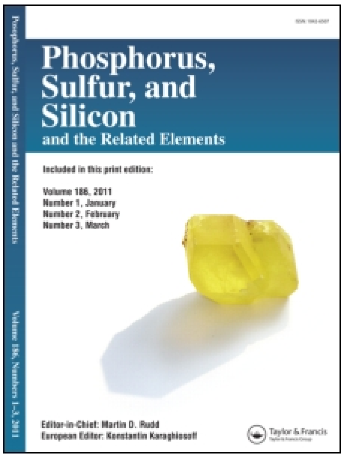

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Unusual Reaction of Epoxynorbornane with Trifluoromethylsulfenyl Chloride

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To cite this Article Munavalli, S. , Schlueter, Robert , Rohrbaugh, D. K. , Longo, R. L. , Mackay, R. A. and Durst, H. D.(2005) 'Unusual Reaction of Epoxynorbornane with Trifluoromethylsulfenyl Chloride', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 2, 309 — 320

To link to this Article: DOI: 10.1080/104265090507740

URL: http://dx.doi.org/10.1080/104265090507740

Phosphorus, Sulfur, and Silicon, 180:309–320, 2005
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090507740

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Unusual Reaction of Epoxynorbornane with Trifluoromethylsulfenyl Chloride

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*The treatment of 1, 2-exo-epoxynorbornane (**1**) with (trifluororomethyl)sulfenyl chloride (**2**) in dry pentane at −80°C furnishes 16 compounds. Of which, 7 are derived from the reaction of the solvent with **2**, 7 others are formed from the substrate (**1**) and the remaining two arise from the reagent (**2**) itself. The probable mechanism of their formation and their mass spectral characterization are presented in this paper.*

Keywords Auto-catalysis; epoxide ring opening; free radical reactions; solvent-derived products

INTRODUCTION

Oxiranes comprise an extremely versatile group of intermediates and as such have attracted considerable attention.[1] Because of their ready availability and exceptional reactivity, the epoxides have found varied applications in synthetic organic chemistry. The oxirane ring can be

Received June 24, 2004; accepted August 27, 2004.

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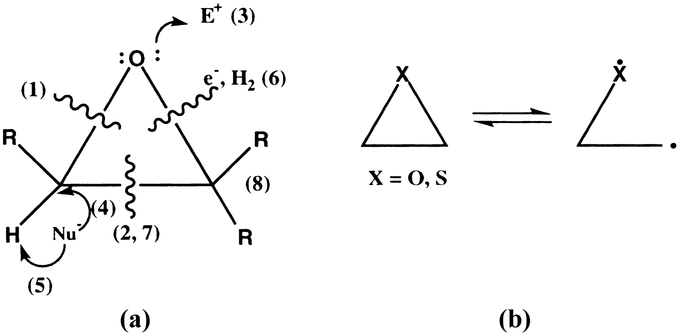

FIGURE 1 (a) Types of oxirane cleavages and reactions. (1, 2) Homolytic cleavages (free radical, photolytic, thermal), (3) Electrophilic attack on the ring oxygen, (4) Nucleophilic attack on the ring carbon, (5) Nucleophilic attack on the ring hydrogen, (6) Reactions with electrons and surface reactions, (7) Cycloadditions, and (8) Reactions of the substituent. (b) Structre of oxirane and thiirane and their diradical equivalents.

opened under almost all conditions: electrophilic, nucleophilic, neutral, gas-phase, thermal and free radical conditions (Figure 1(a)).[1a] The reactivity of the oxiranes is directly attributable to their inherent polarity and ring strain.[1k] The structures of the free radical species generated from the oxiranes and thiiranes have been discussed (Figure 1(B)).[2] It is interesting to note the presence and the participation of the diradical in chemical reactions. An excellent review on the preparation and synthetic applications of the oxiranes has appeared.[1f] We have recently examined the free radical cleavage of styrene oxide with trifluoromethylthiocopper and and dimethyl hydrogenphosphonate and reported the formation of products arising from the cleavage of the C—C and C—O bonds.[3–6]

In continuation of our interest in the chemistry of the oxirane cleavage reactions[3–6] and with a view to examine whether this reaction can be successfully applied to the decontamination and destruction of mustard, a blister agent, the oxirane ring opening in the presence of (trifluororomethyl)sulfenyl chloride (**2**) has now been examined. This paper presents the probable mechanism of the formation of the various compounds and their GC-MS characterization.

