to occur readily by the following experiment. Benzylchromium ion was produced by the addition of a chromous sulfate solution to benzyl bromide in dimethylformamide. The characteristic blue color of chromous ion was immediately replaced by the yellow to brown color of benzylchromium ion. Subsequent immediate injection of benzylmercuric perchlorate in dimethylformamide generated a green solution. The isolated yield of dibenzylmercury from immediate work-up was 99%.

The generality of the reaction for the formation of disubstituted mercury compounds is indicated by reactions from benzyl, cyclohexyl, phenyl, and 4-phenylbutyl perchlorates in which the yields were 99, 91, 88, and 93%, respectively. It is not necessary to utilize perchlorate salts as the reaction proceeds as readily with the more covalent halides. The reaction is heterogeneous, but the yields are comparable.

As further confirmation of the proposed mechanism and in an attempt to devise an alternate method for the formation of organochromium salts, an inversion of the mode of addition was carried out. Slow addition of benzylmercuric perchlorate in dimethylformamide to 3 equiv. of chromous ion over a 6-hr. period diminished the yield of dibenzylmercury with a corresponding increase in the yield of free mercury. Approximately 72% of the mercury utilized was obtained as free mercury. Similarly, phenylmercuric perchlorate when added over a 12-hr. period yielded 62% of the mercury utilized as free mercury. Under the conditions of the experiment, reaction 1d becomes less favorable than reaction 1a compared with the alternate mode of addition.

Solutions of benzylchromium react instantly with mercuric bromide to give dibenzylmercury when 0.5 mole of mercuric bromide/mole of benzylchromium is utilized. It has been reported that benzylchromium[12] and phenylchromium[13] react with mercuric bromide to yield the substituted mercuric salt. Under the conditions reported either 1 molar equiv. or excess mercuric bromide was utilized. Under our experimental conditions the organochromium compound must react with the organomercuric salt produced. As reported above this reaction is facile. Mixed disubstituted mercury compounds should be produced when an organochromium ion ($R-Cr^{+2}$) and an organomercury ion ($R-Hg^{+}$) are mixed. At present the application of this method is severely limited by the small number of chromium compounds available.

Experimental Section

Chromous Sulfate.—Chromous sulfate was prepared according to the procedure of Castro.[14] The reagent was approximately 0.70 *M* and was stored under nitrogen. Samples were removed with a syringe.

Reduction of Mercuric Perchlorates.—The organomercuric perchlorates were prepared by addition of 1 equiv. of 70% perchloric acid to the organomercuric acetate dissolved in degassed dimethylformamide. The resultant solution was maintained under nitrogen. The chromous sulfate was injected into the system through a serum cap. Finely divided mercury was immediately produced and a green solution resulted. The reaction mixture was centrifuged and the liquid layer was removed. The solid residue was washed consecutively with dimethylformamide, water, acetone, and ether. The mercury was dried under vacuum and dissolved in nitric acid. The acidic solution was diluted with distilled water and an aliquot was analyzed by addition of excess sodium thiocyanate and back titration with silver nitrate. The disubstituted organomercury compound was obtained by dilution of the dimethylformamide solution with water and isolation of the resulting solid by filtration. Recrystallization of the mercury compound was accomplished with either benzene or ethanol.

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[12] F. A. L. Anet and E. LeBlanc, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

[13] W. Herwig and H. H. Zeiss, *ibid.*, **79**, 6561 (1957).

[14] C. Castro, *ibid.*, **83**, 3262 (1961).

Oxidations with Oxygen Difluoride. III

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Received November 10, 1964

Oxygen difluoride was found to react readily with selected olefins at low temperatures.[1] The postulated mechanism involved the direct addition of the fragments F and OF, followed by subsequent decomposition of the unstable fluoroxyalkane. The known fluoroxyalkanes contain no hydrogen[2,3] and, in fact, it was found that the addition of a hydrogen-containing compound resulted in decomposition of the fluoroxy compound.[3] Therefore, the addition of oxygen difluoride to several perfluoro olefins was attempted.

The olefins examined included perfluoroethylene, perfluoropropene, perfluorocyclobutene, and perfluorobutene-2. These olefins were found to be much less reactive than the corresponding alkyl olefins and required either thermal or ultraviolet activation. Each olefin is discussed separately below.

