

INVESTIGATION OF THE STRUCTURE AND THERMOLYSIS  
OF QUATERNARY SALTS OF 2-ALKYL- AND 2-ARYLAMINO  
DERIVATIVES OF THIAZOLINES

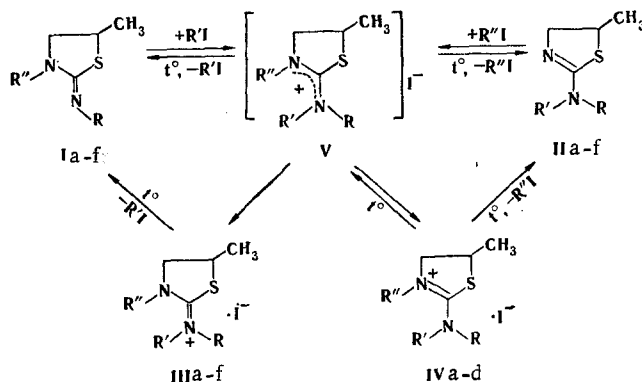
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2-Arylamino derivatives of 5-methylthiazoline react with alkyl iodides to give quaternary salts with primarily an exocyclic orientation of the C=N bond, while the C=N bond is localized in the ring in the corresponding salts of 2-alkylamino derivatives of thiazoline. The decomposition of these salts leads to the corresponding 2-arylaminothiazolidines and 2-alkylaminothiazolines.

A study by means of mass spectrometry of quaternary salts of 2-aminothiazolines that have an aryl grouping attached to the exocyclic nitrogen atom as one of the substituents has made it possible to establish that processes involving primarily the splitting out of an alkyl grouping from the exocyclic nitrogen atom are readily realized in the gas phase [1]. In the present research we studied the structures of the alkyl and aryl derivatives of thiazolinium iodides by means of the PMR spectra and investigated their behavior under thermal decomposition conditions.

We have previously shown [2] that aryl substituents attached to the exocyclic nitrogen atom in 2-aminothiazoline shift the amino-imino equilibrium to favor the imino form, while alkyl substituents make the amino form more stable. We assumed that the C=N bond in the quaternary salts of tautomeric 2-amino-5-methylthiazolines exists in the equilibrium that is characteristic for the starting unfixed base, i.e., that the cations of thiazolinium iodides with 2-N-aryl substituents have preferred structure III, whereas the 2-N-alkyl derivatives have preferred structure IV, although the existence of form V with delocalization of the positive charge over the system of amidine bonds also cannot be excluded.



In fact, a comparison of the PMR spectra of IIIa obtained by the reaction of bases Ia and IIa with methyl iodide shows their completely identical character: Whereas the signal of the N-CH<sub>3</sub> (endo) group in the PMR spectra of base Ia lies at 2.84 ppm, and the signal of the N-CH<sub>3</sub> (exo) group of base IIa is found at 3.30 ppm (Table 1), the spectrum of IIIa contains signals at 2.93 ppm (endo, N-CH<sub>3</sub>) and at 3.70 ppm (exo, N-CH<sub>3</sub>) (Table 2), and this constitutes evidence for considerable localization of the positive charge on the exocyclic nitrogen atom and its correspondingly greater double bond character with the carbon atom in the 2 position of the thiazoline ring. Localization of the charge on the exocyclic nitrogen atom also gives rise to a shift in the signals of the aryl groups in quaternary salts III to 7.50 ppm as compared with 6.95-7.25 ppm in bases I and II.

TABLE 1. Spectral Data for Thiazolines I and II

| Com-<br>pound   | R  | R'                            | R''                           | PMR, $\delta$ , ppm |        |        | IR spec-<br>trum,<br>cm <sup>-1</sup> |
|-----------------|--|-------------------------------|-------------------------------|---------------------|--------|--------|---------------------------------------|
|                 |  |                               |                               | R                   | R'     | R''    |                                       |
| Ia              | C <sub>6</sub> H <sub>5</sub>                            | —                             | CH <sub>3</sub>               | 7,00m               | —      | 2,84 s | —                                     |
| Ib              | C <sub>6</sub> H <sub>5</sub>                            | —                             | C <sub>2</sub> H <sub>5</sub> | 7,00m               | —      | 1,00 t | —                                     |
| Ic              | C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> | —                             | CH <sub>3</sub>               | 7,00q               | —      | 2,84 s | —                                     |
| I <sub>d</sub>  | C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>               | —                             | CH <sub>3</sub>               | 2,22s               | —      | —      | —                                     |
| Ie              | CH <sub>3</sub>  | —                             | CH <sub>3</sub>               | 6,95 q              | —      | 2,84s  | —                                     |
| If              | CH <sub>3</sub>  | —                             | C <sub>2</sub> H <sub>5</sub> | 2,84 s              | —      | 2,70s  | 1645                                  |
| Ig              | CH <sub>3</sub>  | —                             | C <sub>3</sub> H <sub>7</sub> | 2,80 s              | —      | 1,04 t | 1640                                  |
| II <sub>a</sub> | CH <sub>3</sub>  | —                             | C <sub>3</sub> H <sub>7</sub> | 2,84s               | —      | 3,20q  | 1640                                  |
| II <sub>a</sub> | C <sub>6</sub> H <sub>5</sub>                            | CH <sub>3</sub>               | —                             | 7,25s               | 3,30 s | —      | —                                     |
| II <sub>b</sub> | C <sub>6</sub> H <sub>5</sub>                            | C <sub>2</sub> H <sub>5</sub> | —                             | 7,10s               | 1,03 t | —      | —                                     |
| IIc             | C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> | CH <sub>3</sub>               | —                             | 7,10s               | 3,70 q | —      | —                                     |
| II <sub>d</sub> | C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>               | CH <sub>3</sub>               | —                             | 2,25s               | 3,30 s | —      | —                                     |
| IIe             | C <sub>2</sub> H <sub>5</sub>                            | C <sub>2</sub> H <sub>5</sub> | —                             | 7,20s               | 3,30 s | —      | —                                     |
| II <sub>f</sub> | CH <sub>3</sub>  | CH <sub>3</sub>               | —                             | 1,10 t              | —      | —      | 1610                                  |
|                 |  |                               |                               | 3,35 q              | —      | —      | 1610                                  |
|                 |  |                               |                               | 2,83 s (6H)         | —      | —      | 1612                                  |

