Perhalo Ketones. XV.[1] The Preparation and Some Reactions of Perhalocyclopentanones and -hexanones

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Two convenient routes are described for the preparation of perhalogenated cyclopentanones and -hexanones from the corresponding 1,2-dichloroperfluorocyclo olefins. The ketones were converted into a number of derivatives, several of which were obtained through additions to their highly reactive carbonyl groups.

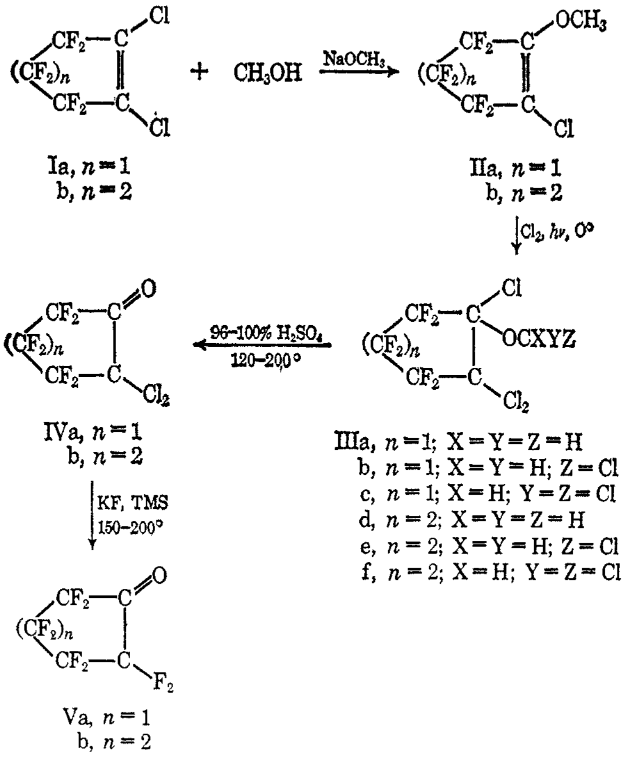
The chemistry of perfluorinated ketones has evoked much interest in recent years as indicated by the large number of patents and publications in this area. The present paper describes the synthesis and some reactions of perhalogenated cyclopentanones and cyclohexanones. Related chemistry in the perhaloacetone and -cyclobutanone areas has been discussed by various workers.[2]

Other preparations of perfluorocyclopentanone and -hexanone have appeared in the literature,[3] but few of their reactions have been reported.

Discussion

The syntheses of 2,2-dichloroperfluorocyclopentanone (IVa) and -hexanone (IVb) were effected in a three-step reaction sequence starting with 1,2-dichloroperfluorocyclopentene (Ia) and -hexene (Ib), respectively. Thus, treatment of these olefins with sodium hydroxide in methanol provided the corresponding 1-chloro-2-methoxyperfluorocycloalkenes (IIa and IIb). Photochlorination of IIa and IIb resulted in saturation of the double bond and partial replacement of the methoxyl hydrogen atoms by chlorine.[4] Hydrolysis of the resulting ethers (IIIa–f) with concentrated sulfuric acid gave the related ketones (IVa and b) in excellent yields; the ethers with partially chlorinated methoxyl groups exhibited increased rates of hydrolysis. The use of 100% sulfuric acid resulted in optimum ketone yields; 95% sulfuric acid gave solutions of ketone hydrates (*vide infra*). The treatment of IVa and IVb with potassium fluoride in polar solvents, such as dimethylformamide and tetramethylene sulfone (TMS), proved to be a good route to perfluorocyclopentanone (Va) and -hexanone (Vb), respectively (see Scheme I).

SCHEME I



Ketones Va and Vb were also prepared by another reaction sequence starting from the 1,2-dichloroperfluoro olefins Ia and Ib. Thus, these materials were epoxidized with basic hydrogen peroxide to provide 1,2-dichloroperfluorocyclopentene epoxide (VIa) and 1,2-dichloroperfluorocyclohexene epoxide (VIb); VIb was obtained in approximately 40% yield, whereas the yield for VIa was somewhat lower. A pure sample of VIb was tested for thermal stability by refluxing for several hours at 114°; there was no indication of decomposition. Treatment of this epoxide with potassium fluoride in tetramethylene sulfone (TMS) afforded a mixture of ketone Vb and 2-chloroperfluorocyclohexanone (VII). A similar treatment of VIa gave Va in very low yields (see Scheme II).

Reactions of Perhalo Ketones.—2,2-Dichloroperfluorocyclohexanone (IVb) was pyrolyzed by passing it through an Alundum tube packed with glass helices and heated to 375°. The recovered products were identified as 2-chloroperfluorocyclohexenone (VIIIa), 2,3-dichloroperfluorocyclohexenone (VIIIb), and silicon tetrafluoride. Compound VIIIb could be converted into VIIIa by treatment with hydrogen fluoride over Cr_2O_3 at 375°. The boiling point and ^{19}F nmr and in-

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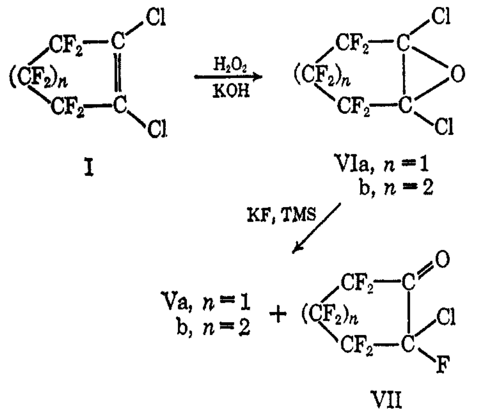
[1] (a) Part XIV: J. J. Murray, *J. Org. Chem.*, in press. (b) R. F. Sweeney, B. Veldhuis, E. E. Gilbert, L. G. Anello, R. J. DuBois, and W. J. Cunningham, *ibid.*, **31**, 3174 (1966).