Recently we have shown that the oxirane ring can be cleaved with dimethyl hydrogen phosphonate[4,5] and with trifluoromethylthiocoper.[3,6] It was considered interesting to investigate whether inexpensive oxiranes (epoxides), such as ethylene oxide, can be used in the decontamination and destruction of mustard, [bis-(2-chloroethyl)sulfide], a known blister agent.[7] This expectation was supported by the fact that

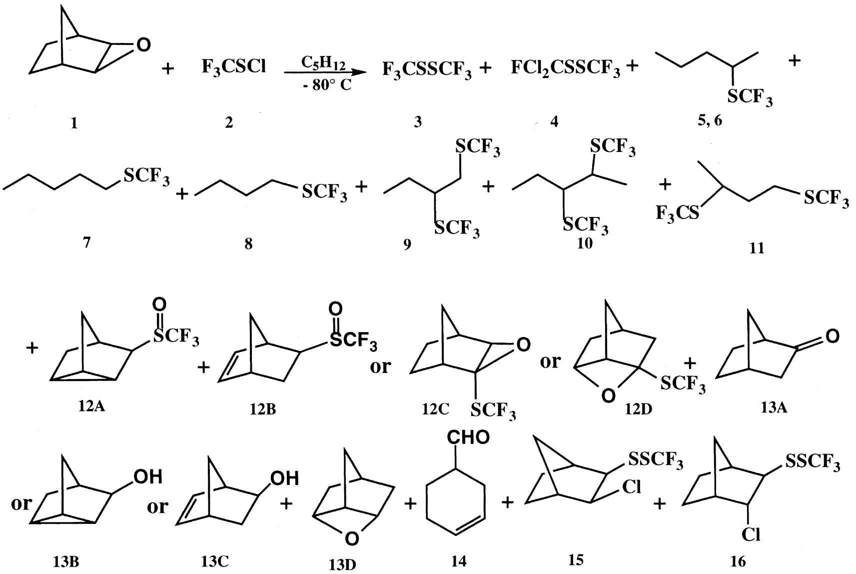

FIGURE 2 Reaction of 1, 2-exo-Epoxynorbornane with F_3CSCl.

the oxiranes react with almost all kinds of reagents.[1] Accordingly, the reaction of 1, 2-exo-epoxynorbornane (**1**) with trifluoromethylsulfenyl chloride (**2**) was examined and found to furnish 16 (**3–16**) compounds (cf. Figure 2).

On treatment with pyridinium chloride compound **1** gives four cholronorborneols and nortricyclanol (**13B**).[8a,b] On reacting with aq. $HClO_4$, it yields four dihydroxynorbornanes and 7-hydroxy-2-norbornene, while on pyrolysis over neutral alumina at 270°C, it furnishes norcamphor (**13A**), nortricyclanol (**13B**), 3-cyclohexene aldehyde (**14**), nortricyclenone and three additional compounds.[8c] In the presence of per acids, **1** gives six dihdroxynorbornanes.[8c] In this quest, sulfonium salts,[8d] trimethylsilyl halides,[8e] phenyl trimethylsilyl sulfide[8f] and trimethylsilyl cyanide[8g–h] have found application. Also, enantioselective epoxide ring opening reactions have been dscribed.[8I–k] In the light of the above discussion,[8a–c] the formation of 16 compounds from **1** on exposure to **2** does not appear to be that unreasonable.

