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TRIFLUOROMETHYLTHIOLATION OF 1, 3- AND 1, 4-CYCLOHEXADIENES

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Treatment of 1, 3-cyclohexadiene with CF₃SCl at –80° furnishes 15 compounds. All but the two dimerized adducts arise from the free radical catalyzed addition of CF₃S and Cl radicals to carbon-carbon double bonds. One dimerized product arises via dimerization of the substrate itself, while the other results from the cross-coupling of the substrate with the reaction product. The same reaction with 1, 4-cyclohexadiene gives 14 compounds. The mass spectral characterization of various compounds and their probable mechanism of formation are presented in this article.

Keywords: Addition and dimerization reactions; cyclohexadienes; trifluoromethylthiyl and chlorine radicals

INTRODUCTION

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 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 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 investigated.^{2b} Although it is widely considered that cyclic episulfonium ions are involved

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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

Acid catalyzed hydration of conjugated dienes using D₂O in the presence of D₂SO₄ has been shown to give the 1, 2-adduct only.^{4a} However, acyclic alkadienes such as substituted butadienes yield allylic alcohols from both 1, 2- and 1, 4-additions.^{4b} The addition of dimethyl(methylthio)-sulfoniumtetrafluoroborate and triethylamine to alkenes in CH₂Cl₂ is said to furnish β -fluoro-alkylmethylthioethers.^{5a} This reaction has been stated to proceed via a cyclic sulfonium ion intermediate.^{5b} In the case of conjugated cycloienes such as 1, 3-cyclohexadiene (**1**, **3-CHD**), three isomeric fluorocyclohexenyl methyl-sulfides resulting from both 1, 2- and 1, 4-adducts were obtained, although the 1, 2-adduct was the major product.^{5c} The 1, 4-addition products have been described as the "allylic rearrangement products." However, with other modes of sulfenylation, no such rearrangements were observed.^{5d-e} The reaction of DBr with 1, 3-CHD gave 85% of the allylic bromide and both 1, 2-anti and 1, 4-syn adducts were formed before the rearrangement occurred.^{5f}

In general, conjugated systems usually involve competition between 1, 2- and 1, 4-additions and the present results appear to reflect this observation.

1, 3-CHD has been reported to undergo facile hydrocarboxylation in the presence of transition metal catalysts.^{6a} Recently hydrophosphorylation of cyclic and acyclic alkenes and alkadienes has been carried at 100°C in the presence a Pd-complex catalyst and found to give quantitative yields of 1, 4-adducts.^{6b} Addition of phenylsulfenyl chloride to 1, 3-CHD and 1, 4-CHD has been found to give the 1, 2-adducts only.^{6c-d} In the presence of rhuthenium carbonate, 1, 3-CHD was found to undergo transformation to benzene, 1, 4-CHD and cyclohexene.^{7a} Low valent tertiary phosphine-zirconium complexes are stated to cause disproportionation of 1, 3-CHD to benzene and cyclohexene.^{7b} Regio- and stereoselective 1, 4-hydroxylation of 1, 3-CHD and 1, 3-cyclooctadiene in the presence of Pd(II) acetate also has been recorded.^{7c-f} A common transient cyclohexadienyl radical has been observed during the laser flash photolysis of both 1, 3- and 1, 4-CHD.^{8a} Addition of metal hydrides to dienes has been reported to proceed via free radical reactions.^{8b} On exposure to UV light, 1, 3-CHD gave cis-2-cyclohexene-1, 4-diol in the presence of O₂, rose bengal, thiourea, and methanol at room temperature.^{8c} 1, 3-CHD has been shown to undergo thermal dimerization when autoclaved at 178 to 186°C for 24 h to give dicyclohexadiene.^{9a} The products of thermal dimerization have been reported to contain 1, 3- and 1, 4-CHD, and benzene.^{9b} The treatment of **1** with a mixture

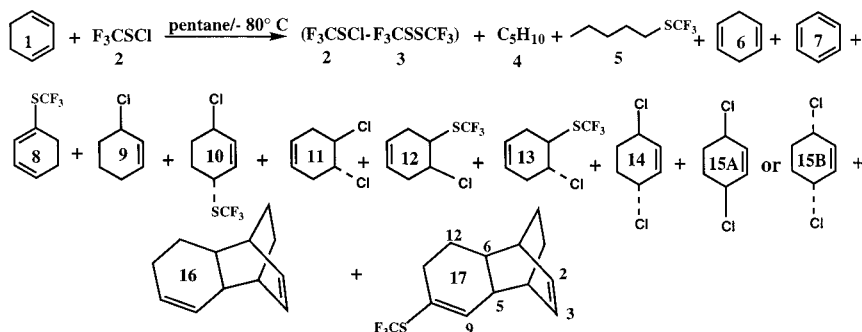


FIGURE 1 Structures of compounds derived from 1, 3-cyclohexadiene.

