SYNTHESIS OF ORGANOSULFUR COMPOUNDS FROM TRICHLOROALLYL ALCOHOL

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UDC 542.91:547.431.3:547.269.1'133

The reactions of trichloroallyl alcohol involving the OH group such as esterification, oxidation, and nucleophilic substitution have been studied rather thoroughly [1]. In this case, the trichlorovinyl group (CCl_2=CCl), which is usually inert relative to nucleophilic reagents [2], remains unchanged.

It was of interest to carry out the nucleophilic thiylation of the halogens in the trichlorovinyl group, which would provide an approach to substituted ketenacetals, which are commonly used as starting materials in a whole series of syntheses [3]. This requires the action of thiolates on trichloroallyl (I) and α-methyltrichloroallyl alcohols (II) in a medium containing DMF and an aprotic solvent with moderate bipolar activity, i.e., under conditions permitting us (as shown earlier in [4]) to carry out the exhaustive substitution of chlorine atoms in tetrachloroethylene by organylthio groups.

We have found that alcohols (I) and (II) extremely readily undergo an exothermal reaction with aliphatic and aromatic thiolates in absolute DMF. In this case, independently of the mole ratio of alcohol (I) or (II) and the thiolates, only the products of the substitution of two chlorine atoms by SR' groups (IIIa)-(IIIi) are formed.

$$\underset{\text{(I), (II)}}{CCl_2{=}CClCHROH} \xrightarrow{R'SNa} \underset{\text{(IIIa—i)}}{C(SR')_2{=}CClCHROH}$$

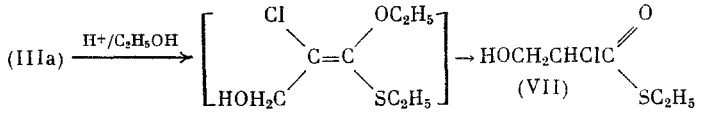
R = H(I), CH_3(II); (III): R = H, R' = C_2H_5 (a), i-C_3H_7 (b), t-C_4H_9 (c), n-C_8H_{17} (d), CH_2CH_2OH (e), C_6H_5 (f), 4-CH_3—C_6H_4 (g); R = CH_3, R' = C_2H_5 (h), C_6H_5 (i).

The reaction of disubstituted alcohol (IIIa) with excess thiolate does not lead to the trisubstituted product.

1,1,2,3-Tetrachloro-1-propene (IV) reacts analogously with thiolates. The products of the consecutive substitution of the allylic (V) and two vinyl chlorine atoms (VI) may be isolated depending on the reagent ratio.

$$\underset{\text{(IV)}}{CCl_2{=}CClCH_2Cl} \xrightarrow{R'SNa} \underset{\text{(V)}}{CCl_2{=}CClCH_2SR'} \xrightarrow{R'SNa} \underset{\text{(VI)}}{C(SR')_2{=}CClCH_2SR'}$$

The geminal structure of the compounds obtained was established by physicochemical methods and confirmed by the conversion of (IIIa) to thioester (VII). Thiocetals of ketenes, while stable in alkaline media, undergo hydrolysis in acid media to give esters of acids or thioacids [5].



The IR spectra of (III) feature a strong band at 1540-1530 cm^{-1} corresponding to the stretching vibrations of $C{=}C(SR)_2$ double bonds [6]. The S-alkyl group protons in the PMR spectra of (III) are anisochronic with a chemical shift difference of 0.03 ppm, which corresponds to the difference in the chemical shifts of the protons of geminal SR groups at a double bond [7, 8]. The nature of the ^{13}C NMR spectra also supports the geminal nature of the SR groups.

A study of the chemical properties of alcohols (III) showed that the replacement of chlorine atoms by SR groups did not have a significant effect on reactions common for alco-

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1928-1931, August, 1988. Original article submitted December 16, 1987.

