V (the reduction wave of dibenzyl) is formed in addition to the IIa-c cations during exhaustive electrolysis. During electrochemical oxidation Ig-i evidently form cation radicals, which undergo fragmentation with the ejection of benzyl radicals, which dimerize to give dibenzyl.

Thus in the cases that we studied the fragmentation of the initially formed cation radicals actually proceeds via two pathways — with cleavage of the C—C (A) and C—H (B) bonds with predominance of pathway A.

The fragmentation of the cation radicals of Ig-i with splitting out of a benzyl radical was also confirmed by EPR spectroscopy. Thus in the oxidation of these compounds in tetrahydrofuran with lead dioxide in the presence of the spin trap C-phenyl-N-tert-butylnitrone we observed the superimposition of several EPR signals, of which two can be interpreted unambiguously: the signal of the benzoyl-tert-butylnitroxyl radical (a_H = 0.9 mT) — the product of oxidation of the nitrone — and a signal of the adduct of the addition of the benzyl radical to the spin trap, C-phenyl-N-tert-butylnitrone (triplet of doublets with a_H = 1.42 mT and a_H = 0.23 mT). The parameters of the EPR spectra of the radicals are close to those presented in [14].

EXPERIMENTAL

The progress of the reactions and the individuality of the compounds were monitored by TLC on Silufol plates with development by means of iodine vapors. The IR spectra of KBr pellets of the compounds were obtained with a Specord 75 spectrometer. The EPR spectra were recorded with a Radiopan SE/X-2543 radiospectrometer in vacuo (10^{-3} mm).

The electrochemical measurements were made with an automated system for scientific measurements [ASNI (ASSM)] consisting of a PI-50.11 pulse potentiostat, a PR-8 programmer, and an Iskra-226 personal-professional computer. The reference points (the E and I peaks) were obtained by construction and processing of the Fourier form of the experimental curve. The ohmic losses were compensated by means of an analog compensator (PI-50) and additionally with the computer. The working electrode was a needle-shaped platinum electrode with an area of $6.25 \cdot 10^{-2}$ cm^2, the reference electrode was a saturated calomel electrode with a waterproof diaphragm, and the auxiliary electrode was a platinum coil. The methylene chloride was purified by fractional distillation over CaH_2. The inert electrolyte was 0.1 mole/liter tetrabutylammonium perchlorate, and the depolarizer concentration was $5 \cdot 10^{-3}$ M.

The results of elementary analysis for C and H were in agreement with the calculated values.

The synthesis of Ig-i was previously described in [15].

9-(4-Methoxyphenyl)-sym-nonahydro-10-oxaanthracene (Ic, $C_{20}H_{24}O_2$). A suspension of 94.2 g (0.3 mole) of 13-oxo-8-(p-methoxyphenyl)tricyclo[7,3,1,$0^{2,7}$]tridecan-2-one [16] in 200 ml of acetic anhydride—acetic acid (1:1) was refluxed for 10 h, after which it was cooled, allowed to stand for 5 h, and filtered to give 63.2 g (72.0%) of colorless Ic with mp 86-87°C (from acetone). IR spectrum: 1670, 1705 cm^{-1} (C=C).

9-(4-Methoxyphenyl)-sym-nonahydro-10-thiaanthracene (Ib, $C_{20}H_{24}OS$). A suspension of 59.2 g (0.2 mole) of Ic in 200 ml of acetic acid was saturated for 0.5 h with hydrogen sulfide, 3 ml of concentrated HCl was added, and the mixture was stirred for 4 h with the continuous admission of hydrogen sulfide. The mixture was then allowed to stand for 12 h, the precipitate was separated, 120 ml of acetone was added to it, and the acetone mixture was refluxed for 1 h. It was then cooled and filtered to give 42.5 g (68.1%) of colorless Ib with mp 66-67°C (from acetone). IR spectrum: 1630, 1695 cm^{-1} (C=C).

9-(4-Methoxyphenyl)-sym-nonahydro-10-selenaanthracene (Ia, $C_{20}H_{24}OSe$). Nitrogen was passed for 1 h into a suspension of 59.2 g (0.2 mole) of Ic in 200 ml of acetic acid, after which the mixture was saturated with hydrogen selenide for 0.5 h. The mixture was treated with 3 ml of concentrated HCl and then stirred for 4 h with the continuous admission of hydrogen selenide. It was then allowed to stand for 15 h, the precipitate was separated, 120 ml of acetone was added to it, and the acetone mixture was refluxed for 1 h. Ethanol (25 ml) was added to the hot solution, after which it was cooled and filtered to give 52.3 g (72.8%) of colorless Ia with mp 83-83.5°C (from acetone). IR spectrum: 1626, 1695 cm^{-1} (C=C).

