

Reaction of Phosphorus Pentafluoride with *t*-Butylamine in Presence of Triethylamine.—A mixture of 6.98 g (0.0955 mol) of *t*-butylamine and 19.4 g (0.181 mol) of triethylamine in 250 ml of benzene was treated with phosphorus pentafluoride at 10° until absorption was complete, then refluxed 5 hr. Filtering the mixture gave 45.9 g (0.186 mol, 97% yield) of insoluble triethylammonium hexafluorophosphate, whereas removal of volatiles from the filtrate at 10 mm left 8.8 g of solids. These were sublimed to give 6.0 g (0.0188 mol, 40% yield) of 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-di-*t*-butyl-1,3,2,4-diazadiphosphetidine.

Anal. Calcd for C₈H₁₈N₂P₂F₆: N, 8.81; P, 19.47; F, 35.83. Found: N, 8.33; P, 19.56; F, 35.58.

Dehydrofluorination of the Adduct of Ammonia and Phosphorus Pentafluoride.—The adduct of ammonia and phosphorus pentafluoride²³ was prepared by several procedures: (1) the addition of phosphorus pentafluoride to ammonia dissolved in ethyl ether at -78° or at 25°, (2) addition of phosphorus pentafluoride to liquid ammonia at -78° until its absorption was complete, and (3) alternate addition at room temperature of ammonia and phosphorus pentafluoride to an evacuated flask until a desired quantity had formed. Finally the flask was kept in an atmosphere of phosphorus pentafluoride for several hours to ensure that no (NH₃)₂PF₅ formed.²³ Procedure 3 gave material with the "cleanest" spectrum. *Warning:* The powdery adduct, even when handled in the hood, at times caused a choking feeling and tightness around the throat. This feeling lasted from 1-8 hr in two workers in the vicinity. Due caution in handling is advised.

The adduct formed above was treated with quantities of triethylamine or diisopropylethylamine-phosphorus pentafluoride stoichiometrically or in slight excess of that required for dehydro-

fluorination to phosphonitrilic fluorides using benzene, diethyl ether, tetrahydrofuran, pyridine, or mixtures as solvent at room to reflux temperatures. Insolubility of the adduct was a problem when benzene was used for the solvent but small yields of phosphonitrilic fluorides (trimer, tetramer, and pentamer) were found. No phosphonitrilic fluorides were formed when pyridine, diethyl ether, or tetrahydrofuran was the solvent. The principal product with each solvent was an oil not readily separated from the by-product tertiary amine hexafluorophosphate salt. Although some concentration of the oil was obtained by centrifugation, analysis was not meaningful. The oil had very strong infrared bands at 1280-1250 and 910-930 and weaker bands at 3350 cm⁻¹. Possibly polymeric products of the type (-NH-PF₄-)_n were formed. The dehydrofluorination of ammonia phosphorus pentafluoride is evidently quite complex. There were indications of other types of products. For example, distillation of the solvent in one instance gave a fraction with a strong phosphine odor and a strong infrared band at 2400 cm⁻¹, characteristic of phosphines.

Analyses were from these laboratories, Galbraith Laboratories, and Schwarzkopf Microanalytical Laboratories. Nmr analyses were made by Varian Associates.

Registry No.—A1, 15199-01-6; A2, 15893-20-6; A3, 15893-21-7; A4, 15893-23-9; A5, 15893-24-0; A6, 15893-22-8; B1, 15893-25-1; B2, 15893-26-2; B3, 15893-27-3; B4, 15893-28-4; C1 (adduct), 15261-57-1; C3 (adduct), 15893-30-8; C5 (adduct), 15893-31-9; C6 (adduct), 15893-32-0; C1 (salt), 12077-62-2; C2 (salt), 12239-94-0; C3 (salt), 12239-95-1; C4 (salt), 12239-97-3; C6 (salt), 12239-90-6; C7 (salt), 12239-93-9; C8 (salt), 12239-96-2; C9 (salt), 12239-91-7; *t*-butylamine hexafluorophosphate, 12239-92-8; phosphorus pentafluoride, 7647-19-0; aniline, 62-53-3.

(23) S. Johnson, Ph.D. Dissertation, Purdue University, Lafayette, Ind., 1952.