0568-5230/88/3708-1727$12.50

TABLE 1. Physical Constants, Elemental Analysis, and Spectral Indices of the Compounds Synthesized

Compound	Chemical formula	Yield, %	Found/Calculated, % C	H	S	Cl	Bp, °C (p, mm Hg), Mp, °C (solvent)	n_D^{20}	IR spectrum, ν, cm^{-1}	PMR and ^{13}C NMR spectrum, δ, ppm
(IIIa)	$C_7H_{13}OS_2Cl$	90	39.94 39,53	6,22 6,12	29,88 30,11	16,52 16,71	115 (2)	1,5843	3400 (OH), 1545 (C=C)	1,22 t (3H, CH_3), 1,25 t(3H, $3H_3$), 2,63–3,25 m (4H, CH_2S), 4,42 s (1H, OH), 4,62 s(2H, CH_2O); ^{13}C: 128,10, 144,29 s (C^2, C^3)
(IIIb)	$C_9H_{17}OS_2Cl$	75	44,85 44,89	7.17 7,12	26,22 26,62	14,50 14,72	66,5–67(acetone)		3300 (OH), 1540 (C=C)	1,25d (6H, CH_3), 1,28 d(6H, CH_3), 3,23–3.63 m (2H, CH+1H, OH), 4,43 s (2H, CH_2O)
(IIIc)	$C_{11}H_{21}OS_2Cl$	60	48,82 49,13	7,54 7,87	23,41 23,85	13,02 13,18	82–86 (0,02)	1,5457	3430 (OH), 1530 (C=C)	0,97 s(9H, CH_3), 1,00 s (9H, CH_3), 4.21 s (1H, OH), 4,52 s (2H, CH_2O)
(IIId)	$C_{19}H_{37}OS_2Cl$	70	57,60 57,88	9,44 9,79	16,73 16,83	9,25 9,31	139–140 (0,08)	1,5152	3400 (OH), 1540 (C=C)	0,88 t(6H, CH_3), 1,29m (24H, CH_2), 2.55–2,95 (4H, CH_2S+1H, OH), 4,45 s (2H, CH_2O)
(IIIe)*	$C_7H_{13}O_3S_2Cl$	66	34,43 34,35	5,91 5,35	25,65 26,20	14,20 14,48	*	1,5882	3360 (OH), 1570 (C=C)	2,60–3,17 m (4H, CH_2S), 3,55–3,85 m (4H, CH_2O), 4,38 m (2H, CH_2O+2H, OH), 4,57 s (1H, OH)
(IIIf)	$C_{15}H_{13}OS_2Cl$	65	58,33 58,34	4,90 4,24	20,33 20,76	11,24 11,48	65 (acetone)		3400 (OH), 1540 (C=C)	4,19 s (2H, CH_2O), 4,27 s (1H, OH), 7,23–7,37 m (10H, C_6H_5); ^{13}C: 133,91, 144,65 s (C^2, C^3)
(IIIg)	$C_{17}H_{17}OS_2Cl$	53	60,96 60,60	5,38 5,09	18,62 19,03	10,30 10,52	77–78 (CH_2Cl_2 : pentane)		3400 (OH), 1545 (C=C)	2,31 s (6H, CH_3), 3,05 s(1H, OH), 4.27 s (2H, CH_2O), 7,03–7,39 m (8H, C_6H_4)
(IIIh)	$C_8H_{15}OS_2Cl$	70	42,24 42,37	6,67 6,66	28,01 28,27	15,94 15,63	100–102 (1)	1,5670	3460 (OH), 1530 (C=C)	1,17–1,35 m(9H, CH_3), 2,90 q_D (4H, CH_2S), 4,01 s (1H, OH), 5,15 q (1H, CH)
