Diethyl 2-[(diphenylmethylene)amino]-2-[(trimethylsilyl)ethynyl]malonate (11a): oil; IR (neat) 2170 (C≡C), 1756 (C=O), 1627 (C=N) cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.10 (9 H, s, Si(CH$_3$)$_3$), 1.24 (6 H, t, J = 7.1 Hz, 2 CH$_2$CH_3), 4.15 and 4.16 (4 H, two q, J = 7.0 and 7.1 Hz, 2 OCH_2CH$_3$), 7.30–7.60 (m, C$_6$H$_5$); ^{13}C NMR (270 MHz, CDCl$_3$) δ 0.48 (SiCH$_3$), 13.7 (CH$_2$CH$_3$), 62.47 (OCH$_2$CH$_3$), 70.05, 93.50, and 98.87 (C≡C), 127.45, 127.88, 128.98, 129.14, 129.30 and 130.72 (C$_6$H$_5$), 136.14 and 140.41 (NC and Ph$_2$C), 166.82 and 172.65 (CO$_2$); MS (M$^+$ – CO$_2$Et) m/z 362.1498 (calcd for C$_{22}$H$_{24}$NO$_2$Si 362.1570). Anal. Calcd for C$_{25}$H$_{29}$NO$_4$Si: C, 68.9; H, 6.72; N, 3.22. Found: C, 69.21; H, 6.78; N, 2.93.

Diethyl 2-[(diphenylmethylene)amino]-2-(phenylethynyl)malonate (11b): light yellow powder; mp 92 °C (from hexane); IR (film) 2236 (C≡C), 1750 (C=O), 1627 (C=N) cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.29 (6 H, t, J = 7.1 Hz, 2 CH$_2$CH_3), 4.23 (4 H, q, J = 7.1 Hz, 2 OCH_2CH$_3$), 7.32–7.41 (m, C$_6$H$_5$); ^{13}C NMR (270 MHz, CDCl$_3$) δ 13.84 (CH$_2$CH$_3$), 62.66 (OCH$_2$CH$_3$), 83.97 and 88.19 (C≡C), 127.32, 127.64, 127.96, 128.49, 128.89, 128.97, 129.32, 130.80, and 131.84 (C$_6$H$_5$), 136.33 and 140.36 (NC and Ph$_2$C), 167.01 and 172.92 (CO$_2$); MS M$^+$ m/z 439.1744 (calcd for C$_{28}$H$_{25}$NO$_4$ 439.1777), (M$^+$ – CO$_2$Et) 366.1537 (calcd for C$_{25}$H$_{20}$NO$_2$ 366.1494). Anal. Calcd for C$_{28}$H$_{25}$NO$_4$: C, 76.50; H, 5.74; N, 3.19. Found: C, 76.48; H, 5.68; N, 3.26.

Diethyl 2-[(diphenylmethylene)amino]-2-*n*-hexynylmalonate (11c): oil; IR (neat) 2244 (C≡C), 1748 (C=O), 1629 (C=N) cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.86 (t, J = 6.9 Hz, CH$_3$), 1.25 (t, J = 7.1 Hz, 2 CH$_2$CH_3), 1.34 (m, 2 CH$_2$), 2.06 (t, J = 6.9 Hz, CH$_2$), 4.17 (q, J = 7.1 Hz, 2 OCH_2CH$_3$), 7.27–7.82 (m, C$_6$H$_5$); ^{13}C NMR (270 MHz, CDCl$_3$) δ 13.53 (CH$_3$), 13.84 (CH$_3$), 18.69 (CH$_2$), 21.83 (CH$_2$), 30.08 (C≡CCH$_2$), 62.45 (OCH$_2$CH$_3$), 76.57 and 89.61 (C≡C), 127.45, 127.90, 128.27, 128.87, 128.95,

129.33, 130.01, 130.64 and 132.35 (C$_6$H$_5$), 136.50 and 140.60 (NC and Ph$_2$C), 164.41 and 172.13 (CO$_2$). Anal. Calcd for C$_{26}$H$_{29}$NO$_4$: C, 74.43; H, 6.97; N, 3.34. Found: C, 74.15; H, 6.82; N, 3.27.

Diethyl 2-[(diphenylmethylene)amino]-2-(3,3-dimethyl-1-butynyl)malonate (11d): white powder; mp 77 °C (from hexane); IR (film) 2245 (C≡C), 1746 (C=O), 1629 (C=N) cm^{-1}; ^{1}H NMR (80 MHz, CDCl$_3$) δ 1.11 (9 H, s, C(CH$_3$)$_3$), 1.23 (6 H, J = 7.2 Hz, 2 CH$_2$CH_3), 4.17 (4 H, br q, J = 7.2 Hz, 2 OCH_2CH$_3$), 7.35, 7.58 (10 H, m, C$_6$H$_5$); ^{1}H NMR (270 MHz, 325 K, CD$_3$Br) δ 1.52 (9 H, s, C(CH$_3$)$_3$), 1.69 and 1.70 (6 H, 2 t, J = 6.9 and 7.1 Hz, 2 CH$_2$CH_3), 4.56 and 4.57 (4 H, 2 q, J = 6.9 and 7.1 Hz, 2 OCH_2CH$_3$), 7.80–9.10 (m, C$_6$H$_5$); ^{1}H NMR (270 MHz, 383 K, CD$_3$Br) δ 1.51 (9 H, s, C(CH$_3$)$_3$), 1.68 (6 H, t, J = 7.1 Hz, 2 CH$_2$CH_3), 4.57 (4 H, q, J = 7.1 Hz, 2 OCH_2CH$_3$), 7.80–9.10 (m, C$_6$H$_5$); ^{13}C NMR (270 MHz CDCl$_3$) δ 13.8 (CH$_2$CH$_3$), 27.5 (C(CH$_3$)$_3$), 30.3 (C(CH$_3$)$_3$), 62.28 (OCH$_2$CH$_3$), 73.8 and 96.6 (C≡C), 127.4, 127.5, 127.8, 128.0, 128.6, 128.9, 129.3 and 130.6 (C$_6$H$_5$), 136.5 and 140.7 (NC and Ph$_2$C), 167.5 and 172.2 (CO$_2$); MS (M$^+$ – CO$_2$Et) m/z 346.1773 (calcd for C$_{23}$H$_{24}$NO$_2$ 346.1801). Anal. Calcd for C$_{26}$H$_{29}$NO$_4$: C, 74.43; H, 6.97; N, 3.34. Found: C, 74.25; H, 6.84; N, 3.53.

Supplementary Material Available: Carbon and proton NMR spectra of compound 11a and 11c (4 pages). Ordering information is given on any current masthead page.

Perhalodioxins and Perhalodihydrodioxins[†]

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Two perhalo-1,4-dioxins, representatives of a previously unknown class of compounds, have been synthesized and shown to exhibit unusual reactivity. In particular, reaction with oxygen is spontaneous and exothermic, and radical-catalyzed homopolymerization will proceed through a fluorinated double bond. Representatives of the perhalo-2,3-dihydro-1,4-dioxin class have also been prepared and found to have reactivity in general intermediate to that of the perhalodioxoles and acyclic trifluorovinyl ethers. Computational studies of the two systems established that introduction of the first double bond raises the energy substantially, while the second double bond results in a near-planar ring with dramatically increased energy content.

Introduction

The effectiveness with which *F*-alkyl trifluorovinyl ethers copolymerize with monomers such as tetrafluoroethylene is well known,[1] but no reports have appeared describing radical-catalyzed homopolymerization of such trifluorovinyl ethers under commonly used pressures. In contrast, *F*-1,3-dioxoles 1 homopolymerize with extraordinary ease.[2] This difference in reactivity may reasonably be ascribed to minimization of steric constraints and/or to the presence of ring strain in the dioxoles 1, raising the question of whether or not the related six-membered vinylene diethers 2 and 3 would exhibit similar high reactivity.

1, X,Y = F or CF$_3$ 2   3
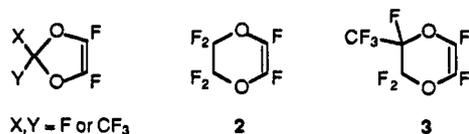
F-2,3-Dihydro-1,4-dioxin (2) has already been obtained by Coe, Dodman, and Tatlow[3] by dehydrofluorination of

Scheme I[a]
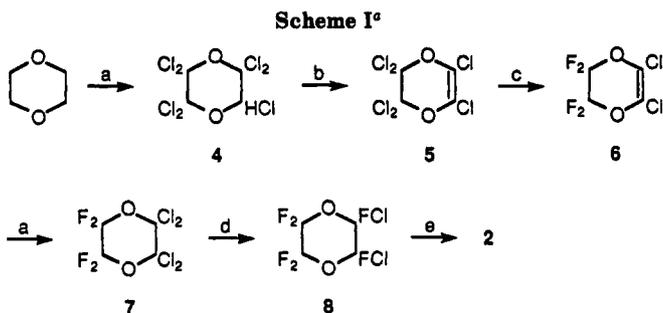
[a] (a) Cl$_2$; (b) NaOH/CH$_3$OH; (c) SbF$_3$/SbCl$_5$/100 °C; (d) SbF$_3$/SbCl$_5$/reflux; (e) Zn + DMF.

F-2*H*-1,4-dioxane, itself one of many products formed during partial fluorination of 1,4-dioxane. The low yields

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(1) Cf.: "*Fluorocarbon and Related Chemistry*;" Banks, R. E., Barlow, M. G., Eds.; The Chemical Society: London, 1976; Vol. 3, pp 280–281.

(2) (a) Polymer Preprints, Vol. 31, No. 1, April 1990, presented at the 199th National ACS Meeting, Boston, MA, by P. R. Resnick. (b) Resnick, P. R. U.S. Patent 3,978,030 (1976). (c) Squire, E. N. U.S. Patent 4,399,264 (1983).

[†] Contribution No. 5649.