Reactions of Hexafluoroacetone or *sym*-Dichlorotetrafluoroacetone with Allylic Olefins

ROBERT L. ADELMAN

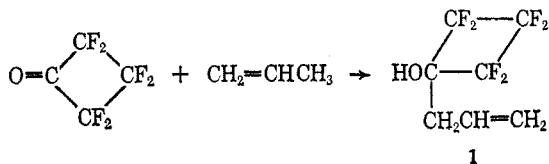
Electrochemicals Department, E. I. du Pont de Nemours and Company, Inc., Experimental Station, Wilmington, Delaware

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The noncatalyzed addition of highly fluorinated perhalo ketones to substituted olefins containing allylic hydrogen atoms leads to 3,4-unsaturated alcohols. The ketones act as strong electrophiles, with significant steric effects. The reaction mechanism offered involves a four-membered, cyclic dipolar intermediate, rather than a concerted mechanism previously postulated. This is based on data such as (a) interception of the intermediate by a very sensitive (difunctional) trapping agent, allyl glycidyl ether, which leads to a homopolymer of the latter, (b) formation of the adduct of β -pinene without rearrangement, and (c) an appreciable solvent effect. Implications of these findings in 1,5 hydrogen shifts, olefin additions, and concerted reactions are discussed.

The uncatalyzed addition reactions of highly fluorinated perhalo ketones to substituted olefins containing allylic hydrogen atoms generally lead to the formation of 3,4-unsaturated alcohols (2-alkenylcarbinols).

This was first demonstrated by D. C. England¹ in reaction of perfluorocyclobutanone with propylene 1.



Davis² and Knunyants and Dyatkin^{3,4} showed that hexafluoroacetone (HFA) or *sym*-dichlorotetrafluoro-

acetone (DCTFA) reacted similarly. Middleton⁵ and Gambaryin, *et al.*,⁶ extended the reaction to allylic compounds containing more polar groups (α -methyl styrene, methyl methacrylate, allyl methyl ether).

In this paper are reported results of uncatalyzed reactions of HFA and DCTFA with various allylic olefins which were carried out under comparable conditions. Qualitative comparisons are made of the effects of structure and solvent on reactivity and product character. Reaction mechanism is considered, as well as implications for other systems.

General Procedure

The reactions were carried out under the mildest conditions which led to appreciable conversion into

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

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

(3) I. L. Knunyants and B. L. Dyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Eng. Transl.)*, 329 (1962).

(4) Belgian Patent 625,425 (1962).

(5) W. J. Middleton, Central Research Department, Du Pont, unpublished work.

(6) N. P. Gambaryin, El. M. Rokhlina, and Yu. V. Zeifman, *Bull. Akad. Sci., USSR, Div. Chem. Sci. (Eng. Trnsl.)*, **8**, 1425 (1965).

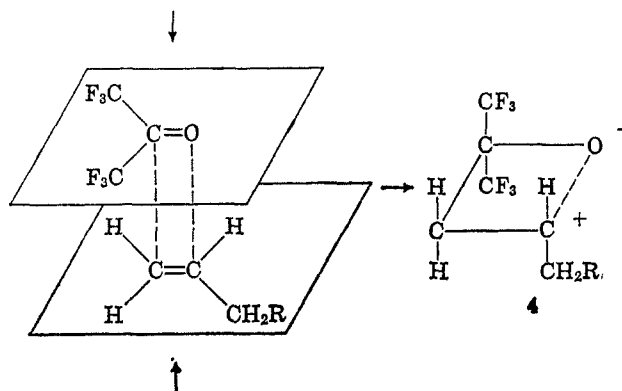


Figure 1.—Suggested approach and planar four-membered cyclic dipolar intermediate resulting from HFA and allylic olefins.

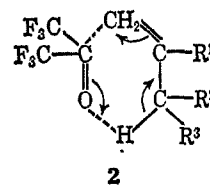
most rapidly when the olefinic double bond was asymmetrically substituted and heavily loaded with groups which were strongly electron donating. Isobutylene, α -methylvinyl methyl ether, α -methyl styrene, and β -pinene reacted rapidly (5–120 min) with HFA near room temperature or below; octene-1 or propylene reacted much more sluggishly (several hours at 100–150°); allyl chloride or methyl methacrylate reacted still more slowly, requiring 150–165°, whereas methacrylonitrile reacted extremely slowly, even at 165–180°. 2-Chloropropene-1 was more sluggish than propylene but not so sluggish as allyl chloride.

