The Preparation and Synthetic Utility of ω-(Vinyl)perfluoroalkanecarboxylates

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The addition of ethylene to ethyl ω-bromoperfluoroalkanecarboxylates under free-radical conditions gave the desired 1:1 adduct, $BrCH_2CH_2(CF_2CF_2)_nCOOC_2H_5$, in good yield along with the 1:2 adduct, $Br(CH_2CH_2)_2(CF_2CF_2)_nCOOC_2H_5$, and a little of the higher telomers. Treatment of the 1:1 adduct with sodium ethoxide resulted in the formation of ethyl ω-(vinyl)perfluoroalkanecarboxylates in high yield. Ethyl 3-(vinyl)perfluoropropionate was converted into 3-(vinyl)perfluoropropionitrile *via* the corresponding amide. The synthetic approach leading to a fluorosilicone–triazine polymer, $[\text{–Si}(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3\text{–}C_3N_3)\text{-}CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiO\text{–}]_x$, by utilization of 3-(vinyl)perfluoropropionitrile is described.

A homologous series of ethyl ω-bromoperfluoroalkanecarboxylates has been previously prepared in this laboratory.[1] Continuing our interest in the synthesis of new versatile fluoroorganic intermediates, we have investigated the preparation of ethyl ω-(vinyl)perfluoroalkanecarboxylates based on ethyl ω-bromoperfluoroalkanecarboxylates as starting materials. After the successful preparation of ethyl ω-(vinyl)perfluoroalkanecarboxylates, the growing interest in poly(perfluoroalkylenetriazines)[2] and our interest in accessing the synthetic utility of the ω-vinyl esters led us to investigate the synthetic feasibility of a poly(fluoroalkylenetriazine) containing a SiOSi linkage *via* a silanol condensation route. This approach would take advantage of the known high degree of reactivity of silanols toward coupling under relatively mild conditions.

Results and Discussion

Ethyl ω-(Vinyl)perfluoroalkanecarboxylates.—A consideration of the replacement of bromine in ethyl ω-bromoperfluoroalkanecarboxylates (I) by vinyl group suggested that an appealing route was the addition of ethylene to the ω-bromo esters followed by dehydrobromination. Although the addition of ethylene to varied haloalkanes including polyfluorinated alkyl halides and a number of functional derivatives has been abundantly documented,[3] only one report concerned with the addition of ethylene to $(\text{–}CF_2)_nBr$ has appeared in the literature.[4]

The addition of ethylene to the ester I was successfully effected under free-radical conditions using di-*t*-butyl peroxide or benzoyl peroxide (eq 1). The typical results of the addition of ethylene to the ester Ia are shown in Table I. Even though the emphasis of this investigation was focused on the formation of the 1:1 adduct ester II, the formation of the higher telomers, namely 1:2 adduct ester III, could not be avoided. Qualitatively, the data in Table I indicate that the IIa/IIIa ratio decreases with an increase in pressure (or concentration) of ethylene as expected and that the ratio of IIa/IIIa increases with increasing the reaction temperature. Similar results were obtained when the reaction was conducted with a given concentration of the reactants in an isolated system (see Table II). The increase of the IIa/IIIa ratio with an increase in the reaction temperature is undoubtedly due, at least in part, to the increase in the chain-transfer constant with increasing the reaction temperature.[5] Under reaction conditions similar to those described above, ester IIb was also prepared. However, no attempt was made to isolate IIIb although a peak corresponding to IIIb was observed in a gas chromatogram of the crude reaction product. The ratio of IIb to presumed IIIb was similar to that of IIa/IIIa.

$$Br(CF_2CF_2)_nCOOC_2H_5 + CH_2{=}CH_2 \longrightarrow \begin{array}{l} \text{Ia, } n = 1 \\ \text{b, } n = 2 \end{array}$$

$$Br(CH_2CH_2)_m(CF_2CF_2)_nCOOC_2H_5 \quad (1)$$

$$\begin{array}{r} \text{IIa, } m = n = 1 \\ \text{b, } m = 1;\, n = 2 \\ \text{IIIa, } m = 2;\, n = 1 \\ \text{b, } m = n = 2 \end{array}$$

