

tip directly in the cooling bath until crystals formed. The molal freezing point constant used for benzene was 5.12°.

The low solubility of *N,N'*-di-*o*-tolylformamidine in benzene allowed determinations of freezing point depressions

in only very dilute solutions where experimental errors were comparatively higher, but there is no doubt about the qualitative result.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, POLAROID CORPORATION]

1,1-Difluoro-2-methylpropene, 3,3-Difluoro-2-methylpropene and 3,3-Difluoro-3-chloro-2-methylpropene¹

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The preparation and properties of $\text{CF}_2=\text{C}(\text{CH}_3)_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$ and a number of derivatives are described.

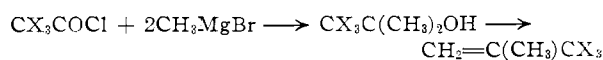
As part of a program on fluorinated monomers, it seemed to us to be of interest to prepare 1,1-difluoro-2-methylpropene, $\text{CF}_2=\text{C}(\text{CH}_3)_2$. During the course of this work, we prepared the isomeric 3,3-difluoro-2-methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$, the related 3,3-difluoro-3-chloro-2-methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$, and the known compounds 3,3,3-trifluoro-2-methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_3$ ² and 1,1-dichloro-2-methylpropene, $\text{CCl}_2=\text{C}(\text{CH}_3)_2$.³

We were unable to prepare $\text{CF}_2=\text{C}(\text{CH}_3)_2$ by removal of fluorine and acetate from $\text{CF}_3\text{C}(\text{CH}_3)_2\text{OCOCH}_3$ or chlorine and acetate from $\text{CF}_2\text{ClC}(\text{CH}_3)_2\text{OCOCH}_3$ by treatment with zinc, although the related chloro compound, $\text{CCl}_2=\text{C}(\text{CH}_3)_2$, was readily prepared by this method³ from $\text{CCl}_3\text{C}(\text{CH}_3)_2\text{OCOCH}_3$. The desired olefin, $\text{CF}_2=\text{C}(\text{CH}_3)_2$, was successfully prepared by (a) reaction of the phosphite, $(\text{CF}_2\text{ClC}(\text{CH}_3)_2\text{O})_3\text{P}$, with zinc and by reduction of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$ with (b) hydrogen with nickel catalyst or (c) lithium aluminum hydride. Method (c) was the only one of preparative significance. The olefin was completely free of isomers on careful 80-plate fractionation and was inert to silica defluorination, as would be expected of a vinylidene fluoride. Structural formulation as $\text{CF}_2=\text{C}(\text{CH}_3)_2$ was demonstrated by preparation of the dibromide, by permanganate oxidation to acetone and by the infrared spectrum ($\text{C}=\text{CF}_2$ absorption⁴ at 1765 cm^{-1} and of very strong intensity due to heightened double bond polarity as compared to other vinylidene fluorides).

The isomeric olefin, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$, was formed in good yield by (a) dehydration of $\text{CHF}_2\text{C}(\text{CH}_3)_2\text{OH}$ by treatment with phosphorus pentachloride and (b) pyrolysis of the acetate ester of this carbinol. Careful fractionation on a 60-plate column gave no indication of the presence of the other isomer, $\text{CF}_2=\text{C}(\text{CH}_3)_2$, and showed a single boiling point plateau. The structure of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$ was confirmed by its infrared absorption spectrum ($\text{C}=\text{CH}_2$ absorption of medium intensity at 1665 and 1850 cm^{-1}),⁴ preparation of the

dibromide and pyrolytic defluorination over silica⁵ to yield methacrolein, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$. It may be noted that difluoromethyldimethylcarbinol was not dehydrated by (a) drastic treatment with phosphorus pentoxide, (b) the Chugaev reaction, (c) the boric ester method⁶ or (d) the Grignard alcoholate pyrolysis method.⁷

The known 3,3,3-trifluoro-2-methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_3$, and the new 3,3-difluoro-3-chloro-2-methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$, were prepared by modification of an established method² *via* dehydration of the appropriate trihalomethyldimethylcarbinol with phosphorus pentachloride.



