

FUNCTIONAL SULFUR-CONTAINING COMPOUNDS.

4. PREPARATION OF CHLORO(BROMO)ALKYL SULFONES BY OXIDATIVE

HALOGENATION OF HYDROXYALKYL SULFIDES AND SULFOXIDES

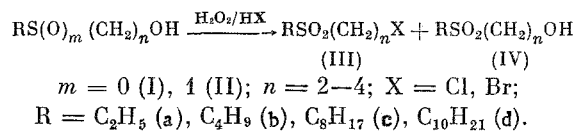
WITH MIXTURES OF HYDROGEN PEROXIDE AND A HYDROHALIC ACID

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The oxidative chlorination of hydroxyalkyl sulfides (I) and sulfoxides (II) with chlorine in water is a convenient method for the preparation of chloroalkyl sulfones, which are important key compounds in the synthesis of a variety of functional sulfur-containing compounds [1-3]. However, replacement of chlorine by bromine does not result in oxidative bromination of hydroxyalkyl sulfides to give the bromoalkyl sulfones in good yield, even with 2-hydroxyethyl, 3-hydroxypropyl, and 4-hydroxybutyl alkyl sulfides and sulfoxides, the oxidative chlorination of which occurs with extreme ease to give the 2-chloroethyl-, 3-chloropropyl-, and 4-chlorobutyl alkyl sulfones [2, 3].

Bearing in mind the special features of the oxidative chlorination of sulfides (I) and sulfoxides (II) [2, 3], it appeared to us that replacement of the halogen-water system by an H_2O_2-HX mixture ($X = Cl$ or Br) should result in the reaction proceeding in a similar way to give the haloalkyl sulfones (III) under milder conditions.



Oxidative chlorination was effected using a molar ratio of sulfide : H_2O_2 : $HCl = 1 : 2-4 : 4-8$, and sulfoxide : H_2O_2 : $HCl = 1 : 1-4 : 2-8$, either in the presence or absence of an organic solvent (such as dioxane or acetonitrile), in the range -10 to $+20^\circ C$.

In the absence of a solvent, the oxidative chlorination of sulfides (I) and sulfoxides (II) is nonselective, giving a mixture of chloroalkyl sulfones (III, $X = Cl$) and (IV) in a ratio of $\sim 1 : 2$ (Table 1). It is noteworthy that the more remote the OH group from the S atom in the sulfide (I) and sulfoxide (II), the greater is the amount of the sulfone (IV) obtained. This is evidently due to the heterogeneous conditions, and the occurrence of competitive oxidation of the starting materials to the sulfones (IV) by $HClO$ or H_2O_2 , catalyzed by HCl .

Increased quantity of H_2O_2 in the reaction medium does not significantly change the ratios of sulfones (III, $X = Cl$) and (IV) being formed. Increased HCl content, on the other hand, significantly affects the process and leads to the formation of (III) with 60-70% yields. At increased molar content of HCl in the reaction medium, the equilibrium of the H_2O_2-HCl system is shifted in the direction of free-chloride formation, which leads to suppression of the concurrent reaction - oxidation of sulfide (I) and sulfoxide (II) to sulfone (IV). This conclusion agrees with earlier results [2, 3].

The organic solvent has a considerable effect on the formation of (III). Thus, in CH_3OH the yield of (III, $X = Cl$) is only 45%. Under homogeneous conditions, using solvents such as dioxane, acetonitrile, or THF, the yields of (III) are 70-80% (Table 1) [4]. The order of addition of the reactants, i.e., addition of the sulfide or sulfoxide to the H_2O_2-HCl mixture, or H_2O_2 to a mixture of the sulfide or sulfoxide and HCl , and the reaction temperature (-15 to $+20^\circ C$), had no marked effects on the formation of (III).

