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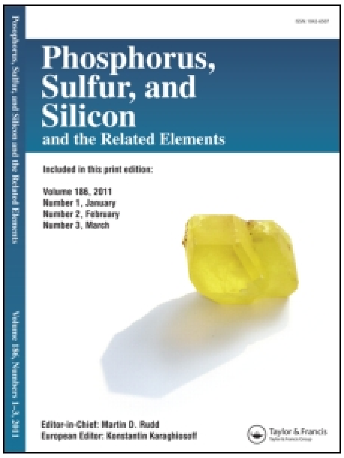

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Unusual Methylene Insertion Reactions

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Unusual Methylene Insertion Reactions

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Spontaneous and unassisted methylene insertions into S—Cl and Se—S, C—S and C—H bonds as well as S—S and Se—S cleavages, double methylene insertions, and a1, 3-addition to diazomethane, which have been observed in the unaided low temperature reactions of diazomethane with sulfenyl halides and dithio-selenide without the need for the photo-generated carbene moiety.

Keywords Diazomethane; double insertions; sulfenyl chlorides and –selenide. 1.3-addition; unassisted low temperature dissociation and reactions

In the one-carbon homologation of organic compounds, diazomethane serves as a versatile reagent, although it is nonselective in methylene insertion reactions. Metal and metal oxides, heat, and ultraviolet light catalyze the so-called Wolff rearrangement of the diazoketones. The mechanism of this rearrangement has been discussed in detail.[1] The thermally catalyzed Wolff rearrangement of methyl diazomalonate furnishes interesting observations; the products correspond to the migration of the methyl moiety of the methoxy group, and the methylene incorporation into methyl part of the methoxy entity to form a lactone intermediate which, readily undergoes decarboxylation to yield vinyl ether and vinyl ester.[2] Although diazomethane has been described as a rod-like nucleophile,[3a] it also exhibits properties of an acid, a base, and a 1,3-dipole.[3b] The *ab initio* Generalized Valence Bond (GVB) and Configurational Interaction (CI) calculations on the ground state and

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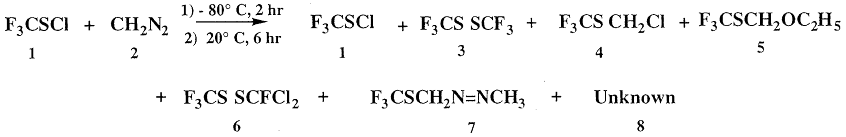
excited states of diazomethane appear to indicate its "ground state is more accurately described as a singlet biradical" and the involvement of 1,3-diradical has been proposed to explain the 1,3-addition of diazomethane.[4] An unusual reaction of carbene derived from diazomethane is its nonselective insertion into a C—H bond.[5] It exhibits little discrimination between the C—H and C═C bonds.[5b] However, it does show preference in two respects: (1) it prefers to insert into a α-C—H bond than to insert into a β-C—H bond,[5c] and (2) it reacts 10 times faster with a C—Cl bond than with a C—H bond.[5d] Two mechanisms have been proposed for methylene insertion into a C—H bond, the first involves a one-step three center cyclic transition state.[6a] The second involves a free-radical initiated direct abstraction of hydrogen.[6b–c] Free-radical generated products may also arise via intermediates formed from direct insertion. The free-radical induced direct hydrogen abstraction by methylene from propane furnishes butane, isobutane, propene, ethane, plus 14 additional compounds, which include alkenes, alkanes, and cyclopropane.[6c] This observation reflects the nonspecificity of the reactions of methyelene. In continuation of our interest in the chemistry of the F_3CS-group,[7] the reaction of sulfenyl chlorides and dithio-selenide with diazomethane at 0°C was examined. This article presents the formation of unusual products and their mass spectral characterization.

RESULTS AND DISCUSSION

The reaction of diazomethane (CH_2N_2, **2**) with trifluoromethylesulfenyl chloride (F_3CSCl, **1**), (trifluoromethyl) (chloromethyl sulfide (F_3CSCH_2Cl, **9**), (chloro-methyl) (methyl) sulfide (H_3CSCH_2Cl, **14**) and bis(trifluororomethythio) selenide ($F_3CSSeSCF_3$, **22**) at low temperature furnishes products corresponding to both single and double methylene insertion reactions, a1,3-addition to diazomethane, vinyl suflides, etc. via free radical reactions. These reactions occur unassisted, which means that no catalysts are needed. The photolysis of diazomethane also is not needed to generate the reactive methylene moiety.

