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OXIDATION OF ALIPHATIC THIOAMIDES IN A SODIUM PEROXYDISULFATE–CUPRIC CHLORIDE SYSTEM

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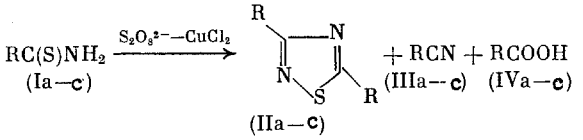
Based on a one-electron oxidation reaction in systems containing sodium peroxydisulfate, we have recently carried out regioselective reactions of remote oxidative functionalization of carbonyl compounds of different types: ketones into γ- and δ-diketones in the $Na_2S_2O_8$–$FeSO_4$ system [1], alkanoic acids, their amides [2-4], and alkanehydroxamic acids [5] into lactones in the $Na_2S_2O_8$–$CuCl_2$ system. In the same system, oxidative cyclization of N-methylsulfonylalkylamines into N-methylsulfonylpyrrolidines takes place [6]. The mechanism of remote oxidative functionalization includes in the first stage the oxidation of carbonyl compounds to oxygen-centered cation-radicals $>C{=}O \rightarrow >C{=}\overset{+}{O}\cdot$ [6].

In a continuation of these studies, and to compare the properties of the carbonyl and thiocarbonyl compounds under one-electron oxidation reaction conditions, we studied the transformations of alkanethioamides and also of N-substituted alkaneselenoamide in the sodium peroxydisulfate–cupric chloride system.

Under the action of the $Na_2S_2O_8$–$CuCl_2$ system, in aqueous solutions at 80-85°C, and with equimolar amounts of the reagents, N-unsubstituted alkanethioamides (Ia-c) convert into 3,5-dialkyl-1,2,4-thiadiazoles (IIa-c). Alkanonitriles (IIIa-c) and alkanoic acids (IVa-c) are also formed (Table 1).



(IIa–c)

R = C_4H_9 (a), C_5H_{11} (b), CH_3 (c).

For alkanethioamides (Ia, b), the predominating reaction is oxidative heterocyclization into (IIa, b), while in the case of thioamide (Ic), hydrolysis into acid (IVc) predominates. Because of the ease of isolation of 1,2,4-thiadiazoles from the reaction mixture (see the Experimental section) and their high yield from (Ia, b), the reaction studied can be regarded as a simple method for synthesizing 3,5-dialkyl-1,2,4-thiadiazoles. The oxidation of thioamides into 1,2,4-thiadiazoles by the action of I_2, $KMnO_4$, tert-butyl hypochlorite, and other oxidizing agents [7, 8] has already been reported, but the objects of the investigation were, in general, readily available arylthioamides.

According to the mechanism of one-electron oxidation of the carbonyl group in systems containing peroxydisulfates [6], during the oxidation of (Ia-c), cation-radicals are most probably first produced, which then split off a proton to form thioamidyl radicals (Va-c). Due to the known tendency of thiocarbonyl compounds to radical addition to the S atom of the C=S group [9], these radicals react with the initial (Ia-c) to form intermediate dimers (VIa-c).

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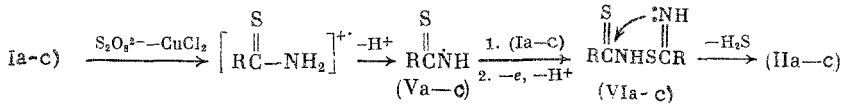
TABLE 1. Oxidation of Thioamides (Ia-c) by $Na_2S_2O_8$–$CuCl_2$ System*

Thioamide	Reaction products and their yield, %†		
	1,2,4-thiadiazole	alkanonitrile	alkanoic acid
(Ia)	(IIa), 60	(IIIa), 10	(IVa), 24
(Ia)‡	(IIa), 32	–	(IVa), 31
(Ib)	(IIb), 55	(IIIb), 11	(IVb), 25
(Ic)	(IIc), 10	(IIIc), 11	(IVc), 60

