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α, β-UNSATURATED SULFENYL CHLORIDES *

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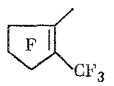
The chemistry of sulfenyl chlorides (SFC), as is well known, extends over more than a century [2]. Their high reactivity, and the possibility of obtaining compounds with biological activity [3, 4], account for the continuing interest in compounds of this type.

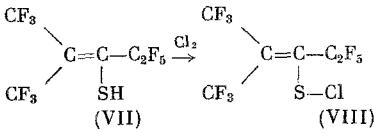
This investigation describes the synthesis of previously unknown perfluorinated α,β-unsaturated SFC. Information on hydrocarbon analogs of the latter is very limited, apparently as a result of their difficult accessibility and low stability [5, 6]. We have found that chlorination of some perfluoroalkenyl 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-benzylthioperfluoro-2-methyl-1-cyclopentene (II), and 1-benzylthioperfluoro-2-methyl-1-propene (III) undergo chlorination at room temperature with the formation of the corresponding unsaturated SFC (IV)-(VI) in high yields

$$R_FS{-}CH_2Ph \xrightarrow{Cl_2} R_F{-}S{-}Cl$$
$$\text{(I)} - \text{(III)} \qquad \text{(IV)} - \text{(VI)}$$

$R_F =$  (I), (IV);  (II), (V); $(CF_3)_2C{=}CF$ (III), (VI)

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



Chlorination of 1-benzylthioperfluoro-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].

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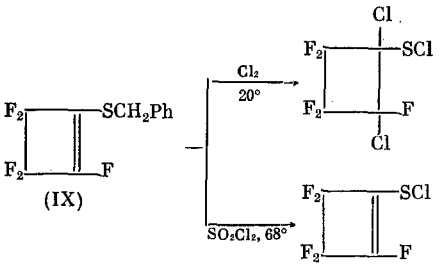
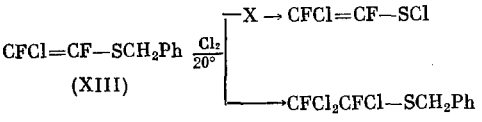
the saturated SFC (X). Perfluoro-1-cyclobutenesulfenyl chloride (XI) has been obtained by reacting the sulfide (IX) with SO_2Cl_2



(X)

(XI)

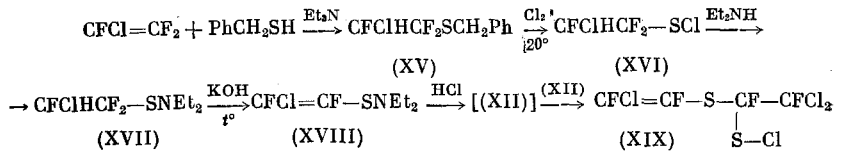
It is not possible to obtain 1,2-difluoro-2-chlorovinyl sulfenyl chloride (XII) by the direct chlorination (Cl_2 at 20°C, or SO_2Cl_2 at 60°C) of 1-benzylthio-1,2-difluoro-2-chloroethylene (XIII). In the first case, the saturated sulfide (XIV) was obtained, and in the second case, resinous products of unknown structure



(XII)

(XIV)

We therefore attempted to obtain (XII) by a more complex multistage route, as follows

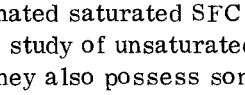


Addition of $PhCh_2SH$ to trifluorochloroethylene under the usual conditions [8] gives the sulfide (XV), which was chlorinated to the SFC (XVI). A known method for the synthesis of the latter is by radical addition of H_2S to trifluorochloroethylene followed by chlorination of the resulting thiol [9].

Successive reaction of (XVI) with Et_2NH and KOH affords the α,β-unsaturated sulfenamide (XVIII). By making use of the well-known property of sulfenamides of reacting with HCl to give the corresponding SFC [3], an attempt was made to convert (XVIII) into the SFC (XII) in this way. It was found that (XII), formed as an intermediate, was not capable of separate existence, but only as the "dimer" (XIX), formed by the addition of one molecule of (XII) to the double bond of another molecule.

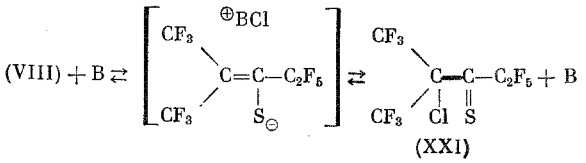
To summarize the results obtained in the synthesis of perfluorinated SFC, it has been found that unsaturated perfluorinated alicyclic and aliphatic SFC are capable of separate existence, except for aliphatic compounds with a terminal double bond.

