CONDENSED HETEROCYCLES CONTAINING A THIAZOLE RING.

19.* NAPHTHOTHIAZOLOPYRIDINIUM(QUINOLINIUM) SALTS

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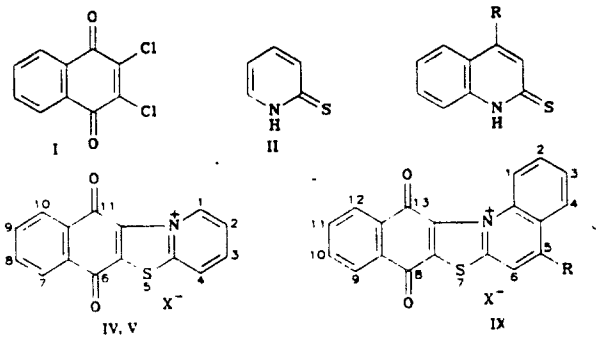
It is shown that the salts of condensed naphthothiazoloazines are formed by the interaction of 2,3, dichloro-1,4-naphthoquinone with 2-mercaptopyridine or 2-mercapto-4-R-quinoline.

For the purpose of obtaining salts of new condensed heterocyclic systems with a nodal nitrogen, we studied the reaction of naphthoquinone (I) with 2-mercaptopyridine (II) and 2-mercapto-4-R-quinolines (IIIa, b). Brief heating of the mixture of initial reagents in acetic acid easily forms salts that can be separated as chlorides or perchlorates. On the basis of the PMR spectra the synthesized compounds were assigned the structures of heterocycles (IV-VII). In the spectra of the naphthothiazolopyridinium salts (IV) and (V) the signal of the proton at position 1 is substantially shifted to the weak field as compared with quaternary pyridinium salts [6, 7]. The 4-H proton signal is also appreciably more shifted to the weak field than the 3-H proton signal. In the PMR spectra of salts (VIa, VIIa, b) the chemical shifts of the 5-H and 6-H protons differ in a similar way. But in the latter cases, due to the anisotropic effect of the electron pair of the adjacent carbonyl the signal of the proton at position 1 is separated only somewhat from that of the multiplet of the aromatic protons.



III a R=H, R=CH_3

The methyl-substituted salt (VIIb) undergoes condensation with the electrophilic reagents used in the synthesis of cyanine dyes. Thus, e.g., when it reacts with p-dimethylaminobenzaldehyde we obtain styrene (IX) (λ_{max} 604 nm).

In the synthesis of (VIa, VIIa, b) (λ_{max} 357 nm) a difficultly soluble colored substance (λ_{max} 484 nm) is also formed. On the basis of its elemental composition and mass spectrum it has been assigned the structure of 5,7,12,14-tetraoxo-5,7,12,14-tetrahydrodibenzo[b,i]-thianthrene [2, 5].

When dichloronaphthoquinone (I) reacts with captax (XI) or with 2-mercaptobenzoxazole (XII), condensed heterocyclic salts are not formed. After the reaction mixture is heated for a short time in acetic acid, only the hetaryl thiosubstituted chloronaphthoquinones (XIII, XIV) can be separated [8]. Further boiling of the reaction mixture, or heating of acetic acid solutions of (XIII, XIV) forms only 5,7,12,14-tetraoxo-5,7,12,14-tetrahydrodibenzo[b,i]thianthrene [2, 5].

*For Communication 18, see [1].

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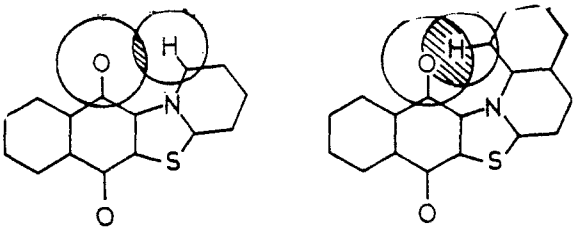
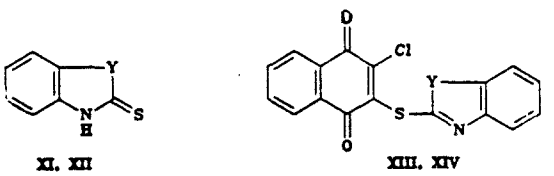


Fig. 1. Projections of dioxonaphthothiazolopyridinium (a) and -quinolinium (b) salts, drawn with allowance for atomic valence angles, covalent radii, and interaction radii [9].

