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# Phototrifluoromethylsulfenylation of phenylcyclopropane

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**Abstract**

Cyclopropane and its derivatives undergo reactions analogous to alkenes as well as free-radical reactions leading to products corresponding to ring-fission, ring-substitution and rearrangement reactions. When a solution of phenylcyclopropane and trifluoromethylsulfenyl chloride in acetonitrile is photolyzed, eight to ten compounds are formed in various amounts depending on the duration of the photolysis. The spectrometric characterization and the mechanism of formation of the various products are presented in this paper. 

*Keywords:* Cyclopropane; Trifluoromethylsulfenyl; Photolysis

## 1. Introduction

The fascinating chemistry of the cyclopropane-ring has been the subject of monograms and reviews [1–5]. The cyclopropanes, under a variety of reaction conditions, undergo a variety of ring-fission, ring-substitution and rearrangement reactions and these processes are facilitated by ring-strain relief. This has made the cyclopropyl moiety a versatile functional group in organic synthesis and transformations [1,3,5]. Substituents present on the cyclopropane ring affect its geometry, thermodynamic and kinetic stabilities and properties [2,6,7]. The presence of fluorine atom(s) on the cyclopropane ring profoundly modifies its behavior and reactivity [8,9]. In fact, the replacement of its hydrogen atom(s) with fluorine atom(s) almost doubles the strain energy of its hydrocarbon analog [10,11]. Highly fluorinated perfluorocyclopropanes undergo thermally catalyzed ring opening in the presence of halogens to furnish 1,3-dihaloperfluoropropanes via biradical intermediates [12].

Recently, considerable interest has been manifested in the study of the substituent effects in the regiochemistry of cyclopropane ring opening during free radical halogenation [13–16]. Hydrogen abstraction and ring fission are commonly observed in free radical reactions of cyclopropanes [17]; the former occurs with highly reactive radicals [18] while the latter takes place with less reactive radicals [19]. The chemoselectivity exhibited by chlorine radicals appears to depend on both the nature of the solvent [15] and the temperature of the reaction [18]. However, the ring cleavage products are exclusively obtained with bromine radicals [13–16,20,21]. The transition state in the homolytic bromination of phenylcyclopropane (**1**) has been suggested to have some charge separation (polar) and the site of attack to be the benzylic carbon (Scheme 1) [22]. Chlorine radicals yielded compounds resulting from both hydrogen abstraction and ring cleavage, while bromine radicals exclusively furnished

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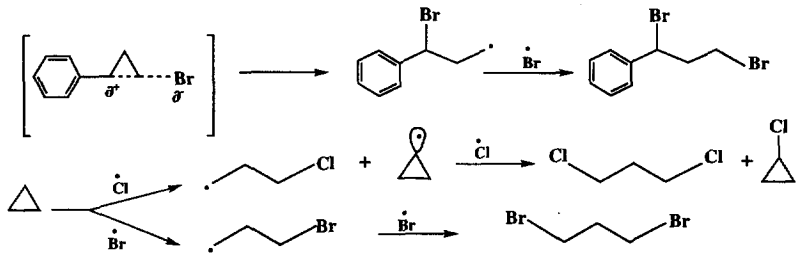


Scheme 1.

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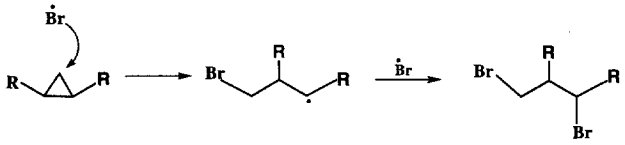
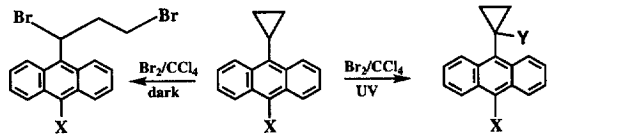


Scheme 2.



