COF_2. The trifluoroamine was characterized by mass spectrometric analysis which showed major peaks at 113, 112, 94, 78, 76, 69, 60, 50, 44, 43, 42, 41, 40, 33, 31, 28, 15, 14, 13 and 12. The fluorine n.m.r. spectrum showed one type of fluorine in the CF_3 region.

Anal. Calcd. for $C_3H_6F_3N$: F, 50.50. Found: F, 49.09.

Since the low fluorine content probably resulted from hydrolysis by trace amounts of water, the compound was purified by gas chromatography (20% Silicone 703 on Columpak at 0°). The infrared spectrum (gas) of the purified sample showed major absorption at 3.29, 3.33, 3.42, 3.47 and 3.53 μ (satd. CH), 6.66, 6.70, 6.74, 6.82, 7.42, 7.82, 8.31, 9.17 and 10.26 μ.

The pressure reactor contained 7 g. of sulfur and 27 g. of dark-colored liquid which yielded on distillation 19 g. (30% conversion) of $(CH_3)_2N\underset{\underset{S}{\|}}{C}{-}F$, b.p. 42–42.5° (1.7 mm.); infrared spectrum (liquid): 3.39 (satd. CH), 6.39 (C=S of N·CSF), 7.10 (N—CH_3), 7.85, 8.53, 9.00, 9.48, 10.76 and 14.90 μ. The fluorine n.m.r. spectrum showed one type fluorine in the $S{=}\underset{|}{C}{-}F$ region.

Anal. Calcd. for C_3H_6FNS: C, 33.70; H, 5.60; F, 17.75; S, 29.90. Found: C, 33.97; H, 6.01; F, 17.92; S, 30.39.

In another experiment in which $(CH_3)_2N\overset{\overset{S}{\|}}{C}{-}F$ (16 g.) and 30 g. of COF_2 were heated with rocking at 75° for 1 hr. and 85° for 1 hr. in a 300-ml. pressure vessel, the trifluoroamine was obtained in 55% conversion; 6 g. of unreacted $(CH_3)_2$ S=CN–F was recovered.

[CONTRIBUTION NO. 774 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON, 98, DEL.]

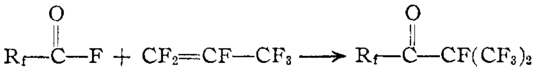
The Chemistry of Carbonyl Fluoride. II. Synthesis of Perfluoroisopropyl Ketones

BY R. D. SMITH, F. S. FAWCETT AND D. D. COFFMAN

RECEIVED APRIL 27, 1962

A convenient synthesis of the new perfluoroisopropyl ketones, $(CF_3)_2CF{-}CO{-}R_f$, has been found in the fluoride ion-catalyzed addition of a fluoroacyl fluoride to hexafluoropropene. Diketones have been prepared by reaction of hexafluoropropene with oxalyl fluoride and with perfluoroglutaryl fluoride.

The addition of carbonyl fluoride to fluoroolefins in the presence of a fluoride ion catalyst and a polar non-protonic solvent to form fluoroacyl fluorides has been reported.[1] In some further studies, this reaction has been extended to the preparation of a family of fluoroketones containing the perfluoroisopropyl group by reaction of hexafluoropropene (HFP) with various fluoroacyl fluorides. In the conversion of carbonyl fluoride and HFP to perfluoroisobutyryl fluoride, bis-(perfluoroisopropyl) ketone is a co-product. This ketone is also obtained in 39% conversion through use of two moles of HFP with one of carbonyl fluoride. The bis-(perfluoroisopropyl) ketone is formed also from preformed perfluoroisobutyryl fluoride and HFP under the same conditions used for the HFP–carbonyl fluoride reaction. The ketones were obtained in conversions up to 75% as shown in Table I.



$$R_f{-}\overset{\overset{O}{\|}}{C}{-}F + CF_2{=}CF{-}CF_3 \longrightarrow R_f{-}\overset{\overset{O}{\|}}{C}{-}CF(CF_3)_2$$

