Simultaneous scission of C–S and S–S bonds of bis(trifluoromethyl)trisulfide by Grignard reagents

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Abstract

Trifluoromethyl mono-, di- and tri-sulfides, and alkyl sulfides and disulfides, as well as dimerized products, are formed as a result of the simultaneous cleavage of the C–S and S–S bonds of bis(trifluoromethyl)trisulfide by Grignard reagents at – 78 °C. The formation of various products has been rationalized on the basis of the involvement of free radicals.

Introduction

Organic mono-, di- and tri-sulfides occur widely in Nature [1]. Because of their importance in determining the structure of proteins [2a], involvement in energy-transfer reactions [2b], industrial applications [2c] and antitumor and antioxidant properties in living systems [1d–e, 2d], the chemistry of these compounds has attracted considerable interest. The redox reactions, mechanism of scission and displacement reactions of the S–S bond and their chemical consequences have been well documented [3]. The attack on the sulfur atom has been described as a cascade of addition–elimination reactions with sulfur expanding its electronic octet, rather than a one-step substitution reaction [4a].

In the reactions of the di-, tri- and tetra-sulfides, the S–S bond is generally cleaved. In contrast, the C–S bond has been described as 'relatively resistant' [3d] and its cleavage as relatively infrequent [4b]. The probability of S–S bond cleavage versus C–S bond scission has been estimated to be 99% to 1% [4b]. This has been attributed to the fact that the C–S bond is stronger than the S–S bond [5a–c]. However, two exceptions to the above generalizations have been reported [5d–e]. The facile fission of the C–S bond observed in these cases is apparently due to the greater stability of the resulting free radicals.

Since methyl-, ethyl-, iso-propyl- and t-butyl-tetrasulfides undergo homolysis more readily than their corresponding disulfides [5d–e, 6a–b], the

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perthiyl radicals thus generated from the former have been stated to be far more stable than the thiyl radicals formed from the latter [6b]. However, there has been no definitive study of the homolysis of the C–S and S–S bonds of the trisulfides [3a, 5d, 6c]. The formation of di- and tetra-sulfides upon irradiation of dimethyl trisulfide [6d] indirectly supports the contention that the trisulfides should undergo homolytic scission more readily than the disulfides. Also, dimethyl-, diethyl- and di-isopropyl-trisulfides were found to give a mixture of di-, tri- and tetra-sulfides due to the disproportionation reaction initiated by S–S fission [6d].

There are not many reports of the simultaneous scission of both C–S and S–S bonds of the trisulfides by Grignard reagents at −78 °C. In fact, to the best of our knowledge this is the first example of the simultaneous cleavage of both C–S and S–S bonds of the perfluoromethyl trisulfide by Grignard reagents at −78 °C and the formation of the perfluoromethyl mixed mono-, di- and tri-sulfides as well as alkyl mono- and di-sulfides. However, it must be said that the credit for observing an unusual but interesting structure-dependent C–S bond cleavage of a perfluoride goes to Tatlow and coworkers [7]. The present communication describes possible mechanisms for the scission of the C–S and S–S bonds of bis(trifluoromethyl)trisulfide (**1**), and the formation and distribution of various products formed during the reaction of Grignard reagents with the said substrate.

Results

The reaction of RMgBr with **1** at −78 °C gave R_fSSSR, R_fSSR, R_fSR, R_fSSSR', RSR and C_8H_{18}, where $R_f = CF_3$, $R = C_2H_5$ and $R' = t\text{-}C_4H_9$ (Table 1). Also, trace amounts of two oxygenated products R_fSCO_2R and RSC(O)F as well as $C(S)F_2$ and RSC(S)Br were identified by their mass spectral data as by-products of this reaction. The reaction of $(CH_3)_2CHMgCl$, on the other hand, yielded R_fSSSR, R_fSSR, R_fSR, RSSR, RSR, RSC_4H_9-t, $R_fSSSC_4H_9$-t, $R_fS_6R_f$ and $C(S)F_2$, where $R_f = CF_3$ and $R = i\text{-}C_3H_7$. In the reaction of **1** with $t\text{-}C_4H_9MgCl$, the mixed trisulfide, namely $R_fSSSC_4H_9$-t was not detected. However, R_fSSR, R_fSR, RSR, R_fSCl and $R_fSSC_5H_9$ ($R_f = CF_3$ and $R = t\text{-}C_4H_9$) were identified as reaction products. Table 2 gives the mass spectral fragmentation of the compounds formed during the reaction of **1** with various Grignard reagents at −78 °C. Molecular ion peaks are observed for all compounds except one. The splitting off of SCF_3 (*m/e* = 101) and CF_3 (*m/e* = 69) appears to be a common characteristic of compounds containing the SCF_3 moiety. In the case of mixed sulfides containing the trifluoromethyl and alkyl groups, the ion corresponding to CSH (*m/e* = 45) is commonly observed. The fragmentation patterns of all sulfides are similar to those reported for alkyl di- and poly-sulfides by others [8].

