fractivities were obtained from tables,[39] and atomic polarization was neglected.[1] The data are summarized in Table VIII.

Acknowledgment.—The authors are indebted to Mr. J. Maul and to Dr. L. Tushaus for some of the rotatory dispersion measurements and to Mr. C. L. Neumann for some of the dipole moment measurements. The authors are also indebted to Dr. M. Emerson for the n.m.r. spectra and helpful discussion regarding them. Experimental approaches to problems similar to some of these reported in this paper have been independently carried out by Drs. A. K. Bose, M. S. Manhas, and E. R. Malinowski, Stevens Institute of Technology; Dr. J. Lehn and Professor G. Ourisson, Universite de Strasbourg; and by Drs. R. J. Abraham and J. S. E. Holker, University of Liverpool. The authors are indebted to them for information regarding their work prior to publication.

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[39] A. I. Vogel, W. T. Cresswell, G. J. Jeffery, and J. Leicester, *Chem. Ind.* (London), 358 (1950).

Fluorocarbon Peroxides. Synthesis and Characterization of *cis*- and *trans*-Perfluoro-3,5-dimethyl-1,2-dioxolane

RICHARD L. TALBOTT

Contribution No. 326 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota 55119

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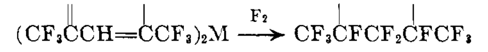
The reaction of fluorine with the copper(II) or the nickel(II) chelate of hexafluoroacetylacetone under mild conditions gives the fluorocarbon cyclic peroxide, perfluoro-3,5-dimethyl-1,2-dioxolane, as a mixture of the *cis* and *trans* isomers. The characterization of the peroxide is described.

With the exception of perfluorodimethyl peroxide,[1] fluorine-containing dialkyl peroxides have received little attention. This paper reports the synthesis and characterization of a member of a new class of organic fluorine-containing compounds, the cyclic fluorocarbon alkyl peroxides.

The reaction of elemental fluorine with the copper(II) or the nickel(II) chelate of hexafluoroacetylacetone gives a volatile, oxidizing liquid readily isolated by vapor phase chromatography. The elemental composition and molecular weight of the product are consistent with the formula $C_5F_{10}O_2$. Quantitative determination of the oxidizing power toward potassium iodide indicates the presence of one oxidizing group capable of undergoing a two-electron change. The infrared spectrum has no strong absorption bands in the region 2.5–7.3 μ, suggesting the absence of any carbon–carbon unsaturation, carbonyl groups, or epoxide functions. Complex absorption peaks are observed in the F^{19} n.m.r. spectrum of this material in the region 75–135 ϕ^*, but there are no other absorption peaks. The proton n.m.r. spectrum of a 69% solution of this substance shows no absorption, indicating that the hydrogen in the starting material has been replaced by fluorine. The only structure consistent with these results is the cyclic structure, perfluoro-3,5-dimethyl-1,2-dioxolane.[2]



$$(CF_3\overset{\overset{\displaystyle O}{\|}}{C}CH{=}\overset{\overset{\displaystyle O^-}{|}}{C}CF_3)_2M \xrightarrow{F_2} CF_3\overset{O\text{——}}{\overset{|}{C}}FCF_2\overset{\text{——}O}{\overset{|}{C}}FCF_3 \qquad (1)$$

$$M = Cu(II), Ni(II)$$

Both *cis* and *trans* isomers of the peroxide are possible. Interpretation of the n.m.r. values was aided by the fact that both isomers were observed in varying ratios in different samples, although the isomer ratio of freshly prepared samples is reproducibly somewhat greater than two, with the *cis* isomer present in greater amount. Assignment of the peak positions can be made with certainty (see Table I), because the *cis* isomer in several samples decomposed, leaving only the *trans* isomer and the decomposition products. The area ratios are consistent with the assignments. In the *cis* isomer the fluorines of the CF_2 group are magnetically nonequivalent. The presence of an AB pattern in the n.m.r. spectrum for the *cis* isomer is consistent with this nonequivalence. The *trans* isomer does not exhibit an AB pattern under the conditions used to obtain the spectrum.