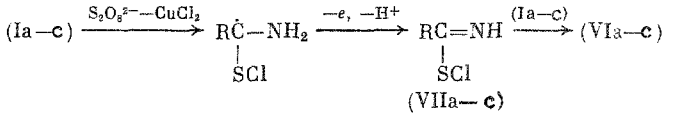
*80-85°C, 50 mmoles of (I), 50 mmoles of $Na_2S_2O_8$, 50 mmoles of $CuCl_2 \cdot 2H_2O$.
†Conversion of (Ia-c) 100%.
‡The reaction proceeds in the absence of $CuCl_2$; conversion of (Ia) 80%.

As a result of intramolecular cyclization of the latter with the elimination of H_2S, 1,2,4-thiadiazoles (IIa-c) are formed:



It is clear that the cyclization of (VIa-c) into (IIa-c) is favored by the presence of oxidizing agents in the reaction mixture, which react with splitting of H_2S.

Another possible path of formation of dimers (VIa-c), which should not be unequivocally excluded, includes the addition of $\dot{C}l$ radicals, generated in the reaction of the components of the oxidation system, to the S atom of the initial (Ia-c) to form S-chloroisothioamides (VIIa-c), as a result of oxidation of the adduct-radicals and elimination of a proton from the N atom. The subsequent condensation of (VIIa-c) with (Ia-c) leads to (VIa-c).



The possible formation of (II), discussed in [8], as a result of cycloaddition of $RC(S^+)=N^-$ [a dehydrochlorination product of isothioamides (VII)] to by-products of the oxidation reaction, nitriles III, can be excluded. This is because during "crossed" oxidation reactions of (Ia) in the presence of (IIIa), or of (Ic) in the presence of C_3H_7CN, we did not detect 3-methyl-5-butyl- and 3-propyl-5-methyl-1,2,4-thiadiazoles, respectively, by the chromatographic/mass spectrometric or PMR spectrometric methods (see the Experimental section):

$$RC\overset{+}{S} = N^- + RC{\equiv}N - \times \rightarrow (IIa{-}c)$$

On splitting of H_2S from (Ia-c) promoted by Cu(II) ions [10], and also, possibly, during dehydrochlorination and elimination of S from (VIIa-c), nitriles (IIIa-c) are formed. Under the reaction conditions, the acid hydrolysis of (Ia-c) leads to alkanoic acids (IVa-c) (cf. [11, 12], which are also formed by the action of $CuCl_2$ only on (I) in the absence of $Na_2S_2O_8$. Compound (Ia) thus converts into (IVa) in a yield of 70%. The hydrolysis of thioacetamide (Ic) into acetic acid (IVc), proceeding in an acid medium at a very high rate [13], is clearly the reason for the low contribution of the heterocyclization reaction of (Ic).

The asymmetric structure of heterocycles (IIa-c) is reliably confirmed by the nonequivalency in the PMR spectrum of protons directly bound to the heterocyclic ring: CH_2 groups in (IIa) (δ 2.97 and 3.10 ppm) and (IIb) (δ 2.90 and 3.05 ppm), CH_3 groups in (IIc) (δ 2.62 and 2.77 ppm).

A thorough investigation of the mixture of the oxidation products of (Ia, b) in the $Na_2S_2O_8$–$CuCl_2$ system by PMR (250 MHz) and mass spectroscopic methods showed the absence in the mixture of thiolactams and thiolactones, the most probable products of oxidative functionalization of thioamides (Ia, b), and intermediate thioamidyl radicals (Va, b). The oxygen

TABLE 2. Physicochemical and Spectral Characteristics of Starting Compounds and Oxidation Products