A feature of the oxidative bromination of the sulfides (I) and sulfoxides (II) is the dependence of the yield of the sulfones (III, $X = Br$) on the order of addition of the reactants and their molar proportions, and furthermore no substantial differences were observed when the reaction was carried out in the presence or absence of organic solvents. Model experiments on the oxidative bromination of 2-hydroxyethyl alkyl sulfides (I, $n = 2$)

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TABLE 1. Oxidative Chlorination of $RS(CH_2)_nOH$ (Ia-d) and $RS(O)(CH_2)_nOH$ (IIa-d) with a Mixture of H_2O_2 and HCl

Compound	n	Molar proportions of (I) or (II): H_2O_2 : HCl	Solvent type*	Yield of sulfones, %	
				(III), X=Cl	(IV)
(Ib)	2	1:2:4	A	75-80	3-6
(IIb)	2	1:1:2	-	36	60
(Ic)	2	1:2:4	A	75-85	10-16
(IIc)	2	1:2:4	-	46	53
(Ia)	2	1:1:2	-	37	63
(Ia)	3	1:2:4	A	70-80	10-17
(Ib)	3	1:2:4	A	70-80	10-15
(IIb)	3	1:1:2	-	33	60
(IIb)	3	1:1:2	A	75-82	10-17
(Ic)	3	1:2:4	A	75-80	10-15
(IIc)	3	1:1:2	-	28	70
(II d)	3	1:1:2	-	28	68
(Ia)	4	1:2:4	A	70-80	10-15
(Ib)	4	1:2:4	A	75-80	10-15
(IIb)	4	1:1:2	-	32	60
(IIb)	4	1:1:8	-	69	29
(Ic)	4	1:2:4	A	75-80	10-16
(Ic)	4	1:4:8	A	70-75	14-18
(Ic)	4	1:4:8	B	45-50	45-50
(Ic)	4	1:4:8	C	55-60	25-36
(IIc)	4	1:1:2	-	31	66
(IIc)	4	1:1:2	A	72-75	23-25
(Id)	4	1:2:4	A	75-80	15-20

*A represents an aprotic solvent such as dioxane, acetonitrile, or THF; B, a hydroxylic solvent such as methanol; and C, a chlorinated hydrocarbon or an aromatic solvent.

showed that increasing the molar proportion of HBr in the reaction mixture above 2 moles per mole of sulfide, and addition of the sulfide to a mixture of H_2O_2 and HBr resulted in a decrease in the yields of the sulfones (III, X = Br, n = 2). In this case, better results were obtained when the H_2O_2 was added to the sulfide- HBr mixture.

In the oxidative bromination of 2-hydroxyethyl alkyl sulfides (I) and sulfoxides (II), the optimum conditions for the preparation of the sulfones (III, X = Br, n = 2) are a molar ratio sulfide: H_2O_2 : HBr = 1: 2: 1.5-2 (sulfoxide: H_2O_2 : HBr = 1: 1: 1.5-2). Under these conditions, it was possible to promote the formation of the bromoalkyl sulfones (III), and to reduce considerably (to 1-3%) the quantities of sulfone by-products (IV, n = 2).

In the oxidative bromination of 3- and 4-hydroxyalkyl sulfides (I, n = 3 or 4) and sulfoxides (II, n = 3 or 4), the optimum molar ratios were sulfide: H_2O_2 : HBr = 1: 2: 4 (sulfoxide: H_2O_2 : HBr = 1: 1: 2-4), the yields of the bromoalkyl sulfones (III) reaching 70-80% (Table 2).

Oxidative halogenation of the hydroxysulfides (I) and sulfoxides (II) is a complex reaction, the mechanism of which has still not been fully elucidated [2, 3]. The first step in this reaction, irrespective of whether it is carried out by oxidation in the X_2/H_2O system or the H_2O_2/HX system, is conversion of the sulfides (I) into the hydroxysulfoxides (II) via the successive formation of intermediates (V) and (VI) [Scheme 1).

