10-CHALCOGENONIAANTHRACENE CATIONS (REVIEW)

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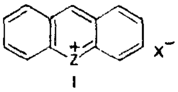
UDC 546.24.07

The literature data on the synthesis and properties of 10-chalcogenoniaanthracene salts are correlated.

Compounds that contain group VIA elements (oxygen, sulfur, selenium, and tellurium) as heteroatoms occupy an important place among 10-heteroniaanthracene cations I.



I

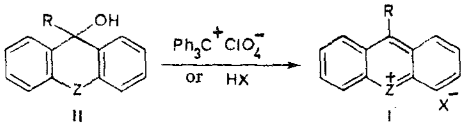
Z = O, S, Se, Te

However, whereas 10-oxoniaanthracene cations constitute a relatively well-studied class of compounds [1], much less study has been devoted to derivatives of 10-thionia- and, particularly, 10-selenonia- and 10-telluroniaanthracene cations. It is sufficient to point out that the overwhelming majority of studies devoted to 10-selenoniaanthracene cations have been carried out in the last 10-15 years, whereas 10-telluroniaanthracene cations were obtained for the first time only in 1980 [2]. The present review is devoted to an examination of methods for the synthesis of 10-chalcogenoniaanthracene cations (I, Z = S, Se, and Te) and their properties; data on 10-oxoniaanthracene cations (primarily data obtained in recent years) will be drawn upon only for comparison with the analogous data on 10-chalcogenoniaanthracene cations.

1. SYNTHESIS OF 10-CHALCOGENONIAANTHRACENE SALTS

The most widely used methods for the preparation of 10-chalcogenoniaanthracene salts are based on the use of the corresponding chalcogen-9H-anthracen-9-ols II [2-19] or 10-chalcogen-9H-anthracenes (chalcogenoxanthenes) as the starting compounds.

One of the most general methods for the preparation of I, which makes it possible to synthesize various 9-substituted 10-chalcogenoniaanthracene cations, is dehydration of chalcogenanthracen-9-ols II with perchloric [2, 3, 5-11, 13-19] or tetrafluoroboric [8] acid:



II I

This reaction is usually realized by treatment of solutions of chalcogenanthracenols in suitable solvents (most often in ether) with excess 70% $HClO_4$ at low temperatures. The yields of I are extremely high; however, in a number of cases the reaction is accompanied by the formation of side products. Thus, 9,9'-bis(thiaxanthenyl) is formed along with 10-thioniaanthracene perchlorate in the reaction of 9H-10-thia-anthracen-9-ol with perchloric acid [6]. Salts with other anions (Hal^- [3-6, 8], Br_3^- [4, 5], $FeCl_4^-$ [3, 4, 6], and $ZnCl_3^-$ [12, 13]) are represented by individual examples.

Another variant of the use of 9-substituted chalcogenanthracen-9-ols for the synthesis of Ia cations is their reaction with trityl perchlorate [6, 18, 19]. This reaction is

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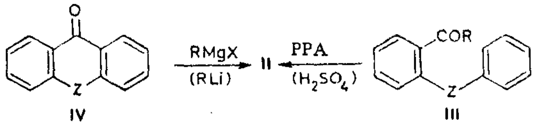
Scientific-Research Institute of Physical and Organic Chemistry at Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 435-446, April, 1983. Original article submitted January 11, 1982.

0009-3122/83/1904-0347$07.50

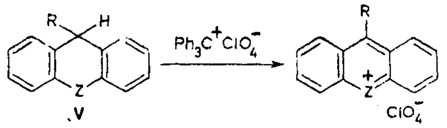
carried out by refluxing equimolar amounts of II and trityl perchlorate in glacial acetic or trifluoroacetic (in the case of telluraanthracenols) acid.

Since the problem of the synthesis of 10-chalcogenoniaanthracene cations reduces, in the reactions presented above, to the problem of the preparation of 9-substituted 10-chalcogenanthracen-9-ols, let us briefly examine methods for the preparation of the latter. The most widely used method for the synthesis of these compounds is the reaction of 10-chalcogenanthracenones IV with organomagnesium [2, 5, 6, 8, 10, 14, 17-21, 24] or organolithium [10, 21-23] compounds. Sometimes the alcohols are not isolated in pure form after hydrolysis of the reaction mixtures, and ether solutions of them are treated immediately with perchloric [6, 8, 10] or tetrafluoroboric [8] acid. The corresponding methylene derivatives are isolated along with 9-R-10-thia-anthracen-9-ols (R = CH_3, C_2H_5, $C_6H_5CH_2$) after workup of the reaction mixtures when 10-thiaanthracenones are treated with Grignard reagents of the CH_3MgX [8, 15] or RCH_2MgZ (R = CH_3 [8], C_6H_5 [8, 24]) type. Chalcogenanthracenols II are also obtained by cyclization of 2-phenylselenobenzophenones [18] or 2-phenylmercaptoacetophenones [25, 26] under the influence of polyphosphoric acid (PPA) or concentrated sulfuric acid.

