Fluorocyclopropanes. II. Synthesis, Properties, and Reactions of Perfluorocyclopropene

P. B. Sargeant[1] and C. G. Krespan

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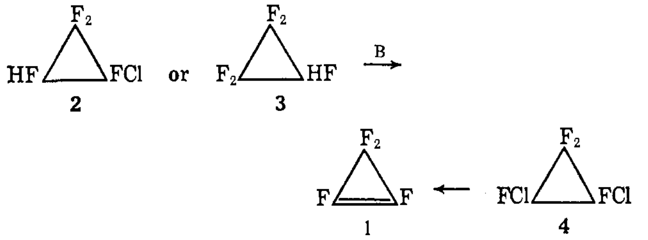
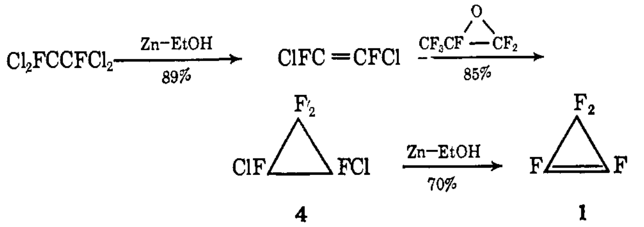
Abstract: Perfluorocyclopropene has been prepared by the dehydrohalogenation of pentafluorocyclopropane and 1-chloro-1,2,2,3-tetrafluorocyclopropane and most conveniently by the dehalogenation of 1,2-dichloro-1,2,3,3-tetrafluorocyclopropane. Perfluorocyclopropene is a flammable, explosive gas. It is surprisingly stable to many conditions, but reacts with nucleophiles, water, and antimony pentafluoride. A Diels–Alder reaction occurs with 1,3-dienes, and a 1,2-cycloaddition reaction was observed with tetrafluoroethylene. Perfluorocyclopropene also undergoes free-radical copolymerization with a variety of unsaturated comonomers.

Cyclopropene[2] and tetrachloro-[3a] and tetrabromocyclopropenes[3b] have been prepared.[4] The availability of several fluorinated cyclopropanes from the reaction of hexafluoropropylene oxide with olefins[5] and consideration of the interesting and often unusual reactions of fluorinated olefins compared to their hydrocarbon and other halogenated analogs[6] led to the preparation and study of perfluorocyclopropene reported in this paper. After completion of this work, the isolation of perfluorocyclopropene from the oxidation of 1,3-perfluorobutadiene was reported.[7]

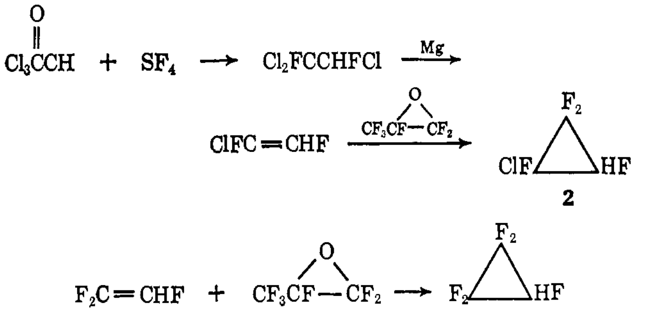
Preparation

Perfluorocyclopropene (**1**) has been prepared by the dehydrohalogenation of 1-chloro-1,2,2,3-tetrafluorocyclopropane (**2**) and pentafluorocyclopropane (**3**) with several bases and by the dehalogenation of 1,2-dichloro-1,2,3,3-tetrafluorocyclopropane (**4**). Isolation of perfluorocyclopropene from the dehydrohalogenation reaction is difficult because it reacts readily with nucleophiles; isolated yields range from 10 to 30%. Perfluorocyclopropene appears to react with bases at a rate at least comparable to that of the cyclopropanes. Therefore, unless the cyclopropene is removed from the reaction mixture as soon as it is produced, it is consumed by reaction with bases present in the reaction medium. The best procedure is addition of the cyclopropane to a stirred 30% aqueous solution of potassium hydroxide at 90–95°. Dehalogenation of 1,2-dichloro-1,2,3,3-tetrafluorocyclopropane, the preferred method of preparation, has proven practical on a 1-*M* scale. Both zinc and magnesium are effective dehalogenation agents. The preferred method uses zinc dust activated by zinc bromide in absolute ethanol at 55°. Yields and conversions vary somewhat from batch to batch, but nine 0.5–1.0-mol runs averaged 53% conversion to product and 70% yield. Recovered starting material was recycled once providing 65% conversion and 72% yield. Starting with the readily available 1,1,2,2-tetrachloro-1,2-difluoroethane, perfluorocyclopropene can be prepared easily in 50–55% over-all yield.





