

The Preparation and Some Reactions of Fluorinated Cyclic Ketones

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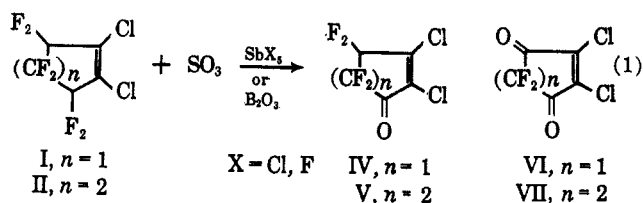
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Sulfur trioxide reacts with 1,2-dichlorohexafluorocyclopentene and 1,2-dichlorooctafluorocyclohexene in the presence of SbF_5 , $SbCl_5$, or B_2O_3 to give mono- and diketo derivatives. 2,3-Dichlorotetrafluoro-2-cyclopentenone, 2,3-dichlorodifluoro-2-cyclopentene-1,4-dione, 2,3-dichlorohexafluoro-2-cyclohexenone, and 2,3-dichlorotetrafluoro-2-cyclohexene-1,4-dione were prepared by this reaction. The five- and six-membered monoketones react with primary and secondary amines to give products containing amino substituents at the 3 position in the ring. These monoketones react with methanol or ethanol to give strongly acidic derivatives to which the structures 2-chloro-3-hydroxytetrafluoro-2-cyclopentenone and 2-chloro-3-hydroxyhexafluoro-2-cyclohexenone have been assigned.

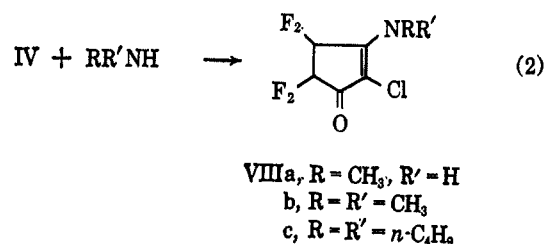
As part of a program directed to the synthesis of highly fluorinated, alicyclic, polyfunctional compounds, the reaction of sulfur trioxide with 1,2-dichlorohexafluorocyclopentene (I) and 1,2-dichlorooctafluorocyclohexene (II) was studied. Halogenated hydrocarbons are known to react with sulfur trioxide to produce oxygen containing derivatives.¹ The reaction of sulfur trioxide with carbon tetrachloride and hexachloroethane affords phosgene and trichloroacetyl chloride, respectively, the co-product in both cases being pyrosulfuryl chloride. It has also been reported that 1,2,3,3,4,4-hexachlorodifluorocyclopentene reacts with sulfur trioxide to give 5,5-difluorotetrachloro-2-cyclopentenone.²

Freshly distilled sulfur trioxide did not react with I or II. If, however, a small amount of antimony pentafluoride, antimony pentachloride, or boric anhydride (B_2O_3) was added to the refluxing mixtures, the corresponding mono- and dicarbonyl compounds were obtained (eq 1).



Although a careful study of the dependence of the reaction rate and product distribution on catalyst concentration was not carried out, certain qualitative observations have been made. Boric anhydride was a less efficient catalyst than antimony pentachloride or antimony pentafluoride. When 0.05 mole % of boric anhydride (based on sulfur trioxide) was used, 10–15 hr were required to effect conversions obtained in about 2 hr using 0.3–1.6 mole % of this catalyst. When 0.3 mole % of antimony pentachloride or antimony pentafluoride was used, the reaction was essentially complete in less than 1 hr.

Reaction of Cyclic Ketones with Ammonia and Amines.—Ammonia as well as primary and secondary amines reacted with IV to effect replacement of the 3-chloro atom by an amino function (eq 2). Compound



V reacted similarly to give the 3-amino derivative when treated with *m*-trifluoromethylaniline. The derivatives prepared by these reactions are listed in Table I.

