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OXIDATION OF ALIPHATIC ALCOHOLS BY A SYSTEM CONTAINING $Na_2S_2O_8$ AND A METAL CHLORIDE

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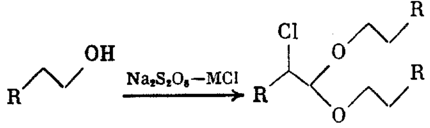
The reaction of sodium peroxydisulfate (PDS) with primary and secondary aliphatic alcohols features the abstraction predominantly of the α-hydrogen atom by $SO_4^{\bar{\cdot}}$ radical-anions generated upon the thermolysis of PDS and the oxidation of the α-hydroxyalkyl radical formed to carbonyl compounds [1, 2]. Alkoxy radicals are mainly formed upon the catalysis of this reaction by Ag(I) and Cu(II) ions. These radicals either fragment with the formation of alkyl radicals and a carbonyl compound or rearrange to δ-hydroxyalkyl radicals [3-5]. The latter are oxidized to give tetrahydrofurans [4]; they can also alkylate protonated heterocyclic bases [6].

In the present work, we carried out the oxidation of primary aliphatic alcohols (Ia)-(Ic) by PDS in conjunction with an alkali metal chloride (MCl). The reaction was carried out at 75-80°C in a two-phase system containing an alcohol and an aqueous solution of PDS, MCl, and H_2SO_4. The major reaction products are 1,1-dialkoxy-2-chloroalkanes (IIa)-(IIc).



(Ia—c) (IIa—c)

Re = Me (a); Et (b); Pr (c); M = Li; Na; K.

TABLE 1. Oxidation of 1-Alkanols by the $Na_2S_2O_8$–MCl System at 75-80°C (4 h, (I):$Na_2S_2O_8$:MCl = 10:1:3; 0.02 mole $Na_2S_2O_8$, 0.02 mole 98% H_2SO_4, 20 ml H_2O; the yield was given assuming 2 mole $Na_2S_2O_8$ per mole (II))

Alcohol (I)	MCl	Yield of (II), % relative to $Na_2S_2O_8$
1-Hexanol	LiCl	31
»	LiCl[a]	26
»	LiCl[b]	27
»	LiCl[c]	—
»	LiCl[d]	34
»	NaCl	22
»	KCl	33
	—	21[e]
»	$CuCl_2$	20[f]
1-Butanol	LiCl	34
»	LiCl[a]	23
1-Propanol	LiCl	40

[a] (I):$Na_2S_2O_8$:LiCl = 2:1:3.
[b] (I):$Na_2S_2O_8$:LiCl = 4:1:3.
[c] Without H_2SO_4.
[d] In the presence of 0.004 mole $AgNO_3$.
[e] 0.015 mole HCl instead of LiCl and H_2SO_4.
[f] Without H_2SO_4; 21% hexyl caproate and 4% 4-chloro-1-hexanol were identified in the reaction mixture in addition to (IIc).

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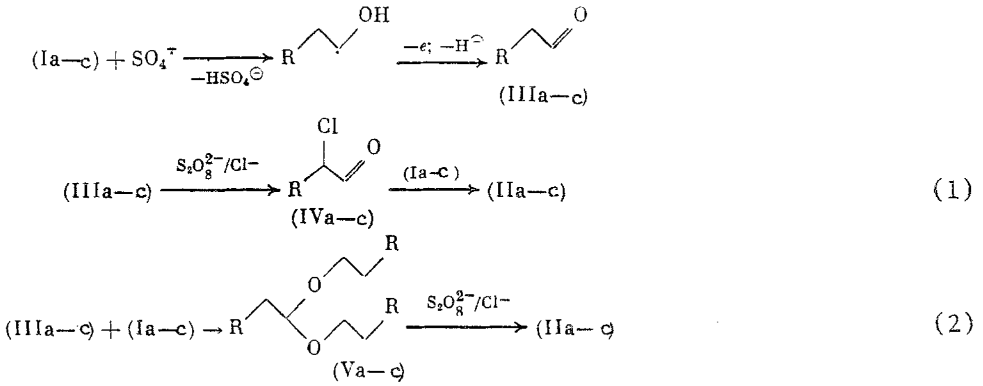
TABLE 2. Properties of Chloroacetals (IIa)-(IIc)

Compound	Bp, °C (p, mm Hg)	Found/Calc., %			Chemical formula	IR spectrum ν, cm^{-1} (C–Cl)	PMR spectrum (δ, ppm, J, Hz)
		C	H	Cl			
(IIa)	97–98(15)	55.43 / 55,53	9.57 / 9,77	18.48 / 18.25	$C_9H_{19}O_2Cl$	–	0,94 t (6H, CH_3, J=7,50), 1,49 d (3H, CH_3, J=6,75), 1,63 m (4H, CH_2), 3,48 m (2H, CH_2O), 3,62 m (2H, CH_2O), 4,00 m (1H, CHCl), 4,41 d (1H, OCHO, J=5,50)
(IIb)	115–116(0,4)	60.55 / 60,89	10.07 / 10,57	14.85 / 15,01	$C_{12}H_{25}O_2Cl$	695	0,92 t (6H, CH_3, J=7,25), 1,30 t (3H, CH_3, J=7,63), 1.30–1.95m (10H, CH_2), 3,52m (2H, CH_2O), 3.65m (2H, CH_2O), 3,82 m (1H, CHCl), 4.44 d(1H, OCHO, J=5,92)
(IIc)	170–172(0,3)	67,27 / 67,39	11,37 / 11,54	11.31 / 11,08	$C_{18}H_{37}O_2Cl$	695	0,99 m (9H, CH_3), 1.25–1,90 m (22H, CH_2), 3,51 m (2H, CH_2O), 3,65 m (2H, CH_2O), 3,87 m (1H, CHCl), 4,44 d (1H, OCHO, J=6,00)

The corresponding esters and acetals (1,1-dialkoxyalkanes) (Va)-(Vc) are also formed to a slight extent. The total yield of these products is 2-5%. 4-Chloro-1-hexanol was detected upon the oxidation of 1-hexanol in about 1% yield by gas-liquid chromatography.