The reaction sequence for cyclopropanes **2** and **3** was



Properties

Perfluorocyclopropene is a colorless gas, bp ~−13° (from distillation), mp −60°, d_4^{-45} ~1.6, which is flammable and burns with a very smoky flame generating a considerable quantity of carbon. Perfluorocyclopropene is probably toxic; crude experiments with drosophila (fruit flies) gave 100% kill in 2 min (concentration = one part in 300).

Perfluorocyclopropene is explosive in air at room temperature and 1 atm.[8] The lower explosive limit is

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[1] Address inquiries to: Benger Laboratory, Textile Fibers Department, E. I. du Pont de Nemours and Company, Waynesboro, Va. 22980.

[2] N. Va. Dem'yanov and M. N. Doyarenko, *Bull. Acad. Sci. USSR*, **16**, 297 (1922).

[3] (a) S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963); (b) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964).

[4] For a review see F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

[5] P. B. Sargent, to be published.

[6] See, for example, R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964.

[7] W. Stuckey and J. Heicklen, *J. Am. Chem. Soc.*, **90**, 3952 (1968).

between 1.7 and 3.4% in air. No upper explosive limit was observed because explosions occurred in 1 atm of pure perfluorocyclopropene. The maximum explosion pressure measured was 114 psi, over a range in concentration of 50–67% perfluorocyclopropene in air; the maximum rate of pressure rise, 20,200 psi/sec, occurred at 83% perfluorocyclopropene in air. Although probably not as extreme a case as tetrafluoroethylene, perfluorocyclopropene is similarly more explosive in the presence than in the absence of oxygen. In a thermal stability test, 1 atm of pure perfluorocyclopropene failed to decompose explosively when heated, at 5°/min, to 273°. Detailed results are in the Experimental Section. It should be pointed out that lack of overt activity in the thermal stability test is not a reliable guarantee of acceptable stability. Explosive decomposition is more likely to propagate at higher pressures. If perfluorocyclopropene is handled in glassware or similarly fragile equipment, suitable precautions should be taken. Reactions in pressure vessels would not entail the same hazards at low pressures; but possibly a vapor-phase explosion could propagate to a liquid phase, in which case a force sufficient to rupture the container can be generated. Such behavior is typical of materials which have obscured upper explosive limits, such as tetrafluoroethylene, alkyl leads, and acetylene.

The infrared spectrum had bands at 1945 (w), 1380 (s), 1340 (s), 1200 (m), 1110 (s), 930 (s), 890 (m), and 775 (w) cm^{-1}. The band at 1945 cm^{-1} is attributed to the carbon–carbon double bond stretch and is the highest frequency yet reported. Cyclopropene,[9] and tetrabromo-[3a] and tetrachlorocyclopropene[3a] have double-bond stretching at 1641, 1757, and 1810 cm^{-1}, respectively. The large dependence on substitution of the band in the double-bond stretching region of cyclopropenes has been noted previously.[9,10] The fluorine nmr spectrum consisted of two triplets at 96.7 and 145.1 ppm[11] (J = 43.5 Hz). The mass spectrum of perfluorocyclopropene (Table I) confirms the identification.

Table I. Mass Spectrum of Perfluorocyclopropene[a]

m/e	Postulated ion	Relative abundance, %
112	Parent	30.7
93	$C_3F_3^+$	82.3
74	$C_3F_2^+$	8.4
69	CF_3^+ [b]	4.4
62	$C_2F_2^+$	12.1
55	C_3F^+	2.2
50	CF_2^+	5.1
43	C_2F^+	3.7
31	CF^+	100
24	C_2^+	2.2
12	C^+	2.3

[a] 70 eV ionizing voltage, 0.125 V trap current, 25° inlet temperature. [b] Rearrangement.

Reactions

In the absence of an ignition source, perfluorocyclopropene is remarkably stable. It was stable to heating at 105° for 12 hr (cyclopropene spontaneously polymerizes at −78°),[12] but in 2 hr at 200° it gave a large number of nonvolatile products. Three of the major products were selected for time-of-flight mass spectrometry. The first two exhibited parent ions at m/e 336 [$(C_3F_4)_3$]; these isomeric trimers had quite different cracking patterns. The third product was a tetramer with parent ion m/e 448. The infrared spectrum of the reaction mixture had bands at 1780 (fluorocarbon C=C) and 1200 (C—F) cm^{-1}.