Compound	mp or bp, °C (p, mm Hg)	IR spectrum ν, cm^{-1}	PMR spectrum δ, ppm	Mass spectrum, m/z (relative intensity, %)
Thiopentanamide (Ia)	122–123	3280, 3170, 1630, 1410, 1090	0,92 t (3H), 1,15–2,00 m (4H), 2,68 t (2H), 8,0 br.s (2H)	117 (M^+, 44), 88(17), 75(100), 64(18), 60(40), 54(100), 44(100)
Thiohexanamide (Ib)	115–116	3285, 3170, 1635, 1415, 1085	0,90 t (3H), 1,20–2,00 m (6H), 2,70 t (2H), 7,80 br.s (2H)	131 (M^+, 50), 130(47), 114(40), 98(90), 96(88), 82(80), 81(75), 75(100), 71(50)
3,5-Dibutyl-1,2,4-thiadiazole (IIa)*	122–125(12) **		0,97 t (6H), 1,18–2,20 m (8H), 2,97 t (2H), 3,10 t (2H)	198 (M^+, 6), 183(14), 170(7), 169(24), 156(100), 115(41), 113(13), 84(13), 83(8)
3,5-Dipentyl-1,2,4-thiadiazole (IIb)	130–133(15) ***		0,95 t (6H), 1,20–2,00 m (12H), 2,90 t (2H), 3,05 t (2H)	226 (M^+, 4), 211(5), 197(20), 183(25), 170(100), 129(61), 114(18), 97(14), 96(31), 56(30)
3,5-Dimethyl-1,2,4-thiadiazole (IIc)	45–48(15) ****		2,62 s (3H), 2,77 s (3H)	114 (M^+, 30), 99(21), 85(17), 83(22), 81(27), 79(100), 73(100), 72(30), 71(30), 69(37)
N-Methylthiopentanamide (IXa)	145–150(1,5)	3230, 1550, 1377, 1090	0,86 t (3H), 1,10–1,80 m (4H), 2,50 t (2H), 2,90 d (3H), 7,60 br.s (1H)	131 (M^+, 59), 130(6), 116(9), 103(12), 102(15), 98(30), 91(10), 89(100)
N,N-Diethylthiopentanamide (IXb)	103–107(0,15)	1505, 1070	0,90 t (3H), 1,10–1,80 m (10H), 2,40 t (2H), 3,40 m (4H)	173(M^+, 75), 172(6), 144(24), 140(21), 132(12), 131(42), 130(100), 102(45)
N-Methylpentanamide (Xa)	127–130(15)	3350, 3070, 1640	0,90 t (3H), 1,10–1,80 m (4H), 2,20 t (2H), 2,70 d (3H), 7,35 br.s (1H)	Identical with [3]
N,N-Diethylpentanamide (Xb)	110–111(15)	1640	0,90 t (3H), 1,20–1,75 m (10H), 2,20 t (2H), 3,24 q (4H)	Identical with [3]
Pentaneselenoamide (XI)	43–44	3280, 3150, 1630, 1460, 1420, 1090	0,95 t (3H), 1,10–2,10 m (4H), 2,75 t (2H), 9,40 br.s (2H)	165 (M^+, 100), 163(54), 150(4), 148(2), 136(18), 134(10), 123(80), 121(44), 108(36), 106(20)

*UV spectrum: λ_{max} 236 nm (ε 3250, alcohol).
†Found, %: C 60.22; H 9.18; N 14.03; S 15.77. $C_{10}H_{18}N_2S$. Calculated, %: C 60.56; H 9.15; N 14.12; S 16.17.
‡Found, %: C 63.55; H 9.70; N 12.20; S 14.70. $C_{12}H_{22}N_2S$. Calculated, %: C 63.71; H 9.73; N 12.39; S 14.16.
**See [8].

analogs of (Ia, b), the carboxylic acid amides $RCONH_2$ (VIII), behave differently in the same oxidation system. They transform to a considerable extent through the corresponding amidyl radicals $RC\dot{O}NH$ into γ- and δ-lactones [3, 4].