The compound $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$ was shown to contain no other isomer on careful fractionation and the structure confirmed by the infrared spectrum ($\text{CH}_2=\text{C}$ absorption of medium intensity at 1665 and 1860 cm^{-1} ; no trace of $\text{CF}_2=\text{C}$ absorption at 1765 cm^{-1}). The reduction of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$ to $\text{CF}_2=\text{C}(\text{CH}_3)_2$ is therefore formulated as hydrogenolysis of the allylic chlorine atom accompanied or preceded by allylic rearrangement.⁸

The three similar isobutylenes, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_3$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$, failed to polymerize under a wide variety of conditions.

Acknowledgments.—The authors are glad to acknowledge their indebtedness to Miss Adelaide Sutton for infrared spectroscopy, to Mr. Marshall W. Kane for much preparative help, to Drs. Daniel I. Livingston and Pandurang Kamath for polymerization studies and to Dr. Elkan R. Blout for many helpful discussions.

Experimental⁹

CF_3COCl .—The acid chloride (b.p. -27°) was prepared in 85–92% average yield. Treatment of a sample in ether

(1) This work was sponsored by the Signal Corps, Department of the Army.

(2) (a) E. Swarts, *Bull. Soc. chim. Belg.*, **1927**, 195; **1929**, 108. (b) A. L. Henne, J. W. Shepard and F. J. Young, *THIS JOURNAL*, **72**, 3577 (1950).

(3) Z. Jocitsch and A. Faworsky, *Chem. Zentr.*, **70**, I, 778 (1899).

(4) See, e.g., L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954, pp. 33, 37.

(5) *Cf.*, W. E. Hanford and G. W. Rigby (to du Pont), U. S. Patent 2,409,274 (October 15, 1946).

(6) W. Brandenburg and A. Galat, *THIS JOURNAL*, **72**, 3275 (1950).

(7) F. C. Whitmore and H. S. Rothrock, *ibid.*, **55**, 1106 (1933).

(8) *Cf.* D. G. Kundiger and H. N. Haney, *ibid.*, **76**, 615 (1954); Maurice Prober, *ibid.*, **76**, 4189 (1954).

(9) All m.p.'s are corrected. Combustion analyses are by the Clark Microanalytical Laboratory, Urbana, Illinois, and Dr. Carol K. Fitz, Needham, Massachusetts.

solution with aqueous ammonia gave trifluoroacetamide, m.p. 74–75° (reported¹⁰ 75°).

$\text{CF}_3\text{C}(\text{CH}_3)_2\text{OH}$.—Treatment of the acid chloride with methylmagnesium bromide gave an average yield of 55% of the carbinol, b.p. 80–82° (763 mm.), n_{D}^{25} 1.3330 (reported^{2a} b.p. 81.6°).

$\text{CF}_3\text{C}(\text{CH}_3)_2\text{OCOCH}_3$.—The acetate obtained by treatment of the carbinol with acetic anhydride, had b.p. 86–88° (760 mm.), n_{D}^{30} 1.3428 (reported^{2a} b.p. 85.6°).

Anal. Calcd. for $\text{C}_6\text{H}_8\text{F}_3\text{O}_2$: C, 42.4; H, 5.3. Found: C, 42.0; H, 5.6.

Treatment of the acetate with zinc,⁵ even under drastic conditions (3 hr. at 170°), gave no $\text{CF}_2=\text{C}(\text{CH}_3)_2$.

$\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_3$.—Reaction of the carbinol with phosphorus pentachloride and redistillation gave a 74% yield of the olefin, b.p. 5–6° (reported^{2a} 6.4°).

Treatment of the carbinol by several variations of the boric acid dehydration method⁶ gave recovered carbinol and only traces of unsaturated product, even under drastic conditions.

CF_2ClCOCl .—The acid chloride, b.p. 26–28°, was prepared in good yield by reaction with phosphorus pentachloride in 1:1.5 mole ratio for 1.5 hr. at 90–100°. Reaction with aq. ammonia in ether gave difluorochloroacetamide, m.p. 76.5° (reported¹¹ 78°).

