2-Hydrazono-3-oxo-5,5-dimethyl-2,3,5,6-tetrahydropyrrolo[2,1-a]isoquinoline (IIIa). A mixture of 2.27 g (10 mmole) of compound IIa and 0.68 ml (15 mmole) of hydrazine hydrate was boiled in ethanol for 3 h. On cooling, hydrazone IIIa formed a precipitate, which was filtered off, dried, and recrystallized.

2-Semicarbazono-3-oxo-5,5-dimethyl-2,3,5,6-tetrahydropyrrolo[2,1-a]isoquinoline (IIIb). A 2.27-g (10 mmole) portion of pyrroledione IIa was dissolved on heating in 30 ml of 70% ethanol; 1.12 g (10 mmole) of semicarbazide hydrochloride was dissolved in 20 ml of water and 1.5 g of sodium acetate and the aqueous alcoholic solution of compound IIa were added. The mixture was agitated and boiled for 2 h. On cooling, substance IIIb precipitated out, and it was filtered off, dried, and recrystallized.

LITERATURE CITED

1. W. J. Houligan, US Patent No. 4100165; Ref. Zh. Khim., 40187P (1979).
2. S. G. Agbalyan and R. D. Khachikyan, Khim. Geterotsikl. Soedin., No. 7, 943 (1979).
3. S. G. Agbalyan, R. D. Khachikyan, and K. K. Lulukyan, Arm. Khim. Zh., 29, 527 (1976).
4. T. Sano, I. Holiguchi, and Y. Tsuda, Heterocycles, 3, 65 (1973).
5. V. S. Shklyaev, B. B. Aleksandrov, M. I. Vakhrin, and G. I. Legotkina, Khim. Geterotsikl. Soedin., No. 11, 1560 (1983).
6. Yu. S. Andreichikov, V. S. Shklyaev, B. B. Aleksandrov, and Yu. V. Ionov, Khim. Geterotsikl. Soedin., No. 3, 420 (1982).

DIAZABICYCLOALKANES WITH NITROGEN ATOMS IN BRIDGEHEAD POSITIONS.

15.* REACTIONS OF BENZO[b]-1,4-DIAZABICYCLO[2.2.2]OCTENE MONOQUATERNARY SALT DERIVATIVES WITH NUCLEOPHILIC REAGENTS

N. P. Luk'yanchuk, N. I. Sagalaeva, V. K. Soboleva, and G. V. Shishkin

UDC 547.863.13'895: 543.878:541.127

Monoquaternary salt derivatives of benzo[b]-1,4-diazabicyclo[2.2.2]octene react with piperidine and sodium methoxide or 4-tert-butylthiophenoxide to give primarily N,N-disubstituted tetrahydroquinoxalines. Rate constants have been measured for these bimolecular reactions. Based on their levels of reactivity, these quaternary salts behave as typical alkylating agents.

Methyl iodide salts of cyclic amines can react via three pathways with sodium methoxide: demethylation, ring opening via a Hofmann reaction, and ring opening via nucleophilic substitution [2, 3]. The third pathway predominates as the ring strain of the cyclic amine increases [2]. Quaternary salt derivatives of benzo[b]-1,4-diazabicyclo[2.2.2]octene contain strained bicyclic diamine fragments, and thus would be expected to react with nucleophilic reagents primarily via the ring opening pathways. This is indicated indirectly by the earlier observation [4] that an equilibrium mixture of 1-(2-bromoethyl)-1,2,3,4-tetrahydroquinoxaline and benzo[b]-1,4-diazabicyclo[2.2.2]octene (I) is formed when the latter is heated in concentrated hydrobromic acid.

Our goal in the present paper was to determine the main reaction pathway and obtain a quantitative estimate of the reactivities of quaternary salt derivatives of benzo[b]-1,4-diazabicyclo[2.2.2]octene with nucleophilic reagents.

Methyl iodide, benzyl bromide and 4-nitrobenzyl bromide derivatives of benzo[b]-1,4-diazabicyclo[2.2.2]octene (compounds II, IV, and V) were prepared by treatment of compound

*For communication 14, see [1].

