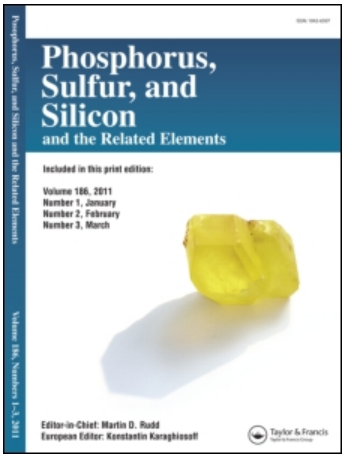

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1-(TRIMETHYLSILYL)-1,2,4-TRIAZENE: A NOVEL FREE RADICAL INITIATOR

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The reaction of 1-(trimethylsilyl)-1,2,4-triazene with trifluoromethylsulfenyl chloride in dry n-pentane furnishes a complex mixture containing 11 compounds. All but six of them are derived from the reaction of the thiyl or chlorine radicals with n-pentane. The probable mechanism of their formation and mass spectral characterization are presented in this article.

Keywords: Mono- and bis-(trifluoromethylthio)- and mono- and dichloropentanes; new free radical initiator; triazene

INTRODUCTION

In continuation of our interest in the synthesis of trifluoromethylthiolating agents[1] and in the chemistry of the trifluoromethylthio-group,[2] the reaction of trifluoromethylsulfenyl chloride (**1**) in n-pentane (**2**) with 1-(trimethylsilyl)-1,2,4-triazene (**3**) was examined and found to furnish 11 compounds. Instead of the expected, 1-(trifluoromethylthio)-1,2,4-triazene (**4**), 1-(trifluoromethylthio)-1,3,4-triazene (**6**), and compounds derived from n-pentane (**9–11** and **13–18**) were identified from their mass spectral fragmentation patterns. Because of insufficient information in its mass spectrum, compound **12** could not be characterized. Compound **6** results from the reaction of the triazenyl radical with trifluoromethylthiyl radical formed from **1**. Also, the presence of 1,2,4-triazene (**5**) was detected. That compound **3** appears to behave as a free radical initiator was amply demonstrated by the characterization of ring cyclization product from an acyclic precursor, namely

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1-bromo-5-hexene. The mechanism of the formation and mass spectral characterization of the above compounds are described in this article.

RESULTS AND DISCUSSION

The chemistry, reactivity, spectral and biological properties, and industrial uses of 1,2,4-triazene derivatives have been documented in an excellent review.[3] With a view to synthesize 1-(trifluoromethylthio)-1,2,4-triazene (**4**), 1-(trimethylsilyl)-1,2,4-triazene (**3**) was treated with a stoichiometric amount of trifluoromethylsulfenyl chloride (**1**) in dry n-pentane (**2**) at -80°C. Gas chromatographic analysis of the reaction mixture showed it to be a highly complex mixture. This inference was confirmed by its GC-MS analysis, which revealed the fact that all but six of the compounds arise from the free radical induced reaction involving the solvent, namely n-pentane (**2**), with thiyl or chlorine radicals. Among the compounds not derived from n-pentane are: (1) 1,2,4-triazene (**5**); (2) 1-(trifluoromethylthio)-1,3,4-triazene (**6**); (3) bis-(trifluoromethyl)disulfide (**7**) formed via the dimerization of trifluoromethylthiyl radicals; and (4) trimethylsilyl chloride (**8**) (Figures 1 and 2).

It appears that 1-(trimethylsilyl)-1,2,4-triazene (**3**) is functioning as a free radical initiator in this reaction, in a similar manner as azobisisobutyronitrile (AIBN) does. The triazene molecule seems to be photostable. The above inference stands supported by the observation that it affords protection against x-rays.[3] The triazenyl radical thus formed abstracts hydrogen from the solvent to yield 1,2,4-triazene (**5**). This compound formed about 45% of the reaction product as determined by

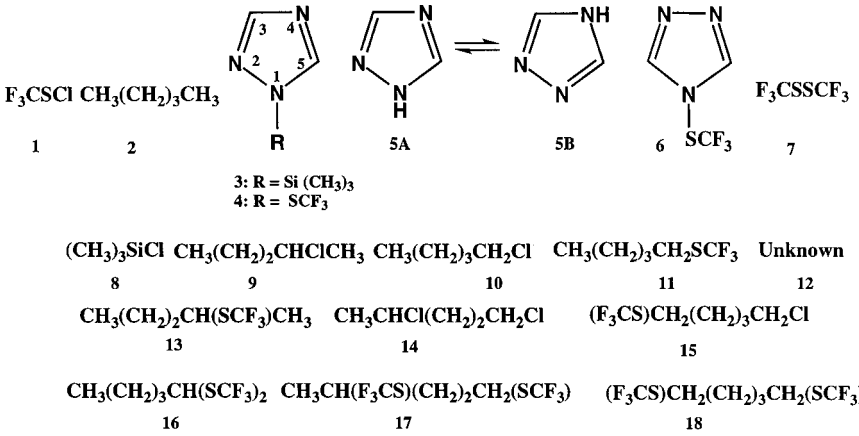

FIGURE 1 Structures of compounds cited in the narrative.