Evidence for displacement of chloride at the 3 position was obtained by comparing the products from the reaction of IV with methylamine, dimethylamine, and di(*n*-butyl)amine with similar derivatives prepared by alternate routes as described in the recent literature.³ Parker prepared 2-chloro-3-(dimethylamino)tetrafluoro-2-cyclopentenone (VIIIb) and 2-chloro-3-(methylamino)tetrafluoro-2-cyclopentenone (VIIIa) by hydrolysis of the products of the reactions of 1,2-dichlorohexafluorocyclopentene with dimethylamine and methylamine, respectively. Compounds VIIIa and b as prepared in our laboratory were found to be identical on the basis of melting points and mixture melting points with the respective methyl- and dimethylamino derivatives prepared by the procedure described by Parker.

The reaction of di(*n*-butyl)amine with 1-methoxy-2-chlorohexafluorocyclopentene-1 was recently reported to give 2-chloro-3-[di(*n*-butyl)amino]tetrafluoro-2-cyclopentenone (VIIIc).⁴ The melting point as well as the wavelengths of the carbonyl and carbon-carbon double-bond infrared absorption bands reported for this compound were identical with those of VIIIc prepared by us.

Reactions with Alcohols and Water.—The reaction of lower alcohols with IV gave a mixture of 2-chloro-3-alkoxytetrafluoro-2-cyclopentenone (IX) and 2-chloro-3-hydroxytetrafluoro-2-cyclopentenone (X) (eq 3).

The alkoxy group in IX is apparently cleaved by alcoholic hydrogen chloride to give the enol X. Weil and Linder⁵ have reported that alcohols react with hexachloro-2-cyclopentenone forming a crystalline enol, 3-hydroxy-2,4,4,5-pentachloro-2-cyclopentenone, presumably formed by cleavage of the intermediate ether 3-alkoxy-2,4,4,5,5-pentachloro-2-cyclopentenone.

(1) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience Publishers, Inc., New York, N. Y., 1965, pp 371–373.

(2) (a) D. H. Campbell, Ph.D. Dissertation, Purdue University, 1954. (b) Campbell has evidence that in this case the attack is by addition of sulfuric acid to the double bond followed by elimination of hydrogen chloride and hydrolysis of the adduct rather than by hydrolysis of the allylic chlorine atoms.

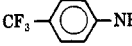
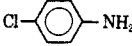
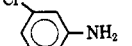
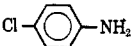
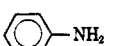
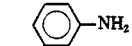
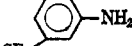
(3) C. O. Parker, *J. Am. Chem. Soc.*, **81**, 2183 (1959).

(4) F. Drier, W. Duncan, and T. Mill, *Tetrahedron Letters*, 1951 (1964).

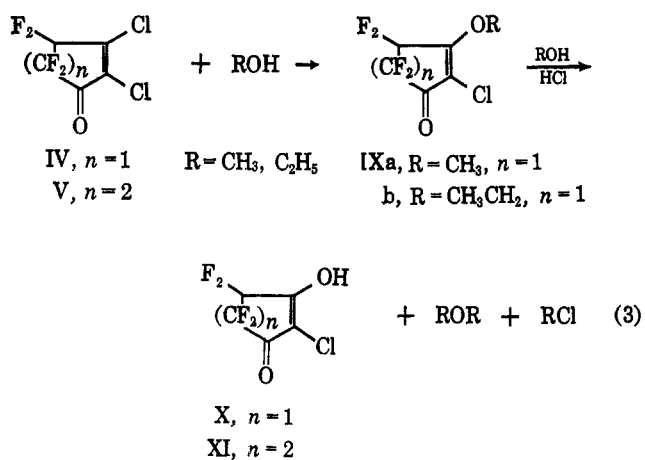
(5) E. D. Weil and J. Linder, *J. Org. Chem.*, **28**, 2218 (1963).