Photosensitized (acetone, up to 15%) gas-phase irradiation at 3500 Å in a Rayonet Griffin-Srinivasan photochemical reactor resulted in no change, even after 4 days. A condensed sample containing 15% acetone was irradiated at 3500 Å for 3 days with no change. Condensed-phase irradiation at 2537 Å for 3 days gave only acetone condensation products.

Perfluorocyclopropene was bombarded with X-rays from the Van de Graaff accelerator. A 25-Mrad dosage of a solid sample at −78° gave largely unchanged starting material but produced enough impurities to melt the sample. Fluorine nmr suggested the presence of CF_3CF_2– groups indicating rearrangements. Continued dosage of 125 Mrads provided very little additional change. Bombardment of a liquid sample at 0° (25 Mrads) produced no observable change.

Perfluorocyclopropene reacts readily with nucleophiles to yield what appears to be a mixture of addition–elimination products. With triethylamine and no solvent, a violent explosion occurred at −100°; in 1,1,2-trichloro-1,2,2-trifluoroethane solvent, triethylamine and perfluorocyclopropene gave a dark oil which was a mixture of products. This oil could not be characterized. Perfluorocyclopropene and *n*-propylamine in trichlorofluoromethane also gave a product mixture which was not characterized. With catalytic quantities of triethylamine, *n*-propylamine, *n*-butyllithium, or cesium fluoride, perfluorocyclopropene did not homopolymerize anionically from −196 to 100°. Perfluorocyclopropene and excess water in a sealed tube gave an immiscible mixture; after 1 month, only one phase was present. The reaction products were silicon tetrafluoride, hydrogen fluoride, and malonic acid. The reaction can be rationalized as a series of addition–eliminations leading eventually to ring opening and isomerization to malonic acid. No evidence supporting this mechanism was obtained, nor was the desired perfluorocyclopropenone isolated. The same result was obtained in 25% sulfuric acid.

The abundance of the $C_3F_3^+$ perfluorocyclopropenium ion in the mass spectrum of perfluorocyclopropene indicated the stability of the cyclopropenium ions could be extended to the fluorinated system. Addition of perfluorocyclopropene to excess antimony pentafluoride at 0° gave a white precipitate soluble in liquid sulfur dioxide but insoluble in trichlorotrifluoroethane. The white crystalline solid was not stable in air at room temperature. The fluorine nmr spectrum showed antimony pentafluoride and a single resonance band

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(8) We are indebted to Dr. B. W. Richards of the E. I. du Pont de Nemours and Company for determining the explosive properties of perfluorocyclopropene.

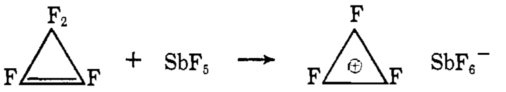
(9) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, 83, 1226 (1961).

(10) W. von E. Doering and T. Mole, *Tetrahedron*, 10, 65 (1960); G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 85, 99 (1963); E. Ciganek, *ibid.*, 88, 1979 (1966).

(11) Referenced to externally substituted trichlorofluoromethane.

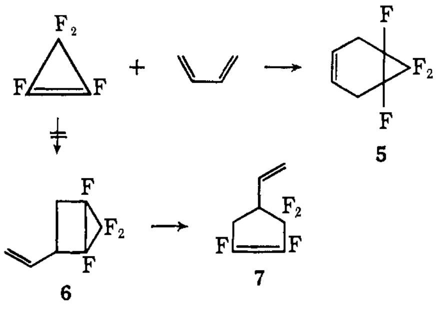
(12) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, 82, 6375 (1960).

