a (0.19, 0.54, 0.68), *trans*-3-hystach (0.19, 0.54, 0.68), isomer b (0.21, 0.57, 0.70), and *cis*-3-hystach (0.21, 0.57, 0.70).

Acknowledgment.—The authors wish to thank Dr. J. W. Cornforth for the samples of 3-hydroxystachydrine and isomers a and b.

Fluoroolefins. X. The Reaction of Propynyllithium with Fluoroolefins

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England and his associates[1] reported briefly that the sodium salt of 1-hexyne and phenylacetylene reacted with tetrafluoroethylene to give, respectively, 30 and 9% of the corresponding difluoroethylene derivative.

$$2\mathrm{R{-}C{\equiv}CNa} + \mathrm{CF_2{=}CF_2} \longrightarrow \mathrm{RC{\equiv}CCF{=}CFC{\equiv}CR} + 2\mathrm{NaF}$$

We now wish to report an extension of this reaction to other fluoroolefins in which propynyllithium was employed as the acetylenic compound and yields of product as high as 73% were realized.

The reactions were carried out by passing the gaseous fluoroolefin into a solution of the acetylide in tetrahydrofuran (THF) at either 0 or −22°. The products were separated by distillation and characterized by elemental analysis and n.m.r. and infrared analysis. The absorption at 4.49 μ served as an indication of the $\mathrm{C{\equiv}C}$ system while peaks at 5.90 to 6.15 μ showed the $\mathrm{C{=}C}$ group with varying amounts of fluorine.

The infrared absorption due to the triple bond is shifted toward lower wave lengths in the conjugated systems over that in methylacetylene which is noted at 4.67 μ, the values for the $\mathrm{C{\equiv}C}$ absorption varying from 4.46 to 4.49 μ. On the other hand the absorption in the double-bond region is shifted toward higher wave lengths; thus chlorotrifluoroethylene exhibits $\mathrm{C{=}C}$ absorption at about 5.6 μ whereas 1-chloro-1,2-difluoropent-1-en-3-yne (III) exhibited the double bond stretching absorption at 5.90 μ. Similar shifts were noted for the other enynes. Only one peak in the double-bond region of the spectra was observed in $\mathrm{CH_3C{\equiv}CCF{=}CFCH{=}CH_2}$, at 6.01 μ, which presumably is due to the difluoroethylene unit.

Perhalogenated ethylenes reacted readily with the lithium salt to give a mixture of *cis–trans*-substituted ethylenes wherever possible. Tetrafluoroethylene gave only the disubstituted difluoroethylene even with a 50% molar excess of the olefin. Presumably the presence of the triple bond in III causes a drift of electrons away from the difluoromethylene group, thus making it more susceptible to further attack than the difluoromethylene groups in tetrafluoroethylene. Thus no monoelimination product (III) was isolated. In this respect, propynyllithium is different from butyllithium, for Dixon[2] has reported the formation of 80% of 1,1,2-trifluoro-1-hexene in the reaction with tetrafluoroethylene.

$$\mathrm{II} + \mathrm{CF_2{=}CF_2} \longrightarrow \underset{\mathrm{III}}{\mathrm{CH_3C{\equiv}C{-}CF{=}CF_2}} + \mathrm{LiF} \xrightarrow{\mathrm{II}} \underset{\mathrm{IV}}{\mathrm{CH_3C{\equiv}C{-}CF{=}CF{-}C{\equiv}C{-}CH_3}} + \mathrm{LiF}$$

Trifluorovinyl bromide normally reacts with nucleophilic reagents to give products formed by attack on the difluoromethylene carbon atom. However, methyl- and butyllithium form trifluorovinyllithium and the alkyl halide.[3] It therefore was of some interest to note that propynyllithium attacked in the normal manner to give the bromenyne.

