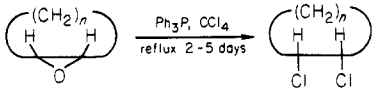
dichlorocycloheptane was unsuccessful. Monitoring the reaction by GLC analysis of the reaction mixture for unconsumed cycloheptene oxide revealed that the reaction was very slow and required several days of refluxing for completion.

By making adjustments for the slower than anticipated reaction and for release for the desired products from occlusion within the triphenylphosphine oxide mass, *cis*-1,2-dichlorocycloalkanes **2a–c** were prepared in 70–80% yields (eq 1). Contamination of the *cis*-1,2-dichloro-



(1)

1a, $n = 5$
b, $n = 6$
c, $n = 10$

2a–c

cycloalkane products by the corresponding *trans*-dichlorides was undetectable by GLC (<1%). In an attempt to shorten the reaction time, epoxide **1b** and triphenylphosphine in carbon tetrachloride were heated at 150 °C in a sealed tube for 24 h. GLC analysis revealed the presence of unconsumed epoxide (27%), *cis*-1,2-dichlorocyclooctane (47%), and *trans*-1,2-dichlorocyclooctane (30%). Thus the use of higher temperature is found to destroy the stereospecificity.

Experimental Section

Materials. Carbon tetrachloride, triphenylphosphine, and petroleum ether (30–60 °C) were reagent grade and were used as received. Epoxide **1a** was obtained from Aldrich Chemical Co. Epoxides **1b** and **1c** were prepared from cycloheptene (Aldrich) and *cis*-cyclododecene,[7] respectively, by reaction with *m*-chloroperbenzoic acid, using the general method of Servis et al.[8]

Preparation of Medium-Ring *cis*-1,2-Dichlorocycloalkanes. The epoxides **1a–c** (0.10 mol) and triphenylphosphine (0.15 mol) in 100 mL of carbon tetrachloride were refluxed under nitrogen. Periodically, an aliquot of the reaction mixture was removed and petroleum ether (30–60 °C) was added. The supernant liquid was analyzed by GLC for unconsumed epoxide. Upon completion of the reaction, the mixture was allowed to cool and was poured into 250–500 mL of petroleum ether (30–60 °C). The supernant liquid was decanted and the residual brown solid was ground (in portions) in a mortar and pestle with portions of the petroleum ether decantate until only light tan triphenylphosphine oxide crystals and a yellow petroleum ether solution remained. The solid was removed by filtration and the filtrate was evaporated on a rotary evaporator. The residual liquid was distilled under reduced pressure to yield (compound, reaction time, yield, boiling point): **2a**,[3] 3 days, 80%, 70 °C (1.1 torr); **2b**,[4] 2 days, 74%, 80–81 °C (0.8 torr); **2c**,[5] 5 days, 70%, 145–147 °C (2.5 torr). IR and ^{1}H NMR spectra were consistent with the proposed structures. Compound **2c** was further characterized by reaction with $NaNH_2$–NaO-*t*-Bu in THF followed by stereospecific dehalogenation[9,10] of the resulting vinyl chloride to yield *cis*-cyclododecene.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. **1a**, 76519-87-4; **1b**, 4925-71-7; **1c**, 1502-29-0; **2a**, 32718-96-0; **2b**, 16250-67-2; **2c**, 86782-61-8; Ph_3P, 603-35-0; CCl_4, 56-23-5.

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Novel Trialkoxymethyl Disulfides via Nucleophilic Addition to Thionocarbonates: Tris(2-fluoro-2,2-dinitroethoxy)methyl Trichloromethyl Disulfide and Related Products

