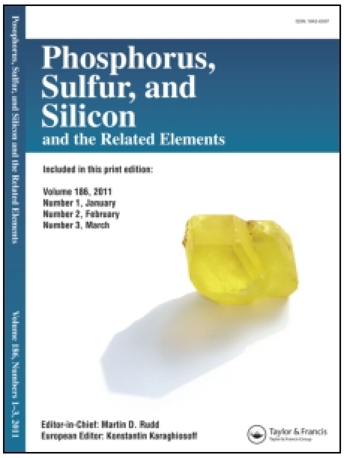

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Trifluoromethylthiocubanes and (Trifluoromethylthio)cubylcubanes

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Trifluoromethylthiocubanes and (Trifluoromethylthio)cubylcubanes

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Reaction of trifluoromethylthiocopper with 1,4-diiodo- and 1-bromo-4-iodocubanes furnishes 1-iodo-4-(trifluoromethylthio)-, 1-bromo-4-(trifluoromethylthio)-, and 1,4-bis(trifluoromethylthio)cubanes in respectable yields (Scheme 1). However, the reaction of iodocubane with trifluoromethylthiocopper under identical conditions yields a complex mixture of mono- and di-substituted cubanes and mono- and di-substituted cubylcubanes (Figure 1). The probable mechanism of their formation and mass spectrometric characterization of the title compounds are presented in this article.

Keywords Cubane radical; cubanediyne (cubane diradical); cubylcubane; dehydrocubane; free radical catalyzed dimerization; trifluoromethylthiocopper

Since its synthesis, cubane with its unique symmetrical molecular geometry and rigdity and exceptionally strained structure has created continued curiosity and interest. The molecule is also attractive from an aesthetic point of view. The chemistry of the molecule is equally fascinating. After its spectacularly successful synthesis in the 1960s,[1] all was quiet on the cubane front until the 1980s! Then, all of a sudden there was an explosion of activity in the functionalization of cubane since it

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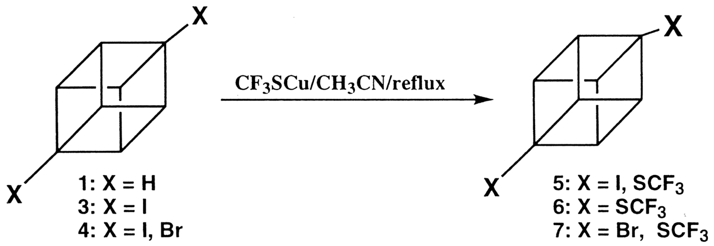


SCHEME 1 Trifluoromethylthiocubanes.

was reported that "polynitrocubanes possess a very high heat of formation and exceptionally high density".[2] May be the polynitrocubanes exhibit better explosive characteristics than TNT! A historical overview on the synthesis and the chemistry of cubane along with related highlights had appeared.[3]

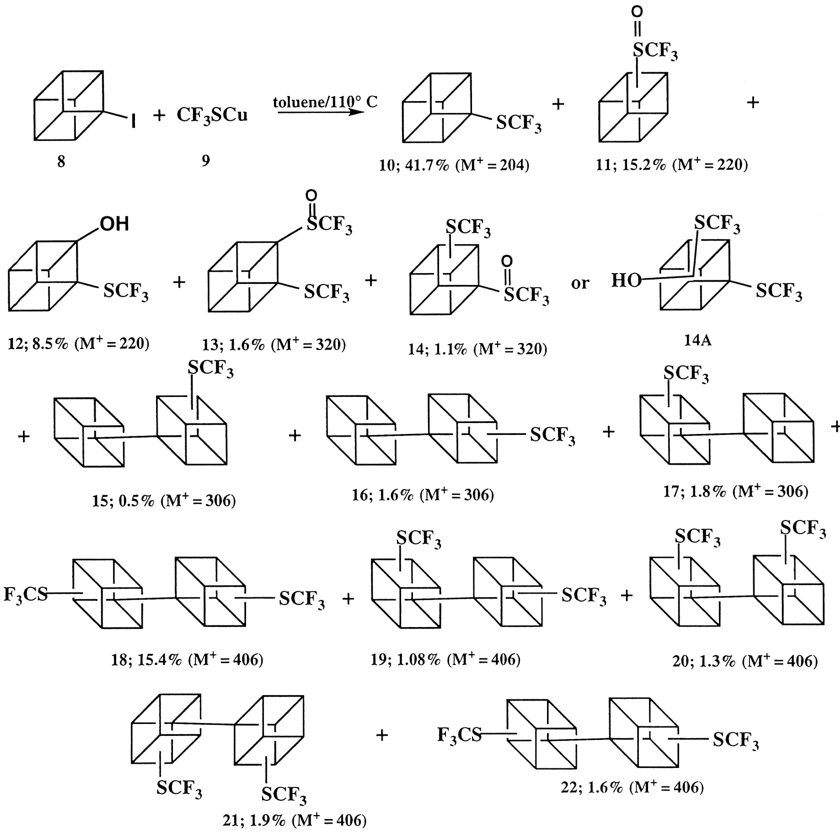
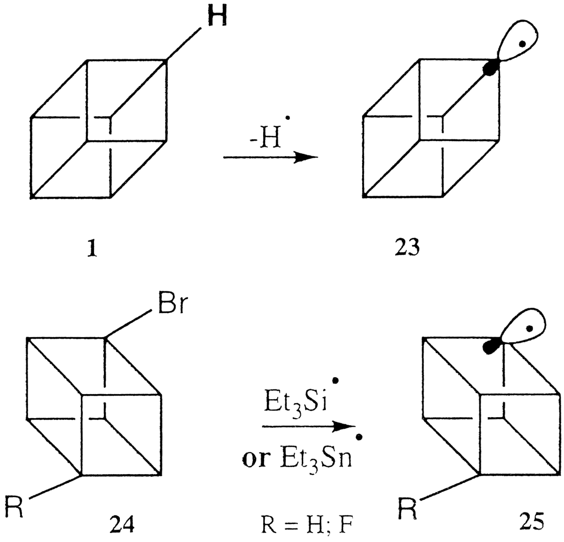