It is known that the reactivity of fluorinated saturated SFC does not differ significantly from that of their nonfluorinated analogs [3, 4]. A preliminary study of unsaturated SFC has shown that, in addition to the properties inherent in this class of compounds, they also possess some special features. Thus, the SFC (V), like its saturated analogs [3, 4], reacts with Et_2NH to give the sulfenamide (XX), indicating the ability of the chlorine atom in these compounds to undergo nucleophilic displacement.



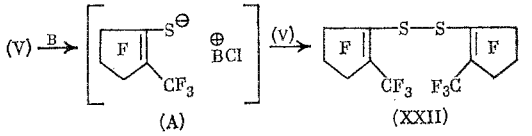
(XX)

However, some aprotic bases attack the Cl rather than the S atom in unsaturated SFC, resulting finally in a shift of the formally positive halogen. This is shown by the chlorotropy which we have observed in the system (VIII)-(XXI) in the presence of basic catalysts ($Et_3N \cdot BF_3$) or solvents (Et_2O) [7].



(XXI)

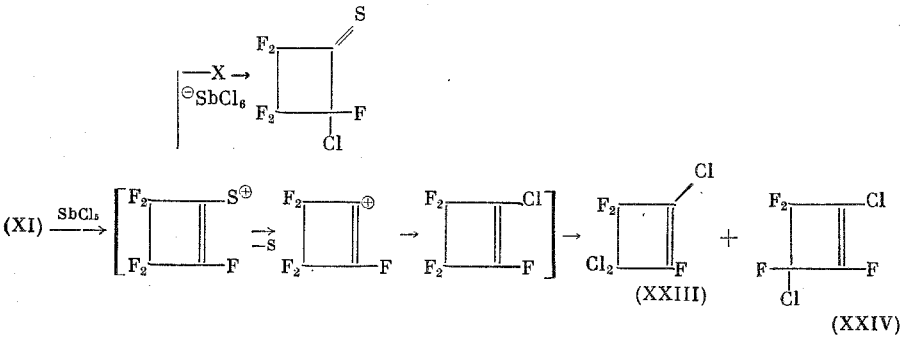
Unsaturated alicyclic SFC do not isomerize under these conditions to the corresponding α-chlorothioketones. For instance, in the presence of bases (N-methylpyrrolidone or $Et_3N \cdot BF_3$), (V) is dechlorinated to the disulfide (XXII)



(A) (XXII)

This reaction may be rationalized as an initial halophilic reaction [10] to give the mercaptide (A), followed by reaction of the latter with another molecule of the SFC by nucleophilic displacement.*

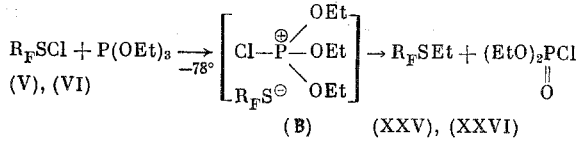
An anionotropic shift of Cl in the CCS triad, such as could take place in the presence of a Lewis acid ($SbCl_5$ or BF_3), failed to occur. In the presence of $SbCl_5$, perfluoro-1-cyclibutenylsulfenyl chloride (XI) loses sulfur. This reaction results in partial replacement of the fluorine atoms by chlorine to give the fluorochlorocyclobutenes (XXIII) and (XXIV)



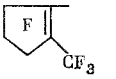
(XXIII) (XXIV)

Trichloromethanesulfenyl chloride reacts similarly with an excess of $SbCl_5$ to give CCl_4 [12]. Sulfenyl chlorides (V), (VI), and (VIII) failed to react with $Et_2O \cdot BF_3$.

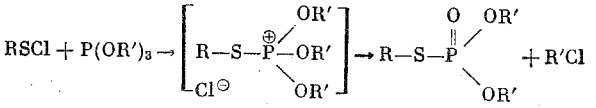
The reactions of the unsaturated SFC (V) and (VI) with $P(OEt)_3$ may also be rationalized in terms of attack of the latter on the Cl atom with the formation of the unstable intermediate (B), which decomposes to the perfluoroalkenyl ethyl sulfides (XXV) and (XXVI), and diethyl chlorophosphate.



