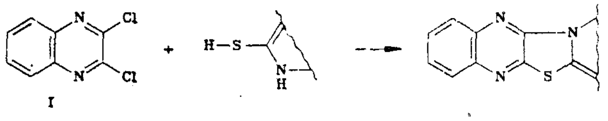
CONDENSED HETEROCYCLES WITH A THIAZOLE RING.
13.* AZINOTHIAZOLOQUINOXALINIUM SALTS

Yu. A. Nesterenko and N. N. Romanov

UDC 547.789.6'863.07:832.1

The condensation of 2,3-dichloroquinoxaline with 2-mercaptopyridines and 2-mercaptoquinolines gave the corresponding derivatives of new heterocyclic systems, viz., azino[1',2':3,2]thaizolo[4,5-b]quinoxalinium salts, which can be used for the synthesis of cyanine dyes.

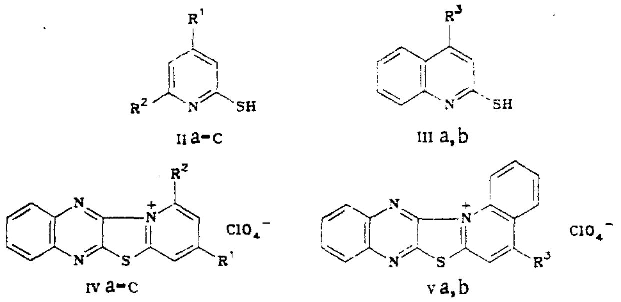
It is known that diverse condensed heterocycles, the compositions of which contain thiazole and quinoxaline rings [2], have a broad spectrum of physiological activity [3, 4]. Compounds of this type are usually obtained by the reaction of 2,3-dichloroquinoxaline (I) with derivatives of mercapto-substituted nitrogen heterocycles containing S—H and N—H groups in the ortho position relative to one another [3-7].


I

The substances obtained in this way are not salts and do not contain active methyl groups; as a consequence of this, they cannot be used for the synthesis of cyanine dyes.

To obtain new condensed heterocyclic systems with a nodal nitrogen atom that contain the indicated structural fragment we studied the reaction of 2,3-dichloroquinoxaline (I) with α-mercapto azines with a tertiary nitrogen atom in the ortho position relative to the S—H group, viz., with 2-mercaptopyridines IIa-c and 2-mercaptoquinolines IIIa, b.

We found that when we carried out the reaction in acetic or formic acid, new salts, which were isolated in the form of perchlorates, to which structures IVa-c and Va, b, respectively, should be assigned on the basis of PMR spectral data, were readily formed.


IIa-c IIIa,b IVa-c Va,b

II—V a $R^1=R^2=R^3=H$; b $R^1=R^3=CH_3$, $R^2=H$; c $R^1=H$, $R^2=CH_3$

Signals that are characteristic only for derivatives of condensed heterocycles of the indicated structures are observed in the PMR spectra of perchlorates IV and V (see Table 1). It should be noted that the signal of the proton in the 1 position (IVa, b and Va, b) is shifted significantly to weak field as compared with the signals of the remaining aromatic protons. The chemical shifts of the signals of the protons of the methyl groups in the 1 and 3 positions (3.40 and 2.70 ppm for IVc and IVb, respectively) differ similarly; this can be explained by the shielding effect on the protons of these groups of the unshared electron pair of the

---

*See [1] for Communication 12.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 551-553, April, 1987. Original article submitted October 28, 1985; revision submitted March 3, 1986.

0009-3122/87/2304-0460$12.50

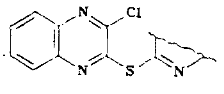
TABLE 1. Characteristics of the Synthesized Compounds

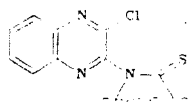
Compound	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calculated, %			Yield, %
			Cl	N	S		Cl	N	S	
IVa*	363 (4,15), 382 (4,15), 400 (4,07)	7,8—8,7 (m, 7H); 9,90 (d, 1H, J=7Hz)	10,8	12,4	9,6	$C_{13}H_8ClN_3O_4S$	10,5	12,5	9,5	80
IVb	360 (4,15), 377 (4,18), 390 (4,15)	2,70 (s, 3H); 7,7—8,5 (m, 6H); 9,70 (d, 1H, J=7 Hz),	9,8	11,8	8,8	$C_{14}H_{10}ClN_3O_4S$	10,1	12,0	9,1	66
IVc	355 (4,03), 380 (4,05), 400 (4,11)	3,40 (s, 3H); 7,7—8,6 (m, 7H)	10,1	12,0	9,3	$C_{14}H_{10}ClN_3O_4S$	10,1	12,0	9,1	71
Va	400 (4,33), 414 (4,39)	7,9—8,6 (m 8H); 8,83 (d, 1H, J=9 Hz); 10,80 (d, 1H)	9,5	10,7	8,3	$C_{17}H_{10}ClN_3O_4S$	9,1	10,8	8,3	85
Vb	395 (4,40), 410 (4,51)	2,73 (s, 3H); 7,7—8,6 (m, 8H); 10,80 (d, 1H, J=9 Hz)	8,9	10,4	8,0	$C_{18}H_{12}ClN_3O_4S$	8,8	10,4	8,0	80
VI	546 (5,05)		6,9		12,2	$C_{23}H_{17}ClN_4O_4S_2$	6,9		12,5	39
VII	600 (4,57)		6,6	10,7		$C_{23}H_{17}ClN_4O_4S_2$	6,9	10,9		47
VIII	561 (5,06)		6,3		11,7	$C_{27}H_{19}ClN_4O_4S_2$	6,3		11,7	80

*This compound melted with decomposition above 260°C; the remaining compounds melted above 300°C.

