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CRDEC-TR-391

NOVEL REACTIONS OF PERFLUORO-2-(TRIFLUOROMETHYL)-PROPENE

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July 1992

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420191

24 pg.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
1992 July

3. REPORT TYPE AND DATES COVERED
Final, 88 Apr - 90 Apr

4. TITLE AND SUBTITLE
Novel Reactions of Perfluoro-2-(Trifluoromethyl)-Propene

5. FUNDING NUMBERS
PR-1C162622A554

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
GEO-CENTERS, Inc., Fort Washington, MD 20744
CDR, CRDEC, ATTN: SMCCR-RSC-O, APG, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER
CRDEC-TR-391

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Unlike its hydrocarbon counterpart, perfluoro-2-(trifluoromethyl)-propene is a highly reactive compound. It participates in both heterolytic and homolytic reactions. It readily reacts with nucleophiles and sluggishly with electrophiles. It reacts as well with common organic solvents, such as acetonitrile, dimethyl formamide, ethanol and others. In this technical report, we describe its reactions with trifluoromethylthiocopper, sulfur trioxide and tributyltin cyanide, the mechanism of formation of the various products and their mass spectral data.

14. SUBJECT TERMS
Perfluoroalkenyl fluorosulfonate
Trifluoromethylthio-copper
Allylic and vinylic substituted products
Perfluoroisobutylene [Perfluoro-2-(trifluoromethyl)-propene]

15. NUMBER OF PAGES
25

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

Standard Form 298 (Rev 2 89)
Prescribed by ANSI Std Z39-18
298-102

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PREFACE

The work described in this report was authorized under Project No. 1C162622A554, Chemical Munitions. This work was started in April 1988 and completed in April 1990.

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This report has been approved for release to the public.

Acknowledgments

The authors thank Professor Donald J. Burton, University of Iowa for the gift of 1,1-dibromo-2-(trifluoromethyl)-perfluoropropene and Linda Szafraniec, William Beaudry and Richard O'Connor, CRDEC, for ^{13}C and ^{19}F NMR spectra.

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NOVEL REACTIONS
OF PERFLUORO-2-(TRIFLUOROMETHYL)-PROPENE

1. INTRODUCTION

Perfluoro-organic compounds possess and exhibit properties and reaction characteristics quite different from those of their hydrocarbon analog. Perfluoro-2-(trifluoromethyl)-propene (1), also known as perfluoroisobutylene (**PFIB**), unlike its hydrocarbon counterpart, is a unique molecule displaying unusual reactivity. Its interesting chemistry has been the subject of an exhaustive review [1]. It is endowed with unusually high electrophilic reactivity [1-4]. It readily reacts with nucleophiles and solvents such as acetonitrile and dimethylformamide and sluggishly with electrophiles [1]. It has three sites of activity; namely, the allylic, vinylic and π bond. These three centers of reactivity bring **1** closer in reactivity to α, β - conjugated carbonyl compounds. With the aid of the Huckel and CNDO calculations, the dynamic distribution of electron density of **1** has been mapped [5]. It undergoes 1, 2- and 1, 3- type cycloadditions. It participates in both heterolytic and homolytic reactions, though there are not many examples of the latter type of reactions. Because of the carbanion stabilizing influence of the trifluoromethyl group, **1** is highly susceptible to attack by alcohols even in neutral media [6]. The perfluorocarbanion of **1**, formed by the addition of a fluoride ion in the presence of metal fluorides, serves as an important intermediate for the introduction of the perfluoromethyl moiety into organic compounds [7].

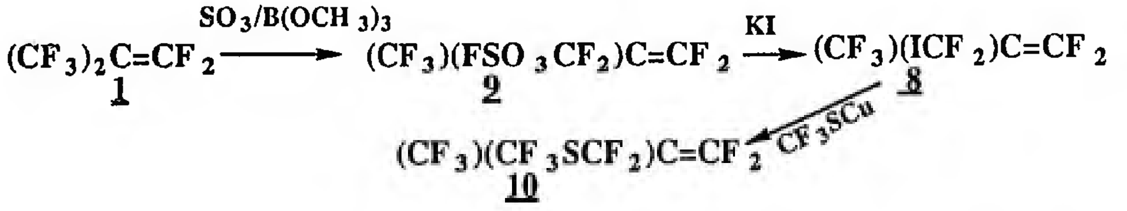
In the presence of CsF, **1** reacts with "active methylene" groups to furnish substituted allenes [8]. Since the vinylic fluorines of **1** are highly labile, they readily exchange with bromine and chlorine [9]. In the case of conjugated nucleophiles, it is the vinylic fluorine that undergoes substitution. However, products corresponding to allylic substitution resulting from the loss of a fluoride ion from CF_3 are obtained in many instances [1]. Often, it is the nucleophile that dictates the nature of the products formed. In fact, it appears that both allylic and vinylic substitutions compete with each other. Such is the case in the reaction of **1** with alkyl Grignard reagents [10]. In the reaction of **1** with arylmagnesium halides, only trisubstituted "inner" olefins are formed from the migration of the double bond [11]. With aryllithium, both vinyl mono- and di-substitution occur [12a]. However, with sodioderivatives, the vinylic fluorine is attacked first [12b]. It reacts with elemental sulfur in the presence of SbF_5 to yield perfluoro-t-butyl sulfide [13]. However, **1** reacts with pentafluorophenyl disulfide in the presence of SbF_5 to furnish a mixed disulfide carrying the perfluoro-t-butyl moiety [13a]. With sulfuryl chloride, it yields a mixed sulfide [13b]. In the presence of CsF, thiazyl fluoride reacted with **1** to give excellent yields of the dimerized product [14]. When **1** is passed over moist granular coal based carbon, hexafluoroisobutyric acid (**2**), 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-propane (**3**), 1,1,3,3,3-pentafluoropropylene (**4**), 1,1,1,3,3,3-hexafluoropropane (**5**) and HF are formed [15].