Carbene (**:CH**$_2$) has been described as "the most indiscriminate reagent in organic chemistry" [8a] and its insertion into carbon-hydrogen bond is said to "depend on the type of bonds."[5,8b] It should be stated that a highly selective methylene insertion has been observed in the reaction of diazomethane with bis(trifluoro-methyl)ketene.[9] In the reaction with trimethylsilyl halide and trimethylsilyltriflate, reactive methylene has been reported to get inserted into S–shalide and Si-triflate bonds.[10] Some carbenes are more reactive than others; for example, a (**:Cl**$_2$) insertion is only effective with an activated carbon-hydrogen bond, while others require the presence of adjacent oxygen atoms. In other cases, the presence of the phenyl ring is required for the reaction to occur.[10b] Methylene insertion into carbon-chlorine was described 40 years ago.[11a] Insertion into a P—S bond;[12a] insertion to form a S—CH_2—S linkage,[12b] and an addition to a C=S bond to form thiacyclopropyl (thiirane) derivative[12c] have all been reported. It must be stated that though insertion into the C—S bond does occur, it has been described as "not a major contributor."[1e] Although the 1,3-addition mechanism has been employed to rationalize the stereospecific formation of the adduct, the involvement of a free-radical catalyzed reaction has not been altogether discounted.[12c] The photolysis of diphenyldiazomethane gives tetraphenylethylene and the same reaction in the presence of methanol yields diphenylmethyl methyl ether.[13a] Addition of diphenyl carbene to diphenyldiazomethane has been studied in a single crystal.[13b] Products arising from moderate dichlorocarbene insertion were obtained via phase-catalyzed insertion reactions of CCl_2 and CBr_2 carbene into benzylic, tertiary C—H bonds of hydrocarbons and α-C—H bonds of ethers.[10a] The major product of the phase-transfer reaction of the *in-situ* generated $\mathbf{:Cl_2}$ has been shown to result from the preferential addition to tertiary carbon.[14] "An interesting and unexpected phenomenon" involving the ($\mathbf{:CF_2}$) insertion has been observed in the *in situ* metathesis of trifluoromethylcopper.[15] In a sense, cyclopropanation via the addition of carbene to a carbon-carbon double bond can be regarded as a methylene addition/insertion reaction.[16]

The reaction of F_3CSCl (**1**) with CH_2N_2 (**2**) first at −80°C and then at 0°C furnishes five compounds (Scheme 1): (1) bis(trifluoromethyl)disulfide (**3**), (2) (chloromethyl) (trifluoromethyl) sulfide (**4**), (3) [(ethoxy)methyl] (trifluoro-methyl) sulfide (**5**), (4) (dichlorofluoromethyl) (trifluoromethyl) disulfide (**6**) [(trifluoromethylthio)methyl] azomethane (**7**), and (**5**) an unknown compound, whose structure could not be ascertained as it undergoes exhaustive disintegration in the mass spectrometer prior to its M^+ ion getting recorded. The formation of the above-cited products implies and indicates free radical reactions. Compound **4**, namely (chloromethyl) (trifluoromethyl) sulfide (**4**), arises via the carbene insertion into the sulfur-chlorine bond, while (ethoxymethyl) (trifluoromethyl) sulfide (**5**) is derived from



$$\underset{1}{F_3CSCl} + \underset{2}{CH_2N_2} \xrightarrow[2)\ 20°\ C,\ 6\ hr]{1)\ -80°\ C,\ 2\ hr} \underset{1}{F_3CSCl} + \underset{3}{F_3CS\,SCF_3} + \underset{4}{F_3CS\,CH_2Cl} + \underset{5}{F_3CSCH_2OC_2H_5}$$

$$+ \underset{6}{F_3CS\,SCFCl_2} + \underset{7}{F_3CSCH_2N{=}NCH_3} + \underset{8}{\text{Unknown}}$$

SCHEME 1 Reaction of trifluoromethylsulfenyl chloride with diazomethane.