Scheme II[a]
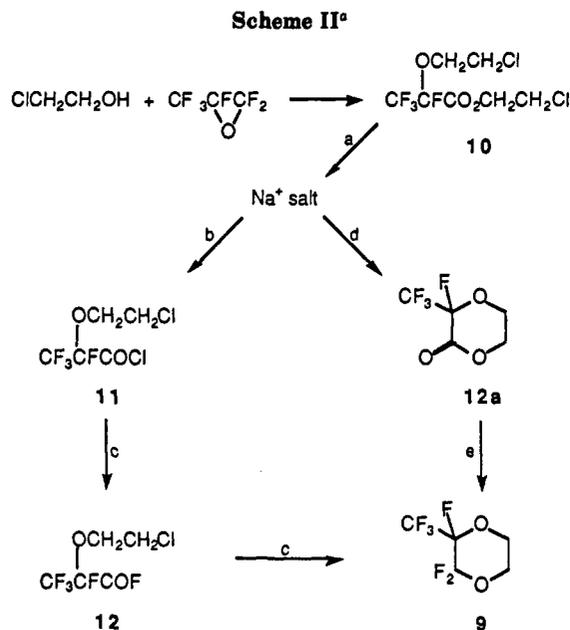
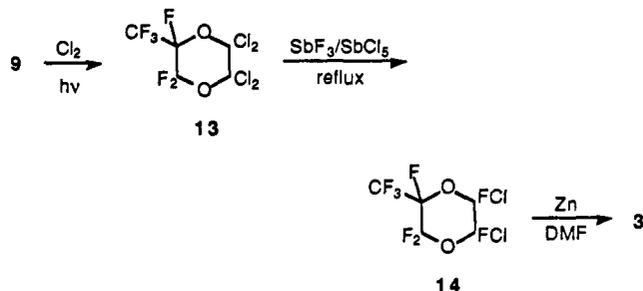[a] (a) NaOH; (b) SOCl₂/DMF; (c) KF; (d) 185 °C; (e) SF₄/HF/ 160 °C.

inherent in this sequence led us to consider other syntheses of **2** and **3**.

***F*-2,3-Dihydro-1,4-dioxin.** Our route to dihydrodioxin **2** involved perfluorination of one side of the ring in the first stage followed by introduction of the difluorovinylene unit in the second stage. Heptachloro-1,4-dioxane (**4**) was readily obtained in quantity from 1,4-dioxane and chlorine,[4] and dehydrochlorination of **4** with base rapidly gave hexachloro-2,3-dihydro-1,4-dioxin (**5**). Treatment of **5** with SbF₃/SbCl₅ reagent at elevated temperature served to introduce four fluorine atoms to give dihydrodioxin **6**. Then chlorination of **6** to form **7**, partial fluorination of **7** to give difluoro compound **8**, and dechlorination of **8** with zinc all proceeded normally to afford pure monomer **2**. Scheme I depicts this synthesis.

***F*-2-Methyl-2,3-dihydro-1,4-dioxin.** A variant of the method used by Schwertfeger and Siegemund[5a] served to prepare dioxane **9**, an intermediate having one side in the desired perfluoro stage. In the older method, trifluoropyruvyl fluoride was condensed with ethylene glycol dimesylate and KF to give **9** in 4% yield. Alternatively, chlorination of an ethoxy side chain was used to form the 2-chloroethoxy substituent in **11**, albeit with very poor selectivity.[5b] As indicated in Scheme II, these difficulties with poor yield were circumvented by reacting 2-chloroethanol and hexafluoropropene epoxide to give chloroethoxy derivative **10**. Conversion of **10** to acid chloride **11**, and then ring closure to dioxane **9** via acid fluoride **12** proceeded normally. An alternate route to **9**, also depicted in Scheme II, involved heating the sodium salt of **10** to form lactone **12a** followed by reaction with SF₄/HF.

Photochemical chlorination of dioxane **9** cleanly gave tetrachloro derivative **13**, which was converted by the usual fluorination–dechlorination reactions to *F*-2-methyl-2,3-dihydro-1,4-dioxin (**3**).

Polymers from Dihydrodioxins 2 and 3. Polymerizations were carried out under conditions similar to those under which dioxoles **1** rapidly form amorphous homo-


polymers with T_g in the range 175–330 °C. The neat monomers held at 40–45 °C under nitrogen were treated intermittently with small amounts of *F*-propionyl peroxide catalyst while viscosity slowly increased over a period of days. Workup afforded in both cases about 30% conversions to amorphous solid homopolymer along with recovered monomer. DSC measurements indicated glass transition temperatures of 110 °C (polymer of **2**) and 150 °C (polymer of **3**). The level of reactivity exhibited by these monomers is clearly much greater than that of the acyclic trifluorovinyl ethers since homopolymerization does occur, but lower than that of dioxoles **1**, since the latter polymerize much more rapidly. Furthermore, the observed glass transitions are well above those of many fluoro polymers, yet not as high as those from the *F*-dioxole class of monomers.

Perhalodioxin Synthesis. Dehydrochlorination of a very impure sample of heptachloro–1,4-dioxane produced crude **5**, which became exceedingly hot when filtered to remove drying agent. This phenomenon was shown to arise from the reaction of oxygen with an unexpected byproduct, **15**. To the extent that underchlorination produced hexachloro–1,4-dioxane isomers with hydrogen atoms distributed one on each side of the ring, dehydrochlorination led to tetrachloro-1,4-dioxin (**15**). Both **15** and **5** are, surprisingly, new compounds. Evidence was also obtained for the presence of 2,2,3,3,5-pentachloro-2,3-dihydro-1,4-dioxin (**16**). Fractionation of the mixture under a nitrogen atmosphere easily afforded **15** of 90–95% purity.
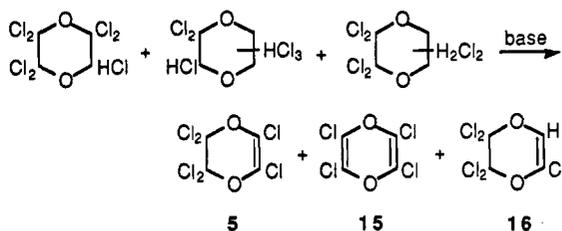
Related dioxin **17** was also prepared, starting from dihydrodioxin **5**. Partial fluorination at 55 °C gave **18** in high yield. Then dechlorination of **18** with zinc in dimethylformamide gave 2,3-dichloro-5,6-difluoro-1,4-dioxin (**17**) as a distillate contamination with dimethylformamide. This mixture could be stirred in air without noticeable reaction, but reaction of **17** with oxygen proved to be even more vigorous than that of **15** after the dimethylformamide had been removed by a water wash.
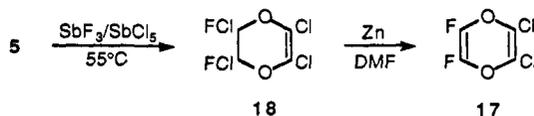
Reactions of the Perhalodioxins. Since **15** was exposed to a larger excess hydroxide/methoxide during synthesis, the halodioxin system is apparently not sensitive to attack by base. The reaction with oxygen, however, is spontaneous and exothermic. A sample of **15** stirred in

(3) Coe, P. L.; Dodman, P.; Tatlow, J. C. *J. Fluorine Chem.* **1975**, *6*, 115.
(4) Luedicke, M.; Stumpf, W. *Naturwiss.* **1953**, *40*, 363.
(5) (a) Schwertfeger, W.; Siegemund, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 126. (b) U.S. Patent 4,343,742 (1982).

air until the reaction subsided and then allowed to stand open gave hydrated oxalic acid as the residue. When exposed to oxygen in a controlled manner, **15** absorbed somewhat over 0.5 mol of oxygen to form one major product, epoxide **19**, in 60–70% yield along with phosgene, oxalyl chloride, and several unidentified minor products.
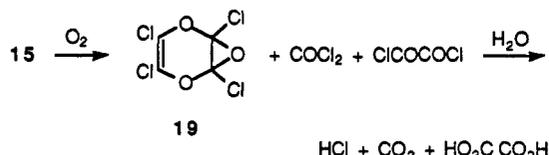
The formation of **19** along with products of C=C cleavage from direct reaction with oxygen is reminiscent of the behavior of many fluoro olefins. Tetrafluoroethylene, hexafluoropropylene, and chlorotrifluoroethylene, for example, all react with oxygen to form epoxides and acyl fluorides.[6a] Such reactions have been shown to proceed through oxygen- and carbon-based free-radical intermediates,[6b] and a similar chain mechanism would explain the products derived from dioxin **15** and oxygen. The reproducibly spontaneous nature of the latter reaction, however, indicates a facile initiation step which we propose arises because of unusually weak π bonding (vide infra).

The thermal stability of **15** up to about 150 °C is good, and attempts to cycloadd either maleic anhydride or tetrafluoroethylene were carried out there. Little interaction occurred in either case, and **15** was largely recovered. Very slow cycloaddition of dimethylbutadiene to **15** did occur to produce a low yield of **20** in competition with polymerization of the diene.
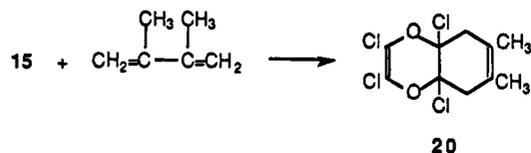
As mentioned above, purified difluorodichlorodioxin **17** reacts vigorously with oxygen. The spectrum of products identified by GC/MS indicates that both double bonds of **17** were subject to attack, but that some selectivity for oxidation of the fluorinated double bond was present. The formation of oligomeric polyethers is particularly revealing, since fluoro epoxides are known to polymerize,[7] and epoxide **21** would be expected to do the same.

+ FCO₂CCl₂COF + ClCO₂CFClCOF + low oligomers
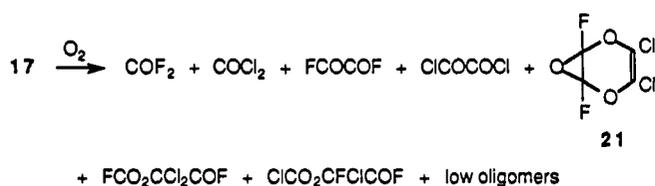
The high reactivity of **17** with oxygen and the tendency to form polyepoxide raised the question as to whether an active *F*-dihydrodioxin such as **3** would add oxygen at 25 °C. Indeed, a slow but steady reaction of **3** with oxygen did occur with continuously increasing viscosity. Nearly 0.5 mol of oxygen had been absorbed before reaction slowed after 8 days. Further exposure to oxygen caused a small general increase in degree of oligomerization.