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As possible starting materials for the synthesis of trialkoxychloromethanes (chloroorthoformates), we were interested in the preparation of trialkoxymethyl disulfides, more specifically, tris(2-fluoro- and/or 2-nitroethoxy)methyl disulfides. However, no examples of trialkoxymethyl disulfides were reported in the literature, presumably because the required trialkoxymethyl thiols[1] are not available. Although it would appear that such thiols could be prepared by the nucleophilic addition of an alkoxide ion to a thionocarbonate (eq 1), in practice the equilibrium

$$RO^- + (RO)_2C{=}S \rightleftarrows (RO)_3C{-}S^- \qquad (1)$$

is unfavorable, and the thiol cannot be isolated. Nevertheless it seemed reasonable to expect that a certain finite concentration of the trialkoxymethanethiolate ion would exist in solution and possibly could be trapped as the disulfide by reaction with a sulfenyl chloride. This expectation has now been realized experimentally. Under basic conditions, 2-fluoro-2,2-dinitroethanol reacted with bis(2-fluoro-2,2-dinitroethyl)thionocarbonate[2] (**1**) in the presence of trichloromethanesulfenyl chloride to give tris(2-fluoro-2,2-dinitroethoxy)methyl trichloromethyl disulfide **2** (eq 2). The thionocarbonate **1** does not have

$$FC(NO_2)_2CH_2OH + \underset{\mathbf{1}}{[FC(NO_2)_2CH_2O]_2C{=}S} + Cl_3CSCl \xrightarrow[CH_2Cl_2/H_2O]{OH^-/PTC} \underset{\mathbf{2}\ (65\text{–}80\%)}{[FC(NO_2)_2CH_2O]_3CSSCCl_3} + \underset{\mathbf{3}\ (6\text{–}11\%)}{([FC(NO_2)_2CH_2O]_3CS)_2} \qquad (2)$$

PTC = phase transfer catalyst

to be present initially but can be formed in situ by the reaction of fluorodinitroethanol with thiophosgene although the yield of **2** is somewhat lessened. The symmetrical disulfide **3** was also isolated as a minor product (6–11%).

At first, it was assumed that **2** was formed in a straightforward manner by nucleophilic attack of the tris(fluorodinitroethoxy)methanethiolate ion on trichloromethanesulfenyl chloride; however, the isolation and identification of the constituents of a partially complete reaction indicated the presence of a considerable concentration of 2-fluoro-2,2-dinitroethyl trichloromethanesulfenate (**4**). When the reaction was followed by TLC, there was an initial increase in the concentration of the ester **4** which then gradually disappeared during the course of the reaction. The ester **4** was independently synthesized by the base-catalyzed reaction of fluorodinitroethanol with trichloromethanesulfenyl chloride[3] (eq 3). Substitution of

(1) The most common precursors for disulfides are thiols or thiol derivatives. For a review, see: Field, L. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; p 303 and references cited therein.
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(3) Compound **4**, in contrast to typical sulfenates, is quite stable. A sample remained unchanged after storage in a desiccator at ambient temperature for 3 years.

the ester 4 for the sulfenyl chloride gave comparable yields of 2.

$$FC(NO_2)_2CH_2OH + Cl_3CSCl \xrightarrow[CH_2Cl_2/H_2O]{OH^-/PTC} \underset{4}{FC(NO_2)_2CH_2OSCCl_3} \quad (3)$$

The experimental evidence suggests the most plausible mechanism for the formation of 2 is that shown in Scheme I.[4] Another possible mechanism[5] (Scheme II) involves

Scheme I

$$FC(NO_2)_2CH_2OH \overset{OH^-}{\rightleftharpoons} FC(NO_2)_2CH_2O^- \quad (a)$$

$$FC(NO_2)_2CH_2O^- + \underset{1}{[FC(NO_2)_2CH_2O]_2C{=}S} \rightleftarrows [FC(NO_2)_2CH_2O]_3C\text{-}S^- \quad (b)$$

$$FC(NO_2)_2CH_2O^- + Cl_3CSCl \rightarrow \underset{4}{FC(NO_2)_2CH_2OSCCl_3} \quad (c)$$

$$[FC(NO_2)_2CH_2O]_3C\text{-}S^- + RSCCl_3 \rightarrow \underset{2}{[FC(NO_2)_2CH_2O]_3CSSCCl_3} + R^- \quad (d)$$

R = $FC(NO_2)_2CH_2O$; Cl

Scheme II

$$4 + 1 \rightarrow [FC(NO_2)_2CH_2O]_2C^+SSCCl_3 + FC(NO_2)_2CH_2O^- \rightarrow 2$$

direct addition of 4 to 1, but this is not a likely route since 1 + 4 in nitromethane at 65 °C for 20 h gives no reaction. Similarly, no reaction occurs when a dichloroethane solution of 1 and trichloromethanesulfenyl chloride is refluxed for 35 h.

