REACTIONS OF p-HYDROXYPHENYL-1-THIOLANIUM COMPOUNDS AND p-(1-THIOLANIA)PHENOXIDE

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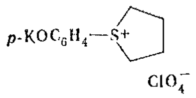
Under the influence of bases p-hydroxyphenyl-1-thiolanium salts readily form compounds with the participation of the p-(1-thiolania)phenoxide zwitterion, including oligomers with an $-S-(CH_2)_4-OC_6H_4-$ cell but with a terminal group with an unopened thiolanium ring. The terminal group is opened under the influence of amines to give an amino sulfide residue. A trissulfonium salt, viz., 1,1'-bis(p-hydroxyphenyl)(1''-thiolaniaphenoxide)dithiolanium diperchlorate, was also obtained with the participation of the indicated zwitterion, and its properties and reaction were studied. It is shown that, despite the previously adopted opinion, p-hydroxyphenylthiobutylpiperidinium salts are not intermediates in the reaction of p-hydroxyphenylthiolanium salts with amines, which leads to the formation of amino sulfides.

Like p-hydroxyphenyl-1-thianium salts [1], p-hydroxyphenyl-1-thiolanium salts readily form compounds with the participation of a zwitterion, viz., p-(1-thiolania)phenoxide, under the influence of bases; peculiarities associated with the lower strength of the C—S bond in the thiolanium ring (as compared with the thianium ring) [2] and with the geometry of the thiolanium ring, which differs from that of the thianium ring, are observed in this case.

The dihydrate (I) of the p-(1-thiolania)phenoxide zwitterion [2] is considerably less stable than p-(1-thiania)phenoxide hydrate (the latter exists in the form of dithianiadiphenoxide dihydrate II) [1]. Compound I gradually loses water even at ordinary temperatures. The anhydrous p-(1-thiolania)phenoxide zwitterion is unstable and undergoes polymerization [2] to give oligomers with an opened thiolanium ring. The mechanism of the oligomerization is probably similar to that for p-(1-thiania)phenoxide [1].

A peculiarity of the oligomerization of p-(1-thiolania)phenoxide as compared with the polymerization of p-(1-thiania)phenoxide consists in the fact that the oligomers obtained on the basis of thiolanium compounds have a terminal group with an unopened ring — the precursor of the monomer.

Potassium perchlorate, which is virtually insoluble in methanol, precipitates during the preparation of I by the action of a solution of potassium hydroxide in methanol on p-hydroxyphenylthiolanium perchlorate (III). However, the amount of the precipitated perchlorate does not exceed 80-85% of the theoretical value. Approximately 20% molar $KClO_4$ does not precipitate, and the K phenoxide of the starting sulfonium salt is possibly formed:



This phenoxide is a polymerization terminator in the dehydration of zwitterion I and subsequent polymerization at ordinary temperatures. In fact, a mixture of oligomers that is soluble (upon heating) in a nonpolar solvent such as anisole and contains perchlorate and potassium ions (which remain in the oligomers even after recrystallization from anisole) is formed. Oligomer IV, with mp 141-146°C, probably consists of mixed crystals with a variable composition. Oligomers IV are insoluble in water, alcohol, and acetone.

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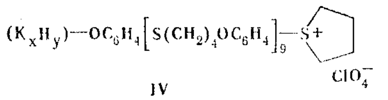
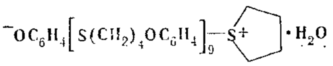
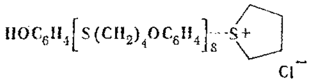
A small amount (12%) of oligomer V, with mp 136-139°C and a terminal cyclic group that does not contain inorganic ions, is obtained in the oligomerization of I by heating after extraction of the reaction product with hot toluene. Oligomers VI with a terminal unopened thiolanium ring are formed in the polymerization of the base obtained by the action of potassium hydroxide on p-hydroxyphenylthiolanium chloride (VII).

