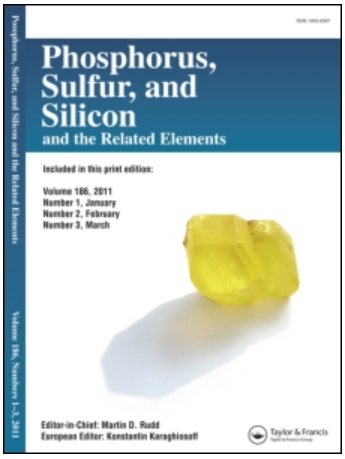

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REACTION OF TRIFLUOROMETHYLSULFENYL CHLORIDE WITH 3-CHLORO- AND 3-HYDROXYPROPYNES

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Vinylsulfides are often obtained via the reaction of substituted acetylenes with sulfur-containing reagents. The presence of other functional groups such as the halide or the hydroxyl moieties enhances the usefulness of the vinylsulfide intermediates. To this end, propargyl alcohol and halides have found wide application. With a view to enhance the biological properties of the end products synthesized from the vinylsulfide intermediates, the trifluoromethylthio function has now been incorporated as a part of the vinylic system. This communication presents the free-radical addition of trifluoromethylsulfenyl chloride to 3-chloro- and 3-hydroxypropynes, and the mechanism of the formation of the various products and their spectral characterization.

Keywords: Multiple bonds; novel free-radical reactions and addition products; trifluoromethylsulfenyl chloride; vinylsulfides

Vinylsulfides constitute one of the most versatile intermediates in organic synthesis.[1] They have been transformed into aldehydes,[2a,b] ketones,[2b] cyclic compounds and oxiranes,[2c] and stereoespecific olefins.[2d] The vinylic sulfide function also forms a part of the biologically potent natural products such as ajoene and antithrombotic agents from garlic[3a] and superconducting "organic metals" such as

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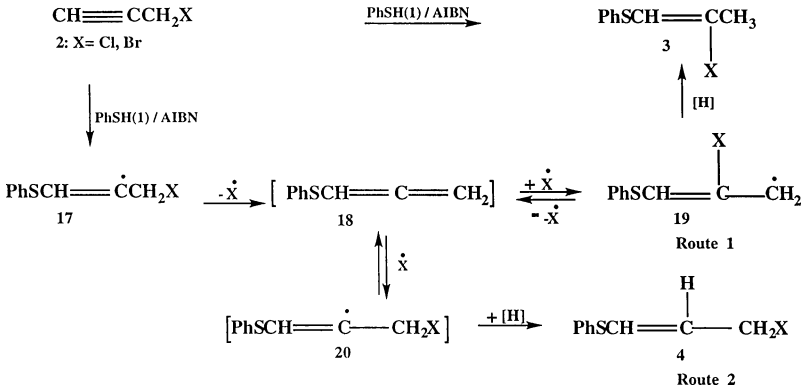
tetrathiafulvanes.[3b] Free-radical catalyzed addition of mercaptans to carbon–carbon triple bond indeed represents an extremely useful synthetic method for the preparation of vinyl sulfide synthons under very mild reaction conditions.[1,4] Addition of the thiyl radicals generated from thiols and disulfides to carbon–carbon triple bond has been discussed in detail.[5] Photo-chemical reaction of methyldisulfide with 1-heptyne yields a 1:1 adduct of the (E)- and (Z)-mixture of 1,2-dialkylmercaptoethylenes.[4a] Thermodynamic control of the formation of the reaction product has been demonstrated by isomerizing the products to an equilibrium mixture.

