UNSATURATED HYDANTOIN DERIVATIVES. 18.* ALKALINE HYDROLYSIS OF 2-THIOXO-5-ARYLIDENEHYDANTOINS AND SOME OF THEIR DERIVATIVES

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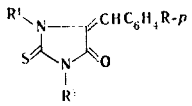
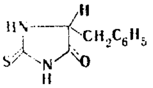
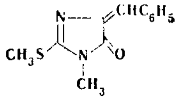
The alkaline hydrolysis of 2-thioxo-5-arylidenehydantoins (R = p-NO_2, p-Br, H, p-Me, and p-OMe) and their mono- and dialkyl derivatives proceeds with the formation of arylpyruvic acids, which undergo subsequent decomposition in the presence of oxygen in alkali solutions. 2-Thioxohydantoin, thioparabanic acid, and thiourea were not detected among the reaction products. Side processes involving the oxidation of the thioxohydantoins also take place under these conditions. The rate of hydrolysis of 2-thioxo-5-arylidenehydantoins varies as the concentration of alkali in solution changes, and the $\log k = f(C_{KOH})$ dependence is S-shaped. The hydrolysis of nonionized hydantoins and their monoanions is a bimolecular reaction and is first-order in substrate and hydroxide ion. The rate-determining step in the hydrolysis is the addition of hydroxide ion to the carbon atom of the $C_4{=}O$ group.

It is known [2-5] that the hydrolysis of hydantoins is used to establish the amino acid composition of poly- and oligopeptides and for the isolation of amino acids from thioxohydantoins formed by treatment of a mixture of amino acids in the hydrolyzates of peptides with isothiocyanates. Examples of the use of the alkaline hydrolysis of thioxohydantoins for practical purposes have already been published [4, 5], but the mechanism of this reaction has not been studied up until now. At the same time, we have previously investigated the mechanism of the rearrangement of 5-carboxymethylidenehydantoins in aqueous alkali solutions [6] and the alkaline hydrolysis of 5-arylidenehydantoins [7, 8] and have established the role of the substituents attached to the C_5 atoms of the hydantoin ring or the C_α atom of the side chain, the composition of the medium, and a number of other factors on the course of these reactions. Moreover, it has been shown [9] that replacement of the oxygen atom attached to the ring C_2 atom by sulfur has a substantial effect on the properties of the compounds under discussion. In this connection, we studied the hydrolysis of substituted 2-thioxo-5-arylidenehydantoins, especially since many problems in the interpretation of the mechanism of the alkaline hydrolysis of cyclic amides and their thio analogs still remain unsolved [10].


I-VII


VIII


IX

I $R^1{=}R^3{=}H$, $R{=}p\text{-}NO_2$; II Br; III H; IV CH_3; V OCH_3; VI $R\text{-}p{=}R^1{=}H$, $R^3{=}CH_3$;
VII $R{=}p\text{-}H$, $R^1{=}R^3{=}CH_3$

Nonionized hydantoins I-VIII exist in the crystalline state and in solutions in both water and organic solvents in the oxo thione form with cis-oriented hydantoin and benzene rings [9]. They are somewhat stronger NH acids than the corresponding 2-oxo analogs ($\Delta pK_a \sim 0.2$ for aqueous solutions) [9]. The ionization of 2-thiohydantoins I-VIII [9] proceeds via detachment of a proton from N_3 and leads to the formation of an anion with the charge delocalized in the ${}^{\delta-}S \dashrightarrow C_{(2)} \dashrightarrow N_{(3)} \dashrightarrow C_{(4)} \dashrightarrow O^{\delta-}$ system, and a dianion is formed due to subsequent detachment of a proton from N_1 [9].

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*See [1] for communication 17.