TABLE 1. Properties of Synthesized Compounds

Compound	Empirical formula	R	X	T_{mp}, °C*	Yield, %
IV	$C_{15}H_8ClNO_2S$	—	Cl	295...300	48
V	$C_{15}H_8ClNO_6S$	—	ClO_4	>280 (разл.)	60
VIa	$C_{19}H_{10}ClNO_2S$	H	Cl	>250 (разл.)	35
VIIa	$C_{19}H_{10}ClNO_6S$	H	ClO_4	315...318	86
VIIб	$C_{20}H_{12}ClNO_6S$	CH_3	ClO_4	300...302	40
IX	$C_{29}H_{21}ClN_2O_6S$	$-CH=CHC_6H_4N(CH_3)_2$	ClO_4	>270 (разл.)	56

*Compounds (V, VIIa, b) and (IX) were crystallized from CH_3COOH.



XI, XII XIII, XIV

XI, XIII Y=O; XII, XIV Y=S

It can also be assumed that hetarylthiochloronaphthoquinones like (XIII, XIV) are also intermediates in the reaction of dichloronaphthoquinone with mercaptoazines. Apparently the difference in reactivity between 2-mercaptopyridine (II) and its benzo homologs (IIIa, b) is due to the increasing steric hindrances to cyclization, that arise in the benzannelation of the dioxonaphthothiazolopyridinium nucleus (Fig. 1). Consequently, other conversions of the corresponding intermediate 2-hetarylthio-3-chloronaphthoquinones, in particular the formation of 5,7,12,14-tetraoxo-5,7,12,14-tetrahydrodibenzo[b,i]thi-anthrene can become highly probable. In going from azines to azoles and their benzo-derivatives, besides the steric factor there also appears a substantial decrease in basicity of the latter [9, 10], which hinders cyclization even more.

EXPERIMENTAL

Electron spectra were obtained in CH_3CN with a SF-8 spectrophotometer; PMR spectra were obtained with a WP-100 SY spectrometer (100 MHz, TMS internal standard).

The properties of the synthesized compounds are shown in Table 1. The elemental contents of Cl, N, and S agree with the calculated values.

6,11-Dioxo-6,11-dihydronaphtho[2',3':4,5]thiazolo[3,2-*a*]pyridinium Chloride (IV). A solution of 0.45 g (2 mmoles) of 2,3-dichloro-1,4-naphthoquinone and 0.22 g (2 mmoles) of 2-mercaptopurine in 5 ml of acetic acid was boiled for 3 min. The precipitate was filtered off and washed with acetone. PMR spectrum (DMSO-D_6): 10.49 (1H, d, 1-H, J = 6 Hz), 9.25 (1H, d, 4-H, J = 8 Hz), 8.70 (1H, d.t, 3-H, J = 8 Hz, J = 2 Hz), 8.3 (3H, m) and 8.1 ppm (2H, m).

6,11-Dioxo-6,11-dihydronaphtho[2',3':4,5]thiazolo[3,2-*a*]pyridinium Perchlorate (V). A mixture of 2.2 g (20 mmoles) of 2-mercaptopyridine and 4.5 ml (20 mmoles) of 2,3-dichloro-1,4-naphthoquinone in 20 ml of acetic acid was boiled for 2 min, then treated with 3 ml of perchloric acid. The precipitate was filtered off. PMR spectrum (CF_3COOD): 10.81 (1H, d, 1-H, J = 6 Hz), 8.89 (1H, d, 4-H, J = 8 Hz), and 8.0-8.7 ppm (6H, m).