Addition of the free-radical entities to the carbon–carbon triple bond gives a mixture of (E)- and (Z)-isomers, though diadducts are sometimes formed.[4] Addition reactions to the triple-bond systems are often complicated by their propensity to undergo skeletal rearrangement to the allenic system. Although radical addition sometimes exhibits low stereoselectivity,[1, 4b,c] highly stereoselective free-radical addition can be accomplished.[6b,c] The reaction of thiophenol with propyne-3-ol in the presence potassium hydroxide and without any solvent yields only a trans-isomer.[6a] However, the same reaction in the presence of 2–2–azobisobutyronitrile (AIBN) furnishes a 7:3 mixture of the (E)- and (Z)-isomers.[4a] Photo-catalyzed sulfenylation of propyne-3-ol with n-butylthiol forms a diadduct, 2, 3-bis(butylthio)propanol as the major product along with small amounts of the expected vinyl sulfide. While the addition of thiols to acetylenic alcohols in the presence of an alkali results in a (E)- and (Z)-isomeric mixture of the Markovnikov and anti-Markovnikov adducts,[7] the regioselectivity of the thiolate addition to the terminal alkynes usually follows Markovnikov orientation to give the major product.[8a,b] The formation of the minor product—the anti-Markovnikov adduct—in the base catalyzed addition of the thiols to the alkynes has been attributed to radical addition.[8c]

The anti-Markovnikov adduct has been reported to predominate in the addition reaction of the thiols to the terminal alkynes[9] and alkynols.[9b] Also, the thiol addition to 3, 3-dimethyl-2-butyne in the presence of a base and air was found to give only the anti-Markovnikov orientation product.[8b] In summary then, the whole picture seems to be somewhat uncertain. In continuation of our interest in the chemistry of the trifluoromethylthio group,[10] we have investigated the addition reaction of the spontaneously formed free radicals from trifluoromethylsulfenyl chloride to the triple-bond system of 3-chloro- and 3-hydroxypropynes. This article presents the unusual results along with the spectral characterization and the probable mechanism of the formation of the various products.

RESULTS AND DISCUSSION

The free-radical–initiated addition thiophenol (**1**) to propargyl chloride (**2**) in the presence of AIBN furnishes 1-phenylthio-2-chloro-1-propene (**3**) via the allene intermediate, **18**. This addition has been stated to proceed through the migration of the halogen atom from the 3-position to the 2-position via the allene intermediate and followed by the abstraction of hydrogen (Scheme 1). Two routes have been implicated in the formation of the expected products, 1-phenylthio-2-chloro-1-propene (**3**, **route 1**) and 1-phenylthio-3-chloro-1-propene (**4**, **route 2**), although **4** has not been observed yet. The formation of **3** has been stated to involve the migration of the halogen from C_3 to C_2 position.[9] It is interesting to note that this migration has not been observed in the case of 3-hydroxypropyne (propargyl alcohol, **5**). It was considered interesting to see whether the addition of trifluoromethylsulfenyl chloride (**6**) to 3-chloropropyne (**2**, **X = Cl**) would follow a similar pathway and furnish a single synthetically useful vinyl sulfide, namely 1-trifluoromethylthio-2, 3-dichloro-1-propene (**7**, Figure 1). However, 11 compounds (**2** and **7–16**, cf. Figure 1), were detected in the reaction product by Gas chromatograph-mass spectrometer (GC-MS). Scheme 2 describes the formation of the expected compounds (**7–8**, **14–16**) if the reaction began with the addition of the thiyl radical and proceeded through the allene intermediate **22**, similar to the proposed allene intermediate (**18**). This scheme also explains the origin of Bis-(1, 3-trifluoromethylthio)-2-chloro-1-propene (**8**). However, if the reaction begins with the addition of the chlorine radical instead of the thiyl radical, what would the product or products be? This was an interesting question. Indeed, that is what appears to occur, at least in part. This



SCHEME 1 Free radical catalyzed addition to propargyl halides.

