0.6 g (57%) of a crystalline product in the form of a mixture of compounds VII and VIII. PMR spectrum of VII (DMSO-D_6), δ, ppm: 2.24 (3H, s, NCH_3), 2.69 (2H, d, NCH_2), 3.53 (6H, N^+CH_3), 3.62 (3H, s, OCH_3), 4.3 and 5.3 (3H, m, H of the ring), 5.84 ppm (1H, s, =CH–). VIII: 2.75 (3H, s, NCH_3), 3.22 (6H, s, N^+CH_3), 3.4 (2H, m, N^+CH_2), 3.62 (3H, s, OCH_3), 3.76 and 5.30 (3H, m, H of the ring), 3.93 ppm (1H, s, =CH–).

LITERATURE CITED

1. M. V. George, S. K. Khetan, and R. K. Gupta, *Advances in Heterocyclic Chemistry*, Vol. 19, New York (1976), p. 279.
2. R. M. Acheson, *Advances in Heterocyclic Chemistry*, Vol. 1, New York (1963), p. 125.
3. A. S. Nakhmanovich and V. N. Elokhina, *Khim. Geterotsikl. Soedin.*, No. 3, 291 (1987).
4. T. E. Glotova, A. S. Nakhmanovich, G. G. Skvortsova, and N. S. Mabarakshina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 858 (1985).
5. A. S. Nakhmanovich, V. N. Elokhina, I. D. Kalikhman, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 11, 2642 (1979).
6. T. E. Glotova, A. S. Nakhmanovich, and T. N. Komarova, *Khim. Geterotsikl. Soedin.*, No. 8, 1144 (1988).
7. A. N. Mirskova, I. D. Kalikhman, S. G. Seredkina, O. B. Bannikova, and M. G. Voronkov, *Zh. Org. Khim.*, 21, 503 (1985).

SYNTHESIS OF 5-(5-AMINO-3,6-DICHLORO-1,4-BENZOQUINON-2-YL)-2-DIMETHYLAMINOTHIAZOLES AND THEIR PROPERTIES

M. F. Utinan, Yu. V. Gulbis, R. É. Valter, É. É. Liepin'sh, G. A. Karlivan, and A. S. Edzhinya

UDC 547.789.1'567.-3'543.422.25

In the reaction of 2-dimethylamino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazole with primary and secondary amines, the chlorine atom at the 5-position of the benzoquinone ring is substituted, according to the ^{13}C NMR spectroscopy data, by an amino group. The chemical, spectroscopic, and electrochemical properties of 5-(5-amino-3,6-dichloro-1,4-benzoquinon-2-yl)-2-dimethylaminothiazoles were revealed.

We have previously developed [1-3] a method for the synthesis of 2-amino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoles simultaneously containing electron-donor and electron-acceptor fragments in the molecule. It is known [4] that haloquinones readily undergo nucleophilic substitution reactions with amines and other nucleophilic agents. The aim of the present work was to study the nucleophilic substitution reaction of 2-dimethylamino-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazole (I) with primary and secondary amines.

In the reactions of thiazole I with primary and secondary amines, a series of N-substituted 5-(5-amino-3,6-dichloro-1,4-benzoquinon-2-yl)-2-dimethylaminothiazoles (IIa-f, Table 1) were obtained. These compounds are deeply colored crystalline substances (IIa, b, d-f — violet; IIc — green). Compared with the starting thiazole, which dissolves readily only in bipolar aprotic solvents, the amino derivatives IIa-f also dissolve in slightly polar solvents.

The reduction of quinones IId, e leads to the formation of 2-dimethylamino-5-(4-piperidino- and -(4-morpholino-2,5-dhydroxy-3,6-dichlorophenyl)thiazoles (IIId, e). Hydroquinones IIId, e are colorless and dissolve readily in organic solvents. They are characterized by comparatively low oxidation potentials, which is confirmed by their prompt oxidation by atmospheric oxygen to colored quinones IId, e (see scheme on page 334).