Table I. Molecular Structures

molecule[a]	$r(C=C),$[b] Å	$r(C—O),$[c] Å	$r(C—O),$[c] Å	$\tau(C—O),$[d] deg
C₄O₂H₄	1.318	1.369	1.369	0
C₄O₂F₄	1.306	1.356	1.356	12
C₄O₂Cl₄	1.312	1.364	1.364	30
C₄O₂H₂F₂ (2,5)	1.313	1.334 (F)	1.388 (H)	0
C₄O₂H₂F₂ (2,6)	1.311	1.353 (F)	1.371 (H)	12
C₄O₂H₂F₂ (2,3)	1.307 (F), 1.317 (H)	1.351 (F)	1.374 (H)	0
C₄O₂Cl₂F₂ (2,5)	1.309	1.344 (F)	1.374 (Cl)	20, 21
C₄O₂Cl₂F₂ (2,6)	1.309	1.353 (F)	1.367 (Cl)	20, 23
C₄O₂Cl₂F₂ (2,3)	1.304 (F), 1.315 (Cl)	1.354 (F)	1.366 (Cl)	24, 24

[a] Fluorine positions given in parentheses. [b] Labels in parentheses for unique double bonds. [c] Labels in parentheses denote other substituent attached to carbon. [d] Torsion angle in degrees about C—O bond. If more than one value is given, the first corresponds to fluorine substitution on the carbon.

GC/MS analysis strongly supported the product structures shown below.
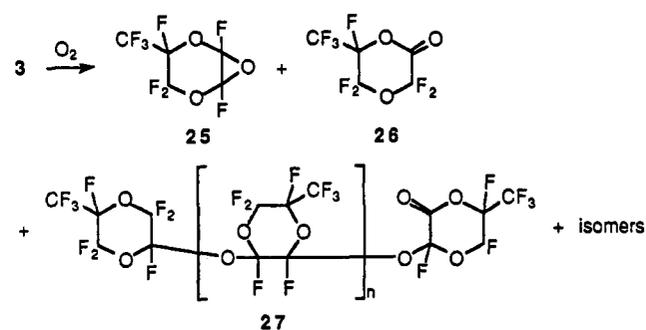
As we have seen, **3** is capable of adding carbon radicals and can participate in free-radical-mediated homopolymerization. If dioxin **17** is hyperreactive toward fluoroalkyl radicals as well as toward oxygen, facile homopolymerization might occur. In fact, polymerization of **17** proceeded only slowly under conditions similar to those for polymerization of **3**. The polymerization appeared to proceed selectively through the fluorinated double bond to give the polymer structure shown, although the level of selectivity is unknown due to the very low intensity of the IR absorption for the cyclic difluorovinylene diether unit.
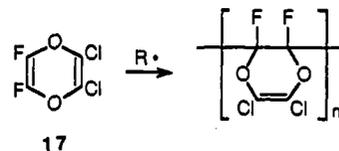
Computational Results

In order to provide better insight into the molecular electronic structure governing the behavior of these molecules, ab initio molecular orbital calculations using an extended basis set have been performed. The calculations[8] were done with the GRADSCF program system[9] on CRAY computers. The basis set is of double ζ quality augmented by polarization functions on the C and O.[10] Such a basis set has been shown to give good structures and reasonable energetics for a wide range of fluorocarbons[11] yet is still

(6) (a) Chapter by Tarrant, P.; Allison, C. G.; Barthold, K. P. In *Fluorine Chemistry Reviews*; Tarrant, P., Ed.; Marcel Dekker: New York, NY, 1971; Vol. 5, pp 105–108. (b) Faucitano, A.; Buttafava, A.; Martinotti, E.; Marchionni, G.; Staccione, A.; De Pasquale, R. J., Abstracts of the Ninth ACS Winter Fluorine Conference, Jan. 29–Feb. 3, 1989, St. Petersburg, FL, p 26.

(7) Reference 6a, pp 96–101.

(8) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab. Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(9) GRADSCF is an ab initio program system designed and written by A. Komornicki at Polyatomics Research.

(10) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977, Chapter 1.

Table II. Total Energies (au)

molecule	E(SCF)	E(MP-2)
1,4-dioxin	−303.502282	−304.327846
2,3-difluoro	−501.226475	−502.260237
2,5-difluoro	−501.233412	−502.267241
2,6-difluoro	−501.230280	−502.265047
tetrafluoro	−698.941622	−700.184926
2,3-difluoro, 5,6-dichloro	−1418.936832	−1420.072989
2,5-difluoro, 3,6-dichloro	−1418.940698	−1420.075287
2,6-difluoro, 3,5-dichloro	−1418.940180	−1420.075113
tetrachloro	−2138.930832	−2139.961158
cis-CHF=CHF	−275.771009	−276.226397
C_2F_4	−473.492467	−474.159363
cis-CHCl=CHCl	−995.775211	−996.114123
cis-CFCl=CFCl	−1193.483032	−1194.037874
C_2Cl_4	−1913.480348	−1914.533999
C_2H_4	−78.042712	−78.288232
C_2H_6	−79.239228	−79.497952
CF_2HCF_2H	−474.732977	−475.404045
1,4-dioxane	−305.887488	−306.733562
1,4-$C_4O_2H_6$	−304.699778	−305.537726
1,4-$C_4O_2F_6$	−897.920791	−899.383931
1,4-$C_4O_2F_8$	−1096.902172	−1098.580673

Table III. Inversion Barriers (kcal/mol)

compound	SCF	MP-2	$i\nu^a$
tetrafluoro	0.04	0.41	17
2,3-difluoro, 5,6-dichloro	0.41	1.92	51
2,5-difluoro, 3,6-dichloro	0.23	1.41	38
2,6-difluoro, 3,5-dichloro	0.26	1.52	44
tetrachloro	1.01	3.25	52

^{a} Imaginary frequency in cm^{-1} for the planar structure.

of a reasonable size for the systems under consideration here. The geometries were optimized using gradient techniques[12] and force fields[13] were determined analytically. Correlation corrections were done at the MP-2 level[14] at the optimized SCF geometry for the valence electrons.

A summary of important molecular parameters for a set of 1,4-dioxins is given in Table I. Total energies are given in Table II. We comapre the halogenated structures to the model hydrocarbon, $C_4O_2H_4$. The parent hydrocarbon is planar with a C=C bond distance 0.004 Å shorter than the calculated value for vinyl alcohol and a C—O distance that is 0.014 Å longer than the value in vinyl alcohol.[15]

As expected, halogenation leads to a decrease in the C=C bond length. Addition of two fluorines can be done in three ways. Addition of one F per double bond leads to a decrease in the C=C bond of 0.005–0.007 Å, consistent with what is observed in the fluoroethylenes.[11a] Addition of two fluorines to a double bond leads to a decrease of 0.011 Å. The comparable shortenings in the fluoroethylenes are 0.011 and 0.013 Å.[11a] The C—O bond adjacent to the C—F bond shortens in these compounds by

Table IV. Isomerization Energies (kcal/mol)^a for Difluoro-1,4-dioxins

compound	SCF	MP-2
2,3-difluoro	4.4	4.4
2,5-difluoro	0.0	0.0
2,6-difluoro	2.0	1.4
2,3-difluoro, 5,6-dichloro	2.6	2.0
2,5-difluoro, 3,6-dichloro	0.0	0.0
2,6-difluoro, 3,5-dichloro	0.3	0.2

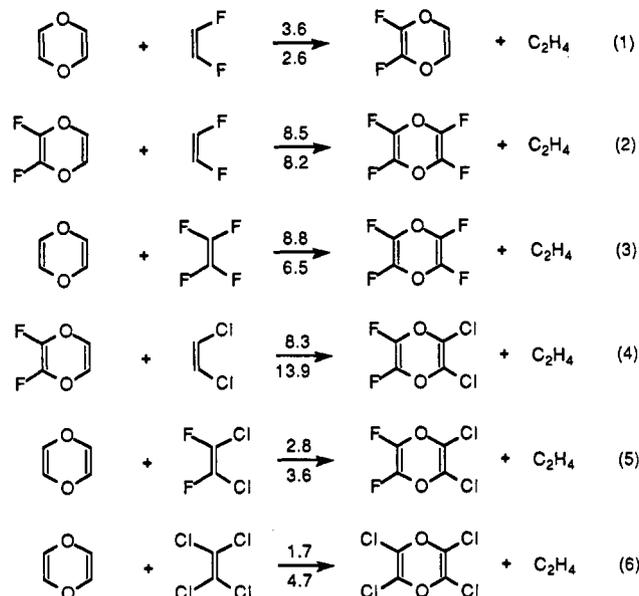^{a} The most stable isomer has zero energy.

Figure 1. Reaction energies ΔE (kcal/mol) for halogenated 1,4-dioxins. (The upper number is the MP-2 value and the lower number is the SCF value.)

as much as 0.035 Å and the C—O bond adjacent to a C—H bond lengthens by as much as 0.019 Å. The shortening of the C—O bond adjacent to the C—F bond is consistent with the result found in the fluoroethylenes[11a] where addition of fluorines leads to a shortening of the C—F bonds. Since O is also quite electronegative, it follows the same trend of a decrease in bond distance with increasing fluorination. The difluoro isomers are planar.

The perfluorinated compounds follows the same structural features as discussed above. It is, however, nonplanar with torsions about the C—O bonds of 12° and an inversion barrier of 0.04 kcal/mol at the SCF level and 0.41 kcal/mol at the MP-2 level (Table III). The imaginary frequency at the planar structure is small as expected from the above energetic differences, 17i cm^{-1}.

Substitution of chlorine for fluorine leads to a significant increase in bending. Substitution of two chlorines in tetrafluorodioxin leads again to three isomers, of which 17 is one. The torsions about the C—O bonds range from 20 to 24°. The inversion barriers are higher than found in the simple fluorinated systems with values between 1.4 and 1.9 kcal/mol at the MP-2 level. The bond distances are similar to those found for the tetrafluoro compound with chlorine substitution for hydrogen leading to less of a shortening of the C=C bond than substitution of fluorine. The C—O bonds adjacent to a fluorine are shorter than those adjacent to chlorine.

