Anal. Calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.54; S, 40.01. Found: C, 52.80; H, 7.64; S, 39.74.

cis-**2,6-Dithiabicyclo[5.3.0]decane (23).**—This compound was prepared from 2.5 g (0.0187 mol) of *cis*-1,2-cyclopentanedithiol, 0.92 g (0.04 g-atom) of sodium metal, and 4.0 g (0.0191 mol) of 1,3-dibromopropane in 40 ml of NH_3 as described for the preparation of **5**. After chromatography the product was distilled to give 1.67 g (51%): bp 91° (0.25 mm); ν_{max}^{film} 2970, 2920, 2860, 2800, 1465, 1445, 1410, 1330, 1310, 1265, 1240, 1215, 1140, 1070, 1050, 1020, 1000, 965, 940, 925, 910, 880, 850, 790, 735, and 680 cm^{-1}; uv end absorption only; nmr ($CDCl_3$) δ 3.10–3.50 (multiplet, 2 H), 2.30–3.05 (multiplet, 4 H), and 1.50–2.20 ppm (multiplet, 8 H); mass spectrum, *m/e* 174 (25%), 106 (100%), 73 (16%), 67 (36%), 45 (40%), and 41 (60%).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.09, S, 36.79. Found: C, 55.35; H, 8.10; S, 36.55.

Registry No.—**4**, 15077-17-5; **5**, 16214-56-5; **6**, 16291-03-5; **7**, 4410-24-6; **14**, 16214-58-7; **15**, 16214-59-8; **21**, 16214-71-4; **22**, 16214-60-1; **23**, 16214-61-2; **24**, 16214-62-3; **25**, 15786-82-0; *cis*-1,2-cyclopentanedithiol, 16214-64-5; *trans*-1,2-cyclopentanedithiol, 2126-11-6; *cis*-1,2-cyclohexene bisthiolacetate, 16214-66-7; *trans*-1,2-cyclohexane bisthiolacetate, 16214-67-8; *cis*-1,2-cyclohexanedithiol, 2242-71-9; 1-cyclopentene thiolacetate, 16214-69-0; *cis*-1,2-cyclopentane bisthiolacetate, 16214-70-3.

Multiple Multicenter Reactions of Perfluoro Ketones with Olefins

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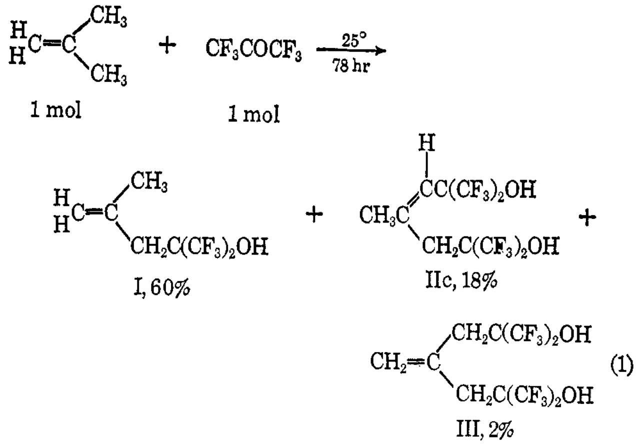
Hexafluoroacetone gives stepwise reactions with olefins $[>\!CH\overset{|}{C}{=}\overset{|}{C}H + CF_3COCF_3 \rightarrow -\overset{|}{C}{=}\overset{|}{C}\overset{|}{C}HC(CF_3)_2OH + CF_3COCF_3 \rightarrow HO(CF_3)_2C\underset{|}{\overset{|}{C}}\overset{|}{C}{=}\overset{|}{C}C(CF_3)_2OH]$ some of which, surprisingly, occur at 25°. Products in a 2:1 ratio are general, and 2-methylpropene also gives a 3:1 product. Terminal olefins are the most reactive with 2-methyl-1-alkenes giving faster rates than 1-alkenes. Otherwise, olefin reactivity is decreased with increased alkyl substitution of their unsaturated carbon atoms. With such tri- and tetrasubstituted olefins or 1:1 products, acid-catalyzed isomerizations (product fluoro alcohols are acidic) occur prior to further reaction with hexafluoroacetone. Reactions giving 2:1 products are stereospecific owing to steric effects.

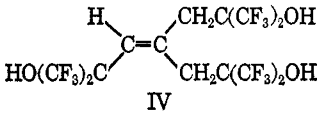
The facile reactions of perfluoro ketones with olefins are known to give 1:1 products;[1-6] and, with 2-methylpropene,[4,5] 2-phenylpropene,[5] and allene,[6] 2:1 products have been reported. The current work shows that the successive reactions occur with comparable rates, and hence 2:1 products are always formed. Indeed, these results suggest that further study of related reactions of olefins with maleic anhydride,[7,8] maleates,[8] fumarates,[8] methylene malonates,[8] pyruvates,[9] or azodicarboxylates[7] may reveal that they also yield such multiple products.

With 2-methylpropene (eq 1), this reaction is unique in its ease and extent (all yields given below are based on olefin used), and the specificity common to them is observed. All of the hexafluoroacetone was consumed (over-all yields based upon it were 100%). Hence, higher ketone/olefin ratios gave more IIc and III, and their yields approached equality at higher reaction temperatures (a ketone/olefin ratio of 2.6 at 25° for 72 hr gave 72% IIc and 8% III; a ratio of 2.0 at 180° for 72 hr gave 56% IIc and 38% III). The reaction of 1,3-dichloro-1,1,3,3-tetrafluoropropanone (2.2 molar excess) with 2-methylpropene at 120° for 72 hr gave products analogous to IIc (54%) and III (29%). To indicate the reaction specificity, no IIt, the *trans*-geometrical isomer of IIc (t or c denotes such products in which the fluorine-containing groups are *trans* or *cis* to each other), was formed in any of the above reactions.



(1)

2-Methylpropene is the only olefin studied that gave a 3:1 product. It (1 mol) with hexafluoroacetone (4.52 mol) at 209° for 150 hr gave 3% IIc, 3% III, and 91% IV. A ketone/olefin ratio of 3.1 at 200° for 60 hr gave 13% IIc, 11% III, and 76% IV.



IV

Other 2-methyl-1-alkenes give these sequential reactions with ease to give 2:1 products. However, 3:1 products were not observed since in general large groups on the terminal olefinic carbon atoms of the allylic systems [C_2H_5– in V, $CH_3(CH_2)_6CH_2$– in VII, and indeed –$C(CF_3)_2OH$ in IIc, VIc, and VIIIc] in-

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(1) D. C. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961).

(2) H. R. Davis. Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept, 1961, p 25M.

(3) I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **2**, 355 (Engl. ed, 329) (1962).

(4) M. H. Litt and G. J. Schmitt, U. S. Patent 3,324,187 (June 6, 1967); British Patent 964,755 (July 22, 1964).

(5) N. P. Gambarjan, E. M. Rolshlina, and Y. V. Zeifman, *Izv. Akad. Nauk SSSR*, **8**, 1466 (Engl. ed, 1425) (1965).

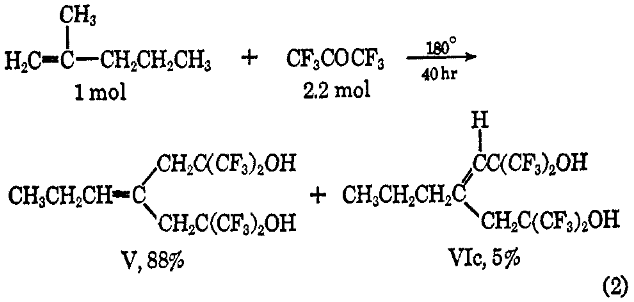
(6) H. R. Davis, U. S. Patent 3,284,516 (Nov 8, 1966).

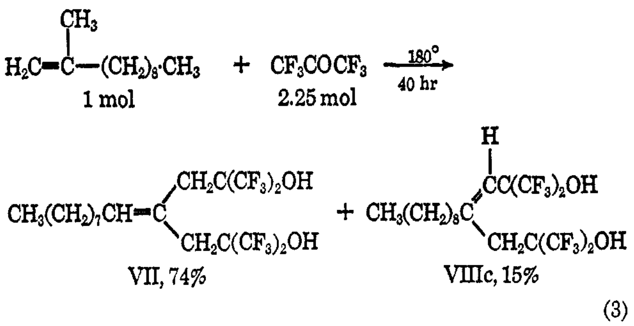
(7) K. Alder, F. Pascher, and A. Schmitz, *Chem. Ber.*, **76**, 27 (1943).

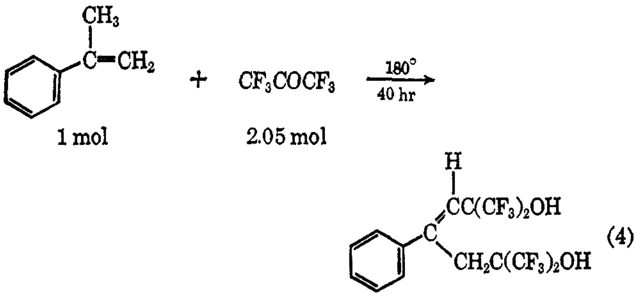
(8) R. T. Arnold and J. S. Showell, *J. Amer. Chem. Soc.*, **79**, 419 (1957).

(9) R. T. Arnold and P. Veeravagu, *ibid.*, **82**, 5411 (1960).

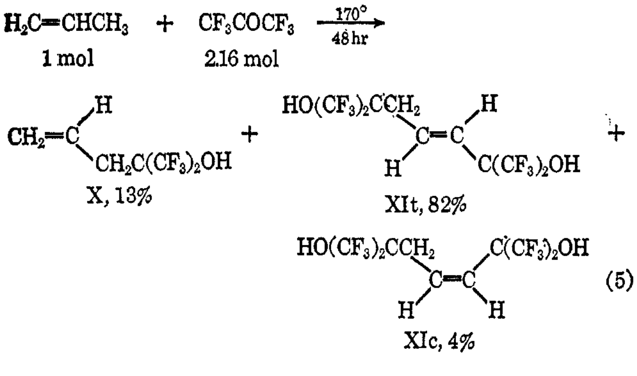
hibit this condensation reaction. Again, only the *cis* forms VIc, VIIIc, and IXc were observed (eq 2–4).