TABLE 1

Products of the reaction of Grignard reagents with bis(trifluoromethyl)trisulfide

$CF_3SSSCF_3 + RMgX \longrightarrow$ Products[a]

$R=C_2H_5$[b]	CSF_2	CF_3SSSR	CF_3SSR	CF_3SR	RSCOF
	3.1%	3.5%	27.5%	–	3.0%
	CF_3SCOOR	RSCSBr	$CF_3S_3C_4H_9$-t	C_8H_{18}	RSR
	1.3%	0.7%	3.1%	7.4%	3.2%
$R=i\text{-}C_3H_7$[c]	CSF_2	CF_3SSSR	CF_3SSR	CF_3SR	RSSR
	0.9%	23.5%	8.9%	–	10.3%
	RSR	RSC_4H_9	$CF_3S_3C_4H_9$-t	$(CF_3SSS)_2$	
	35.5%	2.6%	5.8%	12.9%	
$R=t\text{-}C_4H_9$[d]	CF_3SSR	CF_3SR	RSR	CF_3SCl	$CF_3SSC_5H_9$[e]
	35.0%	6.7%	28.6%	12.9%	0.9%

[a] Data from GC/MS analysis of the products. Starting material and trace amounts of unidentified polymeric materials constituted the rest of the sample.

[b] Ethylmagnesium bromide in diethyl ether and methyl t-butyl ether was supplied as such by the vendor.

[c] Isopropylmagnesium chloride in diethyl ether.

[d] t-Butylmagnesium chloride in diethyl ether and dry heptane was added as a diluent.

[e] The source of this compound has not as yet been determined.

Discussion

In view of the unusual properties of the perfluoroalkyl compounds, our continued interest in the reaction of sulfur-containing compounds with organometallic reagents [9a–c] and the modified synthesis of **1** [9d], it was considered of interest to investigate the reaction of the latter with Grignard reagents. Based on the results presented in Table 1, a number of observations can be made. The formation and identification of the mixed trisulfides, namely R_fSSSR, definitely suggests the scission of the C–S bond of **1** by Grignard reagents at −78 °C. In view of the report that no evidence was observed in the gas-phase reaction of the methyl radical with dimethyl disulfide [10a], our results are indeed interesting. The mixed mono- and di-sulfides (R_fSR and R_fSSR) evidently result from the cleavage of the S–S bond by alkyl radicals derived from Grignard reagents [10b].

What is even more interesting is the detection and characterization of RSR and RSSR. Obviously, these compounds are formed from the attack of the alkyl radicals on the mixed di- and tri-sulfides (R_fSSR and R_fSSSR). The formation of $R_fSSSC_4H_9$-t during the reaction of **1** with C_2H_5MgBr is due to the participation of the solvent, namely methyl t-butyl ether, used to prepare the Grignard reagent. The solvent is split off to generate the t-butyl radical precursor, which then goes on to react with **1** to give the above product. There are precedents for such a participation of solvent in the reactions [11a–b].

Halogen-exchange reactions were noticed in the reactions of **1** with ethylmagnesium bromide and t-butylmagnesium chloride. Again, there are

TABLE 2

Mass spectral fragmentation of compounds formed from the reaction of bis(trifluoromethyl)trisulfide with Grignard reagents