Table I

Addition of Ethylene to Ia[a]

Run	Constant ethylene pressure, psi	Reaction time, hr	Reaction temp, °C	Convn of Ia,[b] %	% yield of adducts[b]	
					IIa	IIIa
1	50	8	130	55.1	67.2	16.2
2	50	20	115	32.5	56.6	30.6
3	75	5	125	33.0	52.4	30.9
4	25	40	70	16.0	56.3	31.1
5	50	22	70	26.0	34.6	46.2

[a] All experiments were made using 200 g of Ia and 7 g of di-*t*-butyl peroxide except the runs 4 and 5, for which benzoyl peroxide (4 g) was employed. [b] Gas chromatographic analysis.

Table II

Reaction of Ethylene with Ia in an Isolated System[a]

Run	Initial ethylene pressure at 25°, psi	Reaction time, hr	Reaction temp, °C	Convn of Ia,[b] %	IIa/IIIa[b]
1	200	15	130–135	57.5	0.613
2	200	80	110–115	58.7	0.428

[a] All experiments were conducted using 75 g of Ia and 2.2 g of di-*t*-butyl peroxide. [b] Gas chromatographic analysis.

Treatment of II with sodium ethoxide in ethanol at room temperature gave rise to the ω-vinyl ester IV in

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(1) Y. K. Kim, *J. Org. Chem.*, **32**, 3673 (1967).

(2) (a) G. A. Grindahl, W. X. Bajzer, and O. R. Pierce, *J. Org. Chem.*, **32**, 603 (1967), and references cited therein; (b) J. A. Young and R. L. Dressler, *ibid.*, **32**, 2237 (1967).

(3) (a) W. E. Hanford and D. E. Sargent in "Organic Chemistry, An Advanced Treatise," Vol. IV, H. Gilman, *et al.*, Ed., John Wiley & Sons, Inc., New York, N. Y., 1953; (b) J. I. G. Cadogan and D. H. Hey, *Quart. Rev.* (London), **8**, 308 (1954); (c) W. A. Skinner, J. D. Johnston, and M. Fisher, *J. Amer. Chem. Soc.*, **79**, 5790 (1957); (d) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, pp 37–40; (e) A. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963); (f) T. Asahara and J. Hirano, *Bull. Jap. Petrol. Inst.*, **7**, 35 (1965).

(4) K. C. Smeltz [U. S. Patent 3,055,953 (1962)] describes the preparation of $Br(CF_2CF_2)_x(CH_2CH_2)_yBr$ and $Br(CH_2CH_2)_z(CF_2CF_2)_x(CH_2CH_2)_yBr$ by the free-radical-catalyzed addition of ethylene to $Br(CF_2CF_2)_xBr$.

(5) R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 3740 (1948).

high yield (eq 2). Since the objective of this dehydrobromination reaction was the preparation of IV and

$$\text{II} \longrightarrow \underset{\substack{\text{IVa}, n = 1\\ \text{b}, n = 2}}{CH_2{=}CH(CF_2CF_2)_nCOOC_2H_5} + \underset{\substack{\text{Va}, n = 1\\ \text{b}, n = 2}}{C_2H_5OCH_2CH_2(CF_2CF_2)_nCOOC_2H_5} \quad (2)$$