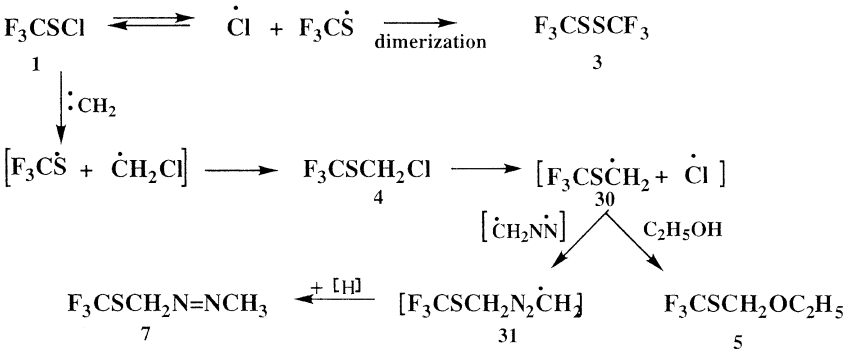


FIGURE 1 Mechanism of formation of compounds from F_3CSCl and CH_2N_2.

the free radical reaction of compound **4** with ethanol, which is itself formed from the reaction of diazomethane with water.[5c] (Dichlorofluoromethyl) (trifluoro-methyl) disulfide (**6**) owes its origin to free radical reactions and its genesis has already been rationalized.[7f] [(Trifluoromethylthio)methyl]azomethane (**7**) is derived from the dissociation of (chloromethyl) (trifluoromethyl) sulfide (**4**) into (trifluoromethylthio) methyl (**30**) and chlorine radicals, and then (**30**) reacts with diazomethane to form a radical intermediate (**31**), which then abstracts hydrogen to give compound **7** (Figure 1).

The reaction of F_3CSCH_2Cl (**9**) with CH_2N_2 (**2**) at 0°C was comparatively simple (Scheme 2), in that only four components were detected by GC-MS. These are (1) dichloromethane (**10**), (2) carbon tetrachloride (**11**), (3) (chloromethyl) (chlorodifluoromethyl) sulfide (**12**), and (4) dimethyl ether (**13**). That dichloromethane (**10**) and carbon tetrachloride (**11**) are really formed as a result of the reaction was ascertained by their absence in the starting materials and the solvent with the aid of GC-MS analysis. Dimethyl ether is formed from the reaction of diazomethane with water[5c] (Chloromethyl) (chlorodifluoromethyl) sulfide (**12**) arises from the displacement of fluorine with chlorine formed from the dissociation of **1** into chlorine and trifluoromethylthiyl radicals. There are precedents for this observation (Figure 2).[7f] Compound **12** also can arise via the intermediate **34** formed by the addition of a

$$\underset{9}{F_3CSCH_2Cl} + \underset{2}{CH_2N_2} \xrightarrow{0^\circ C} \underset{10}{CH_2Cl_2} + \underset{11}{CCl_4} + \underset{12}{ClF_2CSCH_2Cl} + \underset{13}{CH_3OCH_3}$$

SCHEME 2 Reaction of (chloromethyl) (trifluoromethyl) sulfide with diazomethane.

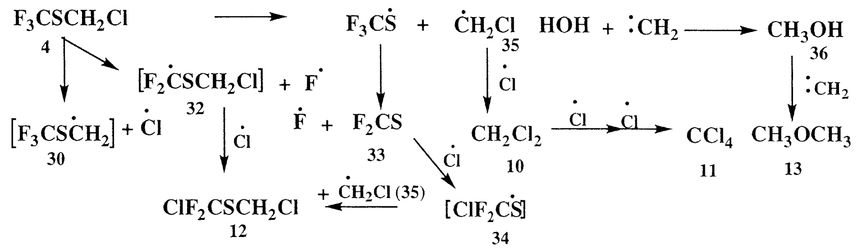


FIGURE 2 Mechanism of formation of compounds from F_3CSCH_2Cl and CH_2N_2.

Cl radical to thiocarbonyl fluoride (**33**), which itself is formed from the F_3CS-radical as shown in Figure 2.

The third reaction involves the treatment of (chloromethyl) (methyl) sulfide (**14**) with diazomethane (**2**, Scheme 3). As in the case of trifluoromethylsulfenyl chloride (**1**), seven compounds were detected by the GC-MS analysis: (**1**) ethylenesulfenyl chloride (**15**), (2) [(methoxy)-methyl]methyl sulfide (**16**), (3) dimethyl disulfide (**17**), (4) bis-(methylthio)methane (**18**), (5) (ethyl)(hydroxyethyl) sulfide (**19**), (6) methyl propyl sulfide (**20**), and [(methylthio)methylazomethane (**21**). Figure 3 attempts to rationalize the mechanism of the formation of the above-mentioned compounds.