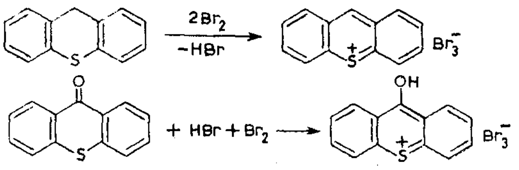


9-Unsubstituted chalcogenanthracenols II (R = H) are obtained in the reduction of ketones IV with various reducing agents, viz., $NaBH_4$ [6, 8, 9, 11, 17, 18], KBH_4 [27], $LiAlH_4$ [2, 19, 28, 29], sodium amalgam [30], and zinc dust in KOH [31] or NaOH [11, 13, 32] solution.

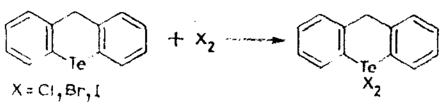
Of less significance for the synthesis of I is a method that uses 10-chalcogen-9H-anthracenes (V) for their preparation, since the latter, particularly the 9-substituted derivatives, are obtained in most cases by reduction of II [2, 11, 19, 23, 33] (see also the literature citations in [15]) or 10-heteroniaanthracene cations (see below). However, if the 10-chalcogen-9H-anthracenes are relatively accessible, the preparation from them of 10-chalcogenoniaanthracene cations by dehydrogenation by means of hydride-ion acceptors (most often trityl perchlorate) takes on preparative significance. The reaction that was first used for the synthesis of 10-oxoniaanthracene perchlorate [34] is usually carried out by brief refluxing equimolar amounts of V with trityl perchlorate in glacial acetic acid [6, 14, 35].



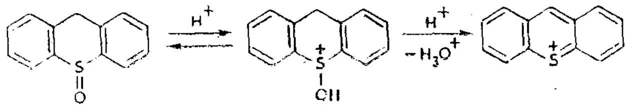
An attempt to obtain 10-telluroniaanthracene perchlorate under similar conditions was unsuccessful [19]. However, when the reaction is carried out in trifluoroacetic acid, 10-telluroniaanthracene perchlorates are formed in close-to-quantitative yields. 10-Thioniaanthracene cations are also obtained in quantitative yields by the action of bromine on 10-thia-9H-anthracene (or by the action of HBr and bromine on 10-thiaanthracen-9-one) in carbon tetrachloride in the dark [36].



9,9'-Bis(10-thioniaanthracene) diperbromide is similarly formed in the reaction of dithiaxanthyl with bromine [36]. This synthetic method cannot, however, be used for the preparation of tellurium (and, probably, selenium) analogs of I because of the much greater (as compared with sulfur) ability of these elements (particularly tellurium) to undergo conversion to tetracoordinates tellurium (selenium) derivatives under the influence of oxidizing agents. In fact, 10,10-dihalotellura-9H-anthracenes rather than 10-telluroniaanthracene cations are formed when 10-tellura-9H-anthracene is treated with halogens in inert solvents [37, 38].



10-Thioniaanthracene cations can also be obtained by treatment of thiaxanthene sulfoxides with an alcohol solution of hydrogen chloride [3] or by the reaction of thiaxanthene sulfoxide with concentrated sulfuric acid [39, 40]. The conversion of sulfoxides to 10-thioniaanthracene cations is evidently realized via the scheme [39, 40]:

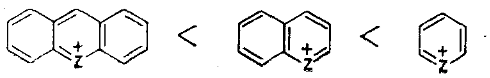


This reaction can hardly find application for the synthesis of 10-selenonia- and 10-telluroniaanthracenes, since telluroxides (and selenoxides) are converted to tetracoordinated tellurium (selenium) derivatives upon reaction with acids that contain sufficiently nucleophilic anions [41], whereas they give stable hydroxytelluronium perchlorates under the influence of acids of the $HClO_4$ type [41].