Subsequent reaction of the sulfoxide (II) with halogen or HOX gives the corresponding intermediates (VIIa) and (VIIb), from which by elimination of HX or H_2O followed by intramolecular cyclization is obtained

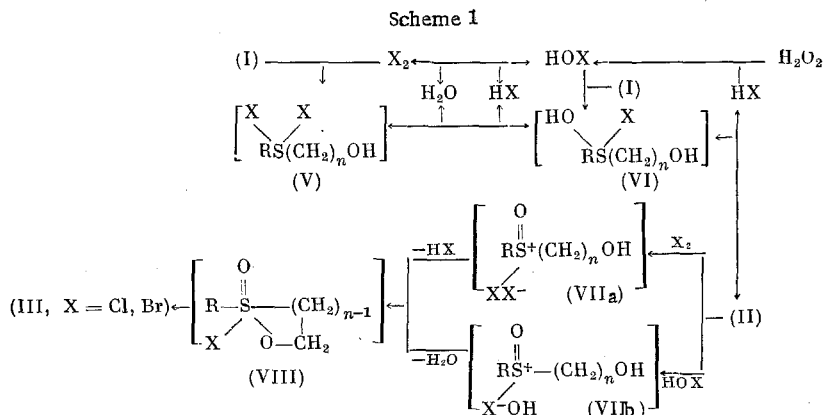


TABLE 2. Oxidative Bromination of $RS(CH_2)_nOH$ (Ia-d) and $RS(O)(CH_2)_nOH$ (IIa-d) with a Mixture of H_2O_2 and HBr

Compound	n	Molar proportions of (I) or (II): H_2O_2 : HBr	Solvent types*	Yield of sulfones, %	
				(III), X=Br	(IV)
(Ia)	2	1:2:1.5	—	76	1
(Ib)	2	1:2:1.5	—	78	2.5
(Ic)	2	1:2:4	A	50-80	3-5
(Id)	2	1:2:2	A	70-80	3-4
(IIc)	2	1:1:2	—	81	12
(Id)	2	1:2:2	A	70-80	3-4
(Ib)	3	1:2:4	A	73-80	3-4
(Ic)	3	1:2:4	—	79	7
(IIc)	3	1:1:2	—	83	10
(Id)	3	1:2:4	A	70-80	5-9
(Id)	3	1:1:2	—	60	33
(Ib)	4	1:2:4	A	75-85	3-5
(Ic)	4	1:2:4	—	82	5
(IIc)	4	1:1:2	—	51	37
(IIc)	4	1:1:8	—	69	4
(Id)	4	1:2:4	A	70-80	5-9
(Id)	4	1:1:2	—	44	43
(Id)	4	1:1:2	A	70-80	8-16

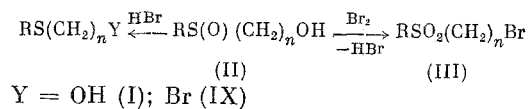
* A represents an aprotic solvent (dioxane, acetonitrile, or nitromethane).

the persulfuran (VIII). Intramolecular rearrangement of the intermediate (VIII), as proposed by us [2, 3], gives the haloalkyl sulfone (III, X = Cl or Br). Thus, oxidative halogenation takes place via the successive conversion of the sulfides (I) into the sulfoxides (II) and the sulfones (III). A necessary condition for the formation of the sulfones (III) is direct participation of the OH group of the sulfoxide (II) in the formation of the sulfonyl group, as demonstrated experimentally in [2, 3]. This scheme for the conversion of the sulfides (I) and sulfoxides (II) does not exclude the possible participation of either free halogen or HOX in the formation of the persulfuran (VIII) (see [5]).

As already remarked, the first stage in the oxidative halogenation is the rapid formation of the hydroxy-sulfoxide (II). Consequently, the differences noted above in the chemical behavior of the hydroxyalkyl sulfides (I) when oxidative halogenation is carried out with an H_2O_2-HCl or an H_2O_2-HBr mixture must mainly originate at the stage of conversion of the hydroxyalkyl sulfoxides (II) into the sulfones (III). For this reason, it was desirable to carry out a comparative study of the halogenation of (II) with free chlorine and bromine.

The oxidative chlorination of the sulfoxides (II) with gaseous chlorine in an organic solvent (CCl_4 , CH_3CN , CH_3NO_2 , dioxane, etc.) takes place selectively over a wide range of temperatures (-25° to $+5^\circ C$) to give high yields (up to 95%) of (III).*

Replacement of chlorine by bromine results in a considerable drop in the yields of bromoalkyl sulfones (up to $\sim 45\%$). Bearing in mind that in the formation of sulfones (III, X = Br), an equimolar amount of HBr is formed, it follows that according to the scheme shown one would expect the competitive formation of sulfides (I) and (IX)



In fact, reaction of the sulfoxide (II, R = C_8H_{17} , n = 2) with bromine in nitromethane at -15 to $-20^\circ C$ affords a mixture of products, the main constituents of which are 2-bromoethyl octyl sulfone (44%), 2-hydroxy- and 2-bromoethyl octyl sulfides (26 and 22%, respectively), and 2-hydroxyethyl octyl sulfone (3%).

