1.2 g. It was crystallized from aqueous ethanol, but with difficulty, to obtain light brown crystals (0.5 g) of 1,2-diisopropylhydrazinecarboxanilide, mp 79.5°. *Anal.* Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 8.97; N, 17.86. Found: C, 66.89; H, 8.41; N, 17.83.

Pyrolysis of 2-Carbethoxyhydrazinecarbonyl Chloride. Heating in Toluene. A solution of 3.5 g of this acyl chloride in 15 ml of dry toluene was refluxed under anhydrous conditions for 17 hr. Hydrogen chloride was evolved, and in duplicate experiments it was absorbed in water and titrated with 0.1 *N* base, showing a total that was 94–96% of theoretical. After evaporation of the toluene there remained 2.5 g of a glassy solid (solid A) that softened at 50–55° and became molten at 63°. It was hygroscopic and failed to crystallize from common solvents. The infrared spectrum showed strong peaks at 5.48, 5.70, and 8.00 μ and medium bands at 3.00, 3.34, 6.60, 6.78, 7.00, 7.24, 7.65, 9.38, and 12.90 μ. *Anal.* Calcd for $C_8H_{12}N_4O_6$: C, 36.95; H, 4.65; N, 21.54; mol wt, 260. Found: C, 36.91; H, 4.56; N, 21.61; mol wt, 276 (Rast).

Solid A dissolved in warm water. The solution was strongly acidic (pH about 2). A trace of carbon dioxide was given off. The solution tested negatively for chlorine ($AgNO_3$) and gave a deep amber-red color with ferric chloride. During a 17-hr reflux period with 0.5715 g of solid A and 10 ml of water there was evolved 0.066–0.070 g of CO_2 (theory 0.097 g for one carbonyl of VII). The resulting solid, after distilling off water and desiccation at 70° (0.05 mm) for 2 hr, looked like the starting material. It softened at 45°, fused at 55°, and had a similar infrared spectrum, except the peak at 5.70 μ was broader and the one at 5.48 μ was absent. *Anal.* Found: C, 34.5; H, 5.14; N, 26.45.

One gram of solid A gradually dissolved in 3 ml of aniline at 100°. After it was cooled, some dilute hydrochloric acid was added. The insoluble brown material (0.12 g) was crystallized from ethanol (Norit) to yield an off-white solid, mp 170–172°. *Anal.* Found: C, 61.3; H, 5.40; N, 16.8. If, instead, the aniline solution was refluxed for 2.5 hr before adding the dilute HCl, then 1.0 g of carbanilide resulted (mp and mmp 236–238°).

One gram of solid A, 2 ml of phenyl isocyanate, and 2 drops of pyridine were warmed at 100° for a few mixtures, cooled, and mixed with ether. The precipitated white solid (0.7 g) was crystallized from dimethylformamide to give 0.4 g of substance, insoluble in camphor at 190°, and melting above 300°. *Anal.* Found: C, 59.7; H, 2.95; N, 19.2.

Heating at Atmospheric Pressure. Ten grams of 2-carbethoxyhydrazinecarbonyl chloride (0.060 mole) was slowly heated to 145° by an oil bath. The flask was connected in series to a trap at −78° and a water trap. A flow of nitrogen gas was maintained. The cold trap collected 2 ml of ethyl chloride (0.03 mole) and the water trap collected 0.033 mole of hydrogen chloride. The glassy residue (6.3 g), solid B, melted higher than solid A; it softened at 100° and melted at 110–115°. Its infrared spectrum was similar to that of solid A except that the peak at 5.48 μ was reduced to a shoulder, and those at 6.60 and 6.78 μ were somewhat stronger. *Anal.* Found: C, 30.9; H, 4.38; N, 28.8.

Potentiometric titration of a solution of 0.4062 g of solid B in water with 0.1 *N* alkali gave a neutral equivalent of 336. Long refluxing (22 hr) of 0.5629 g of an aqueous solution of solid B liberated 0.043 g of carbon dioxide.

Heating at Low Pressure. Nine grams of the acyl chloride lost 2.6 g during 2 hr of heating at 125° (oil bath) and 0.1-mm pressure. The glassy solid residue (solid C) looked like solids A and B. Its infrared spectrum resembled that from solid B except for a strong band at 5.48 μ as from solid A. Its neutral equivalent, determined as for solid B, was 345. *Anal.* Found: C, 34.3; H, 4.54; N, 25.4.

Refluxing a solution of 0.5648 g of solid C in 10 ml of water for 24 hr caused the evolution of 0.067 g of CO_2. The residue, after evaporation of the water, softened at 45° and was molten at 62°. The only significant change in the infrared spectrum was loss of the band at 5.48 μ. *Anal.* Found: C, 32.8; H, 4.85; N, 28.5.

To a solution of 1.0 g of solid C in 5 ml of warm pyridine was added 1.1 ml of 1-naphthyl isocyanate. The white precipitate (2.1 g) that formed during an hour was crystallized from dimethylformamide, yield 0.8 g, mp >300°. *Anal.* Found: C, 65.73, 65.11; H, 4.43, 4.27; N, 14.32, 14.44.

The Free-Radical Chemistry of Fluoro Ketones. I. Reaction with Saturated Substrates

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Wilmington, Delaware 19898. *Received October 10, 1966*

Abstract: Polyfluoro ketones participate in free-radical, chain-addition reactions with the carbon–hydrogen bond. With many types of substrate R–H, addition to the fluoro ketone carbonyl group proceeds readily to give good yields of alcohol $R(R_F)_2COH$ and ether $ROCH(R_F)_2$. A mechanism is suggested to account for the results, including the observed preference for alcohol formation.

The carbonyl group is resistant to free-radical attack; products formed by the addition of free radicals to carbonyl groups have only occasionally been observed.[1a–e] Moreover, in the case of ketones these reactions are nonchain processes. Even with aldehydes the sole known exception is the addition of cyclopentane to formaldehyde[1b] where the kinetic chain length is 2. It is known that radicals are capable of adding to the carbonyl function of molecules like chloranil by a nonchain mechanism to yield products which are mainly ethers of the corresponding hydroquinones or copolymers.[2] In contrast with even such special cases, we find that fluoro ketones will undergo efficient radical chain addition of R–H.

Fluoro ketones are characterized by the electron-withdrawing inductive effect exerted by highly electronegative fluoroalkyl groups. This results in a weakly polarized, electron-deficient carbonyl function, direct

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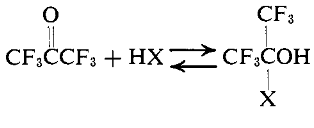
(1) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 282–284; (b) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, 70, 3258, 4253 (1948); (c) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953); (d) M. S. Kharasch, D. Schwartz, M. Zimmerman, and W. Nudenberg, *J. Org. Chem.*, **18**, 1045 (1953); (e) F. R. Rust and G. Fuller, *J. Am. Chem. Soc.*, 80, 6148 (1958); (f) K. Shima and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Soc.*, **64**, 460 (1961); (g) K. Shima, Y. Shigemitsu, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **35**, 1728 (1962); (h) P. W. Jolly and P. DeMayo, *Can. J. Chem.*, **42**, 170 (1964); (i) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964); (j) R. L. Huang and H. H. Lee, *J. Chem. Soc.*, 2500 (1964); (k) W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964); (l) J. F. Harris, Jr., *ibid.*, 30, 2182 (1965); L. Kaplan, *J. Am. Chem. Soc.*, **88**, 1833 (1966).

(2) C. Walling, ref 1a, pp 161–168, 282.

evidence for which is the shift of the carbonyl absorption to shorter than normal wavelengths in the infrared,[3a–c] the rapid attack on the carbonyl carbon atom by weak nucleophiles to form the corresponding adducts,[3b,4a]

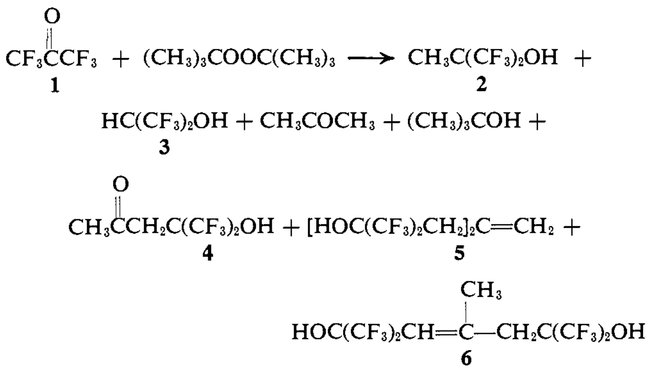


$$CF_3\overset{\overset{O}{\|}}{C}CF_3 + HX \rightleftharpoons CF_3\overset{\overset{CF_3}{|}}{\underset{\underset{X}{|}}{C}}OH$$

and a decrease in the carbonyl oxygen basicity. For example, perfluoroethyl propyl ketone and perfluorodipropyl ketone are insoluble in sulfuric acid, *i.e.*, reluctant to accept a proton.[4b] We suggest the electronic arrangement of the carbonyl function in fluoro ketones more closely resembles the double bond of weakly polarized olefins than it does the carbonyl group in normal hydrocarbon ketones, and fluoro ketones might therefore undergo free-radical reactions more readily than their hydrocarbon counterparts. A study of the free-radical chemistry of fluoro ketones has shown that these carbonyl groups are extremely reactive to radicals.