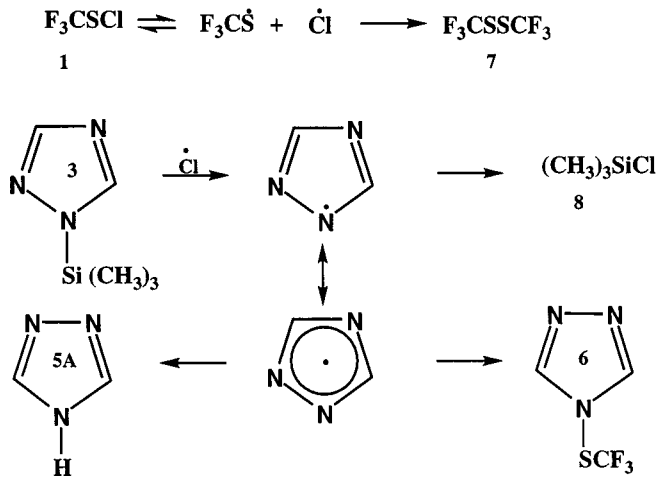

FIGURE 2 Formation of compounds **5a** and **6**.

GC-MS. Its structure was further confirmed by its melting point (cf. experimental part). The above observation that compound **3** acts as a free radical initiator was experimentally ascertained via the synthesis of a cyclic compound from an acyclic precursor in the presence of triazenyl radical generated from it.[4a] That intramolecular radical addition to carbon-carbon double bond leads to cyclic products has been amply demonstrated.[5] Free radical additions, known as the Kharasch or anti-Markovnikov additions, preferentially occur at the unsubstituted terminal of the mono-substituted olefin. When the double bond is δ to the radical the formation of the cyclohexane derivatives appears to be thermodynamically more favored than the formation of the cyclopentane derivatives. However, in reality methylcyclopentanes are exlusively formed.[6] It appears that the temperature and the nature of the solvents exert considerable influence on the course of the reaction.[7] The identification of trimethylsilyl chloride (**8**) as one of the products of the reaction lends additional support to the proposed process (Figure 2). There are precedents for the participation of silyl radicals in organic chemistry.[8]

Two structures, **4** and **6**, were considered for the trifluoromethylthiolated 1,2,4-triazene with the r.t. = 5.17 min. Based on the mass spectral fragmentation of the compound in question, 1-(SCF_3)-1,3,4-triazene (**6**) was selected for it. This assignment is supported by the observation that the elimination of HCN from the M^+ ion would be expected from structure **3**. However, no such elimination was seen in its mass spectrum. Secondly, the presence of two ions, m/e = 140 and 74 support structure **6**. The former results from the loss of the N_2H fragment ($M-N_2H = 140$) from its molecular ion.[9c–d] The latter is due

to the presence of $[HNCHNS]^+$ entity, which arises from the cleavage of the bond between the two nitrogens, namely N_3 and N_4.

The $F_3CS^{\cdot}$ and $Cl^{\cdot}$ radicals thus formed from **1** react indiscriminately with n-pentane to give various products. Such a participation of the solvents in organic reactions has precedents.[8,10] Of the chlorinated compounds present in the reaction product, based on the mass spectral fragmentation behavior, two mono chlorosubstituted pentanes were detected and characterized as 2-chloro- and 1-chorochloropentanes (**9** and **10**, Figure 1). The choice between the two was not too difficult. The α-cleavage in the case of 2-choropentane (**9**), should furnish ions corresponding to m/e = 63 and 91. These ions are seen in its mass spectrum. Similarly, the mass spectrum of 1-choropentane (**10**) shows a low intensity M^+ ion peak. Also, the α-cleavage should lead to an ion with m/e = 49 (CH_2Cl). Indeed, this ion is seen in its mass spectrum. The mass spectra of **9** and **10** bear a striking similarity to those of 1- and 2-chlorohexanes.[11] Two mono-trifluoromethylsulfenylated derivatives (**11** and **13**) were identified and their structures were deciphered based on their mass spectral fragmentation patterns. Turning to the three isomeric bis(trifluoromethylthio)pentanes (**16**, **17**, and **18**), one of them, namely **16**, did not show the M^+ ion peak since it had lost a CF_3 fragment to give the ion with m/e = 203. The structural assignment of these compounds rests on their mass spectral fragmentation behavior. The most intense peak of **16** happens to be m/e = 147 $[F_3CSCH_2S]^+$ suggesting the possibility that the two F_3CS groups are attached to the same carbon and that it also involves the migration of a hydrogen. This arrangement permits the facile loss of the CF_3 moiety from the molecular ion before it gets recorded and thus giving the $M{-}CF_3$ peak. In the case of compound **17**, the presence of three peaks in its mass spectrum, namely m/e = 141 $[F_3CSC_3H_4]^+$, 129 $[F_3CSCH_2CH_2]^+$ and 115 $[F_3CSCH_2]^+$, lends support to the proposed structure. A relatively intense peak at m/s = 101 $[F_3CS]^+$ is also seen. Finally, the assignment of structure **18**, stands supported by the presence of a peak at m/e = 171 corresponding to the $[F_3CSC_5H_{10}]$ moiety.