FIGURE 1 Cubylcubanes from the reaction of F_3CSCu with iodocubane.

RESULTS AND DISCUSSION

Cage molecules have rigid structures, well-defined distances between functional groups, locked-in conformations, nonpolar bridgeheads, and globular shape, all of which are very desirable properties in drug design. Drugs containing cage molecules are fat soluble and are not readily degraded in the physiological matrices. In addition, they are also persistent and long acting. The introduction of the trifluoromethylthio group into the structures of the cage molecules was considered to enhance the biopharmacological properties of the parent compounds. The reaction of iodocubane derivatives with trifluoromethylthiocopper was expected to provide an access to a small library of new and unique molecules with different sizes and shapes endowed with enhanced bioactive properties.

Among the several unusual effects of the cubane molecule, cubyl radical had been predicted to be minor and strongly pyramidal with a high s-character that is highly reactive.[4] The cubyl radicals have been implicated as intermediates in several reactions.[5] Photolysis of cubanecarboxylic acid in Freon 113 in the presence of of t-butylhypoiodate gives iodocubane.[6] Because of the powerful driving forces, the formation of cubyl radicals has been implicated in the tinhydride reduction of halocubanes.[7] Since the bridgehead hydrogens on the cubane skeleton are quite reactive to homolytic cleavage of the carbon–hydrogen bond, the cubyl radicals can be generated directly (**23**, Figure 2). It has been



FIGURES 2 and 3 Formation of cubyl radicals.

shown that t-butoxyl radicals directly abstract bridgehead hydrogens from cubane and substituted cubanes.[5] The bromocubane derivative (**24**, Figure 3) reacts with triethylsilyl and triethylstannyl radicals and forms the respective cubyl radicals (**25**).

Photolysis of 1,4-dicarboxylic cubane in the presence of t-butylhypoiodite furnishes, in addition to the expected 1,4-diodocubane, 1,2,4-triiodocubane. When this mixture was similarly photolyzed, the yields of the triodocubane increased at the expense of the diodocubane. Also detected in the reaction mixture were "11 minute" 1,2,4,7- 1,2,4,6-, and 1,2,3,4-tetra-iodocubanes and a penta-iodocubane.[4c] Photochemical carboxylation of cubanes leads to multiply-substituted derivatives. The exposure of carboxy or carboxylchloride or carbomethoxycubane and oxalyl chloride to UV light, followed by the treatment with methanol, gives a mixture of di-, tri-, tetra-, and pentamethoxycarbonylcubanes.[8] This observation led to the generalization that by virtue of the molecular symmetry, the cubyl radical is truly an exceptional species in that it remains intact and retains "its integrity under a variety of conditions".[9] According to these authors, "Dimerization to give cubylcubanes is a likely dominant termination."[9] Yet, they did not detect any dimerized cubane(s).