Perfluoropropene was completely unreactive to OF_2 at room temperature in the absence of light. After 12 hr. of irradiation in a 500-cc. spherical Pyrex reactor, both reactants were totally consumed, producing the products outlined in Table I. It is apparent that no fluoroxy alkanes were isolated; however, comparable amounts of CF_3COF and CF_4 were found as well as CF_3CF_3 and COF_2. These fragments are believed to result from the decomposition of the two positional alkoxy radicals, $CF_3\overset{O\cdot}{C}FCF_3$ and $CF_3CF_2CF_2O\cdot$, in the presence of fluorine radicals or a fluorine donor. They would be expected to decompose homolytically with cleavage of a carbon–carbon bond.[4] The mode

TABLE I

PERFLUOROPROPENE–OF_2

Product	mmoles
CF_4	0.96
CF_3COF	0.93
COF_2	0.23
CF_3CF_3	0.14
$CF_3CF_2CF_3$	2.68
 $CF_3\underset{O}{CFCF_2}$	2.56

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[1] R. F. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965).

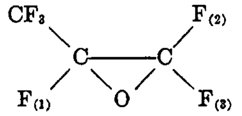
[2] K. B. Kellog and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[3] J. H. Prager and P. G. Thompson, *ibid.*, **87**, 230 (1965).

[4] The relative bond strengths being: C–F, −102 kcal./mole; C–C, −80 kcal./mole: E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 37.

of formation of these radicals is unknown, but they could arise *via* direct addition of oxygen difluoride to the double bond followed by O–F bond cleavage, or by reaction of oxygen and fluorine with the unsaturated center. If a fluoroxy intermediate had been formed it would probably not survive under the reaction conditions employed since irradiation of $(CF_3)_2CFOF$[3] resulted in complete decomposition to CF_4 and $CF_3CF{=}O$. However, the relative amount of this type of reaction is small in comparison with the epoxide-forming process.

The large amount of epoxide[5] formed was unexpected as the other olefins produced no isolable amounts of the corresponding oxide. The F^{19} n.m.r. spectrum of the epoxide (C_3F_6O) is shown in Figure 1. It is apparent that two of the three unique fluorine atoms are nonequivalent and form an AB system. However, it is not possible to determine which two of the three fluorines (omitting the CF_3 group) compose the AB system. The high-field triplet is assigned to the third fluorine which is coupled equally to the other two; J_{FA} = 16.5 c.p.s. and J_{FB} = 16.5 c.p.s. The large low-field doublet is assigned to the CF_3. Coupling occurs between the CF_3 and one of two fluorines in the AB system; $J_{CF_3-A(B)}$ = 8.8 c.p.s. The complex group of peaks in the center portion of the spectrum is assigned to the two fluorines composing the AB system; δ_{AB} = 124.5 c.p.s. and J_{AB} = 43.5 c.p.s. It is evident that one of these fluorines is coupled to only the third fluorine while the other fluorine of the AB pair is coupled to both the third fluorine and the fluorines on the CF_3 group. The F^{19} n.m.r. spectrum was calculated using the above values of the coupling constants and chemical shifts and is also shown in Figure 1.



Perfluorocyclobutene required 6 hr. of irradiation for total consumption of the OF_2. The major product, in 64% yield, is heptafluorobutyryl fluoride accompanied by lesser amounts of smaller fragments (Table II).

TABLE II

PERFLUOROCYCLOBUTENE-OF_2

Product	mmoles
COF_2	0.51
CF_4	0.11
$CF_3CF_2\overset{O}{\overset{/\!/}{C}}{-}F$	0.58
$CF_3CF_2CF_2\overset{O}{\overset{/\!/}{C}}{-}F$	2.49
Perfluorocyclobutane	0.69

The predominant process occurring is probably formation of a cyclobutoxy radical and its subsequent decomposition to heptafluorobutyryl fluoride. No evidence for epoxide formation was observed, although this is perhaps not surprising as the production of the highly strained compound would have to compete with the lower energy process of ring opening. Several other processes are undoubtedly also occurring.

