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SYNTHESIS OF THE UNSYMMETRICAL DISELENANES $CF_3SeSeCF_2Cl$ AND $CF_3SeSeCH_3$

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SUMMARY

Chlorodifluoromethyl(trifluoromethyl)diselenane, $CF_3SeSeCF_2Cl$, has been prepared by the reaction of CF_3SeCl with $Se{=}CF_2$. $CF_3SeSeCH_3$ has been synthesized via a new route from $CF_3SeSeCF_3$ and $CH_3SeSeCH_3$. $CF_3SeSeCF_2Cl$ is unstable with respect to the symmetric diselenanes $CF_3SeSeCF_3$ and $CF_2ClSeSeCF_2Cl$. The new compound $CF_3SeSeCF_2Cl$ has been characterized by ^{77}Se, ^{19}F, and ^{13}C NMR, IR, and mass spectra. Additional data from the ^{77}Se, ^{19}F, ^{13}C, and ^{1}H NMR spectra are reported for the known compounds $CF_3SeSeCH_3$ and $CF_2ClSeSeCF_2Cl$.

INTRODUCTION

In a current NMR spectroscopic study of the selenium-selenium coupling constant in symmetrical and unsymmetrical diselenanes, the compounds $CF_3SeSeCF_2Cl$ and $CF_3SeSeCH_3$ became of interest for comparison. While $CF_3SeSeCH_3$ had recently been prepared by the reaction of CF_3SeBr with CH_3SeH [1], $CF_3SeSeCF_2Cl$ was not known in the literature.

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RESULTS AND DISCUSSION

We were able to synthesize $CF_3SeSeCF_2Cl$ by the reaction of CF_3SeCl with $Se=CF_2$. In this reaction the unstable and reactive compound $Se=CF_2$ [2, 3] is quantitatively inserted into the Se-Cl bond of CF_3SeCl, and $CF_3SeSeCF_2Cl$ is readily formed at low temperatures.

$$CF_3SeCl + Se=F_2 \longrightarrow CF_3SeSeCF_2Cl$$

A new simple synthesis was found for $CF_3SeSeCH_3$. An equimolar mixture of $CH_3SeSeCH_3$ and $CF_3SeSeCF_3$ reacts slowly at room temperature to yield $CF_3SeSeCH_3$. The dismutation is completed after about one week. The progress of the reaction was observed by NMR spectroscopy, and the formation of $CF_3SeSeCH_3$ was proved by the known ^{19}F and ^{1}H NMR data [1].

$$CH_3SeSeCH_3 + CF_3SeSeCF_3 \longrightarrow 2\ CF_3SeSeCH_3$$

$CF_3SeSeCF_2Cl$ is unstable with respect to the symmetrical diselenanes. About 50 % of the neat substance reacted during a period of four months at room temperature in a reaction according to the following equation. Another sample diluted with 10 to 15 % C_6D_6 reacted under the same conditions only to an extent of about 20 %.

$$2\ CF_3SeSeCF_2Cl \longrightarrow CF_3SeSeCF_3 + CF_2ClSeSeCF_2Cl$$

The different thermodynamic stabilities of the diselenanes are noteworthy. The compound with two perhalogenomethyl groups, $CF_3SeSeCF_2Cl$, is unstable with respect to the symmetrical diselenanes. The compound containing one CF_3 and one CH_3 group, $CF_3SeSeCH_3$, is more stable; it is formed from the two symmetric diselenanes.

Besides the well known compound $CF_3SeSeCF_3$, $CF_2ClSeSeCF_2Cl$ could be identified by its ^{19}F NMR signal [3]. $CF_2ClSeSeCF_2Cl$ was also prepared after [3] for further characterization. The NMR data obtained from the ^{77}Se, ^{19}F, ^{13}C, and ^{1}H NMR spectra of