$$\mathrm{CH_3Li} + \mathrm{CF_2{=}CFBr} \longrightarrow \mathrm{CH_3Br} + \mathrm{CF_2{=}CFLi}$$

$$\mathrm{C_4H_9Li} + \mathrm{CF_2{=}CFBr} \longrightarrow \mathrm{C_4H_9Br} + \mathrm{CF_2{=}CFLi}$$

$$\mathrm{CH_3C{\equiv}CLi} + \mathrm{CF_2{=}CFBr} \longrightarrow \mathrm{CH_3C{\equiv}CCF{=}CFBr} + \mathrm{LiF}$$

Neither vinylidene fluoride nor trifluoroethylene gave any of the desired products. Most of the former olefin was recovered. These olefins are lower boiling than most of the others employed, but this is not a contributing factor since tetrafluoroethylene also is volatile. It thus appears that the hydrogen present in these molecules is responsible for their behavior. The compounds may be acid enough to cause the conversion of the propynyllithium to methylacetylene.

Park[4] has recently reported that hexafluorocyclobutene reacts with Grignard reagents to give 75–80% yields of mono- and disubstituted derivatives, and Dixon[2] earlier had found that lithium reagents gave similar results. However, under conditions which gave products with other fluoroolefins, hexafluorocyclobutene gave a black solid product which was not evaluated.

Perfluoropropylene did not give so good a yield of simple products as did the perhalogenated ethylenes. It will be noted that 1,1,2-trifluoro-1,3-butadiene reacted well with propynyllithium to give a conjugated dienyne. A conjugated diynene was obtained from tetrafluoroethylene so that the reaction is a synthetic route to highly conjugated compounds.

The products of the reaction were colorless liquids which generally were thermally unstable. 3,4-Difluorohepta-1,3-dien-5-yne, for example, decomposed at 86° and rapidly turned black at room temperature.

The products from the reaction of propynyllithium and the fluoroolefins are shown in Table I.

It will be noted that increasing the size of the group in $\mathrm{CF_2{=}CFX}$ leads to increasing amounts of the less sterically hindered *trans* isomer, thus bromotrifluoroethylene gives a ratio of *trans–cis* isomer of 1:3, whereas the larger substituents, such as $-\mathrm{CF_3}$ and vinyl, give exclusively the *trans*-substituted ethylene.

The chemical properties of 1-chloro-1,2-difluoropent-1-en-3-yne (III) were studied. Normally acetylenic compounds react with anhydrous hydrogen fluoride to give a vinyl fluoride or difluoroalkane. Compound III reacted at 85° with hydrogen fluoride to give a mixture of fourteen products. At 25°, no reac-

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(1) See D. C. England, L. R. Melby, M. A. Dietrick, and R. V. Lindsey Jr., *J. Am. Chem. Soc.*, **82**, 5112 (1960), for some reactions and references to earlier work.

(2) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

(3) P. Tarrant, P. Johncock, and J. Savory, *ibid.*, **28**, 839 (1963).

(4) J. D. Park and R. Fontanelli, *ibid.*, **28**, 258 (1963).

TABLE I

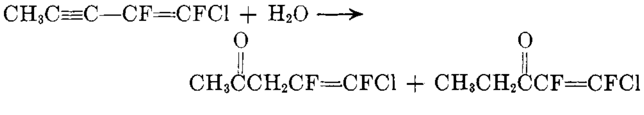
PRODUCTS OF THE REACTION OF PROPYNYLLITHIUM WITH FLUOROOLEFINS

Olefin	Product	Yield, %	*trans–cis* (F–F) ratio
$CF_2{=}CCl_2$	$CH_3C{\equiv}C—CF{=}CCl_2$	51	
$CF_2{=}CFCl$	$CH_3C{\equiv}C—CF{=}CFCl$	73	1:4
$CF_2{=}CFBr$	$CH_3C{\equiv}C—CF{=}CFBr$	56	1:3
$CF_2{=}CFCF_3$	$CH_3C{\equiv}C—CF{=}CFCF_3$	17	∞
$CF_2{=}CF—CH{=}CH_2$	$CH_3C{\equiv}C—CF{=}CFCH{=}CH_2$	64	∞
$CF_2{=}CF_2$	$[CH_3C{\equiv}C—CF{=}]_2$	35	
$CF_2{=}CHF$		0	
$CF_2{=}CH_2$		0	
$\underline{CF_2CF_2CF{=}CF}$		0	

tion occurred and at high temperatures, *i.e. ca.* 100°, carbon was the predominant product.