The examination of quinones I and IId-f by cyclic voltamperometry (Table 2) showed that, compared with the starting quinone I, aminoquinones IId-f are reduced at more negative potentials. At the first stage of the reduction ($Q + e \rightarrow Q^-$), E_1 decreases by approximately 0.3 V. The values of E_2 for aminoquinones IId-f could not be measured by using tetrabutylammonium perchlorate as the polarographic background. They were measured on the background of tetraethylammonium perchlorate and $NaClO_4$ (Fig. 1). According to the data in {5], this can be explained by the fact that E_2 is more strongly influenced by the radius of the M^+ cation than E_1. Increase in its radius leads to a shift

Riga Technical University, Riga. Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 410-415, March, 1991. Original article submitted July 12, 1989.

0009-3122/91/2703-0333$12.50

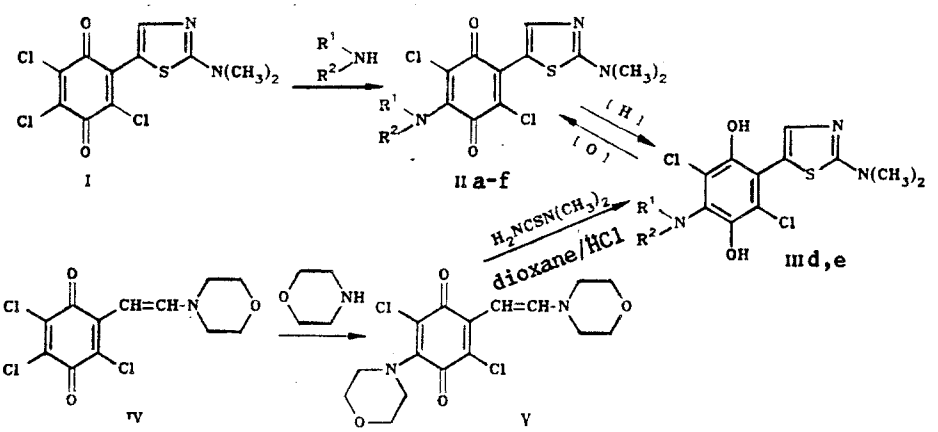
TABLE 1. Characteristics of Compounds IIa-f and IIId, e

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (ε)	Yield, %
II[a]	$C_{15}H_{17}Cl_2N_3O_2S$	159...160	2302, 2962, 2924, 2856, 1650, 1626, 1578, 1511	250 (12 200), 316 (12 400), 491 (16 500), 647 (4 400)	18
II b	$C_{17}H_{13}Cl_2N_3O_2S$	202...203	3234, 2916, 1644, 1621, 1583, 1510	243 (11 000), 274 (10 000), 318 (13 800), 504 (14 200), 650 (4 000)	73
IIc	$C_{13}H_{11}Cl_2N_3O_2S$	193...195	2937, 1655, 1640, 1594, 1575, 1516	244 (12 800), 318 (14 600), 460 (8 100), 634 (5 600)	66
IId	$C_{16}H_{17}Cl_2N_3O_2S$	180...181	2919, 1654, 1624, 1584, 1557, 1524, 1511	246 (13 400), 317 (18 950), 507 (19 850), 679 (3 500)	85
IIe	$C_{15}H_{15}Cl_2N_3O_3S$	205...206	2914, 2860, 1644, 1629, 1594, 1584 sh, 1560, 1540, 1512	250 (4 700), 318 (7 850), 504 (7 480), 660 (1 750)	95
II_f	$C_{16}H_{18}Cl_2N_4O_2S$	191...192	2903, 2776, 1641, 1626, 1589, 1560, 1520	246 (13 200), 317 (17 600), 501 (14 000), 648 (4 600)	78
IIId	$C_{16}H_{19}Cl_2N_3O_2S$	>200 (dec.)	3059, 2911, 2841, 1561		97
IIIe	$C_{15}H_{17}Cl_2N_3O_3S$	>200 (dec.)	3106, 2840, 2812, 1558, 1535		98