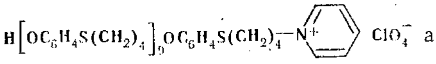

IV


V


VI

x+y=1

The structure of oligomers IV was confirmed by data from the IR spectra: adsorption bands with frequencies that are characteristic for sulfides* (1220-1270 cm^{-1}) and the perchlorate anion (1110 and 628 cm^{-1}). The presence of a terminal thiolanium group is confirmed by the reaction of the oligomers with amines, as a result of which the sulfonium compounds are converted to amino sulfides [3]. This makes it possible to modify the oligomers and convert the terminal ring to an $-S(CH_2)_4NR_2$ group. Thus the following oligomers were obtained from oligomers IV by the action of pyridine or piperidine, respectively: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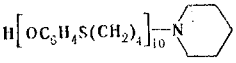

The described modification of the terminal group increases the solubility of the oligomers. Oligomers V also react with piperidine; however, modification of the terminal group proceeds with greater difficulty than in the case of oligomers IV.

The rapid quantitative formation of amino sulfides by the action of excess amounts of secondary amines on the thiolanium compounds was regarded in [3] as a two-step process, in the first step of which an ammonium salt of an aryl aminoalkyl sulfide is formed [for example, (p-hydroxyphenylthiobutyl)piperidinium perchlorate (VIII) in the reaction of perchlorate III with piperidine]. However, splitting out of an anion and the formation of an amino sulfide take place slowly and incompletely when perchlorate VIII or (p-hydroxyphenylthiobutyl)piperidinium hydrochloride (IX) is heated with 1 mole of piperidine in ethanol (the anion is removed more readily by treatment of perchlorate VIII with a strongly basic anion-exchange resin). It is more likely that an amino sulfide is formed as a result of nucleophilic attack by piperidine at the site of the $C-S^+$ bond in the first step of the reaction of a thiolanium compound with 2 moles of an amine, which was described in [3]; the fixation of the anion by a second molecule of piperidine favors the process.

In [1] it was shown that a bissulfonium salt, viz., 1-(p-hydroxyphenyl)(1'-thianiaphenoxide)thianium perchlorate (XI), is formed in the reaction of 1-(p-hydroxyphenyl)thianium perchlorate (X) with base II. In contrast to this base dihydrate I reacts with perchlorate III to give a trissulfonium salt, viz., 1,1'-bis(p-hydroxyphenyl)(1"-thiolaniaphenoxide)dithiolanium diperchlorate (XII). Trissulfonium salt XII is also formed in the reaction of a concentrated solution of the base in methanol with the calculated amount of perchloric acid. According to data from the IR spectrum and x-ray diffraction analysis [5], crystalline salt XII is constructed with the participation of hydrogen bonds. A broad structured band at 900-3200 cm^{-1} due to the stretching vibrations of an OH group that participates in hydrogen bonding is observed in the IR spectrum.

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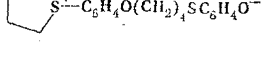
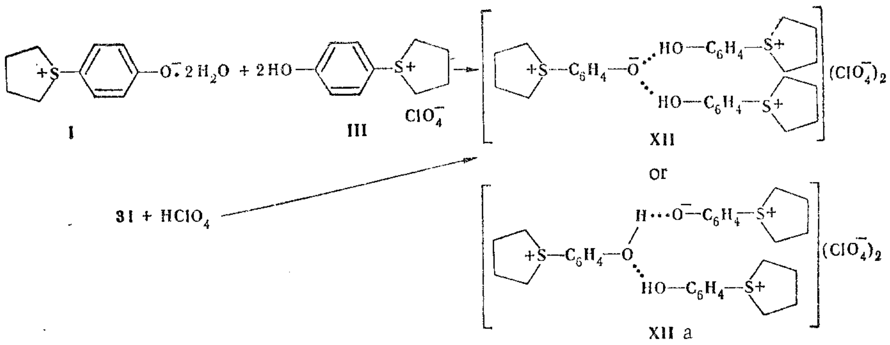
*Considering these data it may be assumed that in the p-(1-thiolania)phenoxide dimer, which we described in [4], one of the rings is probably open, and the structure of the dimer is probably