Scheme 4 describes the reaction of bis(trifluoromethythio) selenide (**22**) with diazomethane (**2**). Compound 22 was synthesized via the reaction of 1 with hydrogen selenide at −80° in the presence of 4-dimethylaminopyridine.[7c] Here again, based on the mass spectral fragmentation behavior seven compounds, (**23–29**) were detected by GC-MS. Interestingly, two vinyl sulfide derivatives were detected and characterized. This appears to be due to the facile loss of hydrogen from the free radical intermediates. They are (trifluorormethythio) [(trifluoromethythio)methyl] selenide (**23**), (trifluoromethyl) (methyl) sulfide (**24**), (methyl) (trifluoromethythio) selenide (**25**), (trifluoromethythio) [(trifluoromethythio) ethyl] selenide (**26**), ethyl (trifluoromethyl) sulfide

$$\underset{14}{H_3CSCH_2Cl} + \underset{2}{CH_2N_2} \xrightarrow{0^\circ C} \underset{15}{CH_2{=}CHSCl} + \underset{16}{H_3CSCH_2OCH_3} + \underset{17}{H_3CSSCH_3}$$

$$+ \underset{18}{H_3CSCH_2SCH_3} + \underset{19}{H_3CCH_2SCH_2CH_2OH} + \underset{20}{H_3CSCH_2CH_2CH_3} + \underset{21}{H_3CSCH_2N{=}NCH_3}$$

SCHEME 3 Reaction of (chloromethyl) (methyl) sulfide with diazomethane.

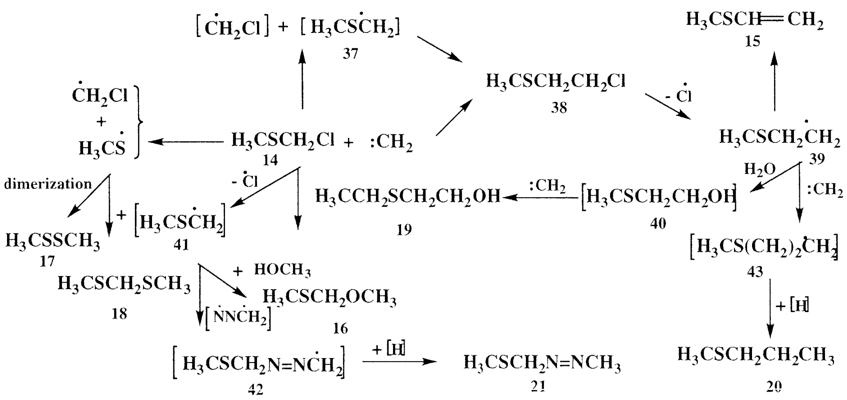
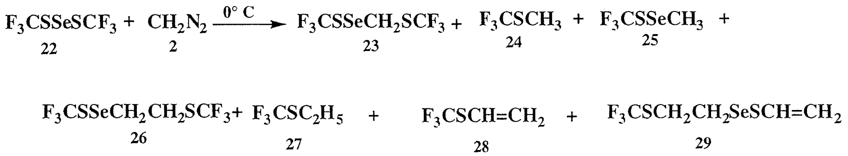


FIGURE 3 Mechanism of formation of compounds from CH_3SCH_2Cl and CH_2N_2.

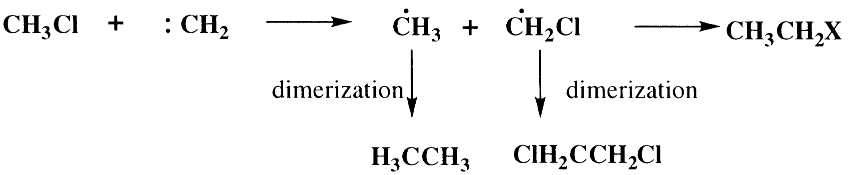
(**27**), (trifluoromethyl) vinyl sulfide (**28**), and [(trifluoromethythio) ethyl] (vinylthio) selenide (**29**) (Figure 4).



SCHEME 4 Reaction of bis-(trifluoromethylthio) selenide with diazomethane.