Bromine reacted with an equimolar amount of III to give a 92% yield of product in which bromine added across the triple bond. N.m.r. analysis indicated the presence of each of the four possible isomers with *cis* (F–F) compounds predominantly. The reaction is in contrast to the bromination of hydrocarbon enynes in which addition to the double bonds takes place preferentially.

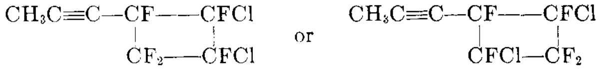
Water added to III to give a mixture of the two possible ketones.



$$CH_3C{\equiv}C—CF{=}CFCl + H_2O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2CF{=}CFCl + CH_3CH_2\overset{\overset{O}{\|}}{C}CF{=}CFCl$$

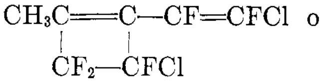
The products were characterized by elemental analysis and spectroscopic methods. Infrared analysis indicated α,β-carbonyl conjugation for one while the other had an n.m.r. spectrum which indicated an isolated methyl group. Somewhat more than twice as much unconjugated ketone was obtained. Such results would indicate that the fourth carbon atom bears a larger partial positive charge than the third, since the oxygen appears preferentially on the fourth carbon atom. The contribution of $CH_3—\overset{+}{C}{=}C\overbrace{—CF{=}}^{-}CFCl$ thus appears more important than $CH_3—\overset{-}{\ddot{C}}{=}C\overbrace{{=}CF—}^{+}CFCl$ in directing the course of the reaction.

Fluoroolefins such as chlorotrifluoroethylene and tetrafluoroethylene form cyclobutane derivatives with other unsaturated compounds. It was found that chlorotrifluoroethylene reacted with III to give three products. The highest boiling material was not identified but is probably the compound resulting from addition of the two molecules of fluoroolefin to the triple bond and the double bond. The lowest boiling compound has been identified as



$$\begin{array}{l}CH_3C{\equiv}C—CF—CFCl\\ \qquad\qquad\;\; |\qquad\;\; |\\ \qquad\qquad CF_2—CFCl\end{array} \quad\text{or}\quad \begin{array}{l}CH_3C{\equiv}C—CF—CFCl\\ \qquad\qquad\;\; |\qquad\;\; |\\ \qquad\qquad CFCl—CF_2\end{array}$$

since the infrared spectrum showed the presence of the triple bond and the absence of the fluorovinyl structure. The n.m.r. spectrum was complex and not enough comparative data has been published to make a judgment distinguishing one cyclobutane structure from the other. The third component has been identified as



$$\begin{array}{l}CH_3C{=}C—CF{=}CFCl\\ \qquad\; |\quad\;\; |\\ \quad\;\; CF_2—CFCl\end{array}$$

or its cyclobutenyl isomer. This type of structure is indicated by n.m.r. and infrared analysis.

Experimental[5]

Preparation of Propynyllithium.—Methylacetylene from a cylinder was slowly passed into a stirred solution of methyllithium in ether (143 ml., 0.2 mole). A white precipitate of propynyllithium (I) was soon formed and methane was evolved from the solution. The reaction was continued for 6 hr. with the addition of more ether as required.

Reaction of I with Fluoroolefins. General Procedure.—The propynyllithium (see above) was allowed to settle overnight and the supernatant liquid was decanted. Anhydrous tetrahydrofuran (THF, 175 ml.) was then added and was sufficient to dissolve most of I. Reactions were then carried out immediately with this solution since any delay might cause unnecessary cleavage of the THF by I.

