Alkali Fluorides as Catalysts in Reactions Involving Unsaturated Fluorocarbons[1]

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Cesium fluoride in the *solid state* has been demonstrated again to be a good fluoride ion catalyst for certain reactions requiring the formation of a carbanion intermediate. For example, $\mathrm{CF_3CF{=}CF_2}$ can be dimerized to *cis* and *trans* isomers of $\mathrm{(CF_3)_2CFCF{=}CFCF_3}$ and $\mathrm{(CF_3)_2C{=}CFCF_2CF_3}$; $\mathrm{CF_3CF{=}CF_2}$ will react with cyclo-$\mathrm{C_5F_{10}NF}$, perfluorpiperidine, to form cyclo $\mathrm{C_5F_{10}N}$—*i*-$\mathrm{C_3F_7}$, perfluoroisopropyl-N-piperidine; $\mathrm{F_2CClCFClCF_2CF{=}CF_2}$ can be isomerized to $\mathrm{F_2CClCFClCF{=}CFCF_3}$; perfluoropentadiene-1,4 and -1,3 can be isomerized to perfluoropentyne-2 in almost 100% yields (and conversions) up to 240°; and the new isomer perfluoromethylcyclobutene-1 can be formed over NaF at between 320 and 440°. The perfluoromethylcyclobutene-1 was oxidized to the new keto acid, $\mathrm{CF_3COCF_2CF_2COOH}$. The dimerization of $\mathrm{CF_3N{=}CF_2}$ to $\mathrm{(CF_3)_2NCF{=}NCF_3}$ appears to proceed *via* a negative ion mechanism. Of the five $\mathrm{C_5F_8}$ isomers tested, only perfluoropentyne-2 tended to undergo significant polymerization on exposure to γ radiation from cobalt-60 source.

The use of $\mathrm{F^-}$ as a catalyst in reactions involving a fluorocarbon carbanion as an intermediate is not novel. There are a number of examples in the chemical and technical literature.[3–7] However, several of these examples[3,5,6] are concerned with ionic fluorides dissolved in polar solvent such as dimethylformamide, dimethyl sulfoxide, chloroform, acetone, or acetonitrile. It is quite possible that fluoride slurries were present. Solvent effects were of some consequence and reaction with solvent were not uncommon from the nature of the products reported. The use of CsF as a catalyst where $\mathrm{CF_3CF{=}CF_2}$ was concerned was suggested also by a number of other reports in which the alkali fluorides were used but in which the role played by the perfluoroisopropyl carbanion was not obvious at the time.[8–10] A recent publication of Andreades[11] demonstrates unambiguously the existence of fluorocarbanions.

TABLE I

REACTION OF $\mathrm{CF_3CF{=}CF_2}$ OVER CsF[a]

Temp., °C.[b]	Time, hr.	—Mole % conversion to products[c]— I	II	III	IV	A	Total conversion, mole %
100	268	19.2	3.1	2.8	0.3	1.6	27.0
150	32	3.2	31.4	5.1	0.5	27.0	67.0
150	64	3.4	33.2	5.4	0.6	28.4	71.0
200	10	0.4	37.5	1.8	0.2	39.5	79.4
200[d]	12	0.4	39.4	1.9	0.2	41.5	83.4
215[e]	87	0.2	46.0	0.6	0.3	23.0	70.1
350[f]	2 min.	0.3	1.4	0.0	1.8	...	3.5

[a] Results are an average of 14 passes. [b] All static runs at 7–9 atm. except where noted otherwise. [c] I, *cis*-$\mathrm{(CF_3)_2CFCF{=}CFCF_3}$; II, $\mathrm{(CF_3)_2C{=}CFCF_2CF_3}$; III, *trans*-$\mathrm{(CF_3)_2CFCF{=}CFCF_3}$; IV, $\mathrm{(CF_3)_2CFCF(CF_3)_2}$; A, various other products with $\mathrm{C_5}$, $\mathrm{C_7}$, $\mathrm{C_8}$, and $\mathrm{C_9}$ skeletons (see Experimental Section). [d] At 90 atm. [e] At 14 atm. [f] Flow run with short contact time.