(B) (XXV), (XXVI)

R_F=$(CF_3)_2C$=CF (VI), (XXV);  (V), (XXVI)

In the analogous reaction with nonfluorinated SFC, trialkyl phosphites attack the S atom to give the alkyl halides and phosphates [4].



* Zeifman et al. [11] observed the formation of $(CF_3)_3CCl$ in the reaction of CCl_3SCl with $(CF_3)_3C^-$, which may also be rationalized as a transfer of formally positive halogen. The formation of the disulfide (XXII) may be interpreted in terms of a one-electron transfer. Rationalization of the tautomeric reactions in the (VIII)-(XXI) system on this basis seems unlikely.

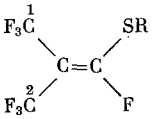
TABLE 1

(δ, ppm)

Compound	n	R	X	$\delta_{CF_2^1}$	$\delta_{CF_2^2}$	$\delta_{CF_2^3}$	$\delta_{CF_2^4}$	δ_X
(IV)	4	Cl	Cl	28,8 m	56,2 m	56,2m	32,4m	
(II)	3	CH_2Ph	CF_3	29,8 m	31,2m	53,0m		−16,7 m
(V)	3	Cl	CF_3	30,6 m	32,7 m	53,8m		−17,1 m
(XX)	3	NEt_2	CF_3	32,0 m	32,0 m	54.0m		−17,2 m
(XXII)	3	$SC{=}C(CF_3)CF_2CF_2CF_2$	CF_3	30,7 m	33,6 m	54,0m		−16,9 m
(XXVI)	3	CH_2CH_3	CF_3	30,2 m	31,5 m	53,5 m		−16,4 m
(IX)	2	CH_2Ph	F	36,6 m	38,0 m			41,5 t.t*
(XI)	2	Cl	F	36,0 m	38,9 m			34,6 m

* $J_{CF_2^1-F} = 18{,}8$; $J_{CF_2^2-F} = 6{,}6$ Hz.

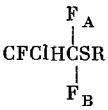
TABLE 2



(δ, ppm, J, Hz)

Compound	R	$\delta_{CF_3^1}$	$\delta_{CF_3^2}$	δF	$J_{F-CF_3^1}$	$J_{F-CF_3^2}$	$J_{CF_3^1-CF_3^2}$
(III)	CH_2Ph	−20,9m	−20,9 m	−11,8 q.q	9,4	24,4	
(VI)	Cl	−20,7d.q	−18,7 d.q	−8,2 q.q	9,4	25,4	9,4
(XXV)	CH_2CH_3	−20,0m	−20,0 m	−8,9 q.q	9,4	24,4	

TABLE 3



(δ, ppm, J, Hz)

Compound	R	δF_A	δF_B	δF	$J_{F_A-F_B}$	J_{F_A-F}	J_{F_A-H}	J_{F_B-F}	J_{F_B-H}	J_{F-H}
(XV)	CH_2Ph	6,9	9,4	68,4 d.d.d	221,0	18,8	5,3	17,1	5,6	49,0
(XVI)	Cl	12,6	16,2	70,4 d.d.d	220,0	17,8	4,7	17,8	7,5	47,0
(XVII)	NEt_2	14,4	19,8	71,1 d.d.d	231,0	18,8	4,7	17,9	9,4	49,9

Trifluoromethanesulfenyl chloride reacts with trimethyl phosphite simultaneously in two different ways, to give the sulfide CF_3SCH_3 and the phosphate $CF_3SP(O)(OCH_3)_2$ [4].

We note in conclusion that α,β-unsaturated SFC open up the possibility of synthesizing unsaturated sulfenic, sulfinic, and sulfonic acids, and of studying cationotropic rearrangements in the triad system C−C−S.

TABLE 4

$^{1}CFCl=C^{2}FSR$
(δ, ppm, J, Hz)

Compound	R	δF^1	δF^2	$J_{F^1-F^2}$	$J_{F^2-CH_2}$
cis-(XIII)	CH_2Ph	9,1 d	34,1 d.t	16,0	1,8
trans-(XIII)	CH_2Ph	26,4 d	44,9 d.t	137,0	1,8
cis-(XVIII)	NEt_2	8,1 d	32,0 d	16,9	
trans-(XVIII)	NEt_2	23,1 d	42,4 d	141,0	

EXPERIMENTAL

^{19}F and ^{1}H NMR spectra were obtained on a Perkin-Elmer R-32 spectrometer (at 84.6 and 90 MHz, respectively), using CF_3CO_2H and TMS as external standards. IR spectra were obtained on a UR-20 spectrometer. The purity of the compounds was checked by GLC on an LKhM-8MD instrument (model 3), using a column packed with 20% QF on Chromaton. Mass spectra were obtained on a Varian MAT CH-8 apparatus (ionizing electron energy 70 eV), and the m/z values and suggested assignments are given.