at 63.1 ppm.[11] The resonance is 57.8 ppm to low field from the average perfluorocyclopropene chemical shifts and consistent with the deshielding observed in other fluorocarbonium ions such as difluorophenylmethyl hexafluoroantimonate.[13] The absence of the SbF_6^- resonance is not understood, although this could be due to a rapid exchange of fluorine between the perfluorocyclopropenium ion and antimony pentafluoride. If this is the case, this exchange is rapid on the nmr time scale even at −70°; and the observed signal for the cyclopropenium ion is a weighted average of the true chemical shift, which would appear even further downfield, and the SbF_6^- chemical shift. An exchange or equilibrium phenomenon would explain the observed instability of the product in the absence of excess antimony pentafluoride. Simple complex formation is considered unlikely because only a single fluorine resonance is observed in the nmr spectrum. A complex should still show two different kinds of fluorine. Reaction of perfluorocyclopropene in trichlorotrifluoroethane at −40° with boron trifluoride also gave a white precipitate which was unstable at room temperature. The data are consistent with the formation of the perfluorocyclopropenium ion. Salts of this ion are apparently not as stable as those of the tetrachlorocyclopropenium ion.[3]



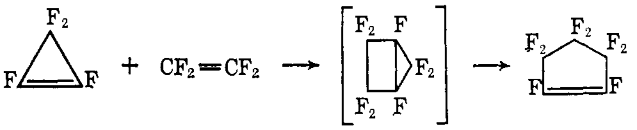
Perfluorocyclopropene did not homopolymerize when treated with catalytic quantities of benzoyl peroxide, azobisisobutyronitrile, or dinitrogen difluoride. Perfluorocyclopropene was recovered unchanged. However, perfluorocyclopropene did undergo free-radical copolymerization with a large variety of unsaturated comonomers, such as ethylene, isobutylene, methyl vinyl ether, and vinyl fluoride. Details of the copolymerization and copolymer properties will be the subject of a subsequent paper.

Cyclopropenes react with 1,3-dienes to yield Diels–Alder adducts.[4,12,14] Perfluorocyclopropene and 1,3-butadiene at 100° gave 1,6,7,7-tetrafluorobicyclo[4.1.0]hept-3-ene (**5**) in ~30% yield.



Identification was based on infrared, hydrogen and fluorine nmr, and mass spectral data. The ^1H nmr spectrum had complex multiplets at 2.4 and 5.0 ppm (area 2 H, 1 H, respectively); the ^{19}F nmr spectrum consisted of an AB pattern of multiplets at 152.5, 156.0, 157.5, and 161.3 ppm ($J_{AB} \sim 200$ Hz) and a multiplet at 211.8 ppm in a 1:1 ratio. In view of the ease with which tetrafluoroethylene cycloadds to olefins, the possibility that the reaction product is a 1,2 cycloadduct (**6**) or its rearranged product (**7**) was considered. The nmr and infrared spectra are inconsistent with such structures. The ^1H nmr spectrum of the product shows saturated and olefinic hydrogens in the ratio 2:1, whereas **6** and **7** require a 1:1 ratio. The ^{19}F nmr spectrum having an AB pattern and a high-field multiplet is consistent with **6**, but **7** would have an AB pattern and two multiplets in the ratio 2:1:1. Further, even if the olefinic fluorines in **7** had identical chemical shifts, 212 ppm is too high field for olefinic fluorines, but expected for tertiary fluorines. Finally, both **6** and **7** would have a strong carbon–carbon double bond stretch in their infrared spectra.[15] This was not observed in the product. However, because of the relatively large quantity of tars isolated in the reaction, one cannot rule out at least partial contribution of the 1,2-cycloaddition reaction. The low yield and high temperature required for this reaction are consistent with the observation[14] that increasing the fluorine content of cyclopropenes decreases their reactivity in Diels–Adder reactions.

A 1,2 cycloaddition was observed between perfluorocyclopropene and tetrafluoroethylene when sealed in a platinum tube and heated at 135° (3000 atm). The product in nearly quantitative yield was perfluorocyclopentene.



Experimental Section

General. Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer. Fluorine nmr spectra were obtained with Varian Associates HR-60 and A56/60 spectrometers operating at 56.4 Hz. Chemical shifts of neat samples were referenced to internal TMSi (^1H) and externally substituted trichlorofluoromethane (^{19}F). Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer calibrated with polystyrene. Mass spectra were obtained on a Bendix Time-of-Flight mass spectrometer at 70 eV ionizing voltage. Syntheses of the olefins and cyclopropanes used in this study have been reported previously.[5] The preparation of pentafluorocyclopropane is reported as an example of the hexafluoropropylene oxide–olefin reaction.[5]

Pentafluorocyclopropane. Trifluoroethylene (80 g, 1.0 mol) and hexafluoropropylene oxide (250 g, 1.5 mol) were charged to a 1-l. stainless steel bomb and heated at 185° for 6 hr. Distillation of the volatile products gave pentafluorocyclopropane (86 g, 0.65 mol, 65% yield, bp −10°)[5,16] along with trifluoroacetyl fluoride (98 g, bp −50 to −40°) and unreacted hexafluoropropylene oxide.