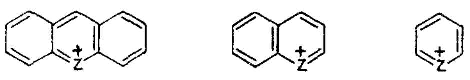
4. PROPERTIES OF 10-CHALCOGENONIAANTHRACENE CATIONS

2.1. Relative Stabilities of 10-Heteroniaanthracene Cations and Related Cations

The relative stabilities of 10-heteroniaanthracene cations I (Z = O, S, Se; data on the tellurium analogs are not available in the literature) and related heteroaromatic benzopyrylium and pyrylium cations were investigated qualitatively in [16] by means of a study of the $R^+ + R'H \rightleftharpoons RH + R'^+$ equilibria, where R^+ and R'H are different combinations of pyrylium (benzopyrylium and xanthylium) salts and pyrans (benzopyrans and xanthenes). The concentrations of the final products were determined by means of the UV or PMR spectra. It was established that the sulfur-containing cations are more stable than the oxygen- and selenium-containing cations; the stability increases in the following order for the same heteroatom:



However, the indicated order is not observed in the case of oxygen-containing cations: The xanthylium cation is more stable than the benzopyrylium cation [42]. A quantitative study of the stabilities of heteroaromatic cations by spectrophotometric determination of the equilibrium constants of the $R^+ + HOH \rightleftharpoons ROH + H^+$ reactions confirms the qualitative results presented above:

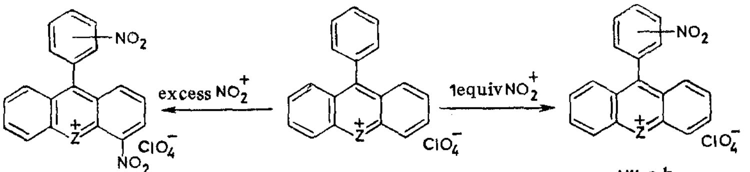


Z	pK_{R^+}	Z	pK_{R^+}	Z	pK_{R^+}
O	−0,83	O	−1,96	–	–
S	−0,21	S	3,15	S	>6
Se	−1,67	Se	1,20	–	–

2.2. Reaction of 10-Chalcogenoniaanthracene Cations with Electrophilic Reagents

The reaction of 10-chalcogenoniaanthracene cations with electrophilic reagents has been investigated in the case of a single reaction, viz., the nitration of 9-phenyl-10-chalcogenoniaanthracene perchlorates (VIa, b) [29, 43-46] [for comparison, data on the nitration of 9-phenyl-10-oxoniaanthracene perchlorate (VIc) [43-45, 47] are presented]. Treatment of VIa-c with the nitrating mixture at an equimolar reagent ratio leads to mixtures of 9-(4-nitrophenyl)- (VIIa) and 9-(3-nitrophenyl)-10-heteroniaanthracenes (VIIb); the ratio of the isomers formed depends on the nature of the heteroatom (in an earlier study it was asserted that only the meta isomer is obtained in 91% yield in the nitration of 9-phenyl-10-oxoniaanthracene perchlorate [47]).

The structure of the products of mononitration of VIa-c is established by conversion of the mixture of perchlorates obtained to the corresponding 9-phenylchalcogenanthracen-9-ols by means of NaOH, reduction of the alcohols to 9-[4(3)-nitrophenyl]-10-chalcogen-9H-anthracenes with formic acid, and subsequent conversion of the nitro groups to an amino group by the action of $SnCl_2$. The resulting 9-[4(3)-aminophenyl]-10-chalcogen-9H-anthracenes were acetylated, the products were separated by chromatography, and their characteristics were compared with the properties of genuine samples synthesized by independent methods. The compositions of the reaction mixtures in the dinitration of (VIa, b) were also determined similarly. The mononitration of 9-phenyl-10-oxoniaanthracene perchlorate gives primarily meta-isomer (VIIb) (Z = 0, 81% yield), whereas the principal product in the nitration of 9-phenyl-10-thioniaanthracene perchlorate is the para isomer (∿55%); 9-phenyl-10-selenoniaanthracene perchlorate occupies an intermediate position, since the reaction mixture contains 40% of the para isomer and 60% of the meta isomer.



VIII a,b

Z = S (VIIIa : VIIIb = 1,2 : 1)
Z = Se (VIII a: VIIIb = 1 : 1,25)

VI a-c

VII a,b

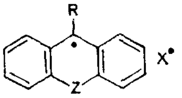
Z=O (VIIa : VIIb = 1: 4,5)
Z=S (VIIa : VIIb = 1,25:1)
Z=Se (VII a: VIIb = 1: 1,5)

The nitration of 9-phenyl-10-oxoniaanthracene perchlorate with excess nitrating mixture under various reaction conditions leads only to mononitro derivatives (VIIa, b) (Z = 0), whereas dinitro derivatives (VIIIa, b) (Z = S, Se), which have the 4-nitro-9-[4(3)-nitrophenyl]-10-chalcogenoniaanthracene perchlorate structure, are formed in the case of the sulfur and selenium analogs with excess nitrating mixture. The ratio of the dinitro derivatives (4, 4' : 4, 3') again depends on the nature of the chalcogen: In the case of sulfur the para isomer (4,4') is formed in ∿55% yield, as compared with an ∿44% yield in the case of selenium.

