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REACTIONS OF F-PROPENE AND ITS DIMER WITH SODIUM DIALKYLDITHIOCARBAMATE

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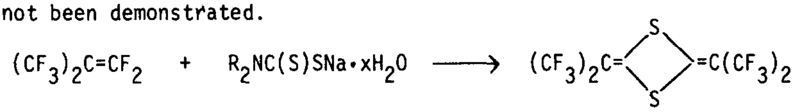
SUMMARY

Sodium dialkyldithiocarbamates readily attacked F-propene to give S-(1,1,2,3,3,3-hexafluoropropyl)-N,N-dialkyldithiocarbamates, $CF_3CHFCF_2SC(S)NR_2$, and Z and E-S-(1,2,3,3,3-pentafluoropropenyl)-N,N-dialkyldithiocarbamates, $CF_3CF{=}CFSC(S)NR_2$. The pyrolysis of the former compound quantitatively gave the dialkylthiocarbamoyl fluoride, $R_2NC(S)F$, while the latter compound and sodium tetraphenylborate formed the corresponding 1,3-dithiolan-2-ylium tetraphenylborate. F-2-Methyl-2-pentene also reacted with sodium dialkyldithiocarbamate to give $(CF_3)_2CH\text{-}C[S\text{-}C(S)\text{-}NR_2]{=}CFCF_3$. The mechanism of this reaction is supposed to involve a 1,4-RSF-elimination.

INTRODUCTION

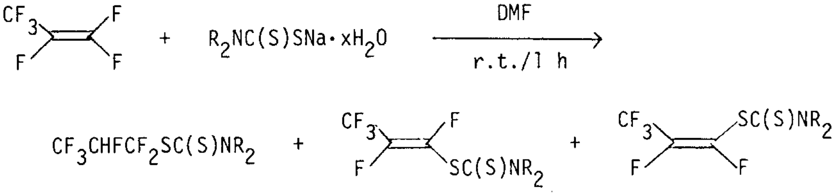
There is considerable research interest in the utilization of dithiocarbamates in synthetic works from the view point of their high nucleophilicity and their remarkable neighboring effects. Although several examples of the utilization of dithiocarbamates are known in hydrocarbon chemistry [1-4], their reactions with perfluoroolefins, excepting that of F-2-methylpropene, leading to 2,4-bis-(F-isopropylidene)-1,3-dithietane [5], have not been demonstrated.



As it seemed interesting to compare the behavior of F-propene with that of F-2-methylpropene, this work was started to clarify the differences in results of nucleophilic reactions between these perfluoroolefins towards N,N-dialkyldithiocarbamates.

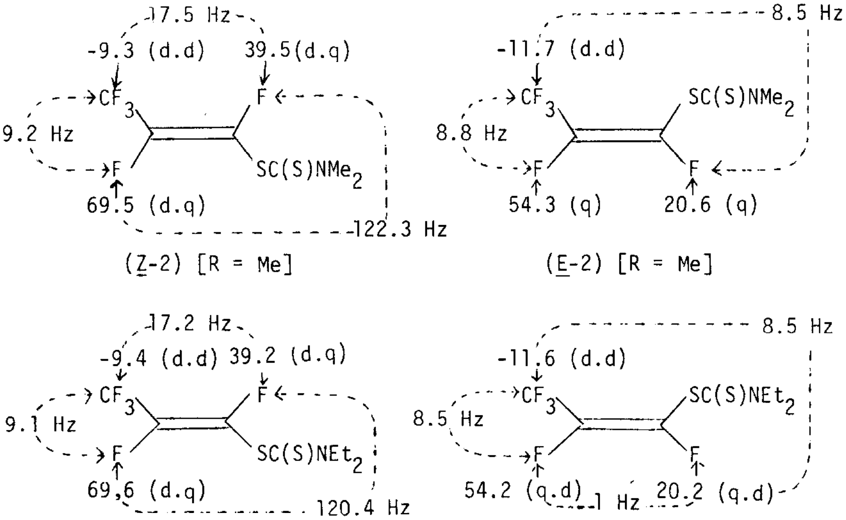
RESULTS AND DISCUSSION

When F-propene was allowed to react with sodium N,N-dialkyldithiocarbamate in DMF, S-(1,1,2,3,3,3-hexafluoropropyl)-N,N-dialkyldithiocarbamate (1) and Z and E-S-(1,2,3,3,3-pentafluoropropenyl)-N,N-dialkyldithiocarbamate (2) resulted as addition and substitution products, respectively.