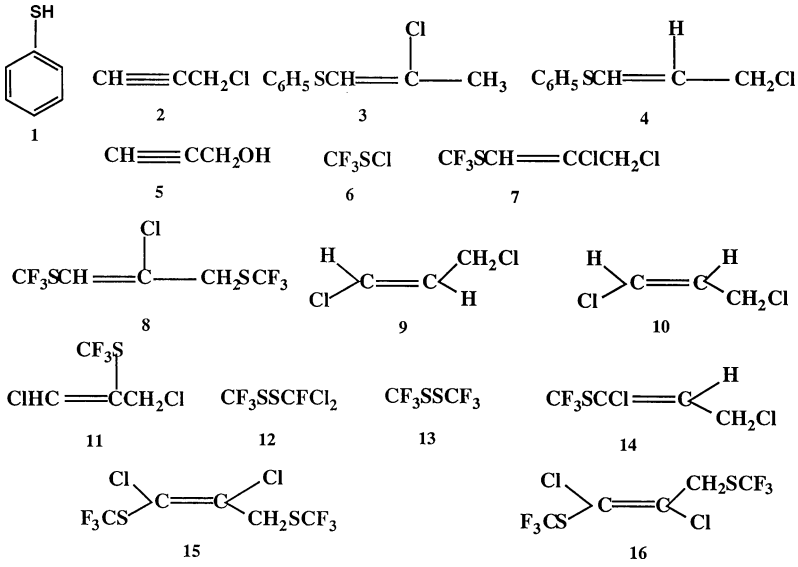
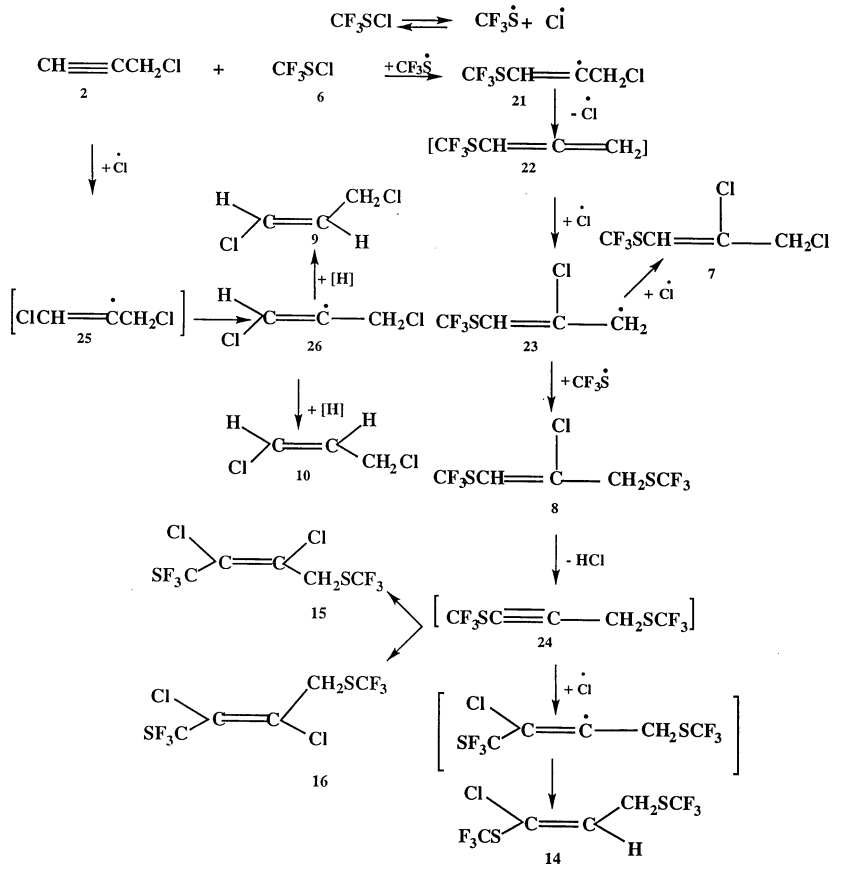


FIGURE 1 Products from the addition to propargyl derivatives.

inference is supported by the characterization of several compounds whose formation cannot be rationalized on the basis of observations found in the literature. That this reaction proceeds via free-radical processes is demonstrated by the characterization of compounds **12** and **13** (cf. Figure 1). The genesis of these two compounds via free-radical reactions has been rationalized.[10f,11]