$C(S)F_2$	$M^+=82$ (100%); 63 (CSF); 50 (CF_2); and 44 (CS)
CF_3SSSEt	$M^+=194$; 166 ($M-C_2H_4$); 125 ($M-CF_3$); 101 (SCF_3); 97 ($125-C_2H_4$); 93 ($125-S$); 82 (CSF_2); 69 (CF_3); 64 (S–S, 100%); and 59 (SC_2H_3)
CF_3SSEt	$M^+=162$ (100%); 147 ($M-CH_3$); 143 ($M-F$); 134 ($M-C_2H_4$); 114 ($134-HF$); 101 (SCF_3); 93 ($M-CF_3$); 78 ($93-CH_3$); 69 (CF_3); 64 (S–S); 61 (SC_2H_5); and 45 (CSH)
EtSC(O)F	$M^+=108$ (100%); 88 ($M-HF$); 80 ($M-C_2H_4$); 63 (CSF); 61 (SC_2H_5); 60 (SCO); and 47 (SCH_3)
$CF_3SCOOEt$	$M^+=174$; 145 ($M-C_2H_5$); 105 ($M-CF_3$); 76 (SCO_2); 73 ($M-SCF_3$, 100%); 69 (CF_3); and 45 (OC_2H_5)
EtSC(S)Br	$M^+=184$; 186 (^{81}Br); 123 ($M-SC_2H_5$); 105 ($M-Br$); 76 (CS_2, 100%); 60 (SC_2H_4); and 45 (CSH)
CF_3SSSBu^t	$M^+=$(not seen); 165 ($M-C_4H_9$); 69 (CF_3); 64 (S–S); 57 (C_4H_9, 100%); and 45 (CSH)
C_8H_{18}	$M^+=112$; 97 ($M-CH_3$); 57 (C_4H_9, 100%); 56 (C_4H_8); and 41 (C_3H_5)
EtSEt	$M^+=90$; 75 ($M-CH_3$, 100%); 62 ($M-C_2H_4$); 61 (SC_2H_5); 59 (SC_2H_3); 47 (SCH_3); 46 (CSH_2); and 45 (CSH)
CF_3SSSPr^i	$M^+=208$; 165 ($M-C_3H_7$); 143 ($CF_3SC_3H_6$); 139 ($M-CF_3$); 130 ($CF_3SC_2H_5$); 107 ($M-SCF_3$); 101 (SCF_3); 82 (CSF_2); 75 (SC_3H_7); 69 (CF_3); 64 (S–S, 100%); 59 (SC_2H_3); and 45 (CSH)
CF_3SSPr^i	$M^+=176$ (100%); 157 ($M-F$); 133 ($M-C_3H_7$); 114 ($157-C_3H_7$); 101 (SCF_3); 82 (CSF_2); 69 (CF_3); 75 (SC_3H_7); 64 (S–S); 59 (SC_2H_3); and 47 (SCH_3)
Pr^iSSPr^i	$M^+=150$; 108 ($HSSC_3H_7$, 100%); 93 ($108-CH_3$); 66 (HSSH); 59 (SC_2H_3); and 45 (CSH)
Pr^iSPr^i	$M^+=118$; 103 ($M-CH_3$); 76 (HSC_3H_7); 61 (SC_2H_5, 100%); 59 (SC_2H_3); and 45 (CSH)
Pr^iSBu^t	$M^+=132$; 117 ($M-CH_3$); 89 (SC_4H_7, 100%); 75 ($M-C_4H_9$); 61 (SC_2H_5); 59 (SC_2H_3); 57 (C_4H_9); 55 (C_4H_7); 47 ($HSCH_2$); and 45 (CSH)
$CF_3S_6CF_3$	$M^+=330$; 266 ($M-SS$); 229 ($M-SCF_3$); 197 ($229-S$); 165 ($197-S$); 133 ($165-S$); 101 (SCF_3); 96 (SSS); 83 (CSF); 69 (CF_3); and 64 (S–S, 100%)
CF_3SSBu^t	$M^+=190$; 171 ($M-F$); 147 ($M-C_3H_7$); 133 ($M-C_4H_9$); 114 ($133-F$); 101 (SCF_3); 87 (SC_4H_7); 82 (CSF_2); 69 (CF_3); 64 (S–S); 57 (C_4H_9, 100%); 45 (CSH); and 41 (C_3H_5)

(*continued*)

TABLE 2 (*continued*)

CF_3SBu^t	$M^+ = 158$; 139 $(M-F)$; 129 $(M-C_2H_5)$; 115 $(M-C_3H_7)$; 89 $(M-CF_3)$; 82 (CSF_2); 69 (CF_3); 56 $(C_4H_8$, 100%); 47 (SCH_3); and 41 (C_3H_5)
Bu^tSBu^t	$M^+ = 146$; 117 $(M-C_2H_5)$; 103 $(M-C_3H_7)$; 90 $(M-C_4H_8)$; 61 $(C_2H_5S$, 100%); 56 (C_4H_8); 47 (SCH_3); 45 (CSH); 41 (C_3H_5); and 39 (C_3H_3)
CF_3SCl	$M^+ = 136$; 101 (SCF_3); 69 (CF_3); 67 (SCl); 51 (SF); and 35 (Cl)
$CF_3SSC_5H_9$	$M^+ = 202$; 173 $(M-C_2H_5)$; 160 $(M-C_3H_6)$; 145 $(M-C_4H_9)$; 133 (CF_3SS); 101 $(SCF_3$ or $SC_5H_9)$; 69 (CF_3); 58 $(SC_2H_2$, 100%); and 41 (C_3H_5)

