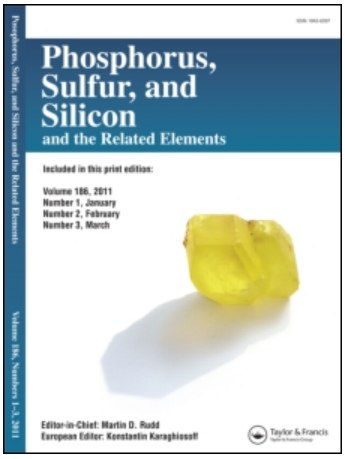

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PHOTO-TRIFLUOROMETHYLTHIOLATION OF CYCLOPROPYL PHENYL PROPARGYL ALCOHOL

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Seven compounds are formed in various amounts when a solution of cyclopropopyl phenyl propargyl alcohol and trifluoromethylsulfenyl chloride in acetonitrile is exposed to UV light. The probable mechanism of formation and the mass spectral characterization of these compounds are described.

Keywords: Cyclopropyl ring cleavage; trifluoromethylthiyl and chlorine radical addition and substitution

INTRODUCTION

Considerable interest has manifested in the study of the cyclopropane ring cleavage during free radical halogenation.[1] Cyclopropanes are converted into olefins when subjected to UV-irradiation.[1e–g] Hydrogen abstraction and/or ring fission are commonly observed in free radical halogenation of cyclopropanes. Ring cleavage products are exclusively obtained with bromine radicals,[1a,2,3] while chlorine radicals have been shown to furnish products resulting from both hydrogen abstraction and ring-cleavage.[3a]

The reaction of $BrCCl_3$ with unsubstituted phenylcyclopropane has been reported to yield unreacted phenylcyclopropane (77%) and 1,3-dibromo-1-phenylpropane (23%), while continued irradiation in the presence benzoyl peroxide gave the staring material, namely phenylcyclopropane (58%) and 1,3-dibromo-1-phenylpropane (42%).[4] Exposure of a solution of phenylcyclopropane and Br_2 to a 450 W Hg arc lamp gave 1,3-dibromo-1-phenylpropane in quantitative yield while the same reaction in the dark resulted in the formation of (4-bromophenyl)cyclopropane.[1d] In continuation of our interest in the

chemistry of the trifluoromethylthio group[5] and the photolytic cleavage of the cyclopropyl ring,[6] the photocatalyzed reaction of cyclopropyl phenyl propargyl alcohol with trifluoro-methylsulfenyl chloride has been examined and the seven compounds thus formed have been characterized. This article describes their formation and mass spectral identification.

RESULTS AND DISCUSSION

The treatment of cyclopropyl phenyl ketone (**1**) with ethynylmagnesium bromide gave cyclopropyl phenyl propargyl alcohol (**2**),[7] which was subjected to photocatalyzed reaction with trifluoromethylsulfenyl chloride (**3**) in acetonitrile with the aid a 100 W mercury lamp and found to furnish a complex mixture of products containing seven compounds (Figure 1). This probably is due to the presence of a reactive carbon center carrying cyclopropyl, hydroxyl and ethynyl functions. In addition to the replacement of the hydroxyl group, addition across the multiple bond as well as the cleavage of the cyclopropyl ring were expected. In this context, it is worth mentioning that an "intriguing" interconversion of the stereochemistry of the carbon center next to the carbonyl carbon of substituted cyclopropyl phenyl ketones during photochrmical reaction has been recorded.[8a] Also, a rearrangement of the diradical formed during the photolysis of cyclopropanes has been reported.[8b]

The complex product formation observed above is reminiscent of the reaction of 1-ethynyl-1-cyclopentanol with trifluoromethylsulfenyl chloride (**3**) at -80° under nonphotochemical conditions.[5g] In the latter case, in all 13 compounds were identified as products of this reaction.

