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REACTION OF PRIMARY ALIPHATIC AMINES IN OXIDATION SYSTEMS CONTAINING SODIUM PEROXYDISULFATE

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Among the large class of nitrogen-centered free radicals, aminyl radicals occupy an important place, in particular, because of their wide use during recent years in organic synthesis [1, 2]. Great progress has been made in the development of methods for the production of these radicals, based on the reactions of amines and some of their derivatives with free radicals [3], in redox systems [4], and under electrochemical conditions [5]. Among the reactions in oxidation systems, the transformations of secondary and tertiary amines has been studied most. The oxidation of primary amines has been studied much less [6-8].

In continuation of our studies on the reactions of nitrogen-centered amidyl and aminyl radicals in the $Na_2S_2O_8-CuCl_2$ and $K_3Fe(CN)_6-NaOH$ systems [9, 10], we studied the oxidation reactions of primary amines and aminyl radicals produced from them in systems containing sodium peroxydisulfate.*

It is known that during oxidation by peroxydisulfates in an alkaline medium catalyzed by Ag^+ ions, primary aliphatic amines transform into Schiff bases [12]. We found that nitriles (IIa-e), 2,3-dichloroalkanals (IIIa-e), alkanoic acids (IVa-e) and chloroalkanes (Va-e) are formed from amines $RCH_2CH_2NH_2$ (Ia-e) by the action of the $Na_2S_2O_8-CuCl_2$ system, using equimolar amounts of the substrate and the oxidation system components in water at 70-80°C (Table 1)

$$\underset{(Ia-e)}{RCH_2CH_2NH_2} \xrightarrow{Na_2S_2O_8-CuCl_2} \underset{(IIa-e)}{RCH_2CN} + \underset{(IIIa-e)}{RCCl_2CHO} + \underset{(IVa-e)}{RCH_2COOH} + \underset{(Va-e)}{RCH_2CH_2Cl}$$
$$R = C_3H_7\,(a),\ C_4H_9\,(b),\ C_5H_{11}\,(c),\ C_6H_{13}\,(d),\ C_7H_{15}\,(e)$$

The transformations of amines (I) into 2,2-dichloroalkanals (III) and chloroalkanes (V) are new reactions of oxidative substitution of the amino group in primary aliphatic amines. The contribution of different oxidation paths of amines (Ia-d) is practically independent of the length of the alkyl fragment in the amine. The main products are the corresponding nitriles (IIa-d) (see Table 1). During the oxidation of (Ie), the selectivity of the oxidation reactions decreases, and products (IIe)-(Ve) are formed in almost the same amounts. It is probable that this is due to a change in the reaction conditions as the result of the decreased solubility of (Ie) in water (compared with other amines studied), as manifested in the nonhomogeneous character of the reaction medium.

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* Preliminary article, see [11].

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TABLE 1. Oxidation of Primary n-Alkylamines (Ia-e) in the $Na_2S_2O_8-CuCl_2$ System*

Amine	Conversion, %	Reaction products, yield per converted amine, %			
		nitrile (IIa-e)	2,2-dichloroalkanal (IIa-e)	acid (IVa-e)	chloroalkane (Va-e)
Amylamine	41	39	17	12	7
Hexylamine (Ib)	36	43	14	17	8
Heptylamine (Ic)	40	44	22	9	7
Octylamine (Id)	42	38	12	19	12
Nonylamine (Ie)	44	22	21	13	15

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* 70-80°C, 4.5 h, 100 mmoles of (I), 100 mmoles of $Na_2S_2O_8$, 100 mmoles of $CuCl_2 \cdot 2H_2O$, 75 ml of water.

To study the mechanism of the oxidative transformations of the amines by the action of $Na_2S_2O_8$, and the dependence of the separate reaction stages on the oxidation system components, we studied the oxidation of hexylamine (Ib) in other oxidation systems containing sodium peroxydisulfate (Table 2).

Hexylamine (Ib) is practically inert to the action of $CuCl_2$ or $NaHSO_4$ (a product of the decomposition of $Na_2S_2O_8$; see Experimental).

The results show that sodium peroxydisulfate by itself, and also in combination with NaCl, has a small effect in the directed oxidation of primary aliphatic amines, causing mainly the resinification of the substrate. The introduction of catalytic amounts of $AgNO_3$ to $Na_2S_2O_8-CuCl_2$ practically does not influence the course of the oxidation, while in the presence of an equimolar amount of NaOH, the formation of nitrile (IIb) is completely inhibited. The last result agrees with the data on the oxidation of amines in the $Na_2S_2O_8-NaOH-AgNO_3$ system [12].