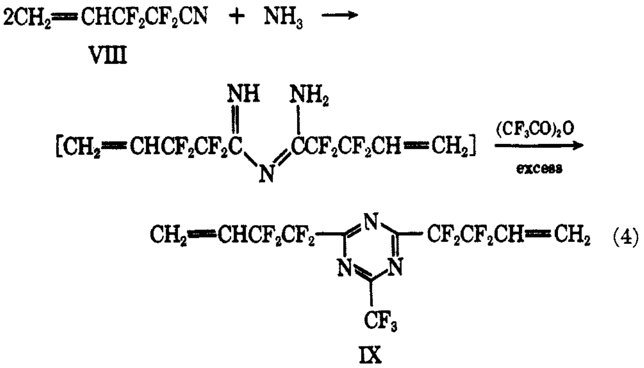
also since a high yield of IV was obtained, no attempt was made to isolate or detect the other possible product, the ω-ethoxy ester V. However, gas chromatographic analysis of the reaction mixture suggested that less than 4% of V might be present. In contrast, the similar treatment of the ester IIIa yielded the ω-ethoxy ester VI as the major product along with the ω-vinyl ester VII (eq 3).[6] The predominant, if not exclusive,

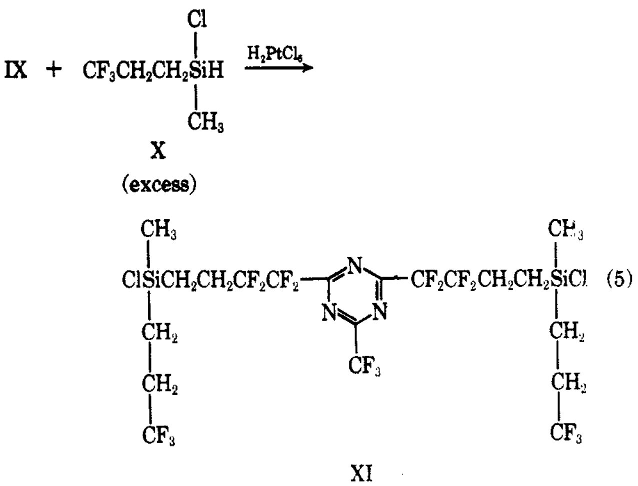
$$\text{IIIa} \longrightarrow \underset{\text{VI}}{C_2H_5O(CH_2)_4CF_2CF_2COOC_2H_5} + \underset{\text{VII}}{CH_2{=}CHCH_2CH_2CF_2CF_2COOC_2H_5} \quad (3)$$

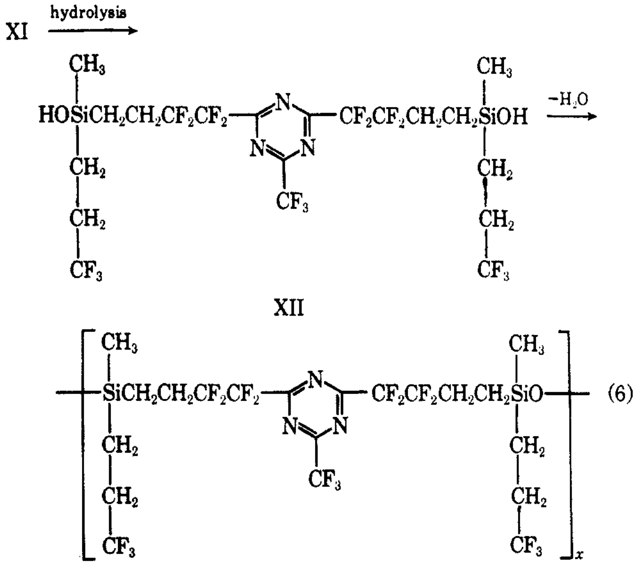
formation of IV in the dehydrobromination of II undoubtedly reflects to a large extent that the electrophilic perfluoroalkyl group activates the proton attached to an adjacent carbon atom, thus promoting attack by base.[7]

