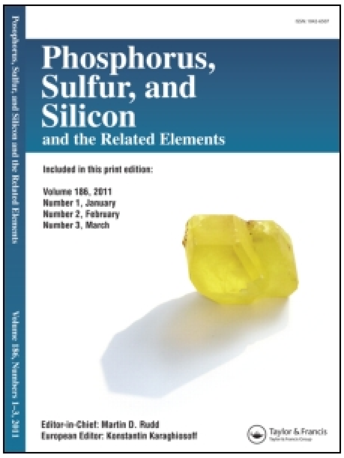

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S. Munavalli[a]; D. K. Rohrbaugh[b]; F. J. Berg[b]; L. R. McMahon[b]; F. R. Longo[a]; H. D. Durst[b]
[a] Gunpowder Branch, Geo-Centers, Inc., Maryland [b] Edgewood Chemical Biological Center, U.S. Army, Maryland

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REACTIONS OF TRIFLUOROMETHYLSULFENYL CHLORIDE WITH 1,5-CYCLOOCTADIENE

S. Munavalli,[1] *D. K. Rohrbaugh,*[2] *F. J. Berg,*[2] *L. R. McMahon,*[2]
F. R. Longo,[1] *and H. D. Durst*[2]
Geo-Centers, Inc., Gunpowder Branch, Aberdeen Proving Ground, Maryland[1] *and U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, Maryland*[2]

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The reaction of 1,5-cyclooctadiene with F_3CSCl at –80°C has been examined and found to furnish both di- and tetrasubstituted adducts. Their mass spectra show the presence of the intact cyclooctyl ring. However, photolyis of a solution of 1,5-cyclooctadiene and F_3CSCl in dry pentane yields addition, isomerization and dimerization as well as free radical products. The rationalization of the formation of the above products along with their mass spectral characterization is described in this communication.

Keywords: Adduct formation; cyclooctadiene; dimerization; free radical reaction products; isomerization; trifluoromethylthiolation

INTRODUCTION

Cyclooctadienes comprise a group of geometrically interesting molecules and often have been used as substrates in a variety of synthetic reactions and in the study of ring strain concepts and considerations. While addition reactions to the carbon–carbon double bonds have yielded simple and transannular bicyclic adducts resulting from the participation of the π-bonds, the photochemical reaction has furnished mono-, di-, and tricyclic hydrocarbons. Since the pioneering investigations of Kharasch, electrophilic addition reactions of sulfenyl halides to π-bonds have been rather well studied.[1] The course of the addition reaction is said to be influenced by the nature of the solvent.[2] The addition appears to go through a two-step process in polar solvents. In

Address correspondence to S. Munavalli, Geo-Centers, Inc., PO Box 68, Gunpowder Branch, Aberdeen Proving Ground, MD 21010. E-mail: sxmunava@SBCCOM.apgea.army.mil

nonpolar solvents and in the absence of ionic intermediates, molecular rearrangements are not usually observed. The reaction has been said to be unaffected by the substituents.[2b] This observation has been contradicted by several authors to the effect that steric factors, in fact, affect the nature of the products formed.[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 SCF-MO calculations.[3]

With pseudohalogens such as NCO, N_3, NO_3, and so on, 1,5-cyclooctadiene (**1**) gives 1,2-monoadducts.[4a–b] No di-adducts were detected in this reaction. So does the addition of the thiols.[4c] Similar 1,2-adduct formation was seen when **1** was reacted with $Me_2S(SO_3)$ and $Me_3S^+(SMe)BF_4^-$ and $NaN_3/MeNO_3/Me_2S$.[4d–e] The treatment of 1,5-cyclooctadiene (**1**) with Cu(II)Cl_2 and LiCl in acetonitrile yields both cis and trans 1,2-dichloro-5,6-cyclooctenes.[5a] The reaction of 1,5-cyclooctadiene (**1**), however, with Br_2 in CH_2Cl_2 yields 1,2-dibromo-5-cyclooctene (95% yields).[5b] A similar reaction with Cl_2 at –30°C gave 1,2-dichloro-5-cyclooctene along with bicylco[3.3.0]octane and -octene. When the solvent was changed to acetonitrile, the only product obtained was 1,4-dichlorobicyclo[3.3.0]octane (90%). Chlorination of **1** with Cu(II)Cl_2 yielded a mixture of four isomeric dichlorocyclooctenes arising from both 1,2- and 1,4-additions.[5c–d] It has been stated that "tetrachlorocyclooctane was not formed from 1,5-cyclooctadiene under any conditions."[5d] The reaction of 1,5-cyclooctadiene (**1**) with antimony(V)Cl_5 in CCl_4 resulted in a mixture of exo- and endo-2-anti-8-dichloro-bicyclo[3.2.1]octanes.[6] However, the treatment of **1** with Br_2 in CCl_4 furnishes in addition to the dibromocyclooctene, a pair of diastereomeric tetrabromocyclooctanes.[7] Based on the x-ray crystallographic structure determination the tetrabromo-derivative (m.p. 137–138°C) was assigned the trans-syn-trans conformation.[8] By analogy, the lower melting isomer was given the trans-anti-trans conformation.[9] Iodine smoothly reacts with 1,5-cyclooctadiene (**1**) to effect solvent dependent transannular cyclization to form a pair of di-iodo bicyclo[3.3.0]octanes.[10] Similar transannular product formation was observed when 1,5-cyclooctadiene (**1**) was treated with thallium(III)trifluoroacetate to give cis-bicyclooctenyl acetates.[11] Trichloromethyl-bicyclo[3.3.0]octane was formed upon the addition of benzoyl peroxide to a solution of **1** in chloroform.[12]