* High yields of sulfones (III) were obtained from the sulfoxides (II) (n = 2-4). With compounds in which for steric reasons the formation of cyclic persulfurans (VIII) is disfavored (for instance when n = 5 or 7), much lower yields of (III) are obtained.

EXPERIMENTAL

GLC analyses were carried out with an LKhM-8MD apparatus with a flame-ionization detector, at 150-250°C, on a 1500 × 3 mm column with 5% silicone XE-60 on Chromaton NAW-DMCS (0.16-0.20 mm). IR spectra were recorded on a UR-10 spectrometer, and PMR spectra on a Varian DA60-IL in CDCl₃, with TMS as internal standard. Mass spectrometric examination was carried out on Varian MAT Ch-6 and Varian MAT-111 instruments.

The 2-hydroxyethyl alkyl sulfides (I, n = 2) were synthesized by a variation of the method given in [6]. To a mixture of the alkyl halide and caustic alkali in n-butanol, in a ratio of ~ 1 : 1 to the reaction mixture, was added at 100°C monothioethylene glycol, at such a rate that the temperature of the reaction mixture did not exceed 120°C, and this temperature was maintained for ~ 6 h. The product was distilled in vacuo. Yields of the 2-hydroxyethyl sulfides averaged 90-96%. The hydroxyalkyl sulfoxides (II) were obtained by oxidizing the sulfides (I) with 30% hydrogen peroxide in a mixture of CHCl₃ and AcOH, in yields of 70-85% [3], and the hydroxyalkyl sulfones (IV) by oxidation with 30% H₂O₂ in glacial acetic acid, in yields of 70-90%, as described in [7] (Table 3). The IR spectra of (II, n = 3 and 4), and (IV, n = 3 and 4) displayed characteristic absorption bands at 3630-3640 and 3370-3390 (OH), 1020-1060 (RSO) for (II), and 3620-3630 (OH), 1300-1320, 1130-1140 cm⁻¹ (RSO₂) for (IV). The most significant chemical shifts in the PMR spectra were (δ, ppm): 2.40-3.20 (CH₂SOCH₂) and 3.55-3.90 (CH₂O) for (II, n = 3, 4), and 2.68-3.30 (CH₂SO₂CH₂), 3.55-3.85 (CH₂O) for (IV, n = 3, 4).

4-Chlorobutyl Octyl Sulfone (III, X = Cl, n = 4). a) To a mixture of 0.5 ml (4 mmole) of 25% H₂O₂ and 0.7 ml (8 mmole) of 36% HCl was added at -10°C a solution of 0.44 g (2 mmole) of 4-hydroxybutyl octyl sulfide in 3 ml of dioxane at such a rate that the temperature of the reaction mixture did not exceed 0-4°C. When all the sulfide had been consumed (by TLC), the temperature was raised to ~ 20°C, and kept for a further ~ 12 h until the 4-hydroxybutyl octyl sulfide had disappeared (by TLC). The mixture was then diluted with water, extracted with CHCl₃, dried over MgSO₄, and the solvent removed. The residue was recrystallized repeatedly from a mixture of CCl₄ and hexane to give 0.08 g (16%) of 4-hydroxybutyl octyl sulfone, mp 66-67°C [3], and 0.43 g (80%) of 4-chlorobutyl octyl sulfone, mp 57.5-58.5°C [3]. PMR spectrum (IIIc, X = Cl, n = 4) (δ, ppm): 0.89 t (3 H, CH₃, J = 5 Hz), 1.33 m (10 H, (CH₂)₅), 1.73-2.18 m (6 H, CH₂)₃, 2.73-3.18 m (4 H, CH₂SO₂CH₂), and 3.56 t (2 H, CH₂CL, J = 5 Hz). Oxidative chlorination proceeded in a similar way in MeCN, THF, DMF, and acetone (Table 1).