of acetic acid and lithium acetate in the presence of LiCl has been reported to yield 1,4-diacetyl-2-cyclohexene.^{10a} 1,4-Cyclohexadiene with bis(pyridine)iodonium (I) tetrafluoroborate furnished trans-1-fluoro-2-iodo-4-cyclohexene.^{10b} However, the reaction of 1,4-CHD (**6**) with KMnO₄, followed by the treatment with acetone dimethyl acetal has been reported to yield a 1,3-CHD derivative.^{10c}

In continuation of our interest in the synthesis of biologically potent organofluorine compounds and in the chemistry of the trifluoromethylthio group,¹¹ the reaction of 1, 3-CHD (Figure 1) and 1, 4-CHD (Figure 2) with F₃CSCl at -80°C has been examined and found to furnish unusual compounds. This article describes the probable mechanism of their formation and mass spectral characterization.

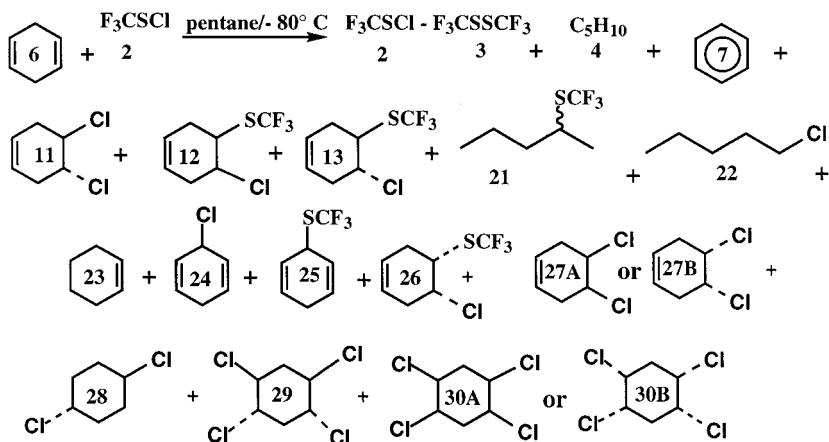


FIGURE 2 Structures of compounds derived from 1, 4-cyclohexadiene.

RESULTS AND DISCUSSION

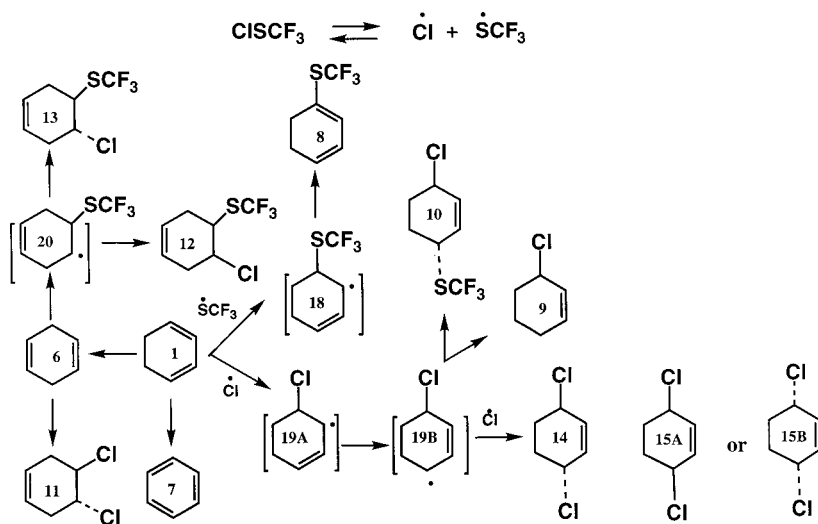
The addition of F_3CSF to methyl- and (trifluoromethyl)ethylenes has been reported.¹² The reaction of dimethyl(methylthio)sulfonium fluoroborate (DMTSF) and $Et_3N/3HF$ with alkenes in CH_2Cl_2 has been said to give fluoroalkylmethyl-thioethers via cyclic sulfonium intermediates.^{12a} Treatment of 1,5-cyclooctadiene with DMTSF has been stated to yield 1-fluoro-2-methylthio-5-cyclooctene and bis-(1,2-methylthio)-5-cyclooctene.^{13a} Although the authors have not said anything about the mechanism of formation of bis-(1,2-methylthio)-5-cyclooctene, it does not seem to involve the cyclic sulfonium intermediates. 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.^{13b}

