SYNTHESIS AND REACTIONS OF 3-AMINOTHIAZOLIDINE-2-THION-4-ONE DERIVATIVES. 5.* POLYMETHINE DYES OF THE THIAZOLO[3,4-b][1,2,4]TRIAZOLE SERIES

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UDC 547.792.9'789. 6.07:543.422

It is shown that the reaction of thiazolo[3,4-b][1,2,4]triazole-5-thiones with alkylating agents gives 5-methylthiothiazolotriazolium salts, which react with the appropriate intermediates to give polymethine dyes.

It has been previously shown [1] that, in contrast to their isoelectronic analogs, viz., thiazolo[4,3-b][1,3,4]thiazole-5-thiones, which are protonated at the sulfur atom of the thione group [2, 3], the protonation of thiazole[3,4-b][1,2,4]triazole-5-thiones Ia-VIa takes place at the carbon atom in the 7 position, i.e., at the terminal carbon atom of the methylenetriazolidene fragment. In analogy with the methylene bases of a number of other heterocycles [4, 5], one therefore might have expected C-alkylation products in the reaction of Ia-VIa with methylating agents.



We have found that thiones Ia-VIa are readily alkylated by the action of dimethyl sulfate or methyl p-toluenesulfonate; in contrast to protonation but like alkylation in the thiazolo-[4,3-b][1,3,4] thiazole-5-thione series, the reaction takes place at the sulfur atom of the thione group to give salts Ib-VIb (Table 1). A signal of an SCH3 group at 2.50 ppm is observed in the PMR spectra (Table 2) of all of the compounds. The signals of the protons of the C--CH₃ and N--CH₃ groups at both salt Ib and starting base Ia are shifted to the weak-field region (0.29-0.67 ppm) as compared with the corresponding signals in the spectra of methylphenyl-substituted analogs IIa,b and IIIa,b. This can probably be explained by the shielding effect of the ring currents of the phenyl group [6, 7], which deviates from the plane of the heterocyclic ring because of steric hindrance. Unfortunately, the evaluation of this effect by the method in [8], like the analysis of the effects of shielding in pyridine and quinoline derivatives [7], is difficult because of the possibility of conjugation of the electron pairs of the nitrogen atoms of the triazole ring with the phenyl groups. The fact that protonation and alkylation of Ia-VIa take place at different centers is probably due to the difference in the hardnesses [9] of the reagents and the reaction centers, as well as to the steric hindrance that arises as the methyl cation approaches the carbon atom in the 7 position.

Like other 2-alkylthio derivatives of quaternary salts of nitrogen heterocycles, 5-methylthiothiazolo[3,4-b][1,2,4]triazolium salts Ib-VIb (Table 1) react readily with compounds that contain an active methyl or methylene group; for example, monomethylidynecyanines Ic-VIc or

*See [1] for Communication 4.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 480-483, April, 1982. Original article submitted January 16, 1981.

| Com- pound | R۱ | R² | R ³ | mp , * °C | λ _{max} , nm (lg ε) | Foun N(Cl) | .d, % s | Emp irica l formula | Calc | •% s | Yield, % |
|---------------|-------------------------------|-------------------------------|-----------------|------------------|---|---------------|------------|--|-------|---------|----------|
| Ίb | CH3 | СН₃ | Н | 182—183 | 235 (3,18), 261 (3,11), | 11,1 | 17,0 | $C_{13}H_{14}ClN_{8}O_{4}S_{2}$ | 11,2 | 17,0 | 71 |
| IIb | СН₃ | C ₆ H ₅ | Н | 209-211 | 350 (3,03) 235 (3,28), 268 (3,26), | 9,5 | 14,6 | $C_{18}H_{16}C1N_3O_4S_2$ | 9,6 | 14,6 | 96 |
| 1116 | C ₆ H₅ | СН₃ | Н | 187—189 | $ \begin{array}{c} 351 \\ 245 \\ 260 \\ (3,26), \end{array} $ | 9,7 | 14,6 | $C_{18}H_{16}C1N_3O_4S_2$ | 9,6 | 14,6 | 95 |
| IVb | C ₆ H ₅ | C ₆ H ₅ | н | 186—187 | $\begin{array}{c} 364 \ (3,12) \\ 247 \ (3,25), \\ 260 \ \ (3,25), \end{array}$ | 8,1 | 12,5 | $C_{23}H_{18}ClN_{3}O_{4}S_{2}$ | 8,4 | 12,8 | 87 |
| Vb | C_6H_5 | C ₆ H ₅ | OCH3 | 185—186 | 366 (3,02) 275 (3,08), 306 (3,23), | (6,8) | 12,2 | $\mathrm{C}_{24}\mathrm{H}_{20}\mathrm{ClN}_3\mathrm{O}_5\mathrm{S}_2$ | (6,7) | 12,1 | 85 |
| VIÞ | C ₆ H ₅ | C ₆ H ₅ | NO ₂ | 225—227 | 362 (3,18) 280 (3,26), 372 (3,10) | (6,6) | 11,9 | $C_{23}H_{17}CIN_4O_6S_2$ | (6,5) | 11,8 | 96 |