(1) (Z-2) (E-2)

Spectroscopic data support the structures of these new compounds. The ^{19}F NMR spectrum of (1) [R = Me] contains three signals at δ -4.4 (CF_3), 10.2 (CF_2) and 128.7 (CF) ppm from external standard CF_3CO_2H, in the ratio 3 : 2 : 1. In the ^1H NMR spectrum, two signals appeared at τ 3.39 (CHF) and 6.51 (CH_3). The ^{19}F NMR data obtained for (2) are also very useful in establishing their respective structures, as shown below (Fig 1).

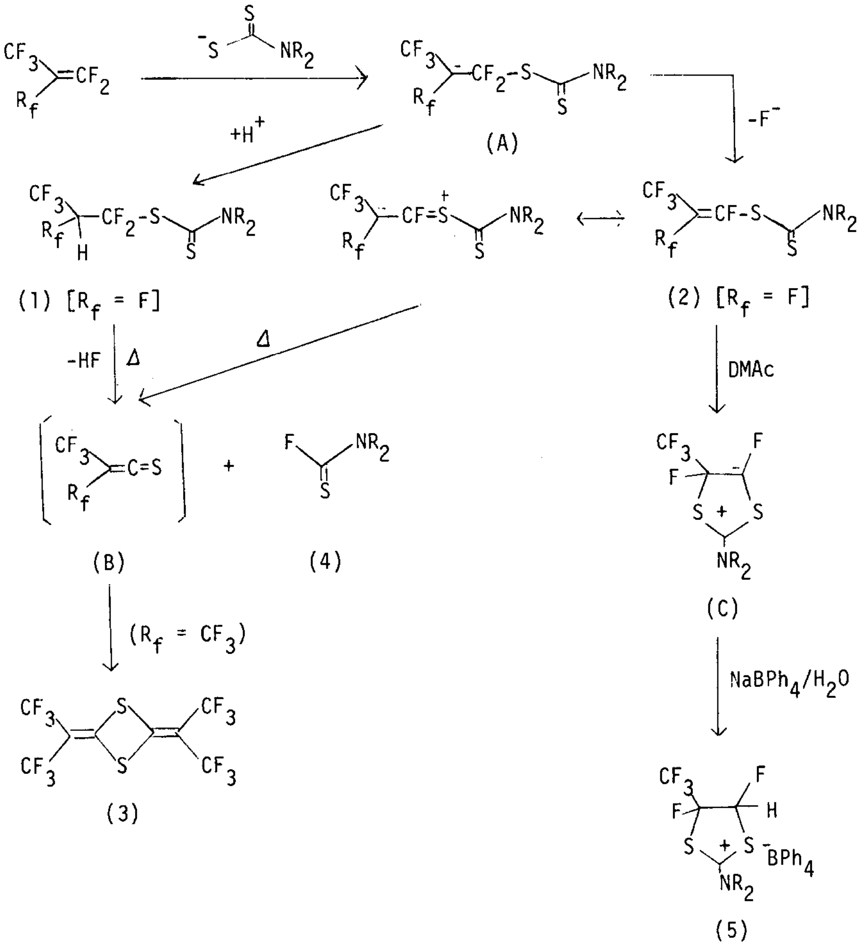


(Z-2) [R = Me] (E-2) [R = Me]

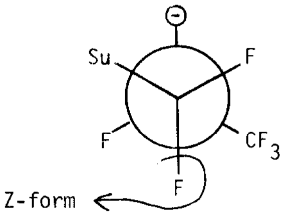
(Z-2) [R = Et] (E-2) [R = Et]

Fig. 1 ^{19}F NMR data for (Z-2) and (E-2)

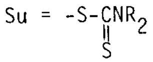
It is well known that perfluoro-terminal-olefins such as F-propene and F-2-methylpropene, are susceptible to the attack of nucleophiles at the terminal difluoromethylene group. In reactions with dithiocarbamates, therefore, it is expected to proceed as shown, and F-propene actually gave the expected products, (1) and (2). However, F-2-methylpropene, which has two strong electron-withdrawing CF_3 groups adjacent to the double bond, underwent decomposition to give (3). The following reaction scheme accounts for the above results.