We believe that the mechanism of reaction of (Ia-e) with the $Na_2S_2O_8-CuCl_2$ oxidation system includes their one-electron oxidation into aminyl radicals $RCH_2CH_2\dot{N}H$, which form aldimines (VIIa-e) oxidative deprotonation

$$\text{(Ia–e)} \xrightarrow{S_2O_8^{2-}-CuCl_2} RCH_2CH_2\overset{+\cdot}{N}H_2 \xrightarrow{-H^+} RCH_2CH_2\dot{N}H \xrightarrow{S_2O_8^{2-}-CuCl_2} \underset{\text{(VIIa–e)}}{RCH_2CH{=}NH}$$

The last compounds oxidize further into nitriles (IIa-e)

$$\text{(VIIa–e)} \xrightarrow{S_2O_8^{2-}-CuCl_2} RCH_2CH{=}\dot{N} \xrightarrow{S_2O_8^{2-}-CuCl_2} \underset{\text{(IIa–e)}}{RCH_2C{\equiv}N}$$

and also hydrolyze into aldehydes (VIa-e)

$$\text{(VIIa–e)} \rightarrow \underset{\text{(VIa–e)}}{RCH_2CHO}$$

The oxidation of (VIIa-e) into nitriles (IIa-e) and hydrolysis into aldehydes (VIa-e) are competing reactions. Aldimines (VIIa-e) apparently readily oxidize in the $Na_2S_2O_8-CuCl_2$ system, which hinders their polymerization to form resinification products. In the presence of sufficiently large amount of alkali in the $Na_2S_2O_8-CuCl_2-NaOH$ system, the hydrolysis of (VIIa-e) clearly becomes accelerated, and the oxidation of these aldimines into (II) is suppressed at the same time, (see Table 2).

Acids (IVa-e) are formed as the result of the oxidation of aldehydes (VIa-e) under the reaction conditions, as confirmed by a control experiment with pentanal (VIa)

$$\underset{\text{(VIa–e)}}{RCH_2CHO} \xrightarrow{Na_2S_2O_8-CuCl_2} \underset{\text{(IVa–e)}}{RCH_2COOH}$$

The oxidative chlorination of (VIa) with the formation of (IIIa) thus does not take place. To convert aldehydes (VIa-e) into 2,2-dichloroalkanals (IIIa-e) by the action of the $Na_2S_2O_8-CuCl_2$ system, an amine must be present in the reaction mixture, as confirmed by the formation of 2,2-dichloropentanal (IIIa) during cooxidation of a mixture of (Ib) and (VIa). A Schiff base $C_4H_9CH{=}NC_6H_{13}$ (VIII) is also formed.

TABLE 2. Oxidation of Hexylamine (Ib) by $Na_2S_2O_8$ and Systems Based on It*

Components of oxidation system, mole % with respect to $Na_2S_2O_8$	Conversion of (Ib), %	Reaction products and their yield, % of converted (Ib)				Resinification products, g
		(IIb)	(IIIb)	(IVb)	(Vb)	
–	60	6	–†	6	–	2,8
$CuCl_2$, 100	36	43	14	17	8	–
$CuCl_2$, 100 + $AgNO_3$, 3	28	42	18	11	11	–
$CuCl_2$, 100 + NaOH, 100	42	–	13	11	1	4,8
NaCl, 100	70	4	–	–	–	5,3
NaCl, 100 + $CuCl_2$, 10	66	1	10	1	1	5,4

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* 70-80°C, 4.5 h, 100 mmoles (9.9 g) of (I), 100 mmoles of $Na_2S_2O_8$, amounts of other components as indicated in Table 2, 75 ml of water.

† Hexanal (VIb) is formed in a yield of 2%.