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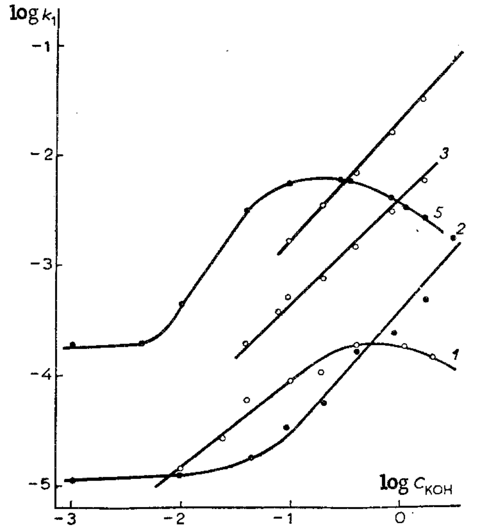

Fig. 1- Logarithmic dependence of the observed first-order rate constants (k_I, sec^{-1}) on the alkali concentration (C_{KOH}, moles/liter) in the hydrolysis of 2-thioxo-5-benzylidenehydantoin at 90°C (1), of 3-methyl-2-thioxo-5-benzylidene-(VI) at 80°C (2), of 1,3-dimethyl-2-thioxo-5-benzylidenehydantoin (VII) at 20°C (3), of 3-methyl-2-methylthio-5-benzylidene-4-imidazolone (IX) at 20°C, and of 2-thioxo-5-benzylhydantoin (VIII) at 90°C (5).

Special experiments and data from thin-layer chromatography (TLC) showed that when the preparative hydrolysis of 2-thioxo-5-benzylidenehydantoins I-VII is carried out in the absence of oxygen, the principle products, regardless of the alkali concentration, are arylpyruvic acids, as in the case of the oxygen analogs. The yields of the arylpyruvic acids reach 80%, although they are lowered when the temperature is raised. Neither thioxohydantoins, thiobarbituric acids, nor thiourea were detected in the reaction mixtures. The appearance of toluenes and benzaldehydes among the hydrolysis products, as demonstrated in [9, 11-13], is associated with cleavage of the arylpyruvic acids (particularly in the presence of oxygen and at increased temperatures). In contrast to 5-benzylidenehydantoins, the thio derivatives, like other 5-substituted 2-thioxohydantoins [14], undergo oxidation in solutions that contain oxygen, no special study was devoted to the structures of these products. Like 5-benzylhydantoin [7], 5-benzyl-2-thioxohydantoin (VIII) undergoes hydrolysis and is converted to phenylalanine with the formation of an N-thiocarbamoylphenylalanine intermediate. 2-Methylthio-3-methyl-5-benzylideneimidazolone (IX) is hydrolyzed to phenylpyruvic acid.

It may consequently be assumed that, as in the case of 5-benzylidenehydantoins [7], the site of hydrolytic attack on the 2-thioxo derivatives is the carbon atom of the carbonyl group rather than the carbon atom of the $C_5=C_\alpha$ bond. This is confirmed by the change in the PMR spectra of samples of the hydrolyzates: the original spectrum of the anion of the 2-thioxo-5-benzylidenehydantoins is transformed with time to the spectrum of the anion of the corresponding arylpyruvic acid, which is absolutely analogous to the situation with 5-benzylidenehydantoins [7]. Singlets of the carbon atoms of the benzene ring (130.7, 131.7, 133.0, and 148.9 ppm), of the methylidyne group (114.1 ppm), and the hydantoin ring [139.0 (C_5), 189.2 (C_4), and 200.5 (C_2)] are observed in the ^{13}C NMR spectra of a solution of 2-thioxo-5-benzylidenehydantoin in 2.14 M NaOD in aqueous (D_2O) hexadeuterodimethyl sulfoxide. The intensities of the signals of the carbon atoms of the carbonyl and thioxo groups decrease gradually during hydrolysis (with heating at 100°C and selection of samples for recording the spectra at 20-25°C), while the signals of the carbon atoms of the benzene ring are shifted and reach the position corresponding to the position of the signals in the spectrum of the dianion of phenylpyruvic acid. In other words, the change in the ^{13}C NMR spectra during the hydrolysis of 2-thioxo-5-benzylidenehydantoin indicates that attack by the hydroxide ion is directed to the ${}^{\delta-}S \cdots C_{(2)} \cdots N_{(3)} \cdots C_{(4)} \cdots O^{\delta-}$ fragment rather than to the $C_5=C_\alpha$ bond, but it does not make it possible to form a strict judgment as to whether the hydroxide ion adds only to C_2 or to C_4 or whether the reaction proceeds simultaneously at the two centers. However, it is well known that in reactions of 2-thioxohydantoins with nucleophilic agents the attack by the nucleophile in most cases is directed to C_4 rather than to C_2. It is evidently appropriate to once again mention that the alkaline hydrolysis of 2-thioxohydantoins and their 5-mono- or 5,5-dialkyl(aryl)derivatives leads to the formation of N-thioureidoamino acids, which subsequently undergo decomposition to free amino acids or their derivatives [2, 3, 5, 14].