2.3. Reactions of 10-Chalcogenoniaanthracene Cations with Nucleophiles

A greater amount of research has been devoted to the study of the reaction of 10-chalcogenoniaanthracene salts with nucleophilic reagents than to the study of their reaction with electrophiles. As expected, the 9 position of the heteroaromatic cations undergoes attack in the case of nucleophilic substitution.

2.3.1. Exchange Reactions with Inorganic Salts. Exchange of the anions in 10-chalcogenoniaanthracene perchlorates leads to various products, depending on the nature of the anion introduced. Thus, according to the data in [8], 9-R-10-thioniaanthracene halides are formed when 9-R-10-thioniaanthracene perchlorates (R = H, CH_3, C_6H_5) are treated with tetraphenylphosphonium halides $Ph_4P^+X^-$ (X = Cl, Br, I). However, according to the data in [48], these compounds exist in the form of radical pairs IX in solution (and in the crystalline state):

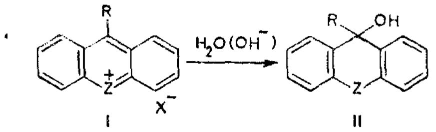


IX

At the same time, the reaction of 10-chalcogenoniaazaanthracene perchlorates I (Z = S, Se) with potassium cyanide [45, 49] or sodium azide [50] leads to 9-R-cyano- or 9-R-azidochalcogenxanthene.

10-Thioniaanthracene perbromide is converted to 10-thioniaanthracene periodide in quantitative yield on treatment with excess periodide anion [36].

2.3.2. Reactions with Water, Alkalis, Alkoxides, and Amines. Upon treatment with water or aqueous solutions of alkalis, 10-chalcogenoniaanthracene salts I are usually converted to the corresponding 10-chalcogen-9H-anthracen-9-ols II [7, 13, 33, 36, 46, 51], which, depending on the nature of the starting reagents and the reaction conditions, may undergo further transformations.



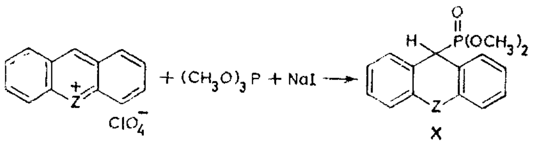
In a number of cases it has been noted that under the influence of excess alkali [7, 15, 51], the resulting compounds of the II type undergo disproportionation to 10-chalcogen-9H-anthracenes and 10-chalcogenanthracenones. A similar reaction occurs when 10-thioniaanthracene perchlorate is heated in isopropyl alcohol: A mixture of 10-thia-9H-anthracene and 10-thiaanthracenone is formed in a ratio of 67:21.

The hydrolysis of 10-thioniaanthracene perbromide (I, Z = S, X = Br_3^-) proceeds peculiarly. Upon reaction with aqueous sodium hydroxide solution, it gives (as a result of disproportionation of the initially formed 10-thia-9H-anthracen-9-ol) a mixture of thiaxanthene and thiaxanthone; the thiaanthracenone is usually obtained in greater amounts than 10-thia-9H-anthracene [36]. This is associated with partial oxidation of 10-thiaanthracen-9-ol by the sodium hypobromite that is formed as a result of hydrolysis of the starting perbromide.

The reaction of 9-phenyl-10-selenoniaanthracene perchlorate with sodium methoxide leads to 9-methoxy-9-phenyl-10-selenaanthracene in 88% yield [46], while a mixture of 10-thiaanthracenone (57%), 10-thia-9H-anthracene (29-45%), and a very small amount of 10-phenylthio-10-thiaanthracene is formed when 10-thioniaanthracene perchlorate is treated with potassium or lithium thiophenoxide [52].

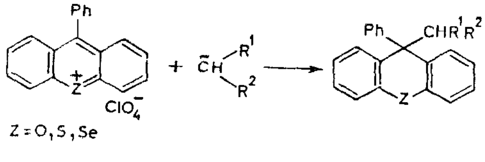
The reaction of 10-selenoniaanthracene perchlorate with aniline gives 9-(4-aminophenyl)-10-selenaanthracene [33].