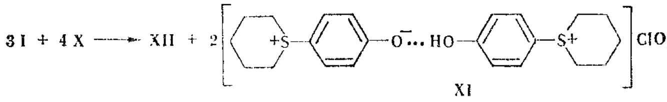


The center of gravity of the band is found at ∿1800 cm^{-1}; according to the correlation in [6], the distance of 2.50 Å between the oxygen atoms that participate in hydrogen bonding corresponds to this value. According to x-ray diffraction data [5], the distances between the oxygen atoms linked by hydrogen bonds are 2.45 and 2.51 Å. According to the equation in [7], the enthalpy of formation of a hydrogen bond is 13.5 ± 0.6 kcal/mole. Data from the IR spectra are included in this equation: $(\Delta H)^2 = 0.11(\Delta\nu - 40)$, where $\Delta\nu = \nu\mathrm{OH(free)} - \nu\mathrm{OH(assoc.)}$. From an approximate estimate νOH(free) = 3500 ± 100 cm^{-1} [8], and νOH(assoc.) = 1800 cm^{-1} with respect to the center of gravity of the OH band. The perchlorate anions in trissulfonium salt XII do not participate in hydrogen bonds. According to data from x-ray diffraction analysis, they have an undistorted tetrahedral configuration. This is responsible for the presence of a narrow absorption band at 1100 cm^{-1} (slightly resolved doublet) in the IR spectrum.

The complex cation of the trissulfonium salt may be formed by two hydrogen bonds in such a way that either the oxygen atom of the zwitterion interacts symmetrically with the hydroxy groups of two hydroxyphenylthiolanium fragments, thereby participating simultaneously in two hydrogen bonds (structure XII), or the zwitterion is linked by a hydrogen bond only with one thiolanium fragment, and the oxygen atom of this fragment is simultaneously an acceptor of a proton of a third thiolanium fragment (structure XIIa). One cannot choose between structures XII and XIIa, since the positions of the hydrogen atoms of the OH groups could not be determined by x-ray diffraction analysis.

Polysulfonium salts with "mixed" complex cations (containing heterorings with different sizes) are not formed in the reaction in methanol solutions of 1-(p-hydroxyphenyl)thianium perchlorate (X) with p-(1-thiolania)phenoxide dihydrate (I) or p-dithianium diperoxide dihydrate (II) with 1-(p-hydroxyphenyl)thiolanium perchlorate (III). Regardless of the conditions, only trissulfonium salt XII and bissulfonium salt XI are formed. The zwitterions are stabilized by "their own" p-hydroxyphenylsulfonium fragments — in other words, hydrogen bonds are formed only between the thianium (salt XI) or only between the thiolanium (salt XII) fragments.

This selectivity is possibly explained by the ratio of the energy contributions to the hydrogen bonding of the proton-donor and proton-acceptor fragments Δh_d and Δh_a (kcal$^{1/2}$·mole$^{-1/2}$). These values are constant for each fragment and are determined by its structure. The product of the contributions gives the bond energy $\Delta h_a \cdot \Delta h_d = \Delta H$ (kcal·mole^{-1}) [8, 9]. Stable crystalline polysulfonium salts with complex cations similar to those examined above are formed if the energy contributions of the acceptor and the donors have approximately equal values. This condition is not satisfied in the case of polysulfonium salts with "mixed" complex cations, and such compounds therefore cannot be formed.



XI

$$\mathrm{II} + 3\,\mathrm{III} \longrightarrow \mathrm{XI} + \mathrm{XII}$$

The mixture of salts XI and XII is readily separated by using the difference in their solubilities.

Dihydrate I adds phenol to give a salt with probable structure XIII.

XIII

Compound XIII, in contrast to a similar thianium derivative, viz., 1-(p-thianiaphenoxide)bisphenol [1], is unstable and readily decomposes to give oligomers of the V type.

The reactions of trissulfonium salt XII are similar to the reactions of thianium bissulfonium salts [1]. The cation of salt XII is decomposed by the action of both acids and bases. Diperchlorate XII is converted to perchlorate III by reaction with perchloric acid; p-hydroxyphenyl 4-piperidinobutyl sulfide (XIV) is formed when salt XII is heated with excess piperidine. Base I, which polymerizes during workup of the mixture, is formed in quantitative yield when a solution of salt XII is passed through an anion-exchange resin (in the OH form).