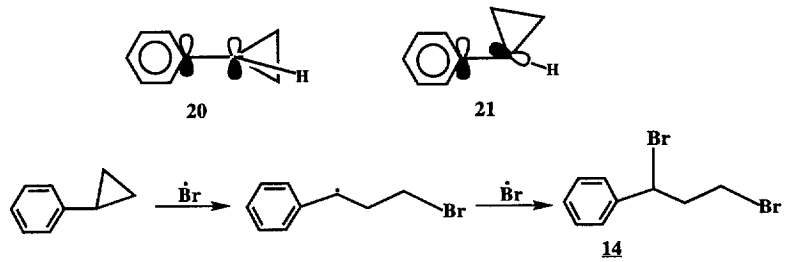
19: X = Cl or Br
16: X = H
18: X = Cl or Br
17: X = H; Y = Cl or Br

Scheme 3.

ring fission products [18]. Condensed-phase free radical chlorination of cyclopropane furnished four products: (i) 1-chlorocyclopropane, (ii) 1,1-dichlorocyclopropane, (iii) 1,3-dichloropropane and (iv) 1,2,3-trichlorocyclopropane in varying yields depending on the solvent [14,18]. The photochemistry of the cyclopropanes and vinylcyclopropanes has been reviewed [23] and the photoisomerization of cyclopropanes to olefins has been discussed [24–26].

In an extensive examination, the bromine radical has been shown to attack from the backside of the least-hindered carbon of alkylcyclopropanes causing inversion of the configuration and yielding products derived from the most stable radical intermediate (Scheme 2) [21]. The reaction of bromotrichloromethane with phenylcyclopropane (**1**) furnished starting material (77%) and 1,3-dibromo-1-phenylpropane (**14**, 23%) and continued irradiation in the presence of benzoyl peroxide yielded **1** (58%) and **14** (42%) [27]. Exposure to a 450 W Hg arc lamp of a solution of **1** and $Br_2$ gave 1,3-dibromo-1-phenylpropane (**14**) in quantitative yield while in the dark (*p*-bromophenyl)cyclopropane (**15**) was formed [16]. However, dilute bromination of 9-cyclopropylanthracene (**16**) in $CCl_4$ gave a 70% yield of 1-(9-anthryl)cyclopropyl bromide (**17**) [12]. Strangely enough, the reaction of 9-halo-10-cyclopropylanthracene (**18**) with $Br_2$ in the dark resulted in the quantitative formation of the cyclopropyl ring cleavage products (**19**) (Scheme 3) [13].

Phenylcyclopropane (**1**) is said to exist in two conformations: (i) bisected (**20**) and (ii) perpendicular (**21**). The bisected conformer (Scheme 4) has been calculated to be more stable than its perpendicular conformer by about 1.4 kcal/mol [14]. The bisected conformer enjoys partial relief of ring strain while the perpendicular conformer suffers additional strain from the change in the hybridization from $sp^3$ to $sp^2$. It is claimed that hydrogen abstraction is possible only



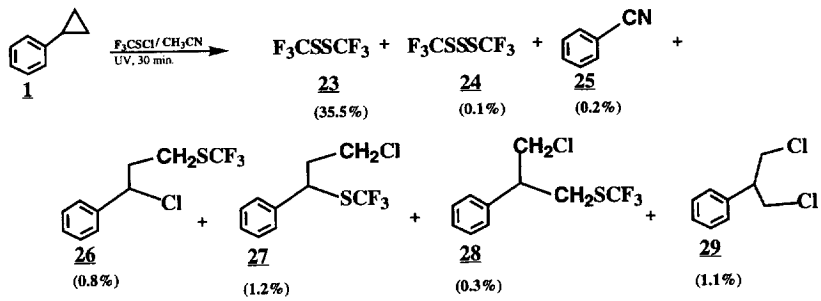
20 21

14

Scheme 4.

**Photo-catalyzed Reaction of Phenylcyclopropane (1) with Trifluoromethylsulfenyl chloride (22)**

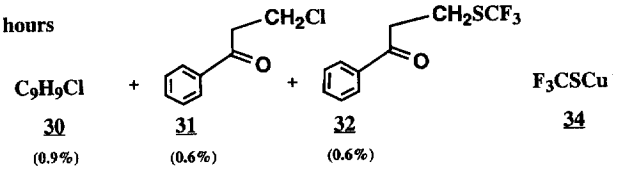
**Part A: For 30 minutes**



1 → $F_3CSSCF_3$ (**23**, 35.5%) + $F_3CSSSCF_3$ (**24**, 0.1%) + (**25**, 0.2%) +

(**26**, 0.8%) + (**27**, 1.2%) + (**28**, 0.3%) + (**29**, 1.1%)

**Part B: Additional 2 hours**



$C_9H_9Cl$ (**30**, 0.9%) + (**31**, 0.6%) + (**32**, 0.6%) + $F_3CSCu$ (**34**)