precedents for halogen-exchange reactions [11c]. The formation of C_8H_{18} and the symmetrical perfluoromethyl hexasulfide $(R_fS_6R_f)$ is a simple case of dimerization of their free-radical precursors, $\dot{C}_4H_9$ and $R_fSS\dot{S}$. The formation of dimerized products is definite proof of the participation of free radicals in these reactions [11d]. Thiocarbonyl fluoride is evidently formed from the trifluoromethylthiyl radical $(CF_3\dot{S})$. The origin of $R_fSSC_5H_9$ is not as yet known.

Schemes 1 and 2 describe the free-radical pathway and the single electron-transfer (SET) process respectively. Although t-BuLi did not cleave the C–S bond of 3-methyl-1-phenylthio-1-trimethylsilylbuta-1,2-diene at −78 °C [11e], the results presented in Table 1 definitely suggest a simultaneous scission of both the C–S and S–S bonds of **1** at −78 °C by Grignard reagents. The involvement of free radicals has been postulated in the reaction of disulfides with Grignard reagents [10b]. The initial process definitely involves the transfer of an electron from the Grignard reagent to the substrate [11f]. Scheme 1 incorporates the free-radical process. Step 1 is similar to the one proposed by Whitesides and coworkers [11g]. Steps 2–4 rationalize the formation of R_fSR, R_fSSR and R_fSSSR. Steps 5–9 explain the formation of RSR and RSSR. The contribution of step 9 is minimal. Steps 10–11 are straightforward and illustrate the formation of dimerized products.

However, in the SET mechanism the initial process is the transfer of an electron from the Grignard reagent to the substrate to form the radical cation/radical anion pair, which subsequently undergoes dissociation in step 2. Steps 3, 5 and 8 describe the formation of R_fSSSR, R_fSSR and R_fSR, respectively. Steps 9–12 explain the origin of RSSR and RSR. Finally steps 13 and 14 describe the dimerization process. Both C–S and S–S bonds are considerably weakened by the presence of the highly electron withdrawing CF_3 group. The SET mechanism proposed here, in a sense, is an extension of the suggestion made by others to account for the products of the Grignard reaction [12]. Although the SET mechanism is helpful in explaining the formation of many of the products, the free-radical process is decidedly more useful in rationalizing the origin of products listed in Table 1. Since

$$CF_3SSSCF_3 + R^{\cdot} \longrightarrow RCF_3 + CF_3SSS^{\cdot} \qquad (1)$$

$$CF_3SSSCF_3 + R^{\cdot} \longrightarrow RSCF_3 + CF_3SS^{\cdot} \qquad (2)$$

$$CF_3SSSCF_3 + R^{\cdot} \longrightarrow RSSCF_3 + CF_3S^{\cdot} \qquad (3)$$

$$CF_3SSSCF_3 + R^{\cdot} \longrightarrow RSSSCF_3 + {}^{\cdot}CF_3 \qquad (4)$$

$$CF_3SSSR + R^{\cdot} \longrightarrow RSSR + CF_3S^{\cdot} \qquad (5)$$

$$CF_3SSSR + R^{\cdot} \longrightarrow RSR + CF_3SS^{\cdot} \qquad (6)$$

$$CF_3SSR + R^{\cdot} \longrightarrow RSSR + {}^{\cdot}CF_3 \qquad (7)$$

$$CF_3SSR + R^{\cdot} \longrightarrow RSR + CF_3S^{\cdot} \qquad (8)$$

$$CF_3SR + R^{\cdot} \longrightarrow RSR + {}^{\cdot}CF_3 \qquad (9)$$

$$2CF_3\dot{S}_3 \longrightarrow CF_3S_6CF_3 \qquad (10)$$

$$2R^{\cdot} \longrightarrow R\text{–}R \qquad (11)$$

Scheme 1. Grignard reagent-catalyzed formation of mixed mono-, di- and tri-sulfides via free-radical intermediates.

new mono-, di- and tri-sulfides containing alkyl group(s) derived from the Grignard reagents are formed, it is apparent that the fission of the C–S bond definitely takes place in these reactions. In view of the free-radical nature of the Grignard reagent itself, the choice between the two processes discussed above is difficult. Recently three competing processes were observed in the SET reaction catalyzed by copper metal [13].

