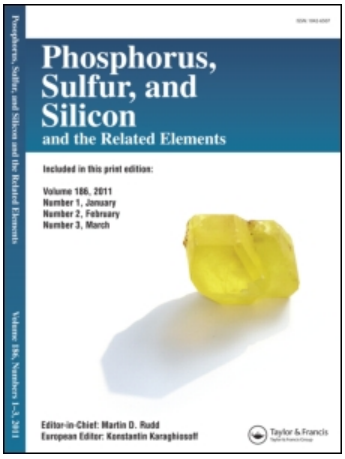

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Treatment of norbornene with trifluoromethylsulfenyl chloride at −80°C furnishes, in addition to trifluoromethylthionortricyclane, four isomeric (chloro) (trifluoromethylthio)-norbornanes and bis-(2, 6-trifluoromethylthio)norbornane. The probable mechanism of the formation of the various compounds via free radical intermediates and their mass spectral characterization are described in this communication.

Keywords: Free-radical–initiated addition reactions; norbornene; trifluoromethylthiolated-norbornanes

Since the poineering investigations of Kharasch, electrophilic addition of sulfenyl halides to π-bonds has been well studied.[1] The course of the addition reaction is said to be influenced by the nature of the solvents.[2] In polar solvents the addition appears to go through a two-step process, while in nonpolar solvents and in the absence of ionic intermediates molecular rearrangements are not usually observed. The reaction has been stated to be unaffected by substituents.[2b] This has been contradicted by several obervations to the effect that steric influence does affect the reaction.[2c–e] The kinetics of addition to scores of alkenes, bridged cycloalkenes, and cycloalkenes have been examined.[2b] Although it is widely considered that cyclic episulfonium ions are involved as reaction intermediates, their actual participation in the reaction has been questioned.[1f] This view appears to be supported by ab initio Self–Consistent Field–Molecular Orbital (SCF—MO) calculations.[3]

In view of their great propensity and willingness to undergo skeletal rearrangements, the chemistry of the fused-ring systems such as

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the bicyclo[2.2.1]heptenes has attracted considerable interest over the years. The reaction of substituted sulfenyl halides with norbornene has been known to furnish products arising from simple addition to C—C multiple bond as well as those formed from skeletal rearrangement of the Wagner-Meerwein type.[4] The addition has been described as giving exclusively trans norbornane derivatives, while the rearrangement products were found to be bicyclic and tricyclic derivatives.[2c] The mechanism of the addition of sulfenyl halides to bridged cycloalkenes has created considerable interest.[4] The frequently employed explanation entails the involvement of nonclassical norbornyl carbonium ion intermediate. Among the various mechanisms proposed to rationalize the formation of the various products are: (1) simple addition across the multiple bond, (2) Wagner-Meerwein type rearrangements, (3) mixed addition reactions accompanied by rearrangements, and (4) elimination of hydrogen or alkyl substituents. The participation of the cyclic sulfonium ion intermediate is the most popular postulate in the addition reaction.[2c] The isolation and characterization of the cyclic sulfonium salts seems to support this suggestion. Other mechanisms considered include: (1) π-complexes,[5a] (2) polyvalent species,[5b] and ion pairs. Although the possibility that sulfenyl halides may react via thiyl and halide radicals had been suggested some time ago,[1a] there are not many examples illustrating the involvement of free radicals in this reaction. Thus, no simple mechanistic picture can accommodate the observed results. However, it is generally agreed that the substitutents present on the norbornyl molecule influence the course of the reaction and the nature of the products formed. It has been said that the chlorine moiety of the sulfenyl chloride may play a "dual role"[4c] and thereby complicate the already complex situation. This is reflected in the observation that the reaction of norborneol with phenylsulfenyl chloride at -80° furnishes a tricyclic oxetane derivative as the primary product[6a] and can be considerably enhanced by the presence of added $LiClO_4$ in the reaction mixture.[6b] Along with furnishing the addition products, F_3CSCl has been stated to cause skeletal rearrangements of the norbornene system.[6c]

In continuation of our interest in the chemistry of the trifluoromethylthio group,[7] and as part of an ongoing project,[7i] the reaction of norbornene (**2**) with trifluoromethylsulfenyl chloride (**3**) was examined and found to furnish (trifluoromethylthio)tricyclene (**1**) and four isomeric (chloro) (trifluoromethylthio)nor-bornanes (**4**, **5**, **6**, and **7**) and bis-(2,6-trifluoromethylthio)norbornane (**8**), respectively (Figure 1). The probable mechanism of formation and the mass spectral characterization of compounds cited in the text are described in this article.