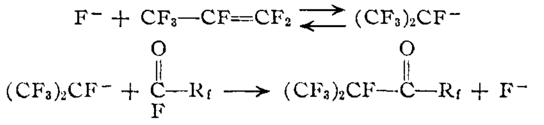
TABLE I

PERFLUOROISOPROPYL KETONES FROM HEXAFLUOROPROPENE AND FLUOROACYL FLUORIDES

Acyl Fluoride	$R\overset{\overset{O}{\|}}{C}CF(CF_3)_2$ ketone; R	% Conv. to ketone
FCOF	$(CF_3)_2CF{-}$	39
CF_3COF	$CF_3{-}$	75
n-C_3F_7COF	$CF_3CF_2CF_2{-}$	60
iso-C_3F_7COF	$(CF_3)_2CF{-}$	38
$H(CF_2)_4COF$	$H(CF_2)_4{-}$	64
$\boxed{F}$ COF	$\boxed{F}$	8
FCOCOF	$(CF_3)_2CFCO{-}$	28
$FCO(CF_2)_3COF$	$(CF_3)_2CFCO(CF_2)_3{-}$	75

In the reaction of trifluoroacetyl fluoride with HFP at 200°, use of cesium fluoride catalyst alone gave 65% conversion to trifluoromethyl perfluoroisopropyl ketone. Similarly, in the conversion of carbonyl fluoride and HFP at 200° to perfluoroisobutyryl fluoride, the use of cesium fluoride catalyst but no solvent gave 46% conversion, while without a catalyst either in the presence or absence of acetonitrile solvent no adduct was obtained. The combined use of a relatively polar solvent, such as acetonitrile, and a catalyst is beneficial, however, as illustrated by the higher conversions (70–75%) observed at lower reaction temperatures (100–125°) for both the carbonyl fluoride[1] and trifluoroacetyl fluoride additions to HFP. Other catalysts which have been found effective include potassium fluoride, potassium bifluoride and quaternary ammonium fluorides.

This ketone synthesis, which is similar to reactions of carbonyl fluoride with unsaturated systems,[1] presumably occurs *via* a fluorocarbanion intermediate that is formed by the reversible addition of a fluoride ion to the fluoroölefin. Reaction of this anion with the acyl fluoride at its highly electrophilic carbonyl group, either by direct displacement or by addition–elimination, would yield the fluoroketone and fluoride ion



$$F^- + CF_3{-}CF{=}CF_2 \rightleftarrows (CF_3)_2CF^-$$

$$(CF_3)_2CF^- + \overset{\overset{O}{\|}}{\underset{F}{C}}{-}R_f \longrightarrow (CF_3)_2CF{-}\overset{\overset{O}{\|}}{C}{-}R_f + F^-$$

The fluoroketones are thermally stable compounds that distil without decomposition. They are non-flammable and resistant to oxidation. They are soluble in diethyl ether and in petroleum ether, whereas the corresponding fluorocarbons are immiscible. Bis-(perfluoroisopropyl) ketone ap-

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(1) F. S. Fawcett, C. W. Tullock and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

pears to be sterically hindered, and, unlike many perfluoroketones, it does not form a hydrate or a hemiketal. Basic reagents, however, bring about cleavage. Thus, treatment with triethylamine and water gives a quantitative yield of 2-hydroheptafluoropropane, while treatment with sodium methoxide and methanol forms 2-hydroheptafluoropropane and methyl perfluoroisobutyrate. Also, ammonia brings about cleavage to form 2-hydroheptafluoropropane and perfluoroisobutyramide. Efforts to prepare the ethylene ketal of bis-(perfluoroisopropyl) ketone by treatment with ethylene chlorohydrin and potassium carbonate caused cleavage with the formation of 2-chloroethyl perfluoroisobutyrate. This behavior is in contrast to that of less hindered α-fluoroketones such as *s*-dichlorotetrafluoroacetone, which form cyclic ketals.[2]

Experimental

The nuclear magnetic resonance (n.m.r.) spectra were measured with a Varian high resolution nuclear magnetic resonance spectrometer and associated electromagnet. Fluorine magnetic resonance spectra were obtained at 40 Mc. using as a reference trifluoroacetic acid contained in a capillary tube in the sample tube unless otherwise specified. The displacements in cycles per second (c.p.s.) from the reference compound were measured and for uniformity were converted to parts per million (p.p.m.) of field strength with reference to CF_3COOH. Negative p.p.m. values refer to the low field side of the reference compound and positive values to the high field side. Infrared spectra were determined with a Perkin–Elmer model 21 double-beam spectrometer.