Results

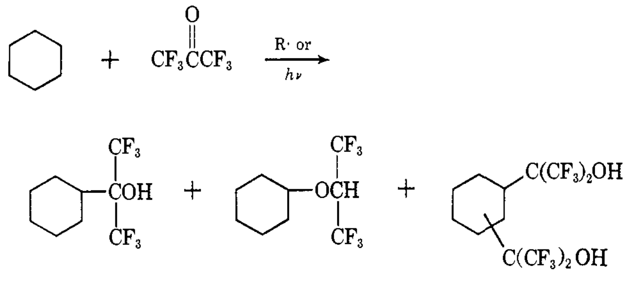
Peroxides. Hexafluoroacetone (**1**) and the methyl free radicals from equivalent amounts of di-*t*-butyl peroxide reacted in nonchain fashion to provide 1,1,-1,3,3,3-hexafluoro-2-methyl-2-propanol (**2**) in 44% yield.



$$\underset{\mathbf{1}}{CF_3\overset{\overset{O}{\|}}{C}CF_3} + (CH_3)_3COOC(CH_3)_3 \longrightarrow \underset{\mathbf{2}}{CH_3C(CF_3)_2OH} + \underset{\mathbf{3}}{HC(CF_3)_2OH} + CH_3COCH_3 + (CH_3)_3COH + \underset{\mathbf{4}}{CH_3\overset{\overset{O}{\|}}{C}CH_2C(CF_3)_2OH} + \underset{\mathbf{5}}{[HOC(CF_3)_2CH_2]_2C{=}CH_2} + \underset{\mathbf{6}}{HOC(CF_3)_2CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2C(CF_3)_2OH}$$

Also formed were 1,1,1,3,3,3-hexafluoro-2-propanol (**3**), acetone, *t*-butyl alcohol, 1,1,1-trifluoro-2-hydroxy-2-trifluoromethyl-4-pentanone (**4**), 1,1,1,7,7,7-hexafluoro-2,6-dihydroxy-4-methyleneheptane (**5**), 1,1,-1,7,7,7-hexafluoro-2,6-dihydroxy-4-methyl-3-heptane (**6**), and several additional unidentified products in lesser amount. Product **2** results from methyl-radical addition to hexafluoroacetone, **4** is formed by the aldol condensation between acetone and hexafluoroacetone, and **5** and **6** from the addition of hexafluoroacetone to isobutylene.[5] The isobutylene arises from dehydration of *t*-butyl alcohol in the acidic reaction mixture. These materials were observed in all reactions of hexafluoroacetone which were initiated with di-*t*-butyl peroxide.

Alkanes and Ethers. Cyclohexane and hexafluoroacetone reacted in the presence of free-radical initiators or ultraviolet irradiation to yield 1,1,1,3,3,3-hexafluoro-2-cyclohexyl-2-propanol (**7**), cyclohexyl 1,1,1,3,3,3-hexafluoroisopropyl ether (**8**), and a mixture of isomeric bis(1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)cyclohexanes (**9**). The ratio of alcohol **7** to ether **8** was dependent upon the reaction temperature as indicated in Table I, formation of ether becoming more important at higher temperatures. It is worth noting that even under conditions of a large excess of cyclohexane, a 7% yield of the 2:1 adduct was obtained.



7 **8** **9**

Table I. Reaction of Cyclohexane and Hexafluoroacetone

Initiator	Temp, °C	Relative amounts, % 7	8	Yield, % 7 and 8	9
hν	−10	100	0	69	14[a]
$(C_6H_5CO_2)_2$	80	95	5	60[b]	7–14[c]
$(t\text{-BuO})_2$	135	83	17	73	17
$C_6H_5C(CH_3)_2OOH$	200	55	45	20[b]	

[a] Ratio of cyclohexane:HFA 2:1. [b] Estimated from vpc data. [c] Ratio of cyclohexane:HFA ranged from 10:1 (7%) to 1:2 (14%).

The minimum kinetic chain length, defined as molecules of product produced per molecule of initiating radical,[6] for the di-*t*-butyl peroxide initiated reaction of cyclohexane with hexafluoroacetone was determined by running the reaction with a quantity of initiator insufficient to consume all the hexafluoroacetone. The results are listed in Table II, as are conditions which result in good yields of product, and indicate a chain

Table II. Effect of Di-*t*-butyl Peroxide Concentration on the Addition of Cyclohexane to Hexafluoroacetone[a]

$(t\text{-BuO})_2$, mole	Adduct, % 1:1	2:1	Alcohol: ether[b]	Minimum kinetic chain length[c] 1:1 adduct	Total product
0.001	28	8	84:16	28	38
0.001	21	7	83:17	21	28
0.002	41	8	. . .	21	25
0.01	72	19	83:17	*d*	. .
0.02	73	7	83:17	*d*	. .

[a] 0.83 mole cyclohexane, 0.2 mole HFA. [b] Vpc data (uncorrected). [c] Assuming each molecule of di-*t*-butyl peroxide initiates two chains. [d] No unreacted HFA remained.

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(3) (a) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957); (b) M. Stacey, J. C. Tatlow, and A. G. Sharpe, *Advan. Fluorine Chem.*, 3, 1 (1963); (c) *ibid.*, 4, 284 (1965).

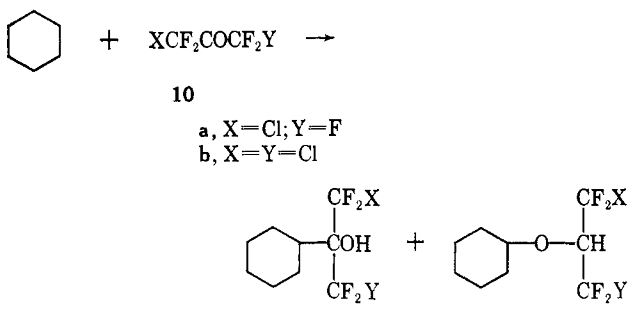
(4) (a) Equilibria of this type lie far to the right, indicating a carbonyl π bond of high energy relative to the saturated adduct. In view of the stabilizing influence of an ionic contribution to a carbonyl bond, as described by L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 190, the more covalent fluoro ketone carbonyl may have a higher energy content (less stable) double bond than its hydrocarbon ketone counterpart. The fluoro ketone carbonyl reactivity is shown in this paper to extend to free radicals. (b) R. N. Haszeldine, W. K. R. Musgrave, F. Smith, and L. M. Turton, *J. Chem. Soc.*, 609 (1951).

(5) (a) H. R. Davis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill. Sept 1961, p 25M; (b) I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 355 (1962); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 329 (1962).

(6) C. Walling and E. S. Heyser, *Org. Reactions*, **13**, 94 (1963).

length of about 25 for 1:1 adduct and 35 on a total product basis.

Similar reactions occurred between cyclohexane and chloropentafluoroacetone (**10a**) to give 1-chloro-1,1,-3,3,3-pentafluoro-2-cyclohexyl-2-propanol (**11a**) and cyclohexyl 1-chloro-1,1,3,3,3-pentafluoroisopropyl ether (**12a**). Cyclohexane and 1,3-dichloro-1,1,3,3-tetrafluoroacetone (**10b**) gave 1,3-dichloro-1,1,3,3-tetrafluoro-2-cyclohexyl-2-propanol (**11b**) and cyclohexyl 1,3-dichloro-1,1,3,3-tetrafluoroisopropyl ether (**12b**).



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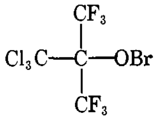
11 **12**

Table III shows the results of these reactions. Cyclohexane and 1,1,3,3-tetrachloro-1,3-difluoroacetone, and

Table III. Free-Radical Addition of Cyclohexane to Fluoro Ketones

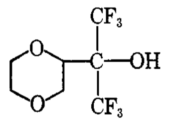
			%		
Fluoro ketone	Initiator	Temp, °C	Alcohol	Ether	Total yield
CF_3COCF_3	$(t\text{-BuO})_2$	135	83	17	73
CF_3COCF_3	$h\nu$	−10	100	0	77
CF_3COCF_2Cl	$(t\text{-BuO})_2$	135	39	61	49
CF_3COCF_2Cl	$h\nu$	10	100	0	59
$CF_2ClCOCF_2Cl$	$(t\text{-BuO})_2$	135	~10	~90	17
$CF_2ClCOCF_2Cl$	$h\nu$	25	70	30	17

cyclohexane and hexachloroacetone gave low yields of many unidentified products. *n*-Butane did not react with hexafluoroacetone when initiated by di-*t*-butyl peroxide, but long ultraviolet irradiation gave a 40% yield of isomeric $C_{10}H_{10}F_{12}O_2$ diols. *n*-Octane and hexafluoroacetone gave a 6% yield of isomeric 1:1 adducts and an 11% yield of isomeric 2:1 adducts with di-*t*-butyl peroxide initiation, and 8 and 10% yields of these adducts with ultraviolet initiation. The products were largely alcohols. Isobutane yielded the isomeric diols **5** and **6** derived from nonradical addition of hexafluoroacetone to isobutylene.[5] Adamantane, chloroform, benzene, toluene, and trifluoromethyl iodide did not react with hexafluoroacetone, but bromotrichloromethane gave an adduct which exploded upon attempted distillation, presumably the hypobromite **13**. Dioxane and hexafluoroacetone gave 1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyldioxane (**14**).



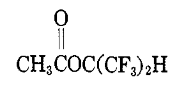
$Cl_3C{-}C(CF_3)_2{-}OBr$

13



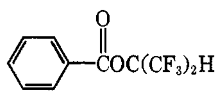
14

Aldehydes. Acetaldehyde and benzaldehyde reacted with hexafluoroacetone to give 1,1,1,3,3,3-hexafluoroisopropyl acetate (**15**) and 1,1,1,3,3,3-hexafluoroisopropyl benzoate (**16**), respectively. Irradiation of hexafluoroacetone and acetaldehyde gave the acetate **15** and a small amount of 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-3-butanone (**17**).