The work reported here on the mild polymerization of $\mathrm{CF_3CF{=}CF_2}$ differs from the cited patent[5] in that no solvents were involved and the reaction conditions were quite different, as were some of the products. At the more elevated temperatures intensive cracking was observed while at lower temperatures (100–200°) cracking was more extensive. Table I incorporates the conditions and results of a series of reaction with $\mathrm{CF_3CF{=}CF_2}$ over dry powdered CsF in various reaction systems. With the exception of compounds III and IV, the main products were those reported in a previous study[5] in solution. The *trans* isomer III shows a temperature dependence which is maximized at about 150°. These results suggest the reaction steps

$$\mathrm{(CF_3)_2CFCF{=}CFCF_3} \xrightarrow{\mathrm{F^-}} \mathrm{(CF_3)_2CFCF\bar{C}F_2CF_3} \longrightarrow \mathrm{(CF_3)_2C{=}CFCF_2CF_3 + F^-}$$

Since free rotation between C-2 and C-3 is possible, *cis–trans* isomerization can result on desorption of the substrate. Evidence for carbon formation, especially in the 350° reaction, was found on the used catalyst. Apparently complete cracking can occur giving quantities of elemental fluorine which accounts for product IV, *viz.*

$$\mathrm{(CF_3)_2CF^- + F\cdot \longrightarrow (CF_3)_2CF\cdot + F^-}$$
$$\mathrm{2(CF_3)_2CF\cdot \longrightarrow \underset{IV}{(CF_3)_2CFCF(CF_3)_2}}$$

At least two different $\mathrm{C_9}$ olefins were observed.[5]

The dimerization of $\mathrm{CF_3N{=}CF_2}$ to form $\mathrm{(CF_3)_2NCF{=}NCF_3}$ probably proceeds *via* an ionic mechanism. That the reaction is more sensitive to solid catalysis is indicated by the fact that in ref. 6, when $\mathrm{CF_3N{=}CF_2}$ was treated with $\mathrm{COF_2}$ in a polar solvent containing $\mathrm{F^-}$, no report of this known dimer[12] was made, although the main reaction to produce $\mathrm{(CF_3)_2NCOF}$ was not rapid.

Attempts to treat $\mathrm{CF_3N{=}CF_2}$ with $\mathrm{NF_3}$ catalytically over CsF resulted only in a high yield of dimer up to 450–500°. At higher temperatures (537°) $\mathrm{NF_3}$ decomposed in quantity and the resulting $\mathrm{(CF_3)_2N\cdot}$ radicals combined to give the stable tetra(trifluorometh-

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(2) This paper was taken in part from the Ph.D. dissertation of F. N. Tlumac, University of Florida, 1961, and part of it was presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 12N.

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yl)hydrazine. It is of interest that, besides dimer, no other compounds were formed at these high temperatures. The contact time was short, 32 sec. $(CF_3)_2CF^-$ ion was capable of F^- displacement in the N–F bond of perfluoropiperidine to form $C_5F_{10}N$-*i*-C_3F_7, *viz.*

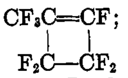
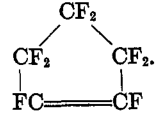
$$(CF_3)_2CF^- + FNC_5F_{10} \longrightarrow (CF_3)_2CFNC_5F_{10} + F^-$$

Table II lists some conditions and results of the isomerization of some C_5F_8 isomers over CsF and NaF as a function of temperature. The two dienes, $CF_2{=}CFCF_2CF{=}CF_2$ (V) and $CF_2{=}CFCF{=}CFCF$ (VI), behave differently over each catalyst. The pentyne (VII) was first prepared by Henne and Latif,[13] and identified unambiguously by Miller.[4] The interesting cyclic isomer 1-perfluoromethylcyclobutene-1 (VIII) was successfully oxidized to the keto acid, perfluorolevulinic acid (X).