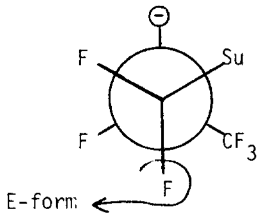
For the conformation of the carbanion (A), the less sterically hindered (A 1) is more likely than (A 2). Thus the formation of (Z-2) should predominate over that of (E-2), because the trans elimination of the fluoride ion from (A 1) and (A 2) will result in (Z-2) and (E-2), respectively.



(A 1)



$Su = -S-\underset{\underset{S}{\|}}{C}NR_2$



(A 2)

The solvent effect on these eliminations is also noticeable. Several solvents were tried in the reaction of F-propene and N,N-dialkyldithiocarbamate, and the results are summarized in the Table 1. Naturally, aqueous solvents increased the yield of the addition product (1) against the substitution product (2).

TABLE 1

Reaction of F-propene with $S\text{-}C(S)\text{-}NR_2 \cdot xH_2O$

Solvent	Time (h)	Products (Yield, %)[a]		
		(1)[R = Et]	(Z-2)	(E-2)
DMAc	1	44	40	11
DMF	1	56	28	8
CH_3CN	3	77	8	4
$CH_3CN + H_2O$ (9 : 1)	3	90	2	trace
Dioxane	96	43	0	0
Dioxane + H_2O (1 : 1)[b]	7	49[b]	0	0
		(1)[R = Me]	(Z-2)	(E-2)
DMAc	1	29	58	15
Dioxane + H_2O (1 : 1)[b]	20	63[b]	0	0

a) Determined by ^{19}F NMR.

b) Yields of isolated products.

When the addition product (1) [R_f = F] was heated at 130°C in a glass vessel, dialkylthiocarbamoyl fluoride (4) [6, 7] was generated quantitatively. This means that HF was eliminated to give unstable thioketene (B) [R_f = F] which instantly decomposed.

On the other hand, when the reaction mixture of F-propene and sodium dialkyldithiocarbamate in dimethylacetamide was treated with an aqueous solution of sodium tetraphenylborate, the formation of tetraphenylborate (5) in addition to (1) and (2) was observed.

The percentage yields of the products are shown in Table 2. From comparison of these ratios with those of Table 1, it is evident that the formation of (5) resulted from an intramolecular nucleophilic attack by the thiocarbonyl sulfur atom to form a cyclic dithiocarbonium salt (C).

TABLE 2

Formation of Tetraphenylborate

R	Products (yield, %)[a]			
	(1)	(Z-2)	(E-2)	(5)
Me	24	1	2	48
Et	35	6	6	19

a) The yields of (1), (Z-2) and (E-2) were determined from their ^{19}F NMR signal intensities whereas (5) was actually isolated.

The structure of the compound (5) [R = Et] was evident from various spectral data. The infrared spectrum showed the absorption band of the C=N double bond at 1610 cm^{-1}. In the mass spectrum, though the molecular ion was absent, other rational fragment peaks, such as m/e 319 ($C_{18}H_{15}B$), 279 ($C_8H_{10}NS_2F_5$), 163 (C_3SF_5) and 116 ($C_5H_{10}NS$) were observed. The ^{19}F NMR data for these compounds were useful in supporting their structures, as shown below (Fig. 2).

The resonance at 80.2 ppm in (5) [R = Me] or 81.0 ppm in (5) [R = Et], assigned to the fluorine atom on the CHF group, was an overlapping split by the geminal hydrogen and other neighboring fluorine atoms. The coupling constant 3.2 Hz (or 3.4 Hz), suggests especially that the vicinal CH-CF bond occupies the cis-position.