$CH_3\overset{O}{\overset{\|}{C}}OC(CF_3)_2H$

15



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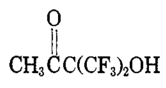


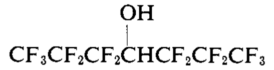
$CH_3\overset{O}{\overset{\|}{C}}C(CF_3)_2OH$

17

Heptafluorobutyraldehyde and hexafluoroacetone gave largely polymeric material; irradiation provided decafluoro-2-trifluoromethyl-2-pentanol (**18**) in 5% yield and a trace of 4H-perfluoro-4-heptanol (**19**)

$CF_3CF_2CF_2C(CF_3)_2OH$

18



$CF_3CF_2CF_2\overset{OH}{\overset{|}{C}}HCF_2CF_2CF_3$

19

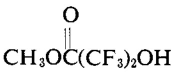
while di-*t*-butyl peroxide initiation gave **19** in 13% yield.

Esters. Methyl acetate and hexafluoroacetone on irradiation gave 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl acetate (**20**) in 88% yield and a trace of 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl 3-trifluoromethyl-3-hydroxy-4,4,4-trifluorobutyrate (**21**).

$$CH_3CO_2CH_3 + CF_3COCF_3 \xrightarrow{h\nu} \underset{\mathbf{20}}{CH_3CO_2CH_2C(CF_3)_2OH} +$$

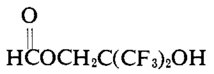
$$\underset{\mathbf{21}}{HOC(CF_3)_2CH_2CO_2CH_2C(CF_3)_2OH}$$

Methyl formate and hexafluoroacetone on irradiation gave methyl 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropionate (**22**), 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl formate (**23**), and a small amount of 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropionate (**24**).



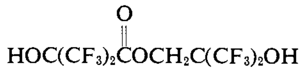
$CH_3O\overset{O}{\overset{\|}{C}}C(CF_3)_2OH$

22



$H\overset{O}{\overset{\|}{C}}OCH_2C(CF_3)_2OH$

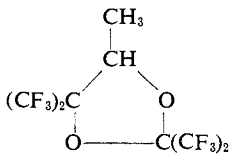
23



$HOC(CF_3)_2\overset{O}{\overset{\|}{C}}OCH_2C(CF_3)_2OH$

24

Ethyl formate and ethyl acetate gave low yields of complex mixtures; from the latter reaction two products were 2,2,4,4-tetrakis(trifluoromethyl)-5-methyl-1,3-dioxolane (**25**) and 1-methyl-2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl acetate (**26**).



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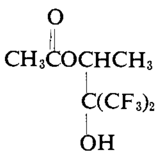

26

Silanes. Hexafluoroacetone with trichlorosilane and dichloromethylsilane gave trichloro(1,1,1,3,3,3-hexafluoro-2-propoxy)silane (**27**) and dichloro(1,1,1,3,3,3-hexafluoro-2-propoxy)methylsilane (**28**), respectively,

$Cl_3SiOC(CF_3)_2H$ **27**

$CH_3SiCl_2OC(CF_3)_2H$ **28**

Table IV. Reaction of Fluorocarbonyl Compounds and Polymers[a]

Polymer	Fluorocarbonyl compound	Initiator/ temp, °C	Product analysis, %
Polyethylene	HFA[b]	None/135	No reaction
Polyethylene (linear)	HFA	t-$(BuO)_2$/135	F, 30.67
Purified polymer from above experiment	HFA	t-$(BuO)_2$/135	F, 40.62
Polyethylene	$(CF_3CF_2CF_2)_2CO$	t-$(BuO)_2$/135	F, 1.11
Polyethylene	$CF_3CF_2CF_2CHO\cdot H_2O$	t-$(BuO)_2$/135	F, 4.60
Polyethylene	CF_3COCF_2Cl	t-$(BuO)_2$/135	Cl, 2.73, F, 6.03

[a] In the system C_6H_6–pressure. [b] HFA = hexafluoroacetone.

on ultraviolet irradiation. A similar result appeared after this work was completed.[7]

Polymeric Substrates. Perfluoro ketones were found to react under free-radical conditions with a number of polymeric substrates to give net insertion of the fluoro ketone into a polymer carbon–hydrogen bond. Table IV records the results of several such polymer modifications. The properties of the polymeric products were quite different from those of the untreated polymer and correspond to those expected for a chain carrying random branches composed largely of fluoro alcohol groups. Crystallinity is greatly reduced, while acidity and an ability to hydrogen bond are markedly developed.[8]

The major new bands found in the infrared absorption spectrum were due to associated and unassociated hydroxyl (3430 and 3600 cm^{-1}), and carbon–fluorine (1200 cm^{-1}) bonds. No gross degradation of the polymer chain occurred, since there was little change in inherent viscosity. Polypropylene absorbed lesser amounts of hexafluoroacetone than did polyethylene in a similar reaction, but some cleavage of C–C bonds also occurred. Polymers bearing negative groups (CN, CO_2CH_3, F) absorbed limited but significant amounts of hexafluoroacetone under the usual conditions.

Discussion

The following reaction sequence utilizing the di-t-butyl peroxide initiated reaction of hexafluoroacetone as a model is proposed to rationalize the experimental facts.

Initiation

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \tag{1}$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \tag{2}$$

$$CH_3\cdot + CF_3COCF_3 \longrightarrow CH_3C(CF_3)_2O\cdot \tag{3}$$

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \tag{4}$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \tag{5}$$

$$CH_3C(CF_3)_2O\cdot + RH \longrightarrow CH_3C(CF_3)_2OH + R\cdot \tag{6}$$

Propagation

$$R\cdot + CF_3COCF_3 \rightleftharpoons RC(CF_3)_2O\cdot \tag{7}$$

$$R\cdot + CF_3COCF_3 \rightleftharpoons RO\dot{C}(CF_3)_2 \tag{8}$$

$$RC(CF_3)_2O\cdot + RH \longrightarrow RC(CF_3)_2OH + R\cdot \tag{9}$$

$$RO\dot{C}(CF_3)_2 + RH \longrightarrow ROC(CF_3)_2H + R\cdot \tag{10}$$

Termination

$$2R\cdot \longrightarrow RR \tag{11}$$

$$2CH_3\cdot \longrightarrow C_2H_6 \tag{12}$$

$$\text{Others} \tag{13}$$

Equations 1 and 2 are well documented.[9] Isolation of substantial amounts of acetone and acetone–hexafluoroacetone condensation products prove the importance of eq 2. Equations 3 and 6 are major initiation steps since significant quantities of hexafluoro-t-butyl alcohol were found in each reaction. Equation 4 is another well-known reaction.[9] No t-butyl alcohol was identified in the reactions studied; however, t-butyl alcohol should readily dehydrate to isobutylene under the reaction conditions used and products derived from reaction of isobutylene and hexafluoroacetone were isolated. The contribution of eq 5 to the initiation cannot be evaluated since no attempts were made to determine the quantity of methane produced in the reactions. However, it is felt this reaction is important since eq 2 has been shown to be a major initiation step and methyl radicals abstract hydrogen efficiently.

No products clearly resulting from chain termination according to eq 11 and 12 have been observed in successful peroxide-initiated reactions of hexafluoroacetone.

The chain nature of these reactions is evident from the fact that small quantities of initiator result in large quantities of product, and the reactions do not proceed in the absence of initiator.

The propagation steps 7–10 are readily derived from the products observed in the reactions, and illustrate the presence of two competing propagation sequences. A radical adds to the carbonyl group either at the carbon atom (eq 7) or the oxygen atom (eq 8); the intermediate radical then abstracts a hydrogen atom from new substrate to give an alcohol (eq 9) or an ether (eq 10) and continues the chain. The observed product distribution might lead one to conclude that radical addition to the carbonyl carbon is generally preferred in the systems studied. However, there are features not in keeping with this rationale. First, considering the competitive addition steps, eq 8, not 7, would be preferred because free radicals are known to add to unsaturated systems at the least sterically hindered point to produce the most stable radical intermediate.[6] In the case of the product from hexafluoroacetone and a radical, the chain intermediate **30** should be more stable than **29** because of electron donation from oxygen and interaction with trifluoromethyls. The stabilization of acyl, α-hydroxyalkyl, and α-alkoxyalkyl

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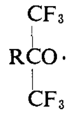
(7) A. F. Janzen and C. J. Willlis, *Can. J. Chem.*, **43**, 3063 (1965).

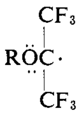
(8) See W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964), for a discussion of properties of fluoro alcohols.

(9) C. Walling, ref 1a, pp 469–472.



$RC(CF_3)_2O\cdot$

29



$R\ddot{O}C(CF_3)_2\cdot$

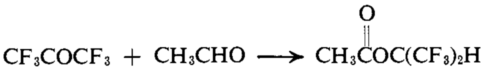
30

free radicals by electron donation from oxygen has been discussed extensively.[10] Stabilization of a free radical by an adjacent trifluoromethyl group has been reported,[11] but the mode of stabilization is not clear. Thus, judging by steric hindrance and intermediate stability, addition to oxygen (eq 8) should be the preferred mode of addition of free radicals to fluoro ketones.

Second, considering the competitive hydrogen abstraction steps, eq 9 is preferred to eq 10. Alkoxy radicals are efficient hydrogen-abstraction agents[12] and as stabilization of the chain-carrying radical increases, the ease of hydrogen abstraction in the chain-propagation step decreases.[6,9] Although steric effects of hydrogen abstraction have not been well established,[9] one would expect a higher entropy requirement for abstraction of hydrogen by the isopropyl radical **30** than by isopropoxy radical **29**.