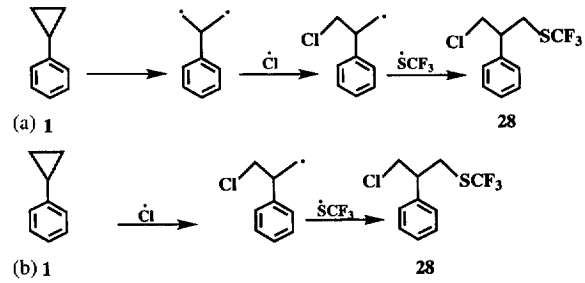
Scheme 5.

in the perpendicular conformer [14]. In continuation of our interest in the chemistry of the trifluoromethylthiyl group [28–35], we have investigated the photocatalyzed reaction of phenylcyclopropane (**1**) with trifluoromethylsulfenyl chloride (**22**). This paper describes the formation and mass spectral characterization of compounds listed in Scheme 5.

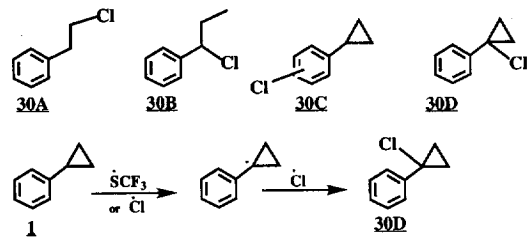
## 2. Results and discussion

An unusual photochemical rearrangement involving the facile fission of the cyclopropyl ring and stereoisomerism of the substituents attached to the cyclopropyl carbon has been reported [25]. Thermolysis and photolysis of the spirocyclopropanes and formation and rearrangement of the 1,3-diradicals have been discussed [24]. Also, the involvement of the diradical intermediate has been implicated in the thermal rearrangement of optically active *trans*-2-methyl-1-(*trans*-2-phenylethynyl)cyclopropane to enantiomeric methylphenylcyclopentenes and 1-phenyl-2,5-hexadiene [36]. It appears that the photochemical reaction of phenylcyclopropane (**1**) with trifluoromethylsulfenyl chloride (**22**) is neither regioselective nor chemoselective, for it yields compounds **23–33**, although it was not possible to characterize **33**. The results are reminiscent of the non-regioselective homolytic chlorination of **1** [15,19]. The formation of the compounds 1-chloro-1-phenyl-3-(trifluoromethylthio)propane (**26**) and 1-phenyl-1-(trifluoromethylthio)-3-chloropropane (**27**) has precedents and can be easily rationalized. The formation of compound 1-chloro-2-phenyl-3-(trifluoromethylthio)-propane (**28**) can be rationalized as shown in Scheme 6a–b. The diradical intermediate may be envisaged as being formed by the fission of the cyclopropyl carbon–carbon bond rather than the cleavage of the bond linking the cyclopropyl ring to the phenyl moiety to give a diradical intermediate which then goes on to give the product (Scheme 6a). A similar thermal cleavage of the carbon–carbon bond of the cyclopropyl ring system has been reported [37,38]. However, it seems more plausible and readily acceptable to infer that compound **28** is formed via the cleavage of the carbon–carbon bond of the cyclopropane ring (Scheme 6b). This inference is supported by the observation that the cleavage of the carbon–carbon bond of the cyclopropanes requires only 61 kcal/mol [39].

The formation of benzonitrile (**25**) can be ascribed to the displacement of the cyclopropyl substituent by the cyano-radical ( CN) formed by the free radical cleavage of acetonitrile, the solvent in which the reaction is carried out. There are precedents for the involvement of the solvents in free radical catalyzed reactions [40–45]. Four isomeric structures, **30A–D** (Scheme 7) can be considered for compound **30** ($C_8H_9Cl$). Structure **30A** owes its origin to the competitive electrophilic aromatic substitution reaction and has a precedent [13]. The presence of ions with $m/e=75$ ($C_3H_4Cl$) and $m/e=77$ ($C_6H_5$) in the mass spectrum led to the assignment of structure **30D** (1-chloro-1-phenylcyclopropane) to compound **30**. Compounds **31** and **32**, appear to




Scheme 6.