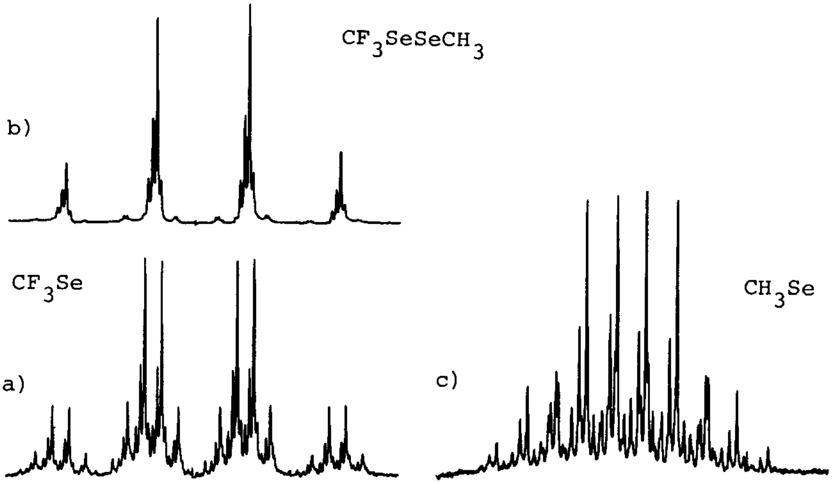


Fig. 1. ^{77}Se NMR spectrum of $CF_3SeSeCH_3$. CF_3Se: a) coupled spectrum, b) ^{1}H decoupled; c) CH_3Se group, coupled spectrum; the fine splitting in the spectra is attributed to isotope effects of neighbouring Se nuclei.

$CF_3SeSeCF_2Cl$, $CF_3SeSeCH_3$, and $CF_2ClSeSeCF_2Cl$ are listed in Table I. The ^{77}Se NMR spectrum of $CF_3SeSeCH_3$ is depicted in Fig. 1.

The coupling constants $^1J(Se-Se)$ and $^1J(Se-C)$ are of particular interest. $^1J(Se-C)$ values are in general much larger in perhalogenoalkyl than in alkyl selenium compounds [5], and the coupling constants $^1J(Se-Se)$ are considerably larger in bis(perhalogenoalkyl)diselenanes than in organyldiselenanes [6]. They reveal that in bis(perhalogenoalkyl)diselenanes multiple bond participation does not only extend over the F-C and C-Se bond, as has been found in CF_3-E-R and CF_2Cl-E-R compounds (E = chalcogen, R = substituent) [7, 8], but over the whole molecule. Although the participation of π-bonding may be very small, the coupling constants $^1J(F-C)$, $^1J(Se-C)$ and $^1J(Se-Se)$ are extremely sensitive to changes in the bond order. Taking into account that the ability of fluorine to form a partial double bond with carbon is much more pronounced than the ability of chlorine, the following formulae may describe the electronic structure of CF_3 substituted chalcogen compounds. The mesomeric formulae for CF_3-Se-R compounds can be represented by the simplified formula I, analogous-

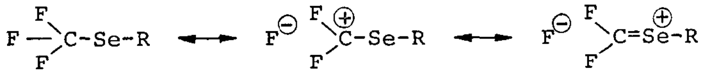
TABLE 1

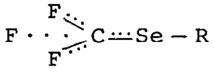
NMR data of $CF_3SeSeCF_2Cl$, $CF_3SeSeCH_3$ and $CF_2ClSeSeCF_2Cl$