These effects indicate that the product ratios (C *vs.* O alkylation) in free-radical reactions with fluoro ketones will depend upon the over-all energy relationship between the paired C-alkylation sequence (eq 7 and 9) and the paired O-alkylation sequence (eq 8 and 10). Any significant energy difference will result in a product derived from the most favorable of the two competing reactions. The preponderance of C-alkylated product derived from most free-radical reactions of fluoro ketones indicates that the hydrogen-abstraction step is reaction controlling. The observed temperature-dependent product distribution in the reaction of cyclohexane with fluoro ketones (Table I) shows an increase in O-alkylated product as the temperature increases. Thus, the free energy of O alkylation is greater than that of C alkylation; it is suggested this result reflects the energy differences in the hydrogen-abstraction steps.

The isolation of O-alkylated product in two of the reactions examined is readily understood on the basis of the previously developed arguments. In addition to the greater gain in energy from forming Si–O and CO–O bonds, hydrogen abstraction from aldehydes[13a]

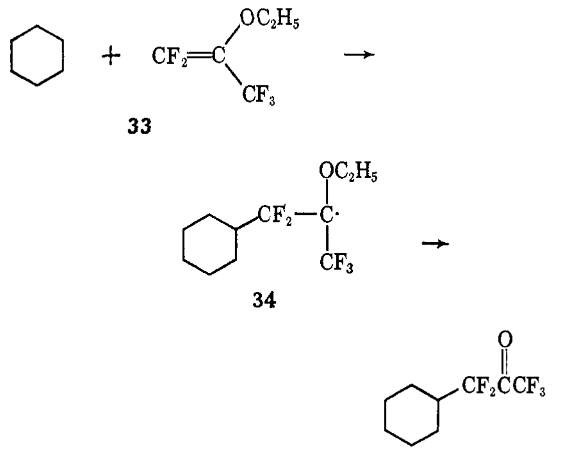


$$CF_3COCF_3 + CH_3CHO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OC(CF_3)_2H \qquad (14)$$

$$CF_3COCF_3 + RCl_2SiH \longrightarrow RCl_2SiOC(CF_3)_2H \qquad (15)$$

and silanes[13b] is relatively more easy than in many carbon–hydrogen systems. This lowering of the energy requirement in the chain-transfer step may allow a favorable energy balance between the O-alkylation steps with the resultant increase in O-alkylated product.

Finally, we propose that the addition of radical to the carbonyl function must be reversible to account for the generally high yields of products and the apparent insensitivity of product distribution to the addition steps. Reversibility of the carbon-addition step (eq 7) is reasonable in light of the work of Greene, *et al.*[14] Reversibility of the oxygen-addition step (eq 8) was tested in the following manner. Free-radical addition of cyclohexane to 2-ethoxy-1,1,3,3,3-pentafluoropropene (**33**), which should generate the intermediate



33

34

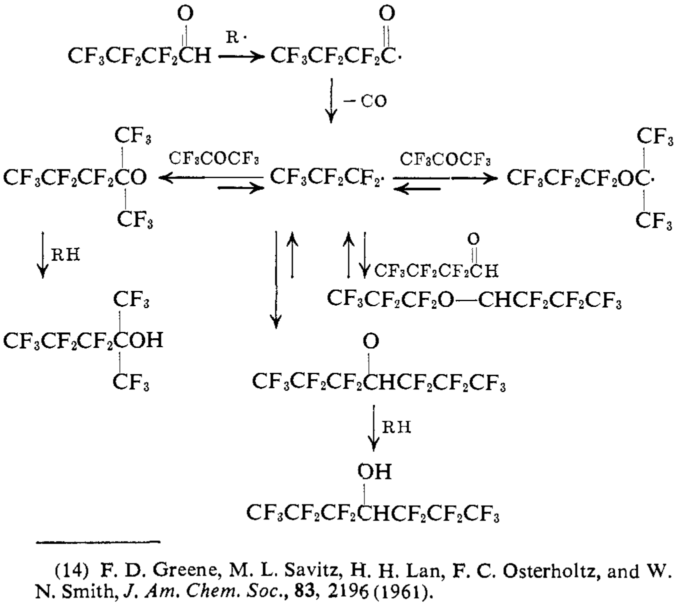
35

(16)

radical **34**, similar to the radical derived from the oxygen addition step (eq 8), gave a 10% yield of 1-cyclohexyl-1,1,3,3,3-pentafluoroacetone (**35**), presumably *via* expulsion of the ethyl radical. This reversibility of addition prevents buildup in the concentration of the O-alkylated radical, and permits channeling of the reaction along the path of C alkylation in the event of an unfavorable O-alkylation, hydrogen-abstraction step.

In the reaction of heptafluorobutyraldehyde with hexafluoroacetone, intermediate stability and steric hindrance, plus consideration of the anticipated electrophilicity of the perfluoroacyl radical, favor preferential addition to oxygen. However, the product, in low yield, is that observed by decarbonylation of the perfluoroacyl radical followed by C alkylation of both hexafluoroacetone and heptafluorobutyraldehyde by the perfluoropropyl radical. These results are readily rationalized (Scheme I) by consideration of reversibility

Scheme I



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[10] C. Walling, ref 1a, pp 51, 285–289.

[11] (a) W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965); (b) P. J. Scheidler and J. R. Bolton, *ibid.*, **88**, 371 (1966); (c) M. T. Jones, *J. Chem. Phys.*, **42**, 4054 (1965).

[12] C. Walling, ref 1a, pp 240–243.

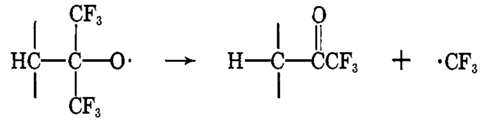
[13] (a) C. Walling, ref 1a, pp 50, 241, 242, 430; (b) C. Walling, ref 1a, pp 343–344.

[14] F. D. Greene, M. L. Savitz, H. H. Lan, F. C. Osterholtz, and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961).

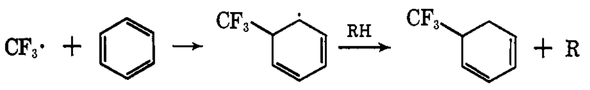
and recognition that hydrogen abstraction from fluoroalkyl aldehydes is difficult.[15]

The preferentially formed O-addition intermediates are apparently unable to abstract hydrogen, thus eliminating O-alkylated product (ether) from the reaction scheme. Reversibility of addition regenerates perfluoropropyl radicals which are consumed by the slower C-addition reactions leading to the observed products. The low yield is the result of increased importance of side reactions and perhaps the increased difficulty of hydrogen abstraction by the fluoroalkoxy radical.

Another mode of intermediate decomposition was observed in the reaction of polyethylene with hexafluoroacetone in benzene solution. The infrared spectrum of the polymeric product revealed the presence of the trifluoroacetyl group attached to the polymer,[16] presumably by loss of CF_3. Furthermore, after reaching a level of 30% F, the reaction stopped; when the product was purified and again treated with hexafluoroacetone, the fluorine content reached 40%. Expulsion of the trifluoromethyl radical from the alkoxy radical depicted in eq 17 would give rise to the observed carbonyl group. Further, the trifluoromethyl radical could attack benzene to yield the trifluoromethylcyclohexadiene **36**, an effective free-radical inhibitor. Purification of the polymer and removal of impurities allows the subsequent treatment by hexafluoroacetone to yield polymer with the additional fluorine content.

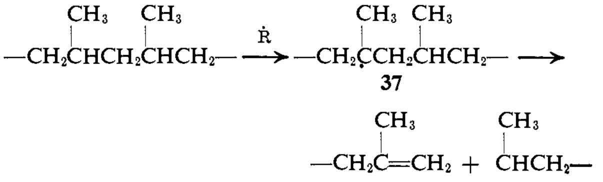


$$\text{HC—}\underset{CF_3}{\overset{CF_3}{\text{C}}}\text{—O}\cdot \rightarrow \text{H—C—}\overset{O}{\overset{\|}{\text{C}}}\text{CF}_3 + \cdot\text{CF}_3 \quad (17)$$



(18)

The failure of moderately stable free radicals to react with hexafluoroacetone is also accommodated by the proposed mechanism. Although an increase in the stability of the incipient free radical R· facilitates hydrogen abstraction from the parent R–H, the endothermic nature of the addition reaction increases.[6,12] With hexafluoroacetone the consequent decrease in the rate of addition can be particularly important in the C-addition reaction (eq 7). A radical substrate with only mild tendency to add can quickly increase the relative importance of alternative paths for utilization of initiator. In these cases, eq 2 and 3 can cause disappearance of initiator without efficient initiation of the desired chain. This is seen in the failure of chloroform and toluene addition to hexafluoroacetone, where hexafluoroacetone and initiator react, but no products derived from substrate addition to hexafluoroacetone were found. The presence of substrate radical in these reactions was proven by the isolation and identification of substrate dimers, *i.e.*, hexachloroethane from the chloroform reaction and bibenzyl from the toluene reaction. Similarly, the degradation of polypropylene by hexafluoroacetone may be explained by suggesting that preferential radical abstraction of the tertiary hydrogen provides the relatively stable radical **37**, which then cleaves to olefin and radical rather than adding to hexafluoroacetone.