$\text{CF}_2\text{ClC}(\text{CH}_3)_2\text{OH}$.—Reaction of the acid chloride by slow distillation into excess ethereal methylmagnesium bromide maintained at 5 to 14° under a –80° condenser gave the carbinol. This was best worked up by evaporation of ether, then fractionation on a 30-plate column after addition of petroleum ether to remove azeotropically the small amount of water which is retained even after thorough drying of the ethereal solution. The carbinol was collected at 106–107° (750 mm.), yield 85–90%. The pure material boils at 106.5° (750 mm.), n_{D}^{25} 1.3841.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{F}_2\text{ClO}$: C, 33.2; H, 4.9. Found: C, 33.2; H, 4.8.

$\text{CF}_2\text{ClC}(\text{CH}_3)_2\text{OCOCH}_3$.—Reaction of the carbinol with acetic anhydride gave the acetate, b.p. 126–127° (770 mm.), n_{D}^{30} 1.3814, yield 65%.

Anal. Calcd. for $\text{C}_6\text{H}_9\text{O}_2\text{ClF}_2$: C, 38.6; H, 4.9; Cl, 19.0. Found: C, 39.1; H, 5.1; Cl, 18.5.

Drastic treatment of the acetate with zinc⁵ under a variety of conditions gave no olefinic product.

$\text{CCl}_2=\text{C}(\text{CH}_3)_2$.—Reaction of $\text{CCl}_3\text{C}(\text{CH}_3)_2\text{OH}$ and acetyl chloride gave the acetate, b.p. 87° (20 mm.), n_{D}^{20} 1.4640, yield 82% (reported¹² b.p. 191° (760 mm.)).

Addition of the acetate to zinc in ethanol, washing out and distillation gave $\text{CCl}_2=\text{C}(\text{CH}_3)_2$, b.p. 107–109° (743 mm.), n_{D}^{20} 1.4584 (reported³ b.p. 107.5–108.5°).

$\text{CH}_2=\text{C}(\text{CH}_3)\text{CF}_2\text{Cl}$. (a) **With Thionyl Chloride**.—A solution of 50 g. (0.345 mole) of $\text{CF}_2\text{ClC}(\text{CH}_3)_2\text{OH}$, 62 g. (0.518 mole), of thionyl chloride and 90 g. of pyridine was heated for 8 hr. at 80–100° and the product distilled from the reaction mixture. Redistillation on a column gave the olefin as a single plateau, b.p. 46° (752 mm.), n_{D}^{20} 1.3635, yield 76%.

Anal. Calcd. for $\text{C}_4\text{H}_5\text{F}_2\text{Cl}$: C, 38.0; H, 4.0; Cl, 28.1. Found: C, 38.2; H, 4.0; Cl, 27.0.

(b) **With Phosphorus Pentachloride**.—A mixture of 132 g. (0.91 mole) of the carbinol and 285 g. (1.37 moles) of phosphorus pentachloride was heated at 90–100° for 1.5 hr. The product collected in a –80° trap was warmed to 0° to remove the bulk of the dissolved HCl, washed with ice water until neutral, dried over MgSO_4 and carefully fractionated on a 30-plate column operated at theoretical efficiency by the intermittent take-off method. All the material distilled at 45.8–46.1° (750 mm.), n_{D}^{21} 1.3603–1.3605, and of this about 80% was constant index material of n_{D}^{21} 1.3605. The total yield was 76%.

$\text{CHF}_2\text{C}(\text{CH}_3)_2\text{OH}$.—Reaction of sodium difluoroacetate with phosphorus oxychloride gave the acid chloride, $\text{CHF}_2\text{C}(\text{CH}_3)_2\text{COCl}$, b.p. 26–28° (reported¹³ b.p. 25°), yield 77–79°. Reaction of the acid chloride with Grignard reagent gave the carbinol, $\text{CHF}_2\text{C}(\text{CH}_3)_2\text{OH}$, b.p. 93–94° (764 mm.), n_{D}^{25} 1.3615, yield 45%.

(10) N. Fukuhara and L. A. Bigelow, *THIS JOURNAL*, **63**, 788 (1941).

(11) F. Swarts, *Bull. acad. roy. Belg.*, 339 (1907).

(12) C. Willgerodt and F. Durr, *J. prakt. Chem.*, [2] **39**, 285 (1889).

(13) F. Swarts, *Chem. Zentr.*, **74**, II, 703 (1903).