2.3.3. Action of Phosphorus-Containing Nucleophiles. Relatively little study has been devoted to the reactions of 10-heteroniaanthracene perchlorates with phosphorus-containing nucleophiles [53, 54]. The corresponding phosphonates X are formed in high yields in the reaction of 10-heteroniaanthracene perchlorates with trimethyl phosphite in the presence of sodium iodide as a result of the Arbuzov reaction:



Phosphonates X are converted via the Wittig–Horner reaction to exo-methylene derivatives in high yields; these products may be of interest as donors in charge-transfer complexes (CTC) that have high electrical conductivities.

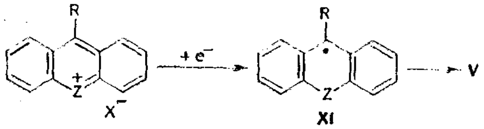
2.3.4. Reaction with Methylene-Active Compounds. Just as in the case of 10-oxoniaanthracene perchlorates [55], products of attack in the 9 position are formed in the reaction of 9-phenyl-10-chalcogenoniaanthracene perchlorates with cyanoacetic, malonic, and acetoacetic esters, malonodinitrile, and acetylacetone [45, 46]:



The reactions are carried out either in tert-butyl alcohol containing an equivalent amount of potassium tert-butoxide [45, 46] or in methylene chloride in the presence of triethylamine [45, 46]. It is interesting to note that 9-phenyl- [45] and unsubstituted 10-oxoniaanthracene [55] perchlorates undergo reaction even with weak CH acids such as acetone [45, 55] and acetophenone [55] both in the presence of bases (potassium tert-butoxide [45]) and in their absence [55]. On the basis of these data and the results of quantum-chemical calculations Hori and co-workers [45, 46] have advanced the assumption that 10-oxoniaanthracene perchlorates have increased reactivities in reactions with nucleophiles as compared with their sulfur and selenium analogs. However, it is obviously premature to draw a definite conclusion, since reactions of this type have not yet been investigated in sufficient detail, and, in addition, data on 10-telluroniaanthracene salts are still not available.

2.3.5. Reduction and Oxidation Reactions. The reduction of 10-heteroniaanthracene salts with various reducing agents (lithium aluminum hydride [6, 12, 14, 17, 19, 46, 56], sodium borohydride [10, 12], and phosphonium iodide [51]) leads to the corresponding 10-chalcogen-9H-anthracenes (V). This reaction can be used as a convenient method for the synthesis of 9R,9H-10-chalcogenanthracenes that are difficult to synthesize by other methods. This is particularly true for 10-telluraanthracenes, methods for the preparation of which have not yet been satisfactorily developed.

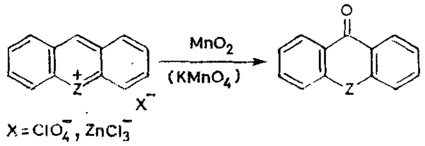
The radical character of the reduction is confirmed by the fact that significant amounts of 9,9'-bis(9H-10-chalcogenanthryls) are formed along with the corresponding 10-chalcogen-9H-anthracenes in the reduction of unsubstituted 10-chalcogenoniaanthracene perchlorates. In particular, the yields of 9,9'-bis(9H-10-thiaanthryl) were quantitative in the reduction of 10-thioniaanthracene perchlorate with zinc powder, sodium dithionate, cobaltocene, or phosphonium iodide [51].



Free radicals XI, the formation of which was proved by the EPR spectra and chemical transformations, are generated by the action on 9-R-10-heteroniaanthracene perchlorates of reducing agents such as zinc or potassium (zinc powder in tetrahydrofuran is most often used) on sulfur [57-59], selenium [56, 59], and tellurium [60] derivatives or vanadium dichloride in the case of 10-oxoniaanthracene perchlorates [61, 62]. 9H-10-Oxaanthryl radicals are most often obtained by different methods, viz., thermal dissociation of bis-(9H-10-oxaanthryls) [63] or reduction of 9H-10-oxaanthracen-9-ols with vanadium dichloride [48, 61]. 9H-10-Heteroanthryl free radicals are also generated in the reaction of 10-heteroniaanthracene salts with organomagnesium or organolithium compounds (see below).

Data that provide evidence for a virtual identical distribution of the spin density in the nuclei of 9-R-10-heteroanthryl radicals, regardless of the nature of the heteroatom, have been obtained on the basis of a complete analysis of the EPR spectra of 9-phenyl-10-oxaanthryl radicals and their sulfur and selenium analogs [56, 57, 61].