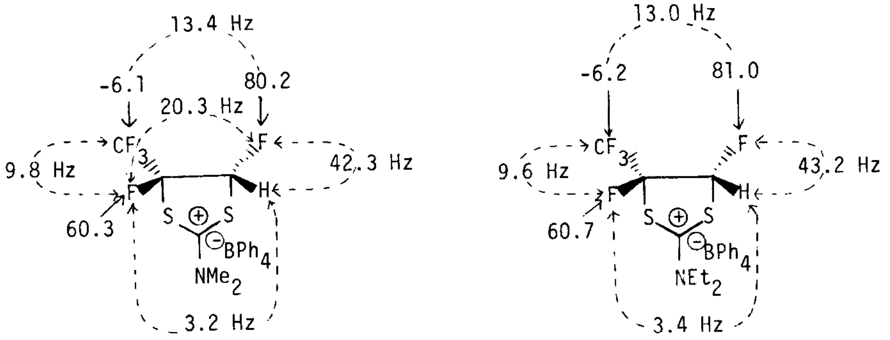
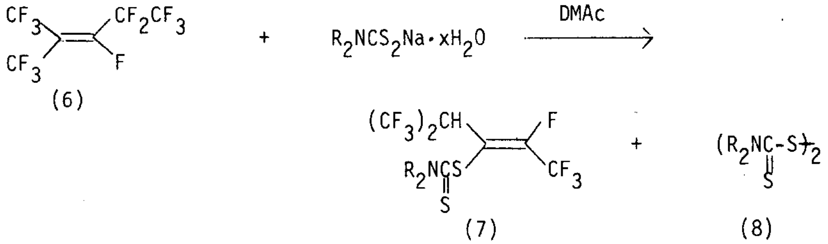


Fig. 2 ^{19}F NMR data for (5)

Further investigation was carried out in the similar nucleophilic reaction of F-2-methyl-2-pentene (6), a dimer of F-propene containing an inner double bond. It reacted with sodium dialkyldithiocarbamate with great ease, with migration of the $>C=C<$ double bond. Thus, the main product was an olefin(7), together with a considerable amount of disulfide (8) of the dialkylaminodithiocarbamate.



Spectroscopic data, particularly those of ^{19}F and ^{1}H NMR, elucidated the structure of (7) undoubtedly.

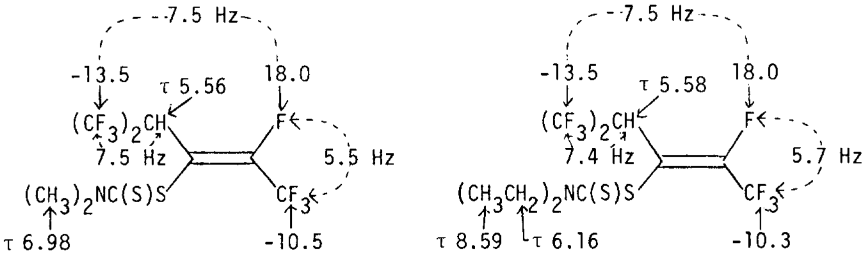
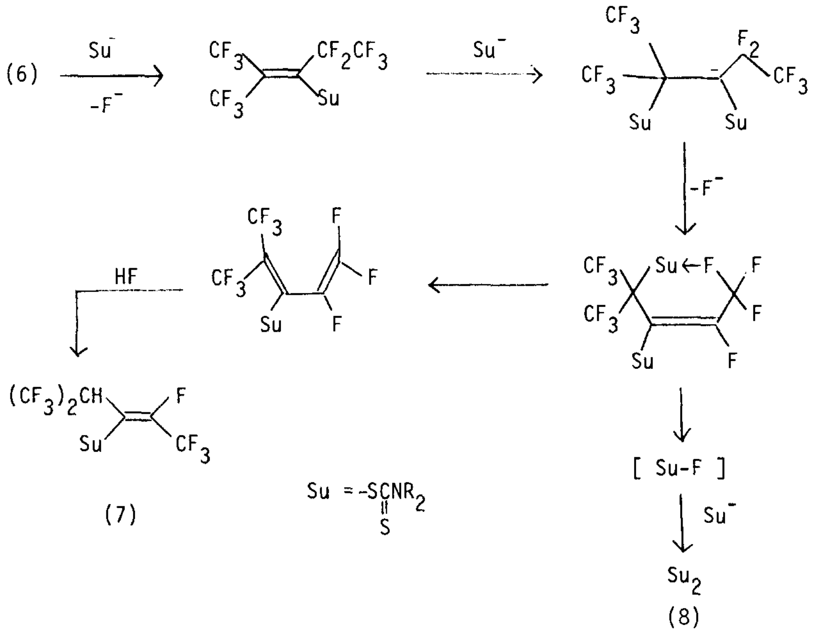


Fig. 3 ^{19}F and ^{1}H NMR data for (7)