TABLE 2. Characteristics and Data from the PMR Spectra of Thiazolium Iodides III and IV

| Com-<br>pound    | R  | R'                            | R''                           | mp, * °C | Start-<br>ing<br>bases | Parameters of the PMR<br>spectra, $\delta$ , ppm |             |        | Decom-<br>position<br>product | Per<br>centage |
|------------------|--|-------------------------------|-------------------------------|----------|------------------------|--|-------------|--------|-------------------------------|----------------|
|                  |  |                               |                               |          |                        | R  | R'          | R''    |                               |                |
| IIIa             | C <sub>6</sub> H <sub>5</sub>                            | CH <sub>3</sub>               | CH <sub>3</sub>               | 160—163  | Ia, IIa                | 7,50m  | 3,70s       | 2,93s  | Ia                            | 100            |
| IIIb             | C <sub>6</sub> H <sub>5</sub>                            | CH <sub>3</sub>               | C <sub>2</sub> H <sub>5</sub> | 134—135  | Ib, IIa                | 7,50m  | 3,70s       | 1,00t  | Ib                            | 100            |
| IIIc             | C <sub>6</sub> H <sub>5</sub>                            | CH <sub>3</sub>               | C <sub>3</sub> H <sub>7</sub> | 91—93    | IIa                    | 7,50m  | 3,68 s      | 3,30q  |                               |                |
| IIId             | C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> - <i>p</i> | CH <sub>3</sub>               | CH <sub>3</sub>               | 141—143  | Ic, IIc                | 7,30q  | 3,65 s      | 0,55 t | Ic                            | 100            |
| IIIe             | C <sub>6</sub> H <sub>4</sub> Cl- <i>p</i>               | CH <sub>3</sub>               | CH <sub>3</sub>               | 165—168  | Id, II <sub>d</sub>    | 2,30 s   | 7,53q       | 3,10m  |                               |                |
| III <sub>f</sub> | C <sub>6</sub> H <sub>5</sub>                            | C <sub>2</sub> H <sub>5</sub> | CH <sub>3</sub>               | 110—115  | IIf                    | 7,50m  | 1,20t       | 2,90 s | Ia                            | 90             |
| IVa              | C <sub>2</sub> H <sub>5</sub>                            | C <sub>2</sub> H <sub>5</sub> | CH <sub>3</sub>               | 80       | IIe                    | 1,40 t   | 3,60s       | 3,82q  | IIb                           | 10             |
| IVb              | CH <sub>3</sub>  | CH <sub>3</sub>               | CH <sub>3</sub>               | 120—122  | Ie, II <sub>f</sub>    | 3,40 s (6H)                                      | 3,60 s (3H) |        | IIe                           | 95             |
| IVc              | CH <sub>3</sub>  | CH <sub>3</sub>               | C <sub>2</sub> H <sub>5</sub> | 105—107  | If, II <sub>f</sub>    | 3,40 s (6H)                                      | 1,35t       |        | Ie                            | 50             |
| IV <sub>d</sub>  | CH <sub>3</sub>  | CH <sub>3</sub>               | C <sub>3</sub> H <sub>7</sub> | 96—99    | II <sub>f</sub>        | 3,40 s (6H)                                      | 3,7—4,1m    |        | II <sub>f</sub>               | 50             |
|                  |  |                               |                               |          |                        |  | 1,00 t      |        | If                            | 60             |
|                  |  |                               |                               |          |                        |  | 3,55—4,00 m |        | Ig                            | 40             |
|                  |  |                               |                               |          |                        |  |             |        | II <sub>f</sub>               | 55             |
|                  |  |                               |                               |          |                        |  |             |        |                               | 45             |

\*Purified by recrystallization from alcohol.