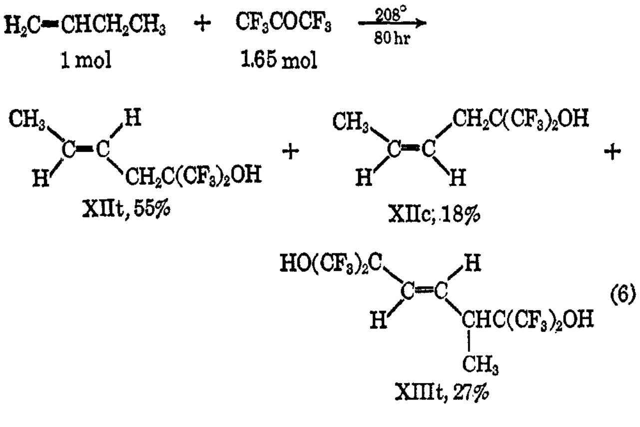

V, 88%
VIc, 5%
(2)


VII, 74%
VIIIc, 15%
(3)

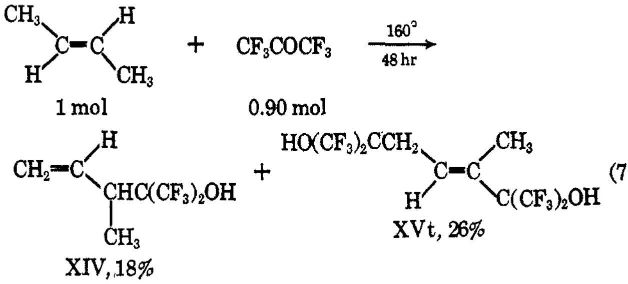

IXc, 97%

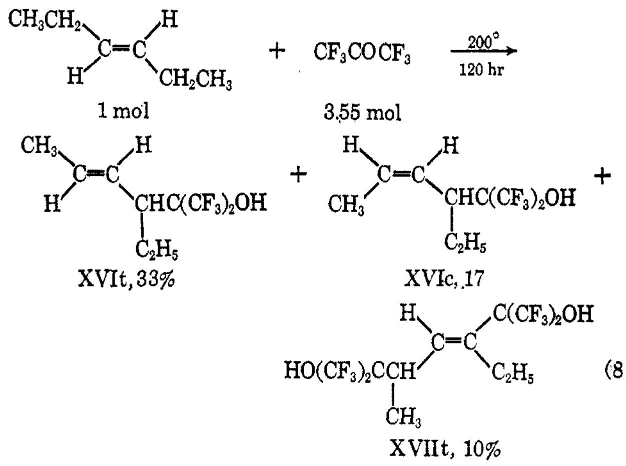
1-Alkenes, such as propene and 1-butene, are less reactive than the olefins above. Apparently, the conversions of X into XI (reaction 5; 0.33 mol of CF_3COCF_3 remained unreacted) and XII to XIII (reaction 6; 0.38 mol of CF_3COCF_3 was unused) are slower than the corresponding reactions with 2-methyl-1-alkenes. The latter reaction (XII → XIII) is also slower than the former (X → XI). Again, the reactions are selective, but here *trans* isomers are dominant. With 1-butene (1 mol) and hexafluoroacetone (0.53 mol) at 25° for 72 hr, only 40% of the latter was consumed to give XIIt (19.5%) and XIIc (1.5%). At the higher temperatures necessary to form 2:1 products (reaction 6), relatively more XIIc was found.


X, 13%
XIt, 82%
XIc, 4%
(5)


XIIt, 55%
XIIc, 18%
XIIIt, 27%
(6)

The 2- and 3-alkenes studied were still less reactive, and again *trans* 1:1 products (reaction 8, XVIt > XVIc) are favored. However, reactions giving 2:1 products are stereoselective—only *trans* isomers are observed. *cis*-2-Butene is less reactive than *trans*-2-butene. Even under more drastic conditions (186°, 72 hr), *cis*-2-butene (1 mol) with hexafluoroacetone (0.91 mol) gave only 4% XIV and 19% XVt.


XIV, 18%
XVt, 26%
(7)


XVIt, 33%
XVIc, 17
XVIIt, 10%
(8)

In reactions 1 and 4–8, the 1:1 and 2:1 products are those expected from successive reactions with hexafluoroacetone without isomerization of either the reactant alkenes or these products. However, when these olefins are highly branched ($RCH{=}CR_2$ or $R_2C{=}CR_2$), their greater rates of acid-catalyzed isomerization (products are acidic; see below) and low reactivity with hexafluoroacetone results in their conversion into more reactive types by the former reaction prior to the completion of the latter. These factors dominate the reactions of 2-methyl-2-butene and 2,3-dimethyl-2-butene, and unexpected products result. Apparently, these olefins are first isomerized to 2-methyl-1-butene or 2,3-dimethyl-1-butene, and these more reactive olefins (see above) then react with hexafluoroacetone. Accordingly, the reaction of 2-methyl-2-butene (0.34 mol) with hexafluoroacetone (0.18 mol) at 165° for 30 hr gave unreacted olefins (0.154 mol)

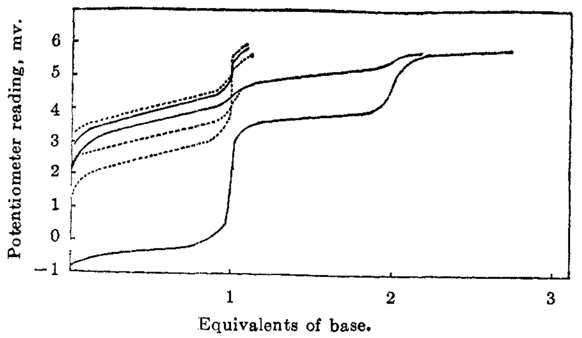
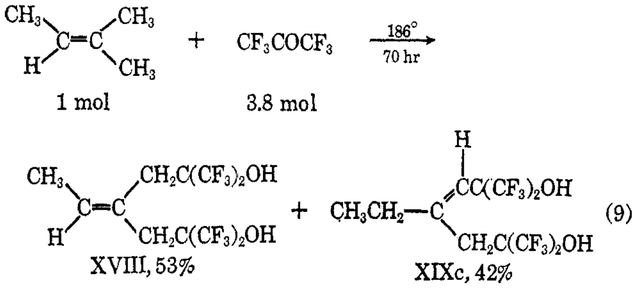


Figure 1.—Potentiometric titrations with tetrabutylammonium hydroxide in dimethylformamide of the products (solid lines) X (upper), IIc (middle), and IV (lower), and the reference substances (dotted lines) phenol (upper), 1,1,3,3,3-hexafluoropropanol-2 (middle), and acetic acid (lower).

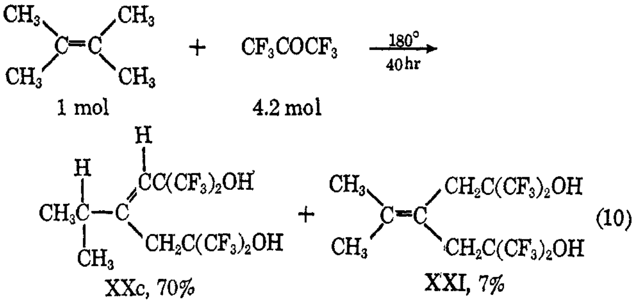
(80% 2-methyl-2-butene and 20% 2-methyl-1-butene), a mixture of 1:1 products (0.13 mol) [the 2-alkenes, $CH_3CH{=}C(CH_3)CH_2C(CF_3)_2OH$, 72% *trans* and 8% *cis*, and 20% of the 1-alkene, $CH_2{=}C(C_2H_5)CH_2C(CF_3)_2OH$], and XVIII and XIXc (0.013 mol). Since only the 1-alkene can react further to give XVIII and XIXc, the major 2-alkene 1:1 products must also isomerize during reaction 9. Similar evidence was obtained for the role of isomerizations in both steps of reaction 10 (see Experimental Section). Under the above reaction conditions, no isomerization of any 2:1 products is observed since only *cis* isomers, and no *trans* ones, are observed. The greater stability of these ultimate products is important since it preserves evidence of reaction specificity, and of relative reactivity of allylic hydrogen atoms.



XVIII, 53%

XIXc, 42%

(9)



XXc, 70%

XXI, 7%

(10)

Reactions where such isomerizations are necessary require high temperatures and long reaction times. One possible reason that vigorous conditions (209° for 150 hr) are needed to obtain IV in the multiple reaction with 2-methylpropene is that the major 2:1 product IIc is unreactive. It is isomerized to the other such product III that reacts to give IV. Also, with the 2-methyl-1-alkenes, reaction 1 is much faster than reactions 2 or 3. In the former, a reactive 2-methyl-1-alkene I is formed first. With 2-methyl-1-pentene or 2-methyl-1-undecene, initial products are the unreactive 2-alkenes [*trans*- and *cis*-$RCH{=}C(CH_3)CH_2C(CF_3)_2OH$] and the reactive 1-alkenes [$CH_2{=}C(CH_2R)CH_2C(CF_3)_2OH$]. The former must be isomerized to the latter before the observed reaction is completed.

The reaction products, and possibly hexafluoroacetone hydrate (no special precautions were taken to make reaction mixtures anhydrous), probably serve as acidic catalysts for these isomerizations. Since 1,1,1,3,3,3-hexafluoro-2-propanol is acidic (pK_a = 9.3),[10] these products were expected to be. Their potentiometric titrations (Figure 1) show that the 1:1 product X is slightly more acidic than phenol, the first dissociation constant of the 2:1 product IIc is greater than that of phenol but less than that of 1,1,1,3,3,3-hexafluoro-2-propanol, and the 3:1 product IV is stronger than acetic acid. Interestingly, the second dissociation constant of IV is approximately equal to the first dissociation constant of IIc.