(IIIi) †	$C_{16}H_{15}OS_2Cl$	62	59,49 59.59	4,97 4,68	21,13 19,86	11,67 10,98	127 (1)	†	3430 (OH), 1540 (C=C)	1,30 d (3H, CH_3), 4,18 s(1H, OH), 5,10q (1H, CH), 7,08–7,52 m(10H, C_6H_5)
(Vf)	$C_9H_7SCl_3$	70	42,91 42,62	2.85 2,78	12,59 12,64	41,78 41,93	127 (3)	1,5995	1595 (C=C)	4,34 s (2H, CH_2), 7,15–7,55m (5H, C_6H_5)
(VIf)	$C_{21}H_{17}S_3Cl$	66	63,22 62,90	4.83 4,27	23.34 23,99	8,61 8,84	70–71 (acetone)		1580 (C=C)	4,10 s(2H, CH_2), 6,93–7,58 m (15H, C_6H_5)
(VIIIe)	$C_{28}H_{28}O_6N_3S_2Cl$	96	55.68 55,85	4,42 4,69	10,44 10,65	5.73 5,89	98–99(ethanol)		3345, 3300 (NH), 1710 (C=O), 1545 (C=C)	3,12 t (4H, CH_2S), 4,23t (4H, CH_2O), 5,00 s (2H, CH_2O), 6,89–7,60 m(15H, C_6H_5+3H, NH)
(VIIIg) ‡	$C_{24}H_{22}O_2NS_2Cl$	98	62,92 63,22	4.63 4,86	13,94 14,06	7,73 7,77	106–106,5 (ethanol)		3340 (NH), 1700 (C=O) 1530 (C=C)	2.15 s (3H, CH_3), 2,25 s(3H, $3H_3$), 4,82 s($1H_A$, CH_AH_B), 4,88 s ($1H_B$, CH_AH_B). 6,50s (1H, NH), 6,93–7,38 m (13H, C_6H_4+C_6H_5)
(IXa)	$C_7H_{13}O_5S_2Cl$	64	30.86 30.38	4,76 4,70	23,03 23,15	12,74 12,84	93–94 (methanol)		3500 (OH), 1580 (C=C) 1320, 1140 (SO_2)	1,33 t (3H, CH_3), 1,35 t (3H, CH_3), 3.43 q (2H, CH_2S), 3,52 q (2H, CH_2S), 4,93 s(2H, CH_2O), 5,97 s (1H, OH); ^{13}C: 141,56, 148,84 s(C^2, C^3)
(IXb)	$C_9H_{17}O_5S_2Cl$	60	35,22 35,46	5,32 5,62	20,92 21,04	11,42 11,63	118–119 (ethanol)		3500 (OH), 1570 (C=C) 1325, 1130 (SO_2)	1,28 d (6H, CH_3), 1,31d (6H, CH_3), 4.05–4,25 m (2H, CHS), 4,80 s(2H, CH_2O), 5,20 s (1H, OH)
(IXc)	$C_{11}H_{21}O_5S_2Cl$	65	39,76 39,68	6,27 6,36	19,00 19,26	10,51 10,65	168–169 (methanol)		3520 (OH), 1560 (C=C) 1310, 1110 (SO_2)	1,45 s(9H, CH_3), 1,48 s (9H, CH_3), 3,38s (1H, OH), 4,80 s(2H, CH_2O)
(IXf)	$C_{15}H_{13}O_5S_2Cl$	70	48,90 48,32	3,64 3,51	17,11 17,20	9.46 9,51	154–155 (methanol)		3510 (OH), 1580 (C=C) 1330, 1150 (SO_2)	4,83 s(2H, CH_2O), 5,64 s (1H, OH), 7,30–7,45 m (10H, C_6H_5)