Perfluoro-olefins have been reported to form polymeric products when heated with bis-(trifluoromethylthio)mercury at 225°C under 300 atm. pressure for 14 hr [16]. Free radical catalyzed addition of Br_2 to **1** has been described [17a]. Contrary to the results of the reaction of **1** with elemental sulfur in the presence of SbF_5, the reaction of perfluoroolefins with elemental sulfur has been reported to proceed via free radical intermediates [17b].

In continuation of our interest in the chemistry of the trifluoromethylthio group [18a-d], it has now been observed that **1** reacts with trifluoromethylthiocopper (**6**) under extremely mild conditions (-78°C) to give a mixture of compounds containing both vinylic and allylic substituted products via free radical intermediates. It was also found that 1,1-dibromohexafluoroisobutylene (**7**) reacts with **6** to furnish both mono- and disubstituted trifluoromethyl sulfides. The treatment of the allylic sulfide (**10**) prepared from **6** and the allylic iodo derivative (**8**) with KI gives a mixture of compounds carrying the trifluoromethylthio moiety. With tributyltin cyanide, the fluorosulfonate derivative (**9**) prepared by the insertion of SO_3, gave three compounds containing the cyano group. This paper describes these unusual results along with the mass spectral fragmentation of the various products formed during the course of these reactions.

2. RESULTS AND DISCUSSION:

The fluorosulfonate derivative **9** was prepared by the allylic insertion of SO_3 into **1**, essentially according to the procedure applied to the synthesis of perfluoropropenefluorosulfonate [20] (Eq.1). It appears that the lability of the allylic



$$\begin{tikzcd} \underset{\mathbf{1}}{(CF_3)_2C{=}CF_2} \arrow[r, "SO_3/B(OCH_3)_3"] & \underset{\mathbf{9}}{(CF_3)(FSO_3CF_2)C{=}CF_2} \arrow[r, "KI"] & \underset{\mathbf{8}}{(CF_3)(ICF_2)C{=}CF_2} \arrow[dl, "CF_3SCu"'] \\ & \underset{\mathbf{10}}{(CF_3)(CF_3SCF_2)C{=}CF_2} & \end{tikzcd}$$

(Eq. 1)

fluorine is the primary reason for the incorporation of SO_3. The transformation of **9** into its corresponding iododerivative, namely perfluoro 2-(difluoroiodomethyl)-

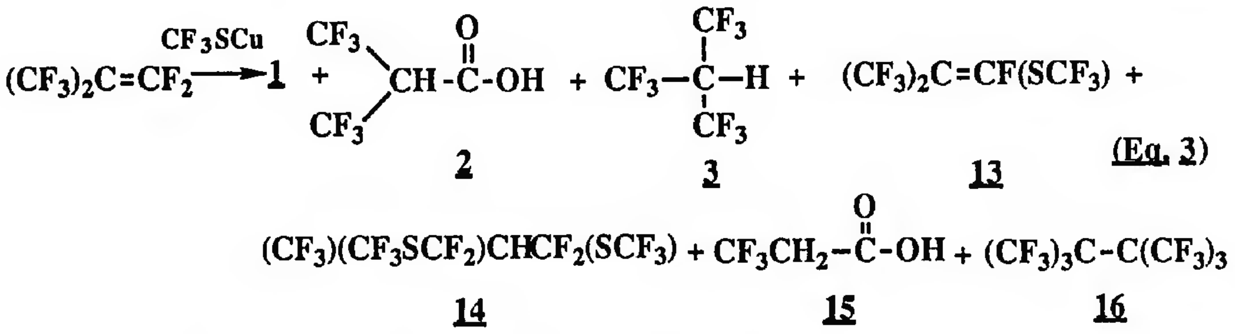
propene (**8**), was carried out as described earlier [20]. Since **8** is light sensitive, its reactions were carried out in the dark. The reaction of **6** with **8** furnished perfluoro- 2-(trifluoromethylthiodifluoromethyl)-propene (**10**).

The reaction of **6** with **7** is straight forward (Eq. 2). One or both of the

$$\underset{\underline{7}}{(CF_3)_2C{=}CBr_2} \xrightarrow{CF_3SCu} \underline{7} + \underset{\underline{11}}{(CF_3)_2C{=}CBr(SCF_3)} + \underset{\underline{12}}{(CF_3)_2C{=}C(SCF_3)_2} + \underset{\underline{19}}{CF_3SSCF_3} \qquad \underline{\text{(Eq. 2)}}$$

vinylic fluorines are replaced by the the trifluoromethylthio group. The formation of **19** via its free radical precursor, **24**, has already been rationalized [18, 21a].