Synthesis of Triazine Derivatives and Polymerization.—Ammonolysis of ethyl 3-(vinyl)perfluoropropionate (IVa) followed by dehydration of the resulting amide yielded 3-(vinyl)perfluoropropionitrile (VIII). The required 2,4-bis[2-(vinyl)perfluoroethyl]-6-(perfluoromethyl)-1,3,5-triazine (IX) was prepared in high yield according to the known synthetic route (see eq 4).[2a,8] The chloroplatinic acid catalyzed addition of (3,3,3-trifluoropropyl)methylchlorosilane (X) to divinyltriazine IX gave the diaddition product XI (eq 5). Unlike the normal addition of ≡SiH to an olefin,[9] a relatively large amount of the catalyst was required to effect the addition of the silane X to IX. Since a *s*-triazine has been known to have a tendency to poison noble-metal hydrogenation catalyst[10] the relatively large amount of the catalyst required may be due to the action of the triazine ring as a poison in the ≡SiH addition reaction. Triazine XI was a viscous liquid and was purified by means of a molecular distillation. The elemental analysis and spectral properties were in complete agreement with the assigned structure (XI). However, the infrared spectrum of the purified XI showed a weak band (~3400 cm^{-1}) attributable to a hydroxy group, suggesting a partial hydrolysis during the work-up.

Hydrolysis of XI was effected in an aqueous sodium bicarbonate–ether system to give rise to a viscous liquid hydrolysate. The analysis of hydroxy content, molecular weight determination, and spectral data suggest that the hydrolysate is principally composed of monomer diol XII and very little of the condensed product. When it stood at room temperature, the viscosity of the hydrolysate increased slowly but noticeably, indicating a partial condensation. The silanol condensation (see eq 6) of XII, catalyzed by tetramethylguanidine–trifluoroacetic acid, yielded polymer XIII. The molecular weight, by vapor phase osmometry, of the polymer was found to be approximately 5100. The raw polymer exists as an elastomeric material that forms a tough film.







Thus the above sequence of reactions demonstrates a successful synthetic route for the preparation of the polymers of type XIII. Further investigation of this synthetic approach and evaluation of polymer XIII will be reported elsewhere in the future.

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(6) No attempt was made to increase the VII/VI ratio.

(7) N. O. Brace, *J. Amer. Chem. Soc.*, **86**, 2430 (1964).

(8) H. C. Brown, P. D. Shuman, and J. Turnbull, *J. Org. Chem.*, **32**, 231 (1967).

(9) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

(10) C. Grundmann and A. Kreutzberger, *ibid.*, **77**, 44 (1955).

Experimental Section

All melting points and boiling points are uncorrected. All melting points were taken on a Thomas–Hoover capillary melting point apparatus. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord. Gas chromatography was conducted on a F & M Model 720 using a 10 ft × 0.25 in. column containing 20% Dow Corning FS 1265 fluid (10,000 cSt) on Anakrom 90–100 mesh ABS. The ^{19}F resonance spectra were measured on a Varian high-resolution nmr spectrometer operating at 56.4 Mc. Chemical shifts were determined in parts per million using CCl_3F as an internal standard (δ 0 ppm) with the positive direction on the high-field side. The proton resonance spectra were obtained on a Varian A-60 nmr spectrometer using tetramethylsilane as an internal standard (δ 0 ppm) with the positive direction in this case on the low-field side.

General Procedure for the Addition of Ethylene to Ethyl ω-Bromoperfluoroalkanecarboxylates (I).—A 250-ml glass pressure reactor, equipped with a magnetic stirrer, a gas inlet, and means for measuring temperature and pressure, was charged with I and peroxide. The system was flushed free of air with ethylene, then closed, and heated under a constant ethylene pressure. The reaction was stopped, and the product was fractionally distilled. The conditions and results of the various runs are summarized in Table I. For the reaction in an isolated system (Table II), a 1-l. stainless steel pressure reactor equipped with a mechanical stirrer was employed. The system containing Ia was flushed and pressurized with ethylene, and then isolated. The reaction pressure increased upon heating, then decreased slowly during the reaction.

Ethyl 2,2,3,3-tetrafluoro-5-bromopentanoate (IIa) had bp 79° (4 mm), n^{25}D 1.4005.