Since cyclohexadienes exhibit great propensity to various types of addition and substitution reactions, they have attracted considerable attention. Both 1, 3- and 1, 4-CHD undergo facile isomerization and dehydration to benzene.¹⁴ Mass spectra of 1, 3- and 1, 4-CHD have been described.¹⁵ In fact, both 1, 3- and 1, 4-CHD have been reported to furnish the same dimerization product, namely dicyclohexadiene.¹⁶ The reactivity of 1, 3-CHD has been attributed to the non-planarity of the conjugated diene system and the stability of the radicals thus formed¹⁷ and to the rearrangement of the radicals.

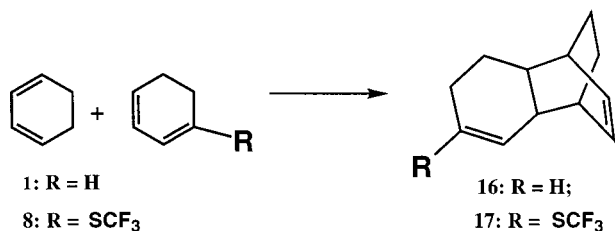
The reaction of 1, 3-CHD (**1**, Figure 1) with F_3CSCl (**2**) gives 15 compounds. Bis-(trifluoromethyl)disulfide (**3**) is formed by the dimerization of the respective thiyl radical. Pentene (**4**), 1-trifluoromethylthiopentane (**5**, cf. Scheme 3), 1, 4-CHD (**6**) and benzene (**7**) were readily detected. Pentene (**4**) arises from pentane, the solvent used in the reaction. There are precedents for the formation of **6** and **7** from **1**.^{7,9b} 1-(Trifluoromethylthio)-1, 3-CHD (**8**) is formed from the addition of the $F_3CS\cdot$ radical to the carbon-carbon double bond, followed by the loss of hydrogen. Compound **9** is formed by the addition of the $Cl\cdot$ radicals, followed by the migration of the double bond and hydrogen abstraction. Also detected was compound **5**, although in trace amounts. 1-Chloro-4-(trifluoromethylthio)-2-cyclohexene (**10**) can be considered to have arisen from a common precursor, namely the 4-chloro-2-cyclohexenyl radical (**19B**, Scheme 1), which can abstract a hydrogen to give **9** or react with the thiyl radical to yield **10** (Figure 1). 1, 2-dichloro-4-cyclohexene (**11**) is formed by the addition of the $Cl\cdot$ radicals to the double bond of 1, 4-CHD (**6**), which is itself obtained from the isomerization of the substrate during the reaction. The same intermediate (**19B**) can also add $Cl\cdot$ radical to give dichlorocyclohexenes (**14** and **15A**). It is possible that **15A** could be **15B**, for it is not always

possible to distinguish two isomers or stereoisomers from their mass spectral breakdown. Compounds **12** and **13** (Figure 1) have a common origin, namely **20**. Their formation can be rationalized as being formed from the addition of the thiyl and chlorine radicals to 1, 4-CHD (**6**), which is formed via the isomerization of **1**. There are precedents for such an isomerization.^{7a} Cyclohexenylbicyclo[2.2.2]octene (**16**) arises via the dimerization of 1, 3-CHD (**1**). This compound has been previously described.^{6,9} Compound **17** is due to cross-coupling or addition of 1, 3-CHD (**1**) and 1-(trifluoromethylthio)-1, 3-CHD (**8**). Scheme 2 describes the origin of **16** and **17**, while Scheme 1 summarizes probable mechanism of formation of compounds cited in Figure 1.