Sulfenyl halides have been shown to react with norbornene.[9a] The reaction of norbornene with t-butylhypochlorite, a low temperature free radical initiator, yields chloronortricyclane and 2-chloro-5-norbornene.[9b] It has been stated that the thiyl radicals add to norbornene via exclusive exo-attack on the double bond.[9c] However, the reaction of 1, 2-exo-epoxynorbornane with Li in ethylenediamine gives predominantly exo-norborneol, accompanied by endo-norborneol, nortricyclanol (**13B**) and 7-hydroxynorbornane.[9d]

The concept of thiyl radicals derived from sulfenyl halides was first advanced by Kharasch.[10] In view of the known propensity of the bicyclo-[2.21]-heptenyl system to undergo facile skeletal rearrangements,[11] the free radical addition reactions to the norbornenyl system appear to be nonspecific; in that both cis and trans additions appear to be the norm rather than the exception. Also, it should be noted that the products of addition are usually accompanied by the products arising from the the aforementioned skeletal rearrangements. It is conceivable that many of the compounds may have been formed from the free radical catalyzed addition reactions to norbornene formed *in situ* (**29**). Indeed, it has been reported that **29** gives six difluoronorbornanes and three dichloronorbornanes and chloronortricyclane when reacted with XeF_2[12a] and chlorine radicals[12b] respectively. Although the free radical reactions of **29** generally occur from the nonhindered side of the molecule, products formed from both exo and endo attacks have been identified.[13a] It seems that with smaller substituents both cis and trans additions are observed, while with bulky attachments steric factors come into play and favor the attack from the less hindered exo-face.[13b,c] These observations have led to the generalization that free radical attack on the norbornene system occurs "exclusively from the exo-side but propagating species transfer from the endo as well as from the exo-face."[13b]

To begin with, F_3CSCl (**2**) undergoes self-catalyzed free radical cleavage of the S—Cl bond to generate the thiyl ($F_3CS^{\cdot}$) and $Cl^{\cdot}$ radicals (cf. Figure 3).[14] The thiyl radicall ($F_3CS^{\cdot}$) radicals dimerize to yield bis-(trifluoromethyl)disulfide (**3**). The formation (dichlorofluoromethyl) (trifluromethyl) disulfide (**4**) during the rections of F_3CSCl (**2**) has been documented.[15] Two compounds, namely bis-(trifluoromethyl)disufide (**3**) and (dichlorofluoromethyl) (trifluoromethyl)disulfide (**4**) are formed from the free radical reactions of the reagent itself (**2**). Their formation has been rationalized.[16]

It is interesting to observe that 7 compounds, namely **5–11**, have their origin in pentane, the solvent used in the reaction. There are several precedents for such a participation of the solvent in the reaction.[17] Figure 3 attempts to describe their genesis. The abstraction of hydrogen by $Cl^{\cdot}$ radical leads to two pentyl radicals (**18** and **19**); radical **18** reacts with the thiyl radical ($F_3CS^{\cdot}$) to form two isomeric 2-(trifluoromethylthio)pentanes (**5** and **6**). While radical **19** simply picks up $F_3CS^{\cdot}$ radical to yield 1-(trifluoromethylthio)pentane (**7**). The intermediate **19** can also split off a methylene moiety to generate a butyl radical ($^{\cdot}\mathbf{C_4H_9}$, **20**), which has two options available to it: (i) to add to the $F_3CS^{\cdot}$ radical to form 1-trifluoromethylthiobutane (**8**) and (ii) to undergo hydrogen migration to yield an isomeric butyl