The largest inversion barrier is found for the tetrachloro compound with a barrier of 3.25 kcal/mol at the MP-2 level. The C=C and C—O bond shortening is not as pronounced as in the tetrafluoro compound.

The relative energetics of the difluoro and difluoro, dichloro isomers are given in Table IV. The most stable

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(12) (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595. (b) McIver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 202. (c) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153.

(13) (a) King, H. F.; Komornicki, A. *J. Chem. Phys.* **1986**, *84*, 5465. (b) King, H. F.; Komornicki, A. In *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jørgenson, P., Simons, J., Eds.; NATO ASI Series C, Vol. 166, D. Reidel: Dordrecht, 1986; p 207.

(14) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

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Table V. Calculated Heats of Formation (kcal/mol)

compound	ΔH_f°	compound	ΔH_f°
1,4-dioxin	−19.8	2,3-difluoro, 5,6-dichloro	−104.8
2,3-difluoro	−99.2	2,5-difluoro, 3,6-dichloro	−106.8
2,5-difluoro	−103.2	2,6-difluoro, 3,5-dichloro	−106.6
2,6-difluoro	−102.2	tetrachloro	−33.2
tetrafluoro	−177.3		

isomer in each case is the one with 2,5 substitution, i.e., the one with the fluorines separated by the largest amount. The least stable form is the one with two fluorines on the same double bond. The isomeric energy differences are smaller in the chlorinated isomers than in the ones with hydrogen.

There are a number of ways of characterizing the reactivity of a molecular system including relative energetics, charge densities, and orbital energetics. We first focus on the stability of the double bond in these systems by examining the isodesmic reactions given in Figure 1. The isodesmic reactions are all calculated with the DZ + Dc,o basis set and values are given at the SCF and MP-2 levels. We employ the MP-2 values in our discussion although, except for reactions 4 and 6, the agreement between the SCF and MP-2 values is satisfactory. For 4 and 6, which involve dichloro- and tetrachloroethylenes, the correlation corrections are bigger, a phenomenon that we have previously observed.[15] A variety of studies have shown that the π bond strength in tetrafluoroethylene is 52 kcal/mol, less than the value in ethylene which is 64 kcal/mol.[16-19] The π bond strength in $CF_2{=}CH_2$ is 65.5 kcal/mol, slightly higher than the value in $CH_2{=}CH_2$. The π bond strength in cis-1,2-difluoroethylene can be taken as the difference in ΔH_f°'s of $CF_2{=}CH_2$ and cis-CFH=CFH which is 10.6 kcal/mol,[11a] giving a π bond strength of 55 kcal/mol. This is 8 kcal/mol below the π bond strength in $CH_2{=}CH_2$. If we account for the difference in the π bond strengths of the two ethylenes, we find that substitution of the FC–CF unit leads to a destabilization of the dioxin by 2 kcal/mol. Substitution of a second FC–CF unit leads to a destabilization of the ring π bonds by 7 kcal/mol. Substitution of a ClC–CCl unit in 2,3-difluorodioxin leads to similar destabilization of the dioxin by 10 kcal/mol. We can also compare the direct addition of the tetrahalogenated olefins to the dioxin. This leads to a destabilization of the dioxin by 21 kcal/mol for the tetrafluoro, by 17 kcal/mol for the 2,3-difluoro, 5,6-dichloro, and 13 kcal/mol for the tetrachloro.[20] Clearly, perhalogenation leads to destabilization of the dioxin in terms of the π bond strengths.

Given heat of formation of the hydrocarbon dioxin, it is possible to derive the heats of formation of the substituted dioxins from the data in Figure 1 and Table IV. The heat of formation of the 1,4-dioxin can be calculated from the following reaction whose ΔE(MP-2) is −8.6 kcal/mol, −9.8 kcal/mol corrected for zero-point energy.

$$\text{c-1,4-}C_4O_2H_8 + 2C_2H_4 \rightarrow \text{c-1,4-}C_4O_2H_4 + 2C_2H_6 \quad (7)$$
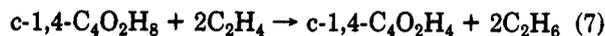
The value of ΔH_f° for 1,4-dioxin is −19.8 kcal/mol. This

Table VI. Orbital Energies

	HOMO, eV	LUMO, eV
$C_4O_2H_4$	8.24	−4.03
$C_4O_2F_4$	10.05	−3.87
$C_4O_2Cl_4$	9.88	−3.22
$C_4O_2H_2F_2$ (2.5)	9.15	−3.89
$C_4O_2H_2F_2$ (2.6)	9.19	−3.93
$C_4O_2H_2F_2$ (2.3)	9.12	−3.67
$C_4O_2Cl_2F_2$ (2.5)	9.92	−3.57
$C_4O_2Cl_2F_2$ (2.6)	9.94	−3.57
$C_4O_2Cl_2F_2$ (2.3)	9.98	−3.43
$C_4O_2F_6$	11.55	−4.18

Table VII. Mulliken Charge Distributions

molecule	$q(C)$,[a] e	$q(C)$, e	$q(O)$,[b] e	$q(X)$[d]	$q(F)$	μ,[c] D
$C_4O_2H_4$	0.01	0.01	−0.37	0.20	−	0
$C_4O_2F_4$	0.32	0.32	−0.33	−	−0.15	0.16
$C_4O_2Cl_4$	0.16	0.16	−0.28	−0.02	−	0.15
$C_4O_2H_2F_2$ (2,5)	0.41 (F)	−0.13 (H)	−0.34	0.23	−0.17	0
$C_4O_2H_2F_2$ (2,6)	0.40 (F)	−0.10 (H)	−0.34 (−0.36)	0.23	−0.17	1.94
$C_4O_2H_2F_2$ (2,3)	0.30 (F)	0.01 (H)	−0.35	0.22	−0.17	3.68
$C_4O_2Cl_2F_2$ (2,5)	0.49 (F)	−0.01 (Cl)	−0.31	−0.02	−0.15	0.08
$C_4O_2Cl_2F_2$ (2,6)	0.49 (F)	0.00 (Cl)	−0.29 (−0.33)	−0.02	−0.15	0.14
$C_4O_2Cl_2F_2$ (2,3)	0.32 (F)	0.17 (Cl)	−0.31	−0.02	−0.16	0.85

[a] Atom in parentheses is substituent on C. [b] If there are unique oxygens, the first value is for O bonded to two CF groups. [c] Dipole moment in Debye. [d] X = H or Cl.

then yields the heats of formation in Table V.

Another way to predict reactivity is to examine the frontier molecular orbitals. The HOMO and LUMO energies are given in Table VI. Addition of halogen stabilizes the HOMO even though the π bond is destabilized in these compounds. The HOMO of the parent hydrocarbon has the following form (with the oxygens at top and bottom), which is derived from the π orbitals of benzene. The LUMO is derived from an antibonding π orbital of benzene. The basic form of the orbital does not change with

substitution of halogens. The fluorine and chlorine π lone pairs come into the HOMO and LUMO in an out-of-phase interaction. There are small perturbations due to the halogen substitution such as which π bond has more density but the differences are not large.

The Mulliken charges are given in Table VII. The charge on the oxygen decreases with halogenation, with the largest decrease found for chlorine substitution. The charges on the hydrogens are positive, 0.20–0.23 e, and the carbon bonded to the hydrogen in the parent is neutral. The fluorines are uniformly negative, −0.15 to −0.17 e, and the carbons bonded to fluorine are always positive. In the difluoro compounds with a fluorine and hydrogen on the same double bond, a very polar double bond is predicted with the C(F) being very positive and the C(H) being negative. The 2,3-difluoro derivative resembles a sum of the parent dioxin and the tetrafluoro derivative. The chlorines have essentially no charge and in the two dichloro derivatives which have an F and a Cl on the same double bond, the carbons bonded to F become the most positive carbons in this set of compounds and the carbons bonded to chlorine are essentially neutral. In the 2,3-difluoro,

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(17) Wu, E.-C.; Rodgers, A. S. *J. Phys. Chem.* 1976, *98*, 6112.

(18) The value for C_2H_4 has been revised upwards by about 1 kcal/mol based on the newest heat of formation data. This has caused minor revisions in other π bond energies.

(19) Pickard, J. M.; Rodgers, A. S. *J. Phys. Chem.* 1976, *98*, 6115.

(20) From available thermodynamic data, it is possible to calculate the π bond energy in C_2Cl_4. This value is 53 kcal/mol. Data is from McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* 1982, *33*, 493. Pedley, J. B., Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.
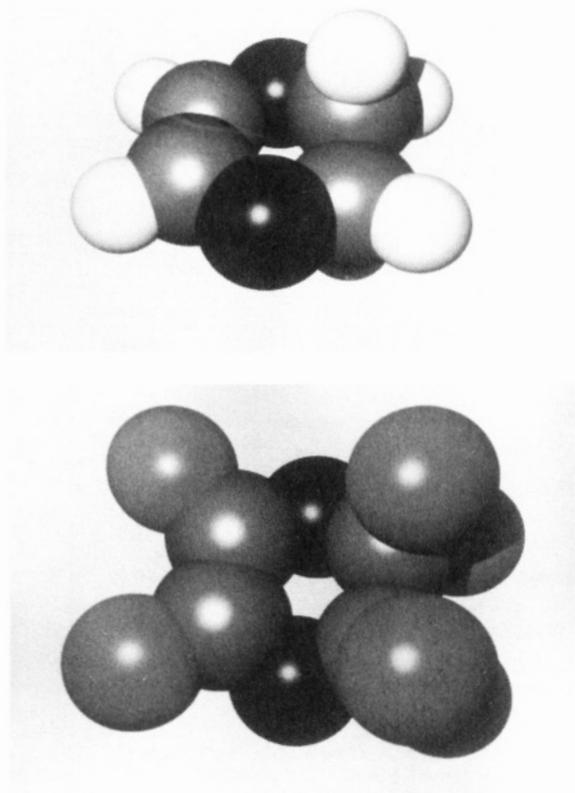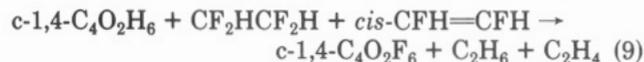
Figure 2. Geometries of the parent dihydrodioxin and the perfluoro derivative. Dark atoms are O, light atoms are H, multiply bonded gray atoms are C and singly bonded gray atoms are F. Image generated using OASIS software on a cray X-MP computer.