The formation of dichloroalkanal (IIIa) only, and the absence of its homolog during the cooxidation of (Ib) and (VIa) can explain the role of amines in the reaction as follows. From amines (Ia-e) and primary products of their oxidation, aldehydes (VIa-e), Schiff bases (IXa-e) are intermediately formed

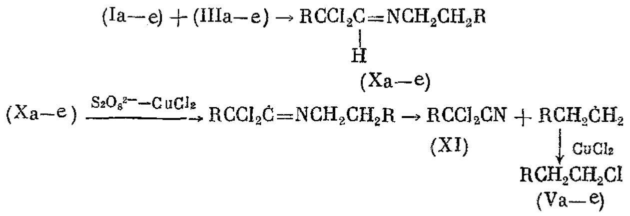
$$\underset{(Ia-e)}{RCH_2CH_2NH_2} + \underset{(VIa-e)}{RCH_2CHO} \rightarrow \underset{(IXa-e)}{RCH_2CH{=}NCH_2CH_2R}$$

The oxidation of (IXa-e) is easier than that of aldehydes (VIa-e), because the CH = N group is a weaker electron-acceptor than the aldehyde group. As the result of the two successive reactions of α-chlorination of (IXa-e) and hydrolysis under the reaction conditions, 2,2-dichloroalkanals (IIIa-e) are formed

$$(IXa-e) \xrightarrow{S_2O_8^{2-}-CuCl_2} R\dot{C}HCH{=}NCH_2CH_2R \rightarrow$$
$$\rightarrow RCHClCH{=}NCH_2CH_2R \xrightarrow[\text{Hydrolysis}]{1.\ S_2O_8^{2-}-CuCl_2} (III\ a-e)$$

In accordance with the proposed mechanism, in the oxidation of N-pentylidenehexylamine (VIII) in the $Na_2S_2O_8-CuCl_2$ system, 2,2-dichloropentanal (IIIa), and also pentanal (VIa) and hexylamine (Ib) are formed.

We believe that chloroalkanes (Va-e), which are unusual products of the direct replacement of the NH_2 group by Cl, are formed as the result of oxidation of Schiff bases (Xa-e), containing two chlorine atoms at the α-position to the C = N group, intermediately formed from 2,2-dichloroalkanals (IIIa-e) and amines (Ia-e), and the "weak" bond in the oxidation is the aldimine C–H bond. As the result of β-fragmentation of the intermediate radicals $RCCl_2\dot{C}{=}NCH_2CH_2R$ with splitting of the N-CH_2 bond, alkyl radicals $RCH_2\dot{C}H_2$ are proposed, which are further oxidized by $CuCl_2$ by a mechanism with ligand transfer [13] into (Va-e)



$$(Ia-e) + (IIIa-e) \rightarrow \underset{(Xa-e)}{RCCl_2\underset{|\atop H}{C}{=}NCH_2CH_2R}$$

$$(Xa-e) \xrightarrow{S_2O_8^{2-}-CuCl_2} RCCl_2\dot{C}{=}NCH_2CH_2R \rightarrow \underset{(XI)}{RCCl_2CN} + RCH_2\dot{C}H_2 \xrightarrow{CuCl_2} \underset{(Va-e)}{RCH_2CH_2Cl}$$

This mechanism is confirmed by a control experiment on the cooxidation of hexylamine (Ib) and 2,2-dichlorohexanal (IIIb), as a result of which 1-chlorohexane (Vb), hexanonitrile (IIb), and hexanoic acid (IVb) are formed.

The proposed mechanism is also confirmed by the identification of 2,2-dichlorohexanonitrile (XIb) in an amount of 1-2% in the oxidation products of hexylamine (Ib) in the $Na_2S_2O_8-CuCl_2$ system. Its structure was confirmed by comparison with an authentic sample. Control experiments showed that (XIb) is stable in the presence of $NaHSO_4$, but readily decomposes in the $Na_2S_2O_8-CuCl_2$ oxidation system.

The proposed scheme for the formation of chloroalkanes (V) is to a certain extent analogous to the von Braun reaction of splitting benzamides by the action of PCl_3 [14].

The structure of all the reaction products was confirmed by GLC using authentic samples for comparison, IR data, and chromatomass spectra. The authentic samples of (IIIa-c) were obtained by an alternative