This main difference in the behavior and direction of oxidation of thioamides (I) and amides (VIII) is due chiefly to the electronic structure of the C=S group in (I). The energy of the highest occupied molecular orbital (HOMO) of the C=S bond, formed due to overlapping of the 2p AO of the C atom and the 3p AO of the S atom, is higher than the HOMO energy of the C=O bond formed due to overlapping of the 2p orbitals of the C and O atoms. Because of the presence of a vacant 3d orbital at the S atom, the energy of the lowest unoccupied molecular orbital (LUMO) of the C=S bond is noticeably lower than that of the LUMO of the C=O bond. These differences in the electronic configuration of the C=S and C=O bonds, together with the higher polarizability of the C=S bond, determine the properties of the latter bond, which is an appreciably more active acceptor of free radicals than the C=O bond. The attack of the free radical is oriented to the "soft" S atom, which is sterically more accessible, and is characterized by low electron negativity and serves as the site for the localization of the LUMO of the C=S bond.

Under the conditions of the $Na_2S_2O_8$–$CuCl_2$ oxidation system, N-substituted thioamides – N-methyl- and N,N-diethylpentanethioamides – convert into O-analogs, N-methyl-, and N,N-diethylpentanamides (Xa, b), in a ~100% yield.

$$\underset{\text{(IXa,b)}}{C_4H_9C(S)NR^1R^2} \xrightarrow{Na_2S_2O_8-CuCl_2} \underset{\text{(Xa,b)}}{C_4H_9C(O)NR^1R^2}$$

$R^1 = CH_3$, $R^2 = H$ (a); $R^1 = R^2 = C_2H_5$ (b).

The oxidative hydrolysis of thioamides into carboxamides is induced by other reagents, in particular H_2O_2 in an alkaline medium, ozone, and $K_3Fe(CN)_6$ [7], tert-butyl hypochlorite [8], nitrous acid [14], and m-chloroperbenzoic acid [15]. Although with some of these reagents [8, 15] a very high yield of O-amides can also be obtained, the oxidation system used by us ($Na_2S_2O_8$–$CuCl_2$) is one of the simplest and convenient.

In the oxidation of $Na_2S_2O_8$–$CuCl_2$ in water, pentaneselenoamide (XI) converts into pentanonitrile (IIIa), pentanoic acid (IVa), and pentanamide (XII) in a yield of 48, 24, and 20%, respectively, with 100% conversion of (XI):

$$\underset{\text{(XI)}}{C_4H_9C(Se)NH_2} \xrightarrow{S_2O_8^{2-}-Cu^{2+}} \underset{\text{(IIIa)}}{C_4H_9CN} + \underset{\text{(IVa)}}{C_4H_9COOH} + \underset{\text{(XII)}}{C_4H_9CONH_2}$$

According to the PMR and mass spectral data, the expected heterocyclization product – 3,5-dibutyl-1,2,4-selenodiazole – does not form, most of all, probably because of the ready hydrolizability and instability of the initial selenoamide (XI) [16].

EXPERIMENTAL

The GLC analysis was carried out on an LKhM-8MD chromatograph with a flame-ionization detector in a N_2 current. Columns: 3000 × 3 mm with 1.5% PEGS on Chromosorb G (120-140 mesh) treated with Me_2SiCl_2, 2000 × 3 mm with 1.5% PEG (mol. wt. 20,000) treated with H_3PO_4 [17], on Chromosorb P-AW (120-140 mesh) treated with Me_2SiCl_2. The PMR spectra of the solutions in $CDCl_3$ and CCl_4 were run on Varian DA-60JL (60 MHz), Tesla BS-497, and Bruker WM-250 (250 MHz) spectrometers. The chemical shifts are given on the δ scale with reference to TMS as internal standard. The mass spectra were obtained on a Varian MAT CH-6 spectrometer. The chromatographic/spectrometric analysis was carried on a Varian MAT CH-111 apparatus (Gnom). The IR spectra were run on a Perkin–Elmer-577 spectrophotometer in a thin layer and in KBr tablets. The UV spectra were obtained on Specord UV-VIS spectrophotometer. Commercial $Na_2S_2O_8$, sp grade, and commercial $CuCl_2$, AR grade, were used without additional purification. Distilled water was used. A commercial preparation of thioacetamide (Ic) was purified by recrystallization from alcohol, mp 113-113.5°C. Thioamides (Ia, b) and (IXa, b) were obtained by the action of freshly prepared P_2S_5 on the corresponding O-amide in m-xylene [18]. Compounds (Ia, b) were purified by chromatography on a column with SiO_2 (eluent: benzene–pentane, 3:1), followed by recrystallization from alcohol. Compounds (IXa, b) were purified by distillation in vacuo. Pentaneselenoamide (XI) was obtained by the action of aluminum selenide on (IIIa) in analogy with [19]. The physicochemical and spectral characteristics of the starting thio- and selenoamides are given in Table 3.