That diazomethane serves as a source of the highly reactive methylene moiety that was first demonstrated by Seyferth.[17] The fact that methylene insertions occur into the C—H, C—O, C—Cl, an O—H bonds has been well accepted.[18] The mechanism of the methylene addition and insertion reactions have been investigated.[19] Roth has presented an interesting demonstration of the use of the chemically-induced nuclear-spin resonance polarization technique in the study of the mechanism of the methylene insertion reactions.[19b]

A gas-phase reaction of methylene with CH_3Cl has been described to preferentially proceed via chlorine abstraction or hydrogen abstraction (cf. Scheme 5) leading to the formation of ethane (30.0%), ethyl chloride (43.0%), and 1,2-dichloroethane (27.0%).[20] Ethane and 1,2-dichloroethane obviously have their origin in radical recombination or dimerization. At a low temperature, hydrogen halides are eliminated to form alkenes and vinyl derivatives. In the gas-phase reactions with CD_3Cl as the substrate it is stated that singlet methylene abstracts halide, while triplet methylene abstractes deuterium.[21] Using



SCHEME 5 Reaction of methyl chloride with methylene.[20]

doubly-labelled reagents, it was shown that methylene abstracts Cl from CH_3Cl to generate CH_3 and CH_2Cl radicals, which form ethyl chloride.[11b] However, in the liquid-phase reactions, the insertion of methylene into a C—Cl bond has been documented.[11a] Photolysis of a mixture of methyl chloride and gaseous diazomethane at −0°C is furnished primarily by ethyl chloride, and is accompanied by trace amounts of dimethyl ether (cf. Scheme 6).[5c] The latter results from the reaction of methylene with water.[5c] It should also be noted that the methyl ethers are said to arise from the decomposition the ethereal solutions of diazomethane.[22]

It appears that there are two mechanisms operating in the reaction of methylene with alkyl halides, depending on the type of the substrates used in the reaction. In an interesting study designed to delineate the mechanism of the methylene reaction with alkyl halides, Olah and

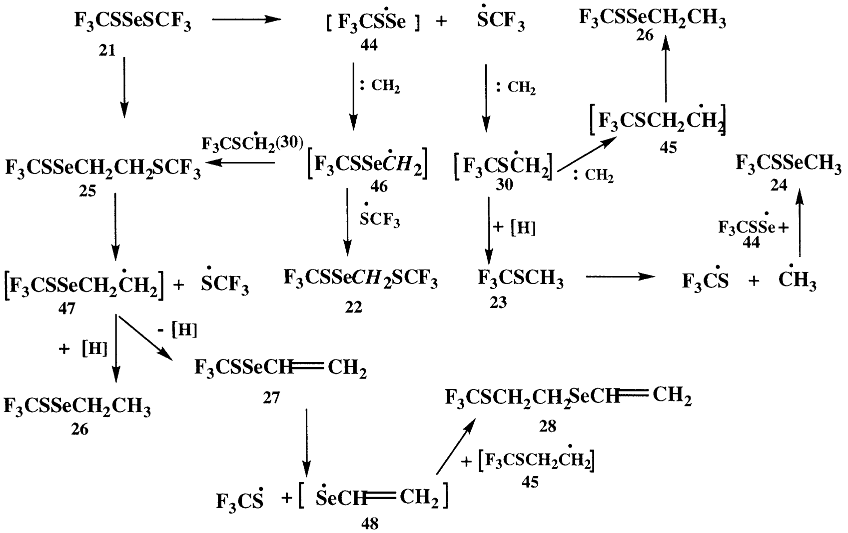
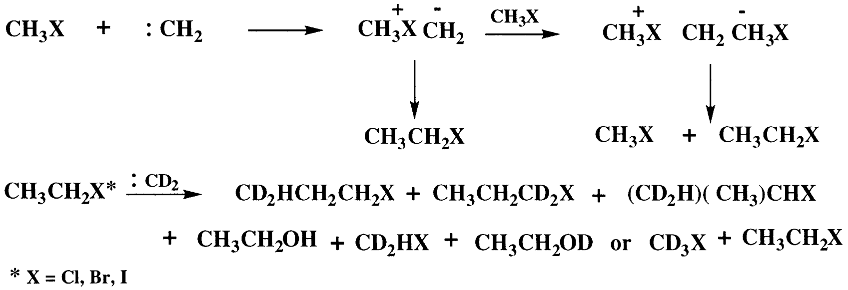


FIGURE 4 Mechanism of formation of compounds from $F_3CSSeSCF_3$ and CH_2N_2.