The solution of I in THF was cooled to 0 or −22° and slowly treated with the desired fluoroolefin. The reactions were exothermic and the solution immediately turned black. In most of the reactions the olefin was a gas and was passed into the reaction mixture three times in order to ensure complete reaction. Hydolysis of unchanged I was effected by pouring the reaction mixture into ice-cold 3 *N* hydrochloric acid (50 ml.). This whole mixture was steam distilled and a residual black tar was obtained. The organic layer from the steam distillation was separated; the aqueous layer was extracted with three 25-ml. portions of ether. Due to the extreme solubility of THF in water there was still some THF left in the aqueous layer. An analytical v.p.c. check, however, showed that the ether extraction had removed all reaction product from this aqueous portion. The combined organic extracts were dried over calcium chloride and the ether and THF were removed by distillation through either an 18-in. Vigreux or 24-in. Heliplate packed column. The residue consisted of product and THF. The last traces of the latter were removed by repeated washing with water. A check by analytical v.p.c. showed no product to be in the aqueous layer. The organic product was dried over calcium chloride and phosphoric anhydride and was vacuum distilled.

1,1-Dichloro-2-fluoropent-1-en-3-yne (II).—Reaction of 1,1-dichlorodifluoroethylene (40 g., 0.3 mole, 50% excess) with I gave 15.7 g. (51%) of II, b.p. 141.5°, n^{25}_D 1.4850.

Anal. Calcd. for: $C_5H_3Cl_2F$: C, 39.25; H, 1.96; F, 12.42. Found: C, 39.16; H, 2.21; F, 12.67.

An infrared spectrum of II had strong bands at 4.49 ($C{\equiv}C$), 7.76, 9.50 (C–F stretching), 10.25, and 12.30, and a medium strong band at 6.15 μ ($C{=}C$).

The ultraviolet spectrum (CH_3OH) had λ_{max} 228, 233, and 245 mμ (ε 12,550, 13,730, and 12,060, respectively).

The n.m.r. spectrum was consistent with the structure assigned.

A black tarry material (9.0 g.) was also formed in the reaction.

1-Chloro-1,2-difluoropent-1-en-3-yne (III).—Reaction of chlorotrifluoroethylene (35 g., 0.3 mole, 50% excess) with I gave 20.0 g. (73%) of III, b.p. 97°, n^{25}_D 1.4300.

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[5] Analyses were by Galbraith Laboratories, Knoxville, Tenn.

Anal. Calcd. for $C_5H_3ClF_2$: C, 44.00; H, 2.20; F, 27.84. Found: C, 44.29; H, 2.42; F, 27.55.

An infrared spectrum of II had strong bands at 4.48 (C≡C), 5.90 (C=C), 7.70, 8.45, 9.51 (C–F stretching), 11.15 μ.

The ultraviolet spectrum (CH_3OH) had λ_{max} 212, 222, and 232 mμ with intensities in the region expected for enynes. The F^{19} n.m.r. spectrum showed peaks corresponding to a mixture of *cis* (F–F) and *trans* isomers in the ratio of 4:1, respectively.

Separation of III into its *cis* and *trans* isomers could be effected to a very limited extent on analytical v.p.c. (dinonyl phthalate on 80–100-mesh Chromosorb, 120°). The two peaks were merged together almost completely and attempts to separate the two compounds by preparative scale v.p.c. were unsuccessful.

A similar reaction was carried out using I (1.3 moles) and chlorotrifluoroethylene (151.5 g., 1.3 moles) and resulted in the formation of 123 g. of III (69.5%) and 10 g. of tar.

1-Bromo-1,2-difluoropent-1-en-3-yne (IV).—Reaction of bromotrifluoroethylene (48 g., 0.3 mole, 50% excess) with I gave 20.0 g. (55.5%) of IV, b.p. 122.0° n^{25}D 1.4590.