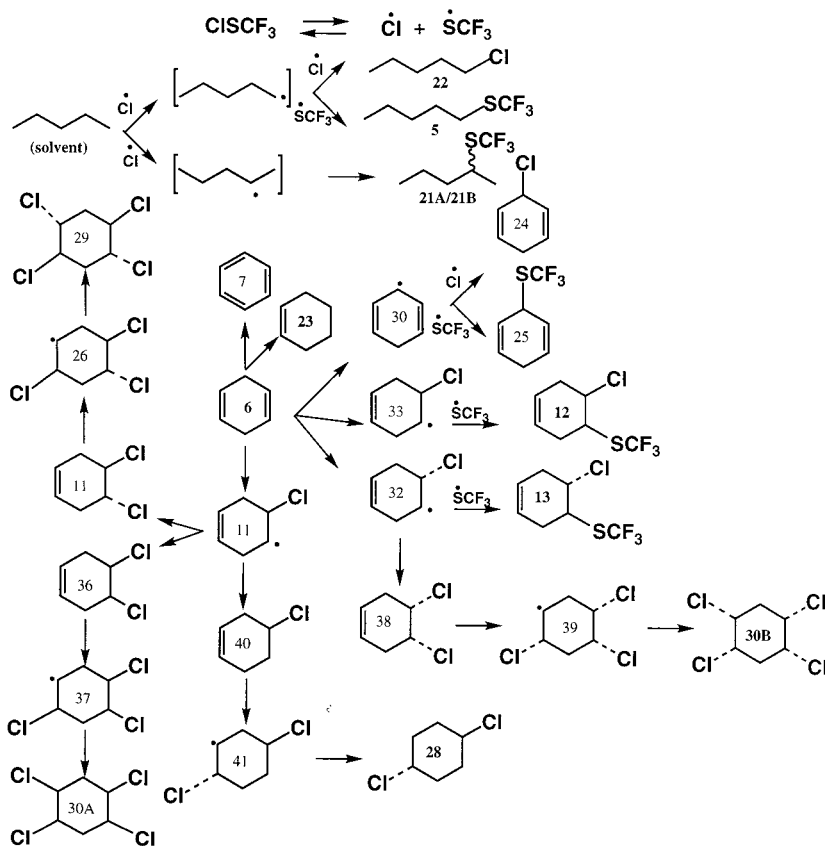
1, 4-CHD (**6**, Figure 2), on the other hand, furnishes 14 compounds when treated with F_3CSCl (**2**) at -80°C . Of the 14 compounds, four compounds (**4**, **21A/21B**, and **22**) arise from the reaction of F_3CSCl (**2**) with



SCHEME 1 Probable mechanism of formation of compounds cited in Figure 1.



SCHEME 2 Formation of the dimerized products.



SCHEME 3 Probable mechanism of formation of compounds cited in Figure 2.

the solvent itself. There are several precedents for this observation.¹¹ Bis(trifluoromethyl)disulfide (**3**) results from the dimerization of the trifluoromethylthiyl radicals. Its formation and mass spectral fragmentation have been described.^{11f} Benzene (**7**) and cyclohexene (**23**) are readily formed from **1** and are easily detected by GC-MS. There are precedents for the formation of these compounds from **1**.^{7,14} 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**12** or **13**) is obtained from the addition of the chlorine and trifluoromethylthiyl radicals, while the addition of the chlorine radicals leads to 1, 2-dichloro-4-cyclohexene (**11**). Compounds **23** and **24** have their origin in the transient cyclohexadienyl radical (**30**), the existence of which has been documented.⁸ This radical reacts with the chlorine and trifluoromethylthiyl radicals to yield compounds **24** and **25** respectively. The tentative structure assigned to