SCHEME 6 Reaction of methylene with alkylhalidess with.[5c]

Colleagues[5c] were not able to conclusively characterize the mechanism of the reaction of methylene with methyl halides. However, experiments with ethyl halides furnished products arising from both a methyelene insertion into the C—H and C—Cl bonds. They were able to characterize seven compounds, including the substrate as well as methyl ethyl and diethyl ethers from the reaction mixture (cf. Scheme 6). This was attributed, in part, to the formation of alkylhalonium methylides intermediates. It must be stated here that during the photolysis, the free radical formation from alkyl halides, in particular from alkyl iodides, must be kept in mind.

There are not many examples of the reaction of methylene with sulfur compounds. Carbene insertion into thiocarbonyl group has been reported to furnish dimerized substituted 1,3-dithiolanes.[12] The treatment of alkenylthioethers with methylene caused methylene insertion rather than effecting cyclopropanation.[23a] The treatment of 1-methyl-3-phenylthio-1-cyclohexene furnished 1-methyl-3-benzylthio-1-cyclohexene rather than the cyclopropanated product. Cycloallylic sulfides also undergo a similar insertion reaction.[23b] Photomethylenation of cyclic thioethers such as tetrahydrothiophene yielded tetrahydrothiopyran, 2-methyl-, and 3-methyltetrahydrothiophenes.[23c] The reaction of methylene with perhaloiodide, namely 3,4-dichloroheptafluorobutyl iodide at room temperature, was found to furnish 5,6-dichloroheptafluorohexyl iodide via double methylene insertions into the C-I bond.[24] The mass spectral fragmentation behavior of the various compounds cited in the narrative is described in Table I.

EXPERIMENTAL

Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.5 mm. i.d. DB-5 capillary column (J and W