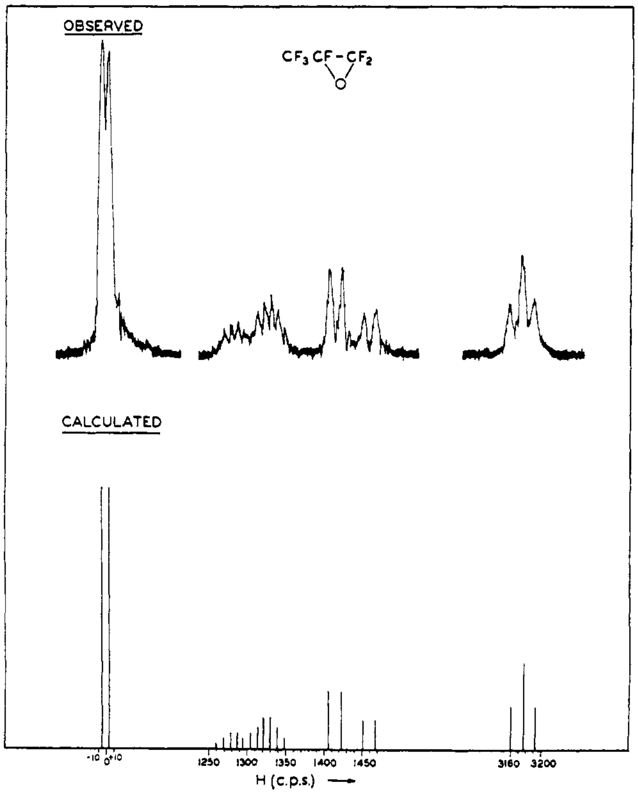


Figure 1.—F^{19} n.m.r. spectrum of perfluoropropene oxide.

Perfluorobutene-2 as a mixture of *cis–trans* isomers required 8 hr. of irradiation to go to completion. Table III lists the fragments and relative amounts of each.

TABLE III

Product	mmoles
CF_4	3.67
COF_2	0.74
CF_3CF_3	0.98
$CF_3\overset{O}{\overset{/\!/}{C}}{-}F$	1.59
$CF_3CF_2\overset{O}{\overset{/\!/}{C}}{-}F$	2.71
$CF_3CF_2CF_2CF_3$	0.62

The observed products can be explained by assuming the decomposition of a perfluoro-2-butoxy radical, which has two possible modes of decomposition by C–C bond cleavage. Cleavage of C-1–C-2 leads to CF_3CF_2COF while C-2–C-3 cleavage leads to the two-carbon acid fluoride CF_3COF. Surprisingly, no epoxide was isolated although its presence in small amounts was indicated in the infrared spectrum of the crude reaction mixture.[5]

Tetrafluoroethylene was found to react rapidly without irradiation to produce an equal molar mixture of CF_4 and COF_2. Traces of C_2F_6 were also isolated, but there was no evidence for the formation of either fluoroxyperfluoroethane or perfluoroethylene oxide.

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(5) A previous preparation of the epoxide contained insufficient physical data to enable a positive identification: E. I. du Pont de Nemours and Co., British Patent 904,877 (1962).

Experimental Section

Materials.—The oxygen difluoride was purchased from Allied Chemical Co. and used without further purification (<1% CO_2). The olefins were obtained from commercial sources and their physical constants were compared with established values to ensure purity. The perfluoro olefins were checked for purity by vapor phase chromatography.

Apparatus.—The oxygen difluoride was stored in large-volume glass bulbs which were an integral part of a standard high-vacuum line. All mercury manometers were protected with a layer of degassed Kel-F KF-10[6] oil and stopcocks were lubricated with Kel-F No. 90[6] grease. Other lubricants are *not* acceptable. The OF_2 can be stored in Pyrex indefinitely without decomposition if the above precautions are taken.

Reaction of the Perfluoro Olefins with OF_2.—The perfluoro olefin additions were conducted by mixing measured quantities of reactants in 500-cc. Pyrex bulbs and irradiating with a high-pressure mercury flood lamp.[7] The bulb was cooled with an air stream to avoid overheating and the temperature was maintained at 35° with the lamp 6 in. from the bulb. As all the additions were performed in a similar manner, only the procedure for perfluoropropylene, given below, will be described in detail. The perfluoropropylene (6.24 mmoles) was admixed with 7.67 mmoles of OF_2 and irradiated for 12 hr. At the end of this period the contents were vacuum distilled and separated into fractions which condensed at −126 and −196°. The total content of the fractions in millimoles was determined by expanding into a known volume and determining the pressure. The −126° condensable fraction contained a total of 6.17 mmoles. Analysis by vapor phase chromatography (15 ft. × 0.25 in., 30% FC-43[8] at 10°) indicated three components.

Compound A (43%, 2.68 mmoles) was purified by chromatography and identified as perfluoropropane by comparison of its infrared and mass spectra with those of an authentic sample. Compound B (42%, 2.56 mmoles) after isolation by chromatography was perfluoropropylene oxide. Molecular weight by mass spectrum effusion method is 165 and by vapor density is 164 (calcd. 166). The F^{19} n.m.r. spectrum is consistent with the epoxide structure (see Figure 1). The infrared spectrum shows strong absorption at 6.45 μ which is indicative of perfluoro olefin epoxides.[5]

Anal. Calcd. for C_3F_6O: F, 68.67. Found: F, 67.10.