TABLE 3. Physicochemical Characteristics of Reaction Products

Compound	IR spectrum (ν, cm^{-1})	Mass spectrum, m/z (relative intensity,%)	Mp 2,4-DNPH, °C
Pentanonitrile (IIa)	2225	see [16]	
2,2-Dichloropentanal (IIIa)	1745	–	95–97
Pentanoic acid (IVa)	1715	see [16]	
1-Chloropentane (Va)	–	see [17]	
Hexanonitrile (IIb)	2225	see [16]	
2,2-Dichlorohexanal (IIIb)*	1747	55(100), 56(69), 57(65), 67(61), 69(56), 85(56), 103(35), 105(28), 112(22), 75(22), 91(20), 114(13), 77(12), 139(9), 141(7), 93(6), 168(M^+, 1), 170(M^+), 172(M^+)	104–106
Hexanoic acid (IVb)	1715	see [16]	
1-Chlorohexane (Vb)	–	see [17]	
Heptanonitrile (IIc)	2225	see [16]	
2,2-Dichloroheptanal (IIIc)	1747	56(100), 55(62), 81(46), 70(27), 69(22), 86(19), 117(16), 112(14), 91(14), 89(14), 75(14), 67(14), 119(4), 182(M^+). 184(M^+), 186(M^+)	101–102
Heptanoic acid (IVc)	1715	see [16]	
1-Chloroheptane (Vc)	–	see [16]	
Octanononitrile (IId)	2225	41(100), 82(80), 43(52), 55(50), 54(48), 83(38), 96(36), 69(36), 97(18), 110(9), 60(8)	
2,2-Dichlorooctanal (IIId)	1745	55(100), 70(60), 82(20), 89(20), 91(17), 112(16), 95(12), 100(12), 114(9), 131(8), 133(3), 167(2), 169(1), 196(M^+), 198(M^+), 200(M^+)	123–125
Octanoic acid (IVd)	1715	see [16]	
1-Chlorooctane (Vd)	–	see [16]	
Nonanonitrile (IIe)	2225	see [16]	
2,2-Dichlorononanal (IIIe)	1750	55(100), 56(74), 57(69), 67(66), 69(55), 109(37), 81(30), 83(28), 112(25), 96(23), 114(20), 91(20), 103(18), 98(18), 89(12), 145(5), 131(3), 167(3), 147(2), 169(2), 210(M^+), 212(M^+), 214(M^+)	150–152
Nonanoic acid (IVe)	1710	see [16]	
1-Chlorononane (Ve)	–	91(100), 43(95), 55(68), 41(66), 57(47), 69(42), 56(34), 93(30), 70(21), 83(16), 71(15), 104(13), 106(4)	
N-Pentylidenehexylamine (VIII)†	1625	–	
2,2-Dichlorohexanonitrile (XIb)	2230	57(100), 54(77), 88(46), 68(36), 67(26), 83(20), 94(17), 90(15), 85(14), 109(13,) 87(6), 111(6), 114(3), 113(2)	

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* PMR spectrum ($CDCl_3$–HMDS, δ, ppm): 0.95 t (3H), 1.50 m (4H), 2.25 m (2H), 9.17 s (1H). ^{13}C NMR spectrum ($CDCl_3$–TMS, δ, ppm); 13.58, 22.13, 26.50, 40.34, 88.72, 184.37.

† PMR spectrum ($CDCl_3$–HMDS, δ, ppm): 0.85 t (6H), 1.25 m (14H), 3.55 t (2H), 8.20 t (1H).

synthesis [15]. Compounds (IIIa–e), formed in oxidation of (Ia–e) were isolated from the mixture of the reaction products and identified in the form of 2,4-dinitrophenylhydrazones (2,4-DNPH).

EXPERIMENTAL

The GLC analysis was carried out on the LKhM-8MD chromatograph with a flame-ionization detector, in a N_2 current, using stainless steel columns: 300 × 0.4 cm with 10% Carbowax 20M, treated with Na_3PO_3 and NaOH, on celite-545 (52-60 mesh); 300 × 0.4 cm with 2% DS-550 on Chromosorb G (60–80 mesh), treated with dimethyldichlorosilane; 300 × 0.3 cm with 5% PEGS on Chromosorb P-AW (120–140 mesh), treated with dimethyldichlorosilane. The NPR spectra of the solutions in $CDCl_3$, CCl_4, and $(CD_3)_2CO$ were measured on the "Tesla BS-497" (100 MHz) and "Bruker WM-250" (250 MHz) spectrometers, using HMDS or TMS as internal standards. The mass spectra were run on the "Varian MAT CH-6" spectrometer with direct introduction of the sample into the ion source, and an energy of the ionizing electrons of 70 eV. The chromatomass-spectrometric analysis was carried out on the "Varian MAT CH-111" ("Gnom") apparatus with chromatographic introduction of the sample into ion source and an energy of the ionizing electrons of 80 eV. The IR spectra were run on the "Specord-75IR" and UR-20" spectrometers in a thin layer and in CCl_4 solution. The $Na_2S_2O_8$ (c.p.), $CuCl_2 \cdot 2H_2O$ (pure for analysis), $NaHSO_4 \cdot H_2O$ (pure for analysis), $AgNO_3$ (pure for analysis), NaCl (c.p.), and NaOH (c.p.) preparations were used without additional purification. Monodistilled water was used. Amines (Ia-e) were purified by distillation under atmospheric pressure in an argon current.