[2] (a) D. C. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961); (b) D. C. England, U. S. Patents 3,036,091 (1961), 3,039,995 (1962), 3,040,058 (1963), 3,140,298 (1964), and 3,148,220 (1964); (c) British Patent (Du Pont) 904,877 (1962); (d) I. L. Knunyants, C. Ch'ing-yun, and N. P. Gambaryan, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 686 (1960); (e) I. L. Knunyants and Yu. A. Cheburkov, *ibid.*, 678 (1960); (f) I. L. Knunyants and Yu. A. Cheburkov, *ibid.*, 2168 (1960); (g) V. F. Plakhova and N. P. Gambaryan, *ibid.*, 681 (1961); (h) A. G. Pittman and D. L. Sharp, *Polymer Letters*, **3**, 379 (1965); (i) A. G. Pittman and D. L. Sharp, *Text. Res. J.*, **35**, 190 (1965); (j) A. G. Pittman, D. L. Sharp, and B. A. Ludwig, Polymer Preprints of Papers, presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 1093; (k) R. P. Graham, *J. Org. Chem.*, **31**, 957 (1966); (l) D. P. Carlson and A. S. Milian, Syntheses and Reactions of Some Perfluorocarbon Expoxides, Presented at the Fourth International Fluorine Symposium on Fluorine Chemistry, Estes Park, Colorado, July 24–28, 1967.

[3] (a) F. F. Holub and H. A. Bigelow, *J. Amer. Chem. Soc.*, **72**, 4879 (1950); (b) W. T. Miller, U. S. Patents 2,712,514 and 2,712,555 (1955); (c) British Patent (Du Pont) 1,019,788 (1966).

[4] R. F. Sweeney, L. G. Anello, and D. Werner, Abstracts, the 154th National Meeting of the Amerian Chemical Society, Chicago, Ill., Sept 1967, p K001.

SCHEME II



frared spectra of VIIIb were identical with those reported earlier.[1b]

Hydrates of the saturated ketones are formed readily; thus the exothermic reaction of IVa, IVb, Va, and Vb with water gave the respective 1:1 adducts (IXa-d) which were well-defined, distillable compounds.

The reduction of IVa, IVb, Va, and Vb with sodium borohydride gave the corresponding secondary alcohols Xa-d.

Ketones Va and Vb undergo reaction with potassium fluoride in polar solvents to afford the perfluorinated alkoxides XIa and XIb which may be isolated, and are stable at ambient temperature.

Hydroxy acids (XIIa and XIIb) are produced upon admixture of Va and b with malonic acid in pyridine.

Ketone Vb was found to undergo the Wittig reaction smoothly. Accordingly, ethyl perfluorocyclohexylidenyl acetate (XIII) was obtained when the ketone was heated with carbethoxymethylenetriphenylphosphorane in ether (see Scheme III).

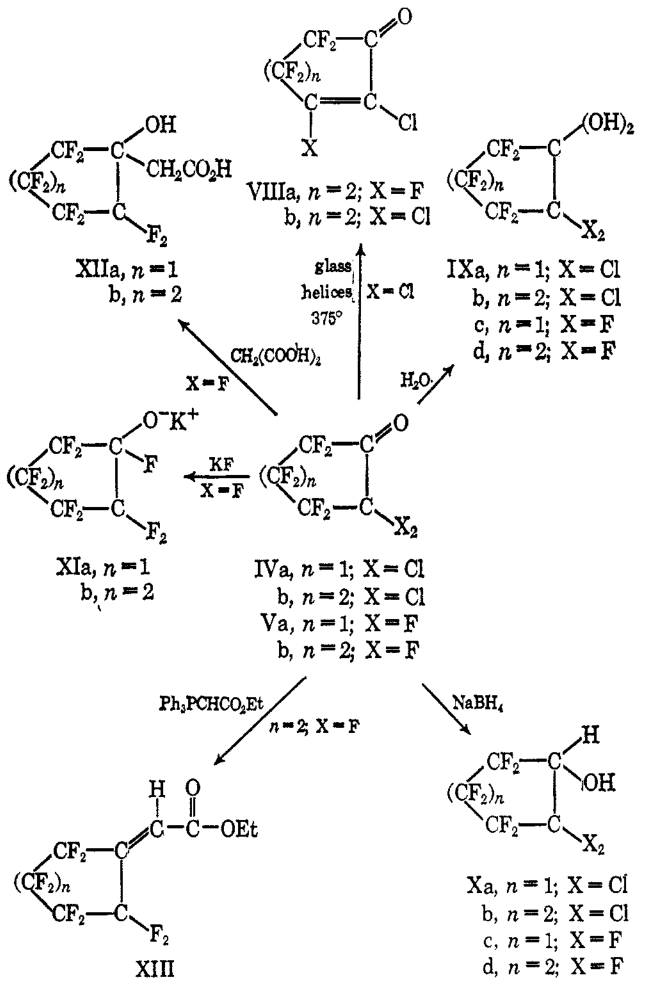
Acrylate Derivatives.—An interesting series of acrylate monomers (XIVa-d) was prepared by the reactions of alcohols Xc and Xd, and alkoxides XIa and XIb with acrylyl chloride. When the alcohols were employed, a by-product, arising from the addition of HCl across the acrylate double bond, was also formed; this was minimized by the use of quinoline as an acid acceptor.