Table II

Isomerization of C_5F_8 Isomers

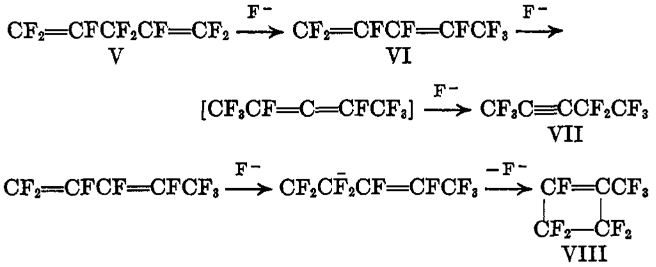
Isomer[a]	Catalyst	Temp., °C.	Contact time, sec.	Isomeric products, mole %[a] V	VI	VII	VIII	IX[b]
V	CsF	240	150	2	..	98	..	..
V	NaF	440	215	5	..	27	58	10
V	NaF	440	100	8	..	26	58	6
V	None[c]	400	72 hr.	94	4	2	..	..
VI	CsF	240	140	..	5	95	..	..
VI	NaF	340	125	..	15	60	25	..
VI	NaF	440	100	..	..	60	40	..
VI	None[c]	400	72 hr.	3	60	..	..	25
VII	CsF	520	118	10	20	40	30	..
VII	NaF	520	83	..	4	92	4	..
VII	None[c]	400	72 hr.	..	..	99	..	..
VIII	CsF	240	200	..	..	1	97	2
VIII	NaF	440	130	3	..	9	85	3
VIII	None[c]	400	72 hr.	..	6	3	91	..

[a] V, $CF_2{=}CFCF_2CF{=}CF_2$; VI, $CF_2{=}CFCF{=}CFCF_3$; VII, $CF_3CF_2C{\equiv}CCF_3$; VIII, ; IX, 

[b] IX failed to react up to 520°. [c] In glass at 11 atm.

The isomerization behavior of V and VI over CsF is explained in ref. 4. The NaF catalysis of V and VI can be explained as shown in Scheme I. These transformations may also be complicated by various thermal processes. The formation of perfluorocyclopentene (IX) from the other isomers may be partly catalytic, but may occur thermally *via* a bicyclo isomer as suggested by Miller and Fainberg.[14]

Scheme I



Of the five C_5F_8 isomers, VI to X, respectively, exposed in glass to 10^7 r. of γ radiation from a cobalt-60 source, only isomer VII showed any gross tendency to react. A polymer was formed which was less stable and less intractable than that made by Brown and Gewanter[15] from $CF_3C{\equiv}CCF_3$ in a similar manner.

In the preparation of VI it was necessary to isomerize the intermediate $CF_2ClCFClCF_2CF{=}CF_2$. This was accomplished over CsF at 240° in a 60% conversion to $CF_2ClCFClCF{=}CFCF_3$.

Experimental Section

Flow reactions were performed (a) by passing gaseous reagents or (b) by vaporizing liquids with a carrier gas, either inert helium or a gaseous reactant, through a 1-in.-o.d. nickel tube packed with catalyst. The reaction tube was heated in a Hoskins furnace. The reported temperatures were measured with a Chromel–Alumel thermocouple which was inserted in a well in the center of the tube. The packed portion of the tube was 13 cm. long. Thus contact times were estimated on the basis of only a small thermal gradient of about 3–5°. Static reactions were performed (A) in a 500-ml. stainless steel Hoke cylinder modified to accommodate a pressure gauge and valve, or (B) a 300-ml. or (C) a 100-ml. stainless steel Aminco high-pressure reactor. These vessels could be heated and rocked in appropriate equipment. Uncatalyzed reactions were run in vessel A or heavy-wall glass ampoules. Each reaction vessel was charged with given amounts of either powdered CsF or NaF (pellets) which was always thoroughly dried at 500° *in vacuo* for at least 1 day each time it was used. Infrared data were obtained mainly on a Perkin-Elmer Model 137B Infracord and to a lesser extent on a Perkin-Elmer Model 21. Gas or vapor samples were studied in a 5-cm. cell with NaCl optics and liquid samples between NaCl plates. N.m.r. data were obtained on a Varian DP-60 high-resolution n.m.r. spectrometer at 56.4 Mc. Trifluoroacetic acid was the external standard in all spectra. Chemical shifts are in p.p.m. Analytical v.p.c. data were obtained with a Perkin-Elmer vapor fractometer, Model 154-B. The analytical columns were packed with either *n*-hexadecane, the ethyl ester of Kel F acid 8114, or dinonylphthalate, each on 65–100-mesh Celite. Each column was 0.25-in.-o.d. copper tubing 2 m. long. Nitrogen or helium was the carrier gas. Mixtures of isomers were analyzed by allowing the whole sample to vaporize in a 5- or 12-l. bulb and to mix for 24 hr. before using an aliquot for analysis. Analysis of known standard mixtures showed that this general procedure was accurate to 2–5% depending on the concentration of a particular isomer. Preparative-scale separations were performed on a noncommercial unit. The column was an 11-m. length of $^3/_8$-in. pipe packed with hexadecane on Celite.