TABLE I

AMINE DERIVATIVES OF 2,3-DICHLOROTETRAFLUORO-2-CYCLOPENTENONE AND 2,2-DICHLOROHEXAFLUORO-2-CYCLOHEXENONE

Amine	Ketone	Time, hr	Yield, %	Mp, °C ^a	Calcd, %				Found, %			
					C	H	Cl	N	C	H	Cl	N
CH ₃ NH ₂ (0.4) ^b	IV ^c (0.2) ^b	1	68 ^d	138-143	33.10	1.84	16.32	6.44	33.50	1.70	16.62	6.42
(CH ₃) ₂ NH ... ^e	IV ^f (0.15)	1	60 ^g	58-61	36.28	2.59	15.33	6.05	36.14	2.69	15.04	5.87
NH ₃ ... ^e	IV ^f (0.15)	1.5	90 ^g	109-111	29.48	0.98	17.44	6.88	30.11	1.05	17.51	6.89
 (0.2)	IV ^h (0.1)	1	86 ^g	96-98	41.44	1.44	...	4.03	42.12	1.56	...	4.20
(<i>n</i> -Bu) ₂ NH (0.3)	IV ^f (0.15)	1.5	73 ^g	65-67	49.44	5.71	11.25	4.44	49.68	5.59	11.21	4.37
 (0.2)	IV ⁱ (0.1)	1	70 ^j	195-196	42.04	1.59	22.61	4.46	42.19	1.73	22.47	4.32
 (0.2)	IV ^h (0.1)	1	75 ^j	107-109	42.04	1.59	22.61	4.46	42.57	1.53	22.25	5.14
 (0.2)	IV ⁱ (0.1)	2	70 ^j	130-131	37.88	1.15	30.56	4.02	38.08	1.19	30.34	3.98
 (0.2)	IV ^f (0.1)	1.5	56 ^g	171-172	49.06	2.73	...	4.77	49.47	2.61	...	5.00
 (0.3)	IV ^h (0.15)	1	68 ^g	137-138	49.06	2.73	...	4.77	49.52	2.95	...	4.96
 (0.07)	V ^h (0.035)	6	79 ^g	90-92	39.25	1.26	8.93	3.52	40.06	1.23	9.08	3.60

^a Melting points uncorrected. ^b Numbers in parentheses refer to moles of starting amines and ketone, respectively. ^c Diethyl ether used as a reaction solvent. ^d Recrystallized from benzene. ^e Excess used. ^f Methylene chloride used as a reaction solvent. ^g Recrystallized from benzene-cyclohexane. ^h Methyl chloroform used as a reaction solvent. ⁱ Acetone used as reaction solvent. ^j Recrystallized from methanol-water. ^k Chloroform used as a reaction solvent. ^l Recrystallized from ethanol-water.

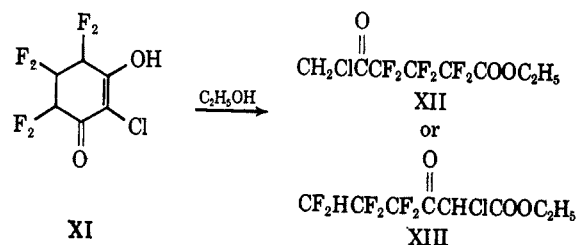


The reaction of ethanol with V proceeded with the formation of 2-chloro-3-hydroxyhexafluoro-2-cyclohexenone XI and an ester XII or XIII which is formed by ring cleavage. No 2-chloro-3-alkoxyhexafluoro-2-cyclohexenone was isolated. It appears that the vinylic ether linkage in IX is more stable than that in the corresponding six-membered ring system.

Compound XI was shown to undergo ring cleavage by refluxing a pure sample with ethanol. As the reaction proceeded, the absorption bands at 5.75 and 6.1-6.4 μ disappeared and a new band appeared at 5.60 μ , a region in which an ester carbonyl would be expected to absorb. The product showed no OH or carbon-carbon double-bond absorptions.