$$\text{—CH}_2\overset{CH_3}{\text{C}}\text{HCH}_2\overset{CH_3}{\text{C}}\text{HCH}_2\text{—} \xrightarrow{\dot{R}} \underset{\textbf{37}}{\text{—CH}_2\overset{CH_3}{\dot{\text{C}}}\text{CH}_2\overset{CH_3}{\text{C}}\text{HCH}_2\text{—}} \longrightarrow \text{—CH}_2\overset{CH_3}{\text{C}}\text{=CH}_2 + \overset{CH_3}{\dot{\text{C}}}\text{HCH}_2\text{—} \quad (19)$$

Evidence is available for the occurrence of intramolecular hydrogen abstraction by the hexafluoroisopropoxy radical as a chain-propagation process in competition with the intermolecular step depicted in eq 9. This reaction, analogous to those observed on decomposition of *t*-alkyl hypochlorides,[14] occurs preferentially at a δ hydrogen. With cyclohexane the yield of the 2:1 hexafluoroacetone:cyclohexane adduct remains relatively constant (7–14%) during a variation in reactant ratio of from 1:10 hexafluoroacetone:cyclohexane to 2:1 hexafluoroacetone:cyclohexane. The appearance of 7% 2:1 product when cyclohexane is present in large excess (10:1) strongly suggests the operation of an intramolecular abstraction mechanism. The photolytic reaction of hexafluoroacetone with *n*-butane to yield only 3:1 hexafluoroacetone:butane adduct may be interpreted as evidence for intramolecular abstraction, as may the reaction of *n*-octane and hexafluoroacetone to yield significant quantities of the 2:1 product. Thus, intramolecular hydrogen abstraction should be an important chain-transfer step in both grafting and copolymerization reactions.

The photolytically induced chain reactions of hexafluoroacetone appear to involve the following primary reactions.

Initiation

$$CF_3COCF_3 \xrightarrow{h\nu} [CF_3COCF_3]^* \quad (20)$$

$$[CF_3COCF_3]^* + RH \longrightarrow (CF_3)_2\dot{C}OH + R\cdot \quad (21)$$

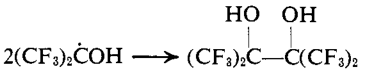
$$(CF_3)_2\dot{C}OH + RH \longrightarrow (CF_3)_2CHOH + R\cdot \quad (22)$$

Propagation

same as eq 7–10

Termination

$$2R\cdot \longrightarrow RR \quad (23)$$



$$2(CF_3)_2\dot{C}OH \longrightarrow (CF_3)_2\overset{HO}{C}\text{—}\overset{OH}{C}(CF_3)_2 \quad (24)$$

The ultraviolet spectrum of hexafluoroacetone shows absorption between 2450 and 3550 A with a maximum at about 3020 A (ϵ 16.9).[17] Photolysis of hexafluoroacetone in the gas phase occurs by two alternative primary processes[18] involving monomolecular dissociation of excited singlet-state molecules in one case and dissociation of triplet-state molecules formed from the excited singlet species by intersystem crossing in the second. The triplet lifetime is estimated to be $\sim 10^{-4}$ seconds. Thus, we presume that the photochemical reactions proceed *via* an excited hexafluoroacetone molecule whose oxygen abstracts a hydrogen atom from the substrate to initiate the chain reaction.

A recent paper by Walling and Gibian[19] reports hydrogen abstraction by the benzophenone triplet.

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(15) J. F. Harris, personal communication.

(16) E. G. Howard and P. B. Sargeant, to be published.

(17) P. B. Ayscough and E. W. R. Steacie, *Proc. Roy. Soc.* (London), A234, 476 (1956).

(18) G. B. Porter, *Angew. Chem. Intern. Ed. Engl.*, 2, 269 (1963).

(19) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, 87, 3361 (1965).

During the course of this work a report[20] concerned with the photolysis of hexafluorobiacetyl appeared. In the presence of hydrocarbon substrates, *e.g.*, neopentane or isobutane, the primary decomposition process was interrupted and several products were obtained. The infrared spectrum of these products showed strong hydroxyl absorption. The identification of hexafluoro-2-propanol and perfluoropinacol as reaction products, and in some cases as the major reaction products, adds weight to the postulated reaction sequence. Perfluoropinacol was previously prepared by irradiation of hexafluoroacetone in the presence of 2-propanol.[8]

Experimental Section

General. ^1H nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 nmr spectrometer, and the chemical shifts are reported in ppm downfield from internal tetramethylsilane. ^{19}F nmr spectra were obtained on a Varian Associates HR 60 or A56/60 nmr spectrometer, both operated at 56.4 Mc. These chemical shifts are reported in ppm upfield from external trichlorofluoromethane. Infrared spectra were obtained on a Perkin-Elmer IR 127 and calibrated with polystyrene. Mass spectra were measured by a Bendix time-of-flight mass spectrometer. Melting points are uncorrected.

Hexafluoroacetone was obtained from the Organic Chemicals Dept., E. I. du Pont de Nemours and Co., and used without further purification.

Ultraviolet irradiations were carried out with a helix-shaped (4 × 2.5 in.) low-pressure, mercury lamp in a previously described system.[21]

Reaction of Di-*t*-butyl Peroxide and Hexafluoroacetone. Hexafluoroacetone (66.4 g, 0.4 mole) and di-*t*-butyl peroxide (29.2 g, 0.2 mole) were heated at 135° for 10 hr in a 240-ml Hastelloy bomb. The liquid product (90 g) was distilled through a 40-cm, spinning-band distillation column. Comparison of vpc, infrared, and ^1H and ^{19}F nmr data established the presence of the following products.

1. 1,1,1,3,3,3-Hexafluoro-2-methyl-2-propanol (**2**) (bp 62–63°, ~32 g, 0.17 mole, 44% yield).[22] The ^1H nmr spectrum had a septet (J = 1 cps, area = 3) at 1.60 ppm and a solvent-dependent hydroxyl absorption. The hydroxyl resonance in the neat liquid was at 3.9 ppm (area = 1). The ^{19}F nmr spectrum had a quartet (J = 1 cps) at 81.2 ppm.

Anal. Calcd for $C_4H_4F_6O$: C, 26.39; H, 2.22; F, 62.63. Found: C, 26.15; H, 2.45; F, 61.14.

2. 1,1,1,3,3,3-Hexafluoro-2-propanol (**3**) (bp 59°, trace).[8] The ^1H nmr had a septet (J = 5.9 cps) at 4.5 ppm and a concentration-dependent hydroxyl peak (area 1:1). ^{19}F nmr had a doublet (J = 5.9 cps) at 78.3 ppm.
3. Acetone (11.5 g, 0.2 mole, 50% yield).
4. *t*-Butyl alcohol (trace).
5. 1,1,1-Trifluoro-2-hydroxy-2-trifluoromethyl-4-pentanone (**4**) (bp 143–145°, 18 g, 0.08 mole, 20% yield, $n^{25}D$ 1.3380). The infrared spectrum had bands at 3350 (OH), 2930 (sat. C–H), 1730 (>C=O), 1430 (CH_2 adjacent to carbonyl), 1370 ($CH_3C(=O)-$), and 1200 (very strong, C–F) cm^{-1}. The ^1H nmr spectrum had absorption at 2.31 (area = 3), 3.08 (area = 2), and a concentration-dependent absorption (area = 1) at 6.98 (neat) ppm. The ^{19}F nmr spectrum had a band at 79.9 ppm.

Anal. Calcd for $C_6H_6F_6O_2$: C, 32.16; H, 2.70; F, 50.87. Found: C, 32.44; H, 2.92; F, 51.05.

6. In reactions of di-*t*-butyl peroxide with hexafluoroacetone in a solvent such as benzene, a solid was isolated and identified (mp 146–146.5°). This solid is a mixture of two isomers, 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)-2,6-dihydroxy-4-methyl-3-heptene (**6**) and 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)-2,6-dihydroxy-4-methyleneheptane (**5**), which apparently form a mixed crystal in the ratio 4:1. The infrared spectrum of the mixture has absorption at 3350 (O–H), 1670, 1640 (C=C), and 1200 (very strong, C–F) cm^{-1}. The ^{19}F nmr spectrum (in CD_3COCD_3) has two bands, equal in area, 77.3 and 78.5 ppm attributed to **6**, and an absorption at 77.2 ppm approximately half the size of the other two, attributed to **5**. The ^1H nmr spectrum had absorptions at 2.10, 3.30, and 5.78 ppm (area 3:2:1) attributed to the methyl, methylene, and vinyl hydrogens of **6**, at 3.03 and 5.33 ppm (area 2:1) attributed to the methylene and vinyl hydrogens of **5**, and a broad absorption between 7 and 10 ppm, concentration and solvent dependent, attributed to the hydroxyl hydrogens. Integration indicated the ratio of **6**:**5** was 4:1. The mass spectrum had a parent ion peak, m/e 388, in agreement with the calculated molecular weight. The same material was independently prepared by the thermal condensation of hexafluoroacetone with isobutylene.

Anal. Calcd for $C_{10}H_8F_{12}O_2$: C, 30.94; H, 2.08; F, 58.43. Found: C, 30.47, 31.02; H, 1.95, 2.24; F, 48.58, 58.47.