Perfluoroazapropene, $CF_3N{=}CF_2$, was made as previously described.[16] Nitrogen trifluoride and $C_5F_{10}NF$ were prepared electrochemically.[17] Perfluoropentadiene-1,4 (V), $CF_2{=}CFCF_2CF{=}CF_2$, was prepared as described by Parks and Lacher.[18]

Static Reactions of $CF_3CF{=}CF_2$ over CsF.—Into reaction vessel A, previously loaded with 75 g. of CsF, were condensed 46 g. of C_3F_6. The vessel was heated over a 50-hr. period to 200°. The pressure rose almost linearly from 8.1 to 14.2 atm. During the next 87 hr. the temperature was raised to 215° as the pressure dropped to 10.0 atm. Heating was discontinued in another 24 hr. as the pressure tended to level off at 9.7 atm. The volatile materials were removed from the vessel at 100°. The C_3F_6, which amounted to 12 g., was stripped from the mixture. The remainder of the products were analyzed by v.p.c. under a set of laboratory standard conditions using a *n*-hexadecane column, and, on the basis of appearance time of a very large number of known fluorocarbon compounds, the composition of the mixture was estimated as follows: (1) 3 mole % C_5F_{10}

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(18) Directions for the preparation from Kel-F acid 683 first appeared in a W.A.D.C. report by J. D. Parks and J. R. Lacher. Pertinent details are also in ref. 10.

isomer, (2) 63 mole % II, (3) 0.5 mole % IV, (4) 4 mole % C_7F_{14} isomers, and (5) 8 and 6 mole % of two different C_9F_{18} isomers.[19] Aliquots of compounds II and IV were separated by v.p.c. from this mixture (and others encountered later) and were found to be $(CF_3)_2C{=}CFCF_2CF_3$ and $(CF_3)_2CFCF(CF_3)_2$.[10]

Anal. Calcd. for C_6F_{12}: C, 76.0; F, 24.0. Found: C, 75.8; F, 24.3.

The compound II had a $C{=}C$ infrared absorption peak at 5.92 μ (m), a boiling point of 50.0°, and a molecular weight of 301 (calcd. 300). The n.m.r. spectrum was [(group), chemical shift in p.p.m., and (relative area)] for $(CF_3)_2{}^{a}C{=}CF^{b}CF^{c}CF_3{}^{d}$: [(a), −20.9 and −17.5, (3 and 3)], [(b), 22.4, (1)], [(c), 44.7, (2)], [(d), 7.3, (3)].

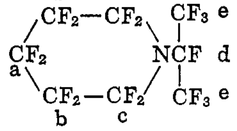
In the other static reactions (Table I) involving C_3F_6 over CsF, the amount of catalyst was 150 g. The amount of olefin charged into vessel B was 70 g. for all the lower pressure reactions between 7 and 9 atm. In the single high-pressure study at 90 atm., 200 g. of catalyst and 73 g. of olefin were used in vessel C. Adequate amounts of compounds I and III were isolated from the various mixtures by preparative-scale v.p.c. using a *n*-hexadecane column. The *trans* isomer showed no infrared absorption in the $C{=}C$ region, but the n.m.r. spectrum was confirmatory, *viz.*, *trans*-$(CF_3)_2{}^{a}CF^{b}CF^{c}{=}CF^{d}CF_3{}^{e}$: [(a], −6.3, (6)], [(b), 111, (1)], [(c), 80, (1)], [(d) 82, (1)], [(e), 0, (3)]. However, the *cis* isomer had a medium strong infrared absorption at 5.72 μ and the following n.m.r. spectrum: [(a), −0.5, (6)], [(b), 109, (1)], [(c), 60.1 (1)], [(d) 63.3, (1)], [(e), −10.9, (3)]. Both isomers had molecular weights of 301 (calcd. 300) and boiled at 51.0 ± 0.5°.