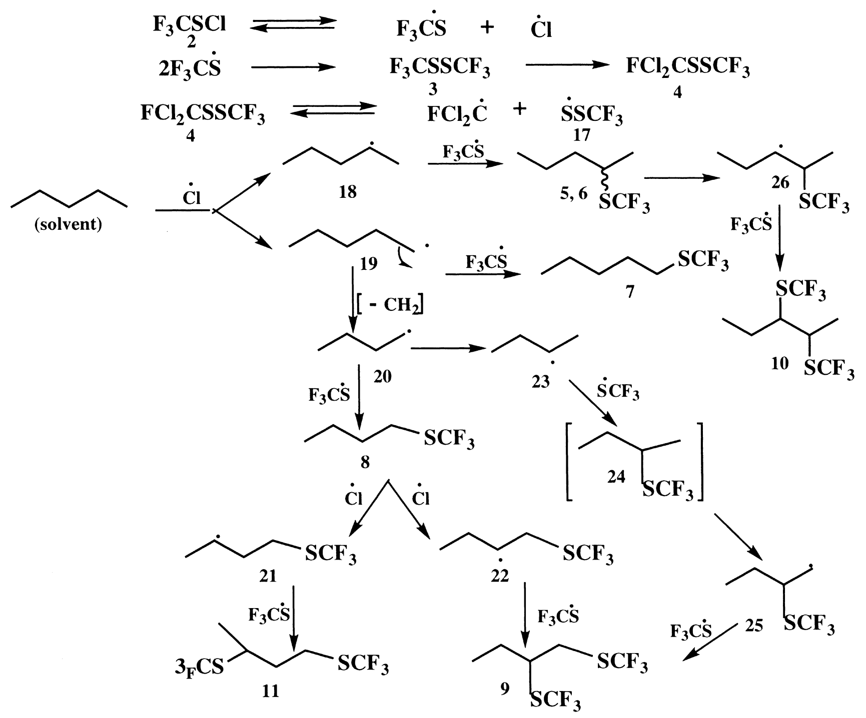

FIGURE 3 Mechanism of formation of compounds derived from the solvent.

radical, namely **21**, which subsequently picks up the $F_3CS^{\cdot}$ radical and furnishes 2-trifluoromethylthiobutane (**24**). Compound **8** can further undergo hydrogen abstraction by $Cl^{\cdot}$ to form 2 more radicals (**21** and **22**), which in turn react with the $F_3CS^{\cdot}$ radical to give 1,2- and 1, 3-bis-(trifluoromethylthio)butanes (**9** and **11**), respectively. Compound **9** can also arise from intermediates **24** and **25**. Bis-2, 3-(trifluoromethylthio)pentane (**10**) is formed via intermediate **26**. The structure of compound **10** stands supported by the presence of the dithiacyclobutenyl entity [$(C_2HS_2)^+$; m/e = 89] in its mass spectrum. All of these compounds have been identified by their mass spectra (cf. Table I).

Figure 4 attempts to explain the origin of the remaining compounds (**12–16**). Compounds **13a**, **13b**, **13c**, **13d** and **14** are artifacts formed from **1** either during the course of the reaction or during the chromatographic work-up (Figure 5). It has been shown that **1** gives rise to these compounds during the course of the chromatographic work-up.[18] The di-radical intermediate, **27**, the equivalent of the oxide moiety, (cf. Figure 4) can be considered to initiate the reaction sequence. The presence of the di-radical species, such as **27**, in the reactions of the epoxide