Anal. Calcd. for $C_5H_3BrF_2$: C, 33.18; H, 1.66; F, 20.99. Found: C, 32.89; H, 1.86; F, 21.22.

Vapor phase chromatography of IV showed that two compounds, IVa and IVb, were present with very similar retention times. The F^{19} n.m.r. spectrum showed four peaks corresponding to a mixture of *cis* (F–F), and *trans* isomers in the ratio of 3:1, respectively. The *cis* isomer, b.p. 122.0°, n^{25}D 1.4589, was isolated in the pure form by preparative scale v.p.c. by collecting a limited amount of material as it first emerged from the column. An infrared spectrum of IVa had strong bands at 4.48 (C≡C), 5.98 (C=C), 7.72, 8.50 (sh), 8.60, 9.70, 11.20, and 11.40 μ. The ultraviolet spectrum (CH_3OH) had λ_{max} 224 and 234 mμ (ϵ 14,280 and 10,440, respectively) with a shoulder at 213 mμ.

An infrared spectrum of the mixture of IVa and IVb had strong bands at 4.48 (C≡C), 5.45, 5.74, 5.98 (C=C), 7.72, 8.50, 8.60, 9.70, 11.20, and 11.40 μ. The ultraviolet spectrum of this mixture was essentially the same as obtained from the *cis* isomer.

1,1,1,2,3-Pentafluorohex-2-en-4-yne (V).—Reaction of hexafluoropropene (45 g., 0.3 mole, 50% excess) with I (0.2 mole) at −22° gave 5.7 g. (17%) of V, b.p. 79.5–80°, n^{21}D 1.3591.

Anal. Calcd. for $C_6H_3F_5$: C, 42.36; H, 1.76; F, 55.89. Found: C, 42.55; H, 1.95; F, 56.17.

An infrared spectrum of V had strong bands at 4.46 (C≡C), 5.90 (C=C), 7.25, 7.80, 8.30, 8.49, 8.70, and 9.43 μ. The ultraviolet spectrum (CH_3OH) had λ_{max} 221 mμ (ϵ 14,880) with a shoulder at 228 mμ. The n.m.r. spectrum was in accord with the above structure with only one *trans* isomer present.

Black tarry material (15 g.) was formed in the reaction. Separation of V from the THF was accomplished using a 24-plate spinning band column and a final purification was carried out using preparative scale v.p.c.

3,4-Difluorohepta-1,3-dien-5-yne (VI).—Reaction of 1,1,2-trifluorobutadiene (27.0 g., 0.21 mole) with I (0.2 mole) gave 16.4 g. (64%) of VI, b.p. 86° dec., n^{21}D 1.4970.

Anal. Calcd. for $C_7H_6F_2$: C, 65.66; H, 4.68; F, 29.67. Found: C, 65.44; H, 4.72; F, 29.92.

An infrared spectrum of VI had strong bands at 4.50 (C≡C), 6.01 (C=C), 7.55, 8.05, 9.22, 9.91, 10.20, and 10.90 μ. The ultraviolet spectrum (CH_3OH) had λ_{max} 260 mμ (ϵ 24,570). The n.m.r. spectrum showed that only the *trans* form was present.

A black solid (4.5 g.) was also formed in the reaction and was not evaluated.

VI was colorless when pure but rapidly turned black at room temperature in the presence of air.

4,5-Difluoroocta-2,6-diyn-4-ene (VII).—Reaction of tetrafluoroethylene (30 g., 0.3 mole, 50% excess) with I at −22° gave, after removal of the THF by distillation and washing with water, 4.9 g. (35%) of VII, m.p. 76–78°, which was purified by sublimation.

Anal. Calcd. for $C_8H_6F_2$: C, 68.60; H, 4.28; F, 27.13. Found: C, 68.71; H, 4.50; F, 27.44.

An infrared spectrum of VII showed strong bands at 4.50 (C≡C), 7.85, 8.95, 9.50, and 12.41, with a medium strong band at 4.38 μ. No band in the double-bond region was present.

