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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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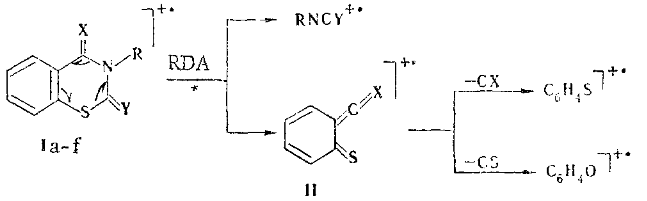
UDC 543.51

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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Karl Marx University, German Democratic Republic, Leipzig 7010. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 329-332, March, 1983. Original article submitted July 17, 1982.

0009-3122/83/1903-0265$07.50

TABLE 1. Mass Spectra of Ia-f (12 eV) and Processes Confirmed by Peaks of the Corresponding Metastable Ions (m*)

| Compound | m/z (relative intensity, %) | m* found | Process |
|---|---|---|---|
| Ia | 287 (100), 210 (14,7), 184 (0,25), 152 (0,25) | 153,66 | $287^{+\cdot} \rightarrow 210^{+} + 77$ |
| Ib | 271 (100), 168 (3,6), 136 (14,4) | 104,15 | $271^{+\cdot} \rightarrow 168^{+} + 103$ |
| | | 68,25 | $271^{+\cdot} \rightarrow 136^{+} + 145$ |
| Ic | 271 (100), 242 (1,9), 194 (12,1), 105 (10,8) | 138,88 | $271^{+\cdot} \rightarrow 194^{+} + 77$ |
| | | 40,68 | $271^{+\cdot} \rightarrow 105^{+} + 166$ |
| Id | 255 (83,5), 136 (100) | 72,53 | $255^{+\cdot} \rightarrow 136^{+} + 119$ |
| Ie | 209 (100), 181 (2,5), 152 (2,4) | 110,54 | $209^{+\cdot} \rightarrow 152^{+} + 57$ |
| If | 193 (100), 136 (37,6) | 95,83 | $193^{+\cdot} \rightarrow 136^{+} + 57$ |

TABLE 2. Products of Pyrolysis of 1,3-Thiazines Ia-f ($\%\Sigma_{11}$)[a]

| Compound | II | $C_6H_5NCS$ | $C_6H_5NCO$ | $C_6H_5SH$ | $C_6H_4CS$ | $C_6H_5CO$ | $C_6H_5CN$ | $C_6H_5NH_2$ | $C_6H_6$ | $CS_2$ | COS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | — | 18,7 | — | 18,0 | 12,2 | — | 16,9 | 5,9 | 6,7 | 10,1 | — |
| Ib | 12,2 | 15,1 | 8,2 | 16,2 | 10,6 | 3,1 | 17,1 | 5,2 | 4,2 | 4,7 | 4,0 |
| Ic | 2,3 | 6,5 | 14,7 | 21,9 | 18,0 | 3,9 | 7,0 | 7,7 | 7,7 | 5,0 | 5,2 |
| Id | 8,5 | 4,4 | 15,4 | 21,1 | 21,2 | 1,7 | 4,2 | 10,0 | 5,8 | 4,1 | 5,1 |
| Ie | 2,3 | 4,4/3,2[b] | –/4,5[c] | 13,9 | 8,7 | — | 3,0 | 2,9 | 4,1 | 9,4 | 5,4 |
| If | 6,0 | 0,8/9,5[b] | –/7,8[c] | 18,4 | 22,5 | — | 7,2 | 5,1 | 7,1 | 8,4 | 8,1 |

[a] The pyrolysis products were identified in the pyrolytic mass spectra in the form of cation radicals or cations.

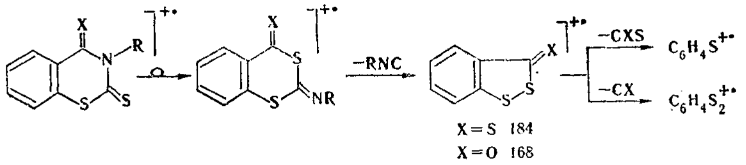
[b] $C_6H_5NCS/CH_3NCS$.