The ^{19}F NMR spectra (δ, ppm, J, Hz) for (II), (IV), (V), (IX), (XI), (XX), (XXII), and (XXVI) are given in Table 1; for (III), (VI), and (XXV) in Table 2; for (XV)-(XVII) in Table 3; and for (XIII) and (XVIII) in Table 4.

1-Benzylthioperfluoro-2-methyl-1-cyclopentene (II). To a mixture of 36.3 g of perfluoro-1-methyl-1-cyclopentene and 20 g of $PhSCH_2SH$ in ether (150 ml) was added slowly with stirring 16.3 g of Et_3N, the temperature being maintained at 20-25°C. The reaction mixture was stirred for a further 2 h, washed with water, dried over $MgSO_4$, and distilled to give 35.0 g (59.5%) of (II), bp 95-97°C (2 mm). Found: C 42.63; H 1.81; F 46.27; S 8.94%. $C_{13}H_7F_9S$. Calculated: C 42.63; H 1.92; F 46.68; S 8.75%.

1-Benzylthioperfluoro-2-methyl-1-propene (III). A steel autoclave containing 35.4 g of perfluoroisobutylene, 19.0 g of $PhCH_2SH$, and 6 ml of N-methylpyrrolidone was heated for 10 h at 90°C. Unreacted gaseous products were collected in a trap cooled to −78°C, and the contents of the autoclave were washed with water, dried over $MgSO_4$, and distilled to give 22.1 g of a mixture consisting of 83% of 1-benzylthio-1,1,3,3,3-pentafluoro-2-trifluoromethylpropane (XXVII) [PMR spectrum: 3.2 m (H), 3.7 s (CH_2), 6.9 s (C_6H_5); ^{19}F NMR spectrum: −15.9 t.d. ($(CF_3)_2$), −6.2 hept. d (CF_2), [$J_{(CF_3)_2-CF_2} = J_{CF_2-H} = 11.3$, $J_{(CF_3)_2-H} = 7.5$] and 17% of (III), bp 61-73°C.

This mixture (14.6 g) was heated with 5.8 g of BF_3NEt_3 for 30 min at 60°C, then washed with dilute HCl, dried over $MgSO_4$, and distilled to give 9.5 g of (III), bp 72-75°C (2 mm). Found: C 43.28; H 2.28; F 43.79; S 10.97%. $C_{11}H_7F_7S$. Calculated: C 43.42; H 2.32; F 43.72; S 10.54%.

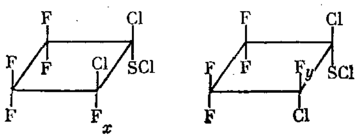
2-Chloroperfluoro-1-cyclohexenylsulfenyl Chloride (IV). Chlorine was passed into 1.9 g of (I) [13] until the exothermic reaction ceased, keeping the temperature at 20°C, then 1 ml of conc. H_2SO_4 was added and the mixture distilled to give 1.0 g (61%) of (IV), bp 65°C (25 mm). Found: C 22.48; F 46.29; S 9.60%. $C_6H_8Cl_2S$. Calculated: C 22.03; F 46.48; S 9.80%. IR spectrum (ν, cm^{-1}): 1590 (C = C).

Perfluoro-2-methyl-1-cyclopentenylsulfenyl Chloride (V). A steel autoclave containing 3.0 g of Cl_2 and 13.7 g of (II) was shaken for 24 h at ~ 20°C. Volatile products were removed from the reaction mixture under vacuum (3 mm) at 20°C and collected in a trap cooled to −78°C. The contents of the trap were then distilled to give 9.0 g (78%) of (V), bp 70°C (130 mm). Found: F 55.37; S 10.32%. C_6F_9ClS. Calculated: F 55.05; S 10.32%. IR spectrum (ν, cm^{-1}): 1610 (C = C).