Anal. Calcd. for C_6F_{12}: C, 24.0; F, 76.0. Found for I: C, 24.3; F, 76.3. Found for III: C, 24.4; F, 75.7.

Flow Reaction of $CF_3CF{=}CF_2$ over CsF at 340°.—Over CsF powder at 340° was passed C_3F_6 (25 g., 0.17 mole) at such a rate that the calculated contact time was 123 sec. As only 1.1 g. of product boiled above 27°, the unconverted olefin was repassed through the reactor 14 times until about 8 g. was converted to products. The products were completely separated by preparative-scale v.p.c. using a *n*-hexadecane column. Only four products were obtained: three as indicated in Table I and a fourth which amounted to only about 1 mole % of the products which had an infrared $C{=}C$ absorption different from the other C_6 olefins formed and could well have been $(CF_3)_2CFC(CF_3){=}CF_2$. From the preponderant amount of IV found, 48 mole %, the substrate was examined for carbon, which was found to be present and visible to the naked eye.

Static Reaction. $CF_3CF{=}CF_2$ with Perfluoropiperidine.—An uncatalyzed reaction was attempted in vessel A using 10 g. (0.35 mole) of $C_5F_{10}NF$ and 5 g. (0.033 mole) of C_3F_6. No reaction was observed to occur below 300°. At 375° ring fragmentation occurred, with no new products formed boiling above −10°. Infrared spectra of the material showed absorptions for $C{=}N$ and $C{\equiv}N$ groups.

In a catalyzed reaction, 30 g. (0.11 mole) of $C_5F_{10}NF$ and 16 g. (0.11 mole) of C_3F_6 were charged into vessel A previously loaded with 75 g. of dried, powdered CsF. The vessel was heated to 200° over a 70-hr. period and, when no further pressure drop was observed for a 24-hr. period, heating was discontinued. Fractionation and estimation of the materials gave the following proximate results: (1) 3 g. of C_3F_8; (2) 3.5 g. of C_3F_6; (3) 11.0 g. of $C_5H_{10}NF$; (4) 5 g. in the C_6 range; (5) 14 g., b.p. 33–34° at 81 mm.; (6) 6.0 g., boiling up to 118°. Fraction 5 had $n^{25}D$ 1.2864 and a molecular weight of 432–433 (calcd. 431). It failed to give a positive test for an N–F bond with K in acetone or acetonitrile. The n.m.r. spectrum was (see the following structure) [(a), 41.2, (2)], [(b), 59.8, (2.1)], [(c), 19.4, (3.9)], [(d), 113 (1.0)], [(e), −1.1, (6.2)].



Anal. Calcd. for $C_8F_{17}N$: C, 22.3; F, 75.0. Found: C, 22.2; F, 74.6.

The yield was in the order of 48% for the amount of $C_5F_{10}NF$ used. It is noted that an isomer perfluoro-4-isopropylpiperidine boils at 124.5° and has $n^{20}D$ 1.3010.[17b]

Dimerization of $CF_3N{=}CF_2$ over CsF by the Flow Method.—In a typical flow reaction, 6.0 g. (0.044 mole) of $CF_3N{=}CF_2$ (b.p. −33°) was passed through a reactor, charged with CsF, at 340° at the rate of 3.6 g. (0.027 mole)/hr. This was equivalent to a theoretical contact time of 83 sec. The products were separated by fractional distillation and analyzed by v.p.c. The dimer, $(CF_3)_2NCF{=}NCF_3$, recovered was better than 99% pure and amounted to 4.6 g. It had a molecular weight of 265 (calcd. 266) and an infrared spectrum identical with an authentic sample.[20] There were no other products and the conversion to dimer was 76%.