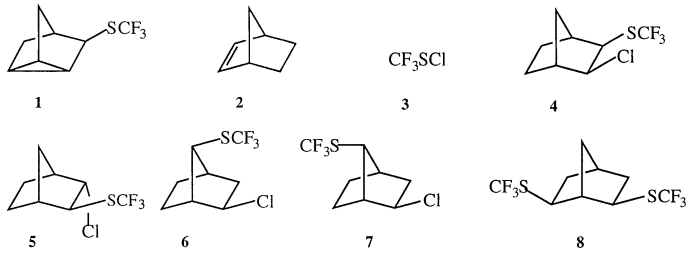
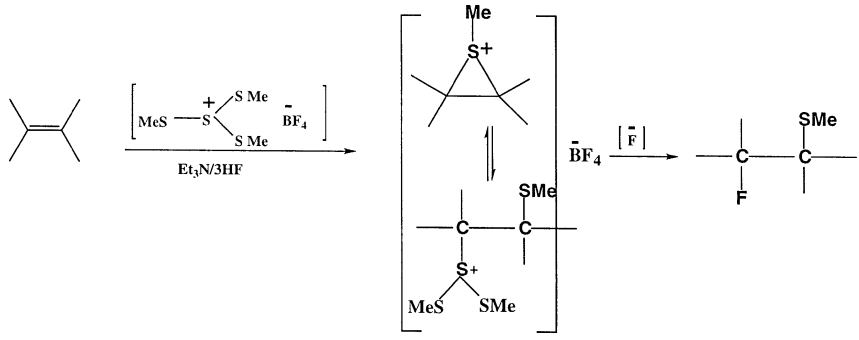


FIGURE 1 Structures of compounds cited in the narrative.

RESULTS AND DISCUSSION

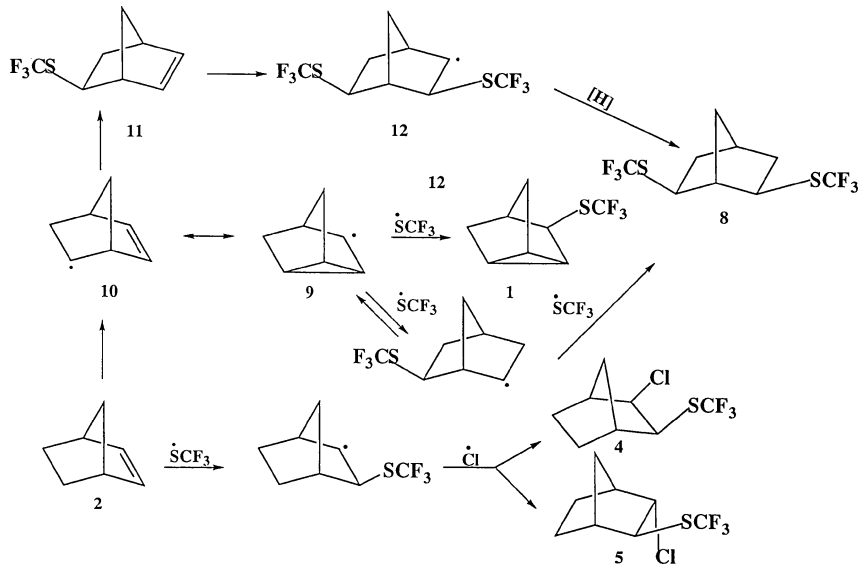
The addition of F_3CSF to methyl- and (trifluoromethyl)ethylenes has been reported.[8] The reaction of dimethyl(methylthio)sulfonium fluoroborate (DMTSF) and $Et_3N/3HF$ with alkenes in CH_2Cl_2 has been shown to give β-fluoroalkylmethylthioethers via cyclic sulfonium intermediates (Scheme 1).[9a] Treatment of 1,5-cyclooctadiene with DMTSF has been stated to yield 1-fluoro-2-methylthio-5-cyclooectene and bis-(1,2-methylthio)-5-cyclooctene.[9a] Although the authors have not said anything about the mechanism of formation of bis-(1,2-methylthio)-5-cyclooctene, it does not appear to go through the cyclic sulfonium intermediates.