Novosibirsk Institute of Bioorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 966-972, July, 1987. Original article submitted January 24, 1986.

0009-3122/87/2307-0792$12.50

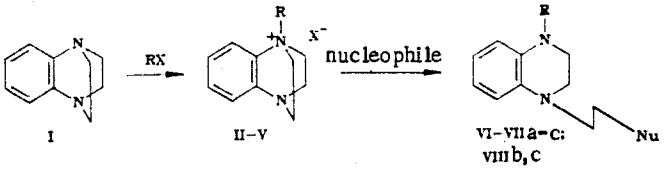
TABLE 1. Quaternary Salt Derivatives of Benzo[b]-1,4-diazabicyclo[2.2.2]octene (II-IV)

Compound	mp, °C *	R_f, system A	UV spectrum (methanol), λ_{max} (log ε)	PMR spectrum (CF_3COOH), δ, ppm				Yield, %
				arom. protons (m)	N^+–CH:Ar (2H, s)	ring CH_2 (m)	N^+–CH_3 (3H, s)	
II	187—188	0,13	205 (4,16)	7,82—7,67 (4H)	—	4,59—4,36 (4H); 4,06—3,74 (4H)	3,91	89
III	198—199	0,35	205 (3,95)	8,29—7,86** (4H)	—	4,04—4,24 (4H); 4,12—3,62 (4H)	3,96	43
IV	155—157	0,38	207 (4,24)	7,47—7,01 (4H); 6,92—6,77 (5H)	4,74	3,76—2,96 (8H)	—	32
V	164—165	0,46	212 (4,16); 258 (4,23)	7,39—7,11 (6H); 6,96—6,54 (2H)	4,47	3,31—2,71 (8H)	—	56

*Correct elemental analyses were obtained for all compounds. Compounds II and IV were crystallized from a methanol—ether mixture, compound III from methanol, and compound IV from ethanol.

**In DMSO-D_6.

(I) with methyl iodide, benzyl bromide, and 4-nitrobenzyl bromide, respectively (Table 1); their reactions were studied with sodium methoxide, sodium 4-tert-butylthiophenoxide, and piperidine.



II, III, VIa—c R=CH_3; IV, VIIa—c R=$C_6H_5CH_2$; V, VIIIb, c R=p-$NO_2C_6H_4CH_2$; VIa, VIIa Nu=OCH_3; VIb, VIIb, VIIIb Nu=4-t-BuC_6H_4S; VIc, VIIc, VIIIc Nu=piperidino; II X=I; IV, V, X=Br; III X=ClO_4

Refluxing methanolic solutions of methyl iodide II, benzyl bromide IV or 4-nitrobenzyl bromide derivative V with sodium methoxide led to the formation of reaction mixtures which, according to TLC analysis, did not contain any residual starting materials. In the case of the reactions of compounds II and IV, the main components of the reaction mixtures, which were isolated chromatographically in ca. 90% yields, were the 1-methyl- and 1-benzyl-4-(2-methoxyethyl)-1,2,3,4-tetrahydroquinoxalines (VIa and VIIa), respectively, (Table 2). These compounds exist as oils, and like the known 1,4-dialkyl-1,2,3,4-tetrahydroquinoxaline derivatives [5], are easily oxidized in air, which makes it difficult to obtain correct elemental analyses of these compounds. The reaction of compound V with sodium methoxide is more complex. Elimination of the 4-nitrobenzyl group occurred even when the reaction was carried out at 20°C, and led to the formation of base I in ca. 40% isolated yield, along with the starting quaternary salt derivative and unidentified impurities.

The reactions proceeded significantly more easily upon treatment of quaternary salts II and IV with sodium 4-tert-butylthiophenoxide in methanol. 1-Substituted 4-[2-(4-tert-butylphenylthio)ethyl]-1,2,3,4-tetrahydroquinoxalines VIb-VIIIb were isolated in up to 90% yields (Table 2). These compounds are also easily oxidized in air, just like their corresponding β-methoxyethyl congeners VIa and VIIa. The presence of base I could not be detected in the reaction mixtures. The ease and uniformity of the ring opening pathways for the quaternary salt derivatives II, IV, and V stand out in remarkable contrast to the reactions of N-substituted N-methylpiperidinium salts, which are easily demethylated, with retention of their cyclic structures, upon treatment with sodium thiophenoxide [6].