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Text

1. Bis-(trifluoromethyl)disulfide (**3**): $M^+ = 202$.
2. (Dichlorofluoromethyl)(trifluoromethyl)disulfide (**4**): $M^+ = 234$; (r.t. = 2.02 min, 0.8%).
3. 2-(Trifluoromethylthio)pentane (**5**): $M^+ = 172$ (CI-mode $M^+ = 173$) (r.t. = 1.50 min, 0.1%); 115 (M-C_4H_7 or CH_2SCF_3); 101 (F_3CS); 82 (CSF_2); 70 (C_5H_{10}); 69 (CF_3 or C_5H9; 100%); 59 (C_2H_3S); 55 (C_4H_7) and 53 (C_4H_5).
4. 2-(Trifluoromethylthio)pentane (**6**): $M^+ = 172$ (r.t. = 2.08 min, 0.1%); 129 (M-C_3H_7); 115 (CH_2SCF_3); 103 (M-CF_3, 100%); 82 (CSF_2); 69 (CF_3); 59 (C_2H_3S) and 55 (C_4H_7).
5. 1-(Trifluoromethylthio)pentane (**7**): $M^+ = 172$ (r.t. = 1.55 min, 0.2%); 143 (M-C_2H_5); 129 (M-C_3H_7); 115 (CH_2SCF_3); 103 (M-CF_3); 82 (CSF_2); 71 (M-SCF_3, 100%); 69 (CF_3); 63 (CSF); 59 (C_2H_3S); 55 (C_4H_7); 53 (C_4H_5) and 47 (SCH 3).
6. 1-(Trifluoromethylthio)butane (**8**): $M^+ = 158$ (r.t. = 1.99 min, 2.3%); 142 (M-CH_4); 115 (CH_2SCF_3; 100%); 101 (F_3CS); 82 (CSF_2); 73 (C_3H_5S); 69 (CF_3); 63 (CSF); 57 (C_4H_9) and 50 (CF_2).
7. Bis-(1, 2-trifluoromethylthio)butane (**9**), $M^+ = 258$ (CI-mode, 259) (r.t. = 2.15 min, 3.5%); 238 (M-HF); 215 (M-C_3H_7); 189 (M-CF_3); 169 (189-HF); 157 (M-SCF_3); 142 (157-CH_3); 129 ($C_2H_4SCF_3$); 115 (CH_2SCF_3); 89 (C_2HS_2, 100%); 77 (CHS_2); 69 (CF_3); 59 (C_2H_3S); 57 (C_4H_9) and 45(CSH).
8. Bis-(2, 3-trifluoromethylthio)pentane (**10**), $M^+ = 272$ (r.t. = 2.4 min, 0.1%);171 (M-SCF_3); 129 ($C_2H_4SCF_3$); 105 ($C_3H_5S_2$); 101 (F_3CS); 89 (C_2HS_2); 82 (CSF_2); 77 (CHS_2, 100%); 69 (CF_3) and 59 (C_2H_3S).
9. Bis-(1, 3-trifluoromethylthio)butane (**11**), $M^+ = 258$ (r.t. = 3.16 min, 0.2%); 115 (CH_2SCF_3, 100%); 82 (CSF_2); 69 (CF_3); 63 (CSF) and 59 (C_2H_3S).
10. Exo-Norbornene oxide (**1**): $M^+ = 110$ (r.t. = 3.42 min, 2.3%).
11. (Nortricyclo)rifluoromethylsulfoxide (**12A**) : $M^+ = 210$ (CI-mode, 211) (r.t. = 4.02 min, 0.2%); 93 (M-$OSCF_3$, 100%); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 69 (CF_3); 65 (C_5H_5); 63 (CSF) and 51 (C_4H_3).
12. 2, 3-Norbornenyl-5-trifluoromethylulfoxide (**12B**): $M^+ = 210$ (not seen) (r.t. = 5.24 min, 4.0%); 117 ($OSCF_3$); 93 (M-$OSCF_3$; 100%); 91 (C_7H_7), 79 (C_6H_7); 77 (C_6H_5); 65 (C_5H_5); 55 (C_4H_7) and 53 (C_4H_5).
13. Norcamphor (**13A**) $M^+ = 110$ (r.t. = 5.41 min, 3.8%), $^{++}$; 95 (M-CH_3); 92 (M-H_2O); 91 (C_7H_7); 81 (M-C_2H_5. 100%); 79 (C_6H_7); 78 (C_6H_6); 68 (C_5H_8); 67 (C_5H_7) and 55 (C_4H_7).
14. Tricyclic oxetane (**13D**) $M^+ = 110$ (r.t. = 5.48 min, 0. 7%); 95 (M-CH_3); 93 (M-OH, 100%); 91 (C_7H_7); 81 (M-C_2H_5 or CHO); 79 (C_6H_7); 77 (C_6H_5); 69 (C_5H_9); 57 (C_4H_9) and 55 (C_4H_7).
15. 3-Cyclohexene aldehyde (**14**) $M^+ = 110$ (r.t. = 6.04 min, 0.8%).
16. Exo, exo-2-(Trifluoromethylthio)-3-chloronorbornyl sulfide (**15**) $M^+ = 262$ (not seen) (r.t. = 6.49 min, 0.8%); 193 (M-CF_3); 129 (M-$SSCF_3$); 101 (SCF_3); 93 (C_7H_9); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_9, 100%); 65 (C_5H_7); 63 (CSF); 55 (C_4H_7) and 53 (C_4H_5).
17. Exo, endo-2-(Trifluoromethylthio)-3-chloronornayl sulfide (**16**) $M^+ = 262$ (not seen) (CI-mode 263) (r.t. = 6.59 min, 0. 8%); 193 (M-CF_3); 129 (M-$SSCF_3$); 101 (SCF_3); 93 (C_7H_9, 100%); 81 (C_6H_9); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_9); 65 (C_5H_7); 63 (CSF); 55 (C_4H_7) and 53 (C_4H_5).