SCHEME 1 Addition via cyclic sulfonium intermediate.

A slow isomerization of threo- and erythro-2-fluoro-3-methylthiobutanes on standing has been reported to furnish stable trans- and cis-1-fluoro-1,2,3-trimethylepisulfurane.[9b] Addition reactions of norbornene have attracted considerable attention over the past 40 years.[4,10a,b] Bromine[10c,d] and sulfenyl halides[10e,f] have been reacted with norbornene. In the former case, the reaction is said to involve free

radicals, while in the latter case cyclic episulfonium intermediates have been implicated. The treatment of norbornene with t-butylhypochlorite, a low-temperature free-radical generator, yields products arising from substitution as well as addition reactions, namely chloronortricyclane, 2-chloronorbornene, and isomeric endo-2-chloro- and exo-2-chloro-3-butoxynorbornanes.[11a] These compounds are said to arise from the resonance radical intermediates (cf. **9**, **10**; Scheme 2), originally suggested by Roberts and coworkers.[11b] Also, free-radical additions to bridged ring systems appear to be nonspecific, in that both cis- and trans-adducts have been characterized.[12]



SCHEME 2 Formation of products via free radical reactions.

In this context, it is worth mentioning that the photochemical addition of thiophenol to norbornene has been described to give primarily the exo-norbornyl phenylsulfide.[13] The addition of CCl_4 in the presence of benzoyl peroxide yielded endo-2-chloro-exo-3-triclormethylnorbornane as the major product, while the exo, exo-adduct was a minor compound.[14] But with $BrCCl_3$ and C_3F_7I, only the trans-adducts were obtained.[12b] While torsional strain as well as hyperconjugation have been implicated,[12c,12g] steric and electronic effects are said not to play any part[12d] in these reactions. An explanation for these observed differences and anomalies has been provided.[13b]

In connection with another project,[7i] (trifluoromethylthio)nortricyclane (**1**) was needed. Reaction of norbornene (**2**) with F_3CSCl (**3**)

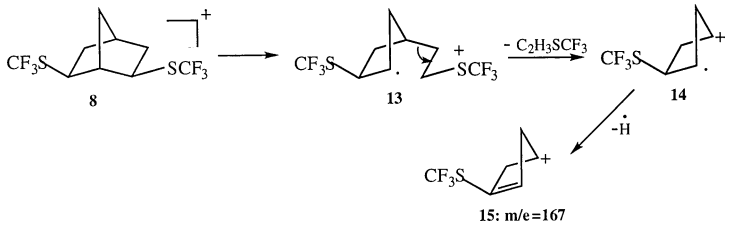


FIGURE 2 Mass spectral fragmentation of Bis-$(SCF_3)_2$ norbornane.

in dry pentane at −80°C furnished six compounds containing the F_3CS moiety (Figure 1). The formation of compound **1** can be ascribed to the reaction of the F_3CS radical with the nortricyclenyl radical (**9**) (Scheme 2). Compounds **4** and **5** arise from the addition of the thiyl and chlorine radicals across the double bond. However, the formation of compounds **6** and **7** appears to involve rearrangements of the free radical intermediates. The formation of compound **8** has a precedent in the free-radical chlorination of nortricyclane.[10a] The structure of compound **8** was deduced from its mass spectral fission (Figure 2). The genesis of this compound apparently involves free-radical processes. Thus, the reaction of the thiyl radical (F_3CS) with one of the resonance hybrids, norbornenyl radical (**10**) gives (F_3CS)norbornene (**11**), which leads to exo, exo-bis-(2, 6-trifluoromethylthio)norbornane (**8**) via the addition of another thiyl radical followed by hydrogen abstraction by **12** from the solvent. This process does not appear to involve the cyclic sulfonium intermediates. The participation of resonance hybrids **9** and **10** and intermediates **9** and **12** in the overall reaction has been previously postulated.[10a–g]