Anal. Calcd for $C_7H_9BrF_4O_2$: C, 29.91; H, 3.23; Br, 28.43; F, 27.04. Found: C, 30.0; H, 3.29; Br, 29.0; F, 27.0.

The infrared spectrum (CCl_4) showed a strong band at *ca.* 1770 cm^{-1} (C=O). The proton resonance spectrum (neat) comprised signals centered at δ 1.38 (3 H, triplet), 2.68 (2 H, multiplet), 3.51 (2 H, triplet), and 4.34 ppm (2 H, quartet).

Ethyl 2,2,3,3-tetrafluoro-7-bromoheptanoate (IIIa) had bp 76° (0.5 mm), n^{25}D 1.4145.

Anal. Calcd for $C_9H_{13}BrF_4O_2$: C, 34.97; H, 4.24; Br, 25.85; F, 24.59. Found: C, 35.0; H, 4.24; Br, 26.5; F, 24.2,

A strong band at *ca.* 1770 cm^{-1} (C=O) was present in the infrared spectrum (CCl_4). The proton resonance spectrum (neat) showed signals centered at δ 1.38 (3 H, triplet), *ca.* 2.3 (6 H, multiplet), 3.38 (2 H, triplet), and 4.34 ppm (2 H, quartet).

Ethyl 2,2,3,3,4,4,5,5-octafluoro-7-bromoheptanoate (IIb) had bp 70° (0.5 mm), n^{25}D 1.3788.

Anal. Calcd for $C_9H_9BrF_8O_2$: C, 28.36; H, 2.38; Br, 20.97. Found: C, 28.7; H, 2.51; Br, 20.2.

The infrared spectrum (CCl_4) showed a strong band at *ca.* 1770 cm^{-1} (C=O). The proton resonance spectrum was consistent with the assigned structure, IIb, and the ^{19}F resonance spectrum consisted of signals centered at δ +115.2, +118.8, +123.6, and +124.7 ppm. The relative areas were equivalent.

In the addition reaction of ethylene to Ia, some amount of ethyl 2,2,3,3-tetrafluoropentanoate, bp 42° (10 mm), n^{25}D 1.3534, was also isolated.

Anal. Calcd for $C_7H_{10}F_4O_2$: C, 41.6; H, 4.99; F, 37.6; mol wt, 202. Found: C, 41.5; H, 5.02; F, 37.6; mol wt, 202.

The ^{19}F and ^{1}H resonance spectra were consistent with the assigned structure, ethyl 2,2,3,3-tetrafluoropentanoate.

Dehydrobromination. A. Ethyl 2,2,3,3-Tetrafluoro-5-bromopentanoate (IIa).—To a stirred sodium ethoxide solution prepared from 35.2 g (1.53 g-atoms) of metallic sodium and 700 ml of ethanol was added slowly 375 g (1.33 mol) of IIa at room temperature. After the addition was completed, the reaction mixture was stirred at room temperature overnight; then the reaction mixture was flush distilled *in vacuo* (*ca.* 0.1 mm) into a receiver cooled by a Dry Ice–acetone bath. The stripping was continued until the still pot was dry. The flush distilled ethanol solution was redistilled to yield, after forecuts, 208 g (78% yield) of analytically pure ethyl 3-(vinyl)perfluoropropionate (IVa), bp 142° (740 mm), n^{25}D 1.3580.

Anal. Calcd for $C_7H_8F_4O_2$: C, 42.01; H, 4.03. Found: C, 42.3; H, 4.18.

The infrared spectrum (CCl_4) showed bands at *ca.* 1770 (C=O) and *ca.* 1650 cm^{-1} (C=C). The ^{19}F resonance spectrum consisted of two triplets, J_{FF} = 3.5 Hz, centered at δ +115.2 and +120.4 ppm with an area ratio of 1:1. Gas chromatographic analysis of the reaction mixture before flush distillation indicated the presence of an unidentified component (less than 4%) whose retention was longer than that of IVa. This unidentified component might have been the ω-ethoxy ester Va or the unreacted IIa.