The kinetics of the alkaline hydrolysis of 5-benzylidene-2-thioxohydantoins I-V and the 3-methyl- (II) and 1,3-dimethyl (III) derivatives, 3-methyl-2-methylthio-5-benzylidene-4-imidazolone (IV), and 5-benzyl-2-thioxohydantoin (V) in aqueous KOH solutions with various concentrations were investigated by a spectrophotmetric method [7, 8]. The rates of hydrolysis (see Table 1 and Fig. 1) of the compounds depend substantially on the alkali concentration in solution; the logarithmic dependences of the first-order rate constants (k_I) on the alkali concentration for I-V and VIII, which are dibasic NH acids, are S-shaped. When the alkali concen-

TABLE 1. Rate Constants in the Alkaline Hydrolysis of 5-Benzylidene-2-thioxohydantoin (III), 3-Methyl-5-benzylidene-2-thioxohydantoin (VI), 1,3-Dimethyl-5-benzylidene-2-thioxohydantoin (VII), 5-Benzylidene-3-methyl-2-methylthio-4-imidazolone (IX), and 5-Benzyl-2-thioxohydantoin (VIII)

Compound, temp. (°C), and λ_{anal} (nm)	$C_{KOH} \cdot 10^2$, moles/liter	$k_I \cdot 10^5$, sec^{-1}	$k_{II} \cdot 10^{-4}$,* liters/mole·sec
III, 90, 380	1,02	1,32	14,80
	2,40	2,76	13,20
	5,07	5,89	14,10
	10,00	8,91	10,90
	20,20	10,50	6,61
	42,50	19,60	5,81
	114,00	19,70	2,10
	212,00	15,60	0,76
VI, 80, 360	0,08	0,11	12,90
	1,00	1,13	12,60
	5,07	1,72	3,43
	10,00	3,55	3,55
	20,20	5,65	3,49
	53,60	16,70	3,95
	88,00	24,20	3,50
	173,00	50,60	3,38
	323,00	169,00	3,30
VII, 20, 364	4,00	16,90	55,50
	8,20	34,90	55,90
	10,00	39,60	62,50
	20,20	75,60	46,70
VII, 20, 364	39,60	148,00	46,80
	88,00	320,00	46,40
	173,00	630,00	42,00
VIII, 90, 290	0,10	19,00	1900,00
	0,43	20,00	503,00
	1,00	33,80	379,00
	5,07	287,00	690,00
	10,00	565,00	695,00
	27,40	595,00	272,00
	42,50	480,00	143,00
	53,60	441,00	105,00
	88,00	400,00	58,00
	114,00	355,00	38,00
	173,00	281,00	18,80
IX, 20, 361	10,00	166,00	209,00
	20,20	358,00	221,00
	43,00	710,00	207,00
	88,00	1660,00	236,00
	173,00	3310,00	220,00
	323,00	8000,00	197,00

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*The second-order rate constants (k_{II}) were calculated with allowance for the activity of the KOH.

tration is changed from 0.01 to 0.2 M for 2-thioxo-5-benzylidenehydantoin (III), from 0.05 to 3.20 M for 3-methyl-2-thioxo-5-benzylidenehydantoin (VI), from 0.04 to 1.70 M for 1,3-dimethyl-2-thioxo-5-benzylidenehydantoin (VII), and from 0.01 to 3.20 M for 3-methyl-2-methylthio-5-benzylidene-4-imidazolone (IX), the $\log K_I = f(\log C_{KOH})$ dependeneces are rectilinear and are described by Eqs. (1)-(4), respectively (see Table 2).