With a view to directly introduce the trifluoromethylthio functionality into **1**, it was treated with **6** under mild conditions. Contrary to an earlier report [16], we have identified **13** as a major product (Eq.3). Of the remaining products of this reaction, **2, 3, 14** and **15** have been characterized by GC/MS data (Table 2). The one explanation for the formation of **2** and **15** is that they are probably formed as a result of the reaction of **1** with moisture. Such a possibility has been reported [15]. Finally, another compound with a molecular weight of 438 has tentatively been identified as **16**.



$$(CF_3)_2C{=}CF_2 \xrightarrow{CF_3SCu} \underline{1} + \underset{\underline{2}}{(CF_3)_2CH{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{\underline{3}}{(CF_3)_3C{-}H} + \underset{\underline{13}}{(CF_3)_2C{=}CF(SCF_3)} + \qquad \underline{\text{(Eq. 3)}}$$

$$\underset{\underline{14}}{(CF_3)(CF_3SCF_2)CHCF_2(SCF_3)} + \underset{\underline{15}}{CF_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{\underline{16}}{(CF_3)_3C{-}C(CF_3)_3}$$

An attempt was made to prepare **10** directly by treating **6** with **9** (Eq.4). This apparently simple reaction turned out to be a complex process. Eight compounds were characterized as products of this reaction. Three others, which have not been identified, appear to be polymeric compounds. Included in this list of eight compounds are: bis-(trifluoromethyl) disulfide (**19**), bis-(trifluoromethylthio)methane (**20**), 3,3,3-trifluoropropionyl fluoride (**21**), **1, 10, 13, 14,** perfluoro-2-(trifluoromethylthiodifluoromethyl)-2H-propane (**22**) and perfluoro-2-(trifluo-

$$\underset{\underline{\mathbf{9}}}{(CF_3)(FSO_3CF_2)C{=}CF_2} \xrightarrow{CF_3SCu} \underset{\underline{\mathbf{1}}}{(CF_3)_2C{=}CF_2} + \underset{\underline{\mathbf{10}}}{(CF_3)(CF_3SCF_2)C{=}CF_2} + \qquad \underline{\text{(Eq. 4)}}$$

$$\underset{\underline{\mathbf{13}}}{(CF_3)_2C{=}CF(SCF_3)} + \underset{\underline{\mathbf{14}}}{(CF_3)(CF_3SCF_2)CH{-}CF(SCF_3)} +$$

$$\underset{\underline{\mathbf{19}}}{CF_3S{-}SCF_3} + \underset{\underline{\mathbf{20}}}{CF_3SCH_2SCF_3} +$$

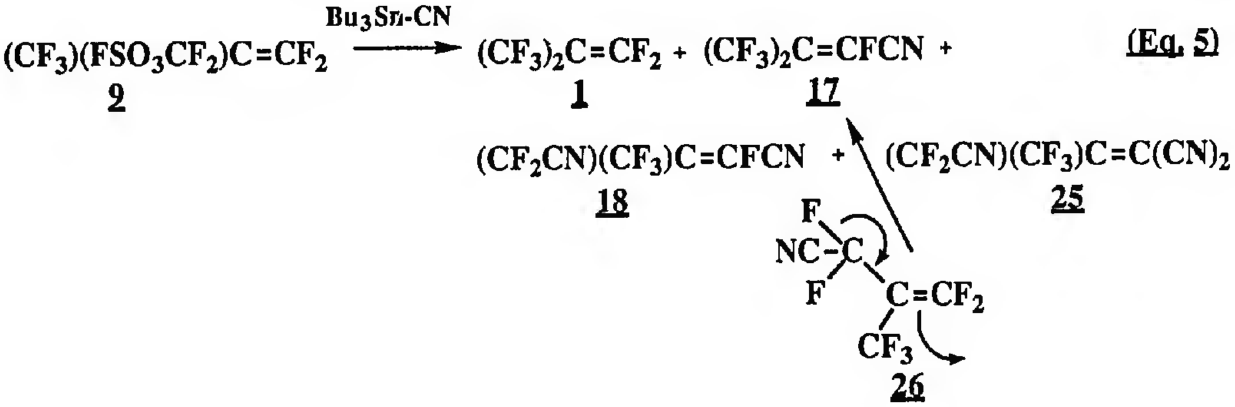
$$\underset{\underline{\mathbf{21}}}{CF_3CH_2C(O)F} + \underset{\underline{\mathbf{22}}}{CF_3SCF_2CH(CF_3)_2} +$$

$$\underset{\underline{\mathbf{23}}}{(CF_3)(CF_3SCF_2)C{=}CF(SCF_3)}$$

romethylthiodifluoromethyl)-1-(trifluoromethylthio)-propene (**23**). For comparison purposes, an authentic sample of **20** found to be prepared by treating **6** with diiodomethane [18f] and its mass spectrum was identical with that of **20**.

Recently it has been reported that **6** reacts with a variety of organic substrates via the trifluorcmethylthiyl radical (**24**) [18e]. The formation of **19** and its higher homologs from **24** has been rationalized [18, 21a]. Free radical catalyzed reactions of trifluoromethylsulfenyl chloride have also been described [21b]. Further, it has been reported that **19** is capable of "quantitatively liberating fluoride" [21c]. The fluorine thus liberated reacts with **9** to generate **1**. The formation of **20** was initially somewhat puzzling. Its formation can be rationalized on the basis of the reaction of **24** with acetonitrile. Acetonitrile is the only source of the methylene moiety in the reaction mixture. Similarly, when reactions are carried out using trifluoromethylthiocopper acetonitrile adduct, the formation of **20** is also observed. There are precedents for the involvement of solvents in chemical reactions [21d-f]. This inference is further substantiated by the identification of two products, **14** and **22** formed by the addition of HF to the double bond of their olefinic precursors, namely, **23** and **10** respectively. The HF required for addition reaction could have come from the dissociation of CF_3SH into $C(S)F_2$ + HF as suggested earlier by Haszeldine and Kidd [22]. The probable origin of CF_3SH can be traced to hydrogen abstraction by the thiyl radical **24** from acetonitrile. Another possibility is that the HF could have originated via hydrogen abstraction from acetonitrile by the fluoride radical generated *in situ* from the thiyl radical **24**. While **10** is the result of allylic substitution, **23** is formed from both allylic and vinylic replacement of fluorine. The formation of **21** has not, as of yet, been rationalized. The only source from which **21** could have originated is **1**, itself formed from the attack by fluoride on **9**. The identification of **1** as a product of this reaction supports the above contention (Eq.4). The reaction of **1** with moisture in the presence of carbon has been reported to give **21** [15].