TABLE 2. Reduction Potentials of Compounds I, IId-f, and V*

Compound	E_1	E_2	E_1	E_2	E_1	E_2
	TBAP/CH_3CN		TEAP/CH_3CN		$NaClO_4/CH_3CN$	
I	−0,17	−0,83	—	—	—	—
IId	−0,47	—	−0,52	−0,97	−0,47	−0,65
IIe	−0,45	—	−0,52	−0,78	−0,45	−0,67
IIf	−0,46	—	−0,52	−1,0	−0,45	−0,65

*TBAP) Tetrabutylammonium perchlorate; TEAP) tetraethylammonium perchlorate.



II, III a R^1=H, R^2=n-Bu; b R^1=H, R^2=Ph; c R^1,R^2=—$(CH_2)_2$—; d R^1,R^2=—$(CH_2)_5$—; e R^1,R^2=—$(CH_2)_2O(CH_2)_2$—; f R^1,R^2=—$(CH_2)_2NMe(CH_2)_2$—

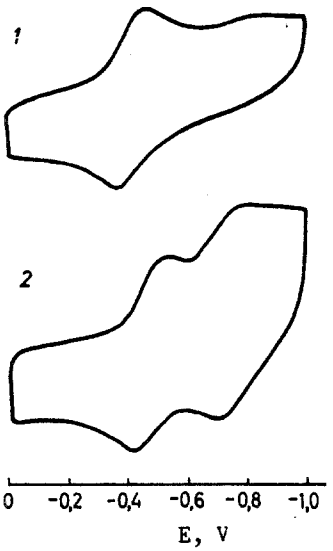


Fig. 1. Cyclic voltamperograms of compound IIe in acetonitrile with 0.1 M TBAP (1) and 0.1 M TEAP (2).

TABLE 3. ^{13}C NMR Spectra of Compounds I, IId, e, VI, and VII

Compound	Chemical shifts, δ, ppm									
	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$	$C_{(6')}$	remaining C
I	175,6	139,2	152,4	176,1	115,4	126,9	170,4	139,4	134,6	40,1 (CH_3)
IId	174,8	133,4	151,5	176,4	115,3	126,5	177,1	149,4	114,8	39,8 (CH_3); 52,5 (α-CH_2); 26,6 (β-CH_2); 23,5 (γ-CH_2)
IIe	174,6	133,4	151,6	176,3	115,3	126,9	177,3	148,5	115,3	40,0 (CH_3); 51,7 (NCH_2); 66,9 (OCH_2)
VI	—	—	—	177,6	116,4	137,3	167,3	141,4	140,8	94,3 (C_α); 153,5 (C_β); 51,3 and 42,4 (CH_2); 14,5 and 11,8 (CH_3)
VII	175,9	139,3	151,9	176,1	117,8	127,3	170,5	139,3	134,9	
CA*	—	—	—	169,6	139,5					

*CA) chloranil.

E_2 in the direction of negative potentials and a sharp decrease in the rate of the second stage of the reduction, due to decrease in the association constant of the reduced form (Q^{2-}) with counterion M^+.

Compound IIe was obtained by countersynthesis. As known [6], 2-(2-N,N-dialkylaminoethenyl)trichloro-1,4-benzoquinones form in reactions with amines the corresponding 5-amino derivatives. From 2-(2-morpholinoethenyl)-3,5,6-trichloro-1,4-benzoquinone (IV) we obtained the 5-morpholino derivative (V), which, according to the method described in [1-3], undergoes reaction with N,N-dimethylthiourea and subsequent oxidation (V → IIIe → IIe). The identity of the thus-synthesized compound with the previously obtained IIe was confirmed by a mixed melting point test, and also by comparison of the IR and UV spectra.