B. Ethyl 2,2,3,3,4,4,5,5-Octafluoro-7-bromoheptanoate (IIb).—Following the procedure outlined above in A, about 15 g (0.039 mol) of IIb was dehydrobrominated. In this case, the reaction mixture was not flush distilled. The mixture was added to water and extracted with ether. The ethereal extract was dried over Drierite and distilled to yield, after forecuts, 8.5 g (72% yield) of analytically pure ethyl 5-(vinyl)perfluoropentanoate (IVb), bp 182–183° (747 mm), n^{25}D 1.3465.

Anal. Calcd for $C_9H_8F_8O_2$: C, 36.01; H, 2.69. Found: C, 36.2; H, 2.80.

C. Ethyl 2,2,3,3-Tetrafluoro-7-bromoheptanoate (IIIa).—Following the procedure outlined above in A, about 130 g (0.42 mol) of IIIa was subjected to dehydrobromination with a sodium ethoxide solution, prepared from 11 g (0.48 g-atom) of metallic sodium and 200 ml of ethanol. The ethanolic reaction mixture was stirred at room temperature for 48 hr and then added to 750 ml of water. The organic layer was separated and dried over Drierite to yield 83 g of crude product. Gas chromatographic analysis showed that the crude product was composed of ~32% ethyl 2,2,3,3-tetrafluoro-5-(vinyl)pentanoate (VII) and ~68% ethyl 2,2,3,3-tetrafluoro-7-ethoxyheptanoate (VI). A fractional distillation gave analytically pure VII, bp 69–70° (11 mm), n^{25}D 1.3790, and VI, bp 113° (11 mm), n^{25}D 1.3870.

Anal. Calcd for $C_9H_{12}F_4O_2$: C, 47.37; H, 5.30; F, 33.31. Found: C, 47.08; H, 5.27; F, 33.7.

Anal. Calcd for $C_{11}H_{18}F_4O_3$: C, 48.17; H, 6.62; F, 27.71; mol wt, 274. Found: C, 48.25; H, 6.64; F, 28.1; mol wt, 267.

The infrared and ^{1}H and ^{19}F resonance spectra were in agreement with the assigned structures, respectively.

Amide and Nitrile.—The amide and nitrile were prepared according to the previously reported methods;[1] the yields were generally greater than 90%. The spectral properties were in agreement with the assigned structures, respectively.

3-(Vinyl)perfluoropropionamide had mp 82–83°.

Anal. Calcd for $C_5H_5F_4NO$: C, 35.09; H, 2.95; F, 44.42; N, 8.19. Found: C, 35.1; H, 3.25; F, 44.5; N, 7.93.

5-(Vinyl)perfluoropentanamide had mp 80–81°. A mixture melting point with 3-(vinyl)perfluoropropionamide was depressed, mmp 58–71°.

Anal. Calcd for $C_7H_5F_8NO$: C, 31.01; H, 1.86; N, 5.17. Found: C, 31.1; H, 1.93; N, 5.04.

3-(Vinyl)perfluoropropionitrile (VIII) had bp 52° (736 mm), n^{26}D 1.3080.

Anal. Calcd for $C_5H_3F_4N$: C, 39.23; H, 1.97; F, 49.65; N, 9.15. Found: C, 39.5; H, 1.94; F, 50.7; N, 8.89.

2,4-Bis[2-(vinyl)perfluoroethyl]-6-(perfluoromethyl)-1,3,5-triazine (IX).—To a stirred solution of 162 g (1.06 mol) of 3-(vinyl)perfluoropropionitrile (VIII) and 250 ml of dry methylene chloride was added 9.4 g (0.55 mol) of dry ammonia under a Dry Ice cooled condenser. The reaction mixture was continuously stirred for 36 hr at room temperature (first 10–15 hr under a Dry Ice cooled condenser). The reaction mixture was then added slowly to a stirred solution of 290 g (1.38 mol) of trifluoroacetic anhydride in 400 ml of dry methylene chloride at 0°. After stirring an additional 18 hr at room temperature, the reaction mixture was added to about 1000 ml of ice-cold water. The methylene chloride layer was separated, washed twice with water, and dried over Drierite. A fractional distillation of the methylene chloride solution yielded, after forecuts, 160 g (72.8% yield) of gas chromatographically pure IX, bp 110–111° (22 mm), n^{25}D 1.3785.