The ultraviolet spectrum (CH_3OH) had λ_{max} 249 and 260 mμ (ϵ 32,690, and 30,250, respectively) with a shoulder at 240 mμ.

The F^{19} n.m.r. spectrum exhibited a single peak at 65.1 p.p.m. relative to external CF_3COOH. The two fluorines were equivalent and therefore no characteristic *trans* F–F coupling would be shown.

Tar (4.0 g.) was obtained.

Attempted Reactions of I with Other Fluoroolefins. Trifluoroethylene.—Reaction of trifluoroethylene (24.6 g., 0.3 mole) with I (0.2 mole) at 0° gave only 8.0 g. of a black solid.

Hexafluorocyclobutene.—Reaction of hexafluorocyclobutene (18.5 g., 0.114 mole) with I gave 25 g. of a black solid which was not evaluated.

1,1-Difluoroethylene.—No reaction was observed when 1,1-difluoroethylene was passed into a solution of I at either −78, −22, 0, or 25°. No discoloring of the solution occurred and most of the 1,1-difluoroethylene was recovered.

Bromination of III.—III (15.0 g., 0.11 mole) was stirred at room temperature and slowly treated with bromine (17.5 g., 0.11 mole). The red liquid formed was shown by analytical v.p.c. to contain no III. Vacuum distillation gave 30.0 g. of 3,4-dibromo-1-chloro-1,2-difluoropenta-1,3-diene (92.5%), b.p. 182–183°, n^{21}D 1.5192.

Anal. Calcd. for $C_5H_3Br_2ClF$: C, 20.42; H, 1.01; F, 12.82. Found: C, 20.51; H, 1.19; F, 13.09.

An infrared spectrum showed strong bands at 5.85 and 6.15 (C=C) and 7 to 10 μ (C–F stretching). There was no absorption between 4 and 5 μ (C≡C) thus showing that additions had occurred only to the triple bond.

Addition of Water to III.—II (20.0 g., 0.147 mole) was stirred and refluxed for 18 hr. with 100 ml. of 10% aqueous sulfuric acid containing mercuric sulfate (5.0 g.). A brown inorganic solid (4.0 g.) was formed during the reaction. Organic material (16.0 g.) was separated from the water and distilled at reduced pressure (50 mm.) through a 18-in. spinning band column into fraction 1, b.p. 34–37°, 5.2 g.; fraction 2, b.p. 50–58°, 1.3 g.; fraction 3, b.p. 65–75°, 2.5 g.; and a residue of 1.3 g. Fraction 1 was starting material. Fraction 2 was identified as 1-chloro-1,2-difluor-1-en-3-one (VIII, 11%), b.p. 122.0°, n^{28}D 1.4148.

Anal. Calcd. for $C_5H_5ClF_2O$: C, 38.88; H, 3.24. Found: C, 39.12; H, 3.28.

An infrared spectrum showed strong bands at 5.80 (C=C), 6.12 (C=O in α,β-unsaturated ketone), 7.95, 8.45, 9.15, 9.44, and 11.29 μ. C–H stretching showed at 3.35, 3.40, 3.44, and 3.47 μ, indicating CH_3 and CH_2.

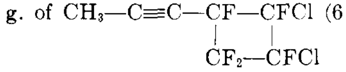
Fraction 2 was shown to consist of two components, one of which was VIII. Preparative scale v.p.c. was used to isolate the other component which was identified as 1-chloro-1,2-difluoropent-1-en-4-one, (3.8 g., 23%), b.p. 148–149°, n^{21}D 1.4154.

Anal. Calcd. for $C_5H_5ClF_2O$: C, 38.88; H, 3.24. Found: C, 39.27; H, 3.15.

N.m.r. indicated an isolated methyl group in the molecule with 40% *cis* and 60% *trans* (F–F) structure.

An infrared spectrum showed strong bands at 5.76 (doublet C=C and C=O) and 7.0 to 10.0 μ (C–F stretching).