The order of olefin reactivity suggested above ($CH_3CR{=}CH_2 > RCH{=}CH_2 >$ *trans*-$RCH{=}CHR$ $>$ *cis*-$RCH{=}CHR > RCH{=}CR_2 > R_2C{=}CR_2$, R = alkyl) is also confirmed by an analysis of the relative rates of the competing reactions (A, olefin + $CF_3COCF_3 \rightarrow$ 1:1 product, *vs.* B, 1:1 product + $CF_3COCF_3 \rightarrow$ 2:1 product) that is possible with those experiments in which neither the olefin nor the 1:1 product was completely consumed [reactions 1, 7 (also that with *cis*-2-butene), and 8]. For example, the average mole fraction of 2-methylpropene (0.35, initial 0.50 and final 0.20) and that of I (0.30, initial 0 and final 0.60) and the ratio of rates of formation of I, and of IIc and III, from the yield ratio [(I + IIc + III)/(IIc + III)] permit calculation of the approximate ratio of rate constants for the two successive reactions (k_A/k_B = 3.4 at 25°). Here, therefore, the first reaction (A) is faster than the second (B).

With the other reactions so examined, the reverse is observed. The reaction (7) of hexafluoroacetone with the 1:1 product XIV is faster than that with *trans*-2-butene (k_B/k_A = 3.0 at 160°), and the corresponding reactions from *cis*-2-butene occur with a greater difference in rates (k_B/k_A = 32 at 186°). As expected, the 2-butenes ($RCH{=}CHR$) are less reactive than the product XIV ($RCH{=}CH_2$). *trans*-2-Butene reacts over ten times faster than *cis*-2-butene. In the reaction (8) of *trans*-3-hexene, where both it and the first product XVI are the same type of olefin ($RCH{=}CHR$), the difference in rates is diminished (k_B/k_A = 2.1). The latter ratio is probably due in part to another factor influencing the relative rates of these reactions—the nature of the allylic hydrogen atom abstracted. A tertiary hydrogen atom is so involved in the reaction of XVI with hexafluoroacetone, while in this reaction with *trans*-3-hexene the hydrogen atom attacked is secondary (general discussion below).

The above identification of geometrical isomers among these products is based upon their nmr spectra. The absorptions due to the methylene hydrogen atoms of $-CH_2C(CF_3)_2OH$ groups *cis* to $-C(CF_3)_2OH$ groups are at lower field than those in which these groups are *trans*. The magnitude of this difference in chemical shift is apparent in the nmr spectrum of IV (methylene singlets at δ 3.58 and 3.14). Evidence for the

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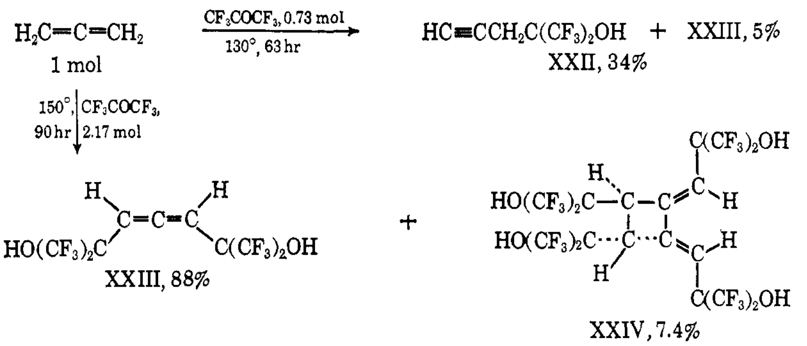
[10] I. L. Knunyants, M. P. Gambajan, C. Y. Chen, and E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **684**, 633 (1962).

assignment is that the doublet due to the methylene group of the *cis* form XIc (olefinic coupling constant, J = 12 cps) is at δ 3.27 and that of the *trans* form XIt (olefinic coupling constant, J = 16 cps) is at δ 2.87. Indeed, the chemical shifts of these methylenes permit classification of the 2:1 products into three groups: (1) those with $-CH_2C(CF_3)_2OH$ *cis* to $-C(CF_3)_2OH$ (IIc, δ 3.47; VIc, 3.18; VIIIc, 3.27; XIXc, 3.23; XXc, 3.27; and XXIXc, 3.17); (2) those with these groups *trans* (IIt, δ 2.75; XIt, 2.80; XVt, 2.85); and (3) those with geminal $-CH_2C(CF_3)_2OH$ groups (III, δ 3.01; V, 3.04; VII, 3.07; XVIII, 3.05; XXI, 3.07). The methylene absorptions of the *trans* 2:1 products (group 2) resemble those in 1:1 products (I, δ 2.68; X, 2.71; XIIt, 2.67; XIIc, 2.83). The corresponding methylene group of IXc (δ 3.87) is sufficiently downfield from that of the 1:1 product from 2-phenylpropene XXXIII (δ 3.01) that IXc probably has the indicated *cis* structure (the methylene of IXt from pyrolysis experiments is at δ 3.10, see below). Again, the coupling constant between the olefinic hydrogen atoms (J = 15.5 cps) of XIIIt indicates that it is the *trans* form. Although the multiplet due to the tertiary hydrogen atom of XIIIt (3.08) is different from that of XVIIt (δ 3.34), the latter probably has the indicated *trans* structure.

The above reactions to give 2:1 products show interesting specificity. Products in a 1:1 ratio with hydrogen atoms attached to the central carbon atoms of their allylic systems react with hexafluoroacetone to give predominantly *trans* 2:1 products (reactions 5–8) while those with more bulky groups (methyl or larger) so attached give *cis* isomers (reactions 1–4, 9, and 10). Study of the molecular models of I and X suggest that the specificity is a steric effect, apparent only when the transition state is considered in three dimensions.

The molecular model of I (solid outline in Figure 2) shows that steric interaction between the $-C(CF_3)_2OH$ group and the methyl or $=CH_2$ groups restricts the former to one side of the molecule (shown below the olefinic system in Figure 2). The attack of hexafluoroacetone can then occur only from the side of the molecule away from that of the $-C(CF_3)_2OH$ group (from above as shown in the dotted outline in Figure 2). The energy of the transition state is presumably minimized by the overlap of the π electrons of the carbonyl and olefinic carbon atoms. As shown in Figure 2, the carbonyl oxygen atom can then more readily reach the methylene hydrogen atom of the $-CH_2C(CF_3)_2OH$ group whose concerted removal leads to the formation of the *cis* isomer IIc.



(11)

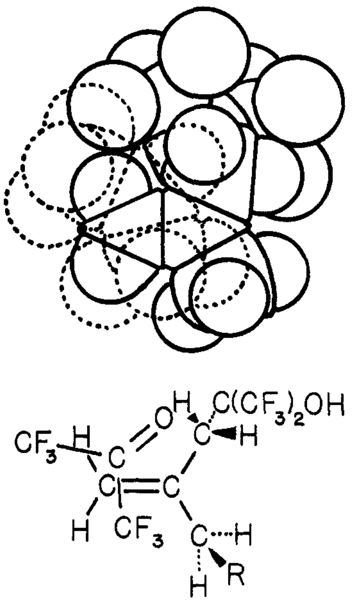


Figure 2.—Perspective drawing of molecular model of I (solid outline above, R = H below) with that of hexafluoroacetone (dotted outline) above it to illustrate its attack to give IIc.

With an hydrogen atom on the middle carbon atom of the allylic system as in X (hydrogen instead of methyl in Figure 2), reduced steric interaction between it and the $-C(CF_3)_2OH$ group permit them to be eclipsed. In this conformation, the hexafluoroacetone molecule has equal access to the allylic system both above and below it, and the methylene hydrogen atom of the $-CH_2C(CF_3)_2OH$ group in position for concerted attack from either direction is that whose removal leads to the *trans* 2:1 product XIt. Previous proposals of concerted reaction mechanisms with six-membered-ring transition states depicted in planar projection[8,9] have ignored such spatial considerations.

A mechanism involving initial formation of the carbon–carbon bond to give a zwitterion intermediate (see below) has been proposed.[11] Such a picture is in keeping with the above discussion if the carbonium ion center preserves the planarity of the olefin-derived system, as it might be expected to do. In fact, this concept is useful in explaining the reaction (11) of allene with hexafluoroacetone. The structure of XXIV is indicated by its ultraviolet [conjugated diene: λ_{max} 241 mμ (ϵ 18,000)], nmr (4 H–OH singlet, 2 H olefinic singlet, and 2 H singlet for ring hydrogen atoms), mass (molecular ion 744) spectra, and steric considerations. Molecular models show that the $-C(CF_3)_2OH$ groups are too large for two of them to be *cis* on the

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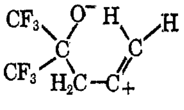
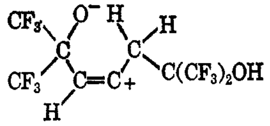
[11] R. L. Adelman, Abstracts of the 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967, p K6.

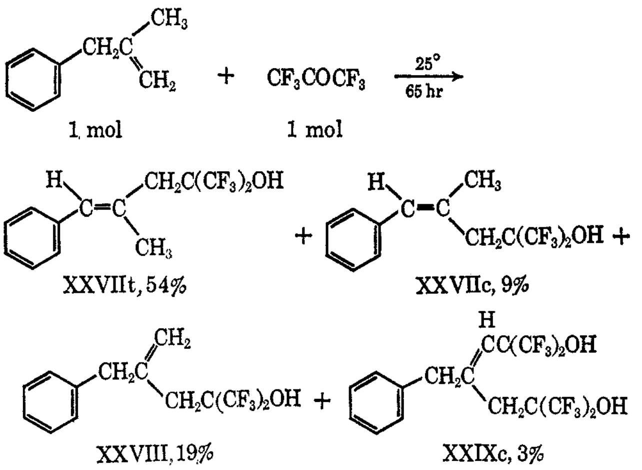
cyclobutene ring, and for the other two to be in the alternative configuration with the $-C(CF_3)_2OH$ groups and olefinic hydrogen atoms transposed.

Obviously, the carbonyl bond of hexafluoroacetone is not of sufficient length to accomplish concerted carbon–carbon bond formation and hydrogen abstraction in either step of its reaction with allene. However, if the zwitterions XXV and XXVI are formed first, the next step to complete the reaction is possible.