Compound C (15%, 0.93 mmole) was collected from the chromatograph and shown to be perfluoroacetyl fluoride by comparison of its infrared and mass spectra with those of an authentic specimen. The −196° condensable fraction contained a total of 2.86 mmoles by *P–V* calculation. Mass spectral analysis showed the following components: SiF_4 (0.27 mmole); COF_2, 8.0% (0.23 mmole); CF_4, 33.6% (0.96 mmole); OF_2, 34.3% (0.98 mmole); CO_2, 9.8% (0.28 mmole); and C_2F_6, 4.9% (0.14 mmole). All compounds were identified by comparison of spectra with those of authentic samples.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. The F^{19} n.m.r. spectra were taken on carbon tetrachloride solutions with a Varian Associates Model HR-40 spectrometer and values are given in cycles per second (c.p.s.) from external trifluoroacetic acid (TFA).

Gas samples were analyzed routinely on a Consolidated Model 21-620 mass spectrometer. Vapor phase chromatograms were obtained with a Wilkens Model A-90-P instrument modified to use low-temperature columns as well as inject and collect gaseous samples.

Acknowledgment.—This work was sponsored under Army Ordnance Contract No. DA-01-021 ORD-11878. We are grateful to Mrs. Carolyn Haney for infrared and n.m.r. spectra.

[6] Minnesota Mining and Manufacturing Co. trade name for perfluorochlorocarbon lubricants.

[7] General Electric Corp., Model H100 PFL 38-4 with Pyrex envelope.

[8] Minnesota Mining and Manufacturing Co. trade name for perfluorotributylamine. Column was loaded with 30% w./w. FC-43 on 80–100-mesh Chromosorb P.

Compounds of Phosphorus and Fluorine. I. Reaction of Trialkyl Phosphites with Saturated Chlorofluorocarbons

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Received April 12, 1965

This is the first paper of a series in which the synthesis and properties of fluorine-containing organophosphorus compounds is explored. Our initial attempts to prepare such compounds by the reaction of trialkyl phosphites with saturated chlorofluorocarbons, described in the present paper, were discontinued when it became evident that products with C–P bonds were not being formed. Subsequent papers will be concerned with reactions which did form products with C–P bonds and with the chemistry of the resulting compounds.

Trialkyl phosphites usually undergo the Arbuzov reaction[2] when treated with saturated alkyl halides, forming products with C–P bonds. In some cases, however, the alkyl halides suffer dehalogenation or dehydrohalogenation, and no C–P bonds are formed. Dehalogenation appears to be the predominant course when the alkyl halides contain two chlorine, bromine, or iodine atoms on adjacent carbon atoms.[3] Some of the alkyl halides also contained fluorine,[3c,h] but in no case was a fluorine atom removed.

The starting point for this investigation was the discovery of an unexpected reaction between tributyl phosphite and Fluorolube® S, one of a group of chlorotrifluoroethylene polymers characterized by a high degree of chemical stability.[4] These polymers should contain few chlorine atoms on adjacent carbon atoms, as they are stabilized by rigorous fluorination. Their structure should therefore be favorable for the replacement of chlorine by phosphonate in the conventional Arbuzov manner. We found, however, that when Fluorolube S was heated with tributyl phosphite in amounts corresponding to a 1:1 ratio of phosphorus to chlorine, a strongly exothermic reaction set in at about 100°, giving butyl chloride and dibutyl phosphorofluoridate as the only identifiable products. The reaction appeared to have proceeded in the manner shown by eq. 1. No butyl fluoride nor dibutyl phosphorochloridate was detected. Efforts to isolate the unsaturated polymer given in eq. 1 were unsuccessful.

$$F[CF_2CFCl]_nF + n(RO)_3P \longrightarrow F[CF{=}CF]_nF + n(RO)_2P(O)F + nRCl \quad (1)$$

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[2] For a recent review, see R. G. Harvey and E. R. De Sombre, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p. 57.

[3] (a) B. A. Arbuzov and B. P. Lugovkin, *Zh. Obshch. Khim.*, **21**, 99 (1951); (b) G. Kamai, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 923 (1952); (c) H. R. Davis, U. S. Patent 2,742,510 (April 17, 1956); (d) V. S. Abramov and N. A. Il'ina, *Zh. Obshch. Khim.*, **26**, 2014 (1956); (e) V. S. Abramov and S. Pall, *Tr. Kazansk. Khim. Tekhnol. Inst.*, **23**, 105 (1957); *Chem. Abstr.*, **52**, 9949 (1958); (f) V. Mark, *Tetrahedron Letters*, 333 (1961); (g) S. Dershowitz and S. Proskauer, *J. Org. Chem.*, **26**, 3595 (1961); (h) I. L. Knunyants and E. Ya. Pervova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1409 (1962); (i) H. Klug and K. Kuchinka, *Ann.*, **677**, 77 (1964).

[4] Technical Bulletin No. 30, "Fluorolubes," Hooker Chemical Corp., Niagara Falls, N. Y., 1952.