Some higher boiling material (0.6 g.) was also isolated from fraction 3, but an infrared spectrum gave no indication of the structure.

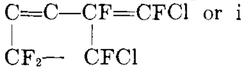
Reaction of III with Chlorotrifluoroethylene.—A 335-ml. stainless steel autoclave was charged with III (19.5 g., 0.143 mole) and chlorotrifluoroethylene (52 g., 0.446 mole) and was shaken at 190° for 7 hr. Unchanged chlorotrifluoroethylene (35 g.) was vented from the autoclave leaving behind 29 g. of liquid product. Fractional distillation at atmospheric pressure afforded 12.1 g. of 1,2-dichlorohexafluorocyclobutane, b.p. 59–60°, lit.[6] b.p. 59.9°, and 6.7 g. of recovered III (65.5% conversion). The distillate was shown by analytical v.p.c. to contain three components. Preparative scale v.p.c. (silicone elastomer 125°) afforded 1.25 g. of 

$$\begin{array}{ccc} CH_3\text{—}C\equiv C\text{—} & CF\text{—} & CFCl \\ & | & | \\ & CF_2\text{—} & CFCl \end{array}$$

(6.5%) or its 1,3-dichlorocyclobutyl isomer, b.p. 148.5°, n^{20}D 1.4064.

Anal. Calcd. for $C_7H_3Cl_2F_5$: C, 33.16; H, 1.19; F, 37.55. Found: C, 33.01; H, 1.43; F, 37.79.

An infrared spectrum showed strong bonds at 4.44 (C≡C) and 7.5 to 9.1 μ (C–F).

The second component was isolated and identified as CH_3— 

$$\begin{array}{ccc} C=C\text{—} & CF= & CFCl \\ | & & | \\ CF_2\text{—} & & CFCl \end{array}$$

or its cyclobutenyl isomer (6.7 g., 29%), b.p. 163.5–164°, n^{20}D 1.4419.

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[6] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

Anal. Calcd. for $C_7H_3Cl_2F_5$: C, 33.16; H, 1.19; F, 37.55. Found: C, 33.09; H, 1.39; F, 37.87.

An infrared spectrum showed strong bands at 4.94 and 6.14 (C=C) and 7.15 to 8.85 μ (C–F).

The third component was not identified.

A similar experiment carried out at 150° for 12 hr. gave very little reaction of III with chlorotrifluoroethylene.

Reaction of III with Hydrogen Fluoride.—III (15.0 g., 0.11 mole) and anhydrous hydrogen fluoride (4.4 g., 0.22 mole) were stirred in a nitrogen atmosphere at −22° for 1 hr. and then kept at 25° for 12 hr. The reaction mixture was then poured onto ice (75 g.), washed with three 10-ml. portions of water, and dried over calcium chloride. Analytical v.p.c. showed that only unchanged III was present.

The same quantities of reactants were sealed in a 335-ml. stainless steel autoclave and heated to 85° for 20 hr. The product was worked up as before to give a black liquid (14.0 g.). This was shown by analytical v.p.c. to consist of at least fourteen components. Some free carbon was deposited on the sides of the autoclave during the reaction.

Acknowledgment.—We are grateful to the U. S. Army Natick Laboratories, Natick, Massachussetts, for financial support of this project. Dr. Malcolm Henry acted as the project officer. We wish to thank Dr. W. S. Brey and Dr. Kermit Ramey for the n.m.r. analyses; their results will be reported in detail elsewhere.