In the IR spectra of crystalline thiazoles IIa-f (Table 1), the C=O bands of the quinone appear at 1650-1640 and 1630-1625 cm^{-1} regions, i.e., they are shifted in the direction of lower frequencies compared with the spectrum of the starting compound I by 20-30 cm^{-1}. This agrees with the data in [7] on the shift of the C=O band of chloranil (1703 cm^{-1}) by approximately 50 cm^{-1} in the direction of low frequencies when the chlorine atoms at the 2- and 5-positions are replaced by dialkylamino groups.

In the IR spectra of hydroquinones IIId, e the C=O absorption band is missing, but an absorption of OH groups appears in the 3050-3110 cm^{-1} region. The low intensity of this band can be explained by the fact that compounds III probably have a betainelike structure.

TABLE 4. ^{1}H and ^{13}C NMR Spectra of Compounds IIIa, b, VIIIa, b, and IX

Compound	Chemical shifts of ^{1}H nuclei, ppm		Chemical shifts of ^{13}C nuclei, ppm									
	4-H	remaining H	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$	$C_{(6')}$	remaining C
IIIa	7,04	8,78 and 8,33 (OH); 3,04 (α-CH_2); 3,04 (CH_3); 1,6 (β,γ-CH_2)	171,4	141,0	116,3	117,6	144,6	119,5	137,2	145,0	120,8	39,7 (CH_3); 50,4 (α-CH_2); 26,1 (β-CH_2); 23,8 (γ-CH_2)
IIIb	7,04	8,84 and 8,18 (OH); 3,69 (OCH_2); 3,01 (NCH_2); 3,02 (CH_3)	171,4	141,0	116,2	118,0	144,9	120,2	136,0	145,1	120,9	39,7 (CH_3); 49,4 (NCH_2); 66,6 (OCH_2)
VIIIa	7,42	10,0 (OH); 9,6 (NH_2)	170,2	127,6	116,6	115,2	143,8	122,4	123,5	146,4	120,4	
VIIIb	7,44	9,2 (OH); 3,22 (CH_3)	169,2	131,6	115,6	115,6	143,8	122,4	123,2	146,3	120,4	41,7 (CH_3)
IX						120,7	141,1					

In the UV spectra of compounds IIa-f (Table 1), run in ethanol, two absorption bands are observed at 244-250 and 316-318 nm which are attributable to $\pi \rightarrow \pi^*$-transitions of a quinone system [8], whereby the 316-318 nm band is probably overlapped by the absorption of the $\pi \rightarrow \pi^*$ system of thiazole, characteristic in this region [9]. Moreover,in the visible part of the spectrum an intense absorption band is observed in the 460-507 nm region and a low-intensity band at 634-679 nm. The absorption band in the 491-507 nm region (for the aziridine derivative IIc — at 460 nm), is not present in the spectrum of the starting compound I and hence its appearance is due to the inclusion of the newly introduced amino group in the conjugation system. The hypsochromic shift of this band on transition from dialkylamino-substituted derivatives to aziridino-substituted haloquinones was also observed [7] in the series of 2,5-diamino-3,6-dihaloquinones. The long-wave bands are due to the interaction between the quinone system and electron—donor substituents (the $n \rightarrow \pi^*$-transitions) [7, 10, 11]. The influence of steric factors on the energy of transition is also observed [11] (the 460-507 nm band). Increase in the volume of the substituent at the 5-position causes a bathochromic shift of this band.