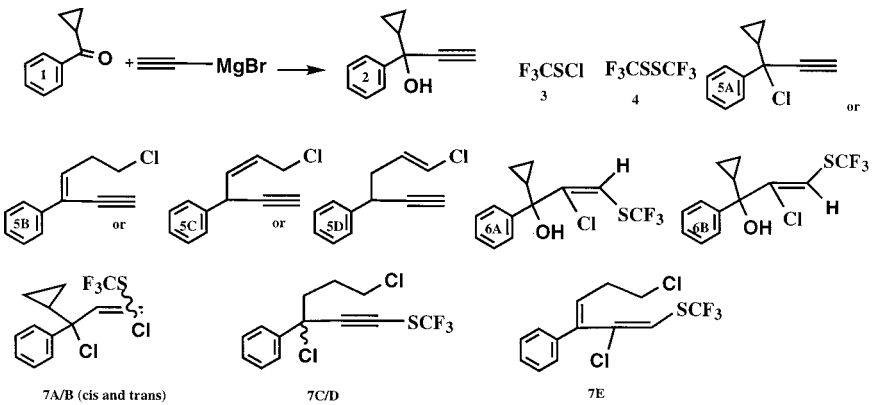

FIGURE 1 Structures of compounds cited in the text.

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Text

1. Bis-(trifluoromthyl)disulfide (**3**)	$M^+ = 202$ (100%; rt = 1.36 min, 1.8%); 183 (M—F); 133 (M—CF_3); 114 (133-F) and 69 (CF_3) [16].
2. Cyclopropyl phenyl ketone (**1**)	$M^+ = 146$ (rt = 6.4 min, 0.5%); 116 (M—C_2H_6); 105 (M—C_3H_5); 77 (C_6H_5); 69 (M—C_6H_5); and 51 (C_4H_3, 100%).
3. Cyclopropyl phenyl propargyl alcohol (**2**)	$M^+ = 172$ (not seen) (rt = 7.56 min, 0.90%); 144 (M—C_2H_4); 115 (M—C_3H_5—O); 105 (C_6H_5CO); 77 (C_6H_5); 53 (C_4H_5, 99.5%) and 51 (C_4H_3, 100%).
4. 1-Chloro-3-ene-4-phenyl-5-hexyne (**5b**)	$M^+ = 190$ (rt = 10.3 min, 26.8%); 153 (M—C_2H_3); 141 (M—CH_2Cl); 115 ($C_6H_5C_3H_2$); 128 (M—C_2H_3Cl); 102 (C_8H_6); 89 (C_4H_6Cl); 77 (C_6H_5); 74 (C_3H_3Cl); 62 (C_2H_3Cl) and 49 (CH_2Cl, 100%).
5. 1-Cyclopropyl-1-hydroxy-1-phenyl-2-chloro-3-(trifluoromethylthio)-2-propene [**6a** (cis) or **6b** (trans)]	$M^+ = 308$ (not seen) (rt = 12.26 min, 48.8%); 280 (M—C_2H_4); 245 (280-Cl); 225 (245-HF); 179 (280-SCF_3); 161 (C_2ClSCF_3); 128 ($F_3CSC_2H_5$); 115 (CH_3SCF_3); 105 ($C_6H_5C_2H_4$); 92 (C_2HSCl); 77 (C_6H_5); 69 (CF_3, 100%); 63 (CSF); 57 (C_2HS); 51 (C_4H_3) and 45 (CSH).
6. 1,4-Dichloro-4-phenyl-6-(trifluoro methylthio)-5-hexyne (**7c**)	$M^+ = 326$ (not seen) (rt = 12.0 min, 10.9%); 291 (M—Cl); 191 ($C_6H_5C_6H_7Cl$); 155 (191-Cl); 141 (155-CH_2); 128 ($C_2H_3SCF_3$); 102 ($HSCF_3$); 77 (C_6H_5); 69(CF_3); 62 (C_2H_3Cl); 51 (C_4H_3) and 49 (CH_2Cl, 100%).
7. 1,4-Dichloro-4-phenyl-6-(trifluoro methylthio)-5-hexyne (**7d**)	$M^+ = 326$ (rt = 12.26 min, 48.8%); 291 (M—Cl); 255 (291-HCl); 153 ($C_6H_5C_6H_6$); 128 ($C_2H_3SCF_3$); 115 (CH_2SCF_3); 92 (C_2HClS); 77 (C_6H_5); 69 (CF_3, 100%); 63 (CSF); 51 (C_4H_3) and 49 (CH_2Cl).
8. 1,5-Dichloro-4-phenyl-6-(trifluoro methylthio)-3,5-hexadiene (**7e**)	$M^+ = 326$ (not seen) (rt = 12.47 min, 1.2%); 291 (M—Cl); 189 (291-F_3CSH); 155 (191-Cl); 128 ($C_2H_3SCF_3$); 92 (C_2HCIS); 77 (C_6H_5); 69 (CF_3, 100%); 62 (C_2H_3Cl); 51 (C_4H_3) and 49 (CH_2Cl).