Cyclohexane and Hexafluoroacetone. Cyclohexane (70 g, 0.83 mole), hexafluoroacetone (33.2 g, 0.2 mole), and di-*t*-butyl peroxide (1.46 g, 0.01 mole) was charged to a 250-ml Hastelloy bomb and heated at 135° for 8 hr with agitation. The reaction mixture (109 g) was distilled through a 4-cm, spinning-band distillation column to provide cyclohexyl 1,1,1,3,3,3-hexafluoroisopropyl ether, bp 50–54° (23 mm), $n^{25}D$ 1.3708, 5.9 g, 0.023 mole, 12% yield, and 1,1,1,3,3,3-hexafluoro-2-cyclohexyl-2-propanol (**7**), bp 65–67° (23 mm), $n^{26}D$ 1.3855, 29.8 g, 0.12 mole, 60% yield, and an isomeric mixture of the bis(1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)cyclohexanes (**9**), bp 60–61° (2 mm), 8 g, 0.019 mole, 19% yield. The ^1H nmr spectrum of the alcohol had cyclohexyl hydrogen bands at 1.23 (equatorial, area = 5) and 1.93 (axial, area = 6) ppm and a concentration- and solvent-dependent hydroxyl absorption at 3.3 ppm (neat liquid, area = 1). The ^{19}F nmr spectrum had a singlet at 73.9 ppm. The mass spectrum of the alcohol gave a parent-minus-F peak (m/e 231), but no parent peak.

The ^1H nmr spectrum of the ether had cyclohexyl absorption at 1.1 and 1.5 (area = 10) ppm, a broad absorption at 3.3 (area = 1) ppm due to the cyclohexyl hydrogen α to the oxygen, and a septet (J_{HF} = 6 cps) at 3.75 ppm due to the isopropyl hydrogen. The ^{19}F nmr spectrum had a doublet (J_{HF} = 6 cps) at 75 ppm. The mass spectrum gave a parent (m/e 250) peak.

Anal. Calcd for $C_9H_{12}F_6O$ (alcohol): C, 43.22; H, 4.84; F, 45.58. Found: C, 43.52; H, 5.04; F, 45.41.

Anal. Calcd for $C_{12}H_{12}F_{12}O_2$: C, 34.62; H, 2.91; F, 54.68. Found: C, 34.93; H, 3.01; F, 54.76.

Cyclohexane (33.6 g, 0.40 mole) and hexafluoroacetone (33.2 g, 0.20 mole) in 1,1,2-trichlorotrifluoroethane (25 ml) were irradiated in a quartz tube under a Dry Ice–acetone condenser by a low-pressure mercury coil lamp for 1.5 hr. No hexafluoroacetone remained; distillation gave 1,1,1,3,3,3-hexafluoro-2-cyclohexyl-2-propanol (bp 70–71° (25 mm), 34.6 g, 0.138 mole, 69% yield) and the isomeric bis(1,1,1,3,3,3-hexafluoroisopropyl)cyclohexanes (6.29 g, 0.015 mole, 15% yield).

Cyclohexane and Chloropentafluoroacetone. Chloropentafluoroacetone (18.2 g, 0.1 mole), cyclohexane (45 ml), and di-*t*-butyl peroxide (0.73 g, 0.005 mole) were sealed in a Carius tube and heated without agitation at 135° for 8 hr. Distillation gave cyclohexyl 1-chloro-1,1,3,3,3-pentafluoroisopropyl ether (**12a**) (bp 59–60° (10 mm), $n^{25}D$ 1.3907, 8 g, 30% yield) and 1-chloro-2-cyclohexyl-1,1,3,3,3-pentafluoro-2-propanol (**11a**) (bp 69–70° (10 mm), $n^{25}D$ 1.4140, 5 g, 19% yield). The ^1H nmr spectrum of the ether had cyclohexyl hydrogen absorption at 1.30 and 1.80 ppm (area = 10), a broad absorption at 3.62 ppm (area = 1, hydrogen α to oxygen), and a gross septet at 4.02 ppm (area = 1) which is a 16-line pattern (doublet to doublets to quartets) arising from coupling of the isopropyl hydrogen with five fluorines of three different kinds. The ^{19}F nmr spectrum consisted of an AB pattern (CF_2Cl, J_{AB} = 176 cps) and a higher field multiplet (CF_3). The A portion (δ = 60.7 ppm) was a quartet (J_{FA} = 10.5 cps) to doublets (J_{HF_A} = 6.5 cps); the B portion (δ = 61.6 ppm) was a quartet ($J_{F_BF_C}$ = 10.5 cps) to doublets (J_{HF_A} = 6.5 cps); the B portion (δ = 61.6 ppm) was a quartet ($J_{F_BF_C}$ = 10.5 cps) to doublets (J_{HF_B} = 8 cps); the CF_3 area (δ = 73.5 ppm) was a triplet ($J_{F_{AB}F_C}$ = 10.5 cps) to doublets (J_{HF_C} = 5.9 cps).

The alcohol (neat) ^1H nmr spectrum had absorption at 1.3 and 2.0 ppm (area = 11) and 3.25 ppm (area = 1). The ^{19}F nmr spectrum had a multiplet [δ = 58.1 ppm, quartet (J_{FF} = 11 cps) to doublets[23] (J = 10 cps)] and a triplet ((J_{FF} = 11 cps) at 70.6 ppm).

The mass spectra of the alcohol and the ether were similar; both spectra had parent ^{35}Cl and parent ^{37}Cl ions.

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[20] T. M. Whitemore and M. Szwarc, *J. Phys. Chem.*, **67**, 2492 (1963).

[21] J. F. Harris, Jr., and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 1553 (1962).

[22] I. L. Knunyants, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 686 (1960); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 647 (1960).

[23] The doublet may be a result of HF coupling or the result of overlap of the two strong bands of an AB pattern where $\delta_{F_B} - \delta_{F_A}$ is so small that the weak wings are lost in the instrument noise.

Anal. Calcd for $C_9H_{12}ClF_5O$: C, 40.54; H, 4.54; Cl, 13.30; F, 35.63. Found (for ether): C, 40.87; H, 4.87; Cl, 12.79; F, 35.96. Found (for alcohol): C, 41.16; H, 4.72; Cl, 13.33; F, 35.88.

Chloropentafluoroacetone (18.2 g, 0.1 mole) and cyclohexane (45 ml) were irradiated 18 hr to give 1-chloro-2-cyclohexyl-1,1,3,3,3-pentafluoro-2-propanol (15.7 g, 59% yield). None of the corresponding ether was found. Repetition of the above experiment with benzophenone (2.5 g) added as a sensitizer gave only the alcohol (11.3 g, 42% yield).

Cyclohexane and 1,3-Dichloro-1,1,3,3-tetrafluoroacetone. 1,3-Dichloro-1,1,3,3-tetrafluoroacetone (20 g, 0.1 mole), cyclohexane (45 ml), and di-*t*-butyl peroxide (0.73 g, 0.005 mole) were sealed in a Carius tube and heated at 135° for 8 hr. Distillation gave some recovered ketone, cyclohexane, and cyclohexyl 1,3-dichloro-1,1,3,3-tetrafluoroisopropyl ether (**12b**) (bp 53–58° (2 mm), 4.75 g, 0.017 mole, 17% yield). One fraction [bp 58–59° (2 mm)] was mostly ether, but also contained a small amount of 1,3-dichloro-2-cyclohexyl-1,1,3,3-tetrafluoro-2-propanol (**11b**).

The H nmr spectrum of the ether had the cyclohexyl hydrogens at 1.4 and 1.9 ppm (area = 10), the hydrogen α to the oxygen at 3.8 ppm as a broad multiplet (area = 1), and the isopropyl hydrogen at 4.28 ppm as a pentuplet (J_{HF} = 7 cps, area = 1). The ^{19}F nmr was a complex A_2B_2 pattern centered at 58.8 ppm.

The mixture of alcohol and ether had the following properties attributed to the alcohol: ^1H nmr spectrum, cyclohexyl hydrogens at 1.4 and 1.9 ppm and the hydroxyl hydrogen at 3.07 ppm; ^{11}F nmr spectrum, singlet at 55.5 ppm.

The mass spectra of the alcohol and the ether were similar; both isomers showed parent ^{35}Cl and ^{37}Cl ions.

Anal. Calcd for $C_9H_{12}Cl_2F_4O$: C, 38.18; H, 4.27; Cl, 25.05; F, 26.85. Found (for ether): C, 38.34; H, 4.42; Cl, 24.87; F, 27.05.

1,3-Dichloro-1,1,3,3-tetrafluoroacetone (20 g, 0.1 mole) and cyclohexane (45 ml) were irradiated for 19 hr. Distillation gave a mixture of alcohol and ether containing a few additional products (5 g total, 17% yield). Vpc indicated the alcohol to ether ratio was 70:30 (uncorrected). A second reaction containing benzophenone (2.5 g) as a sensitizer gave identical results.

***n*-Butane and Hexafluoroacetone.** *n*-Butane (11.6 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) in $CFCl_2CF_2Cl$ (15 ml) were irradiated 5 days at −10°. At this point 6.5 ml of unreacted starting materials was recovered. Distillation of the reaction mixture gave a fraction (bp 186–188°) whose infrared and ^1H nmr spectra indicated the presence of hydroxyl, methyl, and trifluoromethyl groups. Vpc showed three distinct peaks, but analysis suggested these are isomers of the 2:1 HFA-*n*-butane adduct (15.5 g, 0.04 mole, 40% yield).

Anal. Calcd for $C_{10}H_{10}F_{12}O_2$: C, 30.79, H, 2.58; F, 58.46. Found: C, 30.76; H, 2.48; F, 58.13.