TABLE 1. 5-Methylthiothiazolo[3,4-b][1,2,4]triazolium Perchlorates Ib-VIb

*The compounds were crystallized: Ib-IIIb and Vb from alcohol, IVb from ethanol—isopropyl alcohol (1:1), and VIb from alcohol—dimethylformamide (6:1).

TABLE 2. Chemical Shifts ($\delta,$ ppm) of the Protons in the PMR Spectra of Thiazolotriazoles Ia,b-IVa,b

| Solvent | Compound | S—CH₃ | C—CH₃ | N-CH3 | AkH |
|----------------------|--------------------------|--------------------------------------|-------------------|--------------|---|
| CF₃COOH | Ib IIb IIIb IVb | 2,50 2,50 2,50 2,50 2,50 | 2,37 1,83 — | 3,53 | 7,33 7,05 7,05—7,48 6,67—7,20 |
| d ₆ -DMSO | Ia IIa IIIa IVa | | 2,65 1,98 — | 4,06 3,77 | 8,00 7,66—7,95 7,67—8,20 7,00—8,00 |

nullomethylidynemerocyanines Id-IVd (Table 3), respectively, are formed with 2-methyl-3-ethylbenzothiazolium salts or 3-ethylthiazolidine-2-thion-4-one. The absorption maxima of the dyes obtained are close to those observed for their sulfur analogs — the corresponding dyes of 2-phenyl-5-methylthiothiazolo[4,3-b][1,3,4]thiadiazolium derivatives (478 and 488 nm) [3]. It should be noted that for both starting thiones Ia-VIa [1] and the products of their further transformations (Ib-d-IVb-d) replacement of the methyl group by a phenyl group at the nitrogen atom in the 1 position of the thiazolotriazole ring has virtually no effect on the position of the absorption maxima (I, II and III, IV), whereas similar replacement at the carbon atom in the 7 position leads to a shift of the absorption maximum to the long-wave part of the spectrum (~10 nm) (I, III and II, IV). The introduction of an electron-donor or electronacceptor grouping in the para position of the phenyl ring attached to the carbon atom of the triazole ring (V and VI) has only a slight effect on the position of the absorption maxima. This confirms the assumption of a nonplanar orientation of the phenyl groups with respect to the heterocyclic ring.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CF_3COOH were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the standard. The electronic spectra of solutions in CH_3OH were recorded with SF-8 and SF-10 spectrophotometers.