Perfluorocyclopropene. 1. Dehydrochlorination of 1-Chloro-1,-2,3,3-tetrafluorocyclopropane. Aqueous potassium hydroxide (150 g in 300 ml) was heated to 90° in a 500-ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, 50-ml addition funnel, and a cold water condenser leading to a 50-ml trap cooled in Dry Ice-acetone. 1-Chloro-1,2,3,3-tetrafluorocyclopropane (49.5 g, 0.332 mol) was added slowly to the stirring mixture over 30 min. There was obtained a 21-ml product (~34 g) which was 14% perfluorocyclopropene and 86% 1-chloro-1,2,3,3-tetrafluorocyclopropane by vpc. Distillation gave perfluorocyclopropene (4.0 g, 0.036 mol, bp −22°to −15°). Conversion was 12% with a 30% yield (26% isolated).

2. Dehydrofluorination of Pentafluorocyclopropane. Aqueous potassium hydroxide (200 g in 400 ml) was heated to 95° in a 1-l.,

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(13) P. B. Sargeant, unpublished data; G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 362 (1966).

(14) E. Ciganek, *ibid.*, 88, 1979 (1966); S. W. Tobey and D. C. F. Law, *Chem. Eng. News*, **45**, 44 (Oct 2, 1967).

(15) R. A. Mitsch, *J. Am. Chem. Soc.*, 87, 758 (1965).

(16) R. A. Mitsch, *J. Heterocyclic Chem.*, 1, 271 (1964).

three-necked, round-bottomed flask equipped with a mechanical stirrer, gas inlet tube reaching below the surface of the liquid, and a condenser leading to a 50-ml Dry Ice–acetone cooled trap. Pentafluorocyclopropane (38 g, 0.29 mol) was bubbled slowly through the stirring solution (6 hr). The final portion was pushed through by sweeping with N_2 for 15 min. There was obtained a 15.5-ml product (25 g) which was 24% perfluorocyclopropene and 76% pentafluorocyclopropane by vpc (18% conversion, 36% yield).

3. **Dechlorination of 1,2-Dichloro-1,2,3,3-tetrafluorocyclopropane.** Zinc dust (220 g) and zinc bromide (22 g) were suspended in absolute ethanol (300 ml) in a 1-l., three-necked round-bottomed flask equipped with a 250-ml addition funnel, mechanical stirrer, and cold water condenser leading to a 50-ml trap cooled in Dry Ice–acetone, and heated to 55° under N_2. 1,2-Dichloro-1,2,3,3-tetrafluorocyclopropane (136 g, 0.74 mol) in absolute ethanol (75 ml) was slowly added to the stirring suspension. After 18 hr, the system was swept with N_2 for 15 min. Product (50 ml) collected in the trap was distilled through a 40-cm, low-temperature column to give unreacted 1,2-dichloro-1,2,3,3-tetrafluorocyclopropane (27.0 g, 0.14 mol, 80% conversion) and tetrafluorocyclopropene (56 g, 0.50 mol, bp −10 to −3°, 85% yield). The nmr and infrared spectra are presented in the Discussion and the time-of-flight mass spectrum is reported in Table I.

Explosive Properties of Perfluorocyclopropene. Experiments were performed in a 500-cc, stainless steel, cylindrical pressure vessel fitted with end closures and a side inlet. The end closures contained a thermocouple, to measure the vapor temperature, and a quartz pressure transducer. The thermocouple and transducer were connected to appropriate instruments to record the internal temperatures and pressures. An electrically heated coil of nichrome wire served as igniter. The pressure vessel was evacuated, perfluorocyclopropene was admitted to the desired partial pressure, air was admitted up to 1 atm, and the wire was heated to initiate an explosion. Results are in Table II.

Table II. Explosive Properties of Perfluorocyclopropene (PFCP)

Expt no.	% PFCP (in air)	Temp, °C	Explos pressure, ΔP, psi	$(dp/dt)_{max}$, psi/sec	$(\Delta p/\Delta t)_{av}$, psi/sec
4[a]	1.7	32	..	...	..
3	3.4	32	34	145	~50
2	10	31	46	1,880	<1,300
1	15	29	100	5,530	<3,300
6	33	36	105	15,850	<10,000
7	50	27	114	16,550	<10,000
8	67	28	114	18,200	<16,000
9	83	29	105	20,200	<16,000
10	100	30	90	13,000	<14,500
5[b]	100	27	22	560	<430
11[c]	100	≤273	<25	...	...