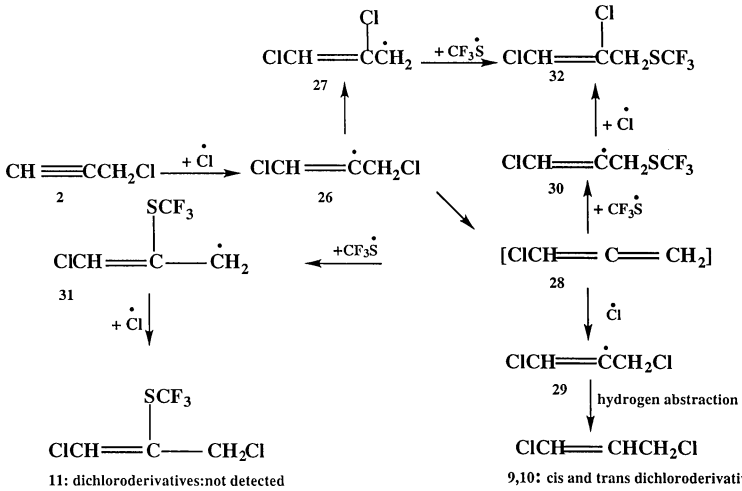
Scheme 2 attempts to rationalize the formation of compounds **7**–**11** and **14**–**16**, which have been characterized from their mass spectral fragmentation behavior. Under the experimental conditions, F_3CSCl reacts with subrates as $F_3CS^{\cdot}$ and $Cl^{\cdot}$ radicals.[11] The addition of the thiyl radical to propargyl chloride (**2**) leads to the intermediate **21**, which goes through a sequence of reactions to give the intermediate, bis-(1, 3-trifluoromethylthio)prop-1-yne (**24**). The latter in turn goes through successive addition of the $Cl^{\cdot}$ radical and hydrogen abstraction to **14** via compound **8**. The intermediate **22** can react with $Cl^{\cdot}$ radical to form **23**, which has two options open to it. First, it can react again with $Cl^{\cdot}$ radical and furnish **7**. The second option entails the reaction with $F_3CS^{\cdot}$ radical to give **8**, as described earlier. If on the other hand the reaction begins with the addition of the $Cl^{\cdot}$ radical instead of the thiyl radical, then the initial formation of the intermediate **25** would be expected. This would then lead to compounds **9** and **10** via the intermediates **26**. Compounds **15** and **16** are considered to arise from the cis- and



SCHEME 2 Mechanism of formation of compounds **7–8** and **14–16**.

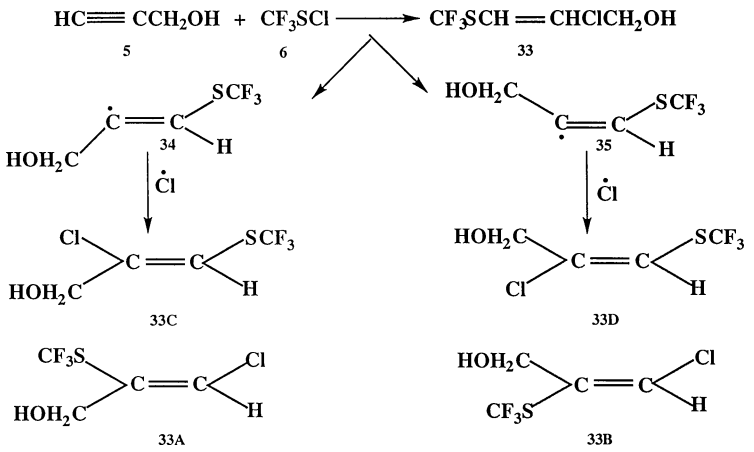
trans-addition of chlorine to the acetylenic intermediate, namely **24**, which is formed in situ from **8** (cf. Scheme 2).

Scheme 3 endeavors to explain the formation of three compounds, namely **9**, **10**, and **11**. The addition of the $Cl^{\cdot}$ radical to **2** gives **26** (cf. Scheme 3), which again has two options open to it. The first one involves the migration of Cl from C_3 to C_2 to form the intermediate **27**, which picks up the $F_3CS^{\cdot}$ radical to furnish compound **33**. The second path involves the rearrangement of the intermediate **26** to chloroallene **28**, which in principle has three avenues available to it, namely to form intermediates **29**, **30**, and **31**, which in turn would lead to compounds **9**, **10**, **11**, and **32**. While compound **32** was not detected, the remaining three compounds **9**, **10**, and **11** were characterized.