Experimental

General procedure

Warning!! Because of the high toxicity associated with 1 via inhalation, extreme care should be exercised in working with it and all reactions should be carried out in efficient hoods. NMR spectra (^{13}C and ^{19}F) were recorded in $CDCl_3$ on a Varian VXR-400 S spectrometer at 100 MHz and 376 MHz, respectively. The external reference for the ^{19}F data was CCl_3F. 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 and W Scientific, Rancho Cordova, CA). 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,

$$CF_3SSSCF_3 + \overset{-}{R}\overset{+}{M}gX \longrightarrow [(CF_3SSSCF_3)^{\bullet -} + R^{\bullet}\ \overset{+}{M}gX] \tag{1}$$

$$(CF_3SSSCF_3)^{\bullet -} \longrightarrow CF_3SSS^{\bullet} + \overset{-}{C}F_3 \tag{2}$$

$$CF_3SSS^{\bullet} + R^{\bullet} \longrightarrow CF_3SSSR \tag{3}$$

$$(CF_3SSSCF_3)^{\bullet -} \longrightarrow CF_3SS^{\bullet} + \overset{-}{S}CF_3 \tag{4}$$

$$CF_3SS^{\bullet} + R^{\bullet} \longrightarrow CF_3SSR \tag{5}$$

$$CF_3SSR + \overset{-}{R}\overset{+}{M}gX \longrightarrow [(CF_3SSR)^{\bullet -} + R^{\bullet}\ \overset{+}{M}gX] \tag{6}$$

$$(CF_3SSR)^{\bullet -} \longrightarrow CF_3S^{\bullet} + \overset{-}{S}R \tag{7}$$

$$CF_3S^{\bullet} + R^{\bullet} \longrightarrow CF_3SR \tag{8}$$

$$(CF_3SSR)^{\bullet -} \longrightarrow RSS^{\bullet} + \overset{-}{C}F_3 \tag{9}$$

$$RSS^{\bullet} + R^{\bullet} \longrightarrow RSSR \tag{10}$$

$$(CF_3SSR)^{\bullet -} \longrightarrow RS^{\bullet} + CF_3\overset{-}{S} \tag{11}$$

$$RS^{\bullet} + R^{\bullet} \longrightarrow RSR \tag{12}$$

$$2CF_3SSS^{\bullet} \longrightarrow CF_3S_6CF_3 \tag{13}$$

$$2R^{\bullet} \longrightarrow R\text{–}R \tag{14}$$

Scheme 2. Grignard reagent-catalyzed formation of the mixed mono-, di- and tri-sulfides via the SET process.

CA). The solvents were dried and freshly distilled before use. The reactions were carried out in a flame-dried, argon-purged 10 or 25 ml three-necked round-bottom flask equipped with a magnetic stirrer, a gas inlet, a pressure equalizing dropping funnel and a reflux condenser carrying a dry ice–acetone trap. The temperature of the coolant passing through the condenser was maintained at −20 °C. All reactions were carried out by adding stoichiometric amounts of the reagents (usually 0.01 mol) of the Grignard reagents to the trisulfide (0.01 mol) cooled to −78 °C. After the addition was over, the reaction mixtures were stirred at −78 °C for 45–60 min. The reactions were terminated by adding moist ether and a saturated solution of ammonium chloride, followed by extraction with ether, drying over anhydrous sodium sulfate, evaporating the solvent under reduced pressure and processing the residue in the usual manner. The results described in Table 1 are based on GC/MS data.

Synthesis of bis(trifluoromethyl)trisulfide (1)

To a slurry of trifluoromethylthiocopper [9b] (3.1 g, 0.19 mol) in dry xylene (5 ml), a solution of sulfur dichloride (3.1 g, 0.024 mol) in dry xylene (5 ml) was added with stirring at ambient temperature. The reaction was exothermic. After the addition was complete, the reaction mixture was stirred for an additional 45 min. The mixture was flash-distilled under reduced pressure and the distillate collected into a receiver cooled to -78 °C. The GC/MS analysis of the distillate indicated the presence of bis(trifluoromethyl)-di-, tetra- and penta-sulfides as minor impurities. Fractional distillation of the distillate through a silvered, vacuum-jacketed, metal helix-packed column gave the desired product (yield, 61%; b.p., 85–87 °C, lit. value [14], 86.2 °C). The purity of the compound was 96% by gas chromatography. The previous procedure [14] required 30 d at room temperature. ^{13}C NMR δ: 128.7 (quartet) ppm; $J=314\pm1$ Hz. ^{19}F NMR δ: 44.5 (singlet) ppm.

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