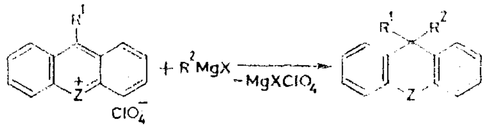
9-Aryl-10-chalcogenanthryl radicals have quite long lives in an inert atmosphere or in vacuo. They undergo reversible dimerization when the temperature is lowered, as indicated by the change in the color of the solution and disappearance of the signal in the EPR spectrum [60]. In the opinion of Price and co-workers [51], the dimerization of the 9-phenyl-10-thiaanthryl radical does not take place in the 9 position, which is sterically hindered, but rather at the sulfur atom. Radicals of the XI type (Z = S, Se) undergo the chemical reactions that are typical for stable hydrocarbon radicals. They can detach a proton from the solvent and thereby undergo conversion to the corresponding 9H-10-chalcogenanthracenes and can react with air oxygen or iodine to give peroxides or 10-thionia-(selenonia)anthracene triiodides [56, 58, 59].



The oxidation of 10-heteroniaanthracene cations with manganese dioxide in chloroform or acetonitrile leads to chalcogenanthracenones in high yields [64]. Similar results were obtained when an alkaline solution of potassium permanganate was used [12]. However, it is most likely that in the latter case the products of hydrolysis of the ketones, viz., 9H-10-chalcogenanthracen-9-ols, rather than the ketones undergo oxidation.

2.3.6. Reaction with Organomagnesium and Organolithium Compounds. 10-Chalcogenanthracenes.

10-Chalcogenoniaanthracene perchlorates react with organomagnesium compounds in an argon or nitrogen atmosphere to give 9-monosubstituted or 9,9-disubstituted 9H-10-chalcogenanthracenes [6, 10, 17, 18, 56, 58, 59, 65].

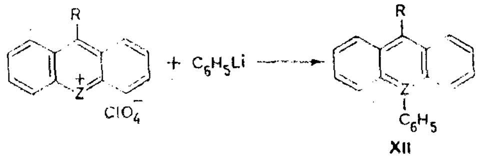


Thus this reaction, like the above-described reduction of I with lithium aluminum hydride, is a preparatively convenient method for the preparation of 9H-10-chalcogenanthracenes, particularly 9,9-disubstituted derivatives.

Although, just as in the case of 10-chalcogenoniaanthracene perchlorates, relatively few organomagnesium derivatives have been subjected to the reaction, it nevertheless seems that this reaction is quite general in character.

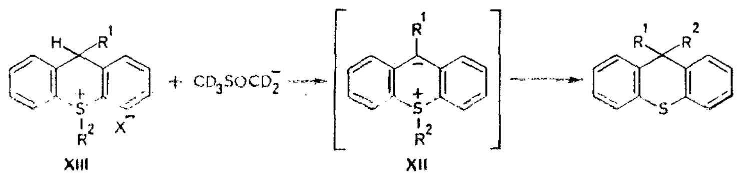
As in the case of 10-oxoniaanthracene perchlorates [66], the reaction of 10-chalcogenoniaanthracene perchlorates with organomagnesium and organolithium compounds [6, 9, 10, 14, 18, 58, 59, 65] proceeds via a radical mechanism. 10-Thia- and 10-selena-9H-anthryl radicals, the formation of which was recorded by means of EPR spectroscopy [56, 58, 59], arise as a result of one-electron reduction of the corresponding cations. In the reaction between 9-phenyl-10-thioniaanthracene perchlorate and phenylmagnesium bromide the concentration of the 9-phenyl-10-thiaanthryl radicals in solution reaches 3% [58]. The reaction of 10-chalcogenanthryl radicals with aryl or methyl radicals leads to the corresponding 9-substituted 9H-10-chalcogenanthracenes, while the recombination of these radicals with one another gives dimers [59]. Recombination is most characteristic for the less stable 9-unsubstituted 10-chalcogenanthryls [6, 17, 59]. 9,9'-Bis(9H-10-chalcogenanthryls) are therefore obtained in 15-20% yields when 10-chalcogenoniaanthracene perchlorates are treated with phenyllithium. Confirmation of the radical mechanism of the reactions of I with organometallic reagents also follows from the fact that the corresponding peroxides are formed when the reaction between them is carried out in the presence of air [59, 66].

In a number of papers [6, 9, 11, 14, 18, 56, 58, 59] it was asserted that stable 10-phenyl-10-chalcogenanthracenes (XII) are formed in the reaction between 10-chalcogenoniaanthracene perchlorates and phenyllithium. The properties (color, solubility in various organic solvents, melting points, and IR, UV, and PMR spectra) of these compounds, which were isolated in low yields, differed markedly from the properties of the isomeric 9-phenyl-10-chalcogen-anthracenes.