TABLE I Mass Spectral Fragmentation of Compounds Cited in Figure 1^a

1. 1, 3-Cyclohexadiene (**1**, *rt* = 1.9 min, 47.8%): $M^+ = 80$.
2. Trifluoromethylsulfenyl chloride (**2**) and Bis-(trifluoromethyl)disulfide (**3**) (*rt* = 1.43 min).
3. Pentene (**4**, *rt* = 1.58 min, 0.2%): $M^+ = 70$ (100%); 55 (C_4H_7) and 53 (C_4H_5).
4. 1-Trifluoromethylthiopentane (**5**, *rt* = 2.14 min, 5.9%): $M^+ = 172, 143$ ($M - C_2H_5$); 129 ($M - C_3H_7$); 115 (CH_2SCF_3); 103 ($M - CF_3$); 71 ($M - SCF_3$, 100%); 70 (C_5H_{10}); 61 (C_2H_5S); 55 (C_4H_7); 53 (C_4H_5) and 47 (CH_3S).
5. 1, 4-Cyclohexadiene (**6**, *rt* = 1.98 min, 0.4%): $M^+ = 80, 79$ ($M - H$, 100%); 77 (C_6H_5); 65 (C_5H_5); 63 (C_5H_3); 54 (C_4H_6); 52 (C_4H_4) and 51 (C_4H_3).
6. **Benzene** (**7**, *rt* = 1.82 min, 5.5%): $M^+ = 78$.
7. 1-Trifluoromethylthio-2, 4-cyclohexadiene (**8**, *rt* = 3.14 min, 5.9%): $M^+ = 180$; 111 ($M - CF_3$); 102 ($HSCF_3$); 96 (C_5H_4S); 85 (C_4H_5S); 79 (C_6H_7 , 100%); 77 (C_6H_5); 69 (CF_3); 63 (CSF); 54 (C_4H_6); and 51 (C_4H_3).
8. 1-Chloro-2-cyclohexene (**9**, *rt* = 3.3 min, 4.9%): $M^+ = 116$; 101 ($M - CH_3$); 88 (C_4H_5Cl); 81 ($M - Cl$); 79 (C_6H_7 , 100%); 77 (C_6H_5); 75 (C_6H_3); 67 (C_5H_7); 65 (C_5H_5); 54 ($M - C_2H_3Cl$); 53 (C_4H_5) and 51 (C_4H_3).
9. 1-Chloro-4-trifluoromethylthio-2-cyclohexene (**10**, *rt* = 4.67 min, 11.1%): $M^+ = 216$; 180 ($M - HCl$); 147 ($M - CF_3$); 128 ($C_2H_3SCF_3$); 115 ($M - HSCF_3$); 88 (C_4H_5Cl , 100%); 77 (C_6H_5 , 100%); 69 (CF_3) and 53 (C_4H_5).
10. 1, 2-Dichloro-4-cyclohexene (**11**, *rt* = 4.8 min, 1.1%): $M^+ = 150$; 115 ($M - Cl$); 109 ($M - C_3H_5$); 88 (C_4H_5Cl); 79 (C_6H_7 , 100%); 77 (C_6H_5); 75 (C_6H_3); 67 (C_5H_7); 65 (C_5H_5) and 51 (C_4H_3).
11. 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**12**, *rt* = 5.08 min, 1.2%): $M^+ = 216$; 180 ($M - HCl$); 154 ($M - C_2H_2$); 128 ($154 - C_2H_2$); 115 ($M - SCF_3$); 97 (C_5H_5S); 85 (C_4H_5S); 80 (C_6H_8); 79 (C_6H_7 , 100%); 77 (C_6H_5); 69 (CF_3); 65 (C_5H_5) and 51 (C_4H_3).
12. 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**13**, *rt* = 5.15 min, 8.5%): $M^+ = 216$; 181 ($M - Cl$); 154 ($M - C_2H_2$); 141 ($M - C_3H_4Cl$); 128 ($154 - C_2H_2$); 115 ($M - SCF_3$); 97 (C_5H_5S); 85 (C_4H_5S); 79 (C_6H_7 , 100%); 77 (C_6H_5); 69 (CF_3); 65 (C_5H_5) and 51 (C_4H_3).
13. 1, 4-Dichloro-2-cyclohexene (**14**, *rt* = 5.29 min, 1.8%): $M^+ = 150$; 122 ($M - C_2H_2$); 114 ($M - HCl$); 101 ($M - CH_2Cl$); 88 (C_4H_5Cl); 79 (C_6H_7 , 100%); 77 (C_6H_5); 65 (C_5H_5) and 51 (C_4H_3).
14. 1, 4-Dichloro-2-cyclohexene (**15A** or **15B**, *rt* = 5.58 min, 0.5%): $M^+ = 150$; 114 ($M - HCl$); 109 ($M - C_3H_5$); 88 (C_4H_5Cl); 79 (C_6H_7 , 100%); 77 (C_6H_5); 65 (C_5H_5) and 53 (C_4H_5).
15. Cyclohexenylbicyclo[2.2.2]octene (**16**, *rt* = 7.13 min, 0.1%): $M^+ = 160$; 105 ($M - C_4H_7$); 91 ($105 - CH_2$); 82 (C_6H_{10}); 80 (C_6H_8 , 100%); 77 (C_6H_5); 65 (C_5H_5); 53 (C_4H_5) and 51 (C_4H_3).
16. (10-Trifluoromethylthiocyclohexenyl) bicyclo[2.2.2]octene (**17**, *rt* = 8.14 min, 0.2%): $M^+ = 260$; 182 ($M - C_6H_6$); 158 ($M - CF_3SH$); 143 ($158 - CH_3$); 132 ($M - C_2H_3SCF_3$); 117 ($132 - CH_3$); 104 ($158 - C_4H_6$); 91 (C_7H_7 , 100%); 77 (C_6H_5); 69 (CF_3); 67 (C_5H_7); 57 (C_4H_9) and 51 (C_4H_3).