In general, the peroxide catalyzed reactions of 1,5-cyclooctadiene (**1**) appear to furnish mainly bicyclo[3.3.0]octanes, arising from transannular reactions.[13a–c] However, the treatment of 1,5-cyclooctadiene (**1**) with

$(CH_3)_3SnH$ in the presence of AIBN was reported to form bicyclo[3.3.0]- and -[4.2.0]octanes as well as cyclooctenyl derivatives.[13d] The photolysis of 1,5-cyclooctadiene (**1**) has provided quite interesting results. Mercury sensitized vapor phase photolysis of 1,5-cyclooctadiene (**1**) gave bicyclo[5.1.0]octene-3; 1,3-cyclooctadiene; 1,4-cyclooctadiene and bicyclo[4.2.0]octene-7.[14a] Experiments using deuterated substrate[15] do not support the free radical mechanism advanced to account for the formation of the said products.[15c] Photoisomerization of 1,5-cyclooctadiene (**1**) in vapor phase using mercury sensitized reaction yielded tricyclo[3.3.0.0]octane and bicyclo[5.1.0]oct-3ene.[14e] Vapor phase as well as solution phase photolysis in the presence of Cu(II)Cl_2 gave tricyclanes as well as compounds mentioned above.[14a,b,f]

In continuation of our interest in the chemistry of the F_3CS-group,[15] the treatment at –80°C and photolysis of 1,5-cyclooctadiene (**1**) with trifluoromethylsulfenyl chloride (**2**) have been investigated and this paper describes the results thus obtained and the mass spectral characterization of the products formed.

RESULTS AND DISCUSSION

Cyclooctadienes are unique compounds, in particular 1,5-cyclooctadiene (**1**), which possesses molecular symmetry and ring strain. These two aspects have made this compound an unusual substrate. In continuation of our interest in the synthesis of organofluorine compounds,[15] we have examined the reaction of 1,5-cyclooctadiene (**1**) with F_3CSCl (**2**) both at –80°C and under photochemical conditions. There is nothing strange about the formation of trans-1-trifluoromethylthio-2-chloro-5-cyclooctenes (**3** and **4**) and there are precedents for this.[1–3,6] Pseudo-halogens also are known to react in a similar way.[4,13]

While the reaction at –80°C yields only one monocyclic adduct (either **3** or its stereomer **4**), the photochemical process furnishes two monocyclic adducts. One of these two isomers shows identical mass spectral fragmentation pattern and has the same retention time as the one obtained from the nonphotocatalyzed cold reaction. The photoadducts have been assigned structures **3** and **4**. The treatment of 1,5-cyclooctadiene (**1**) with Br_2 in CCl_4 has been stated to give a diastereomeric pair of tetrabromocyclooctanes.[6,7] Their structures stand firmly and unambiguously established.[7] What is surprising with our finding is the formation of four tetrasubstituted cyclooctane derivatives arising from bis-addition, namely **5–8**. Nothing comparable to this has been reported in the literature on this substrate. Structures **5** and **6** are