Chloranil in nucleophilic substitution reactions with 4 moles of an amine usually forms 2,5-diamino derivatives [4] which suggests the formation of 5'-amino derivatives in the present case. To obtain irrefutable proof of the substitution site, we used ^{13}C NMR spectroscopy. A detailed assignment of the ^{13}C signals was carried out for the model compounds 2-(2-N,N-diethylaminoethenyl)-3,5,6-trichloro-1,4-benzoquinone (VI) and 2-amino-5-(3,5,6-trichlorobenzoquinon-2-yl)thiazole (VII) (Table 3). On using the ^{13}C NMR spectrum for compound VI without uncoupling of the spin—spin interaction with protons, the $C_{(1')}$ signal is unequivocally separated from the $C_{(4')}$ signal by means of SSCC $^3J_{13C_{(1')}\text{-}C_{(2')}\text{-}C_{\alpha}\text{-}^1H}$ = 8.2 Hz. A characteristic splitting of the $^{13}C_{(3')}\text{-}C_{(2')}\text{-}C_{\alpha}\text{-}^1H$ signal (1.6 Hz) [12] was also observed, enabling the unequivoal identification of the $C_{(3')}$ signal. In order to assign the remaining ^{13}C signals in the spectra of compounds I-III and VI-VIII, we used data from the ^{13}C NMR spectra of substituted benzoquinones [11-14] and 2-aminothiazoles [15]. Comparison of the spectra of compounds I, VI, and VII with the spectrum of chloranil (Table 3) confirms that the introduction of a thiazolyl or β-diethylaminoethenyl substituent into the molecule of chloranil causes a weak-field shift of the signal of the adjacent carbonly carbon atom ($^{13}C_{(1')}$) by 7-8 ppm. The thiazolyl substituent influences the chemical shift of $^{13}C_{(4')}$ much less. The assignment of the $^{13}C_{(4')}$ signal in the spectra of compounds I, VI, and VII agrees well with the data in [12] for 2,6-dichloro—1,4-benzoquinone ($\delta^{13}C_{(1)}$ 172.7 ppm) and 2,3,5-trichloro—1,4-benzoquinone ($\delta^{13}C_{(4)}$ 170.8 ppm). Replacement of the chlorine atom by the dialkylamino group at $C_{(2)}$ in the molecule of 1,4-naphthoquinone [16] or 2-cyclohexenone [12] causes a weak-field shift of the $C_{(1)}$ signal by ~5 ppm, but only slightly influences the $C_{(4)}$ signal and, therefore, the shift of the $^{13}C_{(4')}$ signal in the spectra of compounds IId, e to the weak field of ~6 ppm after the chlorine atom in the molecule of I has been replaced by a piperidino or morpholino group can be caused by the substitution of the chlorine atom at only the $C_{(5')}$ or $C_{(3')}$ atoms. The latter variant is refuted by the constancy of CS of the $C_{(2')}$ atom in compounds I and IId, e. Substitution at the $C_{(5')}$ atom is also confirmed by the weak-field shift of the $C_{(5')}$ atom signal (+10 ppm) and the strong-field shift of the signal of the $C_{(6')}$ atom (—20 ppm) on transition from the spectrum of compound I to the spectra of the amino derivatives IId, e (Table 3), which correlates with the ^{13}C NMR spectral data for 2-chloro- and 2-morpholino-1,4-naphthoquinone (+7 and —24 ppm, respectively) [16]. The presence of a piperidino or morpholino group at the $C_{(5')}$ atom is confirmed by analysis of the increments (see [17, p. 107]) of substituents in screening of ^{13}C nuclei of the benzene ring of hydroquinones IIId, e, 2-amino 5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazole (VIIIa), its 2-dimethylamino analog VIIIb and tetrachlorohydroquinone (IX). The best correlation with the experimental data (Table 4) is obtained from 4'-substitution by the amino group (on transition from quinones to hydroquinones, the numeration of the ring carbon atoms changes 5' → 4').