The chemical properties of perfluoro-3,5-dimethyl-1,2-dioxolane provide further support for the structure assignment. A freshly prepared sample (a mixture of the isomers) was stored in the gas phase in a clean, well-dried borosilicate glass bulb at room temperature in the absence of air. Decomposition was noticeable after 1 day. After 3 days over half of the *cis* isomer had decomposed, while the *trans* isomer remained. After 10 days all of the *cis* isomer had decomposed, but the *trans* isomer was still present in the mixture after 12 weeks. After several months the *trans* isomer was also observed to have decomposed. The major product found was trifluoroacetyl fluoride, while lesser amounts of trifluoroacetic acid, difluoromethyl trifluoroacetate,[3] silicon tetrafluoride, and small amounts of an unidentified material were also observed. Formation of the acid fluoride is explained by cleavage of the molecule at one or both of the positions indicated by the broken lines in eq. 2. The acid itself might have been formed by reaction of the acid fluoride with adventitious moisture at the surface of the glass, and this reaction would also explain the

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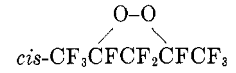
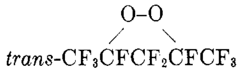
[1] F. Swarts, *Bull. soc. chim. Belges*, **42**, 102 (1933); R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5628 (1957); R. T. Holzmann and M. S. Cohen, *Inorg. Chem.*, **1**, 972 (1962); R. A. Darby and E. K. Ellingboe, U.S. Patent 3,069,404 (1962).

[2] For recent publications regarding substituted hydrocarbon cyclic peroxides, see N. A. Milas, O. L. Mageli, A. Golubović, R. W. Arndt, and J. C. J. Ho, *J. Am. Chem. Soc.*, **85**, 222 (1963); A. Rieche and C. Bischoff, *Chem. Ber.*, **96**, 2607 (1963); G. B. Payne, *J. Org. Chem.*, **26**, 4793 (1961), and references cited therein.

[3] The preparation of $CF_3CO_2CF_2H$ has been reported by N. N. Yarovenko, M. A. Raksha, V. N. Shemanina, and A. S. Vasilyeva [*J. Gen. Chem. USSR*, **27**, 2305 (1957)].

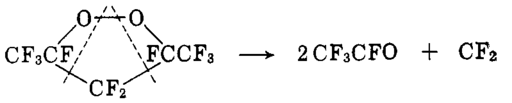
TABLE I

SPECTRAL PROPERTIES OF PERFLUORO-3,5-DIMETHYL-1,2-DIOXOLANE

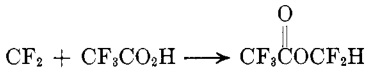
Isomer	F^{19} n.m.r. spectrum: Peak positions (approximate), ϕ^{*} [a]	F^{19} n.m.r. spectrum: Assignments	Infrared spectrum: Characteristic absorption, μ	Infrared spectrum: Other absorptions,[b] μ
 *cis*-$\overset{\text{O–O}}{CF_3CFCF_2CFCF_3}$	+75.7	CF_3	11.6[c]	7.4–9.4
	+128.5	CF		
	110 } AB pattern,	CF_2		
	126 } $J_{AB} = 256$ c.p.s.			
 *trans*-$\overset{\text{O–O}}{CF_3CFCF_2CFCF_3}$	+76.7	CF_3	11.45[c]	7.4–9.4
	+114	CF_2		
	+132.5	CF		

[a] All peaks are broad, complex multiplets. Except for the values for the AB pattern, values given are for the center of the absorption. [b] Both isomers showed several strong complex absorptions in region indicated. [c] Strong.

generation of silicon tetrafluoride (eq. 3). Formation of the ester might have arisen by transfer of difluoromethylene from cleavage fragments of the dioxolane to trifluoroacetic acid (eq. 4). This explanation might well require either a concerted mechanism or a free difluoromethylene species as an intermediate. Formation of difluoromethyl trifluoroacetate has been shown previously by the reaction of the acid with difluoromethylene generated from difluorodiazirine.[4]

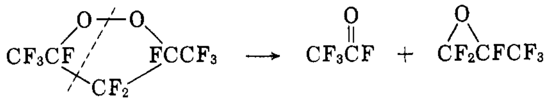

(2)

$$CF_3CFO + \text{glass} \xrightarrow{H_2O} CF_3CO_2H,\ SiF_4 \qquad (3)$$



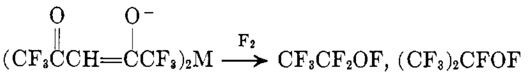
$$CF_2 + CF_3CO_2H \longrightarrow CF_3\overset{\overset{\text{O}}{\|}}{C}OCF_2H \qquad (4)$$

In another experiment no effort was taken to exclude moisture from the reaction, and a dioxolane sample that had been washed with water was allowed to decompose at room temperature in a glass vessel. The rate of decomposition was approximately the same as described above, and the same products were formed but in slightly different amounts. In addition, a small amount of perfluoropropylene oxide[5] was isolated.


(5)

The decomposition products clearly indicate the locations of the oxygen atoms in the parent molecule and demonstrate that no rearrangement took place during the fluorination step. These conclusions are in agreement with the interpretation of the n.m.r. results and the assignments for peaks in the mass-cracking pattern (see Experimental). The decomposition reactions also reveal that the *trans* isomer is more stable than the *cis* isomer toward thermal decomposition, yet both isomers give the same decomposition products.