In a series of similar reactions the following was observed: at 25° conversion was 98% for a contact time of 100 sec., in a (second) reaction at 340° conversion was 65% for a contact time of 55 sec., at 450° the conversion was 55% for a contact time of 31 sec., and at 520° the conversion was 15% for a contact time of 32 sec.

The Reaction of $CF_3N{=}CF_2$ and NF_3 over CsF at 537°. Flow System.—Reaction attempts with these reagents below 500° over CsF in a flow system gave mainly dimer and very small traces of other materials. At 537°, 38 g. (0.54 mole) of NF_3 and 90 g. (0.68 mole) of $CF_3N{=}CF_2$ were passed as a mixture through the flow reactor in 20.4 hr., equivalent to a contact time of 35 sec. The products were stripped of materials boiling below −80°. This amounted to 33 g., most of which was NF_3. Another 43 g., mostly $CF_3N{=}CF_2$, boiled between −36 and −28°; twenty-five grams was isolated which boiled between 31 and 38°. V.p.c. analysis showed that this fraction was mainly a two-component system and the infrared spectrum of the mixture shows that one component was the dimer. An aliquot of the mixture was separated by v.p.c. and a comparison infrared spectrum of the second component showed that it was $(CF_3)_2NN(CF_3)_2$.[20] Based on v.p.c. analysis, the mixture was composed on 45 mole % hydrazine (11.9 g.) and 55 mole % dimer (12.9 g.).

Perfluoropentadiene-1,3 ($CF_2{=}CFCF{=}CFCF_3$, VI) was prepared from Kel-F acid 683. After pyrolysis of the sodium salt of the acid, the resulting $CF_2ClCFClCF_2CF{=}CF_2$ (b.p. 90°) was isomerized to $CF_2ClCFClCF{=}CFCF_3$ as follows. A 29-g. sample was vaporized through a flow reactor heated to 240° and packed with CsF over a 45-min. period. The products contained a fraction, b.p. 73.3–75.0° ($n^{20.5}D$ 1.3298), amounting to 19.0 g. The $C{=}C$ infrared absorption had shifted from 5.60 to 5.86 μ. This material was dechlorinated with Zn dust in isopropyl alcohol to give a product, b.p. 26.5°, mol. wt. 212, with two $C{=}C$ infrared absorptions at 5.59 (s) and 5.77 (m) μ. The yield was 90% for the latter step. The n.m.r. spectrum was for $CF_3{}^{a}CF^{b}{=}CF^{c}CF^{d}{=}CF_2{}^{e}$: [(a), −6.1, (3)], [(b), 83.7, (1)], [(c), 78.3, (1)], [(d), 113, (1)], [(e), 16.8 and 29.2, (1) (1)].

Anal. Calcd. for C_5F_8: C, 28.3; F, 71.7. Found: C, 28.0; F, 72.2.

Perfluorocyclopentene (IX) was prepared from an available sample of 1,2-dichlorohexafluorocyclopentene-1. A 122-g. sample was slowly added to 30 g. of CoF_3 in a flask equipped with a stirrer, dropping funnel, and condenser. The system was refluxed for 37 hr. A fraction of the reaction product, boiling between 82.5 and 84.5°, was examined chromatographically and believed to be approximately 60 mole % c-$C_5F_8Cl_2$ and 40 mole % c-$C_5F_6Cl_2$. The mixture was dechlorinated with Zn in dry isopropyl alcohol. The low-boiling c-C_5H_8 escaped through the ice-cooled condenser with a small quantity of solvent. Volatilizing this mixture over P_2O_5 *in vacuo* removed the solvent. A very pure sample of IX had the characteristic $C{=}C$ infrared absorption at 5.70 μ and boiled at 29.0–29.4°.[18] It failed to isomerize (over catalysts) up to 520°.