The reactions of fluoroacyl fluorides with hexafluoropropene (HFP) were carried out under autogenous pressure in barricaded pressure vessels of Hastelloy equipped with safety relief disks.

The normally solid or liquid components of the reaction mixture, *i.e.*, the polar solvent, the fluoride salt catalyst and the fluoroacyl fluoride, were placed in the pressure vessel at room temperature, and the vessel was closed, cooled to about −80° and evacuated. When the fluoroacyl fluoride was a gas or was very low-boiling, it and the fluoroölefin were then introduced into the cold evacuated vessel. Reaction was brought about by heating and agitating the mixture as indicated. Products normally gaseous at room temperature and atmospheric pressure were collected by venting the pressure vessel to an evacuated stainless steel cylinder cooled in liquid nitrogen, and purification was effected by distillation through a dry low-temperature glass column.

Preparation of Fluoroacyl Fluorides.—Perfluoroisobutyryl fluoride and perfluorocyclobutanecarbonyl fluoride were prepared by addition of carbonyl fluoride to hexafluoropropene and to perfluorocyclobutene, respectively, as previously described.[1] Perfluorobutyryl fluoride was obtained from the acid and carbonyl fluoride.[1,3] Oxalyl fluoride was made from oxalyl chloride and sodium fluoride.[4]

Trifluoroacetyl Fluoride.—A mixture of 150 g. of trifluoroacetic acid and 130 g. of sulfur tetrafluoride in a 1-l. pressure reactor was heated with agitation at 150° for 5 hr. The volatile product was treated with 150 g. of sodium fluoride pellets at room temperature in a 1-l. pressure vessel to remove hydrogen fluoride and was then distilled to obtain 146 g. (95% conv.) of trifluoroacetyl fluoride, b.p. −53 to −50°.

5-Hydroöctafluorovaleryl Fluoride.—A mixture of 123 g. (0.5 mole) of 5-hydroöctafluorovaleric acid, 50 g. (0.75 mole) of carbonyl fluoride and 42 g. (1.0 mole) of sodium fluoride pellets was heated with shaking for 6 hr. at 150°. The vessel and sodium fluoride pellets were rinsed with 30 ml. of xylene, which was then combined with the product. Distillation through a spinning band column gave 82 g. (67% conversion) of the acid fluoride, b.p. 57–59°.

Perfluoroglutaryl Fluoride.—Perfluoroglutaric acid (100 g., 0.41 mole), COF_2 (70 g., 1.1 moles), sodium fluoride pellets (42 g.) and 200 ml. of dry xylene were heated at 175° for 12 hr. under autogenous pressure in a 1-l. pressure vessel. The reactor was cooled, the pressure released, and the mixture filtered. Fractional distillation of the filtrate gave 47 g. (46% conversion) of hexafluoroglutaryl fluoride, b.p. 41–47°.

Synthesis and Chemistry of Fluoroketones. Tetradecafluoro-2,4-dimethyl-3-pentanone (Bis-(perfluoroisopropyl)-Ketone). A. From Perfluoroisobutyryl Fluoride and Hexafluoropropene (HFP).—Perfluoroisobutyryl fluoride[1] (30 g., 0.14 mole), HFP (21 g., 0.14 mole), cesium fluoride (2 g.) and 30 ml. of acetonitrile were heated under autogenous pressure at 100° for 8 hr. in a 240-ml. vessel. The volatile product and the lower phase of the two-phase liquid product were distilled to obtain 19.2 g. (38% conversion) of bis-(perfluoroisopropyl) ketone, b.p. 70–72°.