The symmetrical disulfide 3 was independently synthesized in 48% yield by the reaction of fluorodinitroethanol with the thionocarbonate 1 in the presence of the disulfide 2 (eq 4). The mechanism of this reaction is not

$$FC(NO_2)_2CH_2OH + 2 + 1 \xrightarrow[CH_2Cl_2/H_2O]{OH^-/PTC} \underset{48\%}{3} \quad (4)$$

clear. Although the formation of 3 would appear to result from direct nucleophilic attack of the tris(fluorodinitroethoxy)methanethiolate ion on 2, this process should be quite difficult due to the massive steric repulsions involved in the transition state. The disulfide 3 is not formed from the thionocarbonate 1 and fluorodinitroethoxide in the absence of 2 (even though in one experiment additional oxygen was passed into the system to perhaps aid in oxidation of the thiolate ion to 3), nor is 3 formed when 2 is treated with fluorodinitroethoxide (thereby excluding the possibility that 3 is arising by displacement of chloride from the trichloromethyl group of 2). Another possible mechanism for the formation of 3 would be cleavage of 2 into ions followed by combination with tris(fluorodinitroethoxy)methanethiolate ion.[6]

If the alkoxide used to attack the thionocarbonate is different from the substituents in the thionocarbonate the result is a "mixed" trialkoxymethyl disulfide (Scheme III).

Scheme III

$$R''OH + (R'O)_2C{=}S + ClSCCl_3 \xrightarrow[CH_2Cl_2/H_2O]{OH^-/PTC} \underset{\substack{5,\ R' = CH_2C(NO_2)_2CH_3;\ R'' = CH_2CF(NO_2)_2 \\ 6,\ R' = CH_2CF(NO_2)_2;\ R'' = CH_2CF_3 \\ 7,\ R' = CH_2CF_3;\ R'' = CH_2CF(NO_2)_2}}{(R''O)(R'O)_2CSSCCl_3}$$

The disulfides 5–7 prepared in this way are the major products, although other disulfides are also formed because of the reversibility of the formation of the trialkoxymethanethiolate ion.[7] Since a wide variety of thionocarbonates are available,[2,8,9] a large number of trialkoxymethyldisulfides can now be prepared. The chief limitation is that the reactants must be stable to the required basic conditions.

The trialkoxymethyl disulfides can be readily converted to trialkoxychloromethanes (chloroorthoformates) which are members of a previously unknown class of compounds. This transformation occurs in greater than 95% yield when a dichloroethane solution of the disulfide is treated with gaseous chlorine at 60 °C for 4 h or at ambient temperature for 7 h (eq 5). The preparation of the chloroorthoformates

$$2 + Cl_2 \xrightarrow[60\ °C,\ 4\ h]{ClCH_2CH_2Cl} [FC(NO_2)_2CH_2O]_3CCl \quad (5)$$

as well as numerous derivatives prepared from them will be described in a subsequent paper.[10]

Experimental Section

The compounds described herein are energetic materials, sensitive to impact, and should be handled with care. Reactions should be performed on a small scale behind adequate shielding, and personnel should be equipped with safety glasses and fire-retardant lab coats. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The melting points are uncorrected, and the NMR chemical shifts are relative to Me_4Si as an external standard. The silica gel 60 is 70–230 mesh from EM Reagents (Brinkmann).