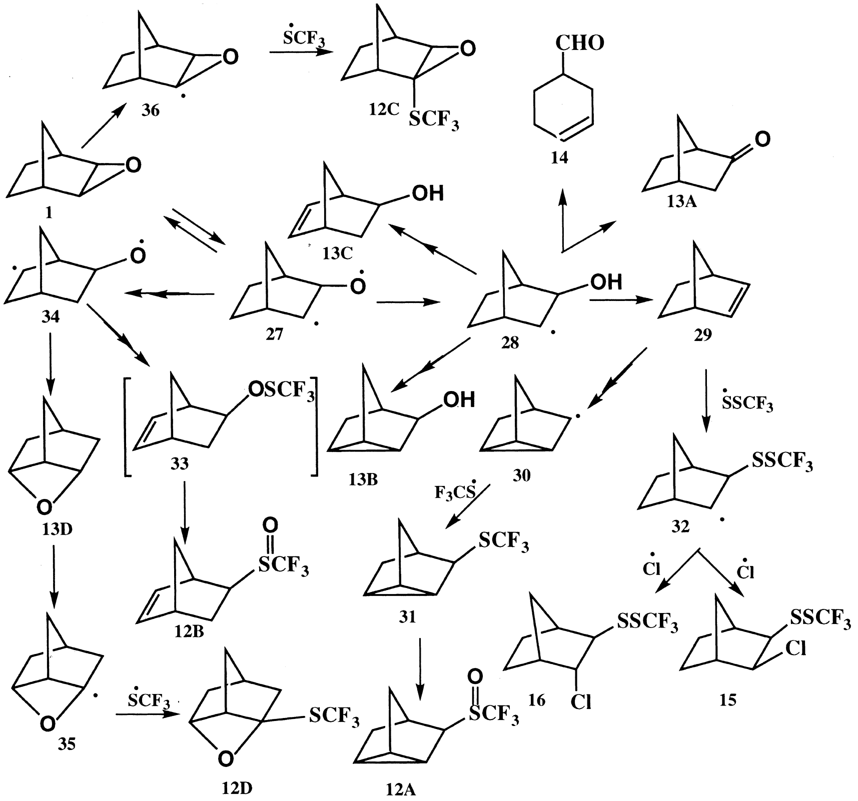

FIGURE 4 Probable mechanism of formation of bi- ant tri-cyclo derivatives.

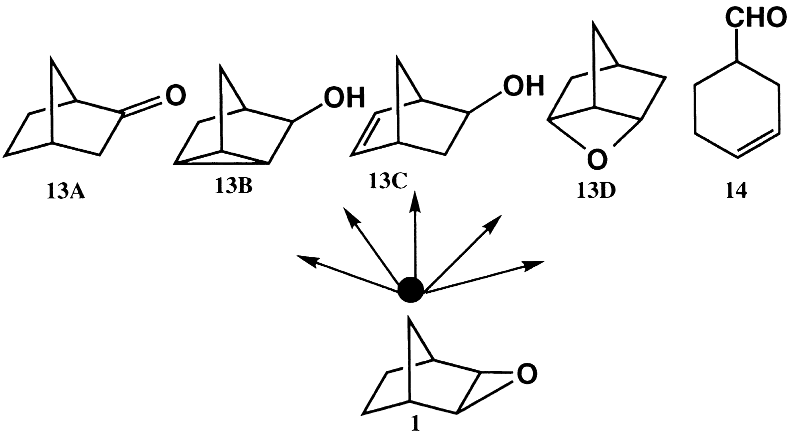

FIGURE 5 Rearrangement of 1, 2-exo-epoxynorbornane.