1,3,3,3-Tetrafluoro-2-trifluoromethylpropenesulfenyl Chloride (VI). Obtained as for (IV) by passing Cl_2 into 3.6 g of (III), and distilling. Yield, 1.7 g (57%) (VI), bp 95-96°C. Found: F 53.93; S 12.85%. $C_4F_7Cl_2$. Calculated: F 53.51; S 12.90%. IR spectrum (ν, cm^{-1}): 1635 (C = C).

1-Benzylthioperfluoro-1-cyclobutene (IX). To a solution of 27.2 g of perfluorocyclobutene in 150 ml of ether was added dropwise with stirring at −3 to −5°C a mixture of 19.1 g of $PhCH_2SH$ and 15.8 g of Et_3N. The mixture was warmed to ~ 20°C, washed with water, the ether layer dried over $MgSO_4$, and distilled to give 20.5 g (41%) of (IX), bp 78°C (2 mm). Found: C 49.53; H 2.65; F 35.54; S 11.87%. $C_{11}H_7F_5S$. Calculated: C 49.62; H 2.63; F 35.71; S 12.03%. PMR spectrum: 3.7 s (CH_2), 6.9 s (C_6H_5). IR spectrum (ν, cm^{-1}): 1678 (C = C).

1,2-Dichloroperfluorocyclobutanesulfenyl Chloride (X). Chlorine was passed into 3.1 g of (IX) at 20°C until the exothermic reaction was complete, and 2 ml of conc. H_2SO_4 was then added. Distillation gave 2.1 g (65%) of (X), bp 61°C (40 mm). Found: C 17.54; F 33.95; S 11.11%. $C_4F_5Cl_3S$. Calculated: C 17.06; F 33.75; S 11.89%. The compound contained two geometrical isomers



The ^{19}F NMR spectrum consisted of 18 multiplets, assigned to four AB quartets for the CF_2 groups and to two CFCl groups. Isomer 1: 32.0 (F_A), 46.0 (F_B) 38.4 ($F_{A'}$), 42.4 ($F_{B'}$), 46.5 (F_x) $J_{F_A-F_B}$ = 211, $J_{F_{A'}-B'}$ = 212 Hz. Isomer 2: 33.6 (F_A), 39.4 (F_B), 37.8 ($F_{A'}$), 46.9 ($F_{B'}$), 39.4 (F_y); $J_{F_A-F_B}$=205, $J_{F_{A'}-F_{B'}}$ = 21 Hz.

Perfluoro-1-cyclobutentylsulfenyl Chloride (XI). A steel autoclave containing 7.4 g of (IX) and 3.6 g of SO_2Cl_2 was kept for 20 h at 68°C. After removing the SO_2 formed, the autoclave was opened, the liquid material placed in a flask, and volatile products distilled at 5 mm vacuum into a trap cooled to −78°C. The condensate was redistilled to give 2.0 g (34.5%) of (XI), bp 102-103°C. Found: C 23.26; F 44.72%. C_4F_5ClS. Calculated: C 22.82; F 45.12%. IR spectrum (ν, cm^{-1}): 1680 (C = C).

1-Benzylthio-1,2-difluoro-2-chloroethylene (XIII). Compound (XV) (21.2 g) was twice distilled over an excess of solid KOH at a vacuum of 20 mm to give 14.4 g (74%) of (XIII), bp 114°C (20 mm). Found: C 48.81; H 3.07; F 17.30; S 14.78%. $C_9H_7F_2ClS$. Calculated: C 48.97; H 3.19; F 17.22; S 14.53%. IR spectrum (ν, cm^{-1}): 1663 (C = C).

1-Benzylthio-1,2-difluoro-1,2,2-trichloroethane (XIV). Chlorine (3.0 g) was passed into 9.5 g of (XIII) at 15-20°C, and the product distilled to give 10.3 g (82.5%) of (XIV), bp 139°C (8 mm). Found: C 37.21; H 2.36; F 13.04; S 11.01%. $C_9H_7F_2ClS$. Calculated: C 37.07; H 2.42; F 13.03; S 11.00%. ^{19}F NMR spectrum: −15.5 d ($CFCl_2$), 6.2 d (CFCl), J_{CFCl_2-CFCl} = 20.6 Hz.