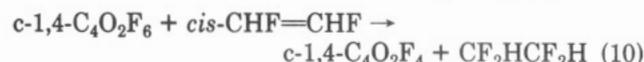5,6-dichloro derivative, the behavior observed for the 2,3-difluoro derivative is also found.

We also calculated the structure of the parent dihydrodioxin and the perfluoro derivative. The geometries are shown in Figure 2, and it is clear that both are folded. However, the hydrocarbon shows twisting about the single bond, but this is not found in the fluorocarbon which has essentially eclipsed CF_2 groups. The C=C bond distance decreases by 0.019 Å on fluorination which is similar to the values found in the dioxins. The C—O bonds to the ethylene moiety shorten by 0.007 Å, again similar to the result found in the dioxins. The heat of formation of the parent can be calculated from reaction 8, similar to reaction 7 above. The value of ΔE(MP-2) for reaction 8 is −8.7 kcal/mol, −9.1 kcal/mol when corrected for zero-point effects.

$$\text{c-1,4-C}_4\text{O}_2\text{H}_8 + \text{C}_2\text{H}_4 \rightarrow \text{c-1,4-C}_4\text{O}_2\text{H}_6 + \text{C}_2\text{H}_6 \quad (8)$$
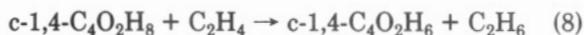
This yields a value for ΔH_f° of −51.8 kcal/mol. From the ΔE(MP-2) of −1.2 kcal/mol for the following reaction, we can calculate the value of ΔH_f° for the perfluoro derivative

$$\text{c-1,4-C}_4\text{O}_2\text{H}_6 + \text{CF}_2\text{HCF}_2\text{H} + cis\text{-CFH}=\text{CFH} \rightarrow$$
$$\text{c-1,4-C}_4\text{O}_2\text{F}_6 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 \quad (9)$$

which is −324.1 kcal/mol. A crude approximation to gain insight into the π bond energies of the *F*-dihydro-1,4-dioxin derivative can be seen in the following reactions
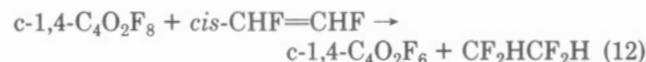
$$\text{c-1,4-C}_4\text{O}_2\text{F}_6 + cis\text{-CHF}=\text{CHF} \rightarrow$$
$$\text{c-1,4-C}_4\text{O}_2\text{F}_4 + \text{CF}_2\text{HCF}_2\text{H} \quad (10)$$

$$\text{c-1,4-C}_4\text{O}_2\text{H}_6 + \text{C}_2\text{H}_4 \rightarrow \text{c-1,4-C}_4\text{O}_2\text{H}_4 + \text{C}_2\text{H}_6 \quad (11)$$

The value for ΔE(MP-2) for reaction 10 is 13.4 kcal/mol

and for the pure hydrocarbon reaction (11), the reaction is thermoneutral (0.1 kcal/mol). The large positive value for reaction 10 suggests that the π bond in the perfluoro dihydro derivative is not very destabilized as compared to the perfluorodioxin. The HOMO of the dihydrodioxin is at 8.81 eV and the LUMO is at 5.29 eV. The HOMO is localized in the π bond. The corresponding values in the perfluoro derivative are 11.55 and 4.16 eV. Clearly fluorination has stabilized the π bond ionization potential. The LUMO is somewhat lower in energy. Comparison to the dioxins shows that the HOMO in the perfluorodihydrodioxin is stabilized with respect to the dioxin values and the LUMO is also stabilized. The charge distributions are similar to those in the dioxins.

The similarities in π bond strength and charge distribution noted above for tetrafluoroethylene and the perhalodioxins lead us to propose that the dioxin reactions reflect ready direct addition of free radicals to π-bonded carbon in the dioxins without initial electron transfer. The products first formed from reaction with oxygen are parallel to those from tetrafluoroethylene, as is the homopolymerization through a difluorinated double bond. The relatively slow dioxin propagation rate may result from low reactivity of the propagating radical end coupled with steric constraints.

Reaction 8 shows that introduction of a double bond into the hydrogen substituted system, 1,4-dioxane, is exothermic by 8.7 kcal/mol at the MP-2 level and by 5.5 kcal/mol at the SCF level. In contrast, reaction 12 with the fluorinated system shows that introduction of a double bond is destabilizing, as reaction 12 is endothermic by 12.2 kcal/mol at the SCF level and 12.0 kcal/mol at the MP-2 level.

$$\text{c-1,4-C}_4\text{O}_2\text{F}_8 + cis\text{-CHF}=\text{CHF} \rightarrow$$
$$\text{c-1,4-C}_4\text{O}_2\text{F}_6 + \text{CF}_2\text{HCF}_2\text{H} \quad (12)$$

The calculations showed further (reaction 11) that introduction of the second difluorovinylene unit to form a perhalo-1,4-dioxin again destabilized the system by about 13 kcal/mol (10.8 kcal/mol at the SCF level), significantly more than for a nonhalogenated system for which no effect of the second double bond was observed. Examination of the nature of this destabilization showed it to arise mainly from weakened π bonding relative to the nonhalogenated system, the π electrons being strongly associated with positively charged carbons. This finding correlates with the ease of radical attack on molecules **2** and **3**, as reflected in their homopolymerization and in spontaneous reaction at 25 °C with oxygen.

Experimental Section[21]

Heptachloro-1,4-dioxane (4). Thermal chlorination of 1,4-dioxane,[4] either neat or in carbon tetrachloride solution, in which the temperature did not exceed 85 °C proved superior to the light-catalyzed reaction because ring-opening products were minimized. A mixture of 264 g (3.0 mol) of 1,4-dioxane and 100 mL of CCl_4 was stirred under a −80 °C condenser and heated to 50 °C. As chlorine gas was introduced, an exothermic reaction occurred which was controlled to 50–70 °C by limiting the rate of Cl_2 addition. As the rate of reaction slowed, the temperature was raised until very slow consumption of Cl_2 occurred at 85 °C after a total of 64 h. Volatiles were distilled off under vacuum, and the residual oil, after heating to 80 °C (0.3 mm), weighed 926 g. When seeded and stored at 0 °C, the mixture deposited 516.4 g (52%) of crystalline 4. The remaining liquid, 406.4 g, was

(21) IR spectra were recorded on 20% solutions in carbon tetrachloride unless otherwise specified. NMR spectra were taken on 20% solutions in $CDCl_3$ with tetramethylsilane and trichlorofluoromethane as internal references; downfield directions were taken as positive.

indicated by GC to contain 47% (191 g, 19% yield) of **4** along with three less highly chlorinated derivatives. The total yield of **4** was thus 71%. Crude **4** had mp 48–52 °C (ref 4 reports mp 56 °C). NMR (CDCl$_3$): ^{1}H δ 6.43 (s).

Hexachloro-2,3-dihydro-1,4-dioxin (5). A solution of 60.1 g (0.183 mol) of crude water-washed **4** in 100 g of CCl$_4$ was cooled at 10–20 °C in an ice bath while a solution of 40.0 g (1.0 mol) of NaOH in 500 mL of methanol was added slowly. The mixture was stirred another 10 min at 10–20 °C and then diluted with 2 L of water. The lower layer was washed with 500 mL of water, dried over CaSO$_4$, and filtered. GC/MS showed **5** to be present in major amounts along with a small amount of **15**. Fractionation afforded 39.4 g (74%) of dihydrodioxin **5**, bp 69–71 °C (2.5 mm). IR (CCl$_4$): 1670 cm^{-1} (C=C). NMR (CDCl$_3$): ^{13}C 124.6 (=CClO) and 108.5 ppm (CCl$_2$O). Anal. Calcd for C$_4$Cl$_6$O$_2$: C, 16.41; Cl, 72.66. Found: C, 16.10; Cl, 72.96.

Reaction of crude **4** with a nearly equivalent amount of base left appreciable amounts of hydrogen-containing impurities in the product. 2,2,3,5,6-Pentachloro-2,3-dihydro-1,4-dioxin [NMR (CDCl$_3$): ^{1}H δ 6.27 (s)] and **16** [NMR (CDCl$_3$): ^{1}H δ 6.41 (s)] appeared as major impurities difficult to separate by fractionation.

Tetrachloro-1,4-dioxin (15). A crude liquid mixture composed mainly of heptachloro-1,4-dioxane and mixed hexachloro-1,4-dioxanes (ca. 2:1 ratio by GC analysis) was obtained as described above. A mixture of 500 g of the crude mixture and 1 L of methanol was stirred under N$_2$ while a solution of 170 g (4.25 mol) of NaOH in 350 mL of water was added with cooling to maintain <30 °C. After addition had been completed and the mixture stirred another 30 min, it remained basic. Water (2 L) was added, and the mixture, still under N$_2$, was stirred. The lower layer was then washed with 4 × 1 L of water and combined with the water-insoluble product from three more runs. The total crude, 1060 g, was dried over MgSO$_4$, filtered, and distilled under N$_2$ to afford 180.7 g of dioxin **15** as a pale yellow oil, bp 50–54 °C (3.5 mm), >90% pure by GC, and 652.9 g of dihydrodioxin **5**, bp 65–70 °C (3.0 mm), >99% pure by GC. For **15**, IR (neat): 1679 (w) and 1663 cm^{-1} (m) (C=C). Raman (neat): 1686 cm^{-1} (C=C). UV (isooctane): ϵ_{225} 1250 with tailing to 350 nm. NMR (CDCl$_3$): ^{13}C 127.4 ppm (s). MS: *m/e* 220, 222, 224, 226, and 228 (M$^+$); 185, 187, and 189 (M$^+$ – Cl); 157, 159, 161, and 162 (M$^+$ – COCl); 129, 131, 133, and 135 (CCl$_2$=CCl$^+$); 94, 96, and 98 (C$_2$Cl$_2^+$); 82, 84, and 86 (CCl$_2^+$); 63 and 65 (COCl$^+$); 59 and 61 (ClC$_2^+$); 47 and 49 (CCl$^+$).