9-(2-Thienyl)-sym-nonahydro-10-selenaanthracene (Id, $C_{17}H_{20}SSe$). A 7.03-g (0.02 mole) sample of 9H-sym-octahydro-10-selenoniaanthracene perchlorate (VIa) [17] was added in portions to a solution of 0.04 mole of thienylmagnesium bromide (prepared from 1 g of magnesium and 6.52 g of 2-bromothiophene) in 50 ml of ether, after which the reaction mixture was decomposed by the successive introduction of 4 ml of water and 30 ml of a saturated aqueous solution of ammonium chloride. The mixture was then extracted with ether (3 × 30 ml), the extract was dried with sodium sulfate, and the solvent was removed by distillation. The oily residue was crystallized from ethanol to give 3.83 g (57.1%) of colorless Id with mp 63-64°C (from ethanol). IR spectrum: 1635, 1695 cm^{-1} (C=C).

Compounds Ie, f. These compounds were similarly obtained from 9H-sym-octahydro-10-thionia(oxonia)anthracene perchlorates.

9-(2-Thienyl)-sym-nonahydro-10-thiaanthracene (Ie, $C_{17}H_{20}S_2$). This compound had mp 111-112°C (from acetone). IR spectrum: 1630, 1690 cm^{-1}. The yield was 68.3%.

9-(2-Thienyl)-sym-nonahydro-10-oxaanthracene (If, $C_{17}H_{20}OS$). This compound had mp 86-87°C (from ethanol). IR spectrum: 1665, 1700 cm^{-1} (C=C). The yield was 52.4%.

Reaction of Ia with Trifluoroacetic Acid. A suspension of 7.19 g (0.02 mole) of Ia in 30 ml of trifluoroacetic acid was stirred for 1 h, 4 g of 70% perchloric acid and 200 ml of ether were added, and 6.74 g (96%) of the known perchlorate Va, with mp 126-127°C (acetone—ether), precipitated [16]. The mother liquor was washed with water (3 × 30 ml), dried with sodium sulfate, and subjected to fractional distillation to give 1.7 g (78.1%) of anisole with bp 154°C and n_D^{20} 1.5170.

Reaction of Ib with Trifluoroacetic Acid. A suspension of 12.4 g (0.04 mole) of Ib in 60 ml of trifluoroacetic acid was stirred for 2 h, after which 6 g of 70% perchloric acid and 400 ml of ether were added to precipitate 11.9 g of a mixture (1:2)* of 9H-sym-octahydro-10-thioniaanthracene (VIb) and 9-(4-methoxyphenyl)-sym-octahydro-10-thioniaanthracene (VIc) perchlorates. The mother liquor was washed with water (4 × 50 ml), dried with sodium sulfate, and distilled to give 1.13 g (26%) of anisole with bp 154°C and n_D^{20} 1.5170. Column chromatography of the oily residue (on aluminum oxide with hexane as the eluent) gave 0.89 g (7%) of IV with mp 158-160°C. The IR spectrum did not contain absorption bands at 1620-1800 cm^{-1}.

Reaction of Id with Trifluoroacetic Acid. A suspension of 3.35 g (0.01 mole) of Id in 10 ml of trifluoroacetic acid was stirred for 1 h, and 2 g of 70% perchloric acid and 200 ml of ether were added to precipitate 3.31 g (94.3%) of perchlorate VIa with mp 126-127°C (acetone—ether). The mother liquor was washed with water (3 × 30 ml) was dried with sodium sulfate and subjected to fractional distillation to give 0.52 g (62%) of thiophene with bp 890°C and n_D^{20} 1.5286.

The reaction of 2.88 g (0.01 mole) of Ie with 10 ml of trifluoroacetic acid was similarly realized. The reaction time was 2 h. The yield of the known perchlorate VIb, with mp 121-122°C [17], was 2.57 g. The yield of thiophene, with n_D^{20} 1.5286, was 0.44 g (53%).

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*The ratio of perchlorates VIb in the mixture was evaluated by analysis of the PMR spectra.

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