The presence of one dichloro-substituted compound (**14**) was noted by its chlorine isotope pattern in its mass spectrum. Its structure was deduced from its mass spectral fragmentation behavior. Of the two remaining compounds, one possessed both F_3CS and Cl functions. Based on its mass spectral breakdown pattern, this compound was designated as 1-chloro-5-(trifluoromethylthio)pentane (**15**). Since complete information was lacking in the mass spectrum of compound **12**, its exact structure could not be ascertained.

Before concluding the discussion of the mass spectral fragmentaion of the compounds cited in the narrative, it would be helpful to take a brief

look at the mass spectral fragmentation of 1,2,4-triazene.[9,12,13] Many cleavages involve hydrogen migration.[9c–9e] The elimination of HCN appears to be the major process from the triazene molecule,[9a] which could be represented by either **5a** or **5b** or an equilibrium mixture.[12] In the solid or gaseous state it is said to be **5a**,[12a] while in solution it exists as **5b**.[12b] Competitive losses of N_2 and HCN have been stated to be due the presence of adjacent nitrogen atoms.[13] In the GC-MS-CI mode, we find that the M^+ ion peak of 1,2,4-triazene (**5**) happens to be the most intense peak. It is interesting to note that the same is true in the case of 1-(trifluoromethylthio)-1,3-4-triazene. After the molecule has lost the trifluoromethylthio group, the fragmentation of the M—SCF_3 entity shows a close similarity to the breakdown of 1,2,4-triazene. The mass spectral fragmentation and characterization of these compounds are described in Table I.

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Narrative

1. 1-Trifluoromethylthio-1,3,4-triazene (**6**): $M^+ = 170$ (CI, M + H, 100%); 150 (M—F); 140 (M—N_2H; 121 (140-F); 112 (140-HCN—H); 102 (121-F); 74 (CH_2N_2S) and 68 (M—SCF_3)
2. Bis(trifluoromethyl)disulfide (**7**): $M^+ = 202$ (100%); 183 (M—F); 133 (M—CF_3); 114 (133-F) and 69 (CF_3)[16]
3. 2-Chloropentane (**9**)[a]: $M^+ = 106$ (not seen); 77 (C_3H_6Cl); 71 (M—Cl); 70 (C_5H_{10}, 100%); 63 (C_2H_4Cl); 62 (C_2H_3Cl); 56 (C_4H_8); 55 (C_4H_7); and 53 (C_4H_5)
4. 1-Chloropentane (**10**)[a]: $M^+ = 106$; 77 (C_3H_6Cl); 71 (M—Cl); 70 (C_5H_{10}, 100%); 69 (C_5H_9); 57 (C_4H_9); 55 (C_4H_7); 53 (C_4H_5) and 49 (CH_2Cl)
5. 1-Trifluoromethylthiopentane (**11**): $M^+ = 172$; 143 (M—C_2H_5); 129 (M—C_3H_7); 115 (M—C_4H_9); 103 (M—CF_3); 71 (C_5H_{11} or M—SCF_3, 100%); 70 (C_5H_{10}); 61 (SC_2H_5); 55 (C_4H_7); and 47 (SCH_3)
6. 2-Trifluoromethylthiopentane (**13**): $M^+ = 172$; 129 (M—C_3H_7); 115 (CH_2SCF_3); 103 (M—CF_3, 100%); 69 (CF_3); 55 (C_4H_7); and 47 (SCH_3)
7. 1,4-Dichloropentane (**14**): $M^+ = 106$ (not seen); 105 (M—Cl); 89 (C_4H_6Cl); 77 (C_3H_6Cl, 100%); 76 (C_3H_5Cl); 69 (C_5H_9); 63 (C_2H_4Cl); 55 (C_4H_7) and 53 (C_4H_5)
8. 1-Chloro-5-trifluoromethylthiopentane (**15**)[a]: $M^+ = 206$; 143 ($C_3H_6SCF_3$, 100%); 137 (M—CF_3); 115 (CH_2SCF_3); 95 (115-HF); 73 (137-C_3H_6); 69 (CF_3); 61 (SC_2H_5); 59 (C_2H_3S); and 45 (CSH)
9. Bis-(1,1-trifluoromethylthio)pentane (**16**): $M^+ = 272$ (not seen); 203 (M—CF_3); 151 (203-$HSCF_3$—HF); 147 (F_3CSCH_2S, 100%); 137 (151-CH_2); 131 (151-HF); 121 ($C_5H_{10}SF$); 115 (CH_2SCF_3); 101 (SCF_3); 96 ($C_2H_2F_2S$); 73 (C_3H_5S); 63 (CSF) and 45 (CSH)
10. Bis-(1,4-trifluoromethylthio)pentane (**17**): $M^+ = 272$; 203 (M—CF_3); 170 (M—$HSCF_3$); 141 (M—C_2H_6—SCF_3); 128 ($C_2H_3SCF_3$); 115 (CH_2SCF_3); 101 (SCF_3); 99 (C_5H_7S); 69 (CF_3, 100%); 67 (C_5H_7 or 99-S); 55 (C_4H_7) and 47 (SCH_3)
11. Bis-(1,5-trifluoromethylthio)pentane (**18**): $M^+ = 272$; 203 (M—CF_3); 171 (M—SCF_3); 129 ($C_2H_4SCF_3$); 115 (CH_2SCF_3); 101 (SCF_3); 73 (C_3H_5S); 69 (CF_3, 100%); 59 (SC_2H_3) and 47 (SCH_3)