Reaction of molecular chlorine with norbornene gives chloronortricyclane, exo-2-syn-7-dichloro-, exo, exo-2, 3-dichloro-, and endo-2-exo-3-dichloro-norbornanes.[10a] The last two compounds are also obtained from the photoreaction of the substrate with iodobenzene dichloride.[10g] Both hydrogen abstraction by radicals and addition to the double bond have been implied in the free-radical reaction of norbornene.[10a] This means that there is competion between the free-radical processes and the ionic reactions in the bridged bicyclic compounds. A similar suggestion has been made by Tobler et al.[11a] While fluorination of norbornene (**2**) with XeF_2 furnishes exo, exo 2, 5-difluoronorbornane, exo-2-endo-5- difluoronorbornane, and 2, 7-difluoronorbornane,[11c] fluorination and halo-fluorination in the presence of polymer-supported HF have been reported to give five compounds.[11]

The mass spectral fragmentation of compounds (cf. Table I) exhibits features similar to those observed in the mass spectra of norbornyl derivatives.[15] The structure of compound **1** was deduced using

TABLE I Mass Spectral Fragmentation of Compounds Described in the Text

Mass spectral fragmentation of Norbornene **(2)**: $M^+ = 94$; 79 (M—CH_3); 67 (C_5H_7); 66 (C_5H_6,100%); 53 (C_4H_5); and 51 (C_4H_3). This has already been described.[14c]

Mass spectral fragmentation of (Trifluoromethylthio)tricyclene **(1)**: $M^+ = 194$ (60%); 166 (M—C_2H_4); 125 (M—CF_3); 97 (166-CF_3); 93 (M—SCF_3, 100%); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 66 (C_5H_6); 58 (C_2H_2S); and 51 (C_4H_3). This has been briefly described.[6c]

Mass spectral fragmentation of exo-2-Chloro-exo-3-(trifluoromethylthio)bicyclo-[2.2.1] heptane **(4)**: $M^+ = 230$ [$^{37}Cl = 232$]; 195 (M—Cl); 181 ($C_7H_8F_3S$); 161 (M—CF_3, 100%); 155 ($C_5H_6F_3S$); 141 ($C_4H_4F_3S$); 129 (M—SCF_3); 125 (M—CF_3-HCl); 115 (CH_2SCF_3); 101 (SCF_3); 97 (125-C_2H_4); 93 (129-HCl or C_7H_9); 91 (C_7H_7); 79 (C_6H_7); 68 (C_5H_8); 67 (C_5H_7); 59 (C_2H_3S); and 53 (C_4H_5).

Mass spectral fragmentation of endo-2-Chloro-exo-3-(trifluoromethylthio)bicyclo-[2.2.1] heptane **(5)**: $M^+ = 230$ [(30%), [($^{37}Cl = 232$)]; 211 (M—F); 195 (M—Cl); 161 (M—CF_3, 100%); 129 (M—SCF_3, < 6%); 125 (M—CF_3—HCl); 115 (CH_2SCF_3); 93 (129-HCl); 79 (C_6H_7); 77 (C_6H_5); 69 (CF_3); 67 (C_5H_7); and 53 (C_4H_5).

Mass spectral fragmentation of exo-2-Chloro-7-syn-(trifluoromethylthio)bicyclo-[2.2.1] heptane **(6)**: $M^+ = 230$ [(70%), ($^{37}Cl = 232$)]; 161 (M—CF_3); 129 (M—SCF_3, 100%); 115 (CH_2SCF_3); 93 (C_7H_9); 91 (C_7H_7); 79 (C_6H_7); 69 (CF_3); 67 (C_5H_7); 59 (C_2H_3S); and 53 (C_4H_5).