Oxidation of Amines (Ia-e) by the $Na_2S_2O_8-CuCl_2$ System (general procedure). A solution of 100 mmoles of $Na_2S_2O_8$ in 50 ml of water was added in the course of 1.5 h, with vigorous stirring, at 75-80°C, to a mixture of 100 mmoles of amine (Ia-e) and 100 mmoles of $CuCl_2 \cdot 2H_2O$ in 25 ml of water. The mixture was stirred for another 3 h at the same temperature, and then cooled and extracted by ether (3 × 100 ml). The ethereal extract was dried over $MgSO_4$ and evaporated, and the residue was analyzed by the GLC method. Distillation of the residue gave the oxidation products: nitriles (IIa-e), 2,2-dichloroalkanals (IIIa-e), acids (IVa-e), and chloroalkanes (Va-e). After the extraction, the aqueous layer was acidified by NH_4OH (20 ml of a 25% solution), and then by a solution of 5 g of KOH in 20 ml of water, and extracted by ether (3 × 100 ml). The ethereal extract was dried over $MgSO_4$ and evaporated. The nonreacted amine (Ia-e) in the residue was determined by the GLC method. A higher or lower homolog of the nitrile formed in the oxidation reaction was used as the standard in the chromatographic determinations. The conversion of amines (I) and the yield of the oxidation products (II)-(V) are listed in Table 1. The spectral characteristics of the oxidation products are reported in Table 3.

Oxidation of hexylamine (Ib) by the action of $Na_2S_2O_8$ and systems based on it was carried out in the same way as described above, by adding a solution of 100 mmoles of $Na_2S_2O_8$ to a solution of 100 mmoles of (Ib) and other components of the oxidation system in amounts indicated in Table 2, in 25 ml of water. The products were isolated as in the general procedure of oxidation. After distillation of the products formed in the oxidation of (Ib) by the action of $Na_2S_2O_8$ and the $Na_2S_2O_8-CuCl_2-NaOH$, $Na_2S_2O_8-NaCl$, and $Na_2S_2O_8-NaCl-CuCl_2$ systems, resinification products are obtained in the residue in amounts listed in Table 2.

Reaction of Hexylamine (Ib) with $NaHSO_4$ or $CuCl_2$. A mixture of 100 mmoles of amine (Ib) and 100 mmoles of $NaHSO_4 \cdot H_2O$ or 100 mmoles of $CuCl_2 \cdot 2H_2O$ in 50 ml of water was vigorously stirred for 6 h at 80°C. After the reaction mixture has been treated as in the general procedure, 90 mmoles (90%) and 93 mmoles (93%) respectively, of unreacted amine (Ib) were isolated.

Oxidation of Pentanal (VIa) in the $Na_2S_2O_8-CuCl_2$ System. A solution of 100 mmoles of $Na_2S_2O_8$ in 50 ml of water was added in the course of 1.5 h at 75-80°C to a mixture of 100 mmoles of (VIa) and 100 mmoles of $CuCl_2 \cdot 2H_2O$ in 25 ml of water. After reaction mixture had been treated according to the general procedure, 20 mmoles of unreacted pentanal (80% conversion) and 79 mmoles (yield 99%) of pentanoic acid (IVa) were obtained.

Cooxidation of Hexylamine (Ib) and Pentanal (VIa) by the $Na_2S_2O_8-CuCl_2$ System. A solution of 100 mmoles of $Na_2S_2O_8$ in 50 mmoles of water was added in the course of 1.5 h, at 75-80°C, to a mixture of 50 mmoles of (Ib), 50 mmoles of (VIa), and 100 mmoles of $CuCl_2 \cdot 2H_2O$ in 30 ml of water. After the reaction mixture had been treated by the general oxidation procedure, 33 mmoles (66%) of unreacted (Ib), 6.5 mmoles (13%) of 2,2-dichloropentanal (IIIa), and 5 mmoles (10%) of N-pentylidenehexylamine (VIII) were isolated.