1-Benzylthio-1,1,2-trifluoro-2-chloroethane (XV). A steel autoclave containing 25.0 g of $PhCH_2SH$, 30.0 g of CF = CFCl and 2 ml of Et_3N was shaken at ~ 20°C for 25 h. The mixture was washed with water, dried over $MgSO_4$, and distilled to give 39.5 g (81.5%) of (XV), bp 87-89°C (2 mm). Found: C 44.87; H 3.09; F 23.50; S 13.10%. $C_9H_8F_3ClS$. Calculated: C 45.00; H 3.33; F 23.75; S 13.33%. PMR spectrum 3.5 s (CH_2), 5.5 d.d.d (CFClH), 6.8 s (C_6H_5).

1,1,2-Trifluoro-2-chloroethanesulfenyl Chloride (XVI). Chlorine was passed into 14.6 g of (XV) until the exothermic reaction ceased, keeping the temperature at 20-25°C, and the product distilled to give 10.5 g (93%) of (XVI), bp 98-100°C (see [9]). Found: F 30.85; S 17.30%. $C_2F_3HCl_2S$. Calculated: F 30.81; S 17.29%. PMR spectrum: 6.4 d.d.d. (CFClH).

1,1,2-Trifluoro-2-chloroethane-N,N-diethylsulfenamide (XVII). To 20 ml of Et_2NH, cooled to −78°C, was added slowly with stirring 10.0 g of (XVI). The reaction mixture was washed with water, dried over $MgSO_4$, and distilled to give 9.2 g (77.5%) of (XVII), bp 79°C (30 mm). Found: C 32.51; H 4.82; F 25.13; S 14.10%. $C_6H_{11}F_3ClNS$. Calculated: c 32.50; H 5.00; F 25.71; S 14.46%. PMR spectrum: 6.1 d.d.d. (CFClH). 3.0 q (CH_2), 1.0 t (CH_3).

1,2-Difluoro-2-chlogovinyl-N,N-diethylsulfenamide (XVIII). Compound (XVII) (11.6 g) was twice distilled over an excess of solid KOH in a vacuum of 130 mm to give 8.5 g (80%) of (XVIII), bp 110°C (130 mm). Found: F 18.77; N 7.45%. $C_6H_{10}F_2ClNS$. Calculated: F 18.84; N 6.94%. IR spectrum (ν, cm^{-1}): 1645 (C = C).

1-(1,2-Difluoro-2-chlorovinylthio)-1,2-difluoro-2,2-dichloroethanesulfenyl Chloride (XIX). A solution of 5.0 g of (XVIII) in 50 ml of $CHCl_3$ was cooled to −78°C, and dry HCl passed in. Distillation of the filtrate gave 2.6 g (63.5%) of a mixture of cis- and trans-isomers of (XIX) in a ratio of 62 : 38, bp 74-75°C (2 mm). Found: C 14.51; S 19.58%. $C_4F_4Cl_4S_2$. Calculated: C 14.56; S 19.43%. IR spectrum (ν, cm^{-1}): 1650 (C=C).

$$\overset{1}{\mathrm{CClF}} = \overset{2}{\mathrm{CF}}\text{—S—}\underset{\mathrm{SCl}}{\overset{3}{\mathrm{CF}}}\overset{4}{\mathrm{CF}}\mathrm{Cl_2}$$

^{19}F NMR spectrum, cis-Isomer: 2.5 d (F^1), 37.3 d.m. (F^2), 11.8 d.d. ($F_3{}^3$), −14.9 d.d. (F^4), $J_{F^1-F^2}$ = 20.7, $J_{F^3-F^2}$ = 7.5, $J_{F^3-F^4}$ = 18.8, $J_{F^4-F^2}$ = 1.9 Hz. trans-Isomer: 19.3 d.m. (F^1), 49.0 d.m (F^2), 12.3 d.d.d (F^3), −14.9 d.d. (F^4), $J_{F^1-F^2}$ = 131.5, $J_{F^3-F^2}$ = 7.5, $J_{F^3-F^4}$ = 18.8, $J_{F^3-F^1}$ = 5.6, $J_{F^4-F^2}$ = 1.9 Hz.

Perfluoro-2-methyl-1-cyclopenten-N,N-diethylsulfenamide (XX). To a solution of 5 ml of Et_2NH in 50 ml of ether, cooled to −78°C, was added slowly 3.8 g of (V). The mixture was washed with water, dried over $MgSO_4$, and distilled to give 2.6 g (62%) of (XX), bp 98-99°C (40 mm). Found: C 34.21; H 3.09; N 4.38; S 9.07%. $C_{10}H_{10}F_9NS$. Calculated: C 34.58; H 2.90; N 4.03; S 9.23%. PMR spectrum: 0.94 t (CH_3), 2.9 q (CH_2). IR spectrum (ν, cm^{-1}): 1600 (C = C).