Perfluoro-1-methylcyclobutene-1 (VIII) was prepared in 58% yields by passing V or VI over NaF at 440° (see Table II). VIII was separated from the mixtures formed by preparative-scale v.p.c. In a typical experiment, 30 g. of V was passed over NaF in 14 hr. The flow rate was 2.1 g./hr. and the theoretical contact 215 sec. The isomers obtained were 5% V, 27% VII, 58% VIII, and 10% IX. VIII had a molecular weight of 212 (calcd. 212), a strong $C{=}C$ infrared absorption at 5.77 μ, and

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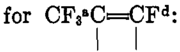
(19) The authors are most grateful to Dr. T. M. Reed, III, a colleague, for providing the equipment and comparison data for this part of the study.

(20) J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Am. Chem. Soc.*, **81**, 1587 (1959).

boiled at 11.5°. The n.m.r. spectrum was for



$CF_3{}^aC{=}CF^d$ / $F_2C^b{-}CF_2{}^c$: [(a), −16.0, (3.1)], [(b), 23.1, (2.0)], [(c), 39.8, (1.9)], [(d), 43.5, (1.0)].

Anal. Calcd. for C_5F_8: C, 28.3; F, 71.7. Found: C, 28.7; F, 71.0.

Perfluoropentyne-2 (VII) was prepared by isomerizing V or VI over CsF at 240°. In a typical reaction, 9.6 g. (0.045 mole) of V was passed over CsF at 240° in 3.6 hr. equivalent to a theoretical contact time of 150 sec. Almost pure VII was obtained in 98% conversion. It boiled at 3.5°, had mol. wt. 212 (calcd. 212), and absorbed in the infrared very weakly between 4.9–5.1 μ (believed to be characteristic of the C≡C grouping). The n.m.r. spectrum was for $CF_3{}^aC{\equiv}CCF_2{}^bCF_3{}^c$: [(a), −21.2, (3.1)], [(b), 29.7, (2.0)], [(c), 10.1, (2.9)].

Perfluorolevulinic acid (X, $CF_3COC_2F_4COOH$) was prepared from VII as follows. Into a round-bottom flask fitted with a cold head was frozen a mixture of dry acetone and $KMnO_4$. Then 7.0 g. of VII was condensed in the flask. The flask was warmed cautiously until no further reflux was noted dropping from the cold head maintained at −78°. The reaction mixture was acidified with a slight excess of H_2SO_4 and filtered. The filtrate was extracted with ether. The ether phase was vacuum stripped and a residue, amounting to 4.3 g., which boiled between 134 and 137° was obtained. This product formed an hydrozone m.p. 149.6–150.0°, readily. The infrared spectrum of the dry acid showed C=O absorptions and one OH absorption. A titration of the acid in water with standard base potentiometrically indicated two end points at about pH 2 and pH 8. Titration with an indicator of color change pH 2–3 gave a molecular weight of 266 (calcd. for the dry acid is 242 and for the hydrate $CF_3C(OH)_2CF_2CF_2COOH$ is 260). The n.m.r. spectrum of the neat, dry acid was for $CF_3{}^aCOCF_2{}^bCF_2{}^cCOOH$: [(a), 4.4, (3.0)], [(b), 41.5, (2.0)], [(c), 46.4, (2.0)].

The γ Irradiation of C_5F_8 Isomers.—Each isomer was exposed to a dose of 10^7-r. γ radiation from a cobalt-60 source. No gross changes (greater than 0.5%) were observed when 3.1 g. of VI 7.5 g. of VIII, and 10.6 g. of IX were exposed in heavy-wall glass ampoules as liquids. V (10.5 g.) under similar conditions formed about 0.5 g. of brownish polymeric substance, while half of a 6.0-g. sample of VII ($CF_3C{\equiv}CCF_2CF_3$) was converted to a soft waxy polymer which on heating began to shrink at 428° and to form a liquid at 434°. At this point the color began to darken until at 458° gas was visibly evolved as the liquid turned brown. An infrared spectrum of the powder between NaCl plates showed no absorptions in the 5.0–6.0-μ region or below.