B. From HFP and Carbonyl Fluoride.—HFP (60 g., 0.4 mole), carbonyl fluoride[1] (13 g., 0.2 mole), cesium fluoride catalyst (2.3 g.) and 50 ml. of acetonitrile were heated under autogenous pressure at 75° for 4 hr. and 100° for 5 hr. in a 240-ml. vessel. Distillation of the combined volatile product and lower phase of the liquid product gave 28.2 g. (39% conversion) of bis-(perfluoroisopropyl) ketone, b.p. 71–72°. With potassium bifluoride as catalyst under otherwise identical conditions a 60% conversion to bis-(perfluoroisopropyl) ketone was obtained.

Bis-(perfluoroisopropyl) ketone is a mobile, colorless liquid having a faint odor. It is immiscible with common solvents such as ethanol and water but is soluble in pentane. In contrast to the straight-chain fluoroketones,[2] bis-(perfluoroisopropyl) ketone appears to be stable to water and to alcohol. The infrared spectrum shows strong absorption at 5.61μ, characteristic of the carbonyl of α-fluoroketones, and in the 7.1–9.1 μ region (C—F). The fluorine n.m.r. spectrum consists of a large CF_3 peak at −2.4 p.p.m. and a small CF peak at +108 p.p.m.

Anal. Calcd. for $C_7F_{14}O$: C, 22.97; F, 72.66. Found: C, 23.43; F, 72.54.

Reaction of Bis-(perfluoroisopropyl) Ketone with Ammonia.[5]—Gaseous ammonia was slowly passed into 10 g. (0.027 mole) of bis-(perfluoroisopropyl) ketone cooled in an ice-bath. A mass of crystals formed, but as more ammonia was introduced the crystals disappeared and were replaced by a light-yellow oil. This material crystallized when subjected to a vacuum, and it was recrystallized from chloroform. There was obtained 3.8 g. (65% conversion) of light-green crystalline perfluoroisobutyramide, m.p. 39–45°. Another recrystallization from chloroform gave colorless crystals of perfluoroisobutyramide, m.p. 46–51°. The infrared spectrum and m.p. of this product were identical with those of perfluoroisobutyramide prepared by Dr. C. M. Langkammerer from ethyl perfluoroisobutyrate and ammonia.

Reaction of Bis-(perfluoroisopropyl) Ketone with Ethanol and Triethylamine.[5]—A solution of 1.5 g. (0.025 mole) of ethanol and 2.52 g. (0.025 mole) of triethylamine was cooled in an ice-bath and 9.15 g. (0.025 mole) of bis-(perfluoroisopropyl) ketone was added all at once. Two immiscible layers were formed, but after stirring for 5–10 min. at room temperature the mixture became homogeneous. The solution was allowed to stand at room temperature overnight and was then distilled to give 0.3 g., b.p. 70–79°, and 8.3 g., b.p. 80–82°. The second fraction was washed with 20% hydrochloric acid and with water. It was then dried and distilled to obtain 1.15 g. of colorless ethyl perfluoroisobutyrate, b.p. 89–91°, n^{25}D 1.3008. These data and also the infrared spectrum of this material were identical with those of an authentic sample of ethyl perfluoroisobutyrate prepared by Dr. C. M. Langkammerer from perfluoroisobutyryl fluoride and ethanol.

Reaction of Bis-(perfluoroisopropyl) Ketone with Water and Triethylamine.[5]—A mixture of 2.52 g. (0.025 mole) of triethylamine and 0.45 g. (0.025 mole) of water was cooled in an ice-bath. Bis-(perfluoroisopropyl) ketone (9.15 g., 0.025 mole) was cooled in an ice-bath and then added in small increments with stirring with provisions for

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(2) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

(3) We are indebted to Dr. E. K. Ellingboe for the procedure of preparing the perfluoroacyl fluorides from the acid and carbonyl fluoride.

(4) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

(5) We are indebted to Dr. W. J. Linn for these experiments.

collecting volatile materials in a trap cooled with solid carbon dioxide. The reaction was extremely exothermic. Shortly after the addition of the ketone, the reaction mixture was colorless, homogeneous and slightly viscous. In the cold trap there was collected 8.0 g. (94% conversion, 2 moles) of gas which was identified as 2-hydroheptafluoropropane by the identity of its infrared spectrum with that of an authentic sample.