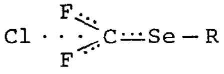
	$CF_3SeSeCF_2Cl$		$CF_3SeSeCH_3$		$CF_2ClSeSeCF_2C$
$\delta(^{19}F)$	-37.7	CF_3	-38.2		-25.2
	-26.2	CF_2Cl	-38.3	[1]	-25.1 [3]
$\delta(^{1}H)$			2.58		
			2.3	[1]	
$\delta(^{13}C)$	118.6	CF_3	118.7	CF_3	116.2
	115.9	CF_2Cl	13.2	CH_3	
$\delta(^{77}Se)$	579	CF_3Se	575	CF_3Se	691
	662	CF_2ClSe	269	CH_3Se	
$^{1}J(FC)$	337.6	CF_3	337.3		349.8
	349.2	CF_2Cl			
$^{1}J(CH)$			143.6		
$^{1}J(SeC)$	175.1	CF_3Se	189.6	CF_3Se	174.7
	173.1	CF_2ClSe	71.7	CH_3Se	
$^{1}J(SeSe)$	57.9		11.3		66.5
$^{2}J(SeF)$	9.8	CF_3Se	20.1		5
	6.5	CF_2ClSe			
$^{2}J(SeH)$			13.0		
$^{3}J(SeF)$	0	$SeSeCF_2Cl$			5
	2.7	$SeSeCF_3$	6.8		
$^{3}J(SeH)$			3.7		
$^{5}J(FF)$	4.0				5.4
$^{5}J(FH)$			0.44		
			0.4	[1]	
$^{1}\Delta^{77}Se(^{13/12}C)$	-0.178	CF_3Se	-0.205	CF_3Se	-0.257
	-0.250	CF_2ClSe			
$^{1}\Delta^{19}F(^{13/12}C)$	-0.1428	CF_3Se			-0.1645
$^{1}\Delta^{19}F(^{13/12}C)$	-0.1618	CF_2ClSe			
$^{1}\Delta^{19}F(^{37/35}Cl)$					-0.0067

$^{1}\Delta^{77}Se$ and $^{1}\Delta^{19}F$ values are isotope shifts. For definition and comparison see [4].

ly the same holds for CF_2Cl-Se-R compounds (formula II). Perhalogenoalkyldiselenanes may be described, for example, by formula III.




(I)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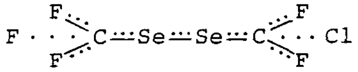
(III)

EXPERIMENTAL

Synthesis of $CF_3SeSeCF_2Cl$

2.0 g $SeCF_2$ [3] and 2.84 g CF_3SeCl [9, 10] were condensed at -196 °C in vacuo into a glass tube (6 mm o.d.). The tube was sealed, warmed to -50 °C and shaken. During a few minutes at this temperature the colour of the mixture changed from red to yellow. Then the tube was warmed up to room temperature to allow the reaction to proceed quickly. After about two hours the tube was opened under vacuum with an "ampoule key" [11] and the substance quantitatively transferred into a NMR tube which was joined to a rotationally symmetrical valve [12]. The ^{19}F and ^{77}Se NMR spectra showed that the product consisted of 96 % $CF_3SeSeCF_2Cl$ and only 1 % CF_3SeCF_3 and 3 % $CF_3SeSeCF_3$ as by-products. The latter could be separated by trap to trap condensation as they are more volatile than $CF_3SeSeCF_2Cl$.

Analysis: Found C, 7.7, $CF_3SeSeCF_2Cl$ requires C, 7.68 %.
Vapour pressure, mbar (°C): 5.5 (0), 9.8 (9.4), 21.0 (24.0).

Mass spectrum: 314 M^+ (69), 279 $[M-Cl]^+$ (30), 229 $CF_3Se_2^+$ (30), 210 $CF_2Se_2^+$ (4), 165 CF_2ClSe^+ (17), 149 CF_3Se^+ (7), 130 CF_2Se^+ (46), 111 $CFSe^+$ (12), 85 CF_2Cl^+ (100), 80 Se^+ (21), 69 CF_3^+ (49), 50 CF_2^+ (5), 31 CF^+ (15). The signals of fragments containing one or two Se atoms exhibited the expected isotope pattern.

IR spectrum (10 mbar): 1272 (w), 1180 (vs), 1109 (vs), 866 (vs), 845 (vs), 743 (s), 635 (w) cm^{-1}.

Spectroscopic Analysis

NMR spectra were obtained with a Brucker WM 250 instrument operating at 250.13 (^1H), 235.36 (^{19}F), 62.90 (^{13}C), and 47.71 MHz (^{77}Se). Absorptions to low field (high frequency) of reference signals (TMS, CCl_3F ext., TMS, $(CH_3)_2Se$ ext., respectively) are assigned positive chemical shift values. Mass spectra were recorded on a Varian MAT CH 7 spectrometer (electron energy 70 eV). IR spectra were run on a Perkin-Elmer 325 spectrophotometer.

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