Coupling of the oxygen atoms in a metal chelate by fluorination constitutes a novel technique for achieving ring closure. The yield based on conversion of the chelate is good. The peroxide is reproducibly found in yields of 40–60 mole % of the total gaseous products in the collection trap, but, under the conditions used, only low conversions have been achieved. Among the other products, which are all of lower molecular weight, are the recently described fluoroxy compounds, fluoroxyperfluoroethane and 2-fluoroxyperfluoropropane.[6]



$$(CF_3\overset{\overset{\text{O}}{\|}}{C}CH{=}\overset{\overset{\text{O}^-}{|}}{C}CF_3)_2M \xrightarrow{F_2} CF_3CF_2OF,\ (CF_3)_2CFOF \qquad (6)$$

Experimental

Apparatus.—All experiments were carried out in well-ventilated areas, and suitable barricades and personal safety equipment, such as face shields and heavy gloves, were used for personnel protection. The fluorination reactions were carried out in a 450-ml. cylindrical copper vessel equipped with a gas inlet tube, a gas outlet tube, and a polychlorotrifluoroethylene rupture disk. The samples to be fluorinated were placed in a copper tray in the reactor. Monel metal fittings were used for the fluorine supply line. Commercially available fluorine (95% pure) was used directly from the cylinder.

Two columns were used for gas chromatography: a 2-m. column (0.5-in. diameter) of silicone gum rubber (20%, commercially available as SE-30, General Electric Co., Inc.) coated on 30–60-mesh acid-washed Celite (80%, diatomaceous earth) for the higher boiling fractions; and an 8.5-ft. column (0.5-in. diameter) of perfluorotributylamine (33%, commercially available as FC-43, Minnesota Mining and Manufacturing Co.) coated on 30–60-mesh acid-washed Celite (67%) for the more volatile fractions.

The infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam infrared spectrophotometer on gas samples. The mass-cracking patterns were obtained on a Consolidated Electrodynamics Corporation mass spectrometer, Type 21-103C, with an ionization potential of 70 v. and an ionization chamber temperature of 250°. The n.m.r. spectra were obtained on a Varian V-4300-2 n.m.r. spectrometer at 40.00 Mc./sec. with trichlorofluoromethane as solvent and internal reference.[7]

Perfluoro-3,5-dimethyl-1,2-dioxolane.—In a typical experiment a 1.6-g. sample of the copper chelate[8] of hexafluoroacetylacetone (m.p. 113–115°, 6.7 mequiv. of hexafluoroacetylacetone) was placed in the copper tray in the reactor. The reactor was immersed in a cooling bath at −20° and flushed for 45 min. with

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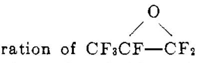
[4] R. A. Mitsch, unpublished work. Generation of difluoromethylene from difluorodiazirine has been reported: R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964).

[5] A convenient preparation of  $\overset{\text{O}}{CF_3CF\text{—}CF_2}$ has been reported by E. P. Moore, Jr., A. S. Milian, Jr., and H. S. Eleuterio [French Patent 1,275,799 (1961)].

[6] (a) J. H. Prager and P. G. Thompson, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, pp. 24K–25K; (b) J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, **87**, 230 (1965).

[7] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[8] A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, *J. Am. Chem. Soc.*, **69**, 1819 (1947).

a stream of dry, prepurified nitrogen. Floruine was introduced into the nitrogen stream, and the fluorine–nitrogen mixture was passed into the reaction vessel. The volatile, entrained products in the effluent stream were passed through an iron tube containing granular sodium fluoride to remove hydrogen fluoride (present in the fluorine supply and also formed in the reaction) and then into a 100-ml. glass trap immersed in liquid air. A stream of 3% (by volume) fluorine in nitrogen was passed through the reactor at a flow rate of approximately 0.016 ft.^{3}/hr. for 3 hr. (a total of 0.10 mole of fluorine). The fluorine flow was discontinued, and the cooling bath was removed. The reactor was thereafter purged with nitrogen for 1 hr. The desired product was formed rapidly during the initial period of fluorine delivery and was produced more slowly during the later stages of fluorination. (If the solid residues were then removed from the reactor, ground into a fine powder, and returned to the reactor, additional quantities of the desired products were obtained by repeating the fluorination procedure.)

The contents of the liquid-air trap were maintained at liquid-air temperature until the purification step. The noncondensable gases were removed from the trap at liquid-air temperature under reduced pressure, and the condensate was then fractionated at 0.1-mm. pressure (while the trap was allowed to warm slowly to room temperature) through traps designated A and B. Trap A was cooled by a bath of solid carbon dioxide–trichloroethylene (−78°) and trap B was cooled by a bath of liquid nitrogen (−196°). Trap A contained 0.38 mmole of crude *cis*- and *trans*-perfluoro-3,5-dimethyl-1,2-dioxolane, which was further purified by preparative gas chromatography on the silicone gum rubber column at room temperature. The yield was 5% of the theoretical amount based on hexafluoroacetylacetone employed as the chelate. No attempts have been made to improve the yield.