Cleavage of Bis-(perfluoroisopropyl) Ketone with Sodium Methoxide in Methanol.[5]—Bis-(perfluoroisopropyl) ketone (9.1 g., 0.025 mole) and absolute methanol (10 ml.) were placed in a still pot, and approximately 0.1 g. of sodium methoxide was added. After one-half hour the mixture was homogeneous, and the product was then distilled. In a cold trap attached to the outlet of the still there was collected 2.2 g. (52% conversion) of liquid identified by means of its infrared spectrum as 2-hydroheptafluoropropane. The liquid product, 11.7 g., boiled at 54–65°. The first portion of the distillate, b.p. 54–55°, appeared to be an azeotrope of methanol and methyl perfluoroisobutyrate. The distillate was washed twice with water, and the insoluble layer was dried and distilled to give 2.4 g. (42% conversion) of colorless liquid methyl perfluoroisobutyrate, b.p. 76–77°. The infrared spectrum of this ester showed absorption at 3.29, 3.35, 3.48 μ (saturated CH), 5.58 μ (C=O), and bands at 7.87, 7.90, 8.07, 8.64, 9.57, 9.67 and 10.1 μ.

Anal. Calcd. for $C_4H_3F_7O_2$: C, 26.33; H, 1.33; F, 58.31. Found: C, 27.05; H, 1.59; F, 58.35.

2-Chloroethyl Perfluoroisobutyrate.—A mixture of bis-(perfluoroisopropyl) ketone (18.3 g., 0.05 mole), anhydrous potassium carbonate (6.9 g., 0.05 mole), ethylene chlorohydrin (4.0 g., 0.05 mole) and pentane (30 ml.) was stirred for 15 hr. at room temperature. Gaseous 2-hydroheptafluoropropane was evolved, but the mixture remained at ambient temperature. Water was added, and the mixture was extracted twice with pentane. The combined pentane extracts were dried over Drierite, and the product was distilled to give 10.67 g. (77% conversion) of 2-chloroethyl perfluoroisobutyrate, b.p. 77–78° (105 mm.). The infrared spectrum was in agreement with the assigned structure with bands at 3.3 μ (C—H stretching) and at 5.56 μ (C=O of ester), and strong absorption in the 7.4–8.7 μ region (C—F).

Anal. Calcd. for $C_6H_4F_7O_2Cl$: C, 26.06; H, 1.46; F, 48.09. Found: C, 26.49; H, 1.51; F, 48.10.

Perfluoropropyl Perfluoroisopropyl Ketone.—A mixture of perfluorobutyryl fluoride (32 g., 0.15 mole), HFP (30 g., 0.2 mole), potassium bifluoride catalyst (2 g.) and 35 ml. of acetonitrile was heated under autogenous pressure at 100° for 4 hr. and at 125° for 5 hr. in a 240-ml. vessel. The lower phase of the liquid product was distilled to obtain 33 g. (60% conversion) of perfluoropropyl perfluoroisopropyl ketone, b.p. 73–75°; infrared spectrum; 5.62 μ strong (C=O of α-fluoroketone) and 7.4–9.1 μ strong (C—F). The fluorine n.m.r. showed five peaks: at −2.5 p.p.m. (large) and +4.8 p.p.m. (medium) for CF_3, two medium-sized peaks at +41.1 (some splitting) and +49.4 p.p.m. for CF_2, and a small broad one at +114 p.p.m. for CF.

Anal. Calcd. for $C_7F_{14}O$: C, 22.97; F, 72.66. Found: C, 23.25; F, 72.35.

4-Hydroöctafluorobutyl Perfluoroisopropyl Ketone.—5-Hydrooctafluorovaleryl fluoride (37 g., 0.15 mole), 30 g. (0.2 mole) of HFP, potassium bifluoride catalyst (2 g.) and 35 ml. of acetonitrile were heated under autogenous pressure at 100° for 4 hr. and at 125° for 5 hr. in a 145-ml. vessel. The volatile products and the lower layer of the two-phase reaction product were combined and distilled to obtain 15.5 g. of a two-phase mixture, b.p. 78–103°, and 38.5 g. (64% conversion) of 4-hydrooctafluorobutyl perfluoroisopropyl ketone, b.p. 112–113°. The two-phase forerun comprised a mixture of acetonitrile with the fluoroketone as judged by infrared spectroscopy. The infrared spectrum of the ketone showed weak absorption at 3.3 μ (C—H), strong absorption at 5.60 μ (C—O of α-fluoroketone) and strong absorption at 7.4–9.1 μ (C—F). The fluorine n.m.r. spectrum consisted of a large CF_3 peak at −2.2 p.p.m. and of four peaks of equal medium size for CF_2 at +40.2, at +46.0 and +52.0 p.p.m. and a doublet centered at +60.7 p.p.m. (split by H). The CF group was indicated by a small broad peak at +114 p.p.m.