[c] $C_6H_5NCO/CH_3NCO$.

time of 3 sec. The fragments observed in the mass spectra are presented in Table 2, from which it is apparent that retrodiene fragmentation products predominate in the mixtures. Thus a large amount of phenyl isothiocyanate or phenyl isocyanate, which reaches 18.7 and 15.4% in the case of Ia,d, respectively, is observed in the mixtures in the case of Ia-d. This is apparently associated with the fact that such fragments can be formed from the indicated compounds not only as a result of an RDA process. A second component (II, Scheme 1) is almost not formed in the case of Ia,c.* Correspondingly, this ion is also absent in the mass spectra of the above-mentioned compounds (Table 1). On the other hand, fragment II is observed in appreciable amounts in both the mass spectra and among the products of pyrolysis of Ib,d.

The presence of significant amounts of benzonitrile among the products of pyrolysis of Ia,b is probably associated with thermal rearrangements of the starting compounds. Similar processes also occur in the case of electron impact (see Scheme 2); this is confirmed by the presence of a rather intense peak of an ion with m/z 168 in the mass spectrum of Ib. However, a peak of the corresponding ion (m/z 184) is absent in the mass spectrum of Ia.

Scheme 2



The formation of a $C_6H_5CO^+$ fragment in both thermal and mass-spectrometric processes is probably explained by migration of a phenyl residue to the carbonyl carbon atom. These fragments are absent in the mass spectra of the products of pyrolysis of methyl-substituted thiazines.

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*The appearance of a very small amount of II in the products of pyrolysis of Ic is apparently associated with partial rearrangement processes of the latter.

Other products of the thermal transformations are thiophenol, aniline, and benzene, as well as a $C_5H_4CS$ fragment, which is formed as a result of ejection of a CX molecule by II. The formation of carbon disulfide is difficult to explain, and a peak of $C_6H_4^+$ ions is superimposed on its signal (m/z 76) in the mass spectrum. At the same time, in complete agreement with the structures of Ic,d, the largest amount of COS is observed among their pyrolysis products. Its presence in the pyrolyzate of Ib is apparently associated with the rearrangement mentioned above (see Scheme 2).

The pyrolytic mass spectra of methyl-substituted Ie and If also contain appreciable amounts of RDA fragmentation products and, except for some features, are similar in many respects to the mass spectra of the phenyl-substituted compounds. Thus the pyrolysis of If gives an unexpectedly large amount of methyl isothiocyanate, and a significant amount of phenyl isocyanate is present in the products of pyrolysis of Ie.

Phenyl isothiocyanate, benzonitrile, aniline, and benzene were identified in the products of pyrolysis at the Curie point during a chromatographic mass-spectrometric study. Their quantitative ratio bears the same character as in the case of pyrolytic mass spectrometry; however, because of the superimposition of the chromatographic peaks and the necessity to subject large amounts of the substance to pyrolysis, which promotes side reactions, the reproducibility of these data is not very high [4, 5].

Thus the processes involved in the pyrolysis of the investigated 1,3-thiazines Ia-f reproduce quite satisfactorily the pattern of the fragmentation of these compounds under electron impact. All of the rearrangements that occur in the molecular ion at both 70 and 12 eV are also observed in the thermal destruction of these substances. This direct relationship between pyrolysis at the Curie point and mass spectrometry promises great possibilities for the prediction of the thermal behavior of organic compounds. This method, in contrast to combination of pyrolysis at the Curie point with chromatographic mass spectrometry, makes it possible to also detect even very reactive unstable fragmentation products that are often similar to the fragments that are formed in the fragmentation of the same compounds under electron impact.

## EXPERIMENTAL

The investigated 1,3-thiazines (Ia-f) were obtained by the methods described in [6, 7].

The mass spectra were recorded with a Varian MAT CH-6 mass spectrometer (Federal Republic of Germany). Pyrolysis at the Curie point was realized in a Fischer pyrolyzer (Federal Republic of Germany). The latter was connected to the mass spectrometer by means of a specially prepared rod with an aperture for direct introduction of samples into the mass spectrometer. The chamber of the pyrolyzer was connected to the rod by means of a ground glass joint. A glass tube secured inside by means of silicone gaskets was inserted into the rod in order to reduce contact of the pyrolysis products with the metal surface to a minimum.