^aChlorine isotope peaks are seen in all compounds containing chlorine.

TABLE II Mass Spectral Fragmentation of the Compounds Cited in Figure 2^a

1. Trifluoromethylsulfenyl chloride (**2**) and Bis-(trifluoromethyl)disulfide (**3**): (cf. Table I).
2. Pentene (**4**): $M^+ = 70$ (100%); 55 (C_4H_7) and 53 (C_4H_5).
3. 1, 4-CHD (**6**): $M^+ = 80$, 79 (M-H, 100%); 77 (C_6H_5); 65 (C_5H_5); 63 (C_5H_3); 54 (C_4H_6); 52 (C_4H_4) and 51 (C_4C_3).
4. Benzene (**7**): (cf. Table I).
5. 1, 2-Dichloro-4-cyclohexene (**11**): $M^+ = 150$; 115 (M - Cl); 88 (M - C_2H_3Cl); 79 (C_6H_9 , 100%); 77 (C_6H_5); 65 (C_5H_5); and 51 (C_4H_3).
6. 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**12**): $M^+ = 216$; 180 (M - HCl); 162 (M - C_4H_6); 147 (M - CF_3); 114 (147 - S); 101 (SCF_3); 85 (C_4H_5S); 75 (180 - SCF_3 , 100%); 77 (C_6H_5); 69 (CF_3); 63 (CSF); and 5 (C_4C_3).
7. 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**13**, rt = 5.08 min, 11.0%): $M^+ = 216$; 180 (M - HCl); 115 (M - SCF_3 or C_6H_8Cl); 97 (C_5H_5S); 85 (C_4H_5S); 79 (C_6H_7 , 100%); 77 (C_6H_5); 69 (C_5F_3); 65 (C_5H_5); and 51 (C_4H_3).
8. 2-Trifluoromethylthiopentane (**21A**): $M^+ = 172$, 143 (M - C_2H_5); 129 (M - C_3H_7); 115 (CH_2SCF_3); 103 (M - CF_3); 71 (M - SCF_3 , 100%); 70 (C_5H_{10}); 61 (C_2H_5S); 55 (C_4H_7); 53 (C_4H_5) and 47 (CH_3S).
9. 2-Trifluoromethylthiopentane (**21B**): $M^+ = 172$, 143 (M - C_2H_5); 129 (M - C_3H_7); 115 (CH_2SCF_3); 103 (M - CF_3); 79 (129 - CF_2); 71 (M - SCF_3 , 100%); 70 (C_5H_{10}); 63 (CSF); 61 (C_2H_5S); 55 (C_4H_7); 53 (C_4H_5) and 47 (CH_3S).
10. 1-Chloropentane (**22**): $M^+ = 106$, 91 (CH_3); 79 (M - C_2H_3); 70 (M - HCl, 100%); 63 (M - C_3H_7); 57 (M - CH_2Cl); 55 (C_4H_7); and 49 (CH_2Cl).
11. Cyclohexene (**23**) (cf. ref. 18).
12. 1-Chloro-2,5-cyclohexadiene (**24**): $M^+ = 114$; 97 (M - CH_4-H); 88 (M - C_2H_2); 83 (97 - CH_2); 79 (M - Cl, 100%); 78 (M - HCl); 77 (C_6H_5); 70 (C_5H_{10}); 67 (C_5H_7); 55 (C_4H_7); 52 (C_4H_4) and 51 (C_4H_3).
13. 1-Trifluoromethylthio-2,5-cyclohexadiene (**25**): $M^+ = 180$; 144 (M - CH_4-F); 124 (M - C_4H_6); 111 (M - CF_3); 95 (111 - CH_4); 83 (124 - C_3H_5); 79 (M - SCF_3 , 100%); 77 (C_6H_5); 70 (C_5H_{10}); 67 (C_5H_7); 65 (C_5H_5); and 51 (C_4H_3).
14. 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**26**, rt = 5.15 min, 12.0%): $M^+ = 216$; 181 (M - Cl); 115 (M - SCF_3 or C_6H_8Cl); 97 (C_5H_5S); 88 (C_4H_5Cl); 79 (C_6H_7 , 100%); 77 (C_6H_5); 69 (CF_3); 65 (C_5H_5); and 51 (C_4H_3).
15. 1, 2-Dichloro-4-cyclohexene (**27A** or **27B**, rt = 5.58 min, 1.0%): $M^+ = 150$; 114 (M - HCl); 88 (C_4H_5Cl); 79 (C_6H_7); 77 (C_6H_5 , 100%); 65 (C_5H_5) and 53 (C_4H_5).
16. 1, 4-Dichlorocyclohexane (**28**): $M^+ = 152$; 115 (M - Cl); 88 (C_4H_5Cl); 79 (C_6H_9 , 100%); 77 (C_6H_5); 65 (C_5H_5); 62 (C_3H_4Cl) and 51 (C_4H_3).
17. 1,2,4,5-Tertachlorocyclohexane (**29**): $M^+ = 220$; 184 (M - HCl); 148 (184 - HCl); 122 (148 - C_2H_2); 113 (C_6H_6Cl , 100%); 109 (C_3H_3Cl); 87 (C_4H_4Cl); 77 (C_6H_5); 75 (C_6H_3); 53 (C_4H_3) and 51 (C_4H_3).
18. 1,2,4,5-Tertachlorocyclohexane (**30A**): $M^+ = 220$; 185 (M - Cl); 149 (184 - Cl); 122 (148 - C_2H_2); 113 (C_6H_6Cl , 100%); 109 (C_3H_3Cl); 87 (C_4H_4Cl); 77 (C_6H_5); 75 (C_6H_3); 53 (C_4H_3) and 51 (C_4H_3).
19. 1,2,4,5-Tetrachloro-2-cyclohexane (**30B**, rt = 6.44 min, 1.0%): $M^+ = 220$; 184 (M - HCl); 149 (184 - Cl); 113 (C_6H_6Cl); 87 (113 - C_2H_2); 77 (C_6H_5 , 100%); 52 (C_4H_4) and 51 (C_4H_3).