The reactions of quaternary salts II, IV, and V with piperidine occur with much more difficulty. Elevated temperatures were required in order to obtain preparative amounts of

TABLE 2. N-R,N'-(2-Nu-Ethyl)-1,2,3,4-Tetrahydroquinoxalines (VI-VIII)

Compound	R_f (system)	M (mass spectroscopic)	PMR spectrum (CCl_4), δ, ppm							yield, %*
			arom. protons	$N-CH_2Ar$ (s, 2H)	$-CH_2-$ (m)	$N-CH_3$ (s, 3H)	$-OCH_3$ (s, 3H)	$-C(CH_3)_3$ (s, 9H)	$-N(CH_2)_5$ (m)	
VIa	0,65 (B)	206	6,7 (4H, s	—	3,89—3,61 (6H); 3,51—3,24 (2H)	3,06	3,54	—	—	98
VIb	0,75 (A)	340	7,31—6,72 (8H, m)	—	3,78—3,42 (6H); 3,22—2,94 (2H)	3,11	—	1,14	—	62,5
VIc	0,75 (B)	—	6,77—6,32 (4H, m)	—	3,54 (2H); 3,48—3,09 (6H)	2,74	—	—	2,91—2,40 (4H); 1,96—1,37 (6H)	8,8
VIIa	0,75 (C)	282	6,44 (4H, s); 7,21 (5H, s)	4,32	3,54—3,32 (8H)	—	3,29	—	—	90
VIIb	0,20 (A)	416	7,37—7,04 (9H, m); 6,47—6,26 (4H, m)	4,29	3,46—2,92 (8H)	—	—	1,27	—	90
VIIc	0,54 (A)	335	7,21 (5H, s)**; 6,47 (4H, s)	4,39	3,57 (2H); 3,42—3,15 (6H)	—	—	—	2,67—2,32 (4H); 1,71—1,36 (6H)	59
VIIIb	0,20 (A)	461	8,14—7,84 (2H, d); 7,46—7,31 (2H, m); 7,19 (4H, s); 6,46—6,11 (4H, m)	4,36	3,51—3,19 (8H)	—	—	1,29	—	90
VIIIc	0,60 (A)	380	8,36—8,02** (2H, d); 7,57—7,24 (2H, d); 6,56—6,21 (4H, m)	4,41	3,57—3,02 (8H)	—	—	—	2,64—2,62 (4H); 1,64—1,39 (6H)	79

*The reaction products were viscous oils which darkened upon exposure to air.
**In CCl_4 and CD_3OD.

TABLE 3. Rate Constants for the Reactions of Quaternary Salts of Benzo[b]-1,4-diazabicyclo[2.2.2]octene (II, IV, V) with Sodium Methoxide, Piperidine, and Sodium 4-tert-Butylthiophenoxide in Methanol*

Quaternary salt	$K \cdot 10^4$, liter/mole·sec, with MeONa			E, kJ/mole	$\Delta S^{\neq}$, J·mole/deg
	60°	70°	80°		
II	2,79	9,79	32,8	120	40
IV	8,2	23,9	68,9	108	12
V**	24,2	75,3	209	106	15
	$K \cdot 10^4$, liter/mole·sec, with piperidine				
	70°	80°	90°		
II	1,40	2,46	4,33	59	−156
IV	1,53	2,69	5,08	63	−140
V	2,58	6,71	14,1	88	−66
	$K \cdot 10^2$, liter/mole·sec, with 4-tert-BuC_6H_4SNa				
	20°	30°	40°		
II	0,23	0,77	1,72	76	−44
IV	0,49	1,58	3,33	72	−52
V	1,46	3,56	7,32	61	−80

*The deviations from the average values did not exceed ±10%.
**More than 50% of the reaction proceeds via debenzylation.

the reaction products. 1-Substituted 4-(2-piperidinoethyl)-1,2,3,4-tetrahydroquinoxalines VIc-VIIIc (Table 2) were isolated in 8.8, 59, and 79% yields, respectively, along with the starting quaternary salts II, IV, and V. Compounds VI-VIIIc are also easily oxidized in air.