***n*-Octane and Hexafluoroacetone.** *n*-Octane (114 g, 1.0 mole), hexafluoroacetone (166 g, 1.0 mole), and di-*t*-butyl peroxide (14.6 g, 0.1 mole) were heated in a stainless steel bomb at 135° for 10 hr. The resulting liquid (289 g, 98%) consisted of many products, some of which were identified by distillation, vpc, nmr, and elemental analysis: (1) unreacted *n*-octane (about 90 g, 80% recovery), (2) 1,1,3,3,3-hexafluoro-2-methyl-2-propanol (about 15 g, 40% yield from di-*t*-butyl peroxide), (3) 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-4-pentanone, (4) 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-4-methyl-4-pentene,[5] (5) acetone, (6) water, (7) 1:1 HFA-*n*-octane adducts (about 17 g, 6% yield) (a number of 1:1 adducts were obtained, but not separated or identified; in most of the isomers HFA was attached as the pendent hexafluoroisopropyl alcohol group), (8) 2:1 HFA-*n*-octane adducts (about 50 g, 11% yield) (a number of 2:1 adducts were obtained, but not separated or identified). The infrared spectrum showed hydrogen-bonded hydroxyl as well as free hydroxyl and the presence of carbonyl groups.

Anal. Calcd for $C_{11}H_{18}F_6O$: C, 47.14; H, 6.48; F, 40.68. Found for fraction 26 [bp 100–108° (40 mm)]: C, 44.88; H, 5.31; F, 42.38.

Anal. Calcd for $C_{14}H_{18}F_{12}O_2$: C, 37.67; H, 4.08; F, 51.05. Found for fraction 36 [bp 102–115° (2 mm)]: C, 36.19; H, 2.94; F, 51.77.

n-Octane (22.8 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) in $CFCl_2CF_2Cl$ (25 ml) were irradiated for 4 days. Distillation gave 1,1,1,3,3,3-hexafluoro-2-propanol, several isomers of the 1:1 adduct (4.4 g, 8% yield) and the 2:1 adduct (9 g, 10% yield).

Isobutane and Hexafluoroacetone. Isobutane (58 g, 1 mole), hexafluoroacetone (166 g, 1 mole), and di-*t*-butyl peroxide (7.30 g, 0.05 mole) were heated at 135° for 10 hr in a 600-ml Hastelloy bomb. The major product was the mixture of 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)-2,6-dihydroxy-4-methyl-3-heptene and 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)-2,6-di-hydroxy-4-methyleneheptane (mp 145–146°, 63 g, 0.16 mole, 32% yield) previously discussed.

Isobutane (11.6 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) in $CFCl_2CF_2Cl$ (20 ml) were irradiated 48 hr. About 50% of the starting materials was recovered. Distillation, vpc, infrared, and nmr indicated the major products were perfluoropinacol[8] (bp 129°, 12 g, 4% yield) and 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-4-methyl-4-pentene[5] (3.6 g, 0.9% yield). Additional minor products were 1,1,1,3,3,3-hexafluoroisopropyl alcohol and the 2:1 HFA-isobutylene isomer mixture previously described.

Dioxane and Hexafluoroacetone. Dioxane (44 g, 0.5 mole), hexafluoroacetone (16.6 g, 0.1 mole), and benzoyl peroxide (2.42 g, 0.01 mole) were heated at 80° for 7 hr in a Carius tube. Unreacted dioxane was partially removed by distillation; the residue was extracted with 1 *N* aqueous sodium hydroxide. The basic solution was acidified and extracted with ether; the ether extract was washed with water and dried over anhydrous magnesium sulfate and most of the ether was removed by distillation. On standing a white solid (mp 73–76°, 13 g) precipitated. The infrared spectrum of this material had O–H stretching at 3300 cm^{-1} and absorption at 1680 cm^{-1} (probably carbonyl). After three recrystallizations from hexane, the product (mp 83–86°) had much stronger O–H stretching and very weak carbonyl stretching. The proton and ^{19}F nmr spectra are explained by assuming the major product was 1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyldioxane (**14**) contaminated with an open-chain isomer. The yield was 25%.

Anal. Calcd for $C_7H_8F_6O_3$: C, 33.08; H, 3.17; F, 44.86. Found: C, 33.11; H, 2.70; F, 45.19.

Dioxane (35.2 g, 0.4 mole) and hexafluoroacetone (33.2 g, 0.2 mole) in $CFClCF_2Cl$ (35 ml) were irradiated 5.5 hr. Distillation provided only starting materials and perfluoropinacol. The distillation residue solidified on standing and after several recrystallizations from hexane, (1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)-dioxane (1.70 g, 0.007 mole, 3% yield) was isolated.

Acetaldehyde and Hexafluoroacetone. Acetaldehyde (8.8 g, 0.2 mole), hexafluoroacetone (16.6 g, 0.1 mole), and di-*t*-butyl peroxide (0.73 g, 0.005 mole) in $CFCl_2CF_2Cl$ (15 ml) were heated at 135° for 8 hr in a Carius tube. Distillation through a 40-cm, spinning-band still gave 1,1,1,3,3,3-hexafluoroisopropyl acetate (**15**) [bp 68–70°, $n^{25}D$ 1.295 (estimated because below instrument scale), 12.95 g, 0.06 mole, 60% yield], a trace of 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-3-butanone (**17**), and 4,4,4-trifluoro-3-trifluoromethyl-3-hydroxybutyraldehyde [bp 63° (31 mm), 27% yield from another run]. The infrared spectrum of the acetate had absorption at 1780 cm^{-1} (>C=O); the ^1H nmr (neat) had a septet (J = 6 cps) centered at 5.90 ppm and a singlet at 2.20 ppm in the ratio 1:3. The ^{19}F nmr spectrum (neat) had a doublet (J = 6 cps) at 75.6 ppm. The mass spectrum had a parent ion (m/e 210) and was consistent with the proposed structure. The infrared spectrum of the butanone had absorption at 3440 (OH) and 1735 (>C=O) cm^{-1}. The proton nmr spectrum had a single broad peak at 5.28 ppm and a septet (J = 0.9 cps) centered at 3.68 ppm in the ratio 1:3. The infrared spectrum of the aldehyde had absorption at 2900 (aldehyde CH) and 1725 (>C=O) cm^{-1}; the proton nmr spectrum (neat) had resonance at 10, 6.12, and 3.12 ppm in the ratio 1:1:2 attributed to the aldehyde, hydroxyl, and methylene hydrogens, respectively.

Anal. Calcd for $C_5H_4F_6O_2$: C, 28.60; H, 1.92; F, 54.29. Found (for acetate): C, 28.83; H, 2.05; F, 53.07. Found (for aldehyde): C, 29.67; H, 2.08; F, 51.55.

Acetaldehyde (8.8 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) in $CFCl_2CF_2Cl$ (15 ml) were irradiated 15 hr. Distillation gave 1,1,1,3,3,3-hexafluoroisopropyl acetate (15.02 g, 0.07 mole, 36% yield) and 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-3-butanone (bp 80–84°, 2.6 g, 0.01 mole, 6% yield).

Benzaldehyde and Hexafluoroacetone. Benzaldehyde (94 g, 1.0 mole), hexafluoroacetone (166 g, 1.0 mole), and di-*t*-butyl peroxide (7.30 g, 0.05 mole) were heated at 135° for 10 hr in a 600-ml Hastelloy bomb. Distillation through a 40-cm, spinning-band still gave a fraction (bp 168–169°) which was a mixture of unreacted benzaldehyde and 1,1,1,3,3,3-hexafluoroisopropyl benzoate (**16**). The yield of product is about 30%. This material occasionally crystallized from methanol-water (mp 52.6–53.5°). The infrared spectrum had carbonyl stretching at 1740 cm^{-1}; the ^1H nmr spectrum (in $CDCl_3$) had two resonances centered at 6.66 and 5.96 ppm and a septet (J = 6 cps) centered at 4.46 ppm, in the ratio

2:3:1; the ^{19}F nmr spectrum (in benzaldehyde) had a doublet (J = 6 cps) at 74.3 ppm.

Anal. Calcd for $C_{10}H_6F_8O_2$: C, 44.13; H, 2.22; F, 41.89. Found: C, 44.19; H, 2.44; F, 41.70.

Benzaldehyde (20.8 g, 0.3 mole) and hexafluoroacetone (49.8 g, 0.3 mole) in $CFCl_2CF_2Cl$ (25 ml) were irradiated 30 hr. Distillation gave a fraction containing benzaldehyde and 1,1,1,3,3,3-hexafluoroisopropyl benzoate. The yield is about 6%.

Heptafluorobutyraldehyde and Hexafluoroacetone. Heptafluorobutyraldehyde was prepared by dropwise addition of heptafluorobutyraldehyde hydrate to a stirred mixture of phosphorus pentoxide (25 g) and concentrated sulfuric acid (50 ml) at 50°. The aldehyde was collected in a trap cooled in Dry Ice–acetone and used immediately.

Heptafluorobutyraldehyde (22.4 g, 0.11 mole), hexafluoroacetone (20 g, 0.12 mole), and di-*t*-butyl peroxide (1.76 g, 0.012 mole) were heated at 135° for 8 hr in a 125-ml stainless steel bomb. The product (26 g, 60%) was largely dark, polymeric tar. Distillation, vpc, infrared, and nmr techniques showed the presence of the usual initiator-derived products and 4H-perfluoro-4-heptanol (**19**) (2.4 g, 13% yield). The ^{19}F nmr spectrum had the trifluoromethyl resonance (triplet) at 82.5 ppm, the β-difluoromethylene at 129 ppm, and the α-difluoromethylene at 127 ppm (quartet to doublets). The ^{1}H nmr spectrum had a quintet at 5.5 ppm and a solvent- and concentration-dependent hydroxyl absorption (ratio 1:1). The mass spectrum did not give a parent ion, but was consistent with the proposed structure.