8,13-Dioxo-8,13-dihydronaphtho[2',3':4,5]thiazolo[3,2-*a*]quinolinium Perchlorate (VIIa). A mix-

ture of 3.2 g (20 mmoles) of 2-mercaptoquinoline, 4.5 g (20 mmoles) of dichloronaphthoquinone, and 25 ml of acetic acid was heated to boiling. The hot solution was filtered from the precipitated thianthrene [2]. To the hot filtrate was added 3 ml of 58% perchloric acid. After cooling, the precipitate was filtered off and washed with acetic acid and acetone. PMR spectrum (CF_3COOD): 8.86 (1H, d, 6-H, J = 9 Hz), 8.78 (1H, d, 1-H, J = 8 Hz), 8.54 (1H, d, 5-H, J = 9 Hz), and 8.0-8.5 ppm (7H, m).

5-Methyl-8,13-dioxo-8,13-dihydronaphtho[2',3':4,5]thiazolo[3,2-*a*]quinolinium perchlorate (VIIb) was obtained analogously to (VIIa) from 2-mercaptolepidine. PMR spectrum (CF_3COOD): 8.0-8.7 (9H, m) and 3.10 ppm (3H, s, CH_3).

5-(p-Dimethylaminostyryl)-8,13-dioxo-8,13-dihydronaphtho[2',3':4,5]thiazolo[3,2-*a*]quinolinium perchlorate (IX). A mixture of 0.4 g (1 mmole) of perchlorate (VIIb), 0.15 g (1 mmole) of p-dimethylaminobenzaldehyde, and 3 ml of acetic anhydride was boiled for 5 min. After cooling the precipitated product was filtered off and washed with acetic anhydride.

LITERATURE CITED

1. N. N. Romanov, O. V. Lazareva, and Yu. M. Volovenko, *Khim. Geterotsikl. Soedin.*, No. 9, 1276 (1990).
2. N. Aundholm and A. Smith, *J. Am. Chem. Soc.*, **73**, 3459 (1951).
3. N. Agarwal and W. Schafer, *J. Org. Chem.*, **45**, 5144 (1980).
4. W. Kang, S. Nan'ya, E. Mackawa, and Y. Ueno, *J. Heterocyc. Chem.*, **25**, 113 (1988).
5. A. Katritzky and W. Fan, *J. Heterocyc. Chem.*, **25**, 901 (1988).
6. M. Yu. Kornilov, L. M. Shulezhko, and A. I. Tolmachev, *Ukr. Khim. Zh.*, **40**, 287 (1974).
7. Yu. A. Nesterenko and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, No. 4, 551 (1987).
8. A. M. Simonov and V. N. Komissarov, *Khim. Geterotsikl. Soedin.*, No. 6, 783 (1976).
9. A. Gordon and R. Ford, *Chemist's Companion* [Russian translation], Mir, Moscow (1976).
10. A. Katritzky, *Physical Methods in the Chemistry of Heterocyclic Compounds* [Russian translation], Khimiya, Moscow (1966).

SYNTHESIS OF 4-SUBSTITUTED 2-AMINOTHIAZOLES AND THIAZOLIUM SALTS DERIVED FROM 2-CHLOROACETYL-1,3-CYCLOHEXANEDIONES

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The reaction of 2-chloroacetyl-1,3-cyclohexanediones with thiourea and substituted thioureas forms 2-amino-4-(1,3-dioxo-2-cyclohexyl)thiazolium chlorides; in the presence of triethylamine 2-aminothiazole bases are formed.

We have previously found that the action of nucleophilic reagents on 2-chloroacetyl-1,3-cyclohexanediones (Ia, b) causes a nucleophilic intramolecular heterocyclization that leads to the formation of 3,4-dioxo-2,3,4,5,6,7-hexahydrobenzo[b]furanes (IIa, b) [1]; α-halocarbonyl compounds, however, react by bimolecular nucleophilic substitution [2]. Since β-triketones are completely enolized and are highly acidic [3-5], the strong anionic nucleophiles that we took for the reaction do not react with the chloroacetyl group; instead they remove a proton from the β-triketone to form an enolate that favors intramolecular attack by the chloroacetyl group, so that hexahydrobenzofurane (II) is obtained.

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