The reaction of **9** with tributyltin cyanide is not as simple as was first considered (Eq.5). This reaction furnishes **1**, perfluoro 1-cyano-2-(trifluoromethyl)-



propene (**17**), perfluoro 1-cyano-2-(cyanodifluoromethyl)-propene (**18**) and perfluoro 1,1-dicyano-2-(cyanodifluoromethyl)-propene (**25**). It is known that nucleophiles readily add to **1**. The formation of **17** can be rationalized as arising from the elimination of fluoride from the allylic substituted intermediate (**26**) and the concomitant migration of the double bond. The identification of **17**, **18** and **25** illustrates the fact that both allylic and vinylic substituted products of **1** are capable of further reactions with nucleophiles [1]. What is interesting in the case of **25** is that both vinylic fluorines are replaced, in addition to the substitution of the allylic fluorine. In contrast, the reaction of **1** with sodium cyanide furnished only a geminally substituted product and no allylic substituted product was detected [23].

Two structures are possible for the tricyano derivative: **25** and 1-cyano-2,2-bis-(cyanodifluoromethyl)-perfluoroethylene (**27**). On the basis of the presence of a dicyanocarbene ion in the GC/MS of the compound, structure **25** was assigned to this compound. It has been suggested that allylic substituted intermediates are capable of eliminating allylic fluorine to give rearranged products [1]. The formation and detection of **17** serve as a direct proof of this suggestion.

When **10** is treated with KF, a host of compounds are formed (Eq.6). The majority of these compounds has been identified by their GC/MS (Table 2). In addition to the starting material **10, 1, 13, 14, 21, 23** or perfluoro bis-2,2-(trifluoromethylthiodifluoromethyl)-ethylene (**28**), perfluoro bis-1,1-(trifluoromethylthio)-2-(trifluoromethylthiodifluoromethyl)-propene (**29**) or 1-(trifluoromethylthio)-2,2-

bis-(trifluoromethylthiodifluoromethyl)-fluoroethylene (**30**), bis-1,1-(trifluoromethylthiodifluoromethyl)-1H-bis-2,2-(trifluoromethyl)-fluoroethane (**31**), or perfluoro bis-1,1-(trifluoromethyl)-1H-bis-2,2-(trifluoromethylthio)-propane (**32**) and perfluoro 1-(trifluoromethyl)-1H-2-(trifluoromethylthio)-propane (**33**) have been identified as products of this reaction (Eq.6). The formation of **1** is simply a case

$$\underset{\underline{10}}{(CF_3)(CF_3SCF_2)C{=}CF_2} \xrightarrow{KF} \underset{\underline{1}}{(CF_3)_2C{=}CF_2} + \underset{\underline{13}}{(CF_3)_2C{=}CF(SCF_3)} + \qquad \underline{(Eq.6)}$$

$$\underset{\underline{14}}{(CF_3)(CF_3SCF_2)CH{-}CF_2(SCF_3)} + \underset{\underline{21}}{CF_3CH_2C(O)F} +$$

$$\underset{\underline{23}}{CF_3(CF_3SCF_2)C{=}CF(SCF_3)} \text{ or } \underset{\underline{28}}{(CF_3SCF_2)_2C{=}CF_2} +$$

$$\underset{\underline{29}}{CF_3(CF_3SCF_2)C{=}C(SCF_3)_2} \text{ or } \underset{\underline{30}}{(CF_3SCF_2)_2C{=}CF(SCF_3)} +$$

$$\underset{\underline{31}}{(CF_3SCF_2)_2CHCF(CF_3)_2} \text{ or } \underset{\underline{32}}{(CF_3)_2CHCF(SCF_3)_2}$$

$$+ \underset{\underline{33}}{(CF_3S)CF_2CH(CF_3)_2}$$

of replacement of the trifluoromethylthio moiety by fluoride. The origin of **21** has been previously discussed. The trifluoromethylthiyl group liberated, as mentioned above, replaces the vinylic fluorine to give **13**. Three structures are possible for the bis-(trifluoromethylthio) derivative: **12, 23** and **28**. Since the mass spectrum of an authentic sample of **12** is different from that of this compound, only structures **23** and **28** remain to be considered as possible structures for this compound. However, a choice between these two structures was not possible. The formation of the saturated compounds containing hydrogen can be rationalized, as already mentioned, on the basis of the addition of HF to the double bond.

The parent molecular ions are observed for all but three compounds; in the latter case, the fragmentation pattern is consistent with the assigned structures (Table 2). The splitting off of CF_3 (m/e = 69); CF_2 (m/e = 50) and (M-F) appear to be a common characteristic. The ion CF_2 (m/e = 50) is due to the difluorocarbene coming off from the CF_3 group. Often, the ion (m/e = 100) representing C_2F_4 is seen. In the majority of cases, the CF_3 ion (m/e = 69) is the most prominent peak. The low energy mass spectral fragmentation of **1** has recently been reported [2,4].