Anal. Calcd. for $C_8F_{15}HO$: C, 24.14; H, 0.25; F, 71.59. Found: C, 24.96; H, 0.54; F, 71.44.

Perfluorocyclobutyl Perfluoroisopropyl Ketone.—Perfluorocyclobutanecarbonyl fluoride[1] (30 g., 0.13 mole), 23 g. (0.15 mole) of HFP, potassium bifluoride (2 g.) and 30 ml. of acetonitrile were heated under pressure at 100° for 4 hr. and at 125° for 5 hr. in a 240-ml. vessel. The volatile product (41 g.) consisted of unreacted starting materials. The lower phase of the two-phase liquid product was distilled to obtain 3.8 g. (8% conversion) of perfluorocyclobutyl perfluoroisopropyl ketone, b.p. 87–92°; infrared spectrum of the crude ketone showed strong absorption at 5.60 μ (C=O of α-fluoroketone) and strong absorption in the range 7.4–8.7 μ (C—F). The fluorine n.m.r. spectrum showed a large peak at −3.1 p.p.m. corresponding to CF_3, two medium-sized peaks at +53 and +56 p.p.m. in ratio 2:1, respectively, corresponding to CF_2, and a small broad peak at +111 p.p.m. corresponding to CF. Although the spectra observed conform to that expected for the structure believed to have resulted from the addition of the fluoroacyl fluoride to fluoroolefin, an analytically pure specimen was not obtained.

Trifluoromethyl Perfluoroisopropyl Ketone.—Trifluoroacetyl fluoride (23 g., 0.2 mole), HFP (30 g., 0.2 mole), potassium bifluoride (2 g.) and 30 ml. of acetonitrile were heated under autogenous pressure at 100° for 4 hr. and at 125° for 5 hr. in a 240-ml. vessel. The gaseous product (54 g.) was distilled to obtain 40 g. (75% conversion) of trifluoromethyl perfluoroisopropyl ketone, b.p. 21–22°; infrared spectrum: strong absorption at 5.55 μ (C=O of α-fluoroketone) and strong absorption in the 7.4–9.1 μ region (C—F). The fluorine n.m.r. spectrum showed a large peak at −1.7 p.p.m. (doublet, *ca.* 10 c.p.s. separation), a medium-sized one at +0.50 p.p.m. for CF_3 and a small broad one at +115 p.p.m. for CF. All peaks showed unresolved multiple splitting.

Anal. Calcd. for $C_5F_{10}O$: F, 71.41. Found: F, 70.96.

In an experiment without solvent, 18 g. of trifluoroacetyl fluoride, 35 g. of HFP and 9.2 g. of cesium fluoride in a 240-ml. pressure vessel at 150° for 2 hr., 175° for 2 hr. and 200° for 10 hr. gave 25.8 g. (65% conversion) of trifluoromethyl perfluoroisopropyl ketone, b.p. 25–27.5°, whose infrared absorption spectrum was the same as that for the above preparation.

Tetradecafluoro-2,5-dimethyl-3,4-hexanedione.—Oxalyl fluoride (12 g., 0.13 mole), HFP (60 g., 0.4 mole), potassium bifluoride (2 g.) and acetonitrile (50 ml.) were heated under pressure at 75° for 4 hr. and at 100° for 5 hr. in a 240-ml. vessel. Distillation of the liquid two-phase reaction product gave 7 g. of bis-(perfluoroisopropyl) ketone, b.p. 72–75°, which undoubtedly originated from carbonyl fluoride formed in the reaction mixture by the decomposition of oxalyl fluoride. A second fraction of 14.5 g., b.p. 91–93°, consisted of the yellow-colored perfluoro-2,5-dimethyl-3,4-hexanedione which was formed in 28% conversion. The infrared spectrum showed strong carbonyl absorption at 5.65 μ and strong absorption in the 7.4–9.1 μ region (C—F). The fluorine n.m.r. spectrum showed a large peak at −2.6 p.p.m. for CF_3 and a small one at +113 p.p.m. for CF.