b) To a mixture of 0.22 ml (2 mmole) of 28% H₂O₂ and 0.34 ml (4 mmole) of 36% HCl at -5°C was added 0.22 g (1 mmole) of 4-hydroxybutyl octyl sulfide, and the reaction carried out as described above. After working up in the usual way, the solid product obtained was recrystallized from a mixture of CCl₄ and hexane to give 0.18 g (72%) of 4-hydroxybutyl octyl sulfone, mp 66-67°C, and 0.07 g (26%) of 4-chlorobutyl octyl sulfone, mp 57.5-58.5°C.

c) To a mixture of 0.05 ml (0.4 mmole) of 25% H₂O₂ and 0.07 ml (0.8 mmole) of 36% HCl was added at -5°C 0.094 g (0.4 mmole) of 4-hydroxybutyl octyl sulfoxide, and the reaction carried out as described above to give 0.066 g (66%) of 4-hydroxybutyl octyl sulfone, mp 66-67°C, and 0.033 g (31%) of 4-chlorobutyl octyl sulfoxide: H₂O₂ : HCl = 1 : 5 : 2.5 gave (IVc) (n = 4) in 78% yield, and (IIIc) (X = Cl, n = 4) in 20% yield when the molar ratio of 4-hydroxybutyl octyl sulfoxide : H₂O₂ : HCl = 1 : 1 : 8; the yields of (IV) and (III) were 37 and 60%, respectively.

d) Chlorine was introduced into a solution of 0.12 g (0.5 mmole) of 4-hydroxybutyl octyl sulfoxide in 3 ml of dry MeCN at -10°C until the color of free chlorine persisted. The product was recrystallized from hexane to give 0.13 g (97%) of 4-chlorobutyl octyl sulfone, mp 57.5-58.5°C.

3-Bromopropyl Octyl Sulfone (IIIc, X = Br, n = 3). a) To a mixture of 0.51 g (2.5 mmole) of 3-hydroxypropyl octyl sulfide and 1.47 ml (0.01 mole) of 40% HBr was added at -10°C 0.51 ml (5 mmole) of 30% H₂O₂ at such a rate that the temperature did not exceed 0°C. The mixture was kept for a further 1 h at -10°C, and ~ 12 h at ~ 20°C. After the usual workup, the product was crystallized from CCl₄-hexane to give 0.59 g (79%) of 3-bromopropyl octyl sulfone, mp 75.5-76.5°C, and 0.04 g (7%) of 3-hydroxypropyl octyl sulfone, mp 72-72.5°C.

b) To a mixture of 0.5 ml (4 mmole) of 25% H₂O₂ and 1.2 ml (8 mmole) of 40% HBr was added at -10°C 0.88 g (4 mmole) of 3-hydroxypropyl octyl sulfoxide, and the reaction carried out as described above. The reaction products were separated by chromatography on silica gel (40-100 μ) (hexane-acetone) to give 0.99 g (83%) of 2-bromopropyl octyl sulfone, mp 75.5-76.5°C (from hexane) (Table 4), and 0.09 g (10%) of 3-hydroxypropyl octyl sulfone, mp 72-72.5°C (CCl₄). PMR spectrum (IIIc, X = Br, n = 3) (δ, ppm): 0.88 t (3 H, CH₃,

TABLE 4. Bromoalkyl Sulfones, $\text{RSO}_2(\text{CH}_2)_n\text{Br}$ (III)