EXPERIMENTAL

Oligomerization of p-(1-Thiolania)phenoxide. A. Production of Oligomers IV. A solution of 2.41 g (43.2 mmole) of potassium hydroxide in 75 ml of methanol was added to a solution of 12.12 g (43.2 mmole) of perchlorate III in 130 ml of methanol. After 12 h, 4.72 g (79.5% of the theoretical value of potassium perchlorate was removed by filtration. The filtrate was evaporated *in vacuo*, and the residue was treated with acetone to precipitate 7.37 g of a mixture of dihydrate I and oligomers IV. After 12 days, the mixture contained S^+_{base} 0.89%, i.e., only 5% dihydrate I.* For the separation of I and III the oligomers were treated repeatedly with methanol. The insoluble part (4.87 g) consisted of oligomers IV with mp 137-142°C. In another experiment a 1.84-g sample of oligomers IV obtained by a similar procedure was recrystallized from anisole to give 1.41 g of oligomers with mp 142-150°C. Part (1.07 g) of this oligomer was once again recrystallized from 3.5 ml of anisole, and the precipitate was washed thoroughly with ether in a Soxhlet apparatus to remove the anisole to give 0.92 g of oligomers IV with mp 141-146°C. Found: C 63.1; H 6.4; Cl 1.9; K 1.0; S 16.8%. $C_{100}H_{120.5}ClK_{0.5}O_{14}S_{10}$ (i.e., $H_{0.5}K_{0.5}[C_{10}H_{12}OS]_{10}ClO_4$). Calculated: C 63.0; H 6.3; Cl 1.9; K 1.0; S 16.7%.

B. Preparation of Oligomers V. As in experiment A, a mixture of I and oligomers was obtained from 7.42 g of perchlorate III and potassium hydroxide. The mixture was heated at 100°C for 14 h (the weight loss due to dehydration was 11.2%), after which the mass of the oligomerization product was 5.26 g. The oligomerization product was extracted with toluene in a Soxhlet extractor. Cooling of the extract precipitated 0.65 g of oligomers V with mp 136-139°C (did not contain either K^+ or ClO_4^-). Found: C 66.3; H 6.5; S 17.6%. Calculated: C 66.1; H 6.7; S 17.6%.

C. Preparation of Oligomers VI. A mixture of 2.16 g (10 mmole) of chloride VII in 80 ml of methanol and 0.56 g (10 mmole) of potassium hydroxide in 20 ml of methanol was refluxed for 6 h, after which the solvent was removed by distillation, and the residue was dehydrated at 150-160°C for 4 h *in vacuo* (at 2 mm at the end of the reaction). The reaction product was extracted with benzene in a Soxhlet apparatus. Cooling of the extract precipitated 0.88 g of oligomers VI with mp 123-125°C. Found: C 63.7; H 6.1; Cl 2.2; S 17.8%. $C_{90}H_{109}ClO_9S_9$ (i.e., $[C_{10}H_{12}SO]_9 \cdot HCl$). Calculated: C 65.2; H 6.6; Cl 2.1; S 17.4%.

Reaction of Oligomer IV with Piperidine. A mixture of 4.20 g of oligomer IV and 15 ml of piperidine was refluxed for 3 h (the mixture became homogeneous near the boiling point). Cooling of the mixture precipitated a colorless oligomer that did not contain halogen. The oligomer was separated and washed with acetone and hexane to give 3.45 g (86.5%) of a product with mp 132-137°C (decomposition temperature 220-240°C), which crystallized from toluene and from anisole. Recrystallization from anisole gave a product with mp 130-134°C. Found: C 66.6; H 6.9; N 0.8; S 17.3%; M (by ebullioscopy in anisole) 1885. $C_{105}H_{131}NO_{10}S_{10}$ (i.e., $[C_{10}H_{12}SO]_{10} \cdot C_5H_{10}N$). Calculated: C 66.6; H 7.0; N 0.7; S 16.9%; M 1845.

Reaction of Oligomer IV with Pyridine. A mixture of 0.77 g of oligomer IV and 25 ml of pyridine was refluxed for 15 h, after which the pyridine was removed by distillation, and the residue was washed with ether, acetone, and methanol. The mass of the oligomer (mp 140-145°C) that was insoluble in these solvents was 0.70 g. Found: 64.4; H 6.4; Cl 1.3; N 0.7%. $C_{105}H_{126}ClNO_{14}S_{10}$ (i.e., $[C_{10}H_{12}SO]_{10} \cdot C_5H_5ClNO_4$). Calculated: C 63.7; H 6.3; Cl 1.8; N 0.7%.