^aMass spectra of benzene (**4**) and cyclohexene (**5**) have been described (cf. ref. 17). Chlorine isotope peaks were seen for all chlorine containing compounds.

1, 4-dichlorocyclohexane (**28**) rests primarily on its M^+ ion and on the presence of two ions corresponding to $m/e = 88$ (C_4H_5Cl) and $m/e = 62$ (C_2H_3Cl). Its formation can be rationalized using intermediates **40** and **41**. The formation of the two isomeric tetrachlorocyclohexanes is straightforward. Scheme 3 endeavors to rationalize the mechanism of the formation of the compounds described in Figure 2. The mass spectra of benzene and cyclohexene have been described.¹⁸ Although Scheme 3 shows how 1,2,4,5-tetrachlorocyclohexanes can be formed via the addition of the chlorine radical across the two double bonds of the substrate, only two were detected by their GC-MS. Based on the mass spectral fragmentation behavior, the two isomers in question appear to be **29** and either **30A** or **30B**. 1,2,4,5-Tetrachlorocyclohexane has been mentioned in the literature.¹⁹

EXPERIMENTAL

F_3CSCl (**2**) is extremely toxic. Extreme care and caution must be exercised when handling it. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m \times 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 \times 0.25 mm. i.d. Rtx-5 capillary column (Restek, Bellefonte, PA). The conditions on 5100 were: oven temperature 60–270°C at 10°C/min, injection temperature was 210°, interface temperature 230°C, electron energy 70 eV, emission current 500 μ A and scan time 1 sec. The conditions on the TSQ-7000 were: oven temperature 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 μ A (EI) or 300 μ A (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 \times 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA).