Di-(perfluoro-2-methyl-1-cyclopentenyl) Disulfide (XXII). To 3 ml of N-methylpyrrolidone was added 2.0 g of (V), and after 10 min the mixture was poured into water. The organic layer was separated, dried over $MgSO_4$, and distilled to give 1.4 g (78%) of (XXII), bp 83°C (5 mm). Mass spectrum (masses down to 175 given): Found: C 26.20; F 62.48; S 11.88%. $C_{12}F_{18}S_2$. Calculated: C 26.19; F 62.15; S 11.65%. 550 (M^+), 531 (M^+-F), 307 ($C_6F_9S_2^+$), 275 ($C_6F_9S^+$), 256 ($C_6F_8S^+$), 243 ($C_6F_9^+$), 237 ($C_6F_7S^+$), 231 ($C_5F_9^+$), 255 ($C_5F_7S^+$), 206 ($C_5F_6S^+$), 193 ($C_5F_7^+$), 187 ($C_5F_5S^+$), 181 ($C_4F_7^+$), 175 ($C_4F_5S^+$). IR spectrum (ν, cm^{-1}): 1625 (C=C).

Reaction of (V) with an equimolar amount of $BF_3 \cdot NEt_3$ gave a mixture which contained, according to GLC and NMR, > 90% of (XXII).

1,3,3-Trichloroperfluoro-1-cyclobutene (XXIII) and 1,3-Dichloroperfluoro-1-cyclobutene (XXIV). To 3 ml of $SbCl_5$ was added at ~ 20°C 1.9 g of (XI). The mixture was stirred for 10 min, and the volatile products removed at a vacuum of 5 mm to a trap at −78°C, giving 1.7 g of a mixture, bp 90-103°, which according to GC-MS contained mainly (XXIII) and (XXIV).

(XXIII). Mass spectrum: 210 (M^+), 191 (M^+-F), 175 (M^+-Cl), 156 (M^+-F-Cl), 141 (M^+-CF_2-F), 132 ($M^+-CF-CCl$), 125 (M^+-CF_2-Cl), 121 (M^+-F-Cl_2), 109 (M^+-CCl_2-F), 106 (M^+-CF_2-F-Cl), 97 (M^+-CCl_2-CF), 93 (M^+-CCl_2-Cl), 90 (C_3FCl^+).

(XXIV). Mass spectrum: 194 (M^+), 175 (M^+-F), 159 (M^+-Cl), 140 (M^+-F-Cl), 137 (M^+-F_3), 125 (M^+-CF_2-F), 116 ($M^+-CF-CCl$), 109 (M^+-CF_2-Cl, 93 ($M^+-CFCl-Cl$), 90 (C_3FCl^+).

1-Ethylthio-1,3,3,3-tetrafluoro-2-trifluoromethylpropene (XXV). To 0.7 g of $P(OEt)_3$ was added at −78°C 1.0 g of (VI). The mixture was warmed to ~ 20°C, and distilled to give 0.5 g of diethyl chlorophosphate, identified by GLC, bp 73°C (5 mm), and 0.6 g (61.2%) of (XXV), bp 126°C (see [14]). IR spectrum (ν, cm^{-1}): 1620 (C = C).

1-Ethylthioperfluoro-2-methyl-1-cyclopentene (XXVI). Obtained as in the preceding example, from 0.9 g of $P(OEt)_3$ and 1.6 g of the sulfenyl chloride (V). Yield 0.7 g of diethyl chlorophosphate and 1.2 g (77%) of (XXVI), bp 62°C (30 mm). Found: C 31.55; H 1.65; F 55.93; S 10.19%. $C_8H_5F_9S$. Calculated: C 31.59; H 1.66; F 56.22; S 10.54%. PMR spectrum: 1.2 t (CH_3), 3.3 q (CH_2). IR spectrum (ν, cm^{-1}): 1600 (C = C).

CONCLUSIONS

A method has been developed for the preparation of perfluorinated α,β-unsaturated sulfenyl chlorides, and their reactions with basic reagents and Lewis Acids have been studied.

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