The formation of (7) and (8) suggests that 1,4-RS-F-elimination, which have been reported in our lab's work [8], also occur in this reaction



EXPERIMENTAL

S-(1,1,2,3,3,3-Hexafluoropropyl)- (1) (nc) and S-(1,2,3,3,3-Pentafluoropropenyl)-N,N-dialkyldithiocarbamates (2) (nc)

(a) With sodium diethyldithiocarbamate

Into a mixture of sodium diethyldithiocarbamate (12.0 g), dioxane (20 ml) and water (20 ml), liquefied F-propene (7.5 g) was introduced at -70°C. The mixture was stirred for 6 h at room temperature, and was poured into water. The oily material was extracted with diethyl ether, and the solvent removed. Distillation under dynamic vacuum gave S-(1,1,2,3,3,3-hexafluoropropyl)-N,N-diethyldithiocarbamate (1) [R = Et] in 49% yield; b.p. 81 - 83 °C/2 mmHg. NMR (CCl_4) : ^1H: τ 8.68 (CH_3), 6.15 (CH_2), 3.44 (CHF); ^{19}F: δ -4.6 (CF_3), 9.3 (CF_2), 127.3 (CFH). Analysis : Calcd for $C_8H_{11}NS_2F_6$: C, 32.10; H, 3.70; N, 4.68%. Found : C, 32.35; H, 3.70; N, 4.63%.

Sodium diethyldithiocarbamate (12.0 g), F-propene (7.5 g) and DMAc (20 ml) were used as in the above reaction and worked up similarly.

The products were separated by preparative gas chromatography (column : 25% Silicon DC 550) giving 44% (1) [R = Et], 40% (*Z*-2) and 11% (*E*-2). Analysis for (2) : Calcd for $C_8H_{10}NS_2F_5$: C, 34.40; H, 3.61; N, 5.02%. Found : (*Z*-2) : C, 34.29; H, 3.58; N, 5.11%. (*E*-2) : C, 34.31, H, 3.38; N, 5.21%.

(b) With sodium dimethyldithiocarbamate

Sodium dimethyldithiocarbamate (10.0 g), *F*-propene (7.5 g), dioxane (20 ml) and water (20 ml) were placed in a Pyrex pressure-vessel allowed to react as in the above examples. Distillation gave 63% (1) [R = CH_3] b.p. 79.5 - 80.5 ^oC/ 5 mmHg. NMR (CCl_4) : ^1H : τ 6.51 (CH_3), 3.39 (CHF): ^{19}F : δ -4.4 (CF_3), 10.2 (CF_2), 128.7 (CFH). Analysis : Calcd for $C_8H_7NS_2F_6$: C, 26.57; H, 2.60; N, 5.16%. Found: C, 24.98; H, 2.53; N, 5.02%.

A mixture of sodium dimethyldithiocarbamate (10.0 g), *F*-propene (7.5 g) and DMAc (20 ml) was stirred for 6 h at room temperature. The products were separated by preparative gas chromatography using a column containing 25% Silicon DC 550, giving 29% (1) [R = CH_3], 58% (*Z*-2) and 5% (*E*-2). Analysis for (2) : Calcd for $C_6H_6NS_2F_5$: C, 28.68; H, 2.41; N, 5.58%. Found : (*Z*-2) : C, 28.61; H, 2.38; N, 5.61%. (*E*-2) : C, 28.81; H, 2.39; N, 5.55%.

2,4-Bis(*F*-isopropylidene)-1,3-dithietane (3)

Liquefied *F*-2-methylpropene (4.0 g, 20 mmol) was introduced at -70^oC into a Pyrex pressure-vessel (100 ml) containing a mixture of sodium diethyldithiocarbamate hydrate (4.5 g) and freshly dried DMF (20 ml). The whole was brought up to and remain at 0 - 5^oC. After 4 h of stirring, the reaction mixture was poured into water and the oily material which separated was extracted with diethyl ether. The extract was dried over magnesium sulfate, and then the solvent was removed under vacuum. Recrystallization of the residue from dichloromethane gave 2,4-bis(*F*-isopropylidene)-1,3-dithietane (3) in a 52% yield. m.p. 84 - 85^oC (lit.[5]: m.p. 83 - 85^oC).