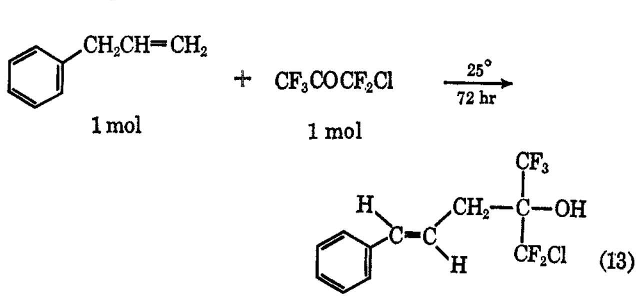

XXV


XXVI

Apparently, the steric effect of the phenyl group is not sufficient to affect the selectivity of this reaction as the $-C(CF_3)_2OH$ group does. The dominant 1:1 product of the reaction (12) of 2-methyl-3-phenylpropene (analogous to I) with hexafluoroacetone is XXVIIt (I gives IIc). The XXVIIc formed is probably due to a limited steric effect of the phenyl group. The following reaction (13) of 3-phenylpropene gave only the *trans* product XXXt.



(12)



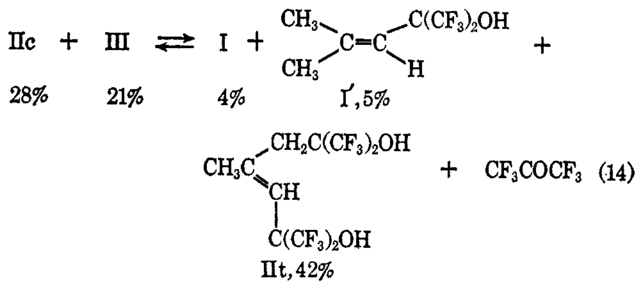
XXXt, 51% (13)

Reaction 12 provides a striking example of the influence of steric effects upon the relative reactivities of allylic hydrogen atoms. Since acid-catalyzed isomerization of the 1:1 products is probably limited at 25°, their yields indicate that, in the competition between the methyl and benzylic hydrogen atoms of 2-methyl-3-phenylpropene, the latter are more reactive (63% XXVIIt and XXVIIc and 22% XXVIII—3% then consumed to give XXIXc). However, the further reaction of XXVIII with hexafluoroacetone gave only XXIXc and none of the isomeric styrene, $C_6H_5CH{=}C(CH_2C(CF_3)_2OH)_2$.

The molecular model of XXVIII indicates the reason for exclusive attack upon a methylene hydrogen atom of its $-CH_2C(CF_3)_2OH$ group. The steric requirements of the $-C(CF_3)_2OH$ and the phenyl groups are so large that they tend to be on opposite sides of the plane of the olefinic and methylene carbon atoms (phenyl in place of the upper hydrogen atom of the methyl group of Figure 2, $R = C_6H_5$). The smaller phenyl group permits attack by the hexafluoroacetone molecule on its side where one of the methylene hydrogen atoms of the $-CH_2C(CF_3)_2OH$ group is accessible (again only the *cis* isomer XXIXc is formed) while the bulky $-C(CF_3)_2OH$ group obstructs the other side where the benzylic hydrogen atoms are.

Such steric effects undoubtedly play a role in other reactions in determining the relative yields of the two 2:1 products formed. The secondary hydrogen atom of the $-CH_2(CF_3)_2OH$ group involved in the reaction of I to give IIc is more reactive than the primary ones of its methyl group that are attacked to give III. This kind of secondary hydrogen atom is less reactive than those of the alkyl methylenes ($C_2H_5CH_2-$ or $C_8H_{17}CH_2-$) in the second steps of reactions 2 (88% V and 5% VIc) or 3 (74% VII and 15% VIIIc). A low reactivity of the tertiary hydrogen atom of the 1:1 product, $CH_2{=}C(CH(CH_3)_2)CH_2C(CF_3)_2OH$, is indicated in its reaction (10) to give 70% XXc and 7% XXI. Presumably, steric repulsion between its two methyl and $-C(CF_3)_2OH$ groups again tends to keep that tertiary hydrogen atom on the unreactive side of the molecule.

Bomb tube pyrolyses of mixtures of IIc and III and of IXc give all of the possible products of their β-hydroxy olefin degradation[12] and isomerization. The evidence supports the above nmr indentifications of *cis* and *trans* isomers and indicates relative stabilities. A neat sample of 60% IIc and 40% III at 275° for 24 hr gave the mixture which is shown in 14 below.



(14)

Equilibrium is here approached by interconversion of the 2:1 products and I and by acid-catalyzed isomerizations. The structure assignments of IIc and IIt are confirmed since IIt is shown to be more stable than IIc. Further, the nmr spectrum of IIt is that characteristic of all such *trans* isomers (methylene singlet at δ 2.73). Also, the rates of formation of IIc, IIt, and III are faster than their rates of degradation, and IV is unstable (none observed), under these conditions.

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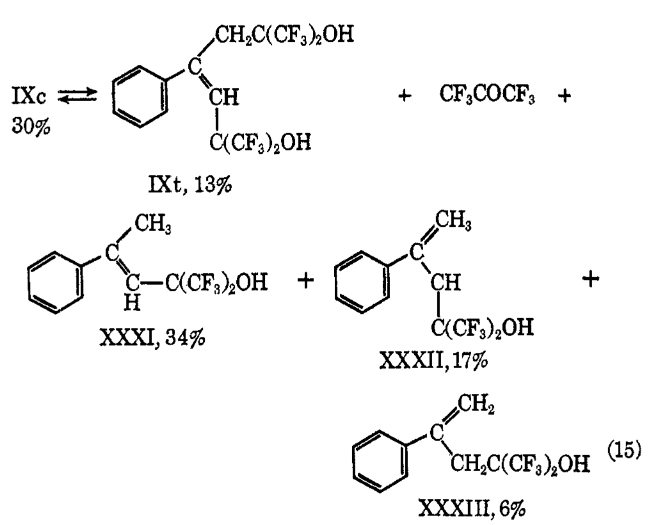
(12) R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **81**, 6443 (1959); **82**, 4918 (1960); *J. Org. Chem.*, **25**, 129 (1960).

In the similar pyrolysis of IXc (250°, 72 hr) the mixture obtained suggests that degradation reactions of IXt and IXc are faster than their formation (eq 15).



Again, the methylene singlet of IXt (δ 3.10) is at higher field than that of IXc (δ 3.87) to confirm the isomeric identification. This degradation and isomerization are too slow to be observed at 184° for 48 hr (conditions of reaction 4). As further evidence for the stability of these 2:1 products, other methods of olefin isomerization (trifluoroacetic acid and perchloric acid at reflux for 48 hr, and palladous chloride in boiling acetic acid for 48 hr) gave back unchanged IXc. Hence, nearly quantitative conversions into 2:1 products occur over a wide range of temperature before their yields are limited and the products multiplied by degradation and isomerization.

Experimental Section

Reactions of Alkenes with Hexafluoroacetone.—With gaseous olefins and this ketone, each of the two reactants was distilled from its supply tank into an evacuated 500-ml stainless steel bomb held at −80°. To determine the weight of each, the bomb was weighed before and after each addition. With liquid olefins, a weighed amount was added to the bomb before it was evacuated. Then each reaction mixture was held at the reaction temperature with rocking for the period specified below. All yields are based upon the olefin used.

2-Methylpropene.—After a reaction mixture containing 2-methylpropene (7.86 g, 0.14 mol) and hexafluoroacetone (23.2 g, 0.14 mol) had been held at 25–30° for 78 hr, the bomb was opened and unreacted 2-methylpropene was allowed to escape. Distillation of the reaction product gave I (18.7 g, 0.084 mol, 60%): bp 117°; ^{1}H nmr in CCl_4 with TMS, 3 H singlet at δ 1.91, 2 H singlet at 2.59, 1 H-OH singlet at 3.17, 1 H narrow multiplet at 4.98 (J = 1.0 cps), and 1 H narrow multiplet at 5.17 (J = 1.3 cps).

Anal. Calcd for $C_7H_8F_6O$: C, 37.8; H, 3.6; F, 51.3. Found: C, 37.6; H, 3.5; F, 51.0.

The distillation residue solidified. Its nmr analysis indicated that it was a mixture of 90% IIc and 10% III (10.9 g, 20%; see below).

With 2-methylpropene (4.5 g, 0.08 mol) and hexafluoroacetone (35.0 g, 0.21 mol) similarly held at 25–30° for 72 hr, the reaction product contained 90% IIc and 10% III (nmr, 25.0 g, 0.064 mol, 80%) after it had been washed with methylene chloride to remove I and reactants. A white solid product (72.0 g, 0.185 mol, 94%) similarly obtained from a reaction of 2-methylpropene (11.0 g, 0.196 mol) and hexafluoroacetone (67.0 g, 0.404 mol) held at 180° for 72 hr was shown by nmr analysis to contain 60% IIc and 40% III. These two products were separated by column chromatography (Fluorosil, Matheson, 60–200 mesh) to give pure III (eluted with 50:50 benzene–petroleum ether of bp 30–60°) [mp 149–150°; ^{1}H nmr in acetone-d_6 with TMS, 4 H singlet at δ 3.01; 2 H broad singlet at 5.33, and 2 H–OH singlet at 6.95; mass spectrum, molecular ion 388, 0.39%; 370, 0.78%; 369, 7.5%; 350, 3.6%; 319, 7.5%; 281, 2.8%; 261, 2.9%; 221, 2.2%; 203, 4.0%; 183, 1.7%; 165, 1.8%; 151, 1.7%; 145, 1.9%; 97, 2.7%; 73, 1.6%; 69, 7.5%; 55, 4.3%; 43, 2.0%; 41, 1.9%; and 39, 2.0% all of Σ_{28}; three base peaks, 369, 319, and 69; metastables, 331.0, 370 → 350; 315.7, 388 → 350; 262.2, 388 → 319; 247.5, 319 → 281; 242.5, 281 → 261; 182.8, 221 → 201; and 165.0, 203 → 183] and IIc (eluted with benzene and benzene–ethyl ether) (mp 142.8–144°; ^{1}H nmr in acetone-d_6 with TMS, 3 H singlet at δ 2.09, 2 H singlet at 3.27, 1 H broad singlet at 5.65, and 2 H–OH singlet at 7.33).

Anal. Calcd for $C_{10}H_8F_{12}O_2$: C, 30.9; H, 2.1; F, 58.7. Found, IIc: C, 31.2; H, 2.3; F, 59.0. Found, III: C, 31.0; H, 2.2; F, 58.5.