Anal. Calcd. for $C_8F_{14}O_2$: C, 24.38; F, 67.50. Found: C, 24.47; F, 68.56.

Perfluoro-2,8-dimethyl-3,7-nonanedione.—A mixture of perfluoroglutaryl fluoride (24.4 g., 0.1 mole), HFP (40 g., 0.27 mole), potassium bifluoride (2 g.) and acetonitrile (35 ml.) was heated at 100° for 4 hr. and at 125° for 6 hr. in a 240-ml. vessel. Distillation of the product through a spinning band column gave 40.6 g. (75% conversion) of perfluoro-2,8-dimethyl-3,7-nonanedione, b.p. 148–151.5°. The major portion of this product boiled at 151–151.5°. The infrared spectrum showed absorption at 5.60 μ (C=O) and at 7.1–9.5 μ (C—F). The fluorine n.m.r. spectrum showed peaks in the CF_3, CF_2 and CF regions, but it was not examined in detail.

Anal. Calcd. for $C_{11}F_{20}O_2$: C, 24.28; F, 69.20. Found: C, 24.88; F, 70.72.

Effect of Solvent and Catalyst on Addition of COF_2 to HFP.—A mixture of 26 g. of COF_2, 30 g. of HFP and 10 g. of cesium fluoride was heated in a 240-ml. pressure vessel at 150° for 2 hr., 175° for 2 hr. and 200° for 10 hr. to give 50 g. of volatile product. Low-temperature distillation gave 20 g. (46% conversion) of perfluoroisobutyryl fluoride, b.p. −4 to +2°, identified by means of its infrared spectrum.[1] A mixture of 26 g. of COF_2, 30 g. of HFP and 30 ml. of acetonitrile under the same conditions gave no material boiling in the neighborhood of 0°, and *ca.* 25 g. distillate, b.p. −24 to −16°, presumably unreacted HFP, was obtained.

In another experiment, 26 g. of COF_2 and 30 g. of HFP under the same conditions likewise gave 25 g. of distillate, b.p. −27 to −24°, presumably recovered HFP. There was no product boiling near 0°.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, THE JACKSON LABORATORY, ORGANIC CHEMICALS DEPARTMENT, AND THE ELASTOMERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Carbodiimides. II. Mechanism of the Catalytic Formation from Isocyanates

BY JOHN J. MONAGLE,[1a] TOD W. CAMPBELL[1b] AND HERBERT F. MCSHANE, JR.

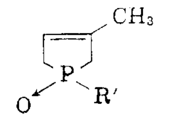
RECEIVED MAY 10, 1962

Isocyanates are smoothly and cleanly converted to carbodiimides by certain phospholene oxides. The kinetics of evolution of carbon dioxide from a variety of isocyanates has been studied, and the rate constants correlated by a Hammett equation. The data indicate that two consecutive reactions are involved with regeneration of the catalyst in the second (fast) step (shown in equations 5 and 6). The reaction is reversible and has a low energy of activation. Although phosphine oxides in general serve as catalysts, the cyclic phospholene oxides are by far the most effective.

Introduction

The formation of dimers and trimers from isocyanates in the presence of catalytic amounts of tertiary phosphines is well known.[2] More recently, it has been shown that certain phosphine oxides[3] have an entirely different catalytic effect on isocyanates.

$$2RNCO \xrightarrow{\text{I or II}} \underset{\text{III}}{RN{=}C{=}N{-}R} + CO_2 \qquad (1)$$



I, R′ = C_2H_5
II, R′ = C_6H_5

The formation of carbodiimides (III) from isocyanates by the catalytic action of the phosphine oxides I and II represents a decided improvement in ease of preparation and purity of product over methods formerly used.[4] The reaction proceeds rapidly and in most cases isolation is simple and yields are high. The unusual nature of the reaction and its potential synthetic applications prompted a study of its mechanism.