Synthesis of N-Pentylidenehexylamine (VIII). Pentanal, 0.2 mmole, was added in the course of 2 h, with vigorous stirring and ice-cooling, to 0.2 mole of amine (Ib), and the mixture was stirred at ~ 20°C for another 15 min. Freshly ground KOH was added, and the mixture was left to stand to separation into two layers. The organic layer was separated, and left to stand overnight in a refrigerator over a new portion of ground KOH, and was then distilled over KOH at reduced pressure. Yield, 0.15 mole (75%) of (VIII), bp 120°C (45 mm).

Oxidation of N-Pentylidenehexylamine (VIII) by the $Na_2S_2O_8-CuCl_2$ System. The reaction and the treatment of the reaction mixture were carried out according to the general procedure for the oxidation of amines. A solution of 100 mmoles of $Na_2S_2O_8$ in 50 ml of water was added to a mixture of 100 mmoles of (VIII) and 100 mmoles of $CuCl_2 \cdot 2H_2O$ in 30 ml of water. From the reaction mixture, 43 mmoles (43%) of hexylamine, 11 mmoles (11%) of pentanal, 10 mmoles (10%) of (VIII), 14 mmoles (14%) of dichloropentanal (IIIa), and 9.2 g of resinification products were isolated.

Cooxidation of Hexylamine (Ib) and 2,2-Dichlorohexanal (IIIb) by the $Na_2S_2O_8-CuCl_2$ System. A solution of 100 mmoles of $Na_2S_2O_8$ in 50 ml of water was added in the course of 1.5 h at 75-80°C to a mixture of 50 mmoles of (Ib), 50 mmoles of (IIIb) and 100 mmoles of $CuCl_2 \cdot 2H_2O$ in 30 ml of water. After the reaction mixture had been treated in accordance with the general oxidation procedure, 5 mmoles (10%) of (Ib), 38.5 mmoles (77%) of (IIIb), 4.5 mmoles (9%) of hexanonitrile (IIb), 1 mmole (2%) of hexanoic acid (IVb), 3.5 mmoles (7%) of chlorohexane (Vb), and 5.6 g of resinification products were isolated.

Synthesis of 2,2-Dichlorohexanonitrile (XIb). Oxidation of 2,2-dichlorohexanal (IIIb) by $KMnO_4$ [15] gave 2,2-dichlorohexanoic acid, bp 124-129°C (11 mm), which was converted by the action of $SOCl_2$–DMFA [18] into an acid chloride, bp 83-85°C (20 mm). In the reaction of the last compound with NH_4OH [19], 2,2-dichlorohexanoic acid amide, mp 47°C, was formed, which was converted by the action of P_2O_5 [20] into (XIb), bp 54-55°C (15 mm). Found: C 43.67; H 5.48; N 8.73; Cl 42.40%. $C_6H_9Cl_2N$. Calculated: C 43.37; H 5.42; N 8.43; Cl 42.77%.

Reaction of 2,2-Dichlorohexanonitrile (XIb) with the $Na_2S_2O_8-CuCl_2$ System. A solution of 5 mmoles of $Na_2S_2O_8$ in 5 ml of water was added in the course of 0.5 h at 75-80°C to a mixture of 5 mmoles of (XIb) and a solution of 5 mmoles of $CuCl_2 \cdot 2H_2O$ in 8 ml of water. After treatment similar to that described in the general procedure, 1.5 mmoles (30%) of unreacted (XIb) were isolated. No other reaction products were detected.

Reaction of 2,2-Dichlorohexanonitrile (XIb) with $NaHSO_4$. A mixture of 3 mmoles of (XIb) and 3 mmoles of $NaHSO_4 \cdot H_2O$ in 8 ml of water was vigorously stirred for 6 h at 80°C. After the reaction mixture had been treated according to the general procedure, 0.27 mmole (90%) of unreacted (XIb) was isolated.

CONCLUSIONS

1. Primary aliphatic amines $RCH_2CH_2NH_2$ are converted by the action of the $Na_2S_2O_8-CuCl_2$ system into nitriles RCH_2CN, 2,2-dichloroalkanals $RCCl_2CHO$, acids RCH_2COOH, and chloroalkanes RCH_2CH_2Cl. The formation of 2,2-dichloroalkanals and chloroalkanes are new reactions of oxidative substitution of the amino group in primary aliphatic amines.

2. A mechanism for the reactions has been proposed, including the production of aminyl radicals $RCH_2CH_2\dot{N}H$ and their oxidation into aldimines $RCH_2CH{=}NH$, predecessors of all the reaction products.

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