However, a thorough investigation of the structures and properties of the hypothetical 10-phenyl-10-chalcogenanthracenes [10, 23, 67-69] showed that these compounds are actually oligomers with undetermined structures and compositions.

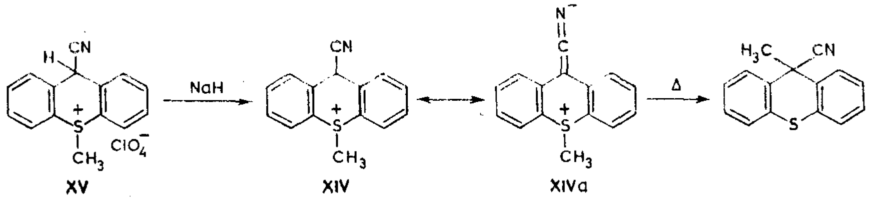
It was found, however, that 10-thiaanthracenes XII may be formed as intermediates in the deprotonation of thioniaanthracene perchlorates XIII with sodium dimsyl in deuterobenzene (toluene) in a nitrogen atmosphere at low temperatures. However, when the temperature is raised, XII undergo rapid and irreversible rearrangement to 9,9-disubstituted 10-thiaanthracenes, which are isolated in high yields.



In fact, a doublet at 1.27 ppm (methyl group of the rearrangement product) and singlets at 6.01 (thiaanthracene 9-H) and 1.05 ppm (thiaanthracene SCH_3) are observed in the PMR spectrum (at −45°C) of the reaction mixture obtained by deprotonation of 9H-10-methyl-10-thioniaanthracene perchlorate with lithium d_5-dimsyl [in toluene–d_8-dimethoxyethane (4:1)]. When the mixture is heated to 40°C, the latter two signals vanish, and only the signal of the rearrangement product remains [10, 67]. The formation of thianthracenes XII can be judged visually from the development (at low temperatures) of intense coloration when XIII are treated with dimsyl derivatives (purple when R^2 = Ar and orange when R^2 = CH_3 [10, 67]); this coloration vanishes when the mixtures are heated. From the fact that only 9-phenyl- and 2-chloro-9-(2,5-dimethylphenyl)-9H-10-thiaanthracenes were obtained in the deprotonation of a mixture of 10-phenyl- and 2-chloro-10-(2,5-dimethylphenyl)-9H,10-thioniaanthracene perchlorates with the d_5-dimsyl anion it follows that the rearrangement of 10-thiaanthracenes XII to the isomeric 9,9-disubstituted 10-thiaanthracenes is intramolecular in character and probably proceeds via a reaction of the Stevens type [10, 67]. The rate of this rearrangement is determined by a number of factors and primarily by the nature of the substituent attached to the sulfur atom in XIII. The rate constants (presented below) for the rearrangement of 10-thiaanthracenes XII (R^1 = H), which were obtained in the deprotonation of XIII with sodium dimsyl, to 10-thiaanthracenes [23] indicate that the rate of rearrangement decreases significantly as the electron-donor properties of the R^2 substituents become more pronounced.

R^2	$k \cdot 10^3$, sec^{-1}
C_6H_5	13
$2,5(CH_3)_2C_6H_3$	8,4
$4\text{-}CH_3OC_6H_4$	0,81
$2,4,6\text{-}(CH_3O)_3C_6H_2$	0,61
$2,4\text{-}(CH_3O)_2C_6H_3$	0,17

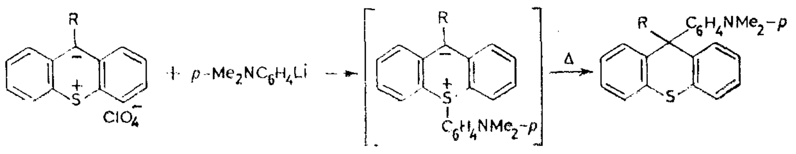
The nature of the solvent also has a significant effect on the rate of the rearrangement. Thus, whereas the half-life of 1-pentafluorophenyl-2-methylthianaphthalene in DMSO is 249 h, it is only 65 h in benzene [68]. Thus an important factor for the stability of thiabenzenes in general and thiaanthracenes in particular is charge delocalization, which indicates the ylid character of XII [10, 23, 68].