[a] Hot wire fused in vapor; no explosion. [b] Total initial pressure, 0.33 atm. [c] Thermal stability; no sudden pressure rise.

Thermal Stability of Perfluorocyclopropene. A sample of perfluorocyclopropene was sealed in an nmr tube and heated at 80° for 3 days. The ^{19}F nmr spectrum indicated no change. Heating was continued at 105° for an additional day. ^{19}F nmr indicated no change. The sample was heated at 200° for 2 hr. The sample yellowed slightly and an increase in viscosity was noted. The ^{19}F nmr spectrum had many new resonance absorptions. Heating at 200° for 66 hr caused no further change. The tube was cooled and opened. No products volatile at room temperature were found. Vpc indicated the presence of numerous products. Three of the larger peaks were selected for time-of-flight mass spectrometry. The first two exhibited parent ions at 336 [$(C_3F_4)_3$]; these isomeric trimers had quite different cracking patterns. The third peak was a tetramer exhibiting the parent *m/e* 448. The infrared spectrum of the reaction mixture had bands at 1780 cm^{-1} (fluorocarbon C=C) and 1200 cm^{-1} (C—F).

Reaction of Triethylamine and Perfluorocyclopropene. Perfluorocyclopropene was condensed on top of triethylamine in an nmr tube. The tube was sealed and slowly warmed from −196°. While both layers were still solid, a black color appeared at the interface followed immediately by a violent explosion. The explosion may have been due to local high concentrations at the interface with no way to dissipate the heat of reaction. The reaction was repeated as follows.

Perfluorocyclopropene (0.5 ml, 0.8 g, 7.1 mmol) was dissolved in trichlorotrifluoroethane (15 ml) and cooled to −40°. Triethylamine (7×10^{-6} mol) was slowly added. No change was apparent, but on warming slowly to room temperature the solution yellowed and a small amount of brown precipitate formed. Vpc showed only unreacted perfluorocyclopropene and solvent. The mixture was cooled to −40° and triethylamine (0.71 g, 7.1 mmol) in trichlorotrifluoroethane (7 ml) was slowly added. A dark precipitate formed instantly. Warming the mixture to room temperature resulted in coagulation and semiliquefaction. The solvent was evaporated to give a residual dark oil which could not be characterized.

Reaction of *n*-Propylamine and Perfluorocyclopropene. Perfluorocyclopropene (0.5 ml, 0.8 g, 7.1 mmol) was dissolved in trichlorofluoromethane (15 ml) and cooled to −78°. *n*-Propylamine (10 μl) was added and the solution was allowed to warm to room temperature. No observable change occurred. The solution was cooled to −78° and *n*-propylamine (0.45 g, 7.6 mmol) in trichlorofluoromethane (5 ml) was added. After stirring 30 min at −78°, slow warming to room temperature resulted in a white precipitate at −20°, which became a dark oil at 25°. The solvent was evaporated to give a residual dark oil which could not be characterized.

Reaction of *n*-Butyllithium and Perfluorocyclopropene. Perfluorocyclopropene (3 mmol) and *n*-butyllithium (10^{-6} mol) were sealed in an nmr tube and warmed to room temperature from −196°. Reaction appeared to occur at ~−100° at the interface to form a small amount of yellow solid. ^{19}F nmr of the sealed tube showed only unreacted perfluorocyclopropene. ^1H nmr showed absorption from 0 to 1 ppm only.

Reaction of Cesium Fluoride and Perfluorocyclopropene. Perfluorocyclopropene (3 mmol) was sealed in an nmr tube with cesium fluoride (5 mg). Warming from −196 to 80° gave slight yellowing of the solution and darkening of the cesium fluoride but no change by ^{19}F nmr. Similar results were obtained with cesium fluoride (5 mg) activated by diglyme (20 μl).