Fluoroolefins. XI. The Conversion of Fluoroolefins to Fluoroalkyl Nitroso Compounds *via* Alkylmercury Compounds

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Fluoroalkyl nitroso compounds have been prepared by the reaction of perfluoroalkyl iodides with nitric oxide,[1] by the addition of nitrosyl chloride to a fluoroolefin,[2] or more recently by the thermal decomposition of perfluoroacyl nitrites.[3] We now wish to report that fluoroalkyl nitroso compounds can be made from the reaction of fluoroalkylmercury compounds with nitrosyl chloride. Since the fluoroalkylmercury compounds are made by adding mercuric fluoride across the double bond of the olefin, the over-all reaction involves the addition of nitrosyl chloride to a fluoroolefin in a two-step operation.

$$2CF_2{=}CFCF_3 + HgF_2 \longrightarrow [(CF_3)_2CF]_2Hg \qquad (1)$$

$$[(CF_3)_2CF]_2Hg + 2NOCl \longrightarrow (CF_3)_2CFNO + HgCl_2 \qquad (2)$$

The addition of mercuric fluoride to a series of fluoroolefins was carried out by Krespan's method[4] in which hydrogen fluoride was used as the solvent instead of arsenic trifluoride. Since the completion of our work, Miller[5] has described the addition of mercuric fluoride to $CF_2{=}CHCF_3$ and $CF_2{=}CFCF_3$ in the presence of hydrogen fluoride, while Aldrich[6] has described similar reactions with 1,1-dichlorodifluoroethene and a series of longer chain polyfluoroolefins containing the $—C{=}CF_2$ group.

It appears that the addition of mercuric fluoride to fluoroolefins is limited to those containing a difluoromethylene group, *i.e.*, terminal olefins, since neither hexafluorocyclobutene nor 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene formed an adduct.

The reaction of $(CF_3CFCl)_2Hg$ and nitric oxide was attempted in the gas phase under the influence of ultraviolet radiation. However, the formation of the blue nitroso compound occurred so slowly that this method was judged unsatisfactory. The reaction of nitrosyl chloride with certain fluoroalkylmercury compounds did take place at a reasonable rate in dimethylformamide (DMF) and $CF_3CFClNO$, $(CF_3)_2CFNO$, and CF_3CCl_2NO were prepared from the corresponding fluoroalkylmercury. This type reaction was first used by Baeyer[8] in preparing nitrosobenzene from diphenylmercury and nitrosyl chloride.

The reaction was carried out at room temperature with DMF. Although the reaction seemed to proceed at a comparable rate in dimethyl sulfoxide, the yield of nitroso compound was considerably lower. In the dimethyl ether of diethylene glycol (diglyme) the reaction was much too slow to be useful while in acetone and in benzene the desired reaction did not take place. It is not practical to increase the temperature of the reaction appreciably since nitroso compounds disproportionate rapidly at elevated temperatures.[9]

The great increase in reaction rate with increase in dielectric constant of the solvent seems to indicate that the formation of a charged species is a factor in the over-all rate.

Qualitatively, the order of reactivity of the alkylmercury compounds with nitrosyl chloride is $(CF_3CFCl)_2Hg > [(CF_3)_2CF]_2Hg > (CF_3CCl_2)_2Hg > (CF_3CHF)_2Hg >> (CF_3CFBr)_2Hg$ and $(CF_3CH_2)_2Hg$. No nitroso compound was obtained from the last two mercury derivatives.

The reaction of $(CF_3CHF)_2Hg$ with nitrosyl chloride did not give the expected nitroso compound nor the oxime that might be derived from it. Instead, 1-chloro-1-nitrosotetrafluoroethane, 1,1-dichlorotetrafluoroethane, and 1-chloro-1,3,3,3-tetrafluoroethane were obtained.

$$(CF_3CHF)_2Hg \xrightarrow{NOCl} CF_3CFClNO + CF_3CFCl_2 + CF_3CHFCl$$

Similar results were obtained in another investigation when nitrosyl chloride was added to trifluoroethylene.

$$CF_2{=}CFH + NOCl \longrightarrow CF_2ClCFClNO$$

It seems unlikely that the hydrogen atoms of such dissimilar compounds as $(CF_3CHF)_2Hg$ and $CF_2{=}CFH$ would be replaced by chlorine and the resulting mercury compound and olefin then undergo the cleavage reactions to give $CF_3CFClNO$ and $CF_2ClCFClNO$.

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