The various acrylates were converted into their corresponding polymers (XVa-d) by free-radical polymerization in aqueous dispersions.

Malonic Acid Derivatives.—When hydroxy acids XIIa and XIIb were heated at 40-60° with thionyl chloride and catalytic amounts of pyridine, their respective acid chlorides (XVIa and XVIb) were formed. Compound XVIa could be isolated readily by glpc separation. In contrast, XVIb decomposed on the column to give primarily the lactone XVII (*vide infra*). Separation of XVIb from unreacted XIIb was achieved by extraction with cold carbon tetrachloride.

Both XVIa and XVIb gave a mixture of products upon heating with catalytic amounts of pyridine at 75°, or upon prolonged heating at lower temperatures. Examination of the product mixture from XVIb showed lactone XVII to be a major constituent. Compound XVII is also the main product when XIIb is heated with phosphorus pentoxide. On the other hand, dehydration of XIIb with 100% sulfuric acid leads to the unsaturated acid, XVIII. In an attempt to convert XVIII into its acid chloride, it was heated with thionyl chloride and a trace of pyridine. Surprisingly enough, the product proved to be the acid fluoride XIX in 47% yield. The acid XVIII was successfully converted into its acid chloride (XX) in high yield upon heating with benzotrichloride. Both XIX and XX reverted to XVIII upon exposure to moisture and gave XIII when warmed with ethanol (see Scheme IV).

SCHEME III



Experimental Section[5]

1-Chloro-2-methoxyperfluorocyclohexene (IIb).—A solution of 142 g (2.53 mol) of potassium hydroxide in 400 g of absolute methanol was added over a period of 4 hr to 748 g (2.53 mol) of 1,2-dichloroperfluorocyclohexene in 100 g of absolute methanol. The rate of addition was regulated to maintain the reaction mixture at about 45°. The product was drowned in a large excess of water; the organic layer was separated, extracted with ether, and dried over P_2O_5. Distillation gave 379 g (51%) of IIb, bp 135-136°.

Anal. Calcd for $C_7H_3OClF_8$: C, 12.2; F, 52.3. Found: Cl, 12.2; F, 52.8.

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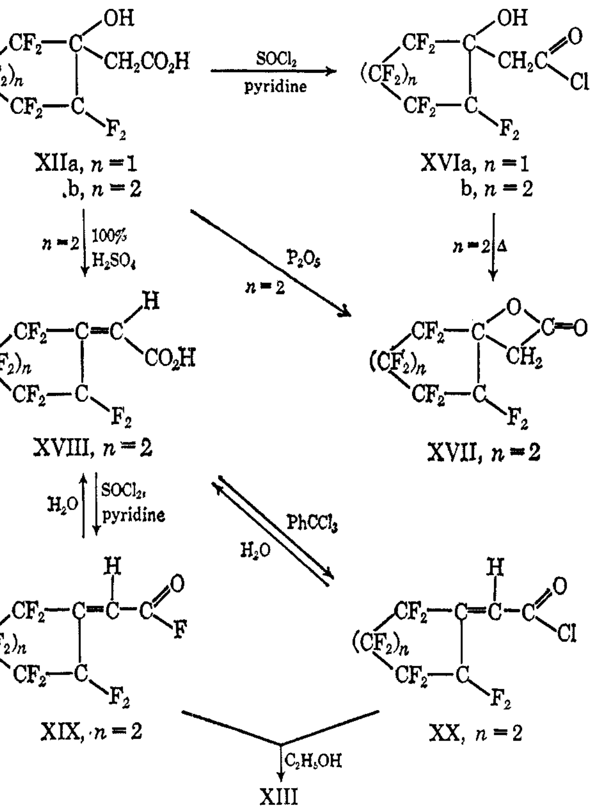
[5] Boiling points and melting points are uncorrected; melting points were taken on a Fisher-Johns hot stage melting point apparatus. The elemental analyses were by the Galbraith Analytical Laboratories and Messrs. G. E. Mohler, R. J. Tepper, and W. Zazulak of the Industrial Chemicals Analytical Laboratory, Morristownship, N. J. Infrared spectra were determined in carbon tetrachloride (unless otherwise noted) on a Perkin-Elmer Model 137 Infracord spectrophotometer. Gas-liquid partition chromatographic analyses and separations were carried out with an Aerograph Autoprep, Model A-700, equipped with a 20-ft column containing 20% QF-1 on 42-60 mesh firebrick.

Scheme IV



1-Chloro-2-methoxyperfluorocyclopentene (IIa).—Following the procedure described above, 315 g (1.29 mol) of 1,2-dichloroperfluorocyclopentene was treated with 724 g (1.29 mol) of potassium hydroxide in 1980 ml of absolute methanol to give 225.8 g (85%) of IIa, bp 130–132°.

Photochlorination of 1-Chloro-2-methoxyperfluorocyclohexene.—Compound IIb (362 g, 1.25 mol), contained in an ice-water-cooled Vycor immersion apparatus, was irradiated with a 450-W, high pressure mercury lamp (Hanovia 79A36L) as chlorine gas (1.6 mol) was bubbled in over a 6-hr period; 0.44 mol of hydrogen chloride was evolved. A 100-g sample of the product was withdrawn and a small portion analyzed by glpc; the remainder was distilled. The analysis showed that the mixture consisted of 11.6 vol % of IIb, 62 vol % of 1,1,2-trichloro-2-methoxyperfluorocyclohexane (IIId), and 18.5 vol % of 1,1,2-trichloro-2-chloromethoxyperfluorocyclohexane (IIIe). Distillation of the product mixture gave mainly IIId (55 g), bp 187° and mp 101–103°, and 22 g of a higher boiling liquid.