has been rationalized.[2] Abstraction of hydrogen by **27** would lead to the intermediate, **28**, which has three options open to it. Firstly, it can form norbornene (**29**), which itself has two options available to it. The first pathway leads to nortricyclyl radical (**30**), which can react with $F_3CS^{\cdot}$ radical to form (trifluoromethylthio)nortricyclane (**31**). The latter subsequently can get oxidized to the sulfoxide (**12A**). The second option for **29** would be to react with the perthiyl (**17**, $F_3CSS^{\cdot}$) radical to form intermediate **32**, which then goes on to react with $Cl^{\cdot}$ radical to give nonspecific addition products, namely exo, exo-1-(trifluoromethylthio)-2-chloronorbornyl sulfide (**15**) and exo-1-(trifluoromethylthio)-endo-2-chloronorbornyl sulfide (**16**), respectively. The second option for intermediate **28** would be to undergo rearrangement to form nortricyclanol (**13B**). There is precedence for the suggested transformation.[19] Here, two points require further clarification: (i) the conversion of **29** to **30**, and (ii) the nature and the reactions of the perthiyl radical ($F_3CSS^{\cdot}$). The passage from norbornene (**29**) to nortricyclyl radical (**30**) via dehydronorbornyl radical was first suggested by J. D. Roberts and coworkers[19a] and subsequently has been discussed by others.[19b–d] The presence and the role of the perthiyl radicals in the formation of (perfluoromethyl)polydisulfides from **2** have been discussed.[15b,20] In this context it is worth noting that compound 31 has been previously identified.[20b,c]

Next, it remains to explain the origin of **12B**, **12C**, and **12D**. The proposed abstraction of hydrogen from exo-norbornene oxide (**1**) to form intermediate (**36**) and the thiolated derivative (**12C**) have precedents (Figure 4).[21]

The diradical intermediate **27** can rearrange to **34**, which can then form the tricyclic oxetane **13D**. The latter can then undergo a similar series of abstraction and addition reactions described above to yield compound **12D** via **13** and intermediate **35**. There are precedents for the suggested formation of the oxetanes.[22] On treatment with t-potassium butoxide, a norbornylepoxide derivative has been reported to give a substituted tricyclic oxetane.[22] The reaction of norborneol with phenylsulfenyl chloride has been described to yield the tricyclic oxetane as the primary product. The sequence of reactions leading to **12A** from **29** via the intermediates **30** and **31** has already been mentioned. Compounds **12A, 12B**, **12C**, and **12D** are isomers. So are **13A, 13B, 13C**, and **13D** (Figure 5).

The mass spectral fragmentation behavior of the norbornyl derivatives has been the subject of detailed investigations.[23] The mass spectrum of nortircyclanol has been described.[23d] Ions with m/e = 79, 77, 65, 53 and 51 are frequently encountered in the mass spectral breakdwon of the norbornyl derivatives. The GC-MS analysis of the complex mixture of products arising from the free radical reaction of the substrate (**1**) with F_3CSCl (**2**) was run using both the EI- and CI-modes to ascertain the exact molecular weight of each of the components described in the text. Table I summarizes the mass spectral fragmentation of compounds described in the narrative.