Reaction of 1, 3-CHD (**1**) with Trifluoromethylsulphenyl Chloride (**2**)

A solution of 1, 3-CHD (**1**, Figure 1) in dry pentane was treated with a stoichiometric amount of F_3CSCl (**2**), drawn in through a vacuum line, at $-80^\circ C$ with stirring and under dry nitrogen for 2 h. The reaction

mixture was stirred overnight at ambient temperature. Routine GC analysis indicated the reaction to consist of a dozen or so components. Thus, the GC-MS analysis permitted the identification of the following from the reaction of 1, 3-CHD with F_3CSCl (Figure 1):

- (a) F_3CSCl (**2**) and F_3CSSCF_3 (**3**) (a) Pentene (**4**, $M^+ = 70$, $rt = 1.58$ min, 0.2%);
- (b) Benzene (**7**, $M^+ = 78$, $rt = 1.72$ min, 5.48%);
- (c) 1, 3-CHD (**1**, $M^+ = 80$, $rt = 1.80$ min, 47.9%);
- (d) 1-Trifluoromethylthiopentane (**5**, $M^+ = 172$, $rt = 2.14$ min, 5.9%);
- (e) 1, 4-Cyclohexadiene (**6**);
- (f) 1-Chloro-2-cyclohexadiene (**9**, $M^+ = 114$, $rt = 3.32$ min, 4.9%);
- (g) 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**10**, $M^+ = 216$, $rt = 4.67$ min, 11.1%);
- (h) 1, 2-Chloro-4-cyclohexene (**11**, $M^+ = 150$, $rt = 4.8$ min, 1.1%);
- (i) 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**12** or **13**, $M^+ = 216$, $rt = 5.08$ min, 1.2%);
- (j) 1-Chloro-2-trifluoromethylthio-3-cyclohexene (**12** or **13**, $M^+ = 216$, $rt = 5.15$ min, 8.6%);
- (k) 1, 4-Dichloro-2-cyclohexene (**14**, $M^+ = 150$, $rt = 5.29$ min, 1.8%);
- (l) 1, 4-Dichloro-2-cyclohexene (**15A** or **15B**, $M^+ = 150$, $rt = 5.58$ min, 0.5%);
- (m) Cyclohexenylbicyclo[2.2.2]octene (**16**, $M^+ = 160$, $rt = 7.13$ min, 0.1%);
- (n) 10-Trifluoromethylthiocyclohexenylbicyclo[2.2.2]octene (**17**, $M^+ = 260$, $rt = 8.14$ min, 0.2%).

Reaction of 1, 4-CHD (**6**) with Trifluoromethylsulfenyl Chloride (**2**)

Thus, the GC-MS analysis enabled the identification of the following compounds from the reaction of 1, 4-CHD **6** with F_3CSCl (Figure 2) as described above:

- (a) Bis-(trifluoromethyl)disulfide (**3**) $M^+ = 202$;
- (b) F_3CSCl (**2**) $M^+ = 136$, $rt = 1.43$ min, 4.08%;
- (c) Benzene (**7**, $M^+ = 78$, $rt = 1.69$ min, 3.7%);
- (d) Cyclohexene (**23**, $M^+ = 82$, $rt = 1.53$ min, 0.8%);
- (e) Pentene (**4**, $M^+ = 70$, $rt = 1.57$ min, 0.2%);
- (f) 1, 4-CHD (**6**, $M^+ = 80$, $rt = 1.59$ min, 24.1%);
- (g) 2-Trifluoromethylthiopentane (**21A**, $M^+ = 172$, $rt = 2.07$ min, 0.2%);
- (h) 2-Trifluoromethylthiopentane (**21B**, $M^+ = 172$, $rt = 2.09$ min, 0.1%);

- (i) 1-Chloropentane (**22**, $M^+ = 106$, $rt = 2.18$ min, 0.2%);
- (j) 1-Chloro-2, 5-cyclohexadiene (**24**, $M^+ = 114$, $rt = 4.32$ min, 0.1%);
- (k) 1-Chloro-2-trifluoromethylthio-4-cyclohexene (**12**, $M^+ = 216$, $rt = 4.61$ min, 37.8%);
- (l) 1-Trifluoromethylthio-2,5-cyclohexadiene (**25**, $M^+ = 180$, $rt = 4.72$ min, 0.2%);
- (m) 1, 2-Dichloro-4-cyclohexene (**27**, $M^+ = 150$, $rt = 4.80$ min, 19.2%);
- (n) 1, 4-Dichlorocyclohexane (**28**, $M^+ = 152$, $rt = 4.91$ min, 0.3%);
- (o) 1,2,4,5-Tetrachlorocyclohexane (**29**, $M^+ = 220$, $rt = 8.11$ min, 0.2%);
- (p) 1,2,4,5-Tetrachlorocyclohexane (**30A** or **30B**, $M^+ = 220$, $rt = 8.65$ min, 0.4%).

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