When methylcubane reacted with t-butoxyl radicals genrated from di-t-butylperoxide at −120°C, the presence of 4-methylcubyl radical (**27**) was detected by ESR. Also detected were 2-methyl- and 3-methylcubyl radicals (**28** and **29**, Figure 4). However, hydrogen abstraction from the methyl moiety was not observed. This suggests that hydrogens from the bridgehead are fair game for free-radical abstraction and that cubyl radical exhibits a high degree of reactivity. The possibility of the existence of 1,2-dehydrocubane (cubene), a compound carrying a bridgehead double bond, an anti-Bredt olefin, was predicted[10] even before its actual synthesis.[11] Based on calculations and other evidence, the presence of three isomeric cubenes, namely 1,2-, 1,3-, and 1,4-dehydrocubanes, has been considered (Figure 4).[12] Although all of the dehydrocubanes exhibit diradical character (cf. Figure 5), the 1, 4-dehydrocubane is said

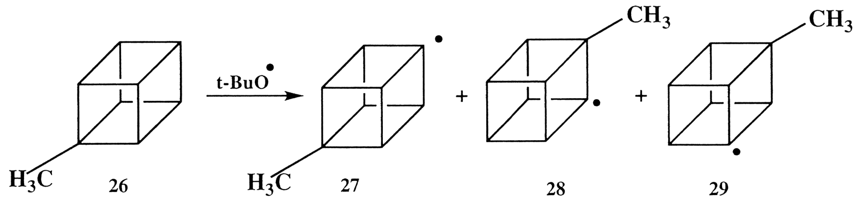
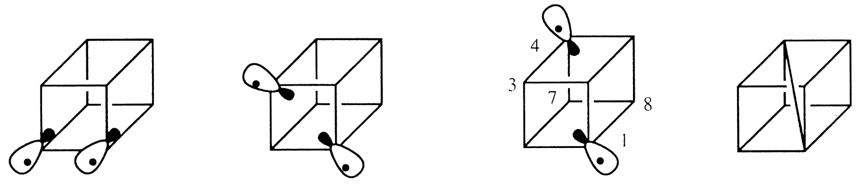


FIGURE 4 Formation of cubyl radicals.



30 31 32 33

FIGURE 5 Formation of cubyl diradicals.

to posses more diradical character than the other counterparts. Dehydrocubanes have been prepared from the reaction of t-BuLi with respective dihalocubanes at −100°C and its reactions have been described to be anionic in nature.[11] Thus starting from, 1,4-diiodocubane, 1,1′-carbomethoxy-4,4′-cubylcubane has been obtained.[13]

Recently, cubane derivatives have been used to create a library of compounds containing aminoacids[13a] and to prepare medicinal compounds.[13b] The incorporation of fluorine and fluorine-containing moieties such as trifluoromethyl and trifluoromethylthio groups have been reported to enhance the biopharmacological properties of the parent compounds.[14] We have been particularly interested in the latter functionlity, namely the trifluoromethylthio group. There are a number of reasons for this. First, the trifluoromethylthio group is highly lipophilic and is retained in the body for an extended period of time. Second, it has been described as a pseudohalogen in that its electronegativity has been calculated to be very close to chlorine. Third, the group is highly stable under acidic conditions; it is said to remain intact even in the presence of concentrated H_2SO_4. Fourth, this work is in continuation of our interest in the chemistry of the trifluoromethylthio group[15] and the reaction of trifluoromethylthiocopper with 1,4-dihalocubane.[15f]

Our work with cubane was initiated with a view to explore its transformation into bioactive compounds(s) containing the SCF_3-function. Reaction of iodocubane (**8**) with trifluoromethylthiocopper (**9**) at 90–100°C gave including the expected trifluoromethylthiocubane (**10**) 12 new compounds (Figure 1). Among these compounds are (1) two mixed cubylcubanes, (2) five dimerized cubylcubanes, (3) two (CF_3S)-[$CF_3S(O)$]-substituted cubanes, and (4) two mono-[$CF_3S(O)$]-substituted cubylcubanes have been identified for the first time from their mass spectral fission patterns. Radical reactions, such as thermolysis, reduction, and photohalogenation, have been employed to functionalize cubane as previously mentioned. Dimerization of cubyl radicals, though stated to be a dominant process, has seldom been observed. Cubylcubanes are usually obtained by the treatment of 1,2- and

1,4-dihalocubanes with organolithium reagents via the resultant 1,2- and 1,4-dehydrocubanes or their equivalent diradicals.