The pyrolytic mass spectra were obtained at 70 eV (11 μA) and 12 eV (24 μA). The temperature of the rod was 125°C, the temperature of the vessel containing the sample and the line leading to the ion source were 180 and 185°C, respectively, and the temperature of the ion source was 190°C. The optimum pyrolysis temperature was found by investigating the temperature dependence in the case of Ic. The most nearly complete pyrolysis was acheived at 800°C for a process time of 3 sec. The pyrolysis time affected only the yields of products — it did not affect the fragmentation process. An ∿100 μg sample of the corresponding compound (in the form of a solution in THF) placed in a special spiral-shaped vessel, from which the solvent was then evaporated, was subjected to pyrolysis. Tetrahydrofuran was the only (of the many tested) solvent that made it possible to obtain a thin film of the substance located very close to the walls — an indispensable condition for obtaining reproducible results in the pyrolysis studies. The relative error in the determination of the individual pyrolysis products ranged from 5 to 10% for the data presented in Table 2. Chromatographic mass-spectrometric analysis of the pyrolysis products was realized with a glass column (6.3 m by 2 mm) containing 8% DS-550 on Chromosorb W. The column temperature was 180°C (isotherm). The pyrolysis conditions were identical to those described above.

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# BASICITIES AND STRUCTURES OF 2H,6H-2,6-DIMETHYL-4-AMINO-1,3,5-DITHIAZINE AND ITS N-ACYL DERIVATIVES

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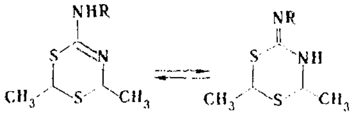
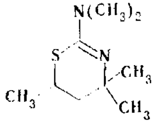
UDC 543.257.1:547.876'869.1:541.623

On the basis of a study of the basic properties of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine and its N-acyl derivatives it was concluded that N-acyldithiazines exist primarily in the amino form in methanol and acetone, regardless of the type of substituent (donor or acceptor) in the acyl fragment of these molecules. The intramolecular interrelationships between the exocyclic substituent and the protonation center in the investigated compounds correspond to the criteria of the ortho effect of nitrogen-containing heteroaromatic compounds.

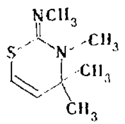
A study of N-acyl derivatives of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine (II-VII) in solution in chloroform, diethyl ether, and ethanol by IR and UV spectroscopy [1] showed that electron-acceptor substituents R' in the acyl fragment of these molecules (COR', where R' = $C_6H_5$, $CH_2Cl$, and $SO_2C_6H_4Me$-4) shift the tautomeric equilibrium to favor imino form b:



a I-VII b



VIII



IX

Ia R=H; IIa,b R=$COCH_3$; IIIa,b R=$COC_3H_7$; IVa,b R=$COC_4H_9$; Va,b R=$COC(CH_3)_3$; VIa,b R=COPh; VIIa,b R=$COCH_2Cl$

The existence of the indicated compounds in solutions in the form of a mixture of two tautomeric forms a and b may evidently be reflected in their reactivities. Thus, for example, a study by PMR spectroscopy of the direction of protonation in substituted 2-amino-4H-1,3-thiazines [2] with fixed amino (VIII) and imino (IX) forms that exclude tautomeric conversion indicates transfer of the protonation center in the imino form from the ring nitrogen atom (as in the case of VIII) to the exocyclic nitrogen atom. The higher basicity of IX as compared with VIII is the result of transfer of the protonation center. It is apparent from structures VIII and IX that 2-amino-4H-1,3-thiazine derivatives have a structure that is similar to that of the N-acyl derivatives of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine (a, b) that we previously investigated. It might therefore be expected that in the protonation of I-VII, which, according to the IR and UV spectroscopic data, are equilibrium mixtures of the a and b forms, the ratios of the basic strengths of their imino and amino forms would be retained in the same way as for the above-indicated VIII and IX, i.e., the basicity of the imino tautomer will be higher than that of the amino form. In this case the experimentally determined dissociation constants ($pK_a$) of the investigated N-acyl derivatives in solutions will be the effective dissociation constants of the equilibrium mixtures, which reflect the overall basicities of the imino and amino forms of these compounds. In conformity with the theory of acid-base protolytic tautomeric equilibria [3, 4] this fact may lead to disruption of the linearity be-

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 333-337, March, 1983. Original article submitted July 14, 1982.

0009-3122/83/1903-0268$07.50