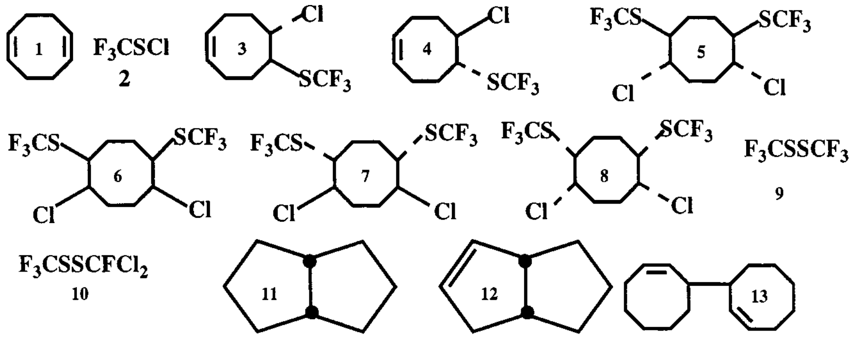

FIGURE 1 Structures of compounds cited in the text.

similar to the ones proposed for the two tetrabromocyclooctanes.[7] However, structures **7** and **8** are different. As far as the mass spectral fragmentation is concerned, the breakdown behavior of compounds **5** and **7** is identical. In the same vein, the mass spectral fragmentation of compound **5** is similar to that of compound **8** (Figure 1).

Compounds **9** and **10**, namely bis(trifluoromethyl)- and (dichlorofluoromethyl)(trifluoromethyl)disulfides, are the result of free radical reactions. The mechanism of formation and the mass spectra of these compounds have been already described.[16] Next to come off the column are two hydrocarbons with $M^+ = 110$ and 108. It was considered that they might have been formed from isomerization of 1,5-cyclooctadiene (**1**). There is ample evidence for such an isomerization of 1,5-cyclooctadiene (**1**) under photolytic and base catalyzed reaction conditions.[14,17] The compound with $M^+ = 110$ has been given the structure **11**, namely cis-bicyclo[3.3.0]octane. Its mass spectrum supports this inference. Several structures were considered for the compound with $M^+ = 108$ (Figure 2). The base catalyzed reaction of 1,5-cyclooctadiene (**1**) has been stated to give cis-bicyclo[3.3.0]oct-2-ene ($M^+ = 108$) along with the 1, 3- and 1,5-cyclooctadienes and 4-vinylcyclohexene (**15**, Figure 2).[17a] That **1** furnishes 9-oxabicyclo[3.3.1]nonane derivatives on treatment with electrophiles under a variety of reaction conditions is rather well know.[17b] The formation of the products is stated to be solvent and electrophile dependent. Halofluorination of 1,5-cyclooctadiene

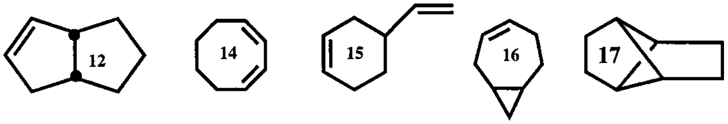

FIGURE 2 Potential candidates for compound 12.

(**1**) with tetrabutylammonium bifluoride yielded 1-fluoro-2-bromo- and 1,2-dibromo-5-cyclooctenes.[17c] But the treatment with dimethyl (methylsulfanyl)sulfonium tetrafluoroborate, followed by the reaction with triethylamine trihydrofluoride has been reported to give a stereospecific product, namely 1-fluoro-2-methylthio-5-cyclooctene.[17d] However, halofluorination using N-bromosuccinimde and triethylamine trihydrofluoride furnished a mixture of three compounds: 1-fluoro-2-bromo-5-cyclooctene and 2-bromo-6-fluorobicyclo-[3.3.0]cycloocatnes via transannular cyclization.[17e]