Anal. Calcd. for $\text{C}_4\text{H}_8\text{F}_2\text{O}$: C, 43.6; H, 7.3; F, 34.5. Found: C, 43.5; H, 7.1; F, 34.5.

The carbinol was completely inert toward the dehydration conditions detailed in the discussion, including heating in a phosphorus pentoxide–phosphoric acid mixture at 140–150°.

$\text{CHF}_2\text{C}(\text{CH}_3)_2\text{OCOCH}_3$.—Treatment of the carbinol with acetic anhydride gave the acetate, b.p. 110–112° (764 mm.), n_{D}^{25} 1.3670.

Anal. Calcd. for $\text{C}_6\text{H}_{10}\text{F}_2\text{O}_2$: C, 47.4; H, 6.6; F, 25.0. Found: C, 45.2; H, 6.6; F, 19.7.

$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$. (a) **From the Carbinol**.—A mixture of 133 g. of $\text{CHF}_2\text{C}(\text{CH}_3)_2\text{OH}$ and 610 g. of phosphorus pentachloride was stirred 0.5 hr. at 25°, then heated for 4 hr. at 100°. The product was distilled from the reaction mixture to give 106 g. (79% yield) of the olefin, b.p. 27°. Fractionation of this material was conducted on a Podbielniak Heligrid column, provided with a silvered vacuum jacket and low temperature head. The throughput was kept at or below 100 ml./hr., at which rate the column has 60 theoretical plates. This efficiency was closely approximated at either end of the isobutylene plateau by using intermittent take-off with an effective reflux ratio of between 100 and 150, allowing time between portions for equilibration. During the plateau the take-off was constant at a reflux ratio of 25. The temperature–distillate volume graph rose steeply at either end of the plateau. The fractions were: (1) 8.5 g., b.p. 6.9–28.1° (760 mm.), n_{D}^{20} 1.3442; (2) 60.2 g., b.p. 28.1 (754 mm.)–28.2° (765 mm.), n_{D}^{20} 1.3426–1.3423; (3) ca. 10 ml., pot residue, b.p. > 28.2°. Fraction (1) was largely HCl, (3) was largely POCl_3 and (2) was $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$ of the following analysis.

Anal. Calcd. for $\text{C}_4\text{H}_8\text{F}_2$: C, 52.2; H, 6.5; F, 41.3. Found: C, 52.1; H, 6.6; F, 40.8.

Molecular weight: calcd., 92.09; found, (1) by Dumas vapor phase method at 48°, 94.9; (2) by bromide–bromate reagent titration (60 min. reaction in the dark), 90.0.

(b) **From the Acetate**.—The vapor of 14.1 g. of $\text{CHF}_2\text{C}(\text{CH}_3)_2\text{OAc}$ mixed with a very slow stream of carbon dioxide was passed during 1 hr. through a 1.5 × 55 cm. combustion tube maintained at 750°. The contact time was ca. 50 sec. The products collected in a cold trap were fractionated to give: (1) 3.9 g. of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$, b.p. 26–28° (769 mm.), n_{D}^{20} 1.3432, and (2) 6.0 g. of a mixture of the carbinol acetate and acetic acid, b.p. 112–118° (769 mm.). Analysis was obtained on fraction (1).

Anal. Calcd. for $\text{C}_4\text{H}_8\text{F}_2$: C, 52.2; H, 6.5; F, 41.3. Found: C, 51.8; H, 6.6; F, 40.6.

Some methacrolein (see below) was found in the higher boiling fraction.

Reactions of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$. (a) **Bromination**.—Bromine (0.68 cc.) was added to 1 ml. of the olefin at 0° until a small coloration remained. The mixture was allowed to stand overnight at 0°, then excess bromine removed by a stream of air and the product distilled through a semi-micro all-glass still to give 1.4 g. of the dibromide, $\text{CHF}_2\text{C}(\text{CH}_3)\text{Br}-\text{CH}_2\text{Br}$, b.p. 156–157° (765 mm.), n_{D}^{25} 1.4726. No HBr was produced during the reaction or distillation.

Anal. Calcd. for $\text{C}_4\text{H}_8\text{F}_2\text{Br}_2$: Br, 63.5. Found: Br, 62.9.