While compounds containing the trifluoromethylthio function usually lose SCF_3 (m/e = 101), ions corresponding to CSF_2 (m/e = 82), CSF (m/e = 63) and CS (m/e = 44) are also found in the mass spectral fragmentation pattern of these compounds. Mass spectral fragmentation data of a large number of compounds containing the SCF_3 group has been recently discussed in a series of papers [25].

3. EXPERIMENTAL SECTION

3.1 General Procedures:

Warning!! Because of the high inhalation toxicity of ***1*** *[19], all reactions should be carried out in an efficient hood.* Mass spectra were recorded on a Finnian model 5100 GC/MS spectrometer equipped with a silica 25 m x 0.31 mm (i.d.) capillary column (J & W Scientific, Rancho Cordova, CA). Routine GC analyses were carried out using a Hewlett Packard 5890A gas chromatograph equipped with a DB-5 30 m x 0.31 mm (i.d.) capillary column (J & W Scientific, Folsom CA). NMR spectra (^{13}C and ^{19}F) were recorded in $CDCl_3$ on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz respectively. The external reference for ^{19}F data was CCl_3F and for the ^{13}C, tetramethylsilane (TMS) was used as an external standard. The reactions were carried out in a flame-dried, argon purged 10 or 25 ml capacity flask equipped with a magnetic stirrer, gas inlet pressure equalizing dropping funnel and a reflux condenser with the coolant maintained at -20°C by a Lauda RC56 refrigerated circulating bath and a dry ice/acetone trap. Perfluoro-2-(trifluoromethyl)-propene (>99% pure by GC) (**1**) was used as received from Armageddon Chemical Company (Durham, NC). Trifluoromethylthiocopper was prepared as described elsewhere [18e]. Acetonitrile was dried over calcium hydride and freshly distilled as needed. All reactions were carried out using stoichiometric quantities of reagents. Reaction mixtures were allowed to come to ambient temperature prior to flash distillation under reduced pressure and products collected at -78°C.

3.2 Synthesis of Perfluoro-2-(trifluoromethylthiodifluoromethyl)-propene (**10**):

(a) Perfluoroalkenylfluorosulfonate (**9**):

A 300 ml capacity Hastalloy stirring autoclave reactor was charged with sulfur trioxide (30 g, 0.38 mol) and trimethylborate (1.5 g, 0.0125 mol) in an argon filled glove bag and quickly sealed. The reactor was cooled to -78°C and **1** (100 g, 0.5 mol) was slowly sparged into the reactor over the course of 1 hr. The reaction mixture was stirred at -78°C for 0.5 hr and allowed to slowly warm up to 20-25°C with stirring. Carefully maintaining the reaction temperature at 30-35°C, the reaction mixture was stirred for 2 hr, then stirred overnight at ambient temperature. A dry ice/acetone trap with a mineral oil bubbler attached to prevent the entrance of moisture was connected to the reactor and the reactor was slowly opened to relieve pressure until no further bubbling was observed. The reaction mixture was transferred from the reactor to a round bottom flask and flash distilled (90 mm Hg) without heating to remove volatile byproducts. The flask was slowly heated to 90°C (oil bath temperature) to yield 37.8 g of product (86% pure by glc, 31% yield). NMR: ^{13}C: δ = 160.3 (J = 313 Hz, $C=\underline{C}F_2$); δ = 5.4 (CF_3-$\underline{C}$=); δ = 120.0 (J = 276 Hz, $\underline{C}F_3$-C=); δ = 119.3 (J = 279 Hz, $\underline{C}F_2OSO_2$). ^{19}F: δ = -64.9 (=CF_2); δ = -60.7 (CF_3); δ = -61.0 (CF_2O-) and δ = 46.1 [J = 9.3 (t), FSO_2-]. MS: 280.

(b) Perfluoro-2-(Difluoroiodomethyl)-propene (**8**):

A mixture of the above fluorosulfonate (8.3 g, 0.03 mol) and dry potassium iodide (7.5 g, 0.045 mol) in dry sulfolane (10 ml) was heated at 90-95°C in the absence of light (the iodo derivative is light sensitive) for one hour. The reaction mixture was cooled to ambient temperature, then flash distilled under reduced pressure into a receiver cooled to - 78°C. Refractionation of the distillate gave an 82% pure sample (GC). NMR: ^{13}C: δ = 156.9 (J = 308 Hz, $C=\underline{C}F_2$); δ = 95.7 ($CF_3\underline{C}$=); δ = 120.5 (J = 271 Hz, $\underline{C}F_3C$=) and δ = 80.3 (J = 314 Hz, $\underline{C}F_2I$). ^{19}F: δ = - 62.0, - 67.3 (=CF_2); δ = -58.3 (CF_3) and δ = -38.2 (CF_2I). MS: 258.

(c) Perfluoro-2-(Trifluoromethylthiodifluoromethyl)-propene (**10**):

A mixture of the allylic ododerivative (**8**) (1.3 g, 4.22 mmol) and trifluoromethylthiocopper (**6**) (1.08 g, 6.54 mmol) in dry freshly distilled acetronitrile (2 ml) was stirred, protected from light, under an argon atmosphere at ambient temperature. Within 1 min, a white precipitate was formed. The reaction mixture was further heated at 80°C for 1 hr. After cooling to ambient temperature, the reaction mixture was flash distilled under reduced pressure into a receiver cooled to -78°C. Redistillation of the sample gave a 97.5% pure sample, b.p. 68-70°C. NMR: ^{19}F: δ = -38.1(t), (J = 9.4 Hz, SCF_3);δ = -67.3 (m) (SCF_2); δ = -58.3 , (J = 27.1 Hz, J = 9.2 Hz, C-CF_3); δ = -59.7 (m) and -60.9 (m) (=CF_2). MS: 282 (Eq.1).