Cleavage of XI could lead to two possible products depending on whether bond cleavage occurs between carbons 1 and 2 giving XII, or between carbons 1 and 6, giving XIII.

Proton nmr data support structure XII. Thus, the spectrum consisted of a triplet centered at 1.4 ppm

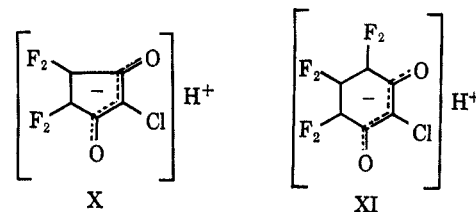


($J = 7$ cps) assigned to the methyl group, a quartet centered at 4.5 ppm ($J = 7$ cps) assigned to the methylene hydrogens of the ethyl group, and a singlet at 4.6 ppm assigned to the protons in the terminal CH₂Cl group. Structure XIII would require a considerably more complex splitting pattern because of the geminal and vicinal fluorine atoms.

Enols X and XI were hygroscopic crystalline solids, forming strongly acidic aqueous solutions which were titrated with 1 equiv of strong base to give sharp end points and neutral equivalents in agreement with the theoretical value. The relative order of decreasing acidity was as follows.



This evidence, taken in conjunction with the spectral data indicate that X and XI are more properly written as stabilized anions.⁶

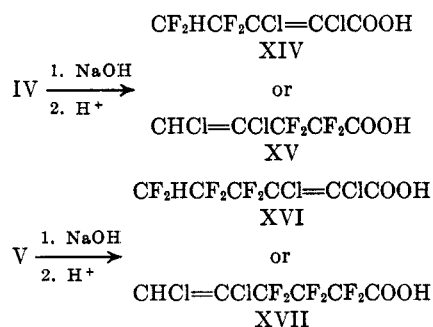


(6) An alternate synthesis of these acids has been described [R. F. Stockel, M. T. Beachem, and F. H. Megson, *J. Org. Chem.*, **30**, 1629 (1965)].

Compound IV which was initially immiscible with water did react with water upon refluxing for 24 hr yielding X and HCl. No evidence was found for the reaction of V with water under identical experimental conditions.

Ring Cleavage with Aqueous Caustic.—Both IV and V were cleaved by dilute aqueous caustic at room temperature, forming carboxylic acids. One might expect these reactions to proceed by formation of X or XI, respectively, followed by cleavage. However, the products obtained have retained two chlorine atoms and, therefore, could not have been formed by this route.

It appears that in the presence of aqueous base the reaction proceeds by attack on the carbonyl group rather than on the 3-chloro atom. Compound IV could form XIV or XV depending on whether the 1-5 or 1-2 carbon-carbon bonds are cleaved. Similarly, V could form XVI or XVII depending on the direction of bond cleavage.



It has been reported that, in the case of 2,3,4,4,5,5-hexachloro-2-cyclopentenone, cleavage occurs at the 1-5 carbon-carbon bond with concomitant elimination of chloride to give 2,3,4,5,5-pentachloropentadien-2,4-oic acid.⁷ In the case of IV and V, a similar reaction would require the elimination of fluoride for which there is no evidence.

The proton nmr spectra of these acids indicated that XV and XVII formed by cleavage of the 1-2 carbon bonds are the correct structures. Both acids exhibited a singlet at 7.12 ppm characteristic of a vinylic hydrogen and a singlet at 10.7 ppm expected for a carboxylic proton. On the other hand, structures XIV and XVI would be expected to have a much more complex spectra owing to splitting of the hydrogen absorption by fluorine.