The dibromide was inert toward silver nitrate at 100° in 5% aq. alcohol. Heating in aq. alcohol in the presence of 1 drop of 5% sodium hydroxide, however, resulted in the release of fluoride and bromide ions.

(b) **Defluorination**.—The vapor of 8 g. of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$ was passed in 1 hr. through a 1.5 × 33 cm. combustion tube filled with dehydrated granular silica gel and maintained at 350°. The product collected in a –80° trap consisted of ca. 1 ml. of water (containing no fluoride ion) and ca. 5 ml. of water-insoluble organic liquid. The water was separated and the organic material fractionated on a 30-plate Bowers–Cooke column to give: (1) 0.9 ml. of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHF}_2$, b.p. 26.5–27.0°, n_{D}^{20} 1.3429; and (2) 1.4 ml. of methacrolein, b.p. 67.0–69.3°, n_{D}^{20} 1.4129 (reported¹⁴ b.p. 68.4°, n_{D}^{20} 1.4144).

The methacrolein from fraction (3), as well as that obtained in pyrolysis of the difluorocarbinol acetate, was further characterized by preparation of the 2,4-dinitrophenylhydrazone, m.p. 204.5–206°, and the semicarbazone, m.p.

(14) G. Hearne, M. Tamele and W. Converse, *Ind. Eng. Chem.*, **33**, 805 (1941); cf. reference 15.

195–195.5°. The melting points of these derivatives were substantially the same as those reported,¹⁶ and mixed melting points with the corresponding derivatives prepared from an authentic sample of methacrolein were not depressed.

On examination of the aqueous phase from the silica pyrolysis, no isobutyric acid was found.

CF₂=C(CH₃)₂. (a) **With Lithium Aluminum Hydride.**—To a solution of 24 g. of lithium aluminum hydride in 160 ml. of purified tetrahydrofuran at 20–25°, 70 g. of CH₂=C(CH₃)CF₂Cl was added slowly with stirring over a period of ca. 1 hr. When addition was complete, the mixture was refluxed for several hours while product was collected in a –80° trap attached to the reflux condenser outlet. A small additional amount of product and a little tetrahydrofuran was also collected when the reduction mixture was decomposed with dilute hydrochloric acid and heated to boiling.

The product was washed by passage together with a slow stream of air through gas washing bottles containing in sequence 5% aq. potassium hydroxide, water, and two tubes of freshly ignited Drierite. The purified product, 38.8 g. (77% yield), was collected in a final –80° trap.

The washed olefin was carefully fractionated at a reflux ratio of ca. 25:1 through a vacuum-jacketed Podbielniak low-temperature column. The entire charge distilled at a constant b.p. 8.6° (768 mm.) with no forerun and no residue other than the ca. 2 ml. of column hold-up. The thermocouple was recalibrated at the ice point and at the boiling points of two pure liquids immediately after the distillation. The distilled CF₂=C(CH₃)₂ weighed 30.7 g. (61% yield).

Anal. Calcd. for C₄H₈F₂: C, 52.2; H, 6.6; F, 41.2. Found: C, 52.2; H, 6.8; F, 41.1.

In a later reduction of a sample of CH₂=C(CH₃)CF₂Cl which had only been distilled and not fractionated on a column, a dangerous contamination with phosphine resulted from reduction of phosphorus impurities. The phosphine was removed by inclusion of a double gas washing bottle containing 50% aq. silver nitrate in the purification line. (We are indebted to Dr. D. I. Livingston for these observations.) Tests on subsequent runs employing fractionated CH₂=C(CH₃)CF₂Cl showed no phosphine present, but washing with the silver nitrate solution was retained as a safety precaution.

(b) **By Catalytic Hydrogenolysis.**—Hydrogenation of 25 g. of CH₂=C(CH₃)CF₂Cl in ethanol in the presence of Raney nickel at 1600 p.s.i. and 100–200° resulted in the uptake of 40% of one mole of hydrogen. After the catalyst was filtered, distillation on a 5-plate column gave ethanol, 10 g. of recovered CH₂=C(CH₃)CF₂Cl and 8 g. of crude product, b.p. 26–30°. Fractionation of the latter on a 30-plate column gave two plateaus: (1) 2.1 g., b.p. 9.5–10.2°; (2) 0.6 g., b.p. 29.0–30.7°. Fraction (1) was a mixture of CF₂=C(CH₃)₂ with, apparently, ethyl chloride (resulting from reaction of HCl with the ethanol).