Anal. Calcd for $C_7H_3Cl_3F_8O$: H, 0.83; Cl, 29.5; F, 42.0. Found: H, 0.80; Cl, 29.7; F, 41.5.

The chlorination of the remaining material was continued with 0.93 mol of chlorine being passed in over 3.5 hr; 0.47 mol of hydrogen chloride was evolved. Another 100-g sample of the reaction mixture was withdrawn and a portion was analyzed by glpc while the remainder was distilled. The analysis showed that the mixture consisted of 5.3% IIb, 18.4% IIId, 68% IIIe, and 8% higher boiler. Distillation of the product mixture gave mainly IIIe (62 g), bp 83–84° (10 mm), and 11 g of a higher boiling liquid.

Anal. Calcd for $C_7H_2Cl_4F_8O$: H, 0.31; Cl, 35.9; F, 38.4. Found: H, 0.45; Cl, 35.6; F, 37.9.

Chlorination of the remaining product mixture was continued with 0.50 mol of chlorine being passed in over a 2-hr period as 0.35 mol of hydrogen chloride evolved. A small portion of the product (278 g) was analyzed by glpc and a 139-g aliquot was distilled. The analysis showed that the product mixture consisted of 50.5% IIIe and 48% 1,1,2-trichloro-2-dichloromethoxyperfluorocyclohexane, IIIf. Distillation gave IIIe (72 g) and IIIf (64 g), bp 94° (10 mm).

Anal. Calcd for $C_7HCl_5F_8O$: H, 0.23; Cl, 41.2; F, 35.0. Found: H, 0.22; Cl, 40.7; F, 35.2.

Photochlorination of 1-Chloro-2-methoxyperfluorocyclopentene.—Using the techniques described above, the photochlorination of IIa gave three analgous compounds.

A.—1,1,2-Trichloro-2-methoxyperfluorocyclopentane IIIa had bp 172–175° and mp 95–100°.

Anal. Calcd for $C_6H_3Cl_3F_6O$: C, 23.1; H, 0.96. Found: C, 23.4; H, 0.80.

B.—1,1,2-Trichloro-2-monochloromethoxyperfluorocyclopentane IIIb had bp 76–78° (8 mm).

Anal. Calcd for $C_6H_2Cl_4F_6O$: H, 0.58; Cl, 41.0. Found: H, 0.50; Cl, 40.6.

C.—1,1,2-Trichloro-2-dichloromethoxyperfluorocyclopentane IIIc decomposed before boiling.

Anal. Calcd for $C_6HCl_5F_6O$: H, 0.26; Cl, 46.6; F, 30.0. Found: H, 0.25; Cl, 46.5; F, 30.0.

2,2-Dichloroperfluorocyclohexanone (IVb).—A mixture of 445 g (0.11 mol) of 1,1,2-trichloro-2-chloromethoxyperfluorocyclohexane and 200 g of 100% H_2SO_4 was slowly heated to 160–185°. At this temperature a rapid evolution of HCl occurred. The reaction was considered to be complete when the flask contents reached 200°. The organic product was distilled as formed using a 36-in. vacuum-jacketed column packed with glass helices. The product (46 g) was redistilled to give a 3-g forecut and 38 g (76%) of 2,2-dichloroperfluorocyclohexanone (IVb), bp 116–117°. The infrared spectrum showed a C=O band at 5.6 μ.

Anal. Calcd for $C_6Cl_2F_8O$: Cl, 22.8; F, 49.0. Found: Cl, 22.9; F, 49.0.

2,2-Dichloroperfluorocyclopentanone (IVa).—A mixture of 1,1,2-trichloro-2-chloromethoxyperfluorocyclopentane and 1,1,2-trichloro-2-dichloromethoxyperfluorocyclopentane, treated as in the previous experiment, gave the ketone IVa (88% yield), bp 87–88°.

Perfluorocyclohexanone (Vb).—2,2-Dichloroperfluorocyclohexanone (68 g, 0.22 mol) was added over a 3-hr period to a stirred mixture of 50 g (0.86 mol) of anhydrous potassium fluoride and 150 g of tetramethylene sulfone at 150°. The product was distilled from the reaction vessel as formed. The product was redistilled through an 18-in. spinning-band column to give a 1.0-g forecut (bp 41–54°), 31 g (74%) of perfluorocyclohexanone (Vb), bp 54–56°, and 22 g of starting material. The infrared spectrum showed a C=O band at 5.55 μ.

Anal. Calcd for $C_6F_{10}O$: C, 25.84; F, 68.34. Found: C, 25.52; F, 67.6.

Perfluorocyclopentanone (Va).—2,2-Dichloroperfluorocyclopentanone, treated as in the previous experiment, gave the ketone Va (50%), bp 23–24°. The infrared spectrum showed a C=O band at 5.49 μ.

Anal. Calcd for C_5F_8O: C, 26.32; F, 66.67. Found: C, 26.15; F, 66.85.

1,2-Dichloroperfluorocyclohexene Epoxide (VIb).—1,2-Dichloroperfluorocyclohexene (90 g, 0.3 mol) was added dropwise over a 75-min period at 0° to a solution of 57 g (1.02 mol) of potassium hydroxide and 151.5 g (1.35 mol) of 30% hydrogen peroxide in 450 ml of methanol. After stirring for an additional 80 min, the mixture was diluted with 400 ml of water, whereupon the lower layer (42.4 g) was separated and dried over sodium sulfate. Infrared analysis indicated that 89% of this layer was the desired epoxide (42% yield); the remainder was mainly the starting olefin.