A portion of this powdered polymer was subjected to X-ray analysis. It demonstrated to diffuse primary spacing of 8.67 ± 1.13 A. It is possible that this represents a fusion of two spacings. The second- and third-order peaks were broad and diffuse. The spectrum was scanned from 1.3–40.0 Å. with no other peaks observed. Microscopic examinations of the polymer showed the material to be isotropic with a refractive index between 1.33 and 1.40 which is high for fluorocarbon material and suggests the formation of strained rings rather than unsaturation.

Acknowledgment.—The authors are most grateful to Dr. W. S. Brey and his students for the n.m.r. spectra reported in this paper. The help of Dr. J. H. Gross of the International Minerals Corporation, Mulberry, Florida, in obtaining the X-ray spectrum of the perfluoropentyne-2 polymer is gratefully acknowledged.

Retention of Configuration in Nucleophilic Vinylic Halide Substitution. Proton Magnetic Resonance Spectra of *cis*- and *trans*-β-Styryldiphenylphosphine Oxides

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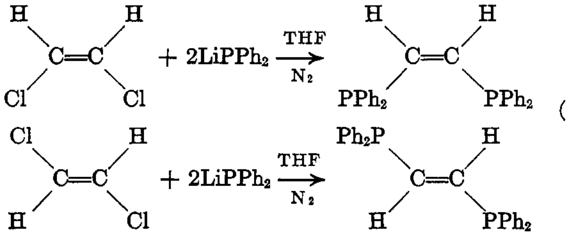
cis- and *trans*-β-bromostyrene were found to react with lithium diphenylphosphide in tetrahydrofuran to produce *cis*- and *trans*-β-styryldiphenylphosphine (isolated as the oxides), respectively, uncontaminated with the other isomer in each case. P.m.r. spectra at 60 Mc. and 100 Mc., along with "spin tickling" results at 100 Mc., are reported for these compounds. Possible mechanistic explanations for the observed retention of configuration are discussed. The addition of lithium diphenylphosphide to the styryldiphenylphosphines and oxides, giving rise to phenylethylenebis(diphenylphosphine) dioxide, is reported and discussed, as is isomerization of *cis*-β-styryldiphenylphosphine to the *trans* isomer by lithium diphenylphosphide.

We recently reported the stereospecific substitution of the vinylic chlorides in *cis*- and *trans*-1,2-dichloroethene by the diphenylphosphide ion[1] (eq. 1).

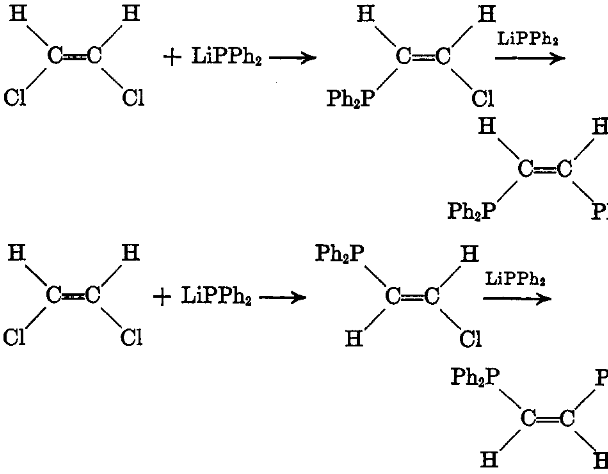


(1)

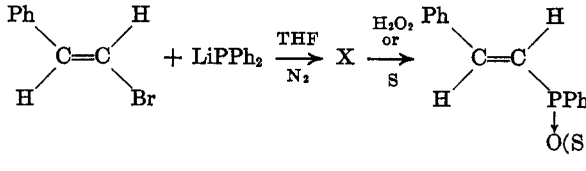
The over-all retention of configuration observed could arise from two replacements with retention of or inversion of configuration at each carbon (eq. 2).

Attempts at isolation of the possible intermediate, β-chlorovinylphosphines (or derivatives) have failed.

In an attempt at clarification of this problem, the replacement of the vinylic bromine in *trans*-β-bromostyrene by the diphenylphosphide ion was studied.[2]



(2)



(3)

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[1] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

[2] A. M. Aguiar and D. Daigle, *J. Org. Chem.*, **30**, 2826 (1965).