The mass spectrum of 1,5-Cyclooctadiene has been described.[18] 1,5-Cyclooctadiene is known to isomerize to 1,3-cyclooctadiene (**1**) under a variety of conditions. The mass spectra of bis-(trifluorometh1) disulfide[19a] and (dichlorofluoromethyl)disulfide (**10**) are known.[19b] Table I gives the mass spectral breakdown of the remaining compounds. In all, five structures **12**, **14**, **15**, **16**, and **17** were considered for the bicylooctene (Figure 2). By the way, compounds **14**, **15**, **16** and **17** have been identified as photoproducts arising from the substrate **1**.[14a,b,f] Compounds **16** and **17** have been characterized from mercury sensitized reaction of 1,5-cyclooctadiene (**1**), in the presence of Cu(II)Cl_2.[14c] Based on the mass spectral fragmenation behavior structure **11** was assigned to this component. The allylic radical intermediate (**18**), gives rise to the bicyclic radical intermediate (**19**) via transannular reaction, which abstracts hydrogen from the solvent to form **12**. Its probable mechanism of formation is described in Figure 3. The last component to come off of the chromatographic column has been given structure **13**. This is supported by its mass spectral data. The molecule splits off into two equal parts with m/e = 109, suggesting that 1,5-cyclooctadiene (**1**) undergoes photodimerization to yield (2-cyclooctenyl)-2-cyclooctene (**13**). The fomation of the dimerized product, **13**, from the substrate has precedents.[20]

EXPERIMENTAL

Care and caution should be exercised in working with trifluoromethylsulfenyl chloride. 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) 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 the 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 sec. The conditions on the TSQ-7000 were: oven temperature

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Text

1. 1,5-Cyclooctadiene (**1**): $M^+ = 108$ (r.t. = 3.52 min, 22.7%); 93 (M—CH_3); 91 (C_7H_7); 80 (M—C_2H_4); 79 (M—C_2H_5); 77 (C_6H_5); 67 (C_5H_7, 100%); 66 (C_5H_6); 55 (C_4H_7); 54 (C_4H_6) and 53 (C_4H_5)
2. 1-Chloro-2-trifluoromethylthio-5-cyclooctene (**3**): $M^+ = 244$ (r.t. = 7.05 min, 61.0%); 216 (M—C_2H_4); 175 (M—CF_3, 100%, ^{37}Cl seen); 139 (175-HCl); 105 (139-H_2S); 91 (C_7H_7); 69 (CF_3); 67 (C_5H_7); 59 (C_2H_3S) and 54 (C_4H_6)
3. 1-Chloro-2-trifluoromethylthio-5-cyclooctene (**4**): $M^+ = 244$ (r.t. = 6.88 min, 0.7%); 175 (M—CF_3, 100% ^{37}Cl seen); 139 (175-HCl); 115 (CH_2SCF_3); 105 (139-H_2S); 91 (C_7H_7); 79 (C_6H_7); 67 (C_5H_7); and 54 (C_4H_6)
4. 1,5-Dichloro-2,6-bis-(trifluoromethylthio)cyclooctane (**5**): $M^+ = 380$ (not seen, r.t. = 9.69 min, 4.2%); 345 (M—Cl); 311 (M—CF_3); 276 ((311-Cl); 275 (311-HCl, 100%); 243 (275-S); 209 ($C_8H_{12}SCF_3$); 175 (276-SCF_3); 141 ($C_8H_{13}S$); 115 (CH_2SCF_3); 105 (C_8H_9); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 65 (C_5H_5) and 53 (C_4H_5)
5. 1,5-Dichloro-2, 6-bis-(trifluoromethylthio)cyclooctane (**6**): $M^+ = 380$ (r.t. = 9.74 min, 3.0%); 345 (M—Cl); 311 (M—CF_3); 275 ((311-HCl); 243 (275-S); 209 (311-$HSCF_3$, 100%); 175 (209-H_2S); 147 (175-C_2H_4); 141 ($C_8H_{13}S$); 128 (243-CH_2SCF_3); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 69 (CF_3); 65 (C_5H_5) and 53 (C_4H_5)
6. 1,5-Dichloro-2,6-bis-(trifluoromethylthio)cyclooctane (**7**): $M^+ = 380$ (not seen, r.t. = 10.13 min, 5.2%); 345 (M—Cl); 311 (M—CF_3); 276 ((311-Cl); 275 (311-HCl, 100%); 243 (275-S); 209 ($C_8H_{12}SCF_3$); 175 (276-SCF_3); 141 ($C_8H_{13}S$); 115 (CH_2SCF_3); 105 (C_8H_9); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 65 (C_5H_5) and 53 (C_4H_5)
7. 1,5-Dichloro-2,6-bis-(trifluoromethylthio)cyclooctane (**8**): $M^+ = 380$ (r.t. = 10.17 min, 3.9%); 345 (M—Cl); 311 (M—CF_3); 275 ((311-HCl); 243 (275-S); 209 (311-$HSCF_3$, 100%); 175 (209-H_2S); 147 (175-C_2H_4); 141 ($C_8H_{13}S$); 128 (243-CH_2SCF_3); 91 (C_7H_7); 79 (C_6H_7); 77 (C_6H_5); 69 (CF_3); 65 (C_5H_5) and 53 (C_4H_5)
8. Bis-(trifluoromethyl)disulfide (**9**): $M^+ = 202$ (100%) (r.t. = 1.42 min, 1.2%); 183 (M—F); 133 (M—CF_3); 114 (183-CF_3); 101 (SCF_3); 69 (CF_3) and 64 (SS)
9. (Dichlorfluoromethyl)(trifluoromethyl)disulfide (**10**): $M^+ = 234$ (r.t. = 2.18 min, 0.5%); 199 (M—Cl); 133 (M—SCF_3); 117 (199-CSF_2); 101 (SCF_3, 100%); 82 (CSF_2) 69 (CF_3) and 63 (CSF)
10. Bicyclo[3.3.0]octane (**11**): $M^+ = 110$ (r.t. = 4.27 min, 0.4%); 109 (M—H); 108 (109-H); 95 (M—CH_3); 94 (M—CH_4); 92 (94-2H); 82 (M-C_2H_4); 81 (M-C_2H_5); 77 (C_6H_5); 69 (C_5H_9); 67 (C_5H_7); 56 (C_4H_8, 100%); 54 (C_4H_6); 54 and 53 (C_4H_5)
11. Bicyclo[3.3.0]2-octene (**12**): $M^+ = 108$ (r.t. = 4.72 min, 0.4%); 107 (M—H, 100%); 92 (107-CH_3, 99%), 80 (C_6H_8); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 65 (C_5H_5); 55 (C_4H_7) and 52 (C_4H_4)
12. (Cyclooctenyl)cyclooctene (**13**): $M^+ = 218$ (r.t. = 11.63 min, 2.7%); 109 (C_8H_{13}, 100%); 94 (109)-CH_3); 82 (C6H10); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7) and 53 (C_4H_5)