Besides bis-(trifluoromethyl)disulfide (**4**), among the products characterized were compounds formed by the addition of the F_3CS and Cl radicals and carrying the tertiary-hydroxyl group as well as compounds in which the hydroxyl group was replaced by Cl.

Based on their mass spectral fragmentation, in all seven compounds have been identified (Figure 1 and Table I). There is nothing unusual about the formation of bis-(trifluoromethyl)disulfide (**4**) in the free radical reactions involving trifluoromethylsulfenyl chloride (**3**).[5] This is formed by the dimerization of the trifluoromethylthiyl radical. Its mass spectrum has been previously described.[5g] The presence of cyclopropyl

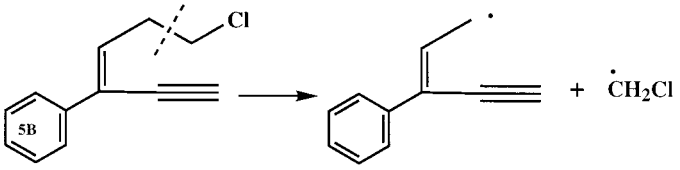

FIGURE 2 Mass spectral fission of compound 5b.

phenyl ketone (**1**, $M^+ = 146$, 0.5%, rt = 6.4 min) can be attributed to the reverse reaction, namely its formation from **2** via the loss of a C_2H_2 entity. Its mass spectrum has been described.[9] Its absence as an impurity in the starting material, namely cyclopropyl phenyl propargyl alcohol (**2**), was confirmed by the GC-MS analysis of the latter.

For the compound containing chlorine in place of the hydroxyl group of cyclopropyl phenyl propargyl alcohol (**2**), four structures, **5a**, **5b**, **5c**, and **5d** were considered. The presence of two ions at m/e = 141 and 49, corresponding to two moities shown in Figure 2, indicated the primary fission of this molecule and led to the structure **5b** for this compound, which is formed from the cleavage of the cyclopropyl ring by Cl radical, followed by dehydration. The ion with m/ = 49 formed the most intense peak in its mass spectrum. The next compound to come off the g.c. column at rt = 12.26 min happens to be the major product of the photochemical reaction. This compound can be represented either by **6a** or **6b**, which can be considered to have been formed from either cis or trans addition to the triple bond of **2**. This inference is due to the fact that its M^+ had increased by 136 and the molecular weight of $F_3CSCl = 136$. Due to steric crowding, this is assumed to be the trans adduct (**6b**). It must be said that no corroborative evidene exists at this point to support the above contention, other than the often-reported facile formation of the trans addition in the addition reactions.