Scheme 7.

result from the oxidation of compounds previously formed by the cleavage of the cyclopropyl ring. It is conceivable that the non-regioselectivity observed here may be due to the fact that the bisected and the perpendicular conformers of phenylcyclopropane (**1**, Scheme 4) may be giving rise to different radical intermediates after the abstraction of the cyclopropyl hydrogen. In addition to this, radical rearrangements may also be occurring simultaneously. Here, it must be stated that the abstraction of the hydrogen has been stated to occur only from the perpendicular conformer of **1** [16]. The cyclopropyl ring remained intact under similar experimental conditions when **1** was reacted with both bis(trifluoromethyl)disulfide (**23**) and trifluoromethylthiocopper (**34**), although the latter successfully opened the oxirane ring [46].

The mass spectral fragmentation behavior of the compounds listed in Scheme 5; namely bis(trifluoromethyl)-disulfide (**23**), bis(trifluoromethyl)-trisulfide (**24**), benzonitrile (**25**), 1-chloro-1-phenyl-3-trifluoromethylthiopropane (**26**), 1-phenyl-1-trifluoromethylthio-3-chloropropane (**27**), 1-chloro-2-phenyl-3-trifluoromethylthiopropane (**28**), 1,3-dichloro-3-phenylpropane (**29**), 1-chloro-1-phenylcyclopropane [**30** or **30D** (Scheme 7)], ω-chloropropiophenone (**31**) and -trifluoromethylthiopropiophenone (**32**); supports the structures assigned to them. The mass spectral and NMR data of compounds **23–24** have already been reported [47–49]. The mass spectrum of benzonitrile (**5**) is identical with that reported [50]. The mass spectral fragmentation of the remaining compounds is given in Table 1. The molecular ion peaks are seen for compounds **26–32**. Compound **33** fragments and loses a large piece of the molecule during the flight and hence its molecular ion peak was not recorded. The first peak in the mass spectrum of **33** is $m/e=105$ ($C_6H_5CO$). This was not sufficient to assign the structure for **33**.

The splitting off of the $SCF_3$ ($m/e=101$) and $CF_3$ ($m/e=69$) appears to be the common characteristic of com-

Table 1
Mass spectral fragmentation of compounds (26–32) cited in the text

| | |
|---|---|
| 1-Chloro-1-phenyl-3-(trifluoromethylthio)propane (**26**) (retention time: 8.33 min) | $M^+$ = 254; 219 (M − Cl); 153 (M − $SCF_3$); 134 (M − $CF_3$–$C_4H_3$); 125 ($C_6H_5CHCl$, 100%); 117 ($C_6H_5C_3H_4$); 105 (M − Cl–$CH_2SCF_3$); 91 ($C_7H_7$); 82 ($CSF_2$); 77 ($C_6H_5$); 63 (CSF) and 51 ($C_4H_3$). |
| 1-Phenyl-1-(trifluoromethylthio)-3-chloropropane (**27**) (retention time: 9.04 min) | $M^+$ = 254; 191 (M − $CH_2CH_2Cl$); 153 ($C_6H_5C_3H_5Cl$); 135 ($C_5H_6SCl$); 117 ($C_6H_5C_3H_4$); 115 ($CH_2SCF_3$); 104 (M − $SCF_3$–$CH_2Cl$); 91 ($C_7H_7$, 100%); 82 ($CSF_2$); 77 ($C_6H_5$); 69 ($CF_3$); 63 (CSF) and 45 (CSH). |
| 1-Chloro-2-phenyl-3-(trifluoromethylthio)propane (**28**) (retention time: 8.46 min) | $M^+$ = 254; 135 ($C_6H_5C_2H_2S$); 126 ($C_2HSCF_3$); 115 ($CH_2SCF_3$); 91 ($C_7H_7$, 100%); 77 ($C_6H_5$); 69 ($CF_3$);63 (CSF) and 51 ($C_4H_3$). |
| 1,3-Dichloro-1-phenylpropane (**29**) (retention time: 9.40 min) | $M^+$ = 188; 153 (M − Cl); 139 (M − $CH_2Cl$); 125 ($C_6H_5CHCl$); 117 ($C_6H_5C_3H_4$); 103 ($C_6H_5C_2H_2$); 91 ($C_7H_7$, 100%); 77 ($C_6H_5$); 63 ($C_2H_4Cl$); 55 ($C_3H_3O$); 51 ($C_4H_3$) and 49 ($CH_2Cl$). |
| 1-Chloro-1-phenylcyclopropane (**30**) (retention time: 7.17 min) | $M^+$ = 152; 137 (M − $CH_3$); 125 (M − $C_2H_3$); 117 (M − Cl, 100%); 91 ($C_7H_7$); 89 (M − $C_2H_2Cl$); 77 ($C_6H_5$); 75 ($C_3H_4Cl$); 65 ($C_5H_5$); 63 ($C_2H_2Cl$) and 51 ($C_4H_3$). |
| ω-Chloropropiophenone (**31**) (retention time: 9.40 min) | $M^+$ = 168; 133 (M − Cl); 105 ($C_6H_5CO$, 100%); 77 ($C_6H_5$); 63 ($C_2H_4Cl$); 55 ($C_3H_3O$); 51 ($C_4H_3$) and 49 ($CH_2Cl$). |
| ω-Trifluoromethylthiopropiophenone (**32**) (retention time: 9.55 min) | $M^+$ = 234 (not seen); 232 (M − 2H); 165 (M − $CF_3$); 147 (165-$H_2O$); 128 ($C_2H_3S\,CF_3$); 105 ($C_6H_5CO$, 100%); 89 (M − $CF_3$–$C_6H_5$); 77 ($C_6H_5$); 69 ($CF_3$); 55 ($C_3H_3O$); 50 ($CF_2$) and 45 (CSH). |