The optimal conditions for the synthesis of chloroacetal (IIc) were determined in the case of the oxidation of (Ic) (Table 1). The best results were obtained using excess (Ic) with (Ic):$Na_2S_2O_8$:LiCl:H_2SO_4 mole ratio equal to 4-10:1:3:1. Product (IIc) is not formed in the absence of H_2SO_4. The yield of (IIc) is somewhat reduced by the replacement of H_2SO_4 and MCl by hydrochloric acid.

Chloroacetals (IIa)-(IIc) are formed from (Ia)-(Ic) probably by two pathways:



In the first step, alcohols (Ia)-(Ic) are oxidized to aldehydes (IIIa)-(IIIc), which are chlorinated to give α-chloroaldehydes (IVa)-(IVc), while (IVa)-(IVc) are acetalyzed to give (IIa)-(IIc) (pathway 1). Indeed, the reaction of (IIIb) with $Na_2S_2O_8$–LiCl–H_2SO_4 gives (IVb), which gives (IIb) upon the addition of 1-butanol. This pathway was also supported by our previous data [7] on the α-chlorination of aliphatic ketones by the $S_2O_8^{2-}$–$CuCl_2$ system under similar conditions. Pathway (2) involves the acetalization of aldehydes (IIIa)-(IIIc), catalyzed by H_2SO_4 and subsequent chlorination of the acetals formed (Va)-(Vc). This sequence was confirmed by a model experiment: the oxidative chlorination of (Vb) by the $S_2O_8^{2-}$–LiCl–H_2SO_4 system leads to the formation of (IIb).

The yield of hexyl caproate is sharply enhanced while the yield of 4-chloro-1-hexanol is slightly increased upon the oxidation of (Ic) by the $S_2O_8^{2-}$–$CuCl_2$ system.

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LKhM-80 chromatograph using a flame ionization detector and 3 m × 3 mm columns packed with 5% XE-60 and 5% Carbowax 20M on Chromaton N-AW-DMCS (0.16-0.20 mm). The nitrogen gas carrier flow rate was 30 ml/min. The product yields were determined using the internal standard method with pentadecane and hexadecane taking account of experimentally determined correction coefficients. The PMR spectra were taken on a Bruker WM-250 spectrometer with $CDCl_3$ as the eluent. The IR spectra were taken neat on a Specord M-80 spectrophotometer. Pure-grade $Na_2S_2O_8$ was used. The starting alcohols were dried and distilled. High-purity-grade $LiCl \cdot H_2O$, pure-grade KCl, chemically-pure-grade NaCl, and pure-grade 98% H_2SO_4 were used.

Oxidation of Primary Aliphatic Alcohols (Ia)-(Ic) by the $Na_2S_2O_8$–LiCl System (General Procedure). Samples of (I), LiCl (see Table 1), 0.02 mole 98% H_2SO_4, and 5 ml water were introduced into a reaction flask and heated to 75-80°C. A solution of 0.02 mole $Na_2S_2O_8$ in 15 ml H_2O was added over 1 h with rapid stirring. Then, the mixture was heated for an additional 4 h and cooled. The organic layer was removed. The aqueous layer was extracted by three 40-ml portions of ether. The combined extract was washed with 30 ml aqueous $NaHCO_3$, dried over Na_2SO_4, and distilled. The preparative yield of (II) is 80-90% of the value determined by gas-liquid chromatography (Table 1). The properties of the chloroacetals are given in Table 2. The esters, 1,1-dialkoxyalkanes, and 4-chloro-1-hexanol were identified by gas-liquid chromatography.

The oxidation of 1-hexanol in the presence of HCl was carried out in the presence of 8 ml 10% hydrochloric acid instead of LiCl and H_2SO_4.

Oxidation of Butyraldehyde by the $Na_2S_2O_8$–LiCl System. A solution of 0.02 mole $Na_2S_2O_8$ in 15 ml water was added over 1 h to a mixture of 5 ml butyraldehyde, 0.06 mole LiCl, and 0.02 mole 98% H_2SO_4 in 5 ml water at 75-80°C. Then, the mixture was heated with stirring for an additional 4 h and 20 ml 1-butanol was added. After 1 h, the mixture was cooled and the organic layer was separated. The aqueous layer was extracted with three 20-ml portions of ether. The combined extract was washed with aqueous sodium bicarbonate, dried, and analyzed by gas-liquid chromatography. The yield of (IIb) was 0.003 mole.

Oxidation of 1,1-Dibutoxybutane by the $Na_2S_2O_8$–LiCl System. A solution of 0.02 mole $Na_2S_2O_8$ in 15 ml water was added with vigorous stirring over 1 h to a mixture of 0.01 mole 1,1-dibutoxybutane, 0.2 mole 1-hexanol, 0.06 mole LiCl, and 0.02 mole sulfuric acid in 5 ml water. The mixture was then heated for 4 h and subjected to ordinary work-up to give 0.003 mole (IIb).

CONCLUSIONS

The oxidation of primary aliphatic alcohols by the $Na_2S_2O_8$–alkali metal chloride system in water in the presence of sulfuric acid gives 1,1-dialkoxy-2-chloroalkanes.

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