<u>1,7-Dimethyl-2-phenyl-5-methylthiothiazolo[3,4-b][1,2,4]triazolium Perchlorate (Ib)</u>. A mixture of 0.52 g (2 mmole) of 1,7-dimethyl-2-phenyl-5H-thiazolo[3,4-b][1,2,4]triazole-5- thione (Ia) and 0.75 g (4 mmole) of methyl p-toluenesulfonate was heated at 100°C for 1.5 h, after which the melt was triturated with ether, and the precipitate was removed by filtration and converted to the perchlorate in solution in alcohol. The yield was 0.23 g.

| Com- | v | mp * °C | λ _{max} , nm | Found, % | | Empirical formula | Calc. % | | Yield, | |
|---|---|--|---|---------------------------------------|--|--|---|---|--|--|
| pound | | шр , О | (lg ɛ) | N(Hal) | s | Empirical formula | N (Hal) | s | <i>0</i> % | |
| IC HIC HIC IVC VC VIC Id HID HID IVD | CIO4 CIO4 CIO4 I CIO4 CIO4 CIO4 | $\begin{array}{c} 258-260\\ 254-255\\ 251-252\\ 256-258\\ 225-226\\ 302-304\\ 241-242\\ 248-250\\ 279-280\\ 293-295\\ \end{array}$ | $\begin{array}{c} 473 & (3,76) \\ 472 & (3,75) \\ 484 & (3,79) \\ 485 & (3,80) \\ 485 & (3,77) \\ 493 & (3,62) \\ 491 & (3,56) \\ 488 & (3,63) \\ 498 & (3,59) \\ 503 & (3,65) \end{array}$ | 11,110,09,8(5,3)(5,2)14,312,312,410,8 | 12,7 11,3 11,1 9,7 9,6 24,7 21,3 21,2 18,6 | $\begin{array}{c} C_{22}H_{21}ClN_4O_4S_2\\ C_{27}H_{23}ClN_4O_4S_2\\ C_{27}H_{23}ClN_4O_4S_2\\ C_{32}H_{25}lN_4S_2\\ C_{33}H_{27}ClN_4O_5S_2\\ C_{32}H_{24}ClN_4O_5S_2\\ C_{17}H_{16}N_4OS_3\\ C_{22}H_{18}N_4OS_3\\ C_{22}H_{18}N_4OS_3\\ C_{27}H_{20}N_4OS_3\\ \end{array}$ | 11,1 9,9 9,9 8,5 (5,4) (5,3) 14,4 12,4 12,4 12,4 10,9 | 12,7 11,3 11,3 9,8 9,7 9,5 24,7 21,3 21,3 18,8 | 54 59 60 78 52 71 52 58 52 89 | |

TABLE 3. Monomethylidynecyanines Ic-VIc and Nullomethylidynemerocyanines Id-IVd

*The compounds were crystallized: Ic-Vc and IId from alcohol and the remaining compounds from alcohol-dimethylformamide (4:1 for Id, 2:1 for IIId and VIc, and 2:3 for IVd).

<u>Perchlorates IIb-VIb.</u> These compounds were similarly obtained from the corresponding thiones IIa-VIa (Table 1).

<u>1,7-Dimethyl-2-phenyl-5-[(3-ethylbenzothiazolin-2-ylidene)methyl]thiazolo[3,4-b][1,2,4]-triazolium Perchlorate (Ic).</u> A 0.41-g (1 mmole) sample of the p-toluenesulfonate of Ib was dissolved by heating in 6 ml of absolute alcohol, 0.28 g (1 mmole) of 2-methyl-3-ethylbenzo-thiazolium perchlorate and 0.1 g (1 mmole) of triethylamine were added, and the precipitated dye was removed by filtration, washed with alcohol and ether, and crystallized. The yield was 0.28 g.

Monomethylidynecyanines IIc-VIc. These compounds were similarly obtained from the corresponding salts (Table 3).

<u>3-Ethyl-5-(1,7-dimethyl-2-phenylthiazolo[3,4-b][1,2,4]triazolin-5-ylidene)thiazolidine-</u> <u>2-thion-4-one (Id).</u> A 0.41-g (1 mmole) sample of the p-toluenesulfonate of Ib and 0.16 g (1 mmole) of 3-ethylthiazolidine-2-thion-4-one were dissolved by heating in 5 ml of absolute alcohol, 0.1 g (1 mmole) of triethylamine was added, and the precipitated dye was removed by filtration, washed with alcohol, and crystallized. The yield was 0.2 g.

Nullomethinylmerocyanines IId-IVd. These compounds were similarly obtained (Table 3).

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