A pure sample of the epoxide (bp 114°) could be obtained by further subjecting this mixture to treatment with basic hydrogen peroxide.

Anal. Calcd for $C_6Cl_2OF_8$: C, 23.2; H, 0.00; Cl, 22.8; F, 48.9. Found: C, 23.13; H, 0.00; Cl, 22.7; F, 49.0.

The infrared spectrum exhibited an absorption band at 7.58 μ which appears to be characteristic of halogenated epoxides.

1,2-Dichloroperfluorocyclopentene Epoxide (VIa).—Following the procedure described above, 245 g of 1,2-dichloroperfluorocyclopentene was treated with 224 g of KOH and 510 ml of 30% hydrogen peroxide in 950 ml of methanol to provide 54 g (19%) of epoxide VIa, bp 86.5–88°.

Anal. Calcd for $C_5F_6Cl_2O$: H, 0.00; F, 43.8. Found: H, 0.00; F, 41.8.

Perfluorocyclohexanone Vb and 2-Chloroperfluorocyclohexanone (VII) from Epoxide VIb.—Potassium fluoride (35 g, 0.6 mol) was slurried in 175 g of tetramethylene sulfone. The temperature was raised to 160° and a slow stream of nitrogen was passed through the system. Epoxide VIb (100 g, 0.32 mol) was added dropwise to this mixture and the resulting products were distilled as they formed. When epoxide addition was complete, the temperature was increased slowly to 200°. A total of 70 g of distillate was collected; subsequent fractional distillation gave, in the early fractions, 22.8 g (27% yield) of perfluorocyclohexanone (Vb), bp 50–55°. In later fractions, approximately 6 g (8% yield) of pure 2-chloroperfluorocyclohexanone (Vb) was obtained. Redistillation provided an analytical sample, bp 85–86.5°.

Anal. Calcd for C_6ClOF_9: C, 24.5; Cl, 12.0; F, 58.0. Found: C, 22.7; Cl, 11.6; F, 59.0.

The infrared spectrum exhibited a carbonyl absorption at 5.52 μ.

In a similar experiment, a mixture of 5.85 g (0.02 mol) of epoxide and about 4.0 g of the olefin was added to a slurry of 8.7 g (0.15 mol) of potassium fluoride in tetramethylene sulfone while the reaction temperature was increased from 130 to 180°. A total of 0.78 g (18% yield) of Vb and 1.94 g (42% yield) of VII were obtained.

Perfluorocyclopentanone (Va) from Epoxide VIa.—Following the above procedure, 15 g of epoxide VIa (containing some of the parent 1,2-dichloroperfluorocyclopentene as an impurity) was treated with 15 g of potassium fluoride in 175 g of tetramethylene sulfone at 160–170° to provide 0.7 g (7%) of ketone Va.

Pyrolysis of 2,2-Dichloroperfluorocyclohexanone.—During a period of 2.75 hr, 55 g (0.18 mol) of 2,2-dichloroperfluorocyclohexanone vapors were passed through a $^5/_8$ in. i.d. × 36 in. long Alundum reactor packed with glass helices; the temperature was maintained at 375° over a 30-in. length by an electric furnace. The products were passed into −78 and −198° cooled traps from which the reaction products were isolated by fractional distillation. The −198° trap contained 28 g of material which was identified by infrared analysis to be almost pure SiF_4, contaminated with traces of CO and CF_2Cl_2. The −78° trap contained 52 g of product which, upon distillation, gave a 1.0-g forecut, 7 g (16%) of 2-chloroperfluoro-2-cyclohexanone (VIIIa), bp 107°, 10 g of 2,2-dichloroperfluorocyclohexenone (IVb), bp 116°, and 28 g (70%) of 2,3-dichloroperfluoro-2-cyclohexenone VIIIb, bp 135–136°. The infrared spectrum of VIIIa showed a C=O absorption at 5.7 and a C=C band at 6.05 μ.

Anal. Calcd for C_6ClF_7O: C, 28.07; Cl, 13.83; F, 51.85. Found: C, 27.65; Cl, 13.64; F, 52.05.

The infrared spectrum of VIIIb showed a C=O band at 5.71 and a C=C band at 6.32 μ.

Anal. Calcd for $C_6Cl_2F_6O$: C, 26.4; Cl, 26.0; F, 41.8. Found: C, 26.1; Cl, 25.7; F, 41.2.

2,2-Dichloroperfluorocyclohexanone Hydrate (IXb).—Water (5 g, 0.28 mol) was slowly added to 25 g (0.08 mol) of 2,2-dichloroperfluorocyclohexanone. After all the water was added, the reaction mixture became a semisolid. Distillation gave a 5-g forecut (mainly water mixed with hydrate) and 22 g (84%) of 2,2-dichloroperfluorocyclohexanone hydrate (IXb), bp 116–118° and mp 95–96°. The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_6H_2Cl_2F_8O_2$: H, 0.61; Cl, 21.6; F, 46.2. Found: H, 0.45; Cl, 21.0; F, 45.8.

2,2-Dichloroperfluorocyclopentanone Hydrate (IXa).—2,2-Dichloroperfluorocyclopentanone, treated as in the previous experiment, gave the hydrate IXa (47%), bp 107–108° and mp 38–40°. The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_5H_2Cl_2F_6O_2$: H, 0.72; Cl, 25.45; F, 40.86. Found: H, 0.85; Cl, 25.1; F, 41.2.