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were obtained on WH 90/DS (^1H, 90 MHz) and WM 360 (^{13}C, 90.5 MHz) spectrometers in DMSO-D_6 solutions. The CS were measured relative to TMS as internal standard. The IR spectra were run in mineral oil and hexachlorobutadiene on Specord M 80 and Specord IR 75 spectrophotometers. The electronic spectra were measured on Specord M 40 and Specord UV Vis spectrophotometers in ethanol solutions (c = $5 \cdot 10^{-5}$ mole/liter). The cyclic voltamperograms were obtained on a PI 50-1 potentiostat using a three-electrode system with reference to a saturated silver chloride electrode. A glass-graphite electrode (0.28 cm^2) was used as a working electrode. The investigations were carried out at room temperature in an anhydrous acetonitrile solution, using tetraethylammonium perchlorate, tetrabutylammonium perchlorate, and $NaClO_4$ as the polarographic background. The concentration of the inert electrolyte was 0.1 mole/liter, the concentration of the depolarizer was 10^{-4} mole/liter. The scanning velocity of the potential was 200 mV/sec.

The course of the reactions and purity of the compounds obtained was monitored by TLC on Silufol UV 254 plates.

The elemental analysis data of compounds II and III for C, H, Cl, N, and S match the calculated values. 2-(2-Morpholinoethenyl)-3,5,6-trichloro-1,4-benzoquinone (IV) was obtained according to [6] and compound I according to [3].

5-(5-n-Butylamino-3,6-dichloro-1,4-benzoquinon-2-yl)-2-dimethylaminothiazole (IIa). A solution of 4 mmoles of n-butylamine in 20 ml of acetone was added with stirring to a solution of 2 mmoles of compound I in 200 ml of acetone. The mixture was stirred for 45 min at 20°C, was then diluted with water, 1:1, and extracted with benzene (2 × 60 ml). The benzene layer was washed with 100 ml of water, separated, and dried over $MgSO_4$. The solution was evaporated to half its volume and chromatographed on a column with silica gel (R_f 0.40, eluent benzene—acetonitrile, 8:1). The solution was evaporated in vacuo to dryness, and the residue was crystallized from a 2-propanol—hexane (1:1) mixture.

5-(3,6-Dichloro-5-phenylamino-1,4-benzoquinon-2-yl)-2-dimethylaminothiazole (IIb). A 4 mmole portion of aniline was added to a solution of 2 mmoles of compound I in 200 ml of ethanol and the mixture was boiled for 2 h. The solution was cooled, diluted with water (1:1), and filtered. A dark precipitate was obtained, which was crystallized from a 2-propanol—benzene (6:1) mixture.

5-(5-Amino-3,6-dichloro-1,4-benzoquinon-2-yl)-2-dimethylaminothiazoles (IIc-f). A) A solution of 8 mmoles of the corresponding amine in 20 ml of acetone was added with stirring to a solution of 2 mmoles of compound I in 200 ml of acetone, and the mixture was stirred for 30 min at 20°C (in the case of IIf at 40-50°C). The solution was diluted with water (1:1), the precipitate was separated and dried. Compounds IId-e were crystallized from a benzene—hexane (1:1) mixture (in the case of IIf, the aqueous solution was extracted with benzene (2 × 50 ml), the organic layer was dried over $MgSO_4$, and was then evaporated in vacuo to dryness.

B) A 1.3 mmole porton of N,N-dimethylthiourea and 1 ml of concentrated HCl were added to a solution of 1.3 mmole of compound V in 40 ml of dioxane. The reaction mixture was stirred for 2 h at 80-90°C. It was then diluted with 100 ml of water, 5 ml of a 25% aqueous ammonia solution, and 20 ml of a 20% aqueous solution of ferric chloride were added. The mixture was stirred for 15 min, and was then extracted with benzene (2 × 40 ml), the benzene layer was dried over calcium chloride and evaporated to dryness. The residue was crystallized from a toluene—hexane (1:1) mixture. Yield 0.25 g (48%) of compound IIe, mp 204-205°C.