Reaction of Oligomer V with Piperidine. A mixture of 0.3 g of oligomer V and 3 ml of

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*Note that $S = S^+_{base} + S^+_{sulfonium}$ in the zwitterion. These values were determined by titration of samples in acetic acid with a solution of perchloric acid in acetic acid by the method in [11].

piperidine was heated, during which the oligomer dissolved rapidly. The solution was refluxed for 3 h, after which it was worked up as in the preceding experiment to give 0.26 g of a mixture of oligomers with mp 135-139°C. Found: C 65.8; H 6.4; N 0.4; S 17.4%; M (by ebullioscopy in benzene) 1637. With allowance for M it was found that the product had empirical formula $(C_{10}H_{12}SO)_9 \cdot 0.5C_5H_{10}N$, i.e., probably only about half of the starting mixture of oligomers, viz., the part that contains sulfonium groups, had reacted with piperidine.

1-[4-(p-Hydroxyphenylthio)butyl]piperidinium Perchlorate (VIII). A 0.85-g (10 mmole) sample of piperidine was added to a hot solution of 2.80 g (10 mmole) of perchlorate III in 7 ml of methanol, and the mixture was refluxed for 6 h. It was then poured into ether, and the liberated oil was washed exhaustively with ether and hot hexane and allowed to stand for a long time in a desiccator over $CaCl_2$ to give 3.37 g (92.5%) of salt VIII with mp 91-93°C. Found: C 49.2; H 6.6; Cl 10.2; S (sulfide) 8.6% (determined by the method in [12]). $C_{15}H_{24}ClNO_5S$. Calculated: C 49.3; H 6.6; Cl 9.8; S 8.9%.

1-[4-(p-Hydroxyphenylthio)butyl]piperidinium Hydrochloride (IX). This compound, with mp 132-137°C, was obtained in 66% yield from chloride VII and 1 mole of piperidine by a method similar to that used to obtain salt VIII. No melting point depression was observed for a mixture of this product with salt IX obtained from amino sulfide XIV and hydrochloric acid by the method in [3].

Reaction of Perchlorate VIII with Piperidine. A 0.42-g (5 mmole) sample of piperidine was added to a refluxing solution of 1.83 g (5 mmole) of VIII in 5 ml of ethanol, and the mixture was refluxed for 8 h. The solvent was removed by distillation, and the residue was extracted successively with hot hexane and benzene to give 0.38 (29%) of (p-hydroxyphenylthio)-butylpiperidine XIV with mp 97.5-104°C. No melting-point depression was observed for a mixture of this product with a genuine sample. The inextractable residue was dissolved in ethanol, and the solution was refluxed with 2 moles (based on salt VIII) of piperidine for 8 h. The mixture was worked up as described above to give another 0.3 g (26%) of sulfide XIV. The inextractable residue (0.76 g) was piperidine perchlorate.

Reaction of Hydrochloride IX with Piperidine. A 0.42-g (5 mmole) sample of piperidine was added to a solution of 1.5 g (5 mmole) of IX in 3 ml of ethanol, and the mixture was refluxed for 8 h. The solvent was evaporated, and the residue was extracted with ether and benzene to give 0.91 g (69%) of XIV with mp 103-107°C. The inextractable residue was dissolved in ethanol, and the solution was refluxed with 2 moles (based on salt IX) of piperidine and extracted to give another 0.22 g (16%) of amino sulfide XIV. The inextractable residue (0.56 g), with mp 225-230°C, was piperidine hydrochloride. No melting-point depression was observed for a mixture of this product with a genuine sample.

Treatment of Hydrochloride IX with an Anion-Exchange Resin. A solution of 0.25 g (0.83 mmole) of IX in 4 ml of absolute methanol was percolated through a column packed with 2 ml of ARA-2p anion exchange resin in the OH form, and the solvent was evaporated from the desorbate to give 0.18 g (84%) of amino sulfide XIV with mp 106-108°C. No melting-point depression was observed for a mixture of this product with a genuine sample.