TABLE I Mass Spetral Fragmentation of Compounds Described in the Text

1. F_3CSCl (**1**): $M^+ = 136(100\%)$ [r.t. = 1.16 min, 47.0%, ^{37}Cl-seen]; 117 (M—F); 101 (M—Cl); 82 (CSF_2); 63 (CSF); and 50 (CF_2).
2. F_3CSSCF_3 (**3**): $M^+ = 202$, [r.t. = 1.18 min, 35.5%], 183 (M—F); 133 (M—CF_3); 114 (133-F); 101 (SCF_3); 95 (133-2F); 82 (CSF_2); 69 (CF_3, 100%); 64 (SS); and 50(CF_2).
3. F_3CSCH_2Cl (**4**): $M^+ = 150$, [r.t. = 1.47 min, 6.1%, ^{37}Cl-seen]; 131 (M—F); 115 M—Cl, 100%); 101 (F_3CS); 82 (CSF_2); 63 (CSF); 51 (SF)and 49 (CH_2Cl).
4. $F_3CSCH_2OC_2H_5$ (**5***): $M^+ = 60$, [r.t. = 2.23 min, 3.4%]; 145 (M—CH_3); 131 (M—C_2H_5); 115 (F_3CSCH_2); 101 (F_3CS). 82 (CSF_2); 69 (CF_3); 63 (CFF); 59 (M—F_3CS, 100%) and 46 (C_2H_6O)
5. $F_3CSSCFCl_2$ (**6***): $M^+ = 234$, [r.t. = 3.22 min, 2.7%, ^{37}Cl-seen]; 199 (M—Cl); 133 (M—$CFCl_2$); 101 (F_3CS). 101 (CFC12); 82 (CSF_2); 69 (CF_3, 100%); 63 (CSF) and 50(CF_2).
6. $F_3CSCH_2NNCH_3$ (**7**): $M^+ = 158$, [r.t. = 3.22 min, 1.3%]; 115 (F_3CSCH_2, 100%): 101 (F_3CS): 82 (CSF_2); 69 (CF_3); 63 (CSF); 57 (M—SCF_3); and 50 (CF_2).
7. CH_2Cl_2 (**10**): $M^+ = 84$ [r.t. = 1.27 min, 0.4%, ^{37}Cl-seen]; 72 (M—C) and 49 (CH_2Cl, 100%).
8. CCl_4 (**11**): $M^+ = 152$ (not seen), [r.t. = 1.43 min, 1.2%, ^{37}Cl-seen]; 117 (M—Cl, 100%); 82 (CC_2) [CCl_2-pattern seen] and 47 (CCl).
9. Cl F_2CSCH_2Cl (**12**): $M^+ = 166$, [r.t. = 2.05 min and 0.2%, ^{37}Cl-seen]; 131 (M—Cl, 100%); 85 (CF_2Cl); 82 (CSF_2); 63 (CSF) and 49 (CH_2Cl).
10. CH_3O CH_3 (**13**): $M^+ = 46$ (100%), [r.t. = 1.22 min, 1.2%].
11. CH_3SCH_2Cl (**14**): $M^+ = 96$, [r.t. = 1.57 min and 26.8%, ^{37}Cl-seen]; 81 ((M—CH_3); 61 (M—Cl, 100%); 59 (SC_2H_3); 49 (CH_2Cl) and 45 (CSH_2).
12. C_2H_3SCl (**15**): $M^+ = 94$, [r.t. = 1.3 8 min and 2.8%, ^{37}Cl-seen]; 79 (M—CH3); 59 (SC_2H_3, 100%) and 49 (CH_2Cl).
13. $CH_3SCH_2OCH_3$ (**16**): $M^+ = 92$, [r.t. = 1.50 min and 0.1%]; 61 (CH_3SCH_2) and 45 (CSH, 100%).
14. CH_3SSCH_3 (**17**): $M^+ = 94$ (100%), [r.t. = 2.02 min and 0.6%]; 79 (M—CH3); 64 (SS); 61 ($CH_3SC_2H_3$); 48 (CH_3SH); 47 (CH_3S) and 46 (CSH_2).
15. $CH_3SCH_2SCH_3$ (**18**): $M^+ = 108$, 100%), [r.t. = 2.58 min and 58.3%]; 93 (M—CH_3); 78 (93—CH_3); 61 (M—SCH_3); 59 (SC_2H_3); 47 (SCH_3) and 46 (CSH_2).
16. $CH_3CH_2SC_2H_4OH$ (**19**): $M^+ = 106$, [r.t. = 2.1 min and 1.7%]; 77 (M—C_2H_5); 61 (M—C_2H_4OH). 59 (SC_2H_3,100%) and 48 (77—C_2H_5).
17. $CH_3SCH_2CH_2CH_3$ (**20**): $M^+ = 90$, [r.t. = 1.31 min and 0.6%]; 89 (M -H, 100%); 75 (M—CH_3); 61 (SC_2H_5); 59 (SC_2H_3) and 45 (CSH).
18. $CH_3SCH_2NNCH_3$ (**21**): $M^+ = 104$, [r.t. = 1.43 min and 9.1%]; 103 (M—H, 100%); 89 ((M—CH_3); 75 (103-N_2); 59 (SC_2H_3) and 47 (SCH_3).

Scientific, Folsom, CA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.25 mm. i.d.Rtx-5 capillary column (Restek, Bellefonte, PA). The conditions on 5100 were oven temperature 60–270°C at 10°C/min, injection temperature was 210°C, interface temperature 230°C, electron energy 70 eV, emission current 500 μA, and scan time 1 s. The conditions on the TSQ-7000 were oven temperature 60–270°C at 15°C/min, injection temperature 220°C, interface temperature 250°C, source temperature

150°C, electron energy 70 eV (EI) or 200 eV (CI), emission current 400 μA (EI) or 300 μA (CI), and scan time 0.7 s. Data was obtained in both the electron ionization mode (range 45–450 da) and chemical ionization mode (mass range 60–450 da). Ultrahigh purity methane was used as the CI agent gas with a source pressure of 0.5 Torr (5100) or 4 Torr (TSQ-7100). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a J and W Scientific 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA). ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Varian 200 (200 MHz) FT-NMR system. The chemical shifts values are reproducible within 0.1 PPM.