5-(4-Amino-2,5-dihydroxy-3,6-dichlorophenyl)-2-dimethylaminothiazoles (IIId, e). A solution of 2 mmoles of the corresponding quinone IId or IIe in 50 ml of benzene was shaken with 50 ml of a 5% solution of $Na_2S_2O_4$ to the complete disappearance of color. The organic layer was separated and dried over $MgSO_4$, benzene was evaporated in vacuo, and colorless crystals of compounds III were obtained.

3,6-Dichloro-5-morpholino-2-(2-morpholinoethenyl)-1,4-benzoquinone (V). A solution of 0.32 ml (3.1 mmoles) of morpholine in 15 ml of acetone was added with stirring to a solution of 0.5 g (1.55 mmole) of compound IV in 70 ml of acetone. The mixture was then stirred for another 15 min, and poured into 200 ml of water. The mixture was filtered, the precipitate was washed with water, and dried. Yield 0.5 g (86%) of compound V, mp 154-155°C.

LITERATURE CITED

1. G. A. Karlivan, R. E. Valter, and M. F. Utinan, USSR Inventor's Certificate, No. 1,131,874; *Byull. Izobret.*, No. 40, 87 (1984).
2. G. A. Karlivan, R. E. Valter, and M. F. Utinan, USSR Inventor's Certificate, No. 1,188,169; *Byull. Izobret.*, No. 40, 82 (1985).
3. M. F. Utinan, R. E. Valter, G. A. Karlivan, E. E. Liepin'sh, and A. S. Edzhinya, *Khim. Geterotsikl. Soedin.*, No. 5, 692 (1982).
4. K. T. Finley, *The Chemistry of the Quinoid Compounds*, Part 2, S. Patai (ed.), Interscience, London (1974), p. 877.
5. C. Küssel and W. Jaenicke, *J. Electroanal. Chem.*, **199**, 139 (1986).
6. D. Buckley, H. B. Henbest, and P. Slade, *J. Chem. Soc.*, No. 12, 4891 (1957).
7. K. Wallenfels and W. Draber, *Tetrahedron*, **20**, 1889 (1964).
8. St. Berger and A. Rieker, *The Chemistry of the Quinoid Compounds*, Part 1, S. Patai (ed.), Interscience, London (1974), p. 163.
9. R. Barone, M. Chanon, and R. Gallo, *Thiazole and Its Derivatives*, Part 2, I. V. Metzger (ed.) Wiley, New York—Chichester—Brisbane—Toronto (1979), p. 9.
10. W. Herre and H. Wunderer, *Tetrahedron*, **28**, 5433 (1972).
11. H.-J. Kallmayer and W. Fritzen, *Arch. Pharm. (Weinheim)*, **321**, 293 (1988).
12. G. Höfle, *Tetrahedron*, **32**, 1431 (1976).

13. R. Neidlein, W. Kramer, and R. Leidholdt, *Helv. Chim. Acta*, **66**, 2285 (1983).
14. St. Berger and A. Rieker, *Tetrahedron*, **28**, 3123 (1972).
15. G. Tóth and B. Podanyi, *J. Chem. Soc., Perkin Trans.* 2, No. 1, 91 (1984).
16. G. Hofle, *Tetrahedron*, **33**, 1963 (1977).
17. G. Levi and G. Nelson, *Handbook on Nuclear Magnetic Resonance of Carbon-13 for Organic Chemists* [in Russian], Mir, Moscow (1975).