Trissulfonium Salt XII. A) A solution of 5 mmole of freshly prepared base I [2] in 2 ml of methanol (2.5 moles/liter) was added gradually to a solution of 2.8 g (10 mmole) of perchlorate III in 15 ml of methanol (0.66 mole/liter). After 2 days, 2.28 g of salt XII was removed by filtration and washed with methanol and acetone to give a product with mp 131-132°C in 61.5% yield. Another 1.15 g (31%) of salt XII was isolated from the mother liquor. Found: C 48.1; H 5.1; Cl 9.9; S 13.2; S^+_{base} 4.2%. $C_{30}H_{38}Cl_2O_{11}S_3$. Calculated: C 48.4; H 5.1; Cl 9.5; S 12.9; S^+_{base} 4.3%. Solubility of salt XII at 20°C: 1.5% in alcohol, 1.4% in acetone, 2.9% in water.

B) A 1.97-g (8 mmole) sample of 42% perchloric acid was added to a solution of 12 mmole of I in methanol (0.6 mole/liter), after which the solvent was evaporated, and the residue was washed with acetone to give 1.93 g (66.5%) of salt XII.

Reaction of Perchlorate X with Base I. A solution of 1 g (5 mmole) in I in 23 ml of methanol was added to a solution of 1.47 g (5 mmole) of salt X in 15 ml of methanol (0.33 mole/liter). After 24 h, 0.75 g (61%) of salt XI was removed by filtration. Recrystallization from alcohol gave 0.45 g of the salt with mp 176-177°C. The composition and IR spectrum were identical to the composition and IR spectrum of perchlorate XI obtained by the method in [1]. No melting-point depression was observed for a mixture of these products. The mother liquor remaining after separation of salt XI was concentrated *in vacuo* to precipitate 0.97 g (quantitative yield) of tris salt XII. Salt XII was recrystallized twice from alcohol to give 0.76 g of a substance that was identical to a sample of XII obtained in the preceding experiments.

Reaction of Dihydrate II with Perchlorate III. A solution of 1 g (5 mmole) of II in 6 ml of methanol was added to a solution of 1.40 g (5 mmole) of salt III in 12 ml of methanol (0.41 mole/liter). Virtually pure perchlorate XI [0.76 g (97%)] precipitated almost immediately. Recrystallization from 38 ml of alcohol gave 0.45 g of perchlorate XI with mp 177-178°C, which was identical to salt XI obtained by the method in [1]. The mother liquor remaining after separation of XI was concentrated *in vacuo* to 5 ml, a few drops of acetone and ether were added until the solution became turbid, and the mixture was cooled to −13°C to precipitate 1.07 g (90%) of crude perchlorate XII. Recrystallization from 8 ml of alcohol gave 0.77 g (64%) of salt XII, which was identical to the compound obtained in the preceding experiments.

Reaction of Dihydrate I with Phenol. A solution of 10 mmole of dihydrate I in methanol was added to a solution of 2.07 g (22 mole) of phenol in 10 ml of dry ether, the solvents were evaporated *in vacuo* without heating, and the residue was dehydrated by distillation with benzene. Extraction with ether gave 0.21 g of phenol. The mass of ether-insoluble XIII, with mp 70-71°C, was 3.83 g. Found: C 69.8; H 6.4; S 9.4%. $C_{38}H_{42}O_5S_2$. Calculated: C 71.0; H 6.5; S 9.2%. Found after 2 days: S^+ 6.6%; S^+ + S (sulfide) by the method in [12] 8.5%. The reaction product was not completely soluble in alcohol (undissolved oligomers remained). An intense band at 1250 cm^{-1} (sulfide group) appeared in the IR spectrum.

Reaction of Diperchlorate XII with Perchloric Acid. A 0.06-g sample of 42% perchloric acid was added to a solution of 0.2 g of salt XII in 4 ml of methanol, and the mixture was refluxed for 5 min. The solvent was removed by evaporation, and the residue was separated and washed with acetone and ether to give 0.11 g (47%) of perchlorate III. No melting-point depression was observed for a mixture of this product with a genuine sample of III.