Anal. Calcd. for $C_5F_{10}O_2$: C, 21.4; F, 67.4; mol. wt., 282. Found: C, 21.4; F, 66.8; mol. wt., 275 (by gas density method).

An analytical sample released 6.8 mequiv. of iodine/g. of sample from aqueous potassium iodide (calcd. for two-electron change, 7.1 mequiv.). The mass-cracking pattern of an analytical sample has peaks at *m/e* 69 (assigned to CF_3), 47 (assigned to CFO), 97 (assigned to CF_3CO), and 263 (assigned to the parent molecule minus one fluorine atom) in addition to many other peaks consistent with the structure. The infrared and n.m.r. data are given in Table I. Both isomers of perfluoro-3,5-dimethyl-1,2-dioxolane are immiscible with water for periods up to 1 hr. with no evidence for hydrolysis. Both isomers are recovered unchanged after exposure to mercury for 30 min. Both isomers have been stored routinely at liquid nitrogen temperature for periods up to 2 years. A mixture of the isomers has a vapor pressure of 320 ± 10 mm. at 25°; the boiling point is estimated at 45° (760 mm.).

Trap B contained approximately 0.37 mmole of a mixture of cleavage products plus a small amount of perfluoro-3,5-dimethyl-1,2-dioxolane. Isolation of the components was accomplished by gas chromatography on the perfluorotributylamine column operated at −30°. The products were identified by comparison of their infrared spectra and gas chromatographic retention times with the spectra and retention times of authentic samples. This fraction consisted of one-carbon fragments and small amounts of perfluoroacetyl fluoride, fluoroxyperfluoroethane, and 2-fluoroxyperfluoropropane.[6] The same procedure was used for fluorination of the nickel chelate of hexafluoroacetylacetone. The yield was the same for either starting material.

The results of the thermal decomposition reactions of perfluoro-3,5-dimethyl-1,2-dioxolane were determined by the infrared and n.m.r. spectra of the samples at convenient time intervals and comparison of these spectra with the spectra of authentic samples of the products.

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Bridgehead-Substituted Bicyclo[2.2.2]octanes. I. Addition of Ethylene to Cyclohexa-1,3-diene-1,4-dicarboxylic Acid Derivatives

J. C. Kauer, R. E. Benson, and G. W. Parshall

Contribution No. 1008 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

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Addition of ethylene and other dienophiles to cyclohexa-1,3-diene-1,4-dicarboxylic acid derivatives yields disubstituted bicyclo[2.2.2]oct-2-enes with functional substituents at both bridgehead positions. These compounds were converted to a variety of 1,4-disubstituted bicyclo[2.2.2]octanes. Contrary to a recent report, the structure dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate originally assigned by Baeyer to the dihydroterephthalate isomer melting at 130° is correct.

Functionally substituted bridgehead structures have been of considerable interest in the study of organic reaction mechanisms. Although many syntheses of the bicyclo[2.2.2]octane ring system have been reported, most are not suitable for the preparation of bridgehead-substituted derivatives. In particular, few 1,4-disubstituted bicyclo[2.2.2]octanes have been described, and these were obtained by rather difficult, multistep syntheses.[1,2]

In general, three approaches have been used for the preparation of bridgehead-substituted bicyclo[2.2.2]octanes and bicyclo[2.2.1]heptanes: (1) free-radical attack at the bridgehead hydrogen atom of a bicyclic hydrocarbon,[3] (2) Wagner–Meerwein rearrangement of an appropriately substituted bicyclic structure,[4] and (3) introduction of a bridge into a substituted cyclohexane derivative.[1,2,5]

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[1] P. C. Guha, *Ber.*, **72**, 1359 (1939); P. C. Guha and C. Krishnamurthy, *ibid.*, **72**, 1374 (1939).

[2] J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, *J. Am. Chem. Soc.*, **75**, 637 (1953).

[3] (a) A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960); (b) R. T. Blickenstaff and H. B. Haas, *J. Am. Chem. Soc.*, **68**, 1431 (1946).

[4] (a) W. von E. Doering and E. F. Schoenewaldt, *ibid.*, **73**, 2333 (1951); (b) W. R. Boehme, *ibid.*, **81**, 2762 (1959); (c) H. Kwart and G. Null, *ibid.*, **81**, 2765 (1959).

[5] See, for instance, (a) S. Hünig and H. Kahanek, *Ber.*, **90**, 238 (1957); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958); (c) J. Colonge and R. Vuillemet, *Bull. soc. chim. France*, 2235 (1961).