Compound	n	mp, °C	Found/calculated, %		Molecular formula
			Br	S	
(IIIa) *	2	19-20	-	-	$\text{C}_4\text{H}_9\text{BrO}_2\text{S}$
(IIIb)	2	51,5-52	34,91	13,90	$\text{C}_6\text{H}_{13}\text{BrO}_2\text{S}$
			34,89	13,56	
(IIIc)	2	55,5-56	27,91	11,20	$\text{C}_{10}\text{H}_{21}\text{BrO}_2\text{S}$
			28,01	11,24	
(III d)	2	56,5-57	25,52	10,20	$\text{C}_{12}\text{H}_{25}\text{BrO}_2\text{S}$
			25,50	10,23	
(III b)	3	61,5-62	32,77	13,15	$\text{C}_7\text{H}_{15}\text{BrO}_2\text{S}$
			32,86	13,19	
(III c)	3	75,5-76,5	27,02	10,80	$\text{C}_{11}\text{H}_{23}\text{BrO}_2\text{S}$
			26,91	10,71	
(III d)	3	83-84	24,20	9,71	$\text{C}_{13}\text{H}_{27}\text{BrO}_2\text{S}$
			24,41	9,80	
(III b)	4	47	31,23	12,53	$\text{C}_8\text{H}_{17}\text{BrO}_2\text{S}$
			31,06	12,46	
(III d)	4	63-64	25,36	10,14	$\text{C}_{12}\text{H}_{25}\text{BrO}_2\text{S}$
			25,50	10,23	
(III)	4	71-72	23,33	9,36	$\text{C}_{14}\text{H}_{29}\text{BrO}_2\text{S}$
			23,41	9,36	

* Mp 19-20°C [8].

$J = 5.5$ Hz), 1.31 m (12 H, $(\text{CH}_2)_6$), 2.18-2.75 m (2 H, CH_2), 2.75-3.28 m (4 H, $\text{CH}_2\text{SO}_2\text{CH}_2$), 3.52 t (2 H, CH_2Br , $J = 6$ Hz).

4-Bromobutyl Octyl Sulfone (IIIc, $X = \text{Br}$, $n = 4$). To 3.52 g (15 mmole) of 4-hydroxybutyl octyl sulfoxide in 20 ml of dry MeCN was added at -25°C over ~ 1 h 2.4 g (15 mmole) of bromine in 10 ml of dry MeCN. The mixture was kept for 1 h at -25°C , the solvent removed, the product extracted with a mixture of ether and hexane, and the extract evaporated. The residue was crystallized from ether-hexane at -10°C to give 2.16 g (46%) of 4-bromobutyl octyl sulfone, mp 63-64°C. The products remaining after crystallization (1.58 g) were analyzed by GC-MS and GLC. Compounds identified were octyl bromide, 4-bromobutyl alcohol, and octane-sulfinyl bromide, m/z (rel. %): 137(51), 135(49), 109(3,5), 107(3,5), 71(70), 69(39), 57(100), 55(80); octane-sulfonyl bromide, m/z (rel. %): 231(6,5), 229(12), 227(6,5), 203(14,6), 201(29,4), 199(14,6), 177(1), 137(10), 135(9,5), 124(10,5), 122(13), 121(39), 119(40), 75(100), 57(47), 55(42,5); and 4-hydroxybutanesulfinyl bromide, m/z (rel. %): 203(2,5), 201(5), 199(3,5), 122(8,5), 121(4,5), 107(14), 55(100). Products insoluble in ether-hexane were separated by chromatography on silica gel (100-160 μ) (hexane-acetone and methanol) to give 0.03 g (0.8%) of 4-hydroxybutyl octyl sulfone, mp 66-67°C (CCl_4 -hexane), and 1 g (24%) of octyl cyclobutyl sulfonium bromide as an oil which after low-temperature recrystallization from dry CHCl_3 -ether was obtained in the form of hygroscopic crystals, mp 120-121°C. Found: C 51.25; H 8.68; Br 28.02; S 11.24%. $\text{C}_{12}\text{H}_{25}\text{BrS}$. Calculated: C 51.24; H 8.96; Br 28.40; S 11.40%. The mass spectrum contained peaks with m/z (rel. %): 282(18), 280(18), 201(66,5), 159(100), 145(8), 137(29), 135(29), 89(16), 88(15), 87(9,5), 71(24), 69(69,5) 57(43), 55(100), 43(59), 41(60). PMR spectrum (X) (δ , ppm): 0.88 t (3 H, CH_3 , $J = 5$ Hz), 1.31 m (12 H, $(\text{CH}_2)_6$), 2.3-2.68 m (4 H, $(\text{CH}_2)_2$), 3.32-4.05 m (6 H, $(\text{CH}_2)_3$).