2,2,3,3-Tetrafluoro-5,6-dichloro-2,3-dihydro-1,4-dioxin (6). To a stirred suspension of 448 g (2.5 mol) of SbF$_3$ in 293 g (1.0 mol) of **5** was added 10 mL of SbCl$_5$. Following an exotherm to 45 °C, the mixture was stirred at 50 °C for 1 h, 60 °C for 2 h, then after addition of 5 mL of SbCl$_5$ at 80 °C for 1 h. Another 5 mL of SbCl$_5$ was added, and the mixture was refluxed (98–93 °C) for 1 h. Then a final 5 mL of SbCl$_5$ was added, and the mixture was refluxed (93–88 °C) for 1 h. Volatile product was removed under vacuum, stirred with NaF, filtered, and distilled to give 118.4 g (52%) of **6**, bp 44–48 °C (200 mm), followed by 22.1 g (9%) of crude 2,5,6-trichloro-2,3,3-trifluoro-2,3-dihydro-1,4-dioxin, bp 72–77 °C (200 mm). For **6**, IR (CCl$_4$): 1675 (C=C), 1250–1100 (CF, C—O), 800 cm^{-1} (CCl). NMR (CDCl$_3$): ^{19}F ϕ –92.8 (s, CF$_2$O). GC/MS: *m/e* 226, 228, and 230 (M$^+$) with expected fragmentation pattern. Anal. Calcd for C$_4$Cl$_2$F$_4$O$_2$: Cl, 31.24. Found: Cl, 30.87.

2,5,6-Trichloro-2,3,3-trifluoro-2,3-dihydro-1,4-dioxin (22), 2,3,5,6-Tetrachloro-2,3-difluoro-2,3-dihydro-1,4-dioxin (18), and 2,2,3,5,6-Pentachloro-3-fluoro-2,3-dihydro-1,4-dioxin (23). A suspension of 429 g (2.4 mol) of SbF$_3$ in 352 g (1.2 mol) of **5** was stirred at 55 °C for 5 h with addition of 8 mL and then 6 mL of SbCl$_5$ catalyst. Volatile products transferred under vacuum were treated with NaF, filtered, and fractionated to give 250 g (80%) of **18** (55/45 isomer mixture), bp 87–90 °C (90 mm). IR (neat): 1675 (C=C), 1250–1000 cm^{-1} (CF, C—O). NMR (CDCl$_3$): ^{19}F ϕ –77.5 (s, CFClO of major isomer), –81.2 (s, CFClO of minor isomer). GC/MS: *m/e* 258, 260, 262, and 264 (M$^+$) with expected fragmentation pattern. Anal. Calcd for C$_4$Cl$_4$F$_2$O$_2$: C, 18.49; F, 14.62. Found: C, 18.36; F, 14.71.

Both **22** and **23** were isolated from separate reactions. For **22**, bp 62–63 °C (100 mm). NMR (CDCl$_3$): ^{19}F ϕ –81.9 (dd, J_{FF} = 17.7, 4.8 Hz, 1 F, CFClO), –87.1. (A branch dd, J_{FF} = 145.1, 4.8 Hz, 1 F, CFFO), –92.3 (B branch dd, J_{FF} = 145.1, 17.7 Hz, 1 F, CFFO). GC/MS: *m/e* 242, 244, 246, and 248 (M$^+$) with expected

fragmentation pattern. For **23**, bp 64 °C (7 mm). IR (neat): 1670 (C=C), 1250–1100 (CF, C—O), 770 cm^{-1} (CCl). NMR (CDCl$_3$): ^{19}F ϕ –75.9 (s, CFClO). GC/MS: *m/e* 274, 276, 278, 280, and 282 (M$^+$) with expected fragmentation pattern.

2,3-Dichloro-5,6-difluoro-1,4-dioxin (17). A suspension of 39.4 g (0.60 mol) of zinc dust in 500 mL of dry DMF was stirred under N$_2$ while about $^1/_3$ of 78.0 g (0.30 mol) of dihydrodioxin **18** (also under N$_2$) was added from a dropping funnel.[22] The entire system, including a stillhead, was evacuated at 120 mm with a N$_2$ bleed-in to maintain the inert atmosphere and heated slowly to reflux (98 °C). As reaction proceeded, product was taken off slowly, bp 69–72 °C (120 mm), while dropwise addition of **18** was completed. Distillation was continued to bp 91 °C (120 mm). GC showed appreciable DMF and **18** to be present along with 54% of dioxin **17**. When a sample was stirred in air, no temperature rise was detectable. After removal of DMF by a water wash, however, reaction of **17** with O$_2$ was vigorously exothermic.

The distillate was washed with 100 mL of water in a N$_2$ atmosphere, dried over CaSO$_4$, filtered, and fractionated under N$_2$ to afford 20.9 g (37%) of pure **17**, bp 42–43 °C (55 mm). IR (neat): 1836 (FC=CF), 1669 cm^{-1} (ClC=CCl). Raman (neat): 1837 (FC=CF), 1670 cm^{-1} (ClC=CCl). UV (isooctane): ϵ_{220} 986 with tailing to 325 nm. MS: *m/e* 188, 190, and 192 (M$^+$); 153 and 155 (M$^+$ – Cl); 141, 143, and 145 (M$^+$ – COF); 125 and 127 (M$^+$ – COCl); 94, 96, and 98 (C$_2$Cl$_2^+$); 63 and 65 (COCl$^+$); 62 (C$_2$F$_2^+$); 47 (COF$^+$). Mass measured M$^+$ 187.9249 (calcd for C$_4$Cl$_2$F$_2$O$_2$ = 187.9243).

2,2,3,3-Tetrachloro-5,5,6,6-tetrafluoro-1,4-dioxane (7). A solution of 118 g (0.52 mol) of **6** in 200 mL of CFCl$_2$CF$_2$Cl was stirred under a 80 °C condenser and irradiated with a sunlamp while chlorine was passed in until reaction ceased. Distillation gave 127.4 g (82%) of **7**, bp 65 °C (40 mm). IR (neat): 1250–1100 (CF, C—O), 760 cm^{-1} (C—Cl). NMR (CDCl$_3$): ^{19}F ϕ –79.6 (s, CF$_2$O). GC/MS: *m/e* 261, 263, 265, and 267 (M$^+$ – Cl), with expected fragmentation pattern.

2,3-Dichloro-2,3,5,5,6,6-hexafluoro-1,4-dioxane (8) and 2,2,3-Trichloro-3,5,5,6,6-pentafluoro-1,4-dioxane (24). A stirred suspension of 143.2 g (0.40 mol) of SbF$_3$ in 117 g (0.39 mol) of **7** was treated with 5 mL of SbCl$_5$ and refluxed for 4 h. An additional 3 mL of SbCl$_5$ was added, and the mixture was stirred at reflux for another 6 h (final temperature = 80 °C). Volatiles were transferred under vacuum, treated with CaSO$_4$, filtered, and distilled to afford 75.1 g (73%) of **8**, bp 79–81 °C. NMR indicated the presence of two isomers in 60/40 ratio, presumed to be trans/cis. For the trans isomer, NMR (CDCl$_3$): ^{19}F ϕ –79.1 (m, 2 F, OCFCl), –82.7 (A branch dm, J_{FF} = 160 Hz, 2 F, OCFF), –86.7 (B branch dm, J_{FF} = 160 Hz, 2 F, OCFF). For the cis isomer, NMR (CDCl$_3$): ^{19}F ϕ –72.3 (d, J_{FF} = 15 Hz, 2 F, OCFCl), –81.8 (A branch dm, J_{FF} = 135 Hz, 2 F, OCFF), –90.2 (B branch dm, J_{FF} = 135 Hz, 2 F, OCFF). Mixed isomers **8** have been reported as products from the addition of chlorine to **2**.[3]

Further fractionation gave 11.8 g (11%) of **24**, bp 113 °C. NMR (CDCl$_3$): ^{19}F ϕ –73.1 (dd, J_{FF} = 20, 3.5 Hz, 1 F, OCFCl), –79.2 (A branch dtd, J_{FF} = 147, 21, 16 Hz, 1 F, OCFF), –82.5 (A' branch ddd, J_{FF} = 149, 21.5, 16 Hz, 1 F, OCFF), –84.8 (B' branch dd, J_{FF} = 149, 16 Hz, 1 F, OCFF), –87.5 (B branch dd, J_{FF} = 147, 16 Hz, 1 F, OCFF).

F-2,3-Dihydro-1,4-dioxin (2). A suspension of 39.2 g (0.60 mol) of zinc dust in 300 mL of dry DMF was stirred under N$_2$ while 5 mL of 1,2-dibromoethane was added. Then a small portion of 74.0 g (0.28 mol) of dichloride **8** was added, and the mixture was stirred and heated. When an exothermic reaction started (about 75 °C), the rest of **8** was added dropwise at a rate sufficient to maintain 110–120 °C in the pot while product was collected in a –80 °C trap. When the addition had been completed, the mixture was heated to reflux to drive out the last of the product. Fractionation of the crude volatile product gave 24.5 g (45%) of **2**, bp 18–18.5 °C (ref 1 reports bp 19.5–20.5 °C). IR (gas): 1845 (w, C=C). GC/MS confirmed the structure as pure **2**. MS: *m/e* 194 (M$^+$), 175 (M$^+$ – F), 119 (C$_2$F$_5^+$), 100 (C$_2$F$_4^+$), 97 (C$_2$F$_3$O$^+$), 81 (C$_2$F$_3^+$), 78 (CF$_2$=C=O$^+$), 69 (CF$_3^+$), 62 (C$_2$F$_2^+$), 50 (CF$_2^+$), 47 (COF$^+$).

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(22) The use of DMF as solvent for dechlorinations with zinc markedly reduces or prevents the formation of hydrogen-containing byproducts, an observation first made by Dr. P. R. Resnick.