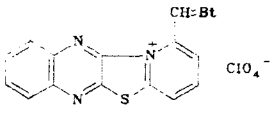
neighboring nitrogen atom of the quinoxaline fragment of the molecule (the nitrogen atom in the 11 position for IV and in the 13 position for V).

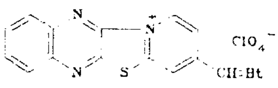
It may be assumed that diheteryl sulfides of the A type, which subsequently undergo intramolecular hetarylation to give new types of heterosystems IV and V, are initially formed in the reaction of 2,3-dichloroquinoxaline with the indicated heterocyclic thiols containing a tertiary nitrogen atom in the α position relative to the mercapto group.

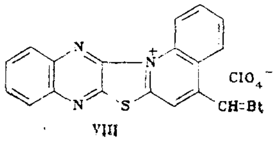

A

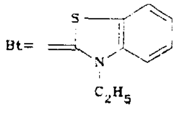

B

An alternative pathway of the first step of the reaction, viz., the initial formation of thiones of the B type, seems unlikely to us, particularly if one takes into account the fact that the process takes place in an acidic medium with the liberation of hydrogen chloride.


VII

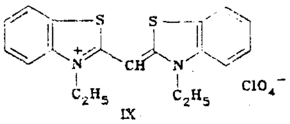

VI


VIII



Further studies showed that methyl-substituted salts IVb, c and Vb react readily with electrophilic intermediates used for the synthesis of cyanine dyes. Thus, for example, monomethylidynecyanine dyes VI-VIII were obtained with 2-methylthio-3-ethylbenzothiazolium tosylate.

Reactions of this type are characteristic for quaternary salts of nitrogen heterocycles that contain an active methyl group; this is an additional confirmation of the structures of the synthesized substances, and the corresponding cyanine dyes find extensive practical application. Of greatest importance is the fact that the thiamonomethylidynecyanines based on the new heterocyclic rings that we synthesized absorb at 546-600 nm, while similarly constructed dyes based on known heterocycles absorb significantly higher. Thus, for example, monomethylidynecyanine IX has an absorption maximum at 422 nm [8].



IX

Since it is known that the stabilities of cyanine dyes decrease sharply with withdrawal of the polymethine chain, it may be assumed that the derivatives of the new heterocyclic systems that we synthesized may find practical application for the purposeful synthesis of new deeply colored cyanine dyes with increased stability.

EXPERIMENTAL

The electronic spectra of solutions of the compounds (in CH_3COOH for IVa-c and Va, b, and in CH_3CN for dyes VI-VIII) were obtained with an SF-8 spectrophotometer. The PMR spectra of solutions in CF_3COOD were recorded with a BS-467 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the external standard.

Data on the properties of the synthesized compounds are presented in Table 1.

Azino[1',2':3,2]thiazolo[4,5-b]quinoxalinium Perchlorates IVa-c and Va, b. A mixture of 0.40 g (2 mmole) of 2,3-dichloroquinoxaline, 2 mmole of the corresponding 2-mercapto azine IIa-c or IIIa, b, and 3 ml of formic acid was refluxed for 15 min, after which 0.26 g (2.2 mmole) of sodium perchlorate or 0.6 ml (3.2 mmole) of 58% perchloric acid was added. The substance was removed by filtration, washed successively with acetic acid, acetone, and ether, and crystallized from acetic acid—formic acid (4:1).

3-[3-Ethyl-2(3H)-benzothiazolylidene[methylpyrido[1',2':3,2]thiazolo[4,5-b]quinoxalinium Perchlorate (VI). A mixture of 0.35 g (1 mmole) of perchlorate IVb, 0.36 g (1 mmole) of 2-methylthio-3-ethylbenzothiazolium tosylate, and 15 ml of alcohol was heated to the boiling point, 0.1 g (1.2 mmole) of anhydrous sodium acetate was added, and the mixture was refluxed for 20 min. The substance was removed by filtration and crystallized from acetic acid—formic acid (3:1).

Monomethylidynecyanines VII and VIII. These compounds were obtained as in the preceding experiment from the corresponding perchlorates IVc and IVb.

LITERATURE CITED

1. A. D. Kachkovskii, Yu. P. Kovtun, and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 12, 1693 (1986).
2. V. N. Charushin, M. g. Ponizovskii, and O. N. Chupakhin, Khim. Geterotsikl. Soedin., No. 8, 1011 (1985).
3. S. Singh and C. Singh, J. Ind. Chem. Soc., 48, 925 (1971).
4. K. Dhaka, K. Mohan, V. Chadha, and H. Pujari, Ind. J. Chem., 12, 966 (1974).
5. K. Jain and R. Handa, Ind. J. Chem., 21, 732 (1982).
6. V. Chadha and V. Saxena, J. Ind. Chem. Soc., 57, 946 (1980).
7. J. Metzger, H. Larive, R. Dennilauler, and R. Baralle, Bull. Soc. Chim. Fr., 1275 (1969).
8. C. Mees, Theory of the Photographic Process, Macmillan (1966).