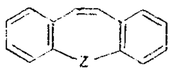
The first crystalline and stable (at room temperature) representative of 10-thiaanthracenes is 9-cyano-10-methyl-10-thiaanthracene (XIV), which was obtained by deprotonation of the corresponding salt XV with sodium hydride in tetrahydrofuran in a nitrogen atmosphere [49]. The significant shift of the band of stretching vibrations of a cyano group in the IR spectrum in the low-frequency region (2170 cm^{-1}) as compared with its usual value (for example, 2240 cm^{-1} in the spectrum of salt XV) indicates that the electron-acceptor cyano group (structure XIVa) participates in delocalization of the negative charge of the carbon atom of this ylid. Consequently, the principal structural factor that increases the stability of 10-chalcogenanthracenes is the presence of electron-donor substituents attached to the onium atom of the chalcogens and strong electron-acceptor groupings attached to the ylid carbon atom that are capable of participating in delocalization of its negative charge.

Like other less stable thiaanthracenes, ylid XIV, which is stable at normal temperature and in the solid state, as well as in solutions, undergoes 1,4 rearrangement to 9-cyano-9-methyl-10-thiaanthracene in high yield.

10-Thiaanthracenes can also be obtained by the action of aryllithium compounds on 10-thioniaanthracene perchlorates but at low temperatures, since the resulting XII undergo rearrangement to the isomeric 9-substituted 9H-10-thiaanthracenes when the temperature is raised. The most stable of the thiaanthracenes obtained in this way is 10-(4-dimethylaminophenyl)-10-thiaanthracene [65], which contains a powerful electron donor, viz., a dimethylamine group, that is capable of delocalization of the positive charge of the ylid sulfur atom:

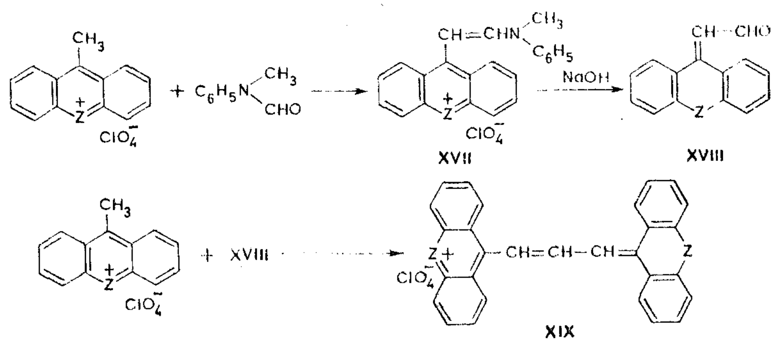


2.3.7. Reaction with Diazomethane. The reaction of 10-thionia- and 10-oxoniaanthracene perchlorates was studied for the first time in [70], and ring-expansion products, viz., dibenzo[b,f]thiepine and the corresponding oxepine (XVI, Z = S, O), were isolated in the 61 and 22% yields:



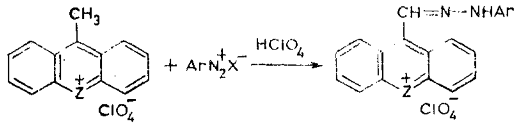
A detailed study of this reaction showed that, in addition to XVI (Z = S), at least another six substances, the relative amounts of which depend on the reaction conditions, are formed [7].

2.3.8. Reactions Involving Condensation of 9-Methyl-10-chalcogenoniaanthracene Perchlorates. It is known that methyl groups in the 2 and 4 positions of pyrylium and benzopyrylium cations readily undergo condensation with aromatic aldehydes, orthoformic ester, etc. [71]. However, in contrast to 9-methyl-10-oxoniaanthracene perchlorate [72], 9-methyl-10-thionia-(and selenonia)anthracene perchlorates, as a consequence of their low reactivities [73], do not react with orthoformic ester. At the same time, they react relatively easily with N-methylformanilide to give 9-[ω-(N-methylanilino)vinyl]-10-chalcogenoniaanthracene perchlorates (XVII), the alkaline hydrolysis of which gives 9-formylmethylene-10-chalcogenanthracenes (XVIII). Condensation of the latter with 9-methyl-10-chalcogenoniaanthracene perchlorates makes it possible to obtain symmetrical chalcogenxanthylotrimethylidynecyanines XIX and, in the case of the reaction with pyrylium, flavylium, xanthylium, and benzothiazolium salts that contain active methylene groups and with 1,1,3-trimethyl-2-formylindoline, the condensation makes it possible to obtain unsymmetrical trimethylidynecyanines [73].



The color of identically constructed trimethylidynecyanine dyes is determined by the nature of the heteroatom and becomes deeper in the order O < S < Se [73].

9-Methyl-10-oxonia- and 9-methyl-10-thionianthracene perchlorates also react with diazonium compounds to give perchlorates of the corresponding azo compounds XX [74].



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