Experimental Section⁸

Reaction of 1,2-Dichlorohexafluorocyclopentene with SO₃ (Procedure A).—A mixture of 50 g (0.20 mole) of 1,2-dichlorohexafluorocyclopentene, 35.2 g (0.440 mole) of Sulfan[®] (B and A reagent grade sulfur trioxide containing 0.25% stabilizing additive), and 2.4 g (0.01 mole) of antimony pentafluoride was heated at reflux temperature for 2.5 hr. The temperature of the flask

contents slowly rose to 85° during this period. The product mixture was distilled using a 36-in. vacuum-jacketed column packed with glass helices to give 22.3 g of a mixture of sulfur trioxide and pyrosulfuryl fluoride (bp 44-58°), 13.0 g of 1,2-dichlorohexafluorocyclopentene (bp 90-97°), 15.9 g (48%) of 2,3-dichlorotetrafluoro-2-cyclopentenone (IV), and 10.2 g (35%) of a yellow solid, 2,3-dichlorotetrafluoro-2-cyclopentene-1,4-dione (VI).

An analytical sample of VI was prepared by redistillation through an 18-in. spinning-band column, bp 127-128°. The infrared spectrum showed a C=O band at 5.61 μ and a C=C band at 6.29 μ. The F¹⁹ nmr spectrum consisted of two triplets, one being centered at 117.0 ppm (*J*_{CF₂,CF₂} = 1.6 cps) assigned to the fluorine atoms in the 4 position, and the other at 125.9 ppm assigned to the fluorine atoms in the 5 position.

Anal. Calcd for C₅Cl₂F₄O: C, 27.0; Cl, 31.8; F, 34.0. Found: C, 26.7; Cl, 31.6; F, 33.5.

An analytical sample of VI was prepared as described above, bp 173-179, mp 74-76. The infrared spectrum showed a triplet in the C=O region at 5.58, 5.68, and 5.57 μ and a C=C at 6.48 μ. The F¹⁹ nmr spectrum was obtained using a Varian Associates Model HR-60 nmr spectrometer operating at 56.4 Mc using CCl₃F as an external reference. It showed a singlet at 124.0 ppm.

Anal. Calcd for C₅Cl₂F₂O: C, 29.8; Cl, 35.3; F, 18.6. Found: C, 29.5; Cl, 35.4; F, 18.9.

Reaction of 1,2-Dichlorohexafluorocyclopentene with SO₃ (Procedure B).—A mixture of 2080 g (8.49 moles) of 1,2-dichlorohexafluorocyclopentene and 2724 g (34.0 moles) of Sulfan[®] containing about 3 g of B₂O₃ was heated to reflux for 6 hr. The product mixture was cooled to room temperature and poured onto wet ice. The organic layer was separated into three equal portions. Each portion was added slowly to 1500 ml of vigorously stirred water. The water-insoluble layers were combined and dried over anhydrous sodium sulfate. The product was distilled to give 68 g of forecut (bp 75-89°), 59.0 g of 1,2-dichlorohexafluorocyclopentene (bp 90-93°), 1040 g (56%) of 2,3-dichlorotetrafluoro-2-cyclopentenone, and 346 g (21%) of 2,3-dichlorodifluoro-2-cyclopentene-1,4-dione.

Reaction of 1,2-Dichlorooctafluorocyclohexene with SO₃ (Procedure A).—A mixture of 267.8 g (0.908 mole) of 1,2-dichlorooctafluorocyclohexene, 151 g (1.89 moles) of Sulfan[®], and 10 g (0.046 mole) of antimony pentafluoride was heated to reflux temperature for 20 hr. The temperature of the reaction mixture slowly rose to 85° during this period. The product mixture was distilled to give a 90-g forecut consisting of a mixture of pyrosulfuryl fluoride and SO₃, 127 g of 1,2-dichlorooctafluorocyclohexene (bp 113-114°), 100.5 g (78%) of 2,3-dichlorohexafluoro-2-cyclohexenone (V, bp 135-136°), and 23.0 g (19%) of 2,3-dichlorotetrafluoro-2-cyclohexene-1,4-dione (VII, bp 161-164°).