Perfluorocyclohexanone Hydrate (IXd).—Perfluorocyclohexanone, treated as previously described, gave the hydrate IXd (85%), mp 129–131°. The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_6H_2F_{10}O_2$: H, 0.68; F, 64.2. Found: H, 0.71; F, 63.3.

Perfluorocyclopentanone Hydrate (IXc).—Perfluorocyclopentanone, treated as previously described, gave the hydrate IXc (97%), bp 124–125° and mp 75–76°. The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_5F_8H_2O_2$: C, 24.39; F, 61.78; H, 0.81. Found: C, 24.75; F, 62.02; H, 0.85.

1-Hydro-2,2-dichloroperfluorocyclohexanol (Xb).—To a mixture of 8 g (0.21 mol) of $NaBH_4$ and 50 ml of anhydrous ether was slowly added 59 g (0.19 mol) of 2,2-dichloroperfluorocyclohexanone. After the addition was complete, the mixture was refluxed for 6 hr. The excess reagent and $NaBH_4$ complex were decomposed by the addition of aqueous sulfuric acid. The lower layer was separated and the upper aqueous layer was extracted with ether. The oil layer and ethereal extracts were combined, dried, and distilled to give 30 g (50%) of 1-hydro-2,2-dichloroperfluorocyclohexanol (Xb), bp 72° (40 mm). The infrared spectrum showed on OH band at 3.0 μ.

Anal. Calcd for $C_6H_2Cl_2F_8O$: C, 23.80; H, 0.64; Cl, 22.68; F, 48.56. Found: C, 22.5; H, 0.78; Cl, 22.2; F, 47.8.

1-Hydro-2,2-dichloroperfluorocyclopentanol (Xa).—2,2-Dichloroperfluorocyclopentanone, treated as in the previous experiment, gave the alcohol Xa (74%), bp 67–69° (76 mm). The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_5H_2Cl_2F_6O$: C, 22.80; H, 0.76; Cl, 26.99; F, 43.34. Found: C, 22.5; H, 0.84; Cl, 26.5; F, 42.7.

1-Hydroperfluorocyclohexanol (Xd).—Perfluorocyclohexanone treated as previously described gave the alcohol Xd (91%), bp 106–108° and mp 66–68°. The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_6F_{10}H_2O$: C, 25.71; F, 67.86; H, 0.71. Found: C, 26.01; F, 67.75; H, 0.80.

1-Hydroperfluorocyclopentanol (Xc).—Perfluorocyclopentanone, treated as previously described, gave the alcohol Xc (77%), bp 86–87°. The infrared spectrum showed an OH band at 3.0 μ.

Anal. Calcd for $C_5H_2F_8O$: H, 0.86; F, 65.5. Found: H, 1.0; F, 66.3.

Perfluorocyclohexanone–Potassium Fluoride Adduct (XIb).—A mixture of 7.0 g (0.17 mol) of anhydrous acetonitrile, 1.5 g (0.025 mol) of potassium fluoride, and 7.0 g (0.025 mol) of perfluorocyclohexanone was stirred at 55° for 1 hr. The resulting product was cooled to room temperature and the organic volatile products were removed under vacuum. A white, crystalline solid (XIb, 92%) was isolated. The infrared spectrum showed no C=O absorption in the 5.5–5.9-μ region.

Anal. Calcd for $C_6F_{11}KO$: C, 21.43; F, 62.20. Found: C, 19.9; F, 61.2.

(1-Hydroperfluorocyclopentyl)acetic Acid (XIIa).—Perfluorocyclopentanone (147 g, 0.64 mol) was added dropwise to a stirred mixture of 93.5 g (0.90 mol) of malonic acid and 180 ml of pyridine; the temperature was maintained at about 10 to 25°. After stirring for an additional 18 hr at ambient temperature, the mixture was diluted with 900 ml of water and then acidified with 192 ml of 12 *N* hydrochloric acid. The resulting solution was extracted with five 200-ml portions of ether. The organic fractions were combined, washed with 150 ml of water, and dried over sodium sulfate. The solvent was removed under reduced pressure. Recrystallization of the residue from carbon tetrachloride afforded 163 g (89% yield) of colorless crystals. Repeated recrystallization provided an analytical sample, mp 117–119°.

Anal. Calcd for $C_7H_4O_3F_8$: C, 29.2; H, 1.4; F, 52.8. Found: C, 30.18; H, 1.87; F, 53.18.

The infrared spectrum (KBr) exhibited absorption bands at 2.8, 3.3, and 5.83 μ corresponding to the hydroxyl and acid functions.

(1-Hydroxyperfluorocyclohexyl)acetic Acid (XIIb).—Following the above procedure, 100 g (0.36 mol) of perfluorocyclohexanone (Vb) was allowed to react with 83.2 g (0.8 mol) of malonic acid in 240 ml of pyridine. A total of 91 g (83% yield) of colorless crystals, mp 122–125°, was obtained.

Anal. Calcd for $C_8H_4O_3F_{10}$: C, 28.4; H, 1.19; F, 56.2. Found: C, 28.22; H, 1.16; F, 56.07.

The infrared spectrum (KBr) showed absorptions at 2.9 (OH), 3.3, and 5.86 μ (CO_2H).

Ethyl (Perfluorocyclohexylidenyl)acetate (XIII).—Perfluorocyclohexanone (Vb) (10 g, 0.036 mol), carbethoxymethylene triphenylphosphorane (5.2 g, 0.015 mol) and ethyl ether (10 ml) were placed in an aerosol compatibility tube and heated for 3 hr at 70–80°. After cooling to ambient temperature, the mixture was filtered to remove the by-product, triphenylphosphine oxide (3.2 g). Ether was distilled from the filtrate to leave a liquid residue; this was purified by glpc separation to provide 3.0 g (57% yield) of a water-white liquid.