*Compound characterized after chromatography on a column packed with 80 g silica gel with 1:3 hexane–CH_2Cl_2 as eluent.
†In an amorphous state at room temperature.
‡(VIIIe), N 6.89/6.98%; (VIIIg), N 3.15/3.07%.

hols. Thus, (IIIe) and (IIIg) react under mild conditions with phenyl isocyanate to form N-phenylurethane, $C(SR')_2=CClCH_2OC(O)NHC_6H_5$ (VIIIe) and (VIIIg) in quantitative yield. In the case of (IIIe), all three hydroxyl groups take part in the reaction.

Alcohols (IIIa)-(IIIc) and (IIIf) are readily oxidized at the sulfide groups by acetyl hydroperoxide in CH_2Cl_2 to give sulfones $C(SO_2R')_2=CClCH_2OH$ (IXa)-(IXc) and (IXf). The compositions of all the compounds obtained were supported by elemental analysis and their structures were supported by IR and NMR spectroscopy (see Table 1).

EXPERIMENTAL

Absolute solvents were used in this work. The reactions with thiolates were carried out in a nitrogen atmosphere. A sample of 1,1,2,3-tetrachloro-1-propene was obtained by the reaction of trichloroallyl alcohol with $SOCl_2$ [1]. The IR spectra were taken on a UR-20 spectrometer neat or in a KBr pellet. The PMR spectra were obtained on a Varian DA-60 IL spectrometer at 60 MHz and Tesla BS-497 spectrometer at 100 MHz in $(CD_3)_2CO$ or CCl_4 solution with HMDS as the internal standard. The ^{13}C NMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz in CD_2Cl_2 or $(CD_3)_2CO$ solution.

General Method for the Preparation of 3,3-Dialkyl- and 3,3-Diarylthio-2-chloro-2-propen-1-ols (IIIa)-(IIIi). A solution of 20 mmoles alcohol (I) or (II) in 20 ml DMF was added with stirring to a suspension of 66 mmoles sodium thiolate in 25 ml DMF such that the temperature did not exceed 30°C. After completion of the exothermal reaction, the mixture was maintained for 2 h at about 20°C. The residue was separated and most of the DMF was distilled off in vacuum. The residue was dissolved in $CHCl_3$, washed with water until neutral, and dried over $MgSO_4$. Chloroform was distilled off. The residue was either distilled in a vacuum or recrystallized from a suitable solvent.

General Method for the Preparation of 3,3-Dialkyl- and 3,3-Diarylthio-2-chloro-2-propenyl-N-phenylurethanes (VIIIe) and (VIIIg). A sample of 20 mmoles phenyl isocyanate was addded to 20 mmoles (IIIe) or (IIIg). The reaction mixture was maintained at about 20°C until the mass partially crystallized and then 10 ml pentane was added. The precipitate formed was separated and recrystallized from ethanol.

General Method for the Preparation of 3,3-Dialkyl- or 3,3-Diarylsulfonyl-2-chloro-2-propen-1-ols (IXa)-(IXc) and (IXf). A solution of 20 mmoles (IIIa)-(IIIc) or (IIIf) in 15 ml CH_2Cl_2 was added with stirring to 88 mmoles acetyl hydroperoxide (72%) in 15 ml CH_2Cl_2, maintaining the temperature of the reaction mixture at 25-30°C. Stirring was continued for an additional 3 h at about 20°C. The mixture was diluted with 100 ml CH_2Cl_2, washed with aqueous $NaHCO_3$ and water, and dried over $MgSO_4$. The solvent was evaporated and the residue was recrystallized from ethanol.

The hydrolysis of 3,3-diethylthio-2-chloro-2-propen-1-ol (IIIa) was carried out according to Seebach and Bürstinghaus [9]. The reaction of 5 g (25 mmoles) (IIIa) and 22.8 g (200 mmoles) CF_3COOH gave 3.1 g (70%) (VII), bp 100-103°C (4 torr), n_D^{20} 1.5701. IR spectrum (ν, cm^{-1}): 3450 (OH), 1670 (C=O). PMR spectrum (δ, ppm): 1.18 t (3H, CH_3), 2.48-2.92 m (2H, CH_2S + 1H, OH), 3.65 t (1H, CH), 3.83 d (2H, CH_2O). Found: C 35.54; H 5.14; S 18.98; Cl 21.24%. Calculated for $C_5H_9O_2SCl$: C 35.62; H 5.38; S 19.02; Cl 21.03%.

CONCLUSIONS

1. The reaction of trichloroallyl alcohol with sodium thiolates in DMF gave previously unreported 3,3-dialkyl- and 3,3-diarylthio-2-chloro-2-propen-1-ols in good yields.

2. The analogous reaction with 1,1,2,3-tetrachloro-1-propene gave the products of the consecutive replacement of the allylic and two vinylic chlorine atoms by SR groups.

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

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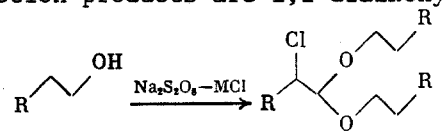
UDC 542.943.7:547.26

The reaction of sodium peroxydisulfate (PDS) with primary and secondary aliphatic alcohols features the abstraction predominantly of the α-hydrogen atom by $SO_4^{\cdot}$ 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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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1932-1934, August, 1988. Original article submitted January 19, 1988.

 0568-5230/88/3708-1730$12.50