The IR spectra of all of the tetrahydroquinoxalines prepared in this paper contain a set of bands which is characteristic of this heterocyclic system (3100-3000, 2990-2800, 1600, 1520, 1370-1350, 1260-1250, and 1120 cm^{-1}); the absorption bands due to the presence of the other functional groups in the molecules are easily discerned against this background: OCH_3 at 2830 and 1150-1100 cm^{-1} in compounds VIa and VIIa, NO_2 at 1560-1500 and 1356-1340 cm^{-1} in compounds VIIb and VIIIc, and aliphatic NR_3 at 1230-1030 cm^{-1} in compounds VIc-VIIIc. In contrast to the UV spectra of the benzo[b]-1,4-diazabicyclo[2.2.2]octene quaternary salt derivatives (cf. Table 1), the UV spectra of the 1,4-disubstituted tetrahydroquinoxalines contain intense absorption bands, with ε values up to 30,000 liter/mole·cm, in the 227-230 nm region. The PMR spectra (Table 2) contain two groups of signals for the aromatic and aliphatic protons, corresponding to the tetrahydroquinoxaline skeleton, as well as nicely resolved signals due to the substituents attached to the nitrogen atoms. The mass spectra exhibited peaks due to the molecular ions for the 1,4-disubstituted tetrahydroquinoxaline derivatives.

It has thus been shown, based on TLC data, that all of the quaternary salts examined herein, with the exception of compound V, react readily with nucleophilic reagents, via ring opening pathways, to form 1,4-disubstituted tetrahydroquinoxalines. The variations in the yields of the tetrahydroquinoxalines are probably associated mainly with the instabilities of these products, which makes it difficult to isolate and purify them.

The absence of any significant side processes in the course of these reactions makes it possible to obtain quantitative estimates of the reactivities of compounds II, IV, and V. These estimates were obtained by measuring the changes in the concentrations of the bases during the course of the reactions, both by potentiometric titration [2], as well as photometrically, based on differences in the UV spectra of the quaternary salt precursors and their ring opening products [7]. The values of the rate constants obtained via these two methods are superimposable on one another, within the limits of experimental error (±10%). The rate orders for these reactions were determined [8], both for the quaternary salts and the nucleophiles, and gave values of close to unity for both, i.e., the total reaction is second order. Average (rate) constant values at different temperatures, as well as the calculated activation parameters, are summarized in Table 3.

As might be expected, the nucleophilic reagents are ordered in the following series, based on their reactivities with respect to the quaternary salts: sodium 4-tert-butylthio-

phenoxide >> sodium methoxide > piperidine. Comparison of the reactivities of quaternary salts II, IV, and V reveals that the rate of reaction with nucleophilic reagents increases as the negative inductive effect of the substituent attached to the nitrogen atom [9] is increased. In the case of piperidine this increase is small (ca. 2 times), whereas the increase is more pronounced (ca. 5 times) in the case of charged nucleophiles. It was also found, based on the reaction of perchlorate III with sodium methoxide, that the anion associated with the quaternary salt has almost no effect on the reaction rate. All of this data points to the fact that the reactions of benzo[b]-1,4-diazabicyclo[2.2.2]octene quaternary salts with nucleophiles take place, as might be expected, according to an S_N2 reaction mechanism. The reaction of sodium methoxide with quaternary salt V appears to be an exception, as mentioned earlier, and leads to the formation of compound I, probably via the predominant intermediate formation of an ylide, which is facilitated by the high basicity of the medium and the increased acidity of the methylene group due to the presence of the p-nitrobenzyl substituent. An S_N2 reaction mechanism is also supported by the values of the activation entropies for the reactions of quaternary salts II, IV, and V with piperidine, which are in the correct range of values characteristic of bimolecular reactions [10]. The positive activation energies obtained for the reactions of quaternary salts with sodium methoxide, however, stand out as contradictory to this proposed reaction mechanism. This contradiction can be resolved if one takes into account the large positive contributions to the measured entropy values arising as a consequence of solvation changes in the transition state due to the disappearance of charged pairs [11]. The large contribution of solvation of the starting material state to $\Delta S^{\neq}$ is confirmed by the intermediate values of the activation entropy obtained for the reactions of compounds II, IV, and V with the bulky p-tert-butylthiophenoxide ion, which is much less solvated than the methoxide anion. Taking into account these deviations, the calculated $\Delta S^{\neq}$ values fit adequately well within the range of values characteristic of S_N2 reactions.