Anal. Calcd for $C_{12}H_6F_{11}N_3$: C, 35.92; H, 1.51; F, 52.10; mol wt, 401. Found: C, 36.0; H, 1.46; F, 53.0; mol wt, 401.

The infrared spectrum (CCl_4) showed a strong band at *ca.* 1550 cm^{-1} (characteristic of triazine) and absorption at *ca.* 1650 cm^{-1} (C=C). The ^{19}F resonance spectrum (neat) consisted of signals centered at δ +72.2 (3 F), +113.5 (4 F), and +117.5 ppm (4 F). The proton resonance spectrum also confirmed the presence of the vinyl group.

Addition of (3,3,3-Trifluoropropyl)methylchlorosilane (X) to the Divinyltriazine IX.—To a stirred mixture of 90 g (0.22 mol) of IX and 157 g (0.89 mol) of X was added 4.2 ml of a 0.1 *M* solution of chloroplatinic acid in isopropyl alcohol. The mixture was then heated under reflux while stirring. At the end of 16 hr of refluxing, an additional 2.5 ml of the chloroplatinic acid solution was introduced, and the mixture was continuously heated under reflux for a total of 87 hr. The excess X and volatile materials were stripped off *in vacuo* at room temperature, and the resulting crude product (148 g) was purified using a molecular still to yield 58 g (34.5% yield) of slightly impure $ClSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3C_3N_3)CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$ (XI), $n^{25}{}_{\mathrm{D}}$ 1.4050. The data for the fractionation are shown in Table III. A large amount of diadduct XI is believed to have been lost during the six passes.

TABLE III

PURIFICATION OF XI BY A MOLECULAR STILL[a]

Run	Temp, °C	Pressure, μ	Time, hr	Distillate, g	Residue, g
1	25–35	25–90	1.5	2	137
2	50–60	30–50	1.5	23	106
3	65–70	20–30	1.0	15	82
4	75–80	70–75	1.0	3	75
5	75–80	20–25	1.3	5	63
6	120–130	~20	4.4	58 (XI)	2

[a] ASCO Model 50-2 Rota-Film molecular still was employed.

Anal. Calcd for $C_{20}H_{22}Cl_2F_{17}N_3Si_2$: C, 31.84; H, 2.93; Cl, 9.40. Found: C, 32.2; H, 2.96; Cl, 8.12.

The ^{19}F resonance spectrum was consistent with the assigned structure, XI. The spectrum ($CDCl_3$) showed a triplet centered at δ +69.2 (6 F), a singlet at +72.2 (3 F), a triplet centered at +114.9 (4 F), and a broad unresolved signal centered at +117.7 ppm (4 F). The infrared spectrum (CCl_4) showed a strong band at *ca.* 1565 cm^{-1} (characteristic of triazine) and a weak band in the $\equiv$SiOH region, indicating the presence of the hydrolysate of XI. The proton resonance spectrum (CCl_4) was in agreement with the assigned structure, XI, with the exception that the spectrum indicated the presence of $(CH_3)(OH)Si<$.

Hydrolysis of Diadduct XI.—To a saturated aqueous sodium bicarbonate solution (120 ml) was added 14 g of XI in 70 ml of ether while stirring at room temperature. After stirring for 1.5 hr, the ether solution was separated, washed with a 5% aqueous sodium chloride solution, and dried over Drierite. After evaporation of the ether *in vacuo* at room temperature, the resulting viscous liquid product was placed under vacuum (*ca.* 0.1 mm) at room temperature for 24 hr to yield 13 g of fairly pure $HOSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3C_3N_3)CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiOH$ (XII).