SCHEME 3 Probable mechanism of formation of compounds **9–11**.

However, the reaction of propargyl alcohol (**5**) with trifluoromethylsulfenyl chloride (**6**) furnishes only one major product (**33**) in 98.1% yields. A minor compound, **8**, (0.15%) was also detected as a product of this reaction. Four isomeric structures, **33A**, **33B**, **33C**, and **33D**, were considered for this major product. Structures **33A** and **33B** were discarded on the consideration that the introduction of the bulky SCF_3 group next to another bulky group, namely hydroxymethyl, would be sterically hindered, and as such its formation not favored. This left us with structures **33C** and **33D**. These are geometrical isomers that arise from the free-radical addition of trifluoromethylsulfenyl chloride (**6**) to the substrate, (**5**). There is no doubt about the free-radical nature of the reaction. The identification of bis-(trifluoromethyl)disulfide as one of the products confirms this inference. Structure **33C** represents the cis-addition of the thiyl and chlorine radicals across the carbon–carbon triple bond, while structure **33D** arises from the trans-addition. The origin of these two addition products is rationalized in Scheme 4. Based on the consideration that trans-addition is generally sterically favored and on the comparison of the simulated ^{1}H NMR and ^{13}C NMR spectra, the structure **33D** was selected for compound **33**. Bis-(1, 3-trifluoromethylthio)-2-chloropropene (**8**) was identified as minor product of this reaction. Scheme 5 traces its origin to the allene intermediate **22**, which serves as its precursor. Compound **5** picks up the $F_3CS^{\cdot}$ radical to initially form **36**, which loses the hydroxyl radical to form the allene intermediate **22**, which then goes on to react successively with thiyl and chlorine radicals to furnish **8**. It is interesting to note that the hydroxyl

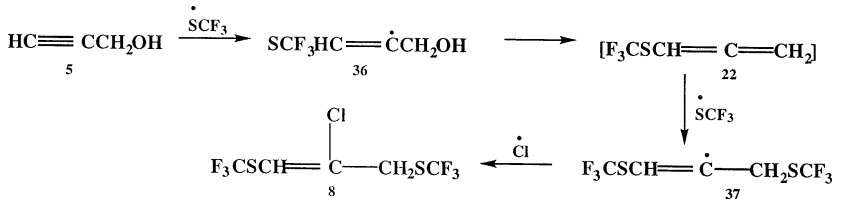


SCHEME 4 Addition Reaction of propargyl alcohol.

moiety of the substrate (**5**) gets replaced by the F_3CS-group in this process. The mass spectral breakdown of the compounds cited in the text is described in Table 1.

EXPERIMENTAL

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.



SCHEME 5 Mechanism of formation of compound **8**.

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Text

Mass spectral fragmentation of Propargyl chloride (**2**): $M^+ = 74$ (100%); 72 (M—2H); 49 (CH_2Cl); and 47 (49–2H).

Mass spectral fragmentation of 1-(Trifluoromethylthio)-2,3-dichloro-1-propene (**7**): $M^+ = 210$; 175(M—Cl, 100%); 155 (175-HF); 127 ($C_3H_2Cl_2F$); 109 (M—SCF_3); 92 (C_2HSCl); 69 (CF_3); 63 (CFS); 49 (CH_2Cl); and 45 (CSH).

Mass spectral fragmentation of Bis-(1, 3-trifluoromethylthio)-2-chloro-1-propene (**8**): $M^+ = 276$; 256 (M—HF); 241 (M—Cl, 100%); 207 (M—CF_3); 187 (207-HF); 159 (207-CHCl); 115 (CH_2SCF_3); 82 (CSF_2); 69 (CF_3); and 45 (CSH).

Mass spectral fragmentation of trans-(1,3-Dichloro)-1-propene (**9**): $M^+ = 110$; 75 (M—Cl, 100%); 61(M—CH_2Cl); and 49 (CH_2Cl).