3.3 Reaction of 1,1-dibromo-2,2-bis(trifluoromethyl)-ethylene (**7**) with trifluoromethylthiocopper (**6**):

A solution of stoichiometric amounts of **7** (3.12 g, 0.01 mol) and **6** (2.05 g, 0.01 mol) in dry freshly distilled acetonitrile (3 ml) was heated at 85-95°C (oil bath temperature) for 5 hr. After cooling to ambient temperature, the reaction mixture was flash distilled under reduced pressure into a receiver cooled to -78°C. GC/MS analysis of the distillate showed the presence of the following three compounds: 1-bromo-1-trifluoromethylthio-2,2- bi-(trifluoromethyl)-ethylene (**11**), 51%; 1,1-bis (trifluoromethylthio)-2,2-bis-(trifluoromethyl)-ethylene (**12**), 15% and bis-(trifluoromethyl)disulfide (**19**), 0.3% (Table 2). The rest was starting material (Eq.2). NMR (compound **11**): ^{13}C: $\delta = 127.0$ ($J = 312$ Hz, $S\underline{C}F_3$); $\delta = 125.4$ [$J = 3$ Hz (m), $=\underline{C}\text{-Br}$];$\delta = 131.1$ [$J = 32.8$ Hz (hep), $=\underline{C}(CF_2)$]; $\delta = 119.6$ [$J = 278$ Hz (q). $\underline{C}F_3$) and d = 119.8 ($J = 278$ Hz (q), $\underline{C}F_3$). ^{19}F: $\delta = -38.7$ [$J = 2.3$ Hz (q). SCF_3]; $\delta = -57.0$ [$J= 2.3$ Hz (q of q), $J = 10.4$ Hz, CF_3] and $\delta = -59.7$ [$J= 10.4$ Hz (q), CF_3]. NMR (compound **12**): ^{13}C: $\delta = 126.6$ ($J = 312$ Hz, SCF_3); $\delta = 137.0$ [$J = 3.0$ Hz (m), $=\underline{C}(SCF_3$]; $\delta = 135.8$ [$J = 32.8$ (hep), $\underline{C}{=}C(SCF_3)_2$] and $\delta = 119.2$ [$J = 280$ Hz (q), CF_3]. ^{19} F: -35.8 [$J = 1.6$ Hz (hep), SCF_3]; $\delta = -57.9$ [$J = 1.6$ Hz (hep), CF_3] (Eq.2).

3.4 Reaction of perfluoro-2-(trifluoromethyl)-propene (**1**) with trifluoromethylthiocopper (**6**):

To a slurry of **6** (2.05 g, 0.01 mol) contained in 5 ml of freshly distilled acetonitrile cooled to -78°C, was sparged an equimolar amount of **1** (2.0 g, 0.001 mol) and the reaction stirred at -78°C for 2 hr, allowed to come to ambient temperature and heated at 55-60°C for 4 hr. After cooling to ambient temperature, the reaction mixture was flash distilled under reduced pressure into a receiver cooled to -78°C. The GC/MS analysis of the distillate showed the presence of **1**, 1-(trifluoromethylthio)-perfluoro-2-(trifluoromethyl)-propene (**13**), 1-(trifluormethylthio)-2H, 2-(trifluoromethylthiodifluoromethyl)-perfluoropropane (**14**), 3,3,3-trifluoropropionic acid (**15**), hexafluoroisobutyric acid (**2**), 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl) - propane (**3**) and 2,2,3,3-tetra-(trifluoromethyl)-perfluorobutane (**16**) (Eq.3).

3.5 Reaction of allylic fluorosulfonate (**9**) with trifluoromethylthiocopper (**6**):

To a slurry of **6** (1.44 g, 7.0 mmol) in freshly distilled acetonitrile (5 ml), **9** (1.71 g, 6.12 mmol) was added dropwise with stirring. An immediate mild exothermic reaction ensued. The reaction mixture was stirred for 0.5 hr at ambient temperature and then at 90°C for 2 hr then flash distilled under reduced pressure into a receiver cooled to -78°C. The distillate was analyzed by GC and GC/MS and was found to contain the desired compound, namely **10**, as one of the major products. The GC/MS of **10** is similar to that obtained earlier (cf. Eq.1). Eight additional compounds were characterized as byproducts of the reaction (Eq.4).

3.6 Reaction of allylic fluorosulfonate **9** with tributyltin cyanide:

To **9** (5.0 g, 17.9 mmol) in dry sulfolane (10 ml) was added with stirring tributyltin cyanide (5.64 g, 17.9 mmol) in small portions via a solid addition funnel. The reaction was exothermic. The mixture was stirred for 1 hr and flash distilled under reduced pressure into a receiver cooled to -78°C. The distillate, as analyzed by GC, showed the presence of three major components identified from their mass spectral fragmentation pattern as 1-cyano-2-(tri-fluoromethyl)-perfluoropropene (**17**), (37.5%); perflouro-2-(trifluoromethyl)-propene (**1**), (16%); and 1-cyano-2-(cyanodifluoromethyl)-perfluoropropene (**18**), (15.1%). Trace amounts of 2-(cyanodifluoromethyl)-2-(trifluoromethyl)-1,1-dicyano-ethylene (**25**) and starting material (**9**) were also detected. Two additional compounds remain unidentified (Eq.5).