Next to come are three isomers having the same molecular weight ($M^+ = 326$). One conspicuous thing about these isomers is the fact that they are all missing the hydroxyl group. The following five possible structures were considered for these three compounds: (a) 1-cyclopropyl-1,2-dichloro-1-phenyl-3-(trifluromethylthio)-2-propene [**7a** (cis) and **7b** (trans) adduct]; (b) 1,4-dichloro-4-phenyl-6-(trifluromethylthio)-5-hexyne (**7c** and **7d**) and (c) 1,5-dichloro-4-phenyl-6-(trifluromethylthio)-3,5-hexadiene (**7e**). Chlorine isotopic fragmentation pattern indicated the presence of two chlorine atoms in the said three compounds. This observation led to the conclusion that the hydroxyl group of **2** has been replaced by chlorine. The above inference was indirectly supported by the absence of ions arising from the

loss OH or H_2O from the parent molecules and/or from their respective fragments. Structures **7a** and **7b** both have their cyclopropyl entity intact and hence can not give rise to ions corresponding to CH_2Cl (me = 49). This left three structures, namely **7c**, **7d**, and **7e** as potential candidates for the three compounds in question. All three compounds (**7c**, **7d**, and **7e**) show intense peaks corresponding to the loss of CH_2Cl (me = 49). This observation confirmed the inference that these compounds do not carry an intact cyclopropyl ring. Their mass spectra show three ions, m/e = 141, 115 (CH_2SCF_3) and 49 (CH_2Cl; ^{37}Cl-ion was also seen) indicating that they do not possess the cyclopropyl entity. The proposed structure **7c** thus nicely accounts for the fragmentation pattern expected of the said compound. The mass spectral fragmentation of **7c** is very similar to that of **7d**. Although the parent peak of **7c** is not seen, its mass spectral breakdown clearly resembles that of **7d**, the molecular ion of which is observed. Structure **7e** with the cleaved cyclopropyl ring was considered for the third isomer. Figure 3 rationalizes its mass spectral breaksown. Structure **7e** represents trans addition to the triple bond. It arises via the addition of the thiyl and chlorine radicals to the triple bond of **5b**. However, the cyclopropyl ring of compounds **7c** and **7d** is cleaved. The photochemical cleavages implicated in the formation of compounds **5b**, **7c**, **7d**, and **7e** have precedents.[1,6,8] A similar type of thermally induced cleavage of the cyclopropyl entity has been reported.[10] In view of the fact that the cleavage of the carbon-carbon bond of cyclopropane requires only 69 kcal/mol,[11] the above observation appears to be on solid ground. Compounds **7c** and **7d** are stereomers (1,4-dichloro-4-phenyl-6-(trifluromethylthio)-5-hexyne), while **7e** is designated as 1,5-dichloro-4-phenyl-6-(trifluromethylthio)-3, 5-hexa-diene. Compound **7e** has an additional peak at m/e = 92 (C_2HClS). Its possible formation is shown in Figure 3. This suggested mechanism draws its support from the reported detection of the thiirane (CH_2CS) moiety, which is an analog of

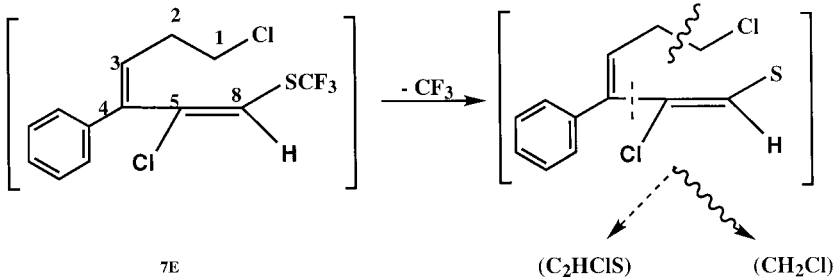

FIGURE 3 Structure elucidation of compound 7E.

ketenes and oxiranes.[12] In addition, the mass spectrum of the compound in question shows a peak at m/e = 49 (CH_2Cl).

Finally, the product formation and distribution of the photocatalyzed reaction were compared with those obtained from the nonphotolytic reaction and found to be almost identical except that the latter did not contain compounds **4** and **5b**. The mass spectral fragmentation and retention times of the rest of the compounds were identical (Table I).