Reaction of Water and Perfluorocyclopropene. Perfluorocyclopropene (1.54 mmol) and distilled water (0.45 ml, 22 mmol) were sealed in an nmr tube. Two layers were observed. The lower (PFCP) layer slowly disappeared (1 month). ^{19}F nmr examination showed only perfluorocyclopropene, a large resonance at 128.7 ppm and a weak resonance at 149.9 ppm. After 3 months, the tube was cooled in Dry Ice and opened. A trace of SiF_4 was observed (infrared); the solution was acidic (pH ~1). Evaporation provided colorless crystals of malonic acid (mp 123–129.5°, malonic acid mp 133°, mmp 133°). The infrared spectrum was identical with the spectrum of an authentic sample, and the ^1H nmr spectrum had bands at 10.7 and 3.4 (area = 1:1) ppm [$H_2C(CO_2Et)$ lit.[17] 3.37 ppm]. The ^{19}F nmr absorption at 128.7 ppm is aqueous HF [Pople, Schneider, and Bernstein report aqueous KF resonance at 125 ppm[18]]. The same result was obtained in 25% (by volume) aqueous sulfuric acid.

Perfluorocyclopropenium Hexafluoroantimonate. Antimony pentafluoride (~3.5 ml, 0.05 mol, redistilled) was added to a 25-ml flask equipped with a rubber septum and a side-arm balloon under N_2, and placed in an ice bath. Perfluorocyclopropene (225 cc, ~0.01 mol) was slowly forced into the flask by a syringe. The white precipitate formed was transferred to an nmr tube and dissolved in liquid sulfur dioxide. ^{19}F nmr showed SbF_5 at 112 ppm and a single line at 63.1 ppm. The nmr spectrum did not change at −39, −60, or −70°. The solid reacted in air, but was stable in the reaction vessel under N_2. The solid was separated from excess antimony pentafluoride by washing with trichlorotrifluoroethane, filtering under N_2, and washing with more trichlorotrifluoroethane. The solid immediately began to turn dark, and the N_2 drying stream fumed in the air.

Reaction of Perfluorocyclopropene and Boron Trifluoride. Perfluorocyclopropene (6.4 g, 57 mmol) was dissolved in trichlorotrifluoroethane (10 ml) in a 125-ml, three-necked, round-bottomed flask equipped with gas inlet tube, Dry Ice condenser, and magnetic stirrer. The solution was cooled to −40°, and boron trifluoride was bubbled through the solution for 1.5 hr. A white precipitate formed which was stored overnight at −78°. On slow warming to

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(17) Varian Associates High Resolution NMR Spectra Catalog, Vol. 1, Palo Alto, Calif., 1962, Spectrum No. 181.

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 318.

room temperature, the precipitate dissolved with gassing. Vpc indicated the presence of only solvent and perfluorocyclopropene. Cooling back to −50° did not cause reprecipitation. Boron trifluoride was bubbled through the solution for 2 hr, resulting in re-formation of the white precipitate. Methanol (2.0 g, 62 mmol) was slowly added to the stirring suspension. On warming to room temperature, vpc showed solvent and perfluorocyclopropene. Examination of the product indicated the presence of a mixture of methanol–BF_3 products.

Free-Radical Polymerization of Perfluorocyclopropene. Benzoyl Peroxide. Perfluorocyclopropene (4 mmol) and benzoyl peroxide (5 mg) were sealed in an nmr tube and heated at 100° for 6 hr ($t_{1/2}$ = 30 min at 100°). ^{19}F nmr showed only unreacted perfluorocyclopropene.

Azobisisobutyronitrile. Perfluorocyclopropene (3 mmol) and AIBN (5 mg) were sealed in an nmr tube and heated at 80° for 2 hr (AIBN $t_{1/2}$ = 1 hr at 84°). The sample yellowed slightly, but did not increase in viscosity. ^{19}F nmr showed only unreacted perfluorocyclopropene.

Dinitrogen Difluoride. Perfluorocyclopropene (6 mmol) and dinitrogen difluoride[19] (9×10^{-4} mol) were sealed in a $^3/_8$-in. platinum tube and heated at 70° under 3000 atm pressure for 4 hr. Perfluorocyclopropene was recovered unchanged (90% recovery).

Copolymers of Perfluorocyclopropene. Equimolar quantities of perfluorocyclopropene and comonomer were added to a glass tube (18 × 4 mm i.d.) containing benzoyl peroxide (5 mg, 2×10^{-5} mol). The tube was degassed, sealed, and heated at 80–85°. The copolymers were characterized by their infrared spectrum, differential thermal analysis, and in most cases by fluorine elemental analysis. All copolymers had infrared bands absent in the homopolymer. Absorption evidently characteristic of the perfluorocyclopropene copolymer appears at 1700–1770 and 1100–1200 cm^{-1}. The 1700-cm^{-1} (unsaturated fluorocarbon) band is substantially decreased upon purification and is probably due to low molecular weight copolymer. Differential thermal analysis charts of the copolymers were different from those of the homopolymers. Several copolymers showed a large exotherm at 250–300°.