The results of the reaction of 1-iodocubane (**8**) with trifluoromethylthiocopper (**9**) were surprising to say the least! In addition to the expected trifluoromethylthiocubane (**10**, 41.7%), 12 other cubane derivatives containing the trifluoromethylthio functionality were detected (Figure 1). We have identified all but two compounds. The presence of the oxygenated species was a real surprise, particularly in the light of the fact that the reaction was carried out in the presence of argon. There is a precedence supporting this observation.[16]

Among the 12 compounds, the major product is trifluoromethylthiocubane (**10**, $M^+ = 204$). There is nothing unusual about its mass spectrum. As expected it undergoes the loss of the SCF_3 moiety to give the C_8H_7 ion. This is followed by two isomers with the molecular weight of 220 corresponding to $C_8H_7S(O)CF_3$. There are two possibilities for these compounds: (i) the sulfoxide and (ii) hydroxy sulfide. In view of the fact that the reaction was carried out under dry argon, the presence of the oxidation products was completely surprising. There is a precedence for the formation of the oxygenated compounds in the presence of argon as stated earlier.[16] The mass spectral breakdown behavior of cubyl trifluoromethyl sulfoxide is somewhat unusual and its structure stands supported by its mass spectral fragmentation. The peak at 119 (100%) is due to ($M—SCF_3$). This suggests that the sulfoxide rearranges to $O—SCF_3$, which subsequently loses SCF_3 to give $(C_8H_7O)^+$. There are precedents for this type of rearrangement. The peaks at 201 and 151 are due to (M—F) and ($M—CF_3$) moieties, respectively. The ion at m/e = 151 loses [O] from sulfur to give the ion at 135. The peak at 103 corresponds to (M-117; $M—SOCF_3$). However, the small peak at 91 is due to (119-CO). The loss of CO supports the sulfoxide rearrangement suggested earlier. The ion $C_5H_7O^+$ gives the peak at 83.

Based on the fragmentation pattern, its isomer has been tentatively assigned the structure of hydroxy (trifluoromethylthio)cubane, **12**. The spectrum shows M + = 220 (100%). The loss of the trifluoromethylthio moiety would then give a peak at 119 (M-101). Incidentally, this is the second-highest peak. This fragment then loses a molecule of H_2O to give a small peak at 101. The small peak at 111 is due to M-(SCF_3-H_2O), while the peak at 103 is due to $C_8H_7^+$. The peaks at 83 and 69 are due to $C_5H_7O^+$ and CF_3^+, respectively. Compound **13** has the $M^+ = 320$. It shows a small peak at 301 (M—F) and an intense peak at 219 ($M—SCF_3$, 100%). The peak at 103 = $C_8H_7^+$. The peak at 77 and 65 may be due to the fragmentation of the cubane moiety. Compound **14** has been tentatively assigned the monosulfoxide and shows an intense M^+ peak. It could also be bis-(trifluoromethylthio)hydroxycubane (**14A**), for it shows a peak at 91 (109-H_2O). The peak at 301 is due to (M—F), while that at m/e = 219 (M—SCF_3, 100%). The third most intense peak at 83 could be due ($C_8H_7O^+$). Next come three components, each with the same molecular weight of 306: **15**, 16, and **17**. They are all cubylcubane isomers carrying one trifluormethylthio group. Their molecular ion is not seen, for they readily lose the SCF_3 moiety to give a peak at 205 (M—SCF_3). Several small peaks are seen, and two of them are at 179 and 103. They are due to (205 – C_2H_2) and $C_8H_7^+$, respectively.

Then we come across a group of five isomeric cubylcubanes (**18–22**); each having a molecular weight of 406 and ranging from 15.4% to 1.0% in yields. They represent dimerized products arising from the trifluoromethylthiocubyl radical (**34**, Figure 6). In the spectra of these components, the M^+ peak is not seen. However, we do see an intense (M—SCF_3) peak in three of them. In the remaining two, we see a moderately intense peak at (M—SCF_3). The cubylcubanes easily lose the trifluoromethylthio moiety. There are precedents for the facile loss of this group from the parent compound.[16] As in the previous cases, we