Four isomeric compounds (**12A**, **12B**, **12C**, and **12D**) have the same molecuar weight, namely $M^+ = 210$. The mass spectral fragmentation of **12A** and **12B** shows the m/e = 93 as the most prominent peak. This corresponds to the moiety $[C_7H_9^+]$ arising from the loss of $\mathbf{OSCF_3}$ from the M^+ and the rest of the breakdown pattern is typical of the norborbornyl derivatives.[23d] Compound **12A** and **12B** definitely have the $F_\#CSO$-moiety which can only come from the $F_\#CSO$-group. This inference is supported by the presence of a peak at m/e = 117 in its mass spectrum. This peak would be absent in the mass spectrum of **12C** or **12D**. Thus, the formation of **12A** and **12B** appears to involve the oxygen atom of the epxoy moiety of the substrate. This suggests the initial formation of the $C{-}O{-}SCF_3$ (**33**). This linkage then rearranges to the sulfoxide $[(C{-}S(O)CF_3]$. There are precedents that support the proposed rearrangement of [C—O—S] entity to [C—S(O)].[24] The mass spectra of **1**, **13A** and **14** have been reported.[18d]

Then come four isomers with $M^+ = 110$, corresponding to $C_7H_{10}O$, which were detected via GC-MS. In addition to the substrate (**1**), five structures, **13A**, **13B**, **13C**, **13D**, and **14** were considered for the said three compounds (cf. Figure 5). The mass spectral breakdown pattern supports structures **1**, **13A**, and **14**.[18d] This inference draws support from the reported facile arrangement of the substrate into compounds **13A**, **13B**, and **13C**.[8]

This left the fourth compound to be identified. Its fragmentation pattern is different from the breakdown behavior of **1** and **13A**. Careful examination of its fragmentation behavior has led us to tentatively assign the oxetan structure (**13D**). Lastly, there is the question of a pair of isomers, namely **15** and **16** (cf. Figure 4). These are the only compounds derived from the substrate (**1**) that do not carry oxygen. The presence of chlorine in the molecule was detected by the presence of ^{35}Cl and ^{37}Cl isotopic peaks in their mass spectra (cf. Table 1). The identification of these two isomers lends support to the presence of norbornene (**29**), the formation of which as well as the probable mechanism of the genesis of the various products is outlined in Figure 4.

EXPERIMENTAL

All solvents were dry and freshly distilled prior to use. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.27 mm. i.d. DB-5 capillary column (J and W Scientific, Folsom, CA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.27 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°, 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°, interface temperature 270°C, source temperature 150°, electron energy 70 eV (EI) or 200 eV (CI) and 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).

Reaction of Exo-Epoxynorbornane (1) with Trifluoromethanesulfenyl Chloride (2)

To exo-norbornene oxide (**1**, 4 g) in freshly distilled dry n-pentane (27 ml), stoichimetric amounts of trifluoromethanesulfenyl chloride (**2**) were added via the vacuum line at −78°C with stirring and under argon. The reaction mixture was stirred at −78°C for additional 4 hr and then overnight at room temperature. The solvent was removed under reduced pressure and the GC analysis of the residue showed it to consist of a complex mixture of 16 compounds. Attempts to fractionate the mixture to separate the components via vacuum distillation were not successful. The GC-MS analysis of the reaction product permitted the characterization of the following compounds: (1) Bis-(trifluromethyl)-disulfide (**3**); (2) (Dichlorofluoromethyl)(trifluoromethyl)disulfide (**4**); (3) 2-(Trifluoromethylthio)pentane (**5**); (4) 2-(Trifluoromethylthio)-pentane (**6**), stereomer of **5**; (5) 1-(Trifluoromethylthio)pentane (**7**); (6) 1-tifluoromethylthio)butane (**8**); (7) Bis-(1, 2-trifluoromethylthio)butane (**9**); (8) Bis-(2, 3-trifluoromethylthio)pentane (**10**); (9) Bis-(1, 3-trifluoromethylthio)butane (**11**); (10) 1,2-epoxynorbornane (**1**); (11) Nortricyclotrifluoromethyl sulfoxide (**12A**); (12) 2, 3-Norbornenyl–5-trilfluoromethyl sulfoxide (**12B**); (13) Norcamphor (**13A**); (14)Tricyclic oxetane (**13D**); (15) 3-Cyclohexene aldehyde (**14**); (16) exo, exo-2- (trifluoromethylthio)-3-chloronorbornylsulfide (**15**); and (17) exo, endo-2-(trifluoromethylthio)norbornyl-3-chlorosulfide (**16**).

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