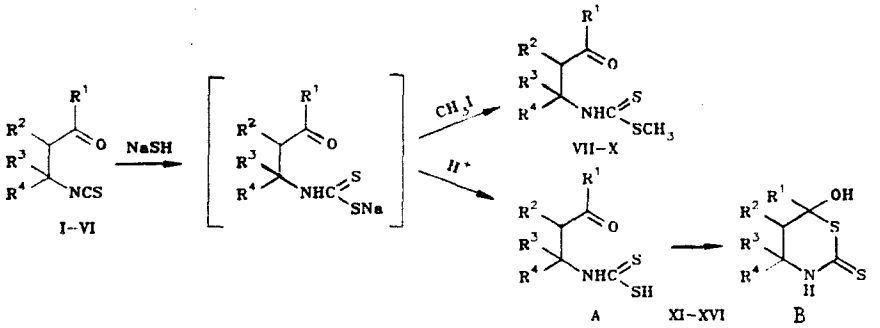
SYNTHESIS OF 6-HYDROXYTETRAHYDRO-1,3-THIAZINE-2-THIONES AND METHYL ESTERS OF 3-OXOALKYLDITHIOCARBAMIC ACIDS FROM 1,3-ISOTHIOCYANATO KETONES

A. S. Fisyuk and B. V. Unkovskii

UDC 547.869.07:543.422.25

Sodium salts of 3-oxoalkyldithiocarbamic acids were obtained by the reaction of 1,3-isothiocyanato ketones with sodum hydrosulfide. These salts were converted by reaction with methyl iodide into the corresponding dithiocarbamates, and with a mineral acid into the 6-hydroxytetrahydro-1,3-thiazine-2-thiones.

The presently known methods for the preparation of 6-hydroxytetrahydro-1,3-thazine-2-thiones and methyl esters of 3-oxoalkyl dithiocarbamic acids from 1,3-isothiocyanato ketones involve the use of the toxic and inflammable carbon disulfide [1, 2]. We found [3] that the reaction of 1,3-isothiocyanato ketones I-VI with sodium hydrosulfide or carbon disulfide in an alkaline medium leads to the formation of sodium salts of 3-oxoalkyldithiocarbamic acids, which convert by the action of methyl iodide into the corresponding esters VII-X, and by the action of mineral acids — into compounds XI-XVI, which in principle can exist in two tautomeric forms: the acyclic form of 3-oxoalkyldithiocarbamic acids XIA-XVIA and in the cyclic form of alkyl-substituted 6-hydroxytetrahydro-1,3-thiazine-2-thiones XIB-XVIB.



I, VII, XI $R^1=R^2=CH_3$, $R^3=R^4=H$; II, VIII, XII $R^1=R^3=R^4=CH_3$, $R^2=H$; III, IX, XIII $R^1=R^2=R^3=R^4=CH_3$; IV, XIV $R^1=C_2H_5$, $R^2=CH_3$, $R^3=R^4=H$; V, XV $R^1=C_2H_5$, $R^2=R^3=R^4=CH_3$; VI, X, XVI $R^1,R^2=(CH_2)_4$, $R^3,R^4=(CH_2)_5$

In contrast to the thioesters VII-X, in the IR spectra of compounds XI-XVI (Table 1), the band at 1680-1710 cm^{-1}, corresponding to the stretching vibrations of the C=O group, is absent, which suggests that in the crystalline state they exist in the cyclic form B.

The PMR spectra of compounds XII, XIII, and XVI, recorded immediately after their dissolution, confirm their presence in the cyclic form B (Table 2). Compound XIII is formed in the form of a mixture of cis- and trans-isomers in a ratio of 93:7, which indicates a dual set of signals corresponding to its structure.

The singlet signals ofthe $COCH_3$ group protons in the 2.08-2.20 ppm region, which are characteristic for acyclic analogs VIII and IX (Table 2), are absent in the case of compounds XII and XIII, while the 6-CH_3 group appears in the form of a singlet at 1.50 and 1.43 and 1.45 ppm, respectively. The proton signals at the $C_{(5)}$ atom of compounds XII and XIII are also present in the stronger-field region, compared with the signals of compounds VIII and IX.

Omsk State University, Omsk. M. V. Lomonosov Moscow Institute of Fine Chemical Technology, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 416-419, March, 1991. Original article submitted May 30, 1989.

0009-3122/91/2703-0339$12.50