The infrared spectrum of V showed a C=O band at 5.71 μ and a C=C band at 6.32 μ. The F¹⁹ nmr spectrum exhibited a complex splitting pattern with three multiplets centered at 110.4, 133.5, and 125.1 ppm. These have been assigned to the 4-6 positions because in these five- and six-membered rings the fluorine atoms adjacent to a vinylic chlorine are more deshielded than fluorine atoms adjacent to a carbonyl group.

Anal. Calcd for C₆Cl₂F₆O: C, 26.4; Cl, 26.0; F, 41.8. Found: C, 26.1; Cl, 25.7; F, 41.2.

The infrared spectrum of VII showed a C=O band at 5.75 μ and a C=C band at 6.53 μ. The F¹⁹ nmr spectrum exhibited a singlet at 124.5 ppm.

Anal. Calcd for C₆Cl₂F₄O₂: C, 28.6; Cl, 28.2; F, 30.2. Found: C, 28.3; Cl, 28.3; F, 29.8.

Reaction of 1,2-Dichlorooctafluorocyclohexene with SO₃ (Procedure B).—A mixture of 143.0 g (0.485 mole) of 1,2-dichlorooctafluorocyclohexene, 77.5 g (0.97 mole) of Sulfan[®], and 6 g (0.020 mole) of antimony pentafluoride was heated to reflux temperature for 6 hr. The temperature of the reaction mixture slowly rose to 85°. The product mixture was poured into approximately 1 l. of water giving 129 g of water-insoluble oil which was dried over anhydrous sodium sulfate. Distillation gave 46.4 g of 1,2-dichlorooctafluorocyclohexene, 54.7 g (66%) of 2,3-dichlorohexafluoro-2-cyclohexenone, and 24 g of residue which consisted of a mixture of 2,3-dichlorotetrafluoro-2-cyclohexene-1,4-dione and 2,3-dichlorohexafluoro-2-cyclohexenone.

General Procedure for the Reaction of Amines with 2,3-Dichlorotetrafluoro-2-cyclopentenone or 2,3-Dichlorohexafluoro-2-cyclohexenone.—All the amine derivatives were prepared using essentially the same procedure except where indicated in

(7) C. J. Pennino, *J. Org. Chem.*, **20**, 530 (1955).

(8) Boiling points and melting points are uncorrected. The elemental analyses were by the Alfred Bernhardt Microanalytisches Laboratorium, Ruhr, and Messrs. G. E. Mohler and R. J. Tepper of the General Chemical Analytical Laboratory, Morristownship, N. J. Infrared spectra were taken on a Perkin-Elmer Model 137 spectrophotometer. Spectra were run in CCl₄ except where indicated. Proton nmr spectra were obtained using a Varian Associates Model A-60 instrument with chemical shifts reported in parts per million from tetramethylsilane and carbon tetrachloride as the solvent. The F¹⁹ nmr spectra were obtained using a Varian Associates Model A-56/60 nmr spectrometer operating at 56.4 Mc and CCl₃F as an internal zero reference except where indicated. Except for solid X and XI, which were in (CD₂)₂CO solution, samples were observed as neat liquids.

Table I. The amine was added slowly to the ketone contained in about 100 ml of solvent. The mixture was heated at reflux for the indicated period and cooled; the solvent was removed under vacuum. The product amine was separated from amine hydrochloride by triturating the product with methylene chloride and filtering off the amine hydrochloride. The methylene chloride was removed under vacuum and the residue was recrystallized from the indicated solvent.