pounds containing this functional group. Other ions that permit the recognition of this moiety are $m/e$ = 82 ($CSF_2$), $m/e$ = 63 (CSF) and $m/e$ = 50 ($CF_2$). Also, seen is $m/e$ = 45 (CSH). An interesting feature of the mass spectral fragmentation behavior is the presence of $m/e$ = 91 and $m/e$ = 77 ions corresponding to ($C_7H_7$) and ($C_6H_5$), respectively. The first ion results from the cleavage of the cyclopropyl moiety and the migration of hydrogen to give the benzylic ion. The second one arises due to the loss of the cyclopropyl moiety itself. Another interesting observation is the presence of the benzylic ion in the mass spectra of the cleavage products presumably formed via hydrogen migration. The $C_6H_5$ ($m/e$ = 77) ion is due to the cleavage of the bond between the phenyl ring and the side chain. Four structures **30A–D** (Scheme 7) merit consideration for compound **30** ($C_9H_9Cl$, M + = 152). Structures **30A–B** were considered in the light of the recent work of Tanko et al. [13]. Since these structures cannot accommodate the formation of ions $m/e$ = 125, 89, 77, 75, 63 and 58, they were rejected. Additionally, their molecular weights are two units greater than that of **30**. Thus, structures **30C–D** are left as contenders for compound **30**. Before deciding the correct structure for **30**, it is appropriate to discuss the mass spectral fragmentation of phenylcyclopropane itself. The mass spectral behavior of the isomeric $C_9H_{10}{}^+$. radical cations and the unstable cyclopropenium ion $C_9H_9{}^+$ has attracted considerable attention [51–54]. Seen in the mass spectrum of phenylcyclopropane (**1**) are the $M^+$, $M+1^+$ and $M+2^+$ ions. However, it is the $M-1^+$ peak that is the most prominent ion (100%). Prominently noticeable in the EI, FI (field ionization) and CAD (collision activated dissociation) spectra of **1**, are $C_9H_9{}^+$, $C_9H_7{}^+$, $C_8H_7{}^+$, $C_7H_7{}^+$, and $C_4H_3{}^+$ ions corresponding to $m/e$ = 117, 115, 103, 91, 77 and 51 respectively. Also, characteristically seen is the fragment ($m/e$ = 580, which has been ascribed to the presence of the doubly charged ion [52]. Although, **1** gives the $M-CH_3$ peak under EI, FI and CAD conditions, it happens to be the prominent ion under FI.

The formation of the phenylcyclopropenium ion ($m/e$ = 115, $C_9H_7{}^+$) resulting from the loss of the $CH_3$ fragment from its parent ion, namely $M^+$ = 152, phenylchloromethylcarbonium ion ($m/e$ = 125, $C_6H_5CHCl^+$) and the chlorocyclopropylium ion ($m/e$ = 75, $C_3H_4Cl^+$) cannot be easily reconciled and accommodated with **30C**. The observation that 1,1-disubstituted cyclopropanes containing a phenyl and heteroatoms undergo diverse fragmentation [51], led to the consideration of **30D** as the most probable structure for **30**. The structure **30D** very nicely accommodates the formation of the above cited ions, namely $m/e$ = 125, 115 and 75. Scheme 7 attempts to rationalize the formation of **30D**.