With a reaction mixture containing 2-methylpropene (6.7 g, 0.12 mol) and hexafluoroacetone (90.0 g, 0.542 mol) held at 209° for 150 hr, a solid product (62.8 g) was obtained. It was triturated with methylene chloride (100 ml), and the portion of it that remained undissolved (12 g) was removed on a filter. Evaporation of the methylene chloride solution gave IV (50.8 g, 0.092 mol, 77%): mp 106–107° after recrystallization from carbon tetrachloride; ^{1}H nmr in acetone-d_6 with TMS, 2 H singlet at δ 3.14, 2 H singlet at 3.58, 1 H singlet with fine splitting at 5.98; and 3 H–OH singlet at 7.27; mass spectrum, molecular ion 554, 0.02%; 536, 0.61%; 515, 0.58%; 498, 1.1%; 485, 1.9%; 477, 1.3%; 468, 0.84%; 467, 6.5%; 449, 1.4%; 447, 0.84%; 429, 3.9%; 428, 1.3%; base peak 427, 10.5%; 387, 0.95%; 385, 1.7%; 379, 0.84%; 349, 1.7%; 347, 1.2%; 327, 0.95%; 279, 3.4%; 147, 1.2%; 145, 1.1%; 97, 2.6%; and 69, 7.4%, all of Σ_{28}; metastables, 457.8, 497 → 477; 456.9, 498 → 477; 449.7, 485 → 467; 437.8, 477 → 457; 427.9, 467 → 447; 409.9, 449 → 429; 407.9, 447 → 427; 390.4, 467 → 427; 287.9, 427 → 407; and 351.8, 387 → 369.

Anal. Calcd for $C_{13}H_8F_{18}O_3$: C, 28.2; H, 1.5; F, 61.7. Found: C, 28.3; H, 1.6; F, 61.7.

Nmr analysis of the solid that did not dissolve in methylene chloride showed that it contained IV (72 mol %, 9.42 g, 0.017 mol, 14%), IIc (14.5 mol %, 1.32 g, 0.0034 mol, 2.9%), and III (13.5 mol %, 1.24 g, 0.032 mol, 2.7%).

The reaction of 2-methylpropene (8.4 g, 0.15 mol) with hexafluoroacetone (77.0 g, 0.464 mol) at 200° for 60 hr gave IIc (7.0 g, 0.020 mol, 13%), III (6.5 g, 0.017 mol, 11%), and IV (63.6 g, 0.115 mol, 76%).

2-Methyl-1-pentene.—Hexafluoroacetone (73 g, 0.44 mol) with this alkene (16.8 g, 0.20 mol) at 180° for 40 hr gave a product mixture (77 g, nmr analysis showed 95% V and 5% VIc) that crystallized when it cooled. The major product V was purified by five recrystallizations from carbon tetrachloride (73.2 g, 0.176 mol, 88%): mp 101.6–103.5°; ^{1}H nmr in acetone-d_6 with TMS, 3 H triplet at δ 0.98 (J = 7.5 cps), 2 H quintet at 2.12 (J = 7.5 cps), 4 H singlet at 3.04, 1 H triplet at 5.78 (J = 7.5 cps), and 2 H–OH singlet at 7.34.

Anal. Calcd for $C_{12}H_{12}F_{12}O_2$: C, 34.6; H, 2.9; F, 54.8. Found: C, 34.5; H, 2.7; F, 54.7.

The presence of VIc (3.8 g, 0.0092 mol, 4.6%, nmr) in the crude product was indicated (nmr methylene singlet at δ 3.18).

2-Methyl-1-undecene.—This olefin (33.6 g, 0.200 mol) and hexafluoroacetone (74 g, 0.45 mol) were held at 180° for 40 hr, and the product mixture (95 g) was crystallized upon cooling. This crude product contained 83% VII and 17% VIIIc (nmr integration of methylene singlets of VII, δ 3.07, and VIIIc, 3.27). Recrystallization from methylene chloride gave pure VII (74.0 g, 0.148 mol, 74%): mp 76–77.8°; ^{1}H nmr in acetone-d_6 with TMS, 3 H triplet at δ 0.92 (J = 6.0 cps), 12 H broad envelope at 1.34, 2 H multiplet at 2.24, 4 H broad singlet at 3.07, 1 H triplet at 5.80 (J = 7.0 cps), and 2 H–OH broad singlet at 7.08.

Anal. Calcd for $C_{18}H_{24}F_{12}O_2$: C, 43.2; H, 4.8; F, 45.6. Found: C, 43.3; H, 4.7; F, 45.9.

2-Phenylpropene.—Hexafluoroacetone (68 g, 0.41 mol) and this styrene (23.6 g, 0.200 mol) were heated at 184° for 48 hr. The crystalline product was nearly pure IXc (86.8 g, 0.193 mol, 97%): mp 141.5–142.5° after recrystallization from carbon tetrachloride;[4,5] ^{1}H nmr in acetone-d_6 with TMS, 2 H singlet at δ 3.87, 1 H singlet at 6.06, 5 H multiplet (two large peaks) at 7.52, and 2 H–OH broad singlet at 7.92; mass spectrum, molecular ion system 452, 0.09%; 451, 0.78%; 450, 4.7%; 381, 1.6%; base peak 363, 8.6%; 345, 1.2%; 293, 1.1%; 284, 1.3%; 232, 1.1%; 197, 3.6%; 196, 4.4%; 177, 2.1%; 147, 1.0%;

146, 1.2%; 145, 2.1%; 117, 3.8%; 116, 1.6%; 115, 4.6%; 103, 1.6%; 97, 2.4%; 91, 2.2%; 78, 1.4%; 77, 1.9%; 69, 6.2%; 51, 1.5%; 50, 1.0%; 39, 1.2%; and 28, 2.0%, all of Σ_{28}; metastables, 345.9, 381 → 363; 327.9, 363 → 345; 325.1, 364 → 344; 324.1, 363 → 343; 322.6, 450 → 381; 306.2, 345 → 325; 287.4, 363 → 323; 276.0, 311 → 293; 274.3, 313 → 393; 159.8, 196 → 177; 159.0, 197 → 177; 113.0, 117 → 115; and 94.4, 145 → 117.

Propene.—This olefin (15.5 g, 0.37 mol) with hexafluoroacetone (133.0 g, 0.80 mol) was held at 170° for 48 hr. After this reaction mixture had cooled, the bomb valve was opened to allow unreacted ketone to escape. The white solid that had precipitated from the reaction mixture was separated on a filter, and it was shown to be XIc (6.0 g, 0.014 mol, 4%): mp 136–137° from chloroform; ^{1}H nmr in acetone-d_6 with TMS, 2 H doublet at δ 3.27 (J = 6.8 cps), 1 H doublet at 5.68 (J = 12.0 cps), 1 H two triplets at 6.30 (J = 12.0 and 6.8 cps), and 2 H–OH singlet at 6.85. Distillation of the filtrate gave X (10.0 g, 0.048 mol, 13%) [bp 98°; ^{1}H nmr in CCl$_4$ with TMS, 2 H doublet at δ 2.71 (J = 6.8 cps), 1 H–OH singlet at 2.98 and 3 H vinyl multiplet with 1 H doublet at 5.28 (J = 17.8 cps), 1 H doublet at 5.35 (J = 9.5 cps), and 1 H multiplet at 5.92 (J = 17.8 and 9.5 cps apparent)] and XIt (112.5 g, 0.301 mol, 82%) [bp 175.5–176.5°; ^{1}H nmr in acetone-d_6 with TMS, 2 H doublet at δ 2.80 (J = 7.0 cps), 1 H doublet at 5.67 (J = 16.0 cps), 1 H two triplets at 6.33 (J = 16.0 and 7.0 cps), and 2 H–OH singlet at 5.62; mass spectrum, molecular ion 374, 0.11%; 356, 0.97%; 317, 2.6%; 315, 3.7%; base peak 305, 16.0%; 287, 11.8%; 267, 10.9%; 235, 5.6%, 219, 1.9%; 217, 2.6%, 205, 1.4%; 69, 2.7%; and 44, 2.7% all of Σ_{28}; metastables: 278.3, 317 → 297; 270.1, 305 → 287; 258.5, 297 → 277; 248.7, 347 → 305, 287 → 267; 233.7, 305 → 267; 228.5, 267 → 247; 214.0, 267 → 239; 200.6, 239 → 219; and 200.3, 235 → 217].

Anal. Calcd for $C_6H_6F_6O$: C, 34.6; H, 2.9; F, 54.8. Found: C, 34.9; H, 3.2; F, 55.2.

Anal. Calcd for $C_9H_6F_{12}O_2$: C, 28.9; H, 1.6; F, 60.9. Found (XIc): C, 28.8; H, 1.3; F, 60.7. Found (XIt): C, 28.7; H, 1.7; F, 60.8.

1-Butene.—A reaction mixture containing this olefin (24.0 g, 0.43 mol) and hexafluoroacetone (117.0 g, 0.71 mol) was held at 208° for 80 hr. Distillation then gave a mixture of XIIt and XIIc (69.0 g, 0.311 mol, 73%) [bp 119–120.5°; ^{1}H nmr of XIIt in CCl$_4$ with TMS, 3 H doublet at δ 1.76 (J = 5.0 cps), 2 H doublet at 2.67 (J = 6.2 cps), 1 H–OH singlet at 3.10 and 2 H multiplet at 5.70 (J = 6.2 and 5.0 cps apparent); presence of XIIc shown by upfield peak of methyl doublet at δ 1.65; downfield peak of methylene doublet at 2.83; integration shows 75% XIIt and 25% XIIc] and XIIIt (45.0 g, 0.116 mol, 27%) [bp 186.5–187°; ^{1}H nmr in acetone-d_6 with TMS, 3 H doublet at δ 1.36 (J = 7.0 cps), 1 H quintet at 3.08 (J = 8.0 cps), 2 H–OH singlet at 3.20, 1 H doublet at 5.78 (J = 15.5 cps), 1 H two doublets at 6.58 (J = 15.5 and 8.0 cps)].

Anal. Calcd for $C_7H_8F_6O$: C, 37.9; H, 3.6; F, 51.3. Found: C, 38.2; H, 3.7; F, 51.0.

Anal. Calcd for $C_{10}H_8F_{12}O_2$: C, 30.9; H, 2.1; F, 58.7. Found: C, 31.1; H, 2.2; F, 58.4.