2-Chloro-3-hydroxytetrafluoro-2-cyclopentenone (X).—A mixture of 25 g (0.11 mole) of 2,3-dichlorotetrafluoro-2-cyclopentenone and 6.6 g (0.37 mole) of water was refluxed for 17 hr. The mixture was cooled and about 25 ml of concentrated H_2SO_4 was added slowly. Upon cooling a white crystalline solid formed. This was recrystallized from benzene and gave 20.2 g (75%) of 2-chloro-3-hydroxytetrafluoro-2-cyclopentenone, mp 94–97°, neut equiv 204, calcd 204. The infrared spectrum of X was run in $CHCl_3$ solution and showed an OH band at 2.80 μ , a C=O band at 5.67 μ , and a broad band between 6.1 and 6.5 μ . Compounds having a 1–3 carbonyl system capable of undergoing hydrogen-bond interactions exhibit a broad absorption in this region.⁹ The F^{19} nmr spectrum exhibited a singlet at 124.4 ppm.

Anal. Calcd for $C_5HClF_4O_2$: C, 29.34; Cl, 17.36. Found: C, 29.9; Cl, 17.2.

Reaction of 2,3-Dichlorohexafluoro-2-cyclohexenone with Ethanol.—Ethanol (95%, 220 g) was added to 120 g (0.44 mole) of 2,3-dichlorohexafluoro-2-cyclohexenone with stirring. The mixture was refluxed for 16 hr. Then, 100 ml of benzene was added and the mixture was rapidly distilled to remove benzene, water, and excess alcohol. The residue was carefully distilled to give 60 g (54%) of 2-chloro-3-hydroxyhexafluoro-2-cyclohexenone (XI), bp 182–183°, mp 60–61°, neut equiv 253, calcd 254. The infrared spectrum of XI, run as a film (neat), showed an OH band at 3.0 μ , a C=O band at 5.75 μ , and a broad band between 6.1 and 6.4 μ . The F^{19} spectrum consisted of a triplet centered at 120.8 ppm, assigned to the fluorine atoms of the 4 and 6 positions, and a quintet centered at 134.5 ppm ($J = 10.2$ cps), assigned to the fluorine atoms at the 5 position.

Anal. Calcd for $C_6HClF_6O_2$: Cl, 13.95; H, 0.39. Found: Cl, 13.50; H, 0.45.

In addition, 47 g (36%) of ethyl 1,1,2,2,3,3-hexafluoro-4-oxo-5-chlorohexanoate (XII), bp 210–212°, was obtained.

Anal. Calcd for $C_8H_7ClF_6O_2$: C, 31.95; H, 2.33; Cl, 11.81. Found: C, 32.1; H, 2.12; Cl, 12.10.

2-Chloro-3-ethoxytetrafluoro-2-cyclopentenone (IXb).—Absolute ethanol (124 g, 2.70 moles) was added over a 20-min period to 200 g (0.90 mole) of 2,3-dichlorotetrafluoro-2-cyclopentenone contained in a flask connected to a trap cooled in a Dry Ice-acetone cooled bath. The reaction mixture was refluxed for 48 hr. At the end of this period the trap contained 51 g of a mixture of ethyl chloride and diethyl ether. The product was distilled using an 18-in. spinning-band column to give 18 g of diethyl ether, 41 g of ethanol, and 19 g (9%) of 2-chloro-3-ethoxytetrafluoro-2-cyclopentenone, bp 77–79° (4 mm). The infrared spectrum, run as a film (neat), showed a C=O band at 5.68 μ and a C=C band at 6.19 μ .

Anal. Calcd for $C_7H_5ClF_4O_2$: H, 2.15; Cl, 15.27. Found: H, 2.05; Cl, 15.60.

In addition, a higher boiling fraction consisting of 168 g (90%) of 2-chloro-3-hydroxytetrafluoro-2-cyclopentenone, bp 102–104° (4 mm), was obtained.

2-Chloro-3-methoxytetrafluoro-2-cyclopentenone (IXa).—The procedure was the same as that described for IXb. A mixture of 100 g (0.448 mole) of 2,3-dichlorotetrafluoro-2-cyclopentenone and 22 g (0.69 mole) of anhydrous methanol was refluxed for 4 hr. Distillation of the product gave 31 g (31%) of 2-chloro-3-methoxytetrafluoro-2-cyclopentenone, bp 192–193°. The infrared spectrum, run as a film (neat), showed a C=O band at 5.70 μ and a C=C band at 6.20 μ .