Mass spectral fragmentation of exo-2-Chloro-7-anti-(trifluoromethylthio)bicyclo-[2.2.1] heptane **(7)**: $M^+ = 230$ [$^{37}Cl = 232$]; 211 (M—F); 194 (M—HCl); 166 (194-C_2H_4); 161 (M—CF_3, 100%); 141 ($C_3H_4SCF_3$); 129 (M—SCF_3); 125 (161-HCl); 101 (SCF_3); 97 (C_5H_5S); 91 (C_7H_7); 77 (C_6H_5); 69 (CF_3); and 53 (C_4H_5).

Mass spectral fragmentation of exo, exo-Bis-(2, 6-trifluoromethylthio)bicyclo-[2.2.1] heptane **(8)**: $M^+ = 296$; 227 (M—CF_3); 195 (M—SCF_3); 167 ($C_5H_6SCF_3$); 93 (195-$HSCF_3$, 100%); 91 (C_7H_7); 79 (C_6H_7); 69 (CF_3); 67 (C_5H_7); 59 (C_2H_3S); and 53 (C_4H_5).

the rationale similar to that described in the mass spectral fission of nortricyclane.[15f] Ions with m/e = 79, 77, 55, 53, and 51 have been recorded in the mass spectral fission of chloronorbornane and other norbornyl and bicyclononane derivatives.[15a,b,f,i] The structural assignment of **5** is based on the intensity of the peak at m/e = 129 (M—SCF_3, <6%), while the intensity of the same peak in the case of its isomer **4** is 48%.[16] Compound **7** was assigned its structure based on the facile loss of HCl and the fragmentation of the SCF_3 moiety to yield ions m/e = 194 and 161, respectively. Figure 2 describes the fragmentation of compound **8**.

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 × 0.25 mm. i.d. DB-5 capillary column (J and W Scientific, Folsom, CA, USA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.25 mm. i.d. Rtx-5 capillary column (Restek, Bellefonte, PA, USA). 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 gas chromatograph (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, USA).

Reaction of Norbornene (2) with Trifluoromethanesulfenyl Chloride (3)

To norbornene (**2**, 5 g) in freshly distilled dry n-pentane (25 ml), stoichimetric amounts of trifluoromethanesulfenyl chloride (**3**) were added via the vacuum line at −78°C with stirring, under argon. The reaction mixture was stirred at −78°C for additional 2 hz 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 seven components. Attempts to fractionate the mixture to separate the components via vacuum distillation were not successful. However, the GC-MS analysis of the reaction mixture indicated the presence of seven compounds: (1) norbornene (**2**, $M^+ = 94$, 16%, r.t. = 1.53 min); (2) (trifluoromethylthio)tricyclane (**1**, $M^+ = 194$, 56%, r.t. = 3.43 min); (3) exo-2-chloro-exo-3-(trifluoromethylthio)bicyclo[2.2.1]heptane (**4**, $M^+ = 230$, 12%, r.t. = 5.17 min); (4) endo-2-chloro-exo-3-(trifluoromethylthio) bicyclo[2.2.1]heptane (**5**, $M^+ = 230$, 4%, r.t. = 5.34 min); (5) exo-2-chloro-7-syn-(trifluoromethylthio)bicyclo-[2.2.1]heptane (**6***, $M^+ = 230$, r.t. = 5.43 min); (6) exo-2-Chloro-7-anti-(trifluoromethylthio)bicyclo [2.2.1]heptane (**7**, $M^+ = 230$, 9%, r.t. = 6.11 min) and (7) exo, exo-Bis-(2,-6-trifluoromethylthio)-bicyclo[2.2.1]heptane (**8***, $M^+ = 296$, r.t. = 5.41 min). The presence of compounds **6** and **7** and endo-2-chloro-exo-3-(trifluoromethylthio)bicyclo[2.2.1]heptane inthe reaction mixture has been detected using NMR, and these isomers are said to be rather difficult to separate using vacuum distillation.[6c] Table I gives the mass spectral breakdown of the compounds cited in the text.

*Compounds **6** and **8** co-elute and together form 2% of the yield.

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