A reaction mixture containing 1-butene (16.0 g, 0.285 mol) and hexafluoroacetone (25.0 g, 0.151 mol) held at 25° for 72 hr gave a mixture of XIIt and XIIc (93:7, bp 119–120.5°, 13.0 g, 0.059 mol, 40%).

***trans-* and *cis*-2-Butenes.**—*trans*-2-Butene (29.4 g, 0.52 mol) with hexafluoroacetone (78.0 g, 0.47 mol) at 160° for 48 hr gave XIV (21.0 g, 0.095 mol, 18%) [bp 119.5–120.5°; ^{1}H nmr in CCl$_4$ with TMS, 3 H doublet at δ 1.32 (J = 7.2 cps), 1 H "quintet" (broad peaks) at 2.88 (J = 7.2 cps), 1 H–OH singlet at 3.20, 3 H vinyl multiplet with 1 H doublet at 5.25 (J = 15.0 cps), 1 H doublet at 5.32 (J = 10.5 cps), and 1 H multiplet at 5.93] and XVt (53.0 g, 0.137 mol, 26%) [bp 185°; ^{1}H nmr in acetone-d_6 with TMS, 3 H singlet at δ 1.87; 2 H doublet at 2.85 (J = 8.0 cps), 1 H–OH singlet at 3.09, 1 H–OH singlet at 3.21, and 1 H triplet at 6.28 (J = 8.0 cps)].

Anal. Calcd for $C_7H_8F_6O$: C, 37.9; H, 3.6; F, 51.3. Found: C, 37.9; H, 3.7; F, 51.5.

Anal. Calcd for $C_{10}H_8F_{12}O_2$: C, 30.9; H, 3.1; F, 58.7. Found: C, 31.2; H, 3.3; F, 59.1.

cis-2-Butene (40 g, 0.71 mol) with hexafluoroacetone (108 g, 0.65 mol) even under more vigorous conditions (186° for 72 hr) gave lower conversions to XIV (6.0 g, 0.027 mol, 4%) and XVt (53.5 g, 0.138 mol, 19%).

***trans*-3-Hexene.**—This alkene (10 g, 0.12 mol) with hexafluoroacetone (70 g, 0.42 mol) at 200° for 120 hr gave a liquid product (21 g). Its distillation gave a mixture of XVIt and XVIc (14.7 g, 0.059 mol, 49%): bp 142° and 44–45° (10 mm); ^{1}H nmr of XVIt in CCl$_4$ with TMS, 3 H triplet at δ 0.94 (J = 8.5 cps), 2 H multiplet at 1.43 (J = 8.5 cps), 3 H pair of doublets at 1.90 (J = 6.5 and 1.0 cps), 1 H multiplet at 2.61, 1 H–OH singlet at 3.19, and 2 H multiplet at 6.05, downfield two quartets at 6.08 (J = 17.0 and 6.5 cps); part due to XVIc, methyl doublet pair at δ 1.78 (J = 7.0 and 2.0 cps); downfield part of olefinic multiplet shows two smaller quartets at 6.30 (J = 11.0 and 6.5 cps); integration of methyl doublet of each shows 65% XVIt and 35% XVIc.

Anal. Calcd for $C_9H_{12}F_6O$: C, 43.2; H, 4.8; F, 45.6. Found: C, 43.2; H, 4.7; F, 45.6.

Further distillation gave XVIIt (5.0 g, 0.012 mol, 10%): bp 40° at 0.08 mm; ^{1}H nmr in CCl$_4$ with TMS, 3 H triplet at δ 1.08 (J = 7.5 cps), 3 H doublet at 1.28 (J = 7.8 cps), 2 H quartet at 2.36 (J = 7.5 cps), 2 H–OH singlets at 3.00 and 3.21, 1 H multiplet at 3.34 (two quartets) (J = 11.0 and 7.0 cps), and 1 H doublet at 6.13 (J = 11.0 cps).

Anal. Calcd for $C_{12}H_{12}F_{12}O_2$: C, 34.6; H, 2.9; F, 54.9. Found: C, 34.9; H, 2.8; F, 55.2.

2-Methyl-2-butene.—With this olefin (8.3 g, 0.12 mol) and hexafluoroacetone (76 g, 0.46 mol) at 186° for 70 hr, a white solid product (46 g) was obtained. The crude product contained 56% XVIII (25.8 g, 0.064 mol, 53%) [^{1}H nmr in acetone-d_6 with TMS, 3 H doublet at δ 1.70 (J = 7.0 cps), 4 H broad singlet at 3.05, 1 H quartet at 5.78 (J = 7.0 cps), 2 H–OH broad singlet at 6.70] and 44% XIXc (20.2 g, 0.050 mol, 42%) [^{1}H nmr in acetone-d_6 with TMS 3 H triplet at δ 1.09 (J = 7.5 cps), 2 H quartet at 2.33 (J = 7.5 cps), 2 H singlet at 3.23, 1 H broad singlet at 5.67, and 2 H–OH broad singlet at 6.70]. Six recrystallizations from carbon tetrachloride gave a mixture of 80% XVIII and 20% XIXc (nmr) that nevertheless melted sharply at 126–127°.

Anal. Calcd for $C_{11}H_{10}F_{12}O_2$: C, 32.9; H, 2.5; F, 56.7. Found: C, 32.9; H, 2.5; F, 56.9.

Since products XVIII and XIXc are those expected from 2-methyl-1-butene, such olefin isomerization was confirmed as follows. A reaction mixture containing pure 2-methyl-2-butene (24.0 g, 0.34 mol) [^{1}H nmr in CCl$_4$ with TMS, 3 H doublet at δ 1.54 (J = 8.5 cps), 6 H singlet at 1.56, and 1 H quartet with fine splitting at 5.15; Varian Aerograph A-90-P, 5 ft × 0.25 in. column packed with 20% Dow silicone 710 on Chromosorb W, isothermal 70°, He flow rate 1.18 ml/sec, retention time 1.17 min] single peak] and hexafluoroacetone (30 g, 0.18 mol) was held at 165° for 30 hr. Distillation gave recovered olefin (10.8 g, 0.154 mol) [bp 38–40° (80% 2-methyl-2-butene, nmr above, and 20% 2-methyl-1-butene); ^{1}H nmr in CCl$_4$ with TMS, 3 H triplet at δ 1.00 (J = 7.0 cps), 3 H singlet at 1.63, 2 H quartet at 1.98 (J = 7.0 cps), and 2 H broad singlet, fine splitting at 4.63; vpc as above two peaks, retention times 0.92 and 1.16 min] and a mixture of three 1:1 products (31 g, 0.13 mol, 38%) (bp 133°). The latter contained 80% $CH_3CH{=}C(CH_3)CH_2C(CF_3)_2OH$, 90% *trans* and 10% *cis* [vpc as above, retention time 6.0 min; ^{1}H nmr of *trans* isomer in CCl$_4$ with TMS, 3 H doublet at δ 1.67 (J = 7.0 cps), 3 H singlet at 1.72, 2 H singlet at 2.67, 1 H–OH singlet at 3.22, and 1 H quartet at 5.51 (J = 7.0 cps); *cis* form indicated by methyl doublet at δ 1.92 (J = 7.5 cps), and smaller quartet in olefin region], and 20% $CH_2{=}C(C_2H_5)CH_2C(CF_3)_2OH$ [vpc as above, retention time 4.84 min; ^{1}H nmr in CCl$_4$ with TMS, 3 H triplet at δ 1.03 (J = 7.3 cps), 2 H quartet at 2.18 (J = 7.3 cps), 2 H singlet at 2.77, 1 H–OH singlet at 3.22, 1 H broad singlet at 5.00, and 1 H broad singlet at 5.18].

Anal. Calcd for $C_8H_{10}F_6O$: C, 40.7; H, 4.3; F, 48.3. Found: C, 40.6; H, 4.5; F, 48.1.

The distillation residue (5.0 g, 0.013 mol of XVIII, 55%, and XIXc, 45%; 4%) solidified when it cooled.

2,3-Dimethyl-2-butene.—2,3-Dimethyl-2-butene (8.4 g, 0.10 mol) with hexafluoroacetone (70 g, 0.42 mol) at 180° for 40 hr also gave a mixture of products (32 g) that solidified upon cooling. Nmr analysis showed that it contained 90% XXc (28.8 g, 0.069 mol, 69%) [^{1}H nmr in acetone-d_6 with TMS, 6 H doublet at δ 1.13 (J = 7.0 cps), 1 H heptet at 2.42 (J = 7.0 cps), 2 H singlet at 3.27, 1 H singlet at 5.65, and 2 H–OH broad singlet at 8.28], and 10% XXI (3.2 g, 0.0077 mole, 8%) (^{1}H nmr in acetone-d_6 with TMS, 6 H singlet at δ 1.75, 4 H singlet at 3.07, and 2 H–OH broad singlet at 8.28). Here five recrystallizations (CCl$_4$) gave pure XXc: mp 123.8–125.2°; mass spectrum, molecular ion 416, 0.87%; 401, 0.20%; 398, 0.20%; 397, 0.20%; 347, 0.50%; 250, 1.6%; 249, 6.2%; 235, 2.7%; 231, 1.3%; 207, 1.7%; 147, 1.2%; 145, 1.4%; 127, 1.1%; 97, 1.7% 85, 4.7%; 69, 1.9%; 67, 1.9%; 65, 1.9%; 55, 3.8%; 53, 1.5%; base peak 43, 9.7%; 41, 7.4%; 39, 3.0%; and 29, 1.4%, all of Σ_{28}; metastables, 380.8, 416 → 298; 289.4, 416 → 347, 329 → 309; 214.3, 249 → 331; 200.4, 235 → 217; 196.1, 249 → 221; 182.3, 235 → 207; 178.8, 249 → 211; 172.1, 249 → 207; and 159.0, 197 → 177.

Anal. Calcd for $C_{12}H_{12}F_{12}O_2$: C, 34.6; H, 2.9; F, 54.8. Found: C, 34.3; H, 2.9; F, 54.9.