For comparison, the corresponding equations [(1a) and (2a)] of the rectilinear portions of the $\log k = f(\log C_{KOH})$ dependences for 5-benzylidenehydantoin and its 3-methyl derivative [7] are presented.

The rectilinear portions with a slope close to unity (Eqs. (1)-(4), Table 2) on the graphs of the $\log k_I = f(\log C_{KOH})$ dependences of III and VI correspond to the KOH concentration range over which only the monoanions of substituted 5-benzylidene-2-thioxohydantoins are present in solution. The lower boundary of this section is determined by the pK_a^1 value of the substrate, and the upper boundary is determined by the pK_a^2 value (ionization due to detachment of a proton from the N_1 atom of the monoanion). At a KOH concentration below the lower limit of the rectilinear portion of the $\log k_I = f(\log C_{KOH})$ dependence the rate of reaction of III and VI is higher than one should expect from extrapolation of the lines corresponding to these dependences; this is due to the development in solutions of the nonionized molecules of a substrate, the rate of hydrolysis of which considerably exceeds the rate of hydrolysis of the monoanions. At KOH concentrations above the upper limit of the rectilinear sections of the $\log k_I = f(\log C_{KOH})$ dependences for 5-arylidene-2-thioxohydantoins I-V the reaction rate decreases as compared with the rate expected from the equation $\log k = A \log C_{KOH} + B$; this is due to the development in the mixture of the corresponding dianions, the reactivities of which are considerably lower than in the case of the monoanions because of strong electrostatic repulsion. The pK_a^2 value of 5-benzylidene-2-thioxohydantoin calculated from kinetic data (under the condition that the dianion is unreactive) is 13.5, which is in agreement with the pK_a^2 value of 5-benzylidenehydantoin (13.9 and 14.2 according to data from kinetic and spectrophotometric determinations, respectively) [7] and the pK_a^3 value of 5-carboxymethylidenehydantoin (15.2 and 15.3) [15].

In the case of 2-thioxo-5-benzylhydantoin the rectilinear character of the $\log k = f(\log C_{KOH})$ dependence is observed only over a narrow range of KOH concentrations; this is probably due either to the relatively small difference in pK_a^2 and pK_a^3 or to the comparable reactivities of the anions of this compound.

Dialkyl derivatives VII and IX, which are incapable of ionization, are hydrolyzed substantially more rapidly than the unsubstituted compound; the rate constants for the hydrolysis of the nonionized substrate

TABLE 2. Parameters of the Logarithmic Dependence of the First-Order Rate Constants for the Alkaline Hydrolysis of III, VI, VIII, and IX on the Alkali Concentration, $\log k_I = (A \pm \Delta A) \log C_{KOH} - (B \pm \Delta B)$ (1)-(4)

Equation	Compound	t°	A	±ΔA	B	±ΔB	n	r	S
(1)	III	90	0,850	0,050	3,172	0,077	4	0,997	0,037
(1a)*	III	95	0,833	0,075	2,881	0,125	5	0,989	0,071
(2)	VI	80	1,172	0,106	3,478	0,044	5	0,988	0,099
(2a)	VI	95	0,907	0,027	3,236	0,022	8	0,997	0,047
(3)	VII	20	0,923	0,024	2,440	0,020	7	0,993	0,036
(4)	IX	20	1,094	0,032	1,705	0,018	6	0,998	0,041

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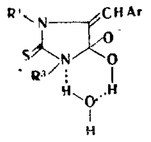
*Equations (1a) and (2a) were borrowed from [7] and pertain to the hydrolysis of 5-benzylidenehydantoin and its 3-methyl derivatives, respectively.