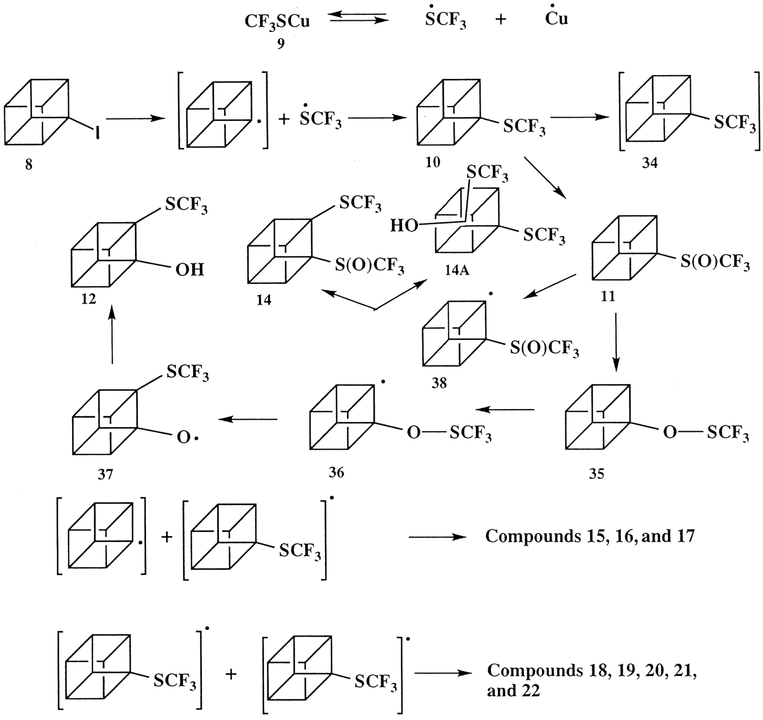


FIGURE 6 Probable mechanism of the formation of the cubylcubanes.

do see the 205, 103, and 83 peaks. Finally, we have the last two components. The M^+ of these could not be determined even using the chemical ionization technique. They appear to be polymeric cubycubanes. There is no doubt about it, for we observe fragmentation similar to that seen in the cubane derivatives. Since the mass spectral breakdown pattern of the isomeric compounds is essentially similar and does not usually permit the assignment of structures to each of the isomers. This holds good in this case. The suggested structures are interchangeable amomg themselves.

Figure 6 attempts to rationalize the probable mode of formation of the compounds cited in the narrative. Iodocubane (**8**) dissociates to form the cubyl radical, which reacts with the F_3CS radical generated from the free-radical dissociation of F_3CSCu to furnish trifluoromethylthiocubane (**10**). The latter undergoes oxidation to form the sulfoxide, **11**, which, though a series of rearrangements (cf. **35–37**, Figure 6) and after hydrogen abstraction, gives **12**. Compound **11** can give rise to the radical intermediate **38**, which in turn forms either **14** or **14A**. The combination of the cubyl radical and the trifluoromethylthiocubyl radical results in the formation of the three momo trifluoromethylthiolated cubylcubane isomers, namely **15**, 16, and **17**. Lastly, the dimerization of the trifluoromethylthiocubyl radicals leads to the four bis-trifluoromethylthiolated cubylcubanes, **18–22**.

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) 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 as follows: oven temperature, 60–270°C at 10°C/min; injection temperature, 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 as follows: 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. 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.

We have previously described the preparation,[17a] the use,[17b] and the X-ray crystal structure[17c] of trifluoromethylthiocopper.

Reaction of Iodocubane (8) with Trifluoromethylthiocopper (9)

A suspension of stochiometric amounts of iodocubane (**8**) and trifluoromethylthiocopper (**9**) in dry toluene was heated over night at 90–100°C under argon. The reaction mixture was cooled to ambient temperature, treated with a saturated solution of ammonium chloride, and extracted three times with CH_2Cl_2. The organic layer was successively passed through a column of anhydrous Na_2SO_4, celite, and silica and concentrated under reduced pressure, and the residue was processed as usual to give, including the expected trifluoromethylthiocubane (**10**, Figure 1), **12** new compounds (Figure 1). Among these **12** compounds, two mixed cubylcubanes, five dimerized cubylcubanes, two (CF_3S)-$CF_3S(O)$]cubanes, and two mono- [$CF_3S(O)$]-substituted cubylcubanes have been identified from their mass spectral fission patterns.[18]

CONCLUSION

The reaction of dihalcubanes with trifluoromethylthiocopper is straightforward and furnishes the expected products.[15f] However, the reaction of iodocubane with the same reagent, namely trifluoromethylthiocopper, yields a complex mixture of compounds. These compounds appear to arise from cubyl and substituted cubyl free radicals. This lends credence to the earlier observation that the cubyl radical is not a localized species. The formation of three isomeric dimethoxycarbonylcubanes, two isomeric trimethoxycarbonylcubanes, three isomeric tetramethoxycarbonylcubanes, and one pentamethoxycarbonylcubane from the photochemical chlorocarbonylation of monomethoxycarbonylcubane has been rationalized.[19] In view of this, the formation of 12 compounds via a freeradical catalyzed reaction of iodocubane with trifluoromethylthiocopper is not unreasonable!

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