Oxidation of Alkanoic Acid Thioamides (Ia-c) and (IXa, b) in a $Na_2S_2O_8$–$CuCl_2$ System (General Procedure). A solution of 50 mmoles of $Na_2S_2O_8$ in 50 ml of water was added dropwise at

80-85°C to a mixture of 50 mmoles of thioamide and 50 mmoles of $CuCl_2 \cdot 2H_2O$ in 70 ml of water. The reaction mixture was held at this temperature for 3 h. When cool, the mixture was extracted by 2 × 100 ml of ether and 100 ml of $CHCl_3$. The combined extract was filtered from CuS precipitate and partially from elementary sulfur, and then dried over $MgSO_4$ and evaporated. The residue was analyzed by GLC, using for the determination of thiadiazoles (II), nitriles (III), and acids (IV), as a standard, a nitrile with one more carbon atom than in the initial (Ia-c). The data on the composition of the oxidation products of (Ia-c) are given in Table 1. To isolate the oxidation products, thiadiazoles (IIa-c) from the oxidation of (Ia-c), and carboxamides (Xa, b) from the oxidation of (IXa, b), the residue was fractionated in vacuo. The physicochemical and spectral characteristics of (IIa-c) and (Xa, b) are listed in Table 2. Nitriles (IIIa-c) and acids (IVa-c) were identified by comparison with authentic samples.

The oxidation of pentaneselenoamide (XI) was carried out in the same way as the oxidation of thioamides. Pentanamide (XI) was identified by comparison with an authentic sample.

Oxidation of Thiopentanamide (Ia) by the $Na_2S_2O_8$–$CuCl_2$ System in the Presence of Acetonitrile (IIIc). A solution of 10 mmoles of $Na_2S_2O_8$ in 10 ml of water was added dropwise, at 80°C, to a mixture of 10 mmoles of (Ia), 10 mmoles of $CuCl_2 \cdot 2H_2O$, and 100 mmoles of (IIIc) in 25 ml of water. The mixture was held at this temperature for 3 h. When cool, it was extracted by 2 × 100 ml of ether and 100 ml of $CHCl_3$. The extracts were combined and dried over $MgSO_4$, and the solvent was evaporated. In the residue, compounds (IIa), (IIIa), (IVa), and (IIIc) were identified by chromatography/mass spectrometry. The expected product of "crossed" oxidative heterocyclization – 3-methyl-5-butyl-1,2,4-thiadiazole (M^+, 156) – was not detected.

The oxidation of thioacetamide (Ic) in the presence of butyronitrile was carried out in a similar way as described above. Chromatography/mass spectrometry analysis of the complex mixture of products showed the absence of 3-propyl-5-methyl-1,2,4-thiadiazole (M^+ 142).

CONCLUSIONS

1. Oxidative cyclization of N-unsubstituted aliphatic thioamides in the $Na_2S_2O_8$–$CuCl_2$ system leads to 3,5-dialkyl-1,2,4-thiadiazoles in a yield of 50-60%.

2. N-Monoalkyl- and N,N-dialkyl-substituted thioamides quantitatively convert in this system into the corresponding O-amides.