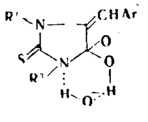
(calculated by the well-known method [15]) are close to the rate constants for the hydrolysis of the dialkyl derivatives (at identical temperatures and KOH concentrations in solution). In addition, as expected, the log $k = f(\log C_{KOH})$ dependences for VII and IX are rectilinear over the entire investigated range of alkali concentrations, while only one inflection is observed for mono-N-methylhydantoin VI.

The rectilinear character of the dependences of the rates of hydrolysis of I-IX on the KOH concentration in logarithmic coordinates (Fig. 1) and the positive slope of the lines described by Eqs. (1)-(4), which in each case is close to unity, constitute evidence that the reactions are first-order in hydroxide ion. This is also confirmed by the rectilinear character of the dependences of the rate constants on the KOH concentration in solution; the $k_I = f(C_{KOH})$ lines for each compound pass through the origin (Fig. 2). This indicates that the rate of noncatalytic hydrolysis of the hydantoins is considerably lower than the rate of their reaction with hydroxide ion. The reaction order in the substrate is also unity for all of the compounds, as shown by special experiments with variation of the substrate concentration at a constant alkali concentration. Using the method in [15], one can easily demonstrate that the order of alkaline hydrolysis with respect to hydroxide ion is also unity for the nonionized molecules of I-VI.

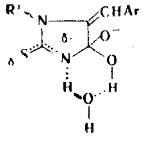
It is extremely interesting that, in contrast to 1,3-dimethyl-5-benzylidenehydantoin [7], the hydrolysis of its 2-thioxo analog is a bimolecular reaction (first-order in both the hydantoin and the hydroxide ion). In all likelihood, this is due to the fact that in the latter case an intermediate complex (X) with participation of a molecule of water rather than the hydroxide ion (structure XI) is realized in the case of transfer of a proton in the tetrahedral intermediate substance. This is in turn probably associated with an increase in the electron density on the N_3 atom in the thioxo derivative as compared with the benzylidenehydantoin because of the effect of the sulfur atom. It may be assumed that transfer of a proton is also realized with the participation of water in the hydrolysis of I-IX. The structure of the complex is similar to structure X for the reaction of nonionized substances, whereas complex XII is realized for the reaction of the anions.



X



XI



XII

Using a procedure similar to that described in [7, 15] and the principle of a steady state, one can show that the observed rate constant for the alkaline hydrolysis of the monoanions of 2-thioxo-5-arylidenehydantoins pertains to the step involving the addition of the hydroxide ion to the C_4 atom and that the remaining processes take place rapidly and are not of kinetic importance.

The similarity in the hydrolysis products, the closeness of the reaction rates, and the similarity in the dependences of the hydrolysis rates on the alkali concentration for substituted 5-benzylidene-2-thioxohydantoins and their oxygen analogs, the mechanism of the alkaline hydrolysis of which has been studied in greater detail [7, 8], constitute evidence for a similarity in the mechanisms of the reactions of the two reaction series.

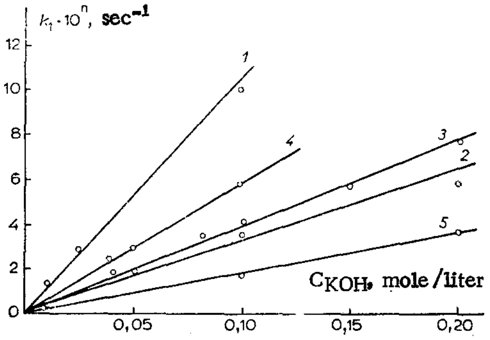
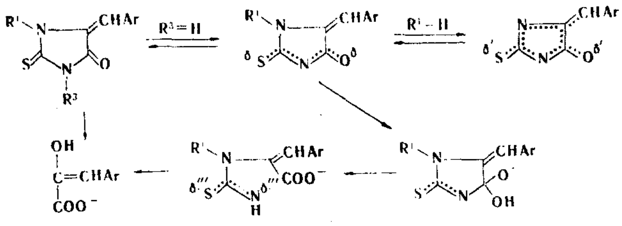