Anal. Calcd for $C_{10}H_6O_2F_{10}$: C, 34.5; H, 1.7; F, 54.6. Found: C, 34.4; H, 1.62; F, 54.6.

The infrared spectrum exhibited absorption bands at 5.72 (ester C=O) and 5.95 μ (C=C stretching).

1-Hydroperfluorocyclohexyl Acrylate (XIVb).—Acrylyl chloride (30 g, 0.33 mol) was rapidly added to 44 g (0.16 mol) of 1-hydroperfluorocyclohexanol containing 0.1 g of hydroquinone. The temperature was raised to 75° and maintained for 10 hr. Hydrogen chloride was evolved during the reaction. Fractionation of the resultant mixture gave 29 g (55%) of 1-hydroperfluorocyclohexyl acrylate (XIVd), bp 51–53° (35 mm), and 17 g (29%) of 1-hydroperfluorocyclohexyl-β-chloropropionate, bp 68° (10 mm).

The infrared spectrum of XIVb showed a C=O band at 5.8 and C=C band at 6.1 μ.

Anal. Calcd for $C_9F_{10}H_4O_2$: F, 56.89; H, 1.20. Found: F, 58.0; H, 1.40.

1-Hydroperfluorocyclopentyl Acrylate (XIVa).—1-Hydroperfluorocyclopentanol, treated as in the previous experiment, gave the acrylate XIVa (32%), bp 57–61° (10 mm).

Anal. Calcd for $C_8F_8H_4O_2$: C, 33.80; F, 53.52; H, 1.48. Found: C, 33.62; F, 53.61; H, 1.52.

The infrared spectrum showed a C=O absorption at 5.8 and a C=C band at 6.1 μ.

Perfluorocyclohexyl Acrylate (XIVd).—Perfluorocyclohexanone (45 g, 0.19 mol) was added to a slurry of 9.3 g (0.16 mol) of KF in 45 g of acetonitrile. The mixture was heated to 50° for 1 hr and then cooled to 20°. Acrylyl chloride (14.5 g, 0.16 mol) was added while the reaction temperature was maintained at 25°. The flask contents were washed with water. The lower layer was dried and distilled to give 36 g (53%) of perfluorocyclohexyl acrylate (XIVd), bp 64° (37 mm). The infrared spectrum showed a C=C band at 5.5 and a C=C band at 6.12 μ.

Anal. Calcd for $C_9F_{11}H_3O_2$: F, 59.37; H, 0.85. Found: F, 58.0; H, 0.90.

Perfluorocyclopentyl Acrylate (XIVc).—Perfluorocyclopentanone treated as in the previous experiment gave the acrylate XIVc (58%), bp 59–61° (58 mm). The infrared spectrum showed a C=O band at 5.5 and a C=C band at 6.1 μ.

Anal. Calcd for $C_8F_9H_3O_2$: F, 56.92; H, 0.99. Found: F, 57.5; H, 1.1.

Preparation of Polyacrylates (XVa–d).—Polymers of the various acrylates were prepared by polymerization of the acrylate ester monomers in aqueous media. In a typical polymerization reaction, 100 g of acrylate ester monomer (XVa), 480 g of deionized water, 3.0 g of sodium lauryl sulfate, and 0.5 g of potassium persulfate were charged to a 1-l., three-necked flask. The mixture was purged by bubbling nitrogen through it, stirred to induce emulsification, and heated to 55° for 6 hr. A latex was obtained containing 21% by weight of solids.

(1-Hydroxyperfluorocyclohexyl)acetyl Chloride (XVIb).—A mixture of 3.0 g (0.01 mol) of (1-hydroxyperfluorocyclohexyl)-acetic acid (XIIb), 1.92 g (0.016 mol) of thionyl chloride and two drops of pyridine was heated for 7 hr while the temperature was raised from 26 to 41°. Infrared analysis of the mixture indicated that most of the starting hydroxy acid had been converted into the hydroxy acid chloride. Attempts to isolate a pure sample of the acid by glpc were unsuccessful; the material eliminated hydrogen chloride on the chromatographic column to give predominantly the corresponding lactone (XVII) (*vide infra*). A portion of the reaction mixture was then added to carbon tetrachloride; refrigeration of this solution caused unreacted hydroxy acid to deposit leaving the acid chloride in the supernatant liquid. The infrared spectrum of this solution exhibited a hydroxyl absorption band at 2.83 and a band corresponding to the acid chloride function at 5.6 μ; no acid or lactone bands were present. Further heating of the orginal reaction mixture for 6 hr at 75° caused about 30% of the hydroxy acid chloride to be converted into the lactone (*vide infra*).

(1-Hydroxyperfluorocyclopentyl)acetyl Chloride (XVIa).—A mixture of 15.3 g (0.05 mol) of (1-hydroxyperfluorocyclopentyl) acetic acid (XIIa), 10.7 g (0.09 mol) of thionyl chloride, and 4 drops of pyridine was heated for 5 hr at 60°. Infrared analysis indicated that the conversion of the hydroxy acid into the hydroxy acid chloride was essentially complete at that time. Further heating for 6 hr at 75° resulted in the formation of some secondary products. However, gas chromatographic analysis showed that approximately 75% of the reaction mixture still consisted of the hydroxy acid chloride. An analytical sample, which was a colorless liquid, was obtained by glpc.