2-Chloroethyl 2-(2′-Chloroethoxy)tetrafluoropropionate (10). A 1-L Hastelloy-lined metal tube was charged with 480 g (6.0 mol) of 2-chloroethanol and 300 g (1.8 mol) of hexafluoropropene epoxide and then heated at 60 °C for 18 h. The liquid product was agitated with 2 L of ice water, washed with 400 mL of water, dried over CaSO₄, filtered, and distilled to afford 351 g (68%) of 10, bp 74–78 °C (1.1 mm). IR (neat): 2970 and 2900 (saturated CH), 1775 (C=O), 1250–1100 cm⁻¹ (CF, C—O). NMR (CDCl₃): ¹H δ 4.57 (t, J_{HH} = 5.5 Hz, 2 H, CO₂CH₂), 4.05 (t, J_{HH} = 5.5 Hz, 2 H, OCH₂), 3.73 (m, 4 H, CH₂Cl); ¹⁹F φ −81.7 (d, J_{FF} = 3 Hz, 3 F, CF₃), −132.0 (q, J_{FF} = 3 Hz, 1 F, CF).

3-Fluoro-3-(trifluoromethyl)-1,4-dioxan-2-one (12a). A solution of 20 g (0.50 mol) of NaOH in 100 mL of methanol was stirred while 66.0 g (0.23 mol) of ester 10 was added slowly. The mixture was stirred 15 min and then evaporated under reduced pressure to a solid mass, which was dried by slowly heating to 150 °C (0.5 mm). Futher heating at 150–185 °C (4.5 mm) caused product to collect in the receiver and cold trap. Fractionation afforded 33.7 g (78%) of 12a, bp 61–63 °C (3 mm). IR (neat): 2980 and 2910 (saturated CH), 1775 (C=O), 1250–1100 cm⁻¹ (CF, C—O). NMR (CDCl₃): ¹H δ 4.58 (m, 2 H, OCH₂), 4.20 (m, 2 H, OCH₂); ¹⁹F φ −82.7 (d, J_{FF} = 5 Hz, 3 F, CF₃), −115.4 (m, 1 F, CF). MS: m/e 189 (M⁺ + H), 188 (M⁺), 144 (M⁺ − CO₂), 141 (M⁺ − COF), 128 (CF₃CFCO⁺), 119 (M⁺ − CF₃), 100 (C₂F₄⁺), 97 (CF₃CO⁺), 69 (CF₃⁺), 50 (CF₂⁺), 47 (COF⁺), 45 (CO₂H⁺), 44 (CO₂⁺). Anal. Calcd for C₅H₄F₄O₃: C, 31.93; H, 2.14; F, 40.41. Found: C, 32.06; H, 2.20; F, 40.55.

2,2,3-Trifluoro-3-(trifluoromethyl)-1,4-dioxane (9). Fluorination of 12a with SF₄ was carried out in the presence of HF (cf. ref 23). A 1-L Hastelloy-lined metal tube charged with 235 g (1.25 mol) of lactone 12a, 140 g (7.0 mol) of HF, and 325 g (3.0 mol) of SF₄ was heated at 140 °C for 1 h and then at 160 °C for 16 h. The product was poured over ice, the aqueous layer was extracted with methylene chloride, and the organic layers were treated with CaSO₄ and distilled to give 209 g (80%) of 9, 56–58 °C (50 mm) (ref 5a: bp 74.5–76.5 °C (100 mm)). IR (neat): 3015, 2970, and 2910 (saturated CH), 1250–1100 cm⁻¹ (CF, C—O). NMR (CDCl₃): ¹H δ 3.7–4.8 (m, OCH₂); ¹⁹F φ −81.7 (td, J_{FF} = 10, 2 Hz, 3 F, CF₃), −86.7 (ddq, J_{FF} = 150, 20, 12 Hz, 1 F, A branch CF), −87.9 (dp, J_{FF} = 150, 9 Hz, 1 F, B branch CF), −139.7 (ddm, J_{FF} = 20, 11 Hz, 1 F, CF). Anal. Calcd for C₅H₄F₆O₂: C, 28.59; H, 1.92; F, 54.26. Found: C, 28.18; H, 2.02; F, 54.26.

2-(2′-Chloroethoxy)tetrafluoropropionyl Chloride (11). Crude sodium salt was prepared from 10 as described above and then evaporated to near dryness under vacuum. Thionyl chloride (179 g, 1.5 mol) was added cautiously, then 1 mL of dimethylformamide, and the mixture was stirred at 60–80 °C until evolution of gas had nearly ceased (6 h). Addition of another 60 g (0.5 mol) of thionyl chloride and heating at 80 °C caused only slight evolution of gas. Volatiles were transferred under vacuum and then fractionated to give 90.1 g (82%) of acid chloride 11, bp 69–70 °C (50 mm). IR (CCl₄): 2960 and 2890 (saturated CH), 1800 (COCl), 1250–1100 cm⁻¹ (CF, C—O). NMR (CDCl₃): ¹H δ 4.08 (t, J_{HH} = 5 Hz, 2 H, OCH₂), 3.68 (t, J_{HH} = 5 Hz, 2 H, CH₂Cl); ¹⁹F φ −79.9 (d, J_{FF} = 3 Hz, 3 F, CF₃), −126.4 ppm (q, J_{FF} = 3 Hz, 1 F, CF).

2-(2′-Chloroethoxy)tetrafluoropropionyl Fluoride (12). Reaction of 11 with potassium fluoride can be made to give either acid fluoride 12 or dioxane 9, depending upon solvent polarity (see also ref 5b). Reaction of 24.3 g (0.10 mol) of 11, 17.4 g (0.30 mol) of spray-dried KF, and 100 mL of diglyme was incomplete after 20 h at 60 °C, but complete after 1 day at 90 °C. Fractionation afforded 15.0 g (66%) of acid fluoride 12, bp 40–49 °C (50 mm). IR (CCl₄): 2960 and 2890 (saturated CH), 1870 (COF), 1250–1100 cm⁻¹ (CF, C—O). NMR (CDCl₄): ¹H δ 4.08 (m, 2 H, OCH₂), 3.65 (t, J_{HH} = 6 Hz, 2 H, CH₂Cl); ¹⁹F φ 29.1 (m, 1 F, COF), −81.5 (dd, J_{FF} = 5.5, 4 Hz, 3 F, CF₃), −131.1 (m, 1 F, CF).

The direct conversion 11 → 9 was carried out in mixed solvents. A mixture of 64.0 g (0.264 mol) of 11, 58.1 g (1.0 mol) of dry KF, 150 mL of acetonitrile, and 150 mL of dry diglyme was stirred and heated at 85–95 °C for 16 h. More KF (29.1 g., 0.50 mol) was added, heating was continued for 16 h, another 29.1 g (0.50 mol) of KF was added, and the reaction was continued at reflux (95

°C) until cyclization was complete (22 h). Distillation afforded a product fraction, bp 85–155 °C, which was washed with 2 × 200 mL of water to give 39.9 g (72%) of virtually pure dioxane 9.

2,2,3,3-Tetrachloro-5,5,6-trifluoro-6-(trifluoromethyl)-1,4-dioxane (13). Neat dioxane 9 (160 g, 0.76 mol) was stirred under nitrogen and irradiated with a sunlamp while chlorine was added as needed and the temperature was slowly raised to 95 °C over 35 h. Fractionation gave 245 g (93%) of pure 13, bp 64–65 °C (30 mm). IR (neat): 1300–1100 (CF, C—O), 800–700 cm⁻¹ (CCl). NMR (CDCl₃): ¹H none; ¹⁹F φ −73.8 (dp, J_{FF} = 160, 17 Hz, 1 F, A branch CF), −77.1 (dd, J_{FF} = 160, 6 Hz, 1 F, B branch CF), −82.0 (d, J_{FF} = 17 Hz, 3 F, CF₃), −127.3 (dd, J_{FF} = 17, 6 Hz, 1 F, CF). Anal. Calcd for C₅Cl₄F₆O₂: Cl, 40.77; F, 32.77. Found: Cl, 41.08; F, 32.32.

2,3-Dichloro-2,3,5,5,6-pentafluoro-6-(trifluoromethyl)-1,4-dioxane (14). A mixture of 69.6 g (0.20 mol) of 13, 71.6 g (0.40 mol) of SbF₃, and 2 mL of SbCl₅ was stirred and heated slowly to 136 °C. Heating was continued for 20 h with two more additions of SbCl₅ while the reflux temperature fell to 107.5 °C. Products were transferred under vacuum and fractionated to afford 33.9 g (54%) of difluoro derivative 14, bp 95–100 °C, as a mixture of isomers. NMR (CDCl₃): ¹⁹F φ −66 to −84.5 (sev. m, 7 F, OCFCl + OCF₂ + CF₃), −127.5 to −133.2 (m, 1 F, OCF (at least three of the four possible isomers)). Anal. Calcd for C₅Cl₂F₈O₂: C, 19.07; Cl, 22.51; F, 48.26. Found: C, 18.98; Cl, 22.77; F, 47.90.

Further distillation gave 21.0 g (32%) of trichloro isomers, bp 79–80 °C (150 mm). NMR (CDCl₃): ¹⁹F φ −69 to −83 (sev. m, 6 F, OCFCl + OCF₂ + CF₃), −127.2 to −132.2 (m, 1 F, OCF (appears to be three isomers)). Anal. Calcd for C₅Cl₃F₇O₂: C, 18.12; Cl, 32.09; F, 40.13. Found: C, 18.14; Cl, 32.23, F, 40.07.