Tris(2-fluoro-2,2-dinitroethoxy)methyl Trichloromethyl Disulfide (2). A well-stirred mixture of 40 g (0.26 mol) of 2-fluoro-2,2-dinitroethanol in 110 mL of CH_2Cl_2 and 2 g of tetrabutylammonium chloride in 100 mL of H_2O was cooled in an ice-salt bath to 0 °C. A solution of 6.06 g (0.05 mol) of 85% thiophosgene[11] and 12.1 g (0.065 mol) of trichloromethanesulfenyl chloride in 30 mL of CH_2Cl_2 was added all at once followed by the dropwise addition (0.5 h) of 11.2 mL of 50% aqueous NaOH, keeping the temperature at 0 to 4 °C. After the reaction solution was kept slightly basic at 0 °C for 40 min by the occasional addition of 50% NaOH, the CH_2Cl_2 layer was separated and dried, and the volatiles were removed to give 45.8 g of an oily residue which was dissolved in 60 mL of $CHCl_3$. Cooling to −20 °C gave 1.55 g (6%) of bis[tris(2-fluoro-2,2-dinitroethoxy)methyl] disulfide (3). Hexane was added to the $CHCl_3$ mother liquor until it began to cloud at room temperature. The solution was treated with charcoal and filtered through a silica gel 60 pad (40 g) which was washed with $CHCl_3$–hexane (3:2). Addition of hexane to the filtrate followed by cooling in dry ice–acetone gave 23.0 g of 2 as white crystals, mp 52–55 °C. Recrystallization from $CHCl_3$–hexane yielded 2: 21.2 g (65%); mp 55–57 °C; ^1H NMR ($CDCl_3$) δ 4.84 (d); mass spectrum (CI), m/e 503, 471. Anal. Calcd for $C_8H_6Cl_3F_3N_6O_{15}S_2$: C, 14.70; H, 0.93; Cl, 16.27; F, 8.72; N, 12.86;

(4) See ref 7.

(5) Subsequent to submission of this article but prior to receiving the reviewer's comments we considered this mechanism and performed the necessary experiments. However, we thank the reviewer for also suggesting this possibility.

(6) The authors thank a reviewer for suggesting other possible mechanisms: (A) disproportionation of 2 either by a homolytic or heterolytic route to give 3 and $(Cl_3CS)_2$ and (B)

$$2 + RO^- \rightarrow (RO)_3CSOR \xrightarrow{1} (RO)_3CSSC^+(OR)_2 \xrightarrow{RO^-} 3$$

However, route B is similar to the addition of 4 to 1 which has been shown not to occur.

(7) That other disulfides are formed further suggests the mechanism involves nucleophilic addition of alkoxides to thionocarbonates. The expected reversibility of these additions would produce mixed thionocarbonates and thus eventually lead to a mixture of products.

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(11) Aldrich Chemical Co.; contains 15% CCl_4.

S, 9.81. Found: C, 14.59; H, 1.07; Cl, 16.32; F, 8.64; N, 12.64; S, 9.61.

A similar experiment starting with bis(2-fluoro-2,2-dinitroethyl) thionocarbonate[2] (17.5 g, 0.05 mol), 2-fluoro-2,2-dinitroethanol (17.7 g, 0.115 mol), and trichloromethanesulfenyl chloride (12.1 g, 0.065 mol) gave 2.79 g (11%) of **3** and 26.05 g (80%) of **2**, mp 55–57 °C.

Bis[tris(2-fluoro-2,2-dinitroethoxy)methyl] Disulfide (3). A solution of 1.96 g (0.003 mol) of **2**, 1.05 g (0.003 mol) of bis-(2-fluoro-2,2-dinitroethyl)thionocarbonate,[2] and 0.6 g (0.004 mol) of 2-fluoro-2,2-dinitroethanol in 10 mL of CH_2Cl_2 was cooled in an ice bath. Tetrabutylammonium chloride (0.3 g) in 6 mL of water was added followed by the dropwise addition (0.25 h) of 0.4 g of 50% NaOH (diluted with 2 mL of H_2O) at 0–3 °C. The reaction solution was allowed to warm to dissolve a solid precipitate into the CH_2Cl_2 layer which was then separated, and the volatiles were removed to give a residue which when treated with $CHCl_3$ gave 1.44 g (48%) of a white solid, mp 130–133 °C. Recrystallization from acetone–$CHCl_3$ gave the product: mp 134–135 °C; ^1H NMR [$(CD_3)_2C{=}O$] δ 5.30 (d); mass spectrum (CI), m/e 471. Anal. Calcd for $C_{14}H_{12}F_6N_{12}O_{30}S_2$: C, 16.71; H, 1.20 F, 11.33; N, 16.70; S, 6.37. Found: C, 16.54; H, 1.15; F, 11.43; N, 16.63; S, 6.14.