With 2,3-dimethyl-2-butene (14 g, 0.17 mol) (vpc as in 2-methyl-2-butene experiment, one peak, retention time 3.36 min; ^{1}H nmr in CCl_4 with TMS, singlet at δ 1.61) and hexafluoroacetone (20 g, 0.12 mol) at 170° for 24 hr, the unreacted olefin was isomerized, and two 1:1 products (vpc) were observed. Distillation gave a mixture (7.6 g, 0.09 mol, bp 56–75°) of unreacted 2,3-dimethyl-2-butene (85%) (above retention time and nmr) and 2,3-dimethyl-1-butene (15%) [vpc retention time 1.45 min; ^{1}H nmr in CCl_4 with TMS, 6 H doublet at δ 1.00 (J = 6.7 cps); 3 H singlet at 1.62, 1 H multiplet at 2.62, and 2 H broad singlet at 4.63]. The 1:1 products [10.6 g, 0.042 mole, 25%, bp 83° (90 mm)] then distilled. Vpc and nmr analysis showed that this mixture contained 70% $CH_2{=}C(CH(CH_3)_2)CH_2C(CF_3)_2OH$ [vpc as above, retention time 5.9 min; ^{1}H nmr in CCl_4 with TMS, 6 H doublet at δ 1.08 (J = 6.8 cps), 1 H heptet at 2.27 (J = 6.8 cps); 2 H singlet at 2.74; 1 H–OH singlet at 3.59; 1 H broad singlet at 5.01, and 1 H broad singlet at 5.22] and 30% $(CH_3)_2C{=}C(CH_3)CH_2C(CF_3)_2OH$ (vpc retention time 11.1 min; ^{1}H nmr in CCl_4 with TMS, 9 H singlet at δ 1.67, 2 H singlet at 2.82, and 1 H–OH singlet at 3.17).

Anal. Calcd for $C_9H_{12}F_6O$: C, 43.2; H, 4.8; F, 45.6. Found: C, 43.1; H, 5.0; F, 45.5.

The distillation residue (90% XXc and 10% XXI, 10 g, 0.024 mol, 14%) solidified upon cooling (see above).

Allene.—This diene (15.0 g, 0.37 mol) and hexafluoroacetone (45 g, 0.27 mol) were held at 130° for 63 hr, and a colorless liquid product (35 g) was obtained. Its distillation gave XXII (25.9 g, 0.126 mol, 34%): bp 94°; ^{1}H nmr in CCl_4 with TMS, 1 H triplet at δ 2.23 (J = 2.5 cps), 2 H doublet at 2.88 (J = 2.5 cps), and 1 H–OH singlet at 3.51.

Anal. Calcd for $C_6H_4F_6O$: C, 35.0; H, 2.0; F, 55.3. Found: C, 34.7; H, 2.0; F, 55.4.

The distillation residue (5.0 g, 0.02 mol, 5%) was the 2:1 product XXIII described below.

In another such reaction, allene (14 g, 0.35 mol) and hexafluoroacetone (126.0 g, 0.76 mol) were heated at 150° for 90 hr. After the reaction mixture had cooled and had been evacuated, the white product (125 g) solidified. The solid that remained undissolved when benzene (200 ml) was added to the crude product was purified by vacuum sublimation to give XXIV (10 g, 0.013 mol, 7.4%): mp 228–229°; ^{1}H nmr in acetone-d_6 with TMS, 2 H singlet at δ 4.37, 2 H singlet at 6.28, and 4 H–OH singlet at 7.92; uv spectrum, λ_{max} 241 mμ (ϵ 18,600); mass spectrum, molecular ion 744, 0.91%; 687, 1.4%; 676, 2.1%; 675, 10.2%; 657, 2.5%; 637, 1.1%; 577, 0.62%; 559, 0.71%; 491, 0.67%; 471, 1.3%; 421, 1.2%; 373, 0.70%; 191, 1.6%; 169, 1.0%; 167, 1.3%; 163, 1.1%; 147, 2.5%; 97, 5.5%; base peak 69, 20.3%; and 28, 1.5%, all of Σ_{28}; metastables: 639.5, 675 → 657; 621.5, 657 → 639; 617.6, 657 → 637; and 612.4, 744 → 675.

Anal. Calcd for $C_{18}H_8F_{24}O_4$: C, 29.0; H, 1.1; F, 61.3. Found: C, 28.9; H, 1.1; F, 61.2.

Evaporation of the benzene solution gave a solid product that was also sublimed (50°) to give XXIII[6] (115 g, 0.309 mol, 88%): mp 70–71°; ^{1}H nmr in acetone-d_6 with TMS, 2 H singlet at δ 5.87 and 2 H–OH singlet at 6.38; mass spectrum, molecular ion 372, 0.72%; 354, 6.7%; 335, 4.7%; 303, 3.2%; 285, 3.3%; 253, 2.2%; 236, 2.7%; 215, 1.5%; 213, 1.7%; 191, 4.8%; 169, 4.7%; 119, 1.5%; 97, 4.7%; 89, 1.5%; base peak 69, 16.7%; 39, 2.3%; and 28, 1.5%, all of Σ_{28}; metastables, 336.9, 372 → 354; 317.0, 354 → 335; 246.8, 372 → 303; 246.4, 285 → 265; and 229.4, 354 → 285.

Anal. Calcd for $C_9H_4F_{12}O_2$: C, 29.0; H, 1.1; F, 61.3. Found: C, 28.8; H, 1.1; F, 61.1.

The dimerization of XXIII to give XXIV apparently is catalyzed by acid. Samples of XXIII (1 g) were sealed in glass ampoules and heated for various times. Since XXIII is soluble in benzene and XXIV is not, these reaction mixtures were triturated with benzene; the XXIV that remained undissolved gave a measure of the extent of reaction. At 150 and 180° for 60 hr, no XXIV was formed, while at 200° (60 hr), 3% conversion into XXIV occurred. Extensive decomposition of XXIII took place when it was so heated at 250° for 12 hr. When 1 drop of concentrated hydrochloric acid and XXIII (1 g) were heated at 200° for 60 hr, a 10% conversion to XXIV was observed.

2-Methyl-3-phenylpropene.—The mixture of this olefin (19 g, 0.14 mol) and the ketone (23 g, 0.14 mol) was held at 25–30° in a shaking bomb for 65 hr. Some unreacted ketone escaped when the bomb was opened. Nmr analysis of the crude product (37 g, 0.12 mol, 86%) indicated 55% XXVIIt, 15% XXVIIc, and 30% XXVIII. The distillation gave little separation of these three products, bp 62–63° at (0.25 mm). Nmr and vpc analysis (F & M 500 chromatograph, 0.25 in. × 5 ft column with 20% Dow silicone 710 on Chromosorb W, isothermal 152°, He flow rate 1.2 ml/sec, retention times of XXVIIc and XXVIII 4.5 min and XXVIIt 6.2 min) gave these compositions (fraction 1, 1.0 g, 20% XXVIIt, 27% XXVIIc, and 53% XXVIII; fraction 2, 4.85 g, 45% XXVIIt, 18% XXVIIc, and 37% XXVIII; and fraction 3, 21.1 g, 61% XXVIIt, 13% XXVIIc, and 26% XXVIII). Fraction 4 was nearly pure XXVIIt (7.3 g, 98%): ^{1}H nmr in CCl_4 with TMS, 3 H singlet at δ 1.98, 2 H singlet at 2.82, 1 H–OH singlet at 3.00, 1 H broad singlet at 6.45, and 5 H singlet at 7.24. It was further purified by preparative vpc.

Anal. Calcd for $C_{13}H_{12}F_6O$: C, 52.4; H, 4.1; F, 38.2. Found: C, 52.5; H, 4.1; F, 38.0. Found (fraction 3): C, 52.5; H, 3.9; F, 38.3.

This study gave the nmr spectra of XXVIIc (^{1}H nmr in CCl_4 with TMS, 3 H singlet at δ 2.03, 2 H singlet at 2.93, 1 H–OH singlet at 3.00, 1 H broad singlet at 6.68, and 5 H singlet at 7.22) and XXVIII [^{1}H nmr in CCl_4 with TMS, 2 H singlet at δ 2.60, 1 H–OH singlet at 3.00, 2 H singlet at 3.45, 2 H multiplet at 5.09 (J = 1.2 cps), and 5 H singlet at 7.21]. It further gave the yields of XXVIIt (0.075 mol, 54%), XXVIIc (0.013 mol, 9%), and XXVIII (0.026 mol, 19%). That the major geometrical isomer is XXVIIt [phenyl *trans* to $-CH_2C(CF_3)_2OH$] and the minor one XXVIIc is based upon a comparison of the chemical shifts of their olefinic hydrogen atoms (XXVIIt, δ 6.45; XXVIIc, δ 6.68). The olefinic hydrogen absorption of IIt [δ 5.46, *cis* to $-CH_2C(CF_3)_2OH$ and *trans* to methyl as in XXVIIt] is at higher field than that of IIc [δ 5.65, *cis* to methyl and *trans* to $-CH_2C(CF_3)_2OH$ as in XXVIIc].

The distillation residue (2 g) crystallized. Complete vacuum sublimation of it gave two fractions, both pure XXIXc: mp 75–76°; ^{1}H nmr in acetone-d_6 with TMS, 2 H singlet at δ 3.17, 2 H–OH singlet at 3.28, 2 H singlet at 3.71, 1 H broad singlet at 5.79, and 5 H singlet at 7.28.

Anal. Calcd for $C_{16}H_{12}F_{12}O_2$: C, 41.4; H, 2.6; F, 49.1. Found: C, 41.5; H, 2.7; F, 49.1.

The chemical shift of the olefinic hydrogen atom of XXIXc (δ 5.79) indicates the structure given rather than that of the alternative substituted styrene. The α-olefinic hydrogen atoms of such styrenes absorb at lower field (XXVIIt, δ 6.45, and XXVIIc, δ 6.68).

The Reaction of 2-Methylpropene with 1,3-Dichloro-1,1,3,3-tetrafluoropropanone.—A reaction mixture containing this olefin (10.7 g, 0.19 mol) and ketone (83.2 g, 0.42 mol) was held at 120° for 72 hr. After the bomb and its contents had cooled, remaining reactants were allowed to escape, and the reaction product (72.0 g, 0.16 mol, 84%) solidified. Its vpc analysis (above chromatograph and column, isothermal 110°, He flow rate 1.18 ml/sec) showed that it contained two substances (65%, retention time 12.3 min, and 35%, retention time 13.1 min). The one of longer retention time, $H_2C{=}C[CH_2(CF_2Cl)_2OH]_2$ (25.2 g, 0.056 mol, 29%) (mp 104.5–106°; ^{1}H nmr in $CDCl_3$ with TMS, 4 H singlet at δ 3.11, 2 H–OH broad singlet at 4.16, and 2 H singlet at 5.20) was obtained pure after five recrystallizations from carbon tetrachloride.