Mass spectral fragmentation of cis-(1, 3-Dichloro)-1-propene (**10**): $M^+ = 110$; 75 (M—Cl, 100%) and 49 (CH_2Cl).

Mass spectral fragmentation of 1, 3-Dichloro-2-(trifluoromethylthio)-1-propene (**11**): $M^+ = 210$; 175 (M—Cl); 109 (M-SCF_3); 69 (CF_3, 100%); 49 (CH_2Cl); 57 (C_2HS); and 45 (CSH).

Mass spectral fragmentation of (Dichlorofluoromethyl) (trifluoromethyl) disulfide (**12**): $M^+ = 234$; 199 (M—Cl); 149 (199-CF_2); 132 (M—$CFCl_2$); 117 (199-SCF_2); 101 ($CFCl_2$, 100%); 98 (CSFCl); 79 (CSCl); 69 (CF_3); and 50 (CF_2).

Mass spectral fragmentation of Bis(trifluoromethyl) disulfide (**13**): $M^+ = 202$; 189 (M—F); 132 (M—CF_3); 114 (132-F); 101 (SCF_3); 82 (CSF_2); 69 (CF_3, 100%); 64 (SS) and 50 (CF_2).

Mass spectral fragmentation of 1, 3-Dichloro-1-(trifluoromethylthio)-1-propene (**14**): $M^+ = 210$; 175 (M—Cl, 100%); 109 (M-SCF_3); 69 (CF_3); 49 (CH_2Cl); and 45 (CSH).

Mass spectral fragmentation of Bis-(1,3-trifluoromethylthio)-cis-(1,2-dichloro)-1-propene (**15**): $M^+ = 310$; 275 (M—Cl, 100%); 241 (M—CF_3); 09 (M—SCF_3); 205 (241-HCl); 193 (275- CSF_2); 171($F_3CSC_2CH_2S$); 145 (C_3F_2ClS); 137 ($C_3H_2ClS_2$); 115 (CH_2SCF_3); 105 (C_3H_2ClS); and 93 (ClC_2SCH_2).

Mass Spectral fragmentation of Bis-(1,3-trifluoromethylthio)-trans-(1,2-dichloro)-1-propene (**16**): $M^+ = 310$; 275 (M—Cl, 100%); 241 (M—CF_3); 222 (241-F); 209 (M—SCF_3); 205 (241-HCl); 193 (275-CSF_2); 171 ($F_3CSC_2CH_2S$); 139 ($C_2SCH_2SCF_3$); 137 ($C_3H_2ClS_2$); 115 (CH_2SCF_3); 105 (C_3H_2ClS); 93 (ClC_2SCH_2); and 69 (CF_3).

Mass spectral fragmentation of 2-Chloro-3-(trifluoromethylthio)propenol (**33D**): $M^+ =$ 192; 171 (M—HF—H); 162 (M—CH_2O); 157 (M—Cl); 137 ($C_4H_3OF_2S$); 126 (M—CH_2OH); 123 (M—CF_3); 115 (CH_2SCF_3); 107 (C_3H_3SCl); 101 (SCF_3); 91 (M—SCF_3, 100%); 87 (C_3H_3OS); 82 (CSF_2); 69 (CF_3); 63 (CSF); 59 (C_2H_3S); 50 (CF_2); and 45 (CSH).

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 GC equipped with a J and W Scientific 30 m $\times$ 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA, USA). Stoichiometric amounts of the respective reagents were mixed in glass vials, vigorously shaken on a vibro-mixer, and heated in the microwave oven for a specified period.

The reaction mixture was allowed to come to ambient temperature, and the cooled product was first analyzed by gas chromatography and then subjected to GC-MS analysis. The NMR spectra (^1H and ^{13}C) were recorded in $CDCl_3$ with TMS (tetramethylsilane) as the internal standard on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz, respectively. The chemical shifts are given as ppm.