Pyrolysis of (1)

In a glass vessel (1) [R = Et] (5.98 g) was placed and heated at 130^oC for 30 min. Distillation of the residue yielded diethylthiocarbamoyl fluoride (4) [R = Et], quantitatively ; b.p. 97 - 98.5 ^{o}C/ 23 mmHg (lit.[6]: b.p. 53^{o}C/16 mmHg).

The diethylamino compound also gave dimethylthiocarbamoyl fluoride quantitatively; b.p. 89 - 90.5^{o}C/31 mmHg (lit.[6]: b.p. 42 - 42.5^{o}C/1.7 mmHg).

2-Dialkylamino-4-trifluoromethyl-4,5-difluoro-1,3-dithiolan-2-ylium phenylborate (5) (nc)

(a) With sodium diethyldithiocarbamate

Liquefied F-propene (1.5 g) was introduced into a Pyrex pressure-vessel containing a mixture of sodium diethyldithiocarbamate (2.25 g) and DMAc (10 ml). The whole was brought to room temperature and kept thay way for 1 h. The reaction mixture was then poured into a solution of aqueous sodium tetraphenylborate (3.24 g) and stirred for 5 h. After being allowed to stand over night, the precipitates were separated by filtration and washed with diethyl ether. Recrystallization from dichloromethane gave (5) [R = Et], m.p. 168 - 169^{o}C. The filtrate was extracted with diethyl ether and the ethereal solution was dried over magnesium sulfate. By evaporation of the solvent, the second portion was obtained. NMR : ^{1}H (acetone-d_6) : τ 1.40 - 2.20 (Ar-H), 6.07 (CH_2), 6.34 (CH_3). IR : 1595 (C=N) cm^{-1}. UV : λ_{max}^{EtOH} = 243 nm. Analysis : Calcd for $C_{32}H_{31}NS_2BF_5$: C, 63.05; H, 4.76; N, 2.45%. Found : C, 62.85; H, 4.71; N, 2.36%.

(b) With sodium dimethyldithiocarbamate

The reaction was carried out similarly, yielding 48% (5) [R = CH_3], m.p. 155 - 157^{o}C. NMR : ^{1}H (acetone-d_6) : τ 1.15 - 2.25 (Ar-H), 6.45 (CH_3). IR : 1610 (C=N) cm^{-1}. UV : λ_{max}^{EtOH}= 243 nm. Analysis : Calcd for $C_{30}H_{27}NS_2BF_5$: C, 64.11; H, 5.21; N, 2.34%. Found: C, 64.29; H, 5.26; N, 2.42%.

S-[1,1,1,2,5,5,5-Heptafluoro-4-(trifluoromethyl)-2-pentene-3-yl]-N,N-dialkyldithiocarbamate (7) (nc)

A mixture of F-2-methyl-2-pentene (6.0 g), sodium dimethyldithiocarbamate (14.0 g) and DMAc (20 ml) was stirred at room temperature for 5 h. The resulting precipitates (NaF) were removed by filtration, and the filtrate was poured into water. Separating oily materials were extracted with diethyl ether, and then subjected to the preparative gas chromatography on Silica using hexane as eluent. Recrystallization of the first portion from pentane yielded 51% of (7) [R = Me], m.p. 66.5 - 67°C. The second portion was recrystallized from chloroform to give 42% of (8) [R = Me], m.p. 146 - 148°C. Analytical data for (7) [R = Me] : Mass : M^+ 383, m/e 263 (C_6HF_{10}), 151 (C_3HF_6), 120 ($C_3H_6NS_2$), 112 (C_3F_4) and 69 (CF_3). Analysis : Calcd for $C_9H_7NS_2F_{10}$: C, 28.20; H, 1.84; N, 3.65%. Found : C, 28.40; H, 1.87; N, 3.70%.

Using diethyldithiocarbamate, (7) [R = Et] (35%; b.p. 64 - 65°C/3mmHg) and (8) [R = Et] (26%; m.p. 71 - 72°C) were obtained. Analytical data for (7) [R = Et]: Mass: M^+ 411. m/e 263 (C_6HF_{10}), 151 (C_3HF_6), 148 ($C_5H_{10}NS_2$), 112 (C_3F_4) and 69 (CF_3). Analysis : Calcd for $C_{11}H_{11}NS_2F_{10}$: C, 32.12; H, 2.70; N, 3.40%. Found: C, 32.36; H, 2.51; N, 3.42%.

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