Fig. 2. Dependence of the observed first-order rate constants on the alkali concentration in the hydrolysis of 2-thioxo-5-benzylidenehydantoin (III) at 90°C ($k_I \cdot 10^5$, sec^{-1}) (1), of 3-methyl-2-thioxo-5-benzylidenehydantoin (VI) at 80°C ($k_I \cdot 10^5$, sec^{-1}) (2), of 1,3-dimethyl-2-thioxo-5-benzylidenehydantoin (VII) at 20°C ($k_I \cdot 10^4$, sec^{-1} (3), of 2-thioxo-5-benzylhydantoin (4) at 90°C, and of 3-methyl-2-methylthio-5-benzylidene-4-imidazolone (IX) at 20°C ($k_I \cdot 10^3$, sec^{-1}) (5).



Thus the rate-determining step of the reaction is the addition of hydroxide ion to the carbon atom of the $C_4{=}O$ group of the hydantoin ring, regardless of the reactive form of the substrate. The monoanions and neutral molecules of the thioxohydantoins under consideration are reactive; the rate of hydrolysis of the monoanions is lower by a factor of more than 1000 than the rate of hydrolysis of the nonionized molecules because of the electrostatic repulsion of the reacting particles. For the same reason, the dianions in all likelihood do not react at all with the hydroxide ion. Water molecules participate in the reaction only in the fast steps. It should be noted that 2-thioxo-5-arylidenehydantoins react somewhat more slowly than the corresponding 5-arylidenehydantoins. This difference is evidently associated with an increase in the electron density on the nitrogen and oxygen atoms (N_3 and $C_4{=}O$) of the reaction center, which leads, on the one hand, to an increase in the electrostatic repulsion of the reacting particles, and, on the other, to a high degree of solvation of it by water molecules and, correspondingly, to large entropy and enthalpy expenditures for resolvation on passing from the starting compounds to the intermediate complexes. It has previously been shown that these processes play a definite role in the change in the reactivities of substituted 5-carboxymethylidene- and 5-benzylidenehydantoins [6-8].

In conclusion, it should be emphasized that a substantial difference between the hydrolysis of 2-thioxo-5-benzylidenehydantoins and the hydrolysis of their oxygen analogs is the ability of the thioxo derivatives to undergo oxidation by air oxygen (or by oxygen dissolved in water); this difference cannot be disregarded in the study of the kinetics of the reaction.

EXPERIMENTAL

The investigated 2-thioxo-5-benzylidenehydantoin (III) and its mono- and dimethyl derivatives (VI and VII) and 5-arylidenehydantoins I, II, IV, and V were obtained [9] by condensation of 2-thioxohydantoins [16-18] with benzaldehydes, 2-methylthio-3-methyl-5-benzylidene-4-imidazolone (IX) was obtained by methylation of 5-benzylidene-2-thioxohydantoin with diazomethane or dimethyl sulfate, and 5-benzyl-2-thioxohydantoin (VIII) was obtained from phenylalanine and ammonium thiocyanate [19]. The compounds obtained were purified by recrystallization until they had constant melting points and molar extinction coefficients in their UV spectra and were dried in vacuo (2-5 mm) at 100-130°C; the individuality of the compounds was monitored by paper and thin-layer chromatography (TLC) [9].

The ^1H and ^{13}C NMR spectra were recorded by Yu. A. Ignat'ev with a Bruker HX-90 spectrometer (at 90 and 22.63 MHz, respectively). The UV spectra were recorded with SF-4A, SF-8, and SF-16 spectrophotometers.