3.7 Reaction of perfluoro-2-(trifluoromethylthiodifluoromethyl)-propene (**10**) with Potassium Fluoride:

Treatment of **10** (0.01 mole) with an equivalent amount of potassium fluoride under an argon atmosphere at -78°C for 1 hr, followed by stirring for an additional hr at ambient temperature, gave a slightly yellow colored solution. GC analysis of the reaction mixture showed the reaction mixture to be a complex one. However, the GC/MS analysis permitted the identification of the prominent components (Table 2). Three trace impurities from the reaction mixture have as yet not been characterized (Eq.6).

3.8 Bis-(trifluoromethylthio) methane (**20**):

A mixture containing **6** (2.0 g, 0.01 mole) and dry, freshly distilled diiodomethane (1.33 g, 0.005 mole) in 5 ml of dry sulfolane, was heated at 85-90°C (oil bath temperature) under an argon atmosphere for 8 hr. The reaction mixture was cooled, then flash distilled under reduced pressure into a dry ice/acetone cooled receiver. The distillate was redistilled through a Vigreaux column to yield a pure sample of the desired product (96.5% by glc). NMR: ^{1}H: $\delta = 4.28$, (s, $-CH_2-$); ^{13}C:$\delta = 129.9$ (SCF_3) and $\delta = 28.6$ ($-CH_2-$).

4. CONCLUSIONS

Perfluoro-2-(trifluoromethyl)-propene, 1,1-dibromoperfluoro-2-(trifluoromethyl)-propene and the allylic fluorosulfonate react with trifluoromethylthiocopper to give complex reaction products. The treatment of perfluoro-2-(trifluoromethylthiodifluoromethyl)-propene with potassium fluoride also furnishes a complex mixture. The reaction of tributyltin cyanide with the allyl fluorosulfonate yields the nitriloderivatives of perfluoro-2-(trifluoromethyl)-propene. The mechanism of the formation of these unusual products has been rationalized in this report. The structures of the various compounds present in the complex reaction mixtures have been deduced from their NMR spectrometric data and from their mass spectral fragmentation

Table 1: Reaction Products

Reaction	Products Formed
$(CF_3)_2C=CBr_2 + CF_3SCu$	$CF_3SSCF_3 + (CF_3)_2C=C(SCF_3)_2 + (CF_3)_2C=C(Br)(SCF_3)$
$(CF_3)_2C=CF_2 + CF_3SCu$	$(CF_3)_2C=C(F)(SCF_3) + (CF_3)_3C\text{-}C(CF_3)_3 + (CF_3)(CF_3SCF_2)CHC(F_2)(SCF_3) + CF_3CH_2CO_2H + (CF_3)_2CHCOOH$
$(FSO_2OCF_2)(CF_3)C=CF_2 + CF_3SCu$	$(CF_3SCF_2)(CF_3)C=CF_2 + (CF_3)_2C=CF_2 + CF_3SSCF_3 + CF_3CH_2C(O)F + (CF_3)_2C=C(F)(SCF_3) + (CF_3)_2CHCF_2SCF_3 + (CF3)(CF3SCF2)C=C(F)(SCF3)$
$(FSO_2OCF_2)(CF_3)C=CF_2 + Bu_3SnCN$	$(CNCF_2)(CF_3)C=C(F)(CN) + (CF_3)_2C=C(F)(CN) + (CF_3)_2C=CF_2 + (CNCF_2)(CF_3)C=C(CN)_2$
$(CF_3)(CF_3SCF_2)C=CF_2 + KF$	$(CF_3)_2C=CF_2 + (CF_3)_2C=C(F)(SCF_3) + (CF_3)(CF_3SCF_2)CHC(F_2)(SCF_3)$ or $(CF_3)_2C=C(SCF_3)_2 + (CF_3)(CF_3SCF_2)C=C(SCF_3)_2$ or $(CF_3SCF_2)_2C=C(F)(SCF_3) + CF_3CH_2C(O)F$ $(CF_3SCF_2)_2CHC(F)(CF_3)_2 + (CF_3)(CF_3SCF_2)CHC(F_2)(SCF_3)$ or $(CF_3)_2CHC(F)(SCF_3)_2$