Anal. Calcd for $C_7H_3ClO_2F_8$: H, 0.99; F, 49.6. Found: H, 0.95; F, 50.7.

The infrared spectrum exhibited bands at 2.85 (hydroxyl) and 5.65 (acid chloride C=O) μ.

(1-Hydroxyperfluorocyclohexyl)acetic Acid β-Lactone (XVII).—An intimate mixture of 5.0 g (0.015 mol) of (1-hydroxyperfluorocyclohexyl)acetic acid (XIIb) and 4.26 g (0.03 mol) of phosphorus pentoxide was heated in a micro distillation apparatus until 3.9 g of distillate, boiling range of *ca.* 135–145°, was collected. Glpc analysis showed this to be 95% pure (77% yield). An analytical sample was obtained by glpc separation.

Anal. Calcd for $C_8H_2O_2F_{10}$: H, 0.63; F, 59.4. Found: H, 0.66; F, 58.92.

The lactone carbonyl absorption occurs at 5.3 with a shoulder at 5.23 μ.

(Perfluorocyclohexylidenyl)acetic Acid (XVIII).—(1-Hydroxyperfluorocyclohexyl)acetic acid (XIIb) (23.5 g, 0.70 mol) was mixed with 35.2 g of 100% sulfuric acid and heated until 22 g of distillate (bp 190–205°) had been collected. This material, which solidified upon cooling to ambient temperature, was recrystallized from petroleum ether (bp 65–110°). A total of 19.9 g (89% yield) of colorless crystals was obtained. An analytical sample, mp 66–67°, was prepared by further recrystallization from petroleum ether.

Anal. Calcd for $C_8H_2O_2F_{10}$: H, 0.63; F, 59.4. Found: H, 0.65; F, 58.94.

The infrared spectrum displays bands at 5.77 (shoulder at 5.65) and 5.94 μ corresponding to the acid and olefinic functions, respectively.

(Perfluorocyclohexylidenyl)acetyl Fluoride (XIX).—(Perfluorocyclohexylidenyl)acetic acid (5.0 g, 0.02 mol), 2.38 g (0.02 mol) of thionyl chloride, and 1 drop of pyridine were mixed and the temperature slowly was raised to 80°. After 30 min, the temperature was increased and 2.7 g of colorless liquid (bp *ca.* 120°) was distilled from the mixture. Glpc and infrared analysis indicated that 93% of this distillate was the acid fluoride (47% yield). An analytical sample was obtained by glpc separation.

Anal. Calcd for C_8HOF_{11}: C, 29.8; H, 0.31. Found: C, 29.8; H, 0.35.

The infrared spectrum showed bands at 5.39 and 5.95 μ corresponding to the acid fluoride and olefinic functions, respectively.

Upon standing in an open vessel the acid fluoride hydrolyzed to the corresponding acid, XVIII, identified by comparison of its melting point and infrared spectrum with those of an authentic sample (*vide ultra*).

Treatment of the acid fluoride with warm ethanol converted it into the ethyl ester XIII, identified by comparison of its infrared spectrum with that of an authentic sample (*vide ultra*).

(Perfluorocyclohexylidenyl)acetyl Chloride (XX).—(Perfluorocyclohexylidenyl)acetic acid (XVIII) (37.0 g, 0.12 mol) and benzotrichloride (35.2 g, 0.18 mol) were mixed and heated in a spinning-band distillation apparatus. The resulting acid chloride was distilled from the reaction mixture, bp 130–140°. Redistillation gave 32.6 g, of colorless liquid, bp 141–142°. Glpc analysis showed this to be 96% pure (78% yield). An analytical sample was purified by glpc separation.

Anal. Calcd for C_8HClOF_{10}: C, 28.4; H, 0.3; Cl, 10.5. Found: C, 26.4; H, 0.26; Cl, 10.4.

Absorption bands for C=O (acid chloride) and C=C stretching appear at 5.52 and 5.93 μ, respectively.

A sample of the acid chloride hydrolyzed upon standing in an open vessel to the parent acid (XVIII) identified by comparison of its melting point with that of an authentic sample (*vide ultra*).

Warming the acid chloride with ethanol produced the ethyl ester (XIII) identified by comparison of its infrared spectrum with that of an authentic sample (*vide ultra*).

Registry No.—IIa, 336-34-5; IIb, 4641-72-9; IIIa, 10363-97-0; IIIb, 10363-96-9; IIIc, 10363-98-1; IIId, 10363-93-6; IIIe, 10363-94-7; IIIf, 10363-95-8; IVa, 5561-34-2; IVb, 5561-36-4; Va, 376-66-9; Vb, 1898-91-5; VIa, 13394-65-5; VIb, 16621-77-5; VII, 16621-78-6; VIIIa, 10534-21-1; VIIIb, 5364-93-2; IXa, 16621-81-1; IXb, 16621-82-2; IXc, 16621-83-3; IXd, 16621-84-4; Xa, 16621-85-5; Xb, 16621-86-6; Xc, 16621-87-7; Xd, 16621-88-8; XIb, 16621-89-9; XIIa, 16621-90-2; XIIb, 16621-91-3; XIII, 16622-02-9; XIVa, 16621-92-4; XIVb, 16621-93-5; XIVc, 16621-94-6; XIVd, 16621-95-7; XVIa, 16621-96-8; XVII, 16621-97-9; XVIII, 16621-98-0; XIX, 16621-99-1; XX, 16622-00-7; 1-hydroxyperfluorocyclohexyl-β-chloropropionate, 16622-01-8.

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