CONCLUSIONS

1. Oxidative halogenation of hydroxyalkyl sulfides and sulfoxides with a mixture of H_2O_2 and HX constitutes a convenient preparative method for chloro- and bromoalkyl sulfones.

2. A possible mechanism for the oxidative halogenation of hydroxyalkyl sulfides and sulfoxides is examined, and it is shown that the differences between oxidative chlorination and bromination in the H_2O_2 -HX system arise at the stage of conversion of the hydroxyalkyl sulfoxides into haloalkyl sulfones. The presence of substantial amounts of free bromine in the reaction mixture results in a considerable reduction in the yields of bromoalkylsulfones.

LITERATURE CITED

1. A. R. Derzhinskii, N. K. Kochetkov, S. A. Nekhoroshev, and V. N. Piottukh-Peletskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2597 (1981).
2. A. R. Dzerhinskii, O. S. Chizhov, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 850 (1977).
3. A. R. Dzerhinskii, L. D. Konyushkin, and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2070 (1978).
4. A. R. Derzhinskii, L. D. Konyushkin, and E. N. Prilezhaeva, *Inventor's Certificate (USSR) No. 690012 (1979)*; *Byull. Izobret.*, No. 37 (1979); *Ref. Zh. Khim.*, 9H89P (1980).
5. S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.*, 348 (B 1967).
6. E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. 2, Chem. Publ. Co., New York (1960), p. 208.
7. E. N. Prilezhaeva, T. E. Pivovarova, V. I. Snegotskii, V. Kh. Syundyukova, V. Z. Sharf, P. V. Saburova, A. L. Petunova, and V. A. Lukin, in: *The Chemistry of Organic Sulfur Compounds Present In Petroleum and Petroleum Products [in Russian]*, Vol. 2, Vysshaya Shkola, Moscow (1972), p. 200.
8. L. Ramberg and B. Backlund, *Arkiv. Kemi, Mineral. Geol.*, 13A, 27, 50 (1940) (German summary); *Chem. Abstr.*, 34, 4725⁶ (1940).

 α , β -UNSATURATED SULFENYL CHLORIDES *

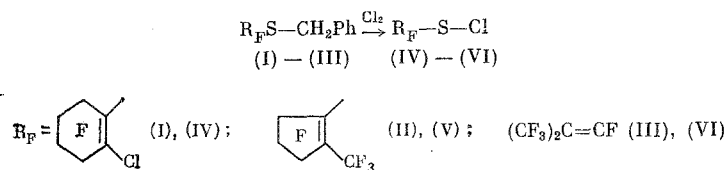
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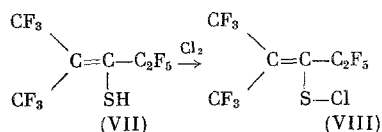
The chemistry of sulfenyl chlorides (SFC), as is well known, extends over more than a century [2]. Their high reactivity, and the possibility of obtaining compounds with biological activity [3, 4], account for the continuing interest in compounds of this type.

This investigation describes the synthesis of previously unknown perfluorinated α, β -unsaturated SFC. Information on hydrocarbon analogs of the latter is very limited, apparently as a result of their difficult accessibility and low stability [5, 6]. We have found that chlorination of some perfluoroalkenyl and perfluorocycloalkenyl benzyl sulfides results in chlorolysis of the C-S bond with retention of the double bond.

Thus, 1-benzylthio-2-chloroperfluoro-1-cyclohexene (I), 1-benzylthio-2-methyl-1-cyclopentene (II), and 1-benzylthio-2-methyl-1-propene (III) undergo chlorination at room temperature with the formation of the corresponding unsaturated SFC (IV)-(VI) in high yields



Perfluoro-2-methyl-2-pentene-3-sulfenyl chloride (VIII) has been obtained by chlorination of the corresponding unsaturated mercaptan (VII) [7]



Chlorination of 1-benzylthio-2-methyl-1-cyclobutene (IX) with elementary chlorine results in the simultaneous formation of the sulfenyl chloride and chlorination of the double bond, the final reaction product being

* For a previous communication, see [1].