Table 2. Mass Spectral Fragmentation of Compounds

$CF_3CH_2CO_2H$:	**M^+ = 128** ; 111($M-OH$); 109($M-F$); 91($CF_2=CH-C=O$); 89(109 83(CF_3CH_2); 64($CF_2=CH_2$, 100%); 59($M-CF_3$); 51(CHF_2); 47(COF); 45($CF=CH_2$, 100%) and 42($CH_2=C=O$).
$CF_3CH_2C(O)F$:	**M^+ = 130** ; 111($M-F$); 91(C_3HF_2O); 83(CF_3CH_2); 69(CF_3, 100%); 64($CF_2=CH_2$) ; 51((CHF_2); 47[$C(O)F$] and 42(111-CF_3).
$(CF_3)_2CHCO_2H$:	**M^+ = 196** ; 179($M-OH$); 132($CF_3CH=CF_2$); 113(132-F); 91(C_3HF_2O); 82(132-CF_2); 75($CF_2=C=CH$); 69(CF_3, 100%); 63(82-F); 51(CHF_2) and 45($CF=CH_2$).
$(CF_3)_2C=CF_2$:	**M^+ = 200** ; 181 ($M-F$); 162(181-F); 150($M-CF_2$); 131($M-CF_3$); 112(131-F); 93(C_3F_3, 100%); 81(150- CF_3); 74(93-F); 69(CF_3); 63(CSF) and 50(CF_2).
CF_3SSCF_3:	**M^+ = 202**; 133($M-CF_3$); 114(133-F); 82(CSF_2); 69(100%, CF_3); 63(CSF); 51(SF) and 44(CS).
$CF_3(CNCF_2)C=CF_2$:	**M^+ = 207** ; 188($M-F$); 181($M-CN$); 162(181-F);143(162-F); 138($M-CF_3$); 131(181-CF_2); 119(138-F)112(138-CN); 100($CF_2=CF_2$); 93($CF_2=C=CF$);76(CF_2CN) and 69(CF_3, 100%
$CF_3(CNCF_2)C=C(F)(CN)$:	**M^+ = 214** ; 200($M-N$); 195($M-F$); 188($M-CN$); 181(200-F); 162(188-CN, 100%); 145($M-CF_3$); 138(188-CF_2); 119($CNCCCF_3$); 107(CF_3CCCN); 100($CNCCCF_2$); 93(119-CN); 76(CF_2CN); 69(CF_3) and 50(CF_2).
$(CF_3S)_2CH_2$:	**M^+ = 216** ;147($M-CF_3$); 115($M-SCF_3$); 101SCF_3); 82(CSF_2); 69(CF_3, 100%); 63(CSF); 50(CF_2); and 45(CSH).
$(CF_3)_3CH$:	**M^+ = 220** (not seen); 201($M-F$); 181(201-HF); 150 [$C(CF_3)_2$]; 132(201- CF_3); 113(132- F); 93(C_3F_3); 82(132-CF_2); 75(113-2F 69(CF_3, 100%); 63(82- F); 50(CF_2); 44(63- F) and 32(CHF).
$CF_3(CNCF_2)C=C(CN)_2$:	**M^+= 221** ; 202($M-F$); 195($M-CN$); 145($M-CF_2CN$); 138(CF_3CCFCN); 119(CF_3CCCN); 100(CF_2CCCN); 81(100 - F); 76(CH_2CN, 100%); 69(CF_3); 64[$C(CN)_2$] and 50(CF_2).
$CF_3(FSO_3CF_2)C=CF_2$:	**M^+ = 280**; 261($M-F$); 211($M-CF_3$); 181($M-SO_3F$, 100%); 159[$CF_2=C(CO)CF_3$]; 131(159-CO); 112($CF_2=C=CF_2$); 100($CF_2=CF_2$); 83(112-F) and 69(CF_3).

Table 2. Mass Spectral Fragmentation of Compounds (Continued)

$CF_3(CF_3SCF_2)C{=}CF_2$:	**M$^+$ = 282** ; 263(M-F); 213(263-CF_2); 194(213-F); 181(M-SCF_3);93(C_3F_3); 82(CSF_2); 69(CF_3, 100%); 63(CSF) and 44(CS).
$(CF_3)_2C{=}CF(SCF_3)$:	**M$^+$ = 282**; 263(M-F); 194(M- CF_3); 175(194-F); 163(194- CF); 144(175- CF); 125(194-CF_3); 106(175-CF_3); 101(SCF_3); 87(106-F); 75(C_2FS); 69(CF_3,100%); 63(CSF) and 50 (CF_2).
$(CF_3)_2CH\text{-}CF_2SCF_3$:	**M$^+$ = 302**; 283(M-F); 200(M- CF_3SH); 151(CF_3SCF_2); 132(201-CF_3);113(132-F, 100%); 107(M-195); 101(SCF_3); 82(CSF_2); 69(CF_3, 100%); 63(CSF);
$(CF_3)_2C{=}C(Br)(SCF_3)$:	**M$^+$ = 342** ; 323(M-19); 263(M-Br); 194(M-CF_3Br); 175(194-F); 144(175-CF); 125(144-F); 106(125-F); 101(SCF_3); 93(C_3F_3); 87(106-F); 69(CF_3, 100%); 63(CSF); 50(CF_2) and 44(CS).
$(CF_3)_2C{=}C(SCF_3)_2$:	**M$^+$ = 364** (not seen); 345(M- F); 263(M-SCF_3); 207($CF_3SCF_2C{=}C{=}S$); 194(263 - CF_3); 175($CF_3SCF{=}C{=}CF$); 151(CF_3SCF_2); 125(CF_3SC_2); 106(125-F); 101(SCF_3); 93($CF_2{=}C{=}CF$); 69(CF_3, 100%);63(SCF) and 51(SF).
$(CF_3)_2C{=}C(SCF_3)_2$:	**M$^+$ = 364** ; 345(M - F); 295(M-CF_3); 257(295-2F); 226[$C_2(SCF_3)_2$]; 213(C_4F_7S); 207(226- F); 194(295- SCF_3); 175(294-F); 157(M-207); 113(C_2F_3S); 106(175- CF_3); 101(SCF_3); 93(C_3F_3); 82(CSF_2);69(CF_3, 100%); 63(CSF); 50(CF_2) and 44(CS).
$CF_3(CF_3SCF_2)CHCF_2SCF_3$:	**M$^+$ = 384**(not seen); 315 (M- CF_3); 283(M- SCF_3); 195 ($CF_3SCF_2\text{-}C{=}CF_2$); 151($CF_3SCF_2$); 113($CF_2{=}CH\text{-}CF_2$); 82($CSF_2$); 69($CF_3$, 100%) and 63(CSF).
$(CF_3)_3CC(CF_3)_3$:	**M$^+$ = 438** ; 419(M-F); 93(C_3H_3); 69(CF_3, 100%) and 50(CF_2).

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