Comparison of the data obtained herein with earlier results [2, 3] reveals that the reaction rates of the quaternary salt derivatives II and IV with sodium methoxide are more than three orders of magnitude greater than that of the N-methylpyrrolidine methyl iodide adduct under analogous conditions, and only one order of magnitude slower than the reaction rate for ring opening of quaternary azetidinium salt derivatives upon treatment with sodium methoxide; the latter salts are well known as highly active alkylating agents. The reactivity of quaternary salt derivatives of benzo[b]-1,4-diazabicyclo[2.2.2]octene, such as II, IV, and V, with respect to nucleophilic reagents is thus of the same level as the reactivity of typical alkylating agents, such as benzyl chloride and p-nitrobenzyl chloride [12].

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer for CCl_4 solutions or KBr pellets. PMR spectra were recorded on a Varian A56/60A spectrometer vs. HMDS as internal standard. Molecular weights were determined using an MS-902 spectrometer. TLC analyses were carried out on Silufol UV-254 plates in the following systems: A, tert-butyl alcohol–methyl ethyl ketone–formic acid–water (8:6:3:3); B, chloroform–methanol (20:1); C, chloroform; D, carbon tetrachloride. Preparative TLC separations were carried out on 30 × 30 cm plates in KSK silica gel. Substances were visualized under UV light. The compounds were then eluted from the silica gel with a mixture of chloroform–methanol, 1:1. Kinetic measurements were made by potentiometric titration using an EV-74 ionometer, with calomel and glass electrodes, or spectrophotometrically on Specord UV-Vis or Beackman DU-8 spectrophotometers.

1-Methylbenzo[b]-1-azonium-4-azabicyclo[2.2.2]octene Iodide (II). A solution of 1 g (6.3 mmole) of compound I [13] in 35 ml ether was treated with 12.5 g (88.2 mmole) of methyl iodide; the solution was maintained at 20°C for 24 h, until all of the starting material had disappeared (as detected by TLC in system A). The precipitate was removed by filtration, washed with ether, and crystallized from a mixture of absolute methanol and ether. Yield 1.69 g of colorless crystals, mp 187-188°C.

1-Methylbenzo[b]-1-azonium-4-azabicyclo[2.2.2]octene Perchlorate (III). A solution of 1 g (6.3 mmole) of compound I in 30 ml ether was treated with an equimolar amount of silver perchlorate in benzene solution (0.18 mole/liter) and 12.8 g (89.9 mmole) of methyl iodide. The mixture was allowed to stand at 20°C for 18 h, after which time the silver iodide precipitate was removed by filtration and extracted with boiling methanol (3 × 15 ml). The residue remained after evaporation of the combined methanol extracts was recrystallized from absolute methanol. Yield 0.73 g colorless crystals, mp 198-199°C.

1-Benzylbenzo[b]-1-azonium-4-azobicyclo[2.2.2]octene Bromide (IV). Compound IV was obtained from 1 g (6.3 mmole) of compound I in 40 ml ether and 1.44 g (8.4 mmole) of benzyl bromide after 19 h at 40°C, and isolated in a manner analogous to compound II to give 0.67 g of rose-colored crystals, mp 155-157°C.