Potassium hydroxide solutions with the required concentrations were prepared by dilution of a saturated solution with deoxygenated distilled water. The KOH concentrations in the solutions were determined by potentiometric titration by means of LPM-60M and pH-121 pH meters with glass and silver chloride electrodes. The starting solutions of the hydantoins were prepared by dissolving weighed samples of the compounds in purified ethanol. Their concentrations were varied in such a way that the hydantoin concentration in a solution formed by the addition of ~0.02 ml of these solutions to 3 ml of the alkali solution ranged from 10^{-4} to 10^{-5} mole/liter.

The kinetics of alkaline hydrolysis of I-IX were investigated by a spectrophotometric method (method A in [20] or the method in [6, 7] when $\tau_{1/2} < 15$ min) with excess alkali in solution (the molar ratio of the hydantoins and KOH in most experiments was no less than 1 : 10). The analytical wavelengths were selected by prior comparison of the UV spectra of the starting hydantoins and the reaction products in KOH solutions (see Table 1). They were refined by a study of the change in the UV spectra of alkaline solutions of the substances (at constant temperature) with time. The conversion of the compounds in most cases was no lower than 75%.

The measurements and the calculations of the rate constants were made as in [6, 7, 20]. Each constant was measured three or more times, and the average value was subsequently used. The error in the determination of the rate constants was no greater than 5%. The results of the kinetic measurements were processed with a computer.

LITERATURE CITED

1. B. A. Ivin, A. I. D'yachkov, G. V. Rutkovskii, and E. G. Sochilin, Zh. Org. Khim., 12, 1836 (1976).
2. E. Stieger and A. Day, in: Heterocyclic Compounds, edited by R. Elderfield, Vol. 5, Wiley.
3. E. Ware, Chem. Rev., 46, 403 (1950).
4. Protein Sequences Determination, Vol. 49, Springer Verlag, Berlin (1970), pp. 79, 211.
5. S. T. Edward, in: Organic Sulfur Compounds, Vol. 2, 287 (1964).
6. B. A. Ivin, G. V. Rutkovskii, N. A. Smorygo, A. I. D'yachkov, G. M. Frolova, and E. G. Sochilin, Zh. Org. Khim., 9, 2405 (1973).
7. B. A. Ivin, G. V. Rutkovskii, T. N. Rusavskaya, and E. G. Sochilin, Zh. Org. Khim., 13, 1970 (1977).
8. B. A. Ivin, G. V. Rutkovskii, T. N. Rusavskaya, and E. G. Sochilin, Reakts. Sposobnost' Org. Soedin., 13, 41 (1976).
9. B. A. Ivin, G. V. Rutkovskii, N. A. Smorygo, A. I. D'yachkov, G. M. Frolova, and E. G. Sochilin, Zh. Org. Khim., 9, 2405 (1973).
10. R. J. E. Talbot, in: Comprehensive Chemical Kinetics, 10, 257 (1972).
11. G. Billek, Monatsh., 92, 335, 343 (1961).
12. H. R. Henze, W. B. Whithney, and M. A. Eppright, J. Amer. Chem. Soc., 62, 540 (1940).
13. C. H. Day, Nature, 24, 529 (1960).
14. B. Africa and F. H. Carpenter, Biochem. Biophys. Res. Commun., 24, 113 (1966).
15. B. A. Ivin, G. V. Rutkovskii, and E. G. Sochilin, Zh. Org. Khim., 8, 1951 (1972).
16. D. T. Elmore, J. K. Ogle, and P. A. Toseland, J. Chem. Soc., No. 1, 192 (1956).
17. J. R. Johnson and J. B. Buchanan, J. Amer. Chem. Soc., 73, 3749 (1951).
18. V. F. Krivtsov and V. M. Stepanov, Zh. Obshch. Khim., 35, 53, 556 (1965).
19. B. H. Nicolet and E. D. Campbell, J. Amer. Chem. Soc., 50, 1155 (1928).
20. B. A. Ivin, G. V. Rutkovskii, E. G. Sochilin, and I. Yu. Tsereteli, Zh. Org. Khim., 8, 640 (1972).