Reaction of Trifluoromethylsulfenyl Chloride (1) with Diazomethane (**2**). To a solution of trifluoromethylsulfenyl chloride (**1**) in dry pentane cooled to −80°C was added: slightly excess amounts of a solution of diazomthane in ether with stirring and under nitrogen. The reaction mixture was stirred for 2 h at this temperature and allowed to come to ambient temperature and stirring was continued overnight. The GC-MS analysis of the reaction product showed it to consist of seven compounds (Scheme 1): (1) trifluoromethylsulfenyl chloride [**1**, $M^+ = 136$, r. t. = 1.25 min]; (2) bis(trifluormethyl) disulfide [**3**, $M^+ = 202$, r. t. = 1.32 min]; (3) (chloromethyl) (trifluoromethyl) sulfide [**4**, $M^+ = 150$, r. t. = 1.54 min]; (4) (ethoxymethyl) (trifluoromethyl) sulfide [**5**, $M^+ = 160$, r. t. = 2.23 min]; (5) (dichlorofluoromethyl) (trifluoromethyl) sulfide [**6**, $M^+ = 150$, r. t. = 3.22 min]; (6) (trifluoromethylthiomethyl)azomethane [**7**, $M^+ =$ **150**, r. t. = 3.22 min]; and (7) an unknown (**8**) with no M^+ ion and since it undergoes extensive fragmentation in ^{13}-NMR of compound **7**: (δ-ppm) N—**C**H_3 (28. 12 ppm); N—**C**H_2—S, (40.55 ppm), and **C**F_3 (−136.26 ppm, JCF = 305. 6 Hz).

Reaction of (Chloromethyl)(trifluoromethyl) Sulfide (**9**) with Diazomethane (**2**): To a solution of (chloromethyl)(trifluoromethyl) sulfide (**9**, 0.6 g, 4 mmole) in dry ether cooled to 0°C was added with stirring and under nitrogen a solution of diazomethane in ether (in slightly excess amounts). The stirring was continued for an additional hour and the yellowish reaction mixture was kept overnight in the refrigerator. The GC-MS analysis of the reaction product showed the presence of 4 compounds in addition to the starting material (**9**) (r. t. = 1.55 min, $M^+ = 150$) (Scheme 2): (1) dichloromethane [**10**, $M^+ = 84$, r. t. = 1.27 min]; (2) carbon tetrachloride, [**11**, $M^+ = 152$, r.t. = 1.43 min]; (3) (chlorodifluoromethyl) (chloromethyl) sulfide [**12**, $M^+ = 150$, r. t. = 2.05 min], and (4) dimethyl ether [**13**, $M^+ = 46$, r. t.= 1.22 min].

Reaction of (Chloromethyl)(methyl)sulfide (**14**) with Diazomethane (**2**): This reaction ran analogously as described above, except that compound **4** was replaced with (chloromethyl)(methyl) sulfide (**14**). The

GC-MS analysis of the reaction product led to the characterization of the following seven compounds in addition to the starting material (r. t. = 1.54 min) (Scheme 3): (1) (ethylene)-sulfenyl chloride [**15**, M^+ = 94, r. t. = 2.02 min.]; (2) (methoxymethyl)-(methyl) sulfide [**16**, M^+ = 92, r. t. = 1.84 min]; (3) dimethyldisulfide [**17**, M^+ = 94, r. t. = 2.03 min]; (4) bis(methylthio)methane [**18**, M^+ = 108, r. t. = 2.97 min]; (5) (ethyl)(2-hydroxyethyl) sulfide, [**19**, M^+ = 106, r. t. = 2.17 min]; (6) (methyl)-(propyl) sulfide, [**20**, M^+ = 90, r. t. = 1.31 min], and (7) methylthiomethyl)-azomethane [**21**, M^+ = 104, r. t. = 1.72 min].

Reaction of bis(trifluoromethythio) selenide (**22**) with diazomethane (**2**): This reaction was run analogously as described above, except that compound **4** was replaced with bis(trifluoromethythio) selenide (**22**). Based on the mass spectral fragmentation behavior, seven compounds (**23–29**, Scheme 4) were detected by GC-MS. Surprisingly, three vinyl suflide derivatives were detected and characterized. This may be due to the facile loss of hydrogen from the SC^2H^4 free-radical intermediates. These compounds are (trifluoromethythio) [(trifluoromethythio)methyl] selenide (**23**, M^+ not seen, M—SCF_3 is seen), (trifluoromethyl) (methyl) sulfide (**24**, M^+ = 116); (methyl) (trifluoromethythio) selenide (**25**, M^+ = 194), (trifluoromethythio) [(trifluoromethythio) ethyl] selenide (**26**, M^+ not seen, M—SCF_3 is seen), ethyl (trifluoromethyl) sulfide (**27**, M^+ not seen, M—CF_3 is seen), (trifluoromethyl) vinyl sulfide (**28**, M^+ = 128), and [(trifluoromethythio) ethyl] (vinylthio) selenide (**29**, M^+ not seen, M—$SCH{=}CH_2$ is seen).

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