Bis(2,2-dinitropropoxy)(2-fluoro-2,2-dinitroethoxy)methyl Trichloromethyl Disulfide (5). A mixture of 20.5 g (0.06 mol) of bis(2,2-dinitropropyl) thionocarbonate,[8] 14.5 g (0.078 mol) of trichloromethanesulfenyl chloride, and 21.2 g (0.138 mol) of 2-fluoro-2,2-dinitroethanol in 110 mL of CH_2Cl_2 was cooled in an ice–salt bath before 3.0 g of tetrabutylammonium chloride in 70 mL of H_2O was added. A 50% aqueous NaOH solution (10.0 g) was diluted with 30 mL of H_2O and added dropwise (0.25 h) at 0–4 °C until the reaction solution turned basic to litmus paper. The CH_2Cl_2 layer was separated and dried, and the volatiles were removed to yield an oil which was washed with 200 mL of hexane and 300 mL of H_2O before it (19.3 g) was purified by chromatography on silica gel 60 (300 g; CH_2Cl_2–hexane as the eluent). The product was then triturated with hexane to give solid: 13.4 g (35%) mp 63–66 °C; ^1H NMR [$(CD_3)_2C{=}O$] δ 5.34 (d, 2 H), 4.91 (s, 4 H), 2.39 (s, 6 H). Anal. Calcd for $C_{10}H_{12}Cl_3FN_6O_{15}S_2$: C, 18.60; H, 1.87; Cl, 16.47; F, 2.94; N, 13.01; S, 9.93. Found: C, 18.80; H, 1.89; Cl, 16.50; F, 2.93; N, 12.96; S, 9.79.

Bis(2-fluoro-2,2-dinitroethoxy)(2,2,2-trifluoroethoxy)-methyl Trichloromethyl Disulfide (6). A solution of 10.5 g (0.03 mol) of bis(2-fluoro-2,2-dinitroethyl) thionocarbonate,[2] 7.25 g (0.039 mol) of trichloromethanesulfenyl chloride, and 6.9 g (0.069 mol) of 2,2,2-trifluoroethanol in 50 mL of CH_2Cl_2 was cooled in an ice–salt bath. Tetrabutylammonium chloride (1.5 g) in 30 mL of H_2O was added followed by the dropwise addition (0.25 h) of 2.8 g of NaOH in 5 mL of H_2O at 0–3 °C. The CH_2Cl_2 layer was separated and dried, and the volatiles were removed to give 16.5 g of an oil which was extracted with boiling hexanes (3 × 50 mL). The cooled extracts were decanted from a small amount of oily precipitate, and the solvent was removed to give 6.0 g (33%) of an oil which was nearly pure by TLC analysis. An analytical sample was obtained by column chromatography on silica gel 60 (115 g) with hexane followed by CH_2Cl_2–hexane as the eluent: ^1H NMR ($CDCl_3$) δ 4.89 (d, 4 H), 4.15 (q, 2 H). Anal. Calcd for $C_8H_6Cl_3F_5N_4O_{11}S_2$: C, 16.02; H, 1.01; Cl, 17.74; F, 15.84; N, 9.34; S, 10.69. Found: C, 16.08; H, 1.02; Cl, 17.97; F, 15.63; N, 9.23; S, 10.81.