EXPERIMENTAL PART

Care and caution should be exercised while working with F_3CSCl (**1**)[13] and F_3CSSCF_3. All solvents were dry and freshly distilled prior to their use. The reactions were carried out at −80°C using stoichiometric amounts of the reactants and the temperature of the coolant circulating through the condenser was maintained at −15°C. The reaction mixture was stirred under argon for two hours at −80°C and stirred overnight at ambient temperature. The reaction mixture was initially analyzed using gas chromatography. For the GC-MS analysis the residue, after the removal of the solvent under reduced pressure, was carefully distilled under vacuum (2∼3 mm Hg) to avoid decomposition. 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 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 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 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).

Cyclopropyl Phenyl Propargyl Alcohol (2)

To a solution of cyclopropyl phenyl ketone (**1**. 3.6 g, 0.025 mmol) in dry ether (50 ml) stoichiometric amounts of ethynylmagnesium bromide

(0.5 M in THF) were added dropwise with stirring and under nitrogen at 0°C. The mixture was stirred for 4 h at 0°C, treated dropwise with an ice-cold solution of saturated ammonium chloride, the organic extract separated, the aq. layer extracted with ether, the combined organic layer washed successively with water, and saturated salt solution, dried over anhydrous sodium sulfate, solvent removed under reduced pressure and the residue distilled under vacuum to give cyclopropyl phenyl propargyl alcohol (**2**, b.p. 110–112°C/5 mm Hg).[7]

Photo-Reaction of Cyclopropyl Phenyl Propargyl Alcohol (2) with Trifluoromethyl-sulfenyl Chloride (3)

A solution of cyclopropyl phenyl propargyl alcohol (**2**, 1 mmol) in freshly distilled dry acetonitrile (5 ml) contained in a 10 ml three necked flask carrying dry ice cooled Dewar condenser was sparged with stoichiometric amounts of trifluoromethylsulfenyl chloride (**3**) at −78°C. The mixture was allowed to come to ambient temperature and was then irradiated with a 100 Watt mercury lamp for 30 min. The GC-MS analysis of the reaction mixture showed it to consist of 8 components including the starting material. The structures of these compounds have been ascertained from the study of their mass spectral fragmenation behavior. The reaction mixture appears to undergo decomposition during distillation. To avoid decomposition, it was analyzed after the removal of the solvent under reduced pressure at room temperature. The percentages in the parenthesis indicate the amount of each compound present in the mixture as determined by GC and GC-MS (Table I). Thus, (a) bis-(trifluoromethyl)disulfide (4), cyclopropyl phenyl propargyl alcohol (**2**), cyclopropyl phenyl ketone (**1**), (d) 1-chloro-4-phenyl-3-ene-5-hexyne (**5b**), (e) 1-cyclopropyl-1-hydroxy-1-phenyl-2-chloro-3-(trifluoromethylthio)-2-propene (**6a** or **6b**, cis or trans adduct), (f–g) 1, 4-dichloro-4-phenyl-6-(trifluoromethylthio)-5-hexyne (**7c–7d**, stereomers), and (h) 1, 5-dichloro-4-phenyl-6-(trifluoromethylthio)-3,5-hexadiene (**7e**) were identified.

Nonphotocatalyzed Reaction of Cyclopropyl Phenyl Propargyl Alcohol (2) with Trifluoromethylsulfenyl Chloride (3)

A solution of cyclopropyl phenyl propargyl alcohol (**2**, 2 mmol) in freshly distilled dry acetonitrile (5 ml) contained in a 10 ml three necked flask carrying a dry ice cooled Dewar condenser was sparged with stoichiometric amounts of trifluoromethylsulfenyl chloride (**3**) at −80°C. The reaction mixture was stirred at this temperature for 2 h and stirring

continued overnight at ambient temperature. The GC-MS analysis of the reaction mixture showed the absence of compounds **4** and **5b**. The rest of compounds were common to both reactions as judged by their GC-MS data and retention times (Table I).

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