Discussion

Examination of the literature did not disclose any reactions of phosphine oxides with isocyanates. Several similar reactions were found, however, in the work of Staudinger on phosphinimides (IV).[5] These compounds were prepared by reaction of aromatic azides with tertiary phosphines.

$$R_3P + R'N_3 \longrightarrow R_3P{=}NR' + N_2 \qquad (2)$$

Both the aliphatic and aromatic phosphinimides were extremely reactive compounds; however, the derivatives of the aromatic phosphines such as triphenylphosphine phenylimide were less reactive than the aliphatic derivatives. Reaction of the molten imide with carbon dioxide yielded phenyl isocyanate and triphenylphosphine oxide. The reaction of *molar* amounts of the imide and phenyl isocyanate with slight warming produced diphenylcarbodiimide and triphenylphosphine oxide exothermically.

$$C_6H_5N{=}P(C_6H_5)_3 + CO_2 \longrightarrow C_6H_5NCO + (C_6H_5)_3PO \qquad (3)$$

$$C_6H_5N{=}P(C_6H_5)_3 + C_6H_5NCO \longrightarrow C_6H_5N{=}C{=}NC_6H_5 + (C_6H_5)_3PO \qquad (4)$$

The aromatic carbodiimides were also formed in an exothermic reaction between triethylphosphine phenylimide and carbon dioxide. Both reactions were considered to go through the initial formation of the isocyanate.

The over-all reaction obtained by a combination of reaction 4 with the reverse of reaction 3 represented a possible mechanism for the formation of carbodiimides from isocyanates.

$$RNCO + R'_3PO \rightleftarrows R\overset{-}{N}\overset{+}{P}R'_3 + CO_2 \qquad (5)$$

$$R\overset{-}{N}\overset{+}{P}R'_3 + RNCO \rightleftarrows RNCNR + R'_3PO \qquad (6)$$

In the present case, considering the extreme reactivity of the phosphine oxides I and II, the intermediate phosphinimides would have to form and react very rapidly in order to account for the catalytic nature of the reaction. However, the high reactivity reported for triphenylphosphine phenylimide with phenyl isocyanate compared to the lack of further reaction between triphenylphosphine oxide and phenyl isocyanate (eq. 3) indicated that the formation of the imide should be rate determining. Therefore, one should be able to deduce kinetically the presence of the imides as true intermediates.

Formation of an intermediate phosphinimide in its simplest form would be expected to exhibit

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[2] (a) J. S. Blair and G. E. P. Smith, *J. Am. Chem. Soc.*, **56**, 907 (1934); (b) W. J. Balon and O. Stallman, U. S. Patent 2,683,144, July 6, 1954 (*C. A.*, **48**, 12465C (1954)); (c) L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, **8**, 230 (1940); (d) H. L. Snape, *J. Chem. Soc.*, **49**, 254 (1886); (e) A. W. Hoffmann, *Jahrb. Fortsch. Chem.*, 335 (1862); (f) K. H. Slotta and R. Tschesche, *Chem. Ber.*, **60B**, 295 (1927).

[3] (a) T. W. Campbell and J. J. Monagle, *J. Am. Chem. Soc.*, **84**, 3673 (1962); (b) T. W. Campbell and J. J. Verbane, U. S. Patent 2,853,473 to du Pont (9/23/58).

[4] (a) H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953); (b) G. Amiard and R. Heymes, *Bull. soc. chim. France*, 1360 (1956); (c) H. Eilingsfeld, M. Seefelder and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960); (d) S. Hunig, H. Leamann and G. Grimmer, *Liebig's Ann.*, **579**, 87 (1953); (e) E. Schmidt, M. Seefelder, R. Jennen, W. Striewsky and H. von Martius, *Ann.*, **571**, 83 (1951); (f) E. Schmidt, E. Kammerl, D. Ross and F. Zaller, *ibid.*, **594**, 233 (1954).

[5] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 636 (1919).