[a] ^{35}Cl and ^{37}Cl isotope peaks were seen for all chlorine containing compounds.

EXPERIMENTAL PART

Care and caution should be exercised while working with trifluoromethylsulfenyl chloride (**1**).[14] All solvents were dry and freshly distilled prior to 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 2 h 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 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 μA (EI) or 300 μA (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 × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA).

Reaction of trifluoromethylsulfenyl chloride (**1**) with 1-(trimethylsilyl)-1,2,4-triazene (**3**): To 1-(trimethylsilyl)-1,2,4-triazene (**3**, 1.69 g, 0.01 mol) in freshly distilled dry pentane (10 ml) trifluoromethylsulfenyl chloride (**1**, 1.36 g, 0.01 mol) was added via the vacuum line at −80°C with stirring and under a blanket of argon. The reaction mixture was stirred at −80°C for 2 h and stirring was continued over night at ambient temperature. The product was initially analyzed using gas chromatography. The reaction mixture was vacuum distilled and the distillate was then subjected to GC-MS analysis. The yields of the compounds cited in the narrative are based on the GC-MS spectral data. In addition to 1,2,4-triazene (**5**, R = H, 45%, r.t. = 2.3 min, m.p. 119, −21°C[15] and 1-trifluoromethylthio-1,3,4-triazene

(6, 0.5%, r.t. = 5.17 min), the following compounds were identified: (a) bis(trifluoromethyl)disulfide[16] (**7**, 2.50%, r.t. = 1.2 min); (b) trimethylsilyl chloride[2,16] (**8**, 14.9%, r.t. = 1.27 min); (c) 2-Chloro-n-pentane (**9**, 2.0%, r.t. = 1.5 min); (d) 1-Chloro-n-pentane (**10**, 4.9%, r.t. = 1.53 min); (e) 1-Trifluoromethylthio-n-pentane (**11**, 18.9%, r.t. = 1.55 min); (f) Unknown (**12**, 0.2%, r.t. = 2.03 min; undergoes extensive fragmentation with no M^+); (g) 2-Trifluoromethylthio-n-pentane (**13**, 4.1%, r.t. = 2.09 min); (h) 1,4-Dichloro-n-pentane (**14**, 0.1%, r.t. = 2.31 min); (i) 1-Chloro-5-trifluoromethyl-thiopentane (**15**, 0.1%, r.t. = 2.50 min); (j) bis-(1,1-trifluoromethylthio)-n-pentane (**16**, 1.6%, r.t. = 2.58 min); (k) bis-(1,4-trifluoromethylthio)-n-pentane (**17**, 0.03%, r.t. = 3.27 min); and (l) bis-(1,5-trifluoromethylthio)-n-pentane (**17**, 0.03%, r.t. = 3.52 min).

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