Anal. Found: Cl, 8.51; F, 34.32. Calculation for a binary mixture of CF₂=C(CH₃)₂ and ethyl chloride based on % Cl gave 84.5% and on % F gave 83.6% CF₂=C(CH₃)₂.

(c) **Via the Phosphite Ester.**—Pure (CF₂ClC(CH₃)₂O)₃P

(15) R. L. Shriner and A. G. Sharp, *THIS JOURNAL*, **62**, 2245 (1940).

was prepared by reaction of 40 g. (0.276 mole) of the pure CF₂ClC(CH₃)₂OH and 21.9 g. (0.276 mole) of A.R. grade pyridine with 25.0 g. (0.0922 mole) of phosphorus tribromide at room temperature in 75 ml. of anhydrous ether. Pyridine hydrobromide precipitated instantly as the PBr₃ was added. The salt was filtered off by suction, the ether distilled off and the residue distilled to give 35.3 g. (83% yield) of the water-insoluble trialkyl phosphite, b.p. 130–131° (7.5 mm.), as the sole volatile product. A mid-cut was taken for analysis.

Anal. Calcd. for C₁₂H₁₈F₆Cl₃O₃P: C, 31.2; H, 3.94. Found: C, 31.1; H, 4.0.

A mixture of 34 g. of the phosphite and 15 g. of acid-washed zinc dust was stirred for 1 hr. at 190°. The volatile product collected in a cold trap attached to the reflux condenser gave, after purification on the gas-washing line, 4.9 g. of CF₂=C(CH₃)₂.

The infrared spectra of the CF₂=C(CH₃)₂ products from methods (a), (b) and (c) were substantially identical throughout, and all displayed the characteristic strong 1765 cm.⁻¹ C=CF₂ absorption band.

Reactions of CF₂=C(CH₃)₂. (a) **Bromination.**—To 0.75 ml. of CF₂=C(CH₃)₂ (from method (c)) was added 1 g. of liquid bromine drop by drop at –80° until a slight bromine color remained on standing 2 days and warming to room temperature. The first ca. 0.5 g. of bromine reacted rapidly with considerable evolution of heat, but the remainder reacted slowly. The product was taken up in ether, washed 4 times with water, dried over magnesium sulfate, the ether distilled off through a short glass helices column and the residue distilled through a semi-micro all-glass Claisen still to give, as the sole distillate, 0.7 g. of CF₂BrCBr(CH₃)₂, b.p. 130° (760 mm.). The dibromide was a colorless, highly refractive liquid.

Anal. Calcd. for C₄H₈F₂Br₂: C, 19.1; H, 2.40; F, 15.0; Br, 63.4. Found: C, 19.5; H, 2.44; F, 14.9; Br, 63.1.

(b) **Silica Pyrolysis.**—Pyrolysis of several 3–4 g. samples of the olefin was conducted over silica at 350° and the resulting gases led through an aniline trap, then a –80° trap. No (CH₃)₂C=C=O was formed as evidenced by no N-phenyl-isobutyramide isolable from the trap containing aniline. Unchanged olefin was isolated from the –80° trap.

(c) **Oxidation.**—A mixture of 3.4 g. of CF₂=C(CH₃)₂ and 7.9 g. of potassium permanganate in 200 ml. of water was stirred at 0° under a –80° reflux condenser. Oxidation was nearly complete in 2 hr. and complete in 4 hr. The slight remaining excess of permanganate and the manganese dioxide were destroyed by addition of sodium bisulfite and the mixture distilled into a solution of 2,4-dinitrophenylhydrazine reagent until ca. 50 ml. had been distilled over. The precipitate of the hydrazone was collected, washed and dried, to give 117 mg., m.p. 118–122°. Half of this, 60 mg., was crystallized to give 30 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 122–124°, mixed m.p. 120–123.5°, with an authentic sample of m.p. 120–123.5°.

Infrared spectra were obtained on the substances as gases at ca. 10 cm. pressure in a 10 cm. cell, using a Perkin-Elmer Corporation Model 21 spectrometer.

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