3. The principal difference in the oxidative reactions of aliphatic thioamides and their oxygen analogs in a $Na_2S_2O_8$–$CuCl_2$ system is determined by the tendency of the S atom of the thiocarbonyl group to add radicals formed in the oxidation process.

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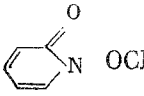
ASYMMETRIC NITROGEN.

COMMUNICATION 47.* GEMINAL SYSTEMS.
COMMUNICATION 31.† AMIDE ROTATION AND NITROGEN INVERSION IN SUBSTITUTED N-ALKOXYUREAS

I. I. Chervin, V. S. Nosova, V. F. Rudchenko, V. I. Shevchenko, and R. G. Kostyanovskii

UDC 543.422.25:541.63:542.91:547.495.3

For N-alkoxyamines, similar values of the barriers to N inversion ($\Delta G^{\neq}_{in}$) and to rotation around the N–O bond ($\Delta G^{\neq}_{ro}$) have been bound, viz., 10-12 kcal/mole [3-6]. Separation of inversion from rotation in $RN(R^1)OR^2$ is achieved by studying the dependence of the barrier on the bulk of substituents R^1 and R^2 [4, 5, 7], and by introducing a substituent R that decreases $\Delta G^{\neq}_{in}$ or effectively applanates the N atom; thus, in PhN(Me)OCH_2Ph or  $\Delta G^{\neq}_{ro}$ = 9-10 kcal/mole [6]. We have previously found a chirality for N-tert-alkyl-N-methoxyamines due to restricted rotation on the NMR time scale around the N–CO and N–C bonds, and have studied the dependence of the barriers to these processes on the type of substituent at N and C=O [8]. In the present work, by means of dynamic NMR we have studied amide rotation and N inversion in substituted N-alkoxyureas $Me_2NCON(OR)X$ (I)-(XVIII), where X is H, Cl, OR, or  (Table 1). Values of $\Delta G^{\neq}_{ro}$ were found from the merging of Me_2N signals (see Table 1). There is an increase of $\Delta G^{\neq}_{ro}$ as the substituent electronegativity increases in going from X = H in (I)-(VII) to X = Cl, RO,  in (VIII)-(XVIII), and also by comparison with $Me_2NCONHPr$-i ($\Delta G^{\neq}_{ro}$ = 9.7 kcal/mole [9]).‡ This can be explained by the weakening of the concurrent conjugation of C=O with the unshared electron pair of the N^3 atom, because $\Delta G^{\neq}_{ro}$ is reduced when one Me in Me_2NCOR, Me_2NCOCl, or Me_2NNO is replaced by MeO [8]. We can therefore expect $\Delta G^{\neq}_{ro}$ to increase in going from X = Cl in (VIII)-(X), to X = RO in (XI)-(XVI) and X=  in (XVII) and (XVIII). But in the series (VIII)-(XVIII), $\Delta G^{\neq}_{ro}$ hardly increases any more (see Table 1). This becomes understandable when compared with $\Delta G^{\neq}_{ro}$ in Me_2NCOX (Table 2), because $\Delta G^{\neq}_{ro}$ depends substantially not only on the +M capability, but also on the bulk and I effect of substituent X. The maximum difference, $\Delta\Delta G^{\neq}_{ro}$, in going from X = i-Pr to X = Br, Cl, F is in all 2.4 kcal/mole.

In the PMR spectra of (XII)-(XIV) the CH_2O signals are broadened, but are not resolved even at −100°, whereas the low-temperature spectra of (XV)-(XVII) show geminal anisochronism of the diastereotopic methylene protons of CH_2O. From the merging of their signals the barrier values were found (see Table 1), which may correspond both to slow inversion of N and to restricted rotation around the N–O bond. These barriers are assigned to $\Delta G^{\neq}_{in}$ of N on the basis of the following data. It is known that the pyramidal stability of amide N increases

*For Communication 44, see [1].
†For Communication 29, see [2].
‡Methyl proton signals in $Me_2NCXNMe_2$, where X = O, S, are not resolved at −120° [9].

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