## 3. Experimental

All solvents were dry and freshly distilled prior to use. The trifluoromethylthiocopper···acetonitrile adduct was prepared from bis(trifluoromethyl) disulfide as described elsewhere [36]. The reactions were carried out in a flame-dried, argon gas-purged 10 or 25 ml three-necked flask equipped with a magnetic stirrer, gas inlet-adaptors and a reflux condenser carrying a dry ice/ acetone cooled trap. The temperature of the coolant passing through the condenser was maintained at −20°C. All reactions were carried out by addition of stoichiometric amounts of trifluoromethylsulfenyl chloride via the vacuum line to the substrate cooled to −78°C. The reaction mixture was initially analyzed by GC and GC/MS, then the solvent was evaporated under reduced pressure and the residue was vacuum distilled and again analyzed by GC/MS. Mass spectra were obtained on a Finnigan Model 5100 GC/MS equipped with a silica 25 m × 0.31 mm i.d. SE-54 capillary column (J&W, Rancho Cordova, CA). Routine GC

analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a J&W 30 m×0.53 mm i.d. DB-5 column (J&W, Folsom, CA).

### 3.1. Reaction of phenylcyclopropane (1) with trifluoromethylsulfenyl chloride (22)

A solution of phenylcyclopropane (**1**, 0.1 g) in freshly distilled dry acetonitrile (1 ml) in a 5 ml round-bottom flask carrying dry ice-acetone cooled Dewar condenser was sparged with trifluoromethylsulfenyl chloride (**22**, 1.1 g) at −78°C. The mixture was allowed to come to room temperature and then irradiated with a 100 Watt mercury lamp for 30 min. The GC/MS analysis of the reaction mixture indicated the presence of eight components. Based on their mass spectral fragmentation behavior, these compounds have been characterized: (a) bis(trifluoromethyl)disulfide (**23**, 35.5%, mol. wt. 202), (b) bis(trifluoromethyl)trisulfide (**24**, 0.1%, mol. wt. 234), (c) benzonitrile (**25**, 0.2%, mol. wt. 103), (d) phenylcyclopropane (**1**, 62.6%, starting material), (e) 1-chloro-1-phenyl-3-(trifluoromethylthio)propane (**26**, 0.8%, mol. wt. 254), (f) 1-phenyl-1-(trifluoromethylthio)-3-chloropropane (**27**, 1.2%, mol. wt. 254), (g) 1-chloro-2-phenyl-3-(trifluoromethylthio)propane (**28**, 0.1%, mol. wt. 254), and (h) 1,3-dichloro-1-phenylpropane (**29**, 0.8%, mol. wt. 254).

### 3.2. Extended reaction of phenylcyclopropane (1) with trifluoromethylsulfenyl chloride (22)

Since the reaction mixture contained relatively large amounts of bis(trifluoromethyl)disulfide (**23**, 35.5%) and the unreacted starting material, the photoreaction was continued for an additional 2 h to see whether the trifluoromethylthiyl radicals generated from **3** would cleave the cyclopropane ring. The GC/MS analysis of the reaction mixture did not show any significant changes in the amounts of the compounds cited above (**23–29**). However, the presence of four more new products was detected. Of these, based on their mass spectral fragmentation behavior, three new compounds have been characterized as: (1) 1-chloro-1-phenylpropane (**30**, 0.9%, mol. wt. 152), (2) -chloropropiophenone (**31**, 0.55%, mol. wt. 168) and (3) -trifluoromethylthiopropiophenone (**32**, 0.6%, mol. wt. of 232). The fourth one (**33**) could not be identified, for it did not show the M+ ion peak.

### 3.3. Attempted photocatalyzed ring cleavage of phenylcyclopropane (1) with bis(trifluoromethyl)disulfide (23)

This reaction was conducted in an analogous manner as described above except that AIBN was added as a free radical reaction initiator. The GC analysis of the reaction mixture indicated it to consist primarily of the starting materials.

### 3.4. Reaction of trifluoromethylthiocopper (34) with phenylcyclopropane (1)

Since the photolysis of a mixture of phenylcyclopropane (**1**) and bis(trifluoromethyl)disulfide (**34**) failed to cleave the cyclopropane ring of phenylcyclopropane (**1**), a solution of **1** and trifluoromethylthiocopper (**23**) in freshly distilled dry acetonitrile was heated at 90–100°C for 4 h. The reaction mixture was allowed to come to room temperature and filtered over celite. The GC/MS analysis of the reaction mixture did not show the presence of products expected of the cleavage of the cyclopropyl ring.

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