1-p-Nitrobenzylbenzo[b]-1-azonium-4-azabicyclo[2.2.2]octene Bromide (V). Compound V was obtained from 1 g (6.3 mmole) of compound I in 60 ml ether and 1.26 g (9.26 mmole) of p-nitrobenzyl bromide, and was isolated after 48 h at 20°C in a manner analogous to compound II, to give 1.33 g of colorless crystals, mp 164-165°C, after recrystallization from ethanol.

1-Methyl-4-(2-methoxyethyl)-1,2,3,4-tetrahydroquinoxaline (VIa). A mixture of 0.45 g (1.49 mmole) of quaternary salt II and 8.5 ml of a solution of sodium methoxide in methanol (0.8 mole/liter) was refluxed for 2 h (monitored by TLC, system B). The reaction mixture was concentrated and the residue was separated by preparative TLC using system C. After drying in a vacuum dessicator, 0.30 g of an oily substance was obtained. This material was purified by molecular distillation at 80°C (2 mm Hg).

1-Benzyl-4-(2-methoxyethyl)-1,2,3,4-tetrahydroquinoxaline (VIIa). In a manner analogous to the preparation of compound VIa, 0.24 g (0.73 mmole) of compound IV in 3.8 ml of sodium methoxide solution in methanol (0.8 mole/liter) gave 0.19 g of an oily substance after 1 h and 30 min (TLC monitor, system B). The latter was purified by molecular distillation at 110°C (2 mm Hg).

1-Methyl-4-[2-(4-tert-butylphenylthio)ethyl]-1,2,3,4-tetrahydroquinoxaline (VIb). A mixture was prepared from 6 ml of sodium methoxide in methanol solution (0.2 mole/liter) and 0.77 ml (4.5 mmole) of 4-tert-butylthiophenol, and 0.35 g of quaternary salt II was added; the mixture was refluxed for 40 min (TLC control, system A). The reaction mixture was worked up as described above for VIa. Yield 0.25 g of an oily substance, which was purified by molecular distillation at 150°C (2 mm Hg).

1-Benzyl-4-[2-(4-tert-butylphenylthio)ethyl]-1,2,3,4-tetrahydroquinoxaline (VIIb). Compound VIIb was obtained in a manner analogous to compound VIb from 0.16 g (0.49 mmole) of quaternary salt IV and a mixture of 2.5 ml sodium methoxide in methanol solution (0.2 mole/liter) and 0.25 ml (1.5 mmole) of 4-tert-butylthiophenol, and gave (after preparative TLC using system D) 0.18 g of an oily substance, which was purified by preparative TLC in system D.

1-p-Nitrobenzyl-4-[2-(4-tert-butylphenylthio)ethyl]-1,2,3,4-tetrahydroquinoxaline (VIIIb). A mixture of 0.15 (0.39 mmole) compound V and a mixture prepared from 2 ml of sodium methoxide in methanol solution (0.2 mole/liter) and 0.27 ml (1.61 mmole) 4-tert-butylthiophenol gave 0.16 g of an oil, after 20 h at 20°C, in a manner analogous to that of compound VIIb.

1-Methyl-4-(2-piperidinoethyl)-1,2,3,4-tetrahydroquinoxaline (VIc). A solution of 0.39 g (1.3 mmole) of quaternary salt II in 23 ml of piperidine in methanol solution (0.19 mole/liter) was heated in an ampul at 90°C for 70 h. Compound VIc was isolated in a manner analogous to that of compound VIa (preparative TLC in system B). Yield 0.03 g of an oily substance after twofold purification (preparative TLC in system B).

1-Benzyl-4-(2-piperidoethyl)-1,2,3,4-tetrahydroquinoxaline (VIIc). A mixture of 0.25 g (0.76 mmole) compound IV and 10 ml of a piperidine in methanol solution (0.19 mole/liter) gave, after 46 h at 90°C, 0.15 g of compound VIIc as an oil, in a manner analogous to compound VIc.