Bis(2,2,2-trifluoroethoxy)(2-fluoro-2,2-dinitroethoxy)-methyl Trichloromethyl Disulfide (7). To a well-stirred solution of 7.26 g (0.03 mol) of bis(2,2,2-trifluoroethyl)thionocarbonate,[12] 6.14 g (0.033 mol) of trichloromethanesulfenyl chloride, and 6.0 (0.039 mol) of 2-fluoro-2,2-dinitroethanol in 40 mL of CH_2Cl_2 cooled in an ice–salt bath was added 1.5 g of tetrabutylammonium chloride in 30 mL of H_2O followed by the dropwise addition (0.25 h) of 5 mL of 10 N aqueous NaOH at 0–5 °C. The reaction solution was then kept slightly basic for 15 min by the addition of a few drops of NaOH solution when required. The CH_2Cl_2 layer was separated, and the solvent was removed to give 18.0 g of oil which was purified by column chromatography on silica gel 60 (115 g; 30:70 CH_2Cl_2–hexane as the eluent). The product was an oil: 9.95 g (61%) ^1H NMR ($CDCl_3$) δ 4.90 (d, 2 H), 4.15 (q, 4 H). Anal. Calcd for $C_8H_6Cl_3F_7N_2O_7S_2$: C, 17.61; H, 1.11; Cl, 19.49; F, 24.38; N, 5.13; S, 11.75. Found: C, 17.62; H, 1.05; Cl, 19.24; F, 24.17; N, 5.19; S, 11.56.

2-Fluoro-2,2-dinitroethyl Trichloromethanesulfenate (4). Trichloromethanesulfenyl chloride (5.6 g, 0.03 mol) and 2-fluoro-2,2-dinitroethanol (5.0 g, 0.033 mol) in 30 mL of CH_2Cl_2 and 0.3 g of tetrabutylammonium chloride in 20 mL of H_2O was cooled at 0 °C during the dropwise addition (0.25 h) of 1.3 g of NaOH in 6 mL of H_2O. Separation of the CH_2Cl_2 layer and removal of solvent gave 8.2 g of oil which was extracted with hexane (2 × 40 mL). The combined extracts were passed through a silica gel 60 pad (40 g, washed with benzene), and the solvent was removed to give 5.9 g (65%) of an oil which was pure by TLC and GLC analysis: ^1H NMR ($CDCl_3$) δ 5.37 (d); mass spectrum (CI), m/e 304, 302, 267, 269. Anal. Calcd for $C_3H_2Cl_3FN_2O_5S$: C, 11.87; H, 0.66; Cl, 35.05; F, 6.26; N, 9.23; S, 10.56. Found: C, 11.85; H, 0.70; Cl, 34.90; F, 6.14; N, 9.05; S, 10.58.

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Registry No. **1**, 70096-91-2; **2**, 86803-34-1; **3**, 86803-35-2; **4**, 86803-39-6; **5**, 86803-36-3; **6**, 86803-37-4; **7**, 86803-38-5; 2-fluoro-2,2-dinitroethanol, 17003-75-7; tetrabutylammonium chloride, 1112-67-0; thiophosgene, 463-71-8; trichloromethanesulfenyl chloride, 594-42-3; 2-fluoro-2,2-dinitroethoxide, 86803-33-0; bis-(2,2-dinitropropyl) thionocarbonate, 80445-01-8; 2,2,2-trifluoroethanol, 75-89-8; bis(2,2,2-trifluoroethyl) thionocarbonate, 83486-43-5.

(12) From thiophosgene and trifluoroethanol with base.

Ionic Fluorination of Adamantane, Diamantane, and Triphenylmethane with $NO^+BF_4^-$/Pyridine Polyhydrogen Fluoride (PPHF)[1]

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The usual laboratory preparation of alkyl or arylalkyl fluorides involves nucleophilic exchange of the corresponding halides (iodides, bromides, chlorides) or other suitable leaving groups by fluoride ion or addition of hydrogen fluoride[3] to olefins. To overcome inconvenience of using volatile, highly corrosive, and difficult to handle anhydrous hydrogen fluoride, we have introduced pyridine polyhydrogen fluoride (PPHF) as a convenient fluorinating agent.[4] Direct fluorination of saturated hydrocarbons is difficult. Fluorination of saturated hydrocarbons using fluoroxytrifluoromethane[5] can be achieved, but the reaction necessitates well-controlled conditions, specific equipment, and precautions. No direct purely ionic fluorination of saturated hydrocarbons was so far reported.[6]

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