Anal. Calcd for $C_{10}H_8F_8Cl_4O_2$: C, 26.5; H, 1. ; F, 33.5. Found: C, 26.3; H, 1.7; F, 33.4.

The other product, *cis*-$CH_3C[CH_2C(CF_2Cl)_2OH]{=}CHC(CF_2Cl_2)OH$ (46.8 g, 0.103 mol, 54%) (mp 73–74°; ^{1}H nmr in CCl_4 with TMS, 3 H singlet at δ 2.07, 2 H singlet at 3.20, 1 H broad singlet at 5.62, 2 H–OH broad singlet at 5.73) was purified by column chromatography of the recrystallization liquors on alumina wherein it was eluted with benzene. It is presumed to be the *cis* isomer since its nmr spectrum resembles that of IIc. The product from evaporation of the benzene solution was then sublimed.

Anal. Calcd for $C_{10}H_8F_8Cl_4O_2$: C, 26.5; H, 1.8; F, 33.5; Cl, 31.2. Found: C, 26.3; H, 1.7; F, 33.3; Cl, 31.1.

The Reaction of 3-Phenylpropene with Chloropentafluoropropanone.—A solution containing this olefin (80.7 g, 0.68 mol) and this ketone (124.5 g, 0.68 mol) was held at 25° for 72 hr. Distillation gave only XXXt (102 g, 0.36 mol, 53%): bp 63–65° (0.3 mm); ^1H nmr in $CDCl_3$ with TMS, 2 H doublet at δ 3.28 (J = 6.5 cps); 1 H–OH singlet at 3.00, 1 H pair of triplets at 6.09 (J = 16.0 and 6.5 cps), 1 H doublet at 6.58 (J = 16.0 cps), and 5 H singlet at 7.28.

Anal. Calcd for $C_{12}H_{10}F_5ClO$: C, 47.9; H, 3.4; F, 31.6; Cl, 11.8. Found: C, 48.1; H, 3.4; F, 31.7; Cl, 11.9.

Thermal Studies.—A bomb tube containing I (2 g, 0.0090 mol) was heated at 300° for 16 hr. When this reaction mixture cooled, a white solid (0.89 g) precipitated. It was collected on a filter and was washed with methylene chloride. Nmr analysis showed that it contained 45% IIc and 55% III. The oil remaining (0.90 g) after the methylene chloride had been removed from the filtrate contained unreacted I and IIt (7:3 molar proportions, nmr analysis) and a small amount of polyisobutene. Major products therefore were IIc (0.39 g, 0.0010 mol), IIt (0.39 g, 0.0010 mol), and III (0.50 g, 0.0013 mol). I (0.51 g, 0.0023 mol) remained unreacted.

The product mixture (2 g, 90% IIc and 10% III) was unchanged after it was held at 150° for 24 hr in a sealed tube. However, extensive reaction occurred when a mixture of 60% IIc and 40% III (14.5 g, 0.0374 mol) was similarly heated at 275° for 24 hr. When it cooled, part of reaction mixture crystallized. It was triturated with carbon tetrachloride (50 ml). Solid products (8.2 g) were separated on a filter, and an oil (5.7 g) remained after carbon tetrachloride had been distilled from the filtrate. Both were analyzed by nmr and vpc methods (Varian Aerograph temperature-programmed chromatograph; 20% SE 30 on Chromosorb P, 0.25 in. × 5 ft; initial temperature 52° increased 10°/min; He flow rate 1 ml/sec; retention times—I, 2.33 min; I′, 2.53 min; IIt, 8.42 min; and IIc and III, 9.0 min). The solid contained 49 mol % IIc (4.02 g, 0.0104 mol), 38 mol % III (3.11 g, 0.0080 mol), and 13 mol % IIt (1.07 g, 0.0028 mol); the oil contained 78 mol % IIt (4.93 g, 0.013 mol, total in both fractions 0.0158 mol), 10 mol % I (0.34 g, 0.0015 mol), and 11 mol % I′ (0.37 g, 0.0017 mol).

Pure IIt ($n^{25}D$ 1.3598; ^1H nmr in $CDCl_3$ with TMS, 3 H singlet at δ 2.15, 2 H singlet at 2.73, 2 H–OH singlet at 3.45, and 1 H broad singlet at 5.46; mass spectrum, molecular ion at 388, 0.48%; 369, 2.1%; 350, 2.8%; 319, 7.1%; 281, 3.7%; 261, 3.7%; 145, 3.4%; 69, 11.4%; 44, 5.5%; 43, 2.1%; base peak at 40, 16.2% all of Σ_{39}) was obtained by preparative vpc of the oil fraction.

Anal. Calcd for $C_{10}H_8F_{12}O_2$: C, 30.9; H, 2.1; F, 58.7. Found: C, 30.8; H, 2.2; F, 58.5.

Less extensive reaction was observed when a sample containing 90% IIc and 10% III was held at 250° for 16 hr. Analysis as above showed IIc (54 mol %), III (18 mol %), and IIt (28 mol %).

The bomb tube pyrolysis of IXc (5.0 g, 0.011 mol) contrasts with those above since the three possible 1:1 products are more important. Again, part of the reaction mixture solidified as it cooled, but here vigorous gas (CF_3COCF_3) evolution occurred when the bomb tube was opened. Trituration with carbon tetrachloride (25 ml) as before gave a solid product (unreacted IXc, 1.5 g, 0.0033 mol) and an oil (2.4 g). Nmr and vpc analysis (as above, except initial temperature 75° with 10° increase per min; retention times—XXXII, 10.55 min; XXXIII, 11.7 min; XXXI, 12.1 min; IXc, 13.25 min; and IXt, 13.65 min) showed that the oil contained 48 mol % XXXI, 25 mol % XXXII, 9 mol % XXXIII, and 18 mol % IXt. Total yields were XXXI (1.05 g, 0.0037 mol, 34%), XXXII (0.54 g, 0.0019 mol, 17%), XXXIII (0.20 g, 0.0007 mol, 6%), IXt (0.63 g, 0.0014 mol, 13%), and unreacted IXc (1.5 g, 0.0033 mol, 30%).

Pure IXt was isolated by preparative vpc ($n^{25}D$ 1.4158; ^1H nmr in $CDCl_3$ with TMS, 2 H singlet at δ 3.10, 2 H–OH singlet at 4.56, 1 H broad singlet at 5.91, and 5 H singlet at 7.44; mass spectrum, molecular ion at 450, 2.9%; 381, 0.6%; 364, 0.5%; 363, 3.4%; 283, 10.0%; base peak at 214, 10.7%; 197, 10.0%; 177, 3.0%; 145, 3.1%; 129, 2.1%; 117, 3.8%; 115, 4.8%; 91, 2.5%; 77, 3.2%; 69, 4.3%; 51, 3.1%; and 39, 3.1% all of Σ_{39}). Nmr spectra of XXXI (^1H nmr in CCl_4 with TMS, 3 H methyl singlet at δ 2.37, 1 H–OH singlet at 3.00, 1 H broad singlet at 5.69, and 5 H singlet at 7.35), XXXII [^1H nmr in CCl_4 with TMS, 3 H methyl doublet at δ 2.12 (J = 1.5 cps), 1 H–OH singlet at 3.00, 1 H broad singlet at 5.69, and 5 H singlet at 7.39], and XXXIII (2 H singlet at δ 3.21, 1 H–OH singlet at 3.00, 1 H broad singlet at 5.32, 1 H broad singlet at 5.51, and 5 H singlet at 7.35) were determined from that of the oil and various preparative vpc fractions of it.

Acidities.—These potentiometric acid–base titrations were performed with a glass electrode as indicator and a saturated calomel electrode, sce, as reference; and with a Leeds and Northrup pH indicator (−700 to 0 and 0 to 700-mV scale). Each sample (References: phenol, 0.27 g; 1,1,1,3,3,3-hexafluoro-2-propanol, 0.54 g; acetic acid, 30 ml of 0.1006 N. Products: X, 0.586 g; IIc, 0.554 g; IV, 0.548 g) in dimethylformamide (100 ml) was titrated with tetrabutylammonium hydroxide (0.34 N; prepared by dilution of 1 N reagent in methanol with 2-propanol). The results are given in Figure 1.

Registry No.—I, 665-05-4; IIc, 16202-90-7; IIt, 16203-24-0; III, 16202-91-8; IV, 16202-92-9; V, 16202-93-0; VII, 16202-94-1; IXc, 16202-95-2; IXt, 16202-96-3; X, 646-97-9; XIc, 16202-98-5; XIt, 16202-99-6; XIIc, 16223-66-8; XIIt, 16203-00-2; XIIIt, 16203-01-3; XIV, 16203-02-4; XVt, 16203-03-5; XVIc, 16203-04-6; XVIt, 16203-05-7; XVIIt, 16203-06-8; XVIII, 16203-07-9; XIXc, 16203-08-0; $CH_3CH{=}C(CH_3)CH_2C(CF_3)_2OH$ (*cis*), 16203-09-1; $CH_3CH{=}C(CH_3)CH_2C(CF_3)_2OH$ (*trans*), 16203-10-4; $CH_2{=}C(C_2H_5)CH_2C(CF_3)_2OH$, 16203-11-5; XXc, 16203-12-6; $CH_2{=}C[CH(CH_3)_2]CH_2C(CF_3)_2OH$, 16203-13-7; $(CH_3)_2C{=}C(CH_3)CH_2C(CF_3)_2OH$, 16203-14-8; XXII, 16203-15-9; XXIII, 16203-16-0; XXIV, 16203-17-1; XXVIIc, 16203-18-2; XXVIIt, 16203-19-3; XXVIII, 16203-20-6; XXIXc, 16203-21-7; $CH_2{=}C[CH_2C(CF_2Cl)_2OH_2]$, 4795-96-4; *cis*-$CH_3C[CH_2C(CF_2Cl)_2OH]{=}CHC(CF_2Cl)_2OH$, 16203-23-9; XXXt, 16223-67-9; XXXI, 16204-30-1; XXXII, 16204-31-2; XXXIII, 16204-32-3.