Examination of the volatile material after each polymerization showed mostly unchanged starting olefin and PFCP with only traces of other fluorine-containing materials.

1,6,7,7-Tetrafluorobicyclo[4.1.0]hept-3-ene. Butadiene (0.15 g, 2.4 mmol) and perfluorocyclopropene (2.9 mmol) were sealed in an nmr tube and heated at 100°. The reaction was followed by ^1H nmr. After 24 hr the amount of butadiene had decreased by about 60%. The tube was cooled and opened, and 1,6,7,7-tetrafluorobicyclo[4.1.0]hept-3-ene was isolated free from perfluorocyclopropene, butadiene, and polymeric by-products by trap-to-trap distillation. The ^1H nmr spectrum had multiplets at 2.4 and 5.0 ppm (area = 2 and 1, respectively); the ^{19}F nmr spectrum had an AB pattern at 152.5, 156.0, 157.5, and 161.3 ppm ($J_{AB} \sim 200$ Hz) and a multiplet (211.8 ppm) in a 1:1 ratio. The infrared spectrum had bands at 3080 (olefinic C—H), 2910, 2850 (aliphatic C—H), 1560 (weak, C=C), 4180, 1430 (CH_2), and 1200 (C—F) cm^{-1}. The time-of-flight mass spectrum had a parent ion (*m/e* 166) and fragmentation pattern consistent with the assigned structure.

Perfluorocyclopentene. Perfluorocyclopropene (3.5 mmol) and tetrafluoroethylene (3.5 mmol) were sealed in a platinum tube and heated at 135° and 3000 atm for 8 hr. The tube was opened, and perfluorocyclopentene was identified by ^{19}F nmr and vpc comparison with an authentic sample. Only traces of other products were noted. Similar results were obtained at 180° for 2 hr.

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The Reaction of Diazonium Salts with Nucleophiles. XIII. Identity of the Rate- and Product-Determining Steps[1]

Edward S. Lewis, Levoy D. Hartung, and Bruce M. McKay

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received July 19, 1968*

Abstract: The effects of several salts on the rates of disappearance of benzenediazonium ion in aqueous solution are studied. The effects are small, but at any concentration the rates increase in the order bisulfate < chloride < bromide < thiocyanate. Rates with various bisulfates are slower than in the absence of added salts. The rate reduction is attributed to the low reactivity of water solvating the cation, and hence the very small rate effect of solutions of sodium bromide or chloride is actually a combination of a retardation due to the sodium ion and an acceleration due to the chloride or bromide ion. These rate accelerations are at least enough to account for all the chlorobenzene or bromobenzene formed. Thus no products are determined by competitions after the rate-determining step—a conclusion supported by a simple reinterpretation of a great deal of earlier data. It is possible to account for the detailed shape of the plot of rate *vs.* salt concentration by a normal salt effect, so an earlier interpretation of this shape in terms of a spirocyclic diazirine cation intermediate is not supported. The relative reactivities of the different nucleophiles toward the diazonium ion differ very little, and it is shown that this unselectivity leads to an inherent and general difficulty in distinguishing between one-step reactions and two-step processes through a highly reactive intermediate.

The hydrolysis of diazonium salts follows a first-order course and is insensitive to many added salts at low concentrations[2,3] and even sometimes at high concentrations.[4] This is not always true. Tetrazotized paraphenylenediamine shows essentially pure bimolecular kinetics with chloride, bromide, or thiocyanate ions;[5] *p*-nitrobenzene diazonium ion dis-

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[1] Based upon portions of the Ph.D. theses of L. D. Hartung (1966) and B. M. McKay (1968), Rice University. Certain parts were presented at Southwest Regional Meetings of the American Chemical Society, Memphis, Tenn., 1965 and Little Rock, Ark., 1967.

[2] D. F. DeTar and A. R. Ballentine, *J. Am. Chem. Soc.*, **78**, 3916 (1956).

[3] H. A. H. Pray, *J. Phys. Chem.*, **30**, 1417 (1926).

[4] J. S. P. Blumberger, *Rec. Trav. Chim.*, **49**, 259 (1930).

[5] E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **82**, 5408 (1960).