Reaction of Propargyl Chloride (2) with Trifluoromethylsulfenyl Chloride (6)

Stoichiometric amounts propargyl chloride (**2**) and trifluoromethylsulfenyl chloride (**6**) delivered through the vacuum line were reacted in dry pentane with stirring at −78°C for 3 h under argon. The reaction mixture was allowed to come to room temperature and was stirred overnight at ambient temperature. The solvent was evaporated under reduced pressure, and the residue was examined by GC and found to be a complex mixture of several components. The GC-MS analysis of the product not only confirmed this inference but also enabled the characterization of the products formed during this reaction. Thus: (1) Bis-(trifluoromethyl) disulfide (**13**, $M^+ = 202$, r.t. = 1.17 min, 1.6%); (2) propargyl chloride (**2**, $M^+ = 74$, r.t. = 1.24 min, 18.0%); (3) 1,3-Dichloro-trans-1-propene (**9**, $M^+ = 110$, r.t. = 1.45 min, 2.8%); (4) 1,3-Dichloro-cis-1-propene (**10**, $M^+ = 110$, r.t. = 1.54 min, 1.0%); (5) (Dichlorofluoromethyl) (trifluoromethyl) disulfide (**12**, $M^+ = 234$, r.t. = 1.59 min, 0.5%); (6) Bis-(1, 3-trifluoromethylthio)-2-chloro-1-propene (**8**, $M^+ = 276$, r.t. = 2.36 min, 0.7%); (7) 1-Trifluoromethylthio-2,3-dichloro-1-propene (**7**, $M^+ = 210$, r.t. = 2.42 min, 29.5%); (8) 1,3-Dichloro-1-(trifluoromethylthio)-1-propene (**14**, $M^+ = 210$, r.t. = 2.44 min, 1.0%); (9) 2-Trifluoromethylthio-1,3-dichloro-1-propene (**11**, $M^+ = 210$, r.t. = 2.44 min, 1.3%); (10) Bis-(1,3-trifluoromethylthio) cis(1,2-dichloro)-1-propene (**15**, $M^+ = 310$, r.t. = 3.36 min, 1.8%); and (11) Bis-(1,3-trifluoromethylthio)-trans-(1,2-dichloro)-1-propene (**16**, $M^+ = 310$, r.t. = 3.44 min, 41.2%) (cf. Figure 1).

Reaction of Propyne-3-ol (5) with Trifluoromethylsulfenyl Chloride (6)

Stoichiometric amounts propyne-3-ol (**5**) and trifluoromethylsulfenyl chloride (**6**) were reacted in dry pentane with stirring at −78°C for 3 h under argon. The reaction mixture was allowed to come to room temperature and was stirred overnight at ambient temperature. The solvent was evaporated under reduced pressure, and the residue was examined by GC and found to consist of three components. The mixture

was subjected to vacuum distillation, and the distillate was then examined by GC-MS analysis. Based on their mass spectral fragmentation behavior and ^{13}C NMR data, all of the components have been characterized and structures have been assigned to them. They are: (a) Bis-(trifluoromethyl)disulfide, trifluoromethylsulfenyl chloride (**6**, M^+ = **136**) and pentane (all coeluted, 1.75%), (b) 2-chloro-3-(trifluoromethylthio)-propenol (**33D**, $M^+ = 192$, 98.1%), and (c) bis-(1, 3-trifluoromethylthio)-2-chloropropene (**8**, $M^+ = 276$, 0.15%) (Scheme 4).

Spectral Data of 2-Chloro-3-(trifluoromethylthio)propenol (**33D**): a ^1H-NMR: $\delta = 6.89$ (s, 1H); 5.2 (s, O—H); and 4.48 (s, 2H).^{13}C-NMR: $\delta =$ 59.7 ($\mathbf{C}H_2$); 128.8 (**C**H); 129.1 (**C**Cl); and 131.7 (S**C**F_3).

SUMMARY

While the apparently kinetically controlled addition reaction of trifluoromethylsulfenyl chloride (**6**) to 3-hydroxypropyne (**5**) gave the only trans-isomer (**33D**, 98.1%), the reaction of trifluoromethylsulfenyl chloride (**6**) with 3-chloropropyne (**2**) led to the formation of ten compounds (**7**–**16**). The mechanism of the formation of the various products in the latter case appears to be much more complicated than considered earlier.

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