Anal. Calcd for $C_6H_5ClF_4O_2$: Cl, 16.25. Found: Cl, 16.3.

The residue was recrystallized from methylene chloride and had an infrared spectrum identical with that of 2-chloro-3-hydroxytetrafluoro-2-cyclopentenone.

Methyl 1,1,2,2,3,3-Hexafluoro-4-oxo-5-chlorohexanoate (XIIa).—A mixture of 35 g (0.13 mole) of 2,3-dichlorohexafluoro-2-cyclohexenone and 12 g (0.38 mole) of absolute methanol was refluxed for 24 hr using the same apparatus as that described for IVb. The Dry Ice-acetone cooled trap contained 11 g of a low boiler which consisted of methyl chloride and dimethyl ether. The product mixture was distilled to give 16 g of a fraction boiling at 62–64° (3 mm). Gas-liquid partition chromatographic analysis¹⁰ of this fraction showed that it consisted of two components, one component having a retention time identical with XI. This fraction was heated with 3 g (0.1 mole) of absolute methanol for 24 hr. The product was distilled using an 18-in. spinning-band column to give a forecut of 1.4 g, bp 44–48° (1 mm), an intermediate fraction of 5.8 g, bp 48–62° (1 mm), and 1 g of methyl 1,1,2,2,3,3-hexafluoro-4-oxo-5-chlorohexanoate, bp 62–66° (1 mm).

Anal. Calcd for $C_7H_5ClF_6O_2$: H, 1.74; Cl, 12.39. Found: H, 1.72; Cl, 12.37.

2,2,3,3-Tetrafluoro-4,5-dichloro-4-pentenoic Acid (XV).—2,3-Dichlorotetrafluoro-2-cyclopentenone (16.3 g, 0.073 mole) was added to 35 ml of 10% aqueous sodium hydroxide solution and stirred until dissolved. The mixture was cautiously acidified with 50% H_2SO_4 . The organic layer was separated, vigorously shaken with a portion of concentrated H_2SO_4 , taken up in benzene, and separated from residual H_2SO_4 . Distillation of the benzene layer gave after removal of the benzene 8.5 g (48%) of 2,2,3,3-tetrafluoro-4,5-dichloro-4-pentenoic acid, bp 208–210°, mp 41–44°, neut equiv 241, calcd 241. The infrared spectrum showed a COOH band at 3.0–3.5 μ , a C=O band at 5.65 μ , and a C=C band at 6.20 μ .

Anal. Calcd for $C_6H_2Cl_2F_4O_2$: Cl, 29.46. Found: Cl, 29.1.

2,2,3,3,4,4-Hexafluoro-5,6-dichloro-5-hexenoic Acid (XVII).—2,3-Dichlorohexafluoro-2-cyclohexenone (20 g, 0.073 mole) was added to 35 ml of 10% aqueous sodium hydroxide and stirred until dissolved. The solution was worked up as described for XV above. Distillation of the product gave 5.9 g (28%) of 2,2,3,3,4,4-hexafluoro-5,6-dichloro-5-hexenoic acid, bp 102–105° (10 mm), neut equiv 303, calcd 291. The infrared spectrum exhibited a COOH band at 3.0–3.5 μ , a C=O band at 5.64 μ , and a C=C band at 6.20 μ .

Anal. Calcd for $C_8H_2Cl_2F_6O_2$: Cl, 24.39; F, 39.17. Found: Cl, 24.13; F, 38.96.

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(9) R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

(10) Separation was carried out using an Aerograph Autoprep Model A-700 with a 20-ft column containing 20% QF-1 on 42–60 mesh firebrick.