Reaction of Diperchlorate XII with Piperidine. A mixture of 0.2 g of salt XII with 3 ml of piperidine was heated to the boiling point, after which the excess piperidine was removed by distillation, and amino sulfide XIV was extracted with benzene by heating and converted to hydrochloride IX by heating with hydrochloric acid and treatment with acetone. This procedure gave 0.1 g of hydrochloride IX with mp 143-148°C. No melting-point depression was observed for a mixture of this product with a genuine sample.

Treatment of Diperchlorate XII with an Anion-Exchange Resin. A solution of 0.37 g (0.5 mmole) of tris salt XII in methanol was percolated through 2 ml of AV-17 anion exchange resin (in the OH form), and the eluate was evaporated *in vacuo* to give 0.23 g (86%) of a substance that did not contain halogen and had mp 142-146°C (chiefly a mixture of oligomers). Found: S^+ 0.3% (i.e., 22% of base I). Treatment of the reaction product with 2 ml of ethanol precipitated 0.09 g of an oligomer with mp 146-149°C. Found: C 66.8; H 6.8; S 16.8%. $C_{10}H_{12}OS$. Calculated: C 66.6; H 6.7; S 17.7%.

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COMPARISON OF THE THERMAL AND MASS-SPECTROMETRIC FRAGMENTATION OF 2,4-THIOXO(OXO)DIHYDRO-5,6-BENZO-1,3-THIAZINES

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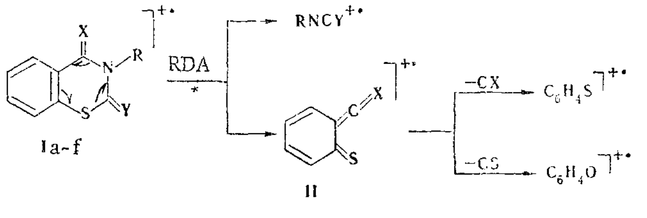
The pyrolysis of a series of phenyl- and methyl-substituted 2,4-thioxo(oxo)dihydro-5,6-benzo-1,3-thiazines at the Curie point was studied. Processes involving retrodiene fragmentation with the formation of, respectively, phenyl isothiocyanate or phenyl isocyanate lie at the foundation of the thermal transformations of these compounds. Among other stable pyrolysis products, aniline, benzonitrile, and benzene were identified by gas chromatography and mass spectrometry. Pyrolysis directly in the mass spectrometer gives a larger number of fragmentation products, since it makes it possible to also record compounds with low stabilities. The results of the two methods of analysis correlate well with one another.

Owing to its good reproducibility, pyrolysis at the Curie point has become widely used. In combination with gas-chromatographic, mass-spectrometric, and, particularly, chromatographic mass-spectrometric methods of analysis it is frequently used to study the processes involved in the destruction of various polymeric products [1]. This method also makes it possible to investigate the thermal fragmentation of low-molecular-weight compounds; pyrolysis at the Curie point in combination with mass- or chromatographic mass-spectrometric analysis of the fragmentation products makes it possible to conduct a comparative study of the behavior of an organic substance both under electron impact and in the case of thermal action. With this in mind, we subjected 2,4-thioxo(oxo)dihydro-5,6-benzo-1,3-thiazines (Ia-f) to this sort of investigation.

It is known that these compounds under the influence of electron impact (70 eV) undergo fragmentation via the scheme of a retro-Diels—Alder (RDA) process (Scheme 1), which is confirmed by the intense peaks of metastable ions [2]. This pathway becomes particularly appreciable when the ionization energy is decreased to 12 eV (Table 1).

Scheme 1



I a $X=Y=S$, $R=C_6H_5$; b $X=O$, $Y=S$, $R=C_6H_5$;
c $X=S$, $Y=O$, $R=C_6H_5$; d $X=Y=O$, $R=C_6H_5$;
e $X=S$, $Y=O$, $R=CH_3$; f $X=Y=O$, $R=CH_3$

The intensity of the peak of the corresponding metastable ion reaches $1 \cdot 10^{-4}$ of the intensity of the daughter ion, and the indicated fragmentation pathways consequently are realized from the ground energy state of the molecular ion [3]. In this case one should expect a pronounced analogy between fragmentation under electron impact and fragmentation in the case of thermal action. We obtained the pyrolytic mass spectra of Ia-f at an ionization energy of 14 eV, an emission current of 24 μA, a pyrolysis temperature of 800°C, and a pyrolysis

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