Heptafluorobutyraldehyde (19.8 g, 0.1 mole) and hexafluoroacetone (16.6 g, 0.1 mole) were irradiated for 24 hr. Distillation gave a trace of 4H-perfluoro-4-heptanol and decafluoro-2-trifluoromethyl-2-pentanol (**18**) (1.90 g, 5% yield). The ^{19}F nmr spectrum of the pentanol had a triplet to triplets at 74.4 ppm owing to the β-trifluoromethyl groups, a triplet at 82.8 ppm owing to the δ-trifluoromethyl group, and the β- and α-difluoromethylene absorptions were at 118 and 127 ppm, respectively.

Methyl Acetate and Hexafluoroacetone. Methyl acetate (22.2 g, 0.3 mole) and hexafluoroacetone (49.8 g, 0.3 mole) in 1,1,2-trichloro-1,2,2-trifluoroethane (22 ml) were irradiated 16 hr. Distillation through a 40-cm, spinning-band still gave 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl acetate (**20**) (bp 78° (35 mm), $n^{27}D$ 1.3418, 42 g, 0.175 mole, 88% yield). A second fraction [bp 72–108° (25 mm)] gave, after preparative vpc, a small amount of 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl 3-trifluoromethyl-3-hydroxy-4,4-trifluorobutyrate (**21**). The infrared spectrum of acetate had strong absorption at 3400 (OH) and 1740 (>C=O) cm^{-1}. The ^{1}H nmr spectrum had single resonances at 5.47, 4.60, and 2.17 ppm in the ratio 1:2:3. The mass spectrum was compatible with the proposed structure. The infrared spectrum of the butyrate showed absorption at 3400 (OH) and 1780 (>C=O) cm^{-1}. The ^{1}H nmr spectrum had absorption at 4.88, 4.35, and 2.78 ppm in the ratio of 1:1:1. The ^{19}F nmr had two singlet resonances equal in area.

Anal. Calcd for $C_6H_6F_6O_3$: C, 30.02; H, 2.52; F, 47.48. Found: C, 30.81; H, 2.68; F, 46.27.

Anal. Calcd for $C_9H_6F_{12}O_4$: C, 26.61; H, 1.49; F, 56.14. Found: C, 26.80; H, 1.77; F, 55.98.

Ethyl Acetate and Hexafluoroacetone. Ethyl acetate (17.6 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) in 1,1,2-trichloro-1,2,2-trifluoroethane (15 ml) were irradiated 41 hr. Distillation followed by preparative vpc gave small amounts of acetic acid, 2,2,4,4-tetrakis(trifluoromethyl)-5-methyl-1,3-dioxolane (**25**), and 1-methyl-2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl acetate (**26**). The infrared spectrum of the dioxolane showed no hydroxyl or carbonyl absorption. The ^{1}H nmr spectrum (neat) had a quartet (J = 6 cps) centered at 5.44 ppm and a doublet (J = 6 cps) centered at 1.43 ppm in the ratio 1:3 and attributed to the methinyl and methyl hydrogens, respectively. The ^{19}F nmr spectrum (neat) had two broadened quartets (J = 7 cps) at 68.4 and 69.6 ppm. The mass spectrum showed the parent mass (360) peak. The fragmentation pattern suggests the proposed structure, rather than an isomer, is corrected. The infrared spectrum of the acetate had absorption at 3400 (OH) and 1725 (>C=O) cm^{-1}. The ^{1}H nmr spectrum (neat) had a quartet (J = 7 cps) centered at 5.23 ppm, a singlet at 5.35 ppm, a singlet at 1.20 ppm, and a doublet (J = 7 cps) centered at 1.35 ppm in the ratio 1:1:3:3 and attributed to the methinyl, hydroxyl, acyl methyl, and alkyl methyl hydrogens, respectively.

Anal. Calcd for $C_8H_4F_{12}O_2$: C, 26.69; H, 1.12; F, 63.33. Found: C, 27.14; H, 1.11; F, 62.98.

Anal. Calcd for $C_7H_8F_6O_3$: C, 33.09; H, 3.17; F, 44.86. Found: C, 32.55; H, 2.87; F, 44.81.

Methyl and Formate and Hexafluoroacetone. Methyl formate (24 g, 0.4 mole) and hexafluoroacetone (49.8 g, 0.3 mole) were irradiated 16 hr. Distillation through a 40-cm, spinning-band column gave a trace (~1.0 g) of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propyl alcohol, methyl 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropionate (**22**) (bp 107°, 30.3 g, 0.15 mole, 50% yield), 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl formate (**23**) (bp 62–69° (24 mm), 8.35 g, 0.041 mole, 13% yield), and a small amount of 2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropyl-2-trifluoromethyl-2-hydroxy-3,3,3-trifluoropropionate (**24**) (mp 82.9–84.1°). The infrared spectrum of the methyl propionate had absorption at 3420 (OH) and 1740 (>C=O) cm^{-1}; the ^{1}H nmr spectrum (neat) showed single resonances at 4.83 and 3.90 ppm in the ratio 1:3; the ^{11}F nmr spectrum (neat) had a single resonance at 76.1 ppm. The infrared spectrum of the formate had absorption at 3400 (OH) and 1725 (>C=O) cm^{-1}; the ^{1}H nmr spectrum (neat) showed singlet resonances at 7.98, 4.98, and 4.58 ppm in the ratio 1:1:2; the ^{19}F nmr spectrum (neat) showed a singlet at 77.5 ppm. The infrared spectrum of the 2:1 adduct had absorption at 3500 and 1770 cm^{-1}; the ^{1}H nmr spectrum (in $CDCl_3$) had a singlet at 4.72 ppm and a broad resonance centered at 3.9 ppm in the ratio 1:1; the ^{19}F nmr spectrum (in $CDCl_3$) showed two singlets, 74.5 and 76.3 ppm.

Anal. Calcd for $C_5H_4F_6O_3$: C, 26.56; H, 1.78; F, 50.42. Found (for the propionate): C, 26.59; H, 1.77; F, 49.91. Found (for the formate): C, 26.38; H, 1.74.

Anal. Calcd for $C_8H_4F_{12}O_4$: C, 24.51; H, 1.03; F, 58.14. Found: C, 25.11; H, 1.09; F, 57.05.

Trichlorosilane and Hexafluoroacetone. A solution of trichlorosilane (27.1 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) was irradiated 22 hr. Distillation under N_2 gave trichloro(1,1,1,3,3,3-hexafluoro-2-propoxy)silane (**27**) (bp 86–88°, 25.9 g, 43% yield). The ^{1}H nmr spectrum had a septet (J = 5 cps) at 4.60 ppm and the ^{19}F nmr spectrum had a doublet (J = 5 cps) at 76.3 ppm.

Anal. Calcd for C_3HClF_6OSi: C, 11.95; H, 0.34; Cl, 35.28; F, 37.81; Si, 9.31. Found: C, 12.47; H, 0.70; Cl, 37.96; F, 36.82; Si, 9.56.

Methyldichlorosilane and Hexafluoroacetone. Methyldichlorosilane (23 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) were irradiated for 16 hr. Distillation gave dichloro(1,1,1,3,3,3-hexafluoro-2-propoxy)methylsilane (**28**) (bp 98°, 25.8 g, 46% yield). The ^{1}H nmr spectrum had a singlet at 0.87 ppm and a septet (J = 5 cps) at 4.70 ppm in the ratio 3:1.

Anal. Calcd for $C_4H_4Cl_2OSi$: C, 17.10; H, 1.44; Cl, 25.24; F, 40.56; Si, 10.00. Found: C, 17.48; H, 1.55; Cl, 25.14; F, 40.56; Si, 9.54.

Polymeric Substrates and Hexafluoroacetone. The grating reaction procedure is illustrated by the following example with linear polyethylene. A mixture of benzene (200 ml), hexafluoroacetone (33.2 g, 0.2 mole), linear polyethylene (20 g), and di-*t*-butyl peroxide[24] (0.2 g, 0.013 mole) was heated with shaking in a stainless steel reactor at 135° for 8 hr. The polymer was filtered and dried under vacuum (33 g). A sample of polymer was purified for analysis by dissolving in hot benzene, filtering the hot solution, and cooling to reprecipitate the polymer.

Anal. Found: F, 26.7.

When the above procedure was repeated on the purified polymer, a product containing 40.6% fluorine was isolated.

Cyclohexane and 2-Ethoxy-1,1,3,3,3-pentafluoropropene. 2-Ethoxy-1,1,3,3,3-pentafluoropropene was prepared from hexafluoroacetone and triethyl phosphite by the procedure of Wiley and Simmons.[25] Cyclohexane (16.8 g, 0.20 mole), 2-ethoxy-1,1,3,3,3-pentafluoropropene (10 g, 0.057 mole), and di-*t*-butyl peroxide (0.15 g, 0.001 mole) were heated at 135° for 8 hr in an 80-ml stainless steel bomb. Distillation gave a little unreacted vinyl ether, cyclohexane, and 1-cyclohexyl-1,1,3,3,3-pentafluoropropanone (**35**) (bp 135–137°, 1.2 g, 0.0052 mole, 10% yield). The infrared spectrum had bands at 2940, 2960 (sat. C–H), 1795 (fluoro ketone), 1465 (CH_2), and 1200 (C–F) cm^{-1}. The ^{1}H nmr had absorption at 1.25 and 1.80 ppm and the ^{19}F nmr had a triplet at 76.3 ppm and a doublet to quartets at 115 ppm.

Anal. Calcd for $C_9H_{11}F_5O$: C, 46.96; H, 4.82; F, 41.27. Found: C, 46.12; H, 5.31; F, 41.28.

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(24) When benzoyl peroxide was used as initiator the reaction temperature was 80°.

(25) D. W. Wiley and H. E. Simmons, *J. Org. Chem.*, **29**, 1876 (1964).