TABLE 3. Characteristics of Thiazolines I-IIe, f

| Com-<br>pound   | bp, °C [mm<br>(mercury<br>column)] | $n_D^{20}$ | Found, % |      |      | Empirical<br>formula                            | Calc., % |      |      |
|-----------------|------------------------------------|------------|----------|------|------|---|----------|------|------|
|                 |                                    |            | C        | N    | S    |   | C        | N    | S    |
| Ie              | 98—100 (2)                         | 1,5300     | 50,4     | 19,0 | 21,8 | C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> S | 50,0     | 19,4 | 22,2 |
| If              | 116 (2)                            | 1,5270     | 53,1     | 17,7 | 20,0 | C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> S | 53,2     | 17,7 | 20,2 |
| IIe             | 113 (2)                            | 1,5278     | 50,2     | 19,1 | 21,7 | C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> S | 50,0     | 19,4 | 22,2 |
| II <sub>f</sub> | 132 (2)                            | 1,5170     | 55,9     | 16,4 | 18,6 | C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> S | 55,8     | 16,3 | 18,6 |

Thus quaternization of 2-N-arylaminothiazolidines I with alkyl iodides does not change the structure peculiar to the base, while quaternization of 2-N-arylaminothiazolidines with the II structure, which takes place at the ring nitrogen atom, is accompanied by its isomerization to amino form III, which is probably thermodynamically more stable.

The PMR spectra of the quaternary salts of 2-alkylaminothiazolines IV, in contrast to the spectra of 2-N-aryl-substituted thiazolines, provide evidence for considerably greater double bond character of the ring nitrogen atom. Thus a shift to weaker field of the signals

of both the exo- and endo-methyl groups is observed in the PMR spectrum of quaternary salt IV. However, this shift is greater for the methyl group attached to the endocyclic nitrogen atom (Table 2).

To exclude the possibility of isomerization during the exothermic quaternization of the thiazolines, the reaction with alkyl iodides was carried out with cooling of the reagents with subsequent maintenance at 0°C until crystallization of the salt was complete. The thiazolinium iodides isolated under such conditions had stable III and IV states. An intermediate salt (mp 122-123°C), which after heating in alcohol was converted to stable salt IVc (mp 105-107°C), was obtained only in the quaternization of base II<sub>f</sub> with ethyl iodide.

The thermal decomposition of the quaternary salts of 2-alkyl- and 2-arylaminothiazolines was directed primarily by the preferred splitting out of a methyl radical (as compared with an ethyl or propyl radical) and secondarily by the splitting out of a radical from the quaternary nitrogen atom [3]. Thus imino compounds I were obtained in the thermolysis of the quaternary salts (IIIa-e) of 2-arylaminothiazolines, whereas a mixture of bases Ia and IIb was obtained in the decomposition of salt III<sub>f</sub>.

In the thermolysis of the quaternary salt (IVa) of a 2-alkylaminothiazoline the preferred splitting out of a methyl radical from the quaternary nitrogen atom leads to the primary production of aminothiazoline II<sub>b</sub>. However, the decomposition of salt IV<sub>b</sub>, which has methyl groups attached to the exocyclic and endocyclic nitrogen atoms, leads, as a consequence of the lability of the charge density within the confines of the amidine fragment, to the production of a mixture of bases with equal percentages of amino- and imino-thiazolines Ie and II<sub>f</sub>. A mixture of thiazolines I and II was also obtained in the thermolysis of quaternary salts IV<sub>c</sub>, d, but the mixture had a higher percentage of the imino derivative.

It should be noted that the PMR spectra proved to be unsuitable for analysis of the products of the decomposition of the quaternary salts (IV) of 2-alkylaminothiazolines because of the closeness of the signals of the exo- and endo-methyl groups in 2-alkylaminothiazolines (I, II). The IR spectra proved to be more suitable, since the significant difference in the absorption bands of the stretching vibrations of the C=N double bond in the amino and imino compounds (30 cm<sup>-1</sup>; Table 1) made it possible to not only carry out the analysis of the decomposition products but also to determine their percentages in the mixtures.

#### EXPERIMENTAL

The IR spectra of thin layers of the compounds between KBr plates without dilution were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl<sub>4</sub> and CDCl<sub>3</sub> were recorded at 20°C with a Tesla BS-467 spectrometer with tetramethylsilane as the internal standard. The chemical shifts are given on the δ scale.

Compounds Ia-d and IIa-d were obtained by the method in [4], Ie, f and IIe, f were obtained by intramolecular cyclization in hydrochloric acid of the corresponding allylthiourea derivatives [5], and Ig was obtained by decomposition of quaternary salt III<sub>g</sub>. The characteristics of Ie, f and IIe, f are presented in Table 3.

The decomposition of the quaternary salts was carried out by heating melts of the salts to 225-250°C with subsequent distillation of the decomposition products *in vacuo*. The percentages of the components in the products of decomposition of salts IIIa-f and IVa were analyzed from the intensities of the signals of the methyl groups in the PMR spectra, while the percentages of the components in the products of decomposition of IV<sub>b</sub>-d were analyzed from the intensities of the ν<sub>C=N</sub> absorption bands in the IR spectra.

#### LITERATURE CITED

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