Anal. Calcd for $C_{20}H_{24}F_{17}N_3Si_2O_2$: OH, 4.74. Found: OH, 4.59.

The ^{19}F resonance spectrum ($CDCl_3$) was comprised of a triplet centered at δ +69.4 (6 F), a singlet at +72.1 (3 F), a triplet centered at +115.1 (4 F), and a broad unresolved signal centered at +117.5 ppm (4 F). The proton resonance spectrum (CCl_4) was in agreement with the assigned structure, XII, but showed that more than a trace amount of ether was present. The molecular weight by vapor phase osmometry was found to be 795 (calcd 717). The infrared spectrum (CCl_4) showed a strong band at *ca.* 1565 cm^{-1} (characteristic of triazine) and bands in the $\equiv$SiOH region (*ca.* 3400 and 3700 cm^{-1}). The above analytical and spectral data suggest that diol XII was fairly pure, although the molecular weight determination suggested that some condensation might have occurred. Diol XII prepared in this manner was used for polymerization without further purification.

Polymerization of Diol XII.—A mixture of 19 g of XII and 5 drops of tetramethylguanidine–trifluoroacetic acid (1:3) solution was heated, while mixing by rotation, at 70–75° *in vacuo* (*ca.* 15 mm) for 27 hr, at 80° under *ca.* 0.3-mm pressure for 16 hr, and at 100° under *ca.* 0.2-mm pressure for 45 min. The resulting polymer, 17.5 g, was a rubbery gum (XIII) which was soluble in isopropyl acetate.

Anal. Calcd for $(-C_{20}H_{22}F_{17}N_3Si_2O-)_n$: C, 34.34; H, 3.17. Found: C, 34.8; H, 3.47.

The infrared spectrum (film) was qualitatively in agreement with the assigned polymer structure, $[-Si(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3C_3N_3)CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiO-]_x$ (XIII).

Registry No.—IIa, 18321-45-4; IIb, 18321-46-5; IIIa, 18321-47-6; IVa, 18339-04-3; IVb, 18320-81-5; VI, 18320-82-6; VII, 18320-83-7; VIII, 18320-84-8; IX, 18320-85-9; XI, 18320-86-0; XII, 18320-87-1; ethyl 2,2,3,3-tetrafluoropentanoate, 18320-88-2; 3-(vinyl)perfluoropropionamide, 18320-89-3; 5-(vinyl)perfluoropentanamide, 18320-90-6.

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Mass Spectra of Bis-1,3-dithiolanes and Bis-1,3-dithianes. Mechanism of the Ring-Cleavage Reactions of Malonaldehyde Bisthioacetals and Structures of Glyoxal Bisthioacetals

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α cleavage and two ring-cleavage reactions constitute the major fragmentation pathways of malonaldehyde bisthioacetals. The mechanisms of the ring-cleavage reactions have been elucidated and one of them has been shown to proceed with McLafferty rearrangement of the angular hydrogen of the distal ring to the departing chain of the fragmenting ring. α cleavage is the only major fragmentation reaction of glyoxal bisthioacetals and biacetyl bisthioketals, establishing the pendant rather than the fused bicyclic systems as the correct structures of these compounds.

We have recently carried out an investigation of the electron-impact-induced fragmentation reactions of bis-1,3-dithiolanylmethanes and bis-1,3-dithianylmethanes.[1] The major fragmentation reactions observed in this system were α cleavage and two ring-cleavage reactions, designated as type I and type II, in which the expelled neutral fragment contained one and two sulfur atoms, respectively.

Both ring-cleavage reactions proceed with the simultaneous loss of an angular hydrogen atom and both reactions were completely blocked when the two angular

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[1] R. H. Shapiro, T. E. McEntee, and D. L. Coffen, *Tetrahedron*, **24**, 2809 (1968).