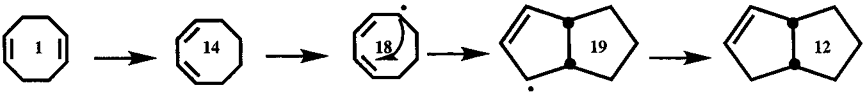

FIGURE 3 Probable mechanism of formation of bicyclooctene.

60–270°C at 15°C/min, injection temperature 220°, interface temperature 250°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 sec. 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 1,5-Cyclooctadiene (1) with Trifluoromethylsulfenyl Chloride (2)

Stoichiometric amounts of trifluoromethylsulfenyl chloride (**2**, 1.36 g, 0,01 mmol) were added via the vacuum line to a solution of 1,5-cyclooctadiene (**1**, 1.08 g, 0.01 mmol) in dry pentane at –80°C with stirring under a blanket of nitrogen. The reaction mixture was stirred at –80°C for 2 h, allowed to come to room temperature with stirring and then stirred overnight at ambient temperature. The reaction mixture was first analyzed by GC. The GC-MS analysis of the product after the solvent had been evaporated at reduced pressure permitted the characterization of 1-trifluoromethylthio-2-chloro-5-cyclooctene (**3**) and two pairs of bis(trifluoromethylthio) dichlorocycloocatnes (**5–8**, Figure 1).

Photolysis of 1,5-Cyclooctadiene (1) with Trifluoromethylsulfenyl Chloride (2)

Stoichiometric amounts of trifluoromethylsulfenyl chloride (**2**, 1.36 g, 0,01 mmol) were added via the vacuum line to a solution of 1,5-cyclooctadiene (**1**, 1.08 g, 0.01 mmol) in dry pentane contained in a three-necked flask fitted with a reflux condenser carrying the dry-ice/acetone device at –80°C with stirring under a blanket of nitrogen. The reaction mixture was allowed to come to room temperature and then exposed to ultraviolet light for 1 h using a GE 100 W mercury lamp. The reaction mixture was cooled to room temperature and the GC analysis indicated it to consist of seven compounds. The

GC-MS analysis of the reaction product permitted the characterization of bis(trifluoromethyl)disulfide (**9**), (trifluoromethyl)(dichlorofluoromethyl)disulfide (**10**), 1-trifluoromethylthio-2-chloro-5-cyclooctenes (**3** and **4**), a pair of bicyclic hydrocarbons (**11** and **12**) and a dimerized product (**13**, Figure 1).

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