F-2-Methyl-2,3-dihydro-1,4-dioxin (3). A mixture of 29.8 g (0.095 mol) of dioxane 14, 150 mL of dry DMF, 13.1 g (0.20 mol) of zinc dust, and 1 mL of 1,2-dibromoethane was stirred and heated under N₂ until the temperature reached 95 °C, where reaction occurred. The mixture was kept at 90–95 °C for 2 h, during which time 15 g of distillate, bp 30–45 °C, was collected. The crude product was washed with water, dried over CaSO₄, filtered, and distilled to give 7.1 g (31%) of 3, bp 43 °C. IR (vapor): 1845 (C=C), 1300–1100 cm⁻¹ (CF, C—O). NMR (CDCl₃): ¹⁹F φ −80.3 (td, J_{FF} = 9, 3.0 Hz, 3 F, CF₃), −82.5 (ddq, J_{FF} = 149.2, 14.7, 10.3 Hz, 1 F, A branch CFF), −92.9 (dm, J_{FF} = 149.2 Hz, 1 F, B branch CFF), −133.8 (t, J_{FF} = 15 Hz, 1 F, CF), −140.7 (dd, J_{FF} = 47.8, 4.3 Hz, 1 F, A branch =CF), −144.2 (d, J_{FF} = 47.8 Hz, 1 F, B branch =CF). MS: m/e 244 (M⁺), 197 (M⁺ − COF), 169 (M⁺ − CO − COF), 150 (CF₃CF=CF₂⁺), 131 (CF₂=CFCF₂⁺), 100 (C₂F₄⁺), 97 (CF₃CO⁺), 81 (C₂F₃⁺), 69 (CF₃⁺), 62 (FC≡CF⁺), 50 (CF₂⁺), 47 (COF⁺).

A similar reaction on a 0.81-mol scale carried out at 100–110 °C gave 103.9 g (53%) of 3.

Homopolymerization of 3. A sealed vial containing 1.3 g (5.3 mmol) of 3 and 8 drops of 3% perfluoropropionyl peroxide in CF₂ClFCl₂ was heated at 40 °C for 1 day. Addition of catalyst was repeated three times while reaction was continued at 40–45 °C for 1.5 days. The viscous solution was evaporated to dryness at 140 °C (0.1 mm) to afford 0.36 g (28%) of a clear, glassy homopolymer, which softened and flowed at 150–160 °C, T_g = 151 °C. IR showed no significant carbonyl absorption, indicating that ring opening did not occur during polymerizations.

Homopolymerization of 2. A mixture of 5.5 g (0.028 mol) of 2 and 0.2 mL of 0.8% perfluoropropionyl peroxide catalyst in CFCl₂CF₂Cl was sealed in a 25-mL polymer tube and heated at 40 °C for 3 days. Then 0.1 mL of catalyst solution was added, and the tube was again thermostated at 40 °C for 1 day. The addition was repeated, and the reaction continued another 3 days. Evaporation of volatiles at 0.1 mm gave 1.90 g (35%) of clear, colorless solid polymer. The polymer was soluble in CFCl₂CF₂Cl as well as in the monomer. On the melting point block, softening and flow occurred at 110–120 °C. DSC gave T_g = 110 °C. TGA showed the polymer to be stable to 350 °C, then 11% wt loss to 440 °C.

2,3-Epoxy-2,3,5,6-tetrachloro-2,3-dihydro-1,4-dioxin (19). Dioxin 15 was unreactive toward iodine on prolonged exposure at 25 °C, but reacted rapidly with O₂.

A 1.01-g sample of 15 was stirred in an open vial until the exotherm subsided and then allowed to stand for 3 days. The solid residue, 0.55 g, was extracted with petroleum ether and dried

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(23) De Pasquale, R. J. *J. Org. Chem.* 1973, *38*, 3025.

to give 0.46 g of white solid, mp 90–100 °C (–H_2O) followed by resolidification and mp 170–175 °C dec. The mp behavior and IR spectrum suggested partially hydrated oxalic acid. Acidified NaI gave only a possible weak test for peroxide.

A sample of **15**, 41.8 g (0.16 mol), was stirred in a system having a total free volume of 1575 mL. Oxygen was added as needed at 500–600 mm while the temperature ranged from 28 to 40 °C. Reaction slowed and practically stopped after a total drop of 980 mm, corresponding to absorption of 2.03 L (~0.084 mol) of oxygen. Analysis by GC/MS established the presence of small amounts of phosgene and oxalyl chloride along with 60–70% of one major product and several unidentified minor products. Fractionation afforded 12.2 g (32%) of epoxide **19**, bp 37–42 °C (4.5 mm). As the pot temperature rose above 120 °C during the distillation, later fractions partially decomposed to $COCl_2$, ClCOCOCl, and higher boilers. For **19**, IR (CCl_4): 1796 (C=C), 1260–840 cm^{-1} (eight distinct bands). NMR ($CDCl_3$): ^{13}C 161.6 (s, ClC=CCl), 77.8 ppm (s, Cl$\overline{CCC}$OCl). MS: m/e 201, 203, and 205 (M$^+$ – Cl); 173, 175, 177, and 179 (M$^+$ – COCl); 145, 147, and 151 (M$^+$ – COCOCl); 117, 119, 121, and 123 (CCl$_3^+$); 110, 112, and 114 (Cl$_2$C=C=O$^+$); 103 and 105 (ClC$_2$OCO$^+$); 94, 96, and 98 (C$_2$Cl$_2^+$); 82, 84, and 86 (CCl$_2^+$); 75 and 77 (ClC=C=O$^+$); 63 and 65 (COCl$^+$); 59 and 61 (C$_2$Cl$^+$); 47 and 49 (CCl$^+$). For highest mass peak, MS (CI): m/e 200.8915 (calcd for C$_4$Cl$_3$O$_3$, 200.8913).

2,3,5,6-Tetrachloro-2,3-(2′,3′-dimethylbut-2′-ene-1′,4′-diyl)-2,3-dihydro-1,4-dioxin (20). A mixture of 2.1 g (0.026 mol) of 2,3-dimethylbutadiene (inhibited with hydroquinone), 5.8 g (0.026 mol) of dioxin **15**, and 10 mL of CCl$_4$ was heated under N$_2$ at 80 °C for 2.5 h. No reaction was detected by GC, so the mixture was heated in a heavy-walled tube at 140 °C for 76 h. GC showed 86% of unreacted **15** still present along with a modest amount of product and considerable diene polymer. Another 2.1 g (0.026 mol) of inhibited diene was added and reaction was continued at 140 °C for 7 days. LC separation of product (present in 8% concentration) was difficult, so that only 0.05 g of purified product **20**, mp 76–80 °C, was obtained. IR (CDCl$_3$): 3000, 2920, 2860 (saturated CH), 1670 cm^{-1} (C=C). NMR (CDCl$_3$): ^1H δ 2.98 (A branch d, J_{HH} = 18.1 Hz, 2 H, CHH), 2.87 (B branch d, J_{HH} = 18.1 Hz, 2 H, CHH), 1.64 (s, 6 H, CH$_3$); ^{13}C 123.4 (ClC=CCl), 121.0 (CH$_3$C=CCH$_3$), 97.4 (bridgehead C), 44.1 (CH$_2$), 18.1 ppm (CH$_3$). MS: m/e 302, 304, 306, and 308 (M$^+$) with appropriate fragmentation pattern.
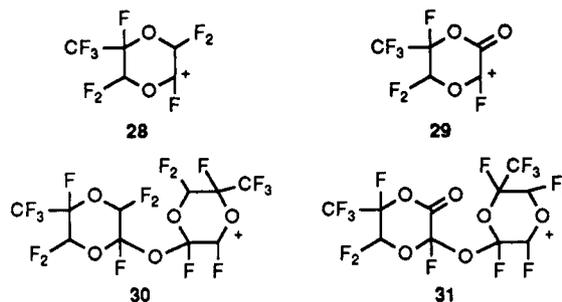
Polymerization of 17. A solution of 5.7 g (0.030 mol) of dioxin **17** in 10 mL of CFCl$_2$CF$_2$Cl was kept under N$_2$ at 25 °C for 5 days, during which time seven portions (5–20 drops each) of peroxide catalyst solution in CFCl$_2$CF$_2$Cl were added while viscosity increased. Volatiles removed under vacuum consisted essentially of solvent and unreacted **17**. The residual solid polymer, 1.3 g, was dried at 0.05 mm. IR (KBr): 1830 (end-group C=O, w), 1750 (CO$_2$H along with 3430 for OH, w), 1685 (ClC=CCl, w), 1180 and 1145 (CF, C—O, s), 1010 (m/s peak), 845 and 750 cm^{-1} (C—Cl, w).

The crude polymer was stirred for 3 h with 50 mL of methanol, filtered, rinsed well with methanol, and dried at 0.1 mm. The white insoluble polymer, 0.43 g, clarified and flowed on the melting point block at 215–225 °C. IR (KBr): 2955 (saturated CH, w), 1780 (ester C=O, w), 1685 (ClC=CCl, w), 1180 and 1150 (sh) (CF, C—O, s), 1010 (m to s), 845 and 750 cm^{-1} (C—Cl, w). DSC (N$_2$): T_g 175–200 °C. TGA (N$_2$): slight wt loss of 300 °C; 50% wt loss to 350 °C.

The methanol filtrate was diluted with 100 mL of water, the precipitated polymer was filtered, rinsed with water, and dried at 0.1 mm to give 0.63 g of soluble polymer. The white, glassy polymer clarified and flowed at 105–120 °C on the melting point block. IR (KBr): 2960 (saturated CH, w), 1780 (ester C=O, m/w), 1685 (ClC=CCl, w), 1180 and 1145 (CF, C—O, s), 845 and 750 cm^{-1} (C—Cl, w). DSC (N$_2$): T_g 70–90 °C. TGA (N$_2$): 5% wt loss to 225 °C, 50% wt loss to 325 °C.

Reaction of 3 with Oxygen. Glass apparatus containing 8.1 g (0.033 mol) of **3** was maintained under an atmosphere of O$_2$ while the liquid was stirred at 25 °C. No noticeable exotherm occurred, but steady absorption of oxygen was made up by occasional recharging to 1 atm. After 8 days, viscosity had increased markedly and gas absorption had ceased after consumption of 350–400 mL (~0.015 mol) of O$_2$. Analysis by GC/MS indicated 54% of a mixture of **3**, epoxide **25**, and an isomer which appeared to be **26**, along with oligomers **27** (34% n = 0, 5% n = 1, 2.8% n = 2, 2.1% n = 3, 1.6% n = 4, 1% n = 5, and a trace n = 6). Evaporation of volatiles from a small sample gave a very tacky residue.

For **27** (n = 0), the mass spectrum is dominated by m/e 263 and 241 from cleavage to cations **28** and **29** (and isomers). For **27** (n = 1–6), masses 263 and 241 are accompanied by high masses 523 and 501, corresponding to fragments **30** and **31** (and isomers).

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