1-p-Nitrobenzyl-4-(2-piperidinoethyl)-1,2,3,4-tetrahydroquinoxaline (VIIIc). A mixture of 0.25 g (0.67 mmole) quaternary salt V and 11 ml of a solution of piperidine in methanol (0.19 mole/liter) gave, after 22 h at 90°C, in a manner analogous to VIc, 0.20 g of an oily substance.

Kinetic Studies of the Reactions of Compounds II-V with Nucleophiles. A. Potentiometric Titration Method. A sample solution in methanol was prepared such that the concentration of quaternary salts II-V was 0.05 mole/liter, and that of the nucleophile, 0.1 mole/liter. An aliquot portion of this solution was placed in a 1.2 ml-ampul, sealed, and thermostatted at 60-90°C. After a fixed time period, the ampul was cooled to 0°C, 1 ml of the reaction mixture was removed, and diluted with 10 ml of methyl ethyl ketone; 0.8 ml of a solution of p-toluenesulfonic acid in 2-propanol (0.13 mole/liter) was added, and the solution was titrated potentiometrically with a solution of tetrabutylammonium hydroxide in isopropyl alcohol (0.02 mole/liter). Reaction rate constants were calculated from the titration data using a second order kinetic equation [8].

B. Spectrophotometric Method. Aliquots containing 0.15 ml of reaction mixture, prepared as described above, were sealed in ampuls. After heating at thermostated temperatures of 60-90°C, they were cooled and 0.1 ml of reaction mixture was removed, diluted 100 times with absolute methanol, and their UV spectra were recorded, measuring the optical density at 227-230 nm. Reaction rate constants were calculated according to [7] using a second order kinetic equation.

In the case of the reactions of quaternary salts with sodium 4-tert-butylthiophenoxide, the reaction mixtures were observed directly in a spectrophotometer at 227-230 nm, using thermostatted cuvettes (l = 0.1 cm), at initial concentrations of quaternary salt of 1 mmole/liter and of sodium 4-tert-butylthiophenoxide equal to 1.5 mmole/liter.

Average rate constant values, calculated based on 3-5 measurements, are summarized in Table 3.

Reaction orders with respect to individual components were determined according to a method described previously [8].

LITERATURE CITED

1. G. V. Shishkin and V. N. Sil'nikov, Khim. Geterotsikl. Soedin., No. 12, 1658 (1986).
2. G. Cerichelli, G. Illuminati, and C. Lillocci, J. Org. Chem., 45, 3952 (1980).
3. G. Cospito, G. Illuminati, C. Lillocci, and H. Petride, J. Org. Chem., 46, 2944 (1981).
4. A. A. Gall' and G. V. Shishkin, Khim. Geterotsikl. Soedin., No. 6, 831 (1980).
5. G. W. H. Cheeseman and R. F. Cookson, The Chemistry of Heterocyclic Compounds, Wiley, New York (1979), Vol. 35, p. 261.
6. T. S. Manoharan, K. M. Madyastha, B. B. Singh, S. F. Bhafnagar, and U. Weiss, Synthesis, No. 10, 261 (1983).
7. O. V. Sverdlova, Electronic Spectra in Organic Chemistry [in Russian], Khimiya, Leningrad (1973), p. 195.
8. G. M. Panchenkov and V. P. Lebedev, Chemical Kinetics and Catalysis [in Russian], Izd. Mosk. Gos. Univ., Moscow (1961), p. 17, 35.
9. M. Charton, Progress in Physical Organic Chemistry, R. W. Taft (ed.), Wiley, New York (1981), Vol. 13, p. 119.
10. N. B. Chapman, J. Biggs, and A. Finch, J. Chem. Soc., B, No. 1, 55 (1971).
11. R. W. Hoffmann, Mechanisms of Chemical Reactions [Russian translation], Khimiya, Moscow (1979), p. 52.
12. V. A. Pal'm and T. L. Tenno, Tables of Rate Constants and Equilibrium Constants for Heterolytic Organic Reactions [in Russian], VINITI, Moscow (1977), Vol. 2, Part 2, p. 186.
13. G. V. Shishkin and G. A. Zloba, USSR Patent No. 749835; Byull. Izobr., No. 27, p. 101 (1980).