On the other hand, reaction of HFA or DCTFA with symmetrically substituted olefins was very slow, unlike the reactivity of such electrophilic reagents as chlorine, bromine, or sulfonyl halides.^{7,8} Thus *cis*- or *trans*-2-butene or cyclohexene reacted extremely slowly, even at 165–180°, and α -pinene also appeared unreactive (see Table I). Therefore, steric effects in addition with HFA or DCTFA appear to be significant. The importance of steric effects is also seen by the low reactivity of DCTFA with camphene or α -pinene, and for HFA with 3,3-dimethylbutene-1.

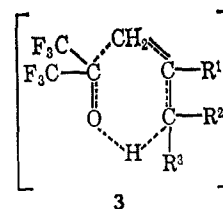
Reaction Course and Mechanism.—In the formation of the adducts, one possibility, an insertion reaction with an allylic hydrogen, analogous to reactions of saturated aliphatic R-H with HFA in a free-radical chain reaction¹⁰ may be ruled out, for the reaction of HFA with butene-1 led to the linear rather than to a branched adduct.¹¹

Further, insertion with a vinylic hydrogen followed by a hydrogen shift seems very unlikely, based on the generally low reactivity of vinylic hydrogen and on the resistance to adduct formation of 3,3-dimethylbutene-1 or camphene.

Thus the reaction course may best be categorized (as pointed out by Davis,² Knunyants and Dyatkin,³ and Gambaryan, *et al.*⁶) as a 1,5-hydrogen shift, accompanied by a double-bond shift, with the over-all electron redistribution as indicated in structure 2.



The realization that a double-bond shift occurred led to the suggestion^{3,12} that the reaction mechanism is concerted and involved a six-membered cyclic transition state 3.¹³



This mechanism is particularly appealing, as other noncatalyzed 1,5-hydrogen shifts involving olefins, for example, with maleic anhydride^{14a} or keto esters,^{14b} are believed to proceed by such a mechanism. Arguments for the concerted mechanism have been primarily based on the high stereospecificity and lack of rearrangement in the reaction products.^{14,15}

In our work, the simple adducts from β -pinene and HFA or DCTFA were also formed, without appreciable (less than 1%) rearrangement. This would, at first glance, also support the view of the concerted mechanism.

Other data, however, led us to conclude that adduct formation proceeds through a dipolar, four-membered, cyclic intermediate 4 (Figure 1),¹⁶ followed by proton migration.

These data are as follows.

(A) Reaction of HFA with an allylic compound containing another reactive functional group (epoxide) did not give the simple adduct, but a polymeric poly-

(7) For review of evidence for electrophilic character of halogens or sulfonyl halide in additions to olefins, see P. B. D. de La Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, pp 75 and 115.

(8) See ref 7: (a) p 168; (b) p 92; (c) p 244; (d) p 32.

(9) W. Honsberg, Elastomers Department, E. I. Du Pont de Nemours and Co., personal communication, 1965.

(10) E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Amer. Chem. Soc.*, **89**, 1422–1430 (1967).

(11) P. B. Sargeant, Central Research Department, Du Pont, personal communication, 1964.

(12) (a) N. P. Gambaryan, Em. Rokhlin, Yu. V. Zeifman, C. Ching-Yun, and I. L. Knunyants, *Angew. Chem. Intern. Ed. Engl.*, **5**, 947 (1966). (b) C. G. Krespan and W. J. Middleton in "Fluorine Chemistry Reviews," P. Tarrant, Ed., Marcel Dekker, Inc., New York, N. Y., 1967.

(13) Davis postulated a six-membered cyclic intermediate, but no details were given.²

(14) (a) R. K. Hill and M. Rabinovitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964), and earlier references quoted therein. (b) R. T. Arnold and P. Veeravagu, *ibid.*, **82**, 5411 (1960), and references therein.

(15) W. J. Middleton, *J. Org. Chem.*, **30**, 1395 (1965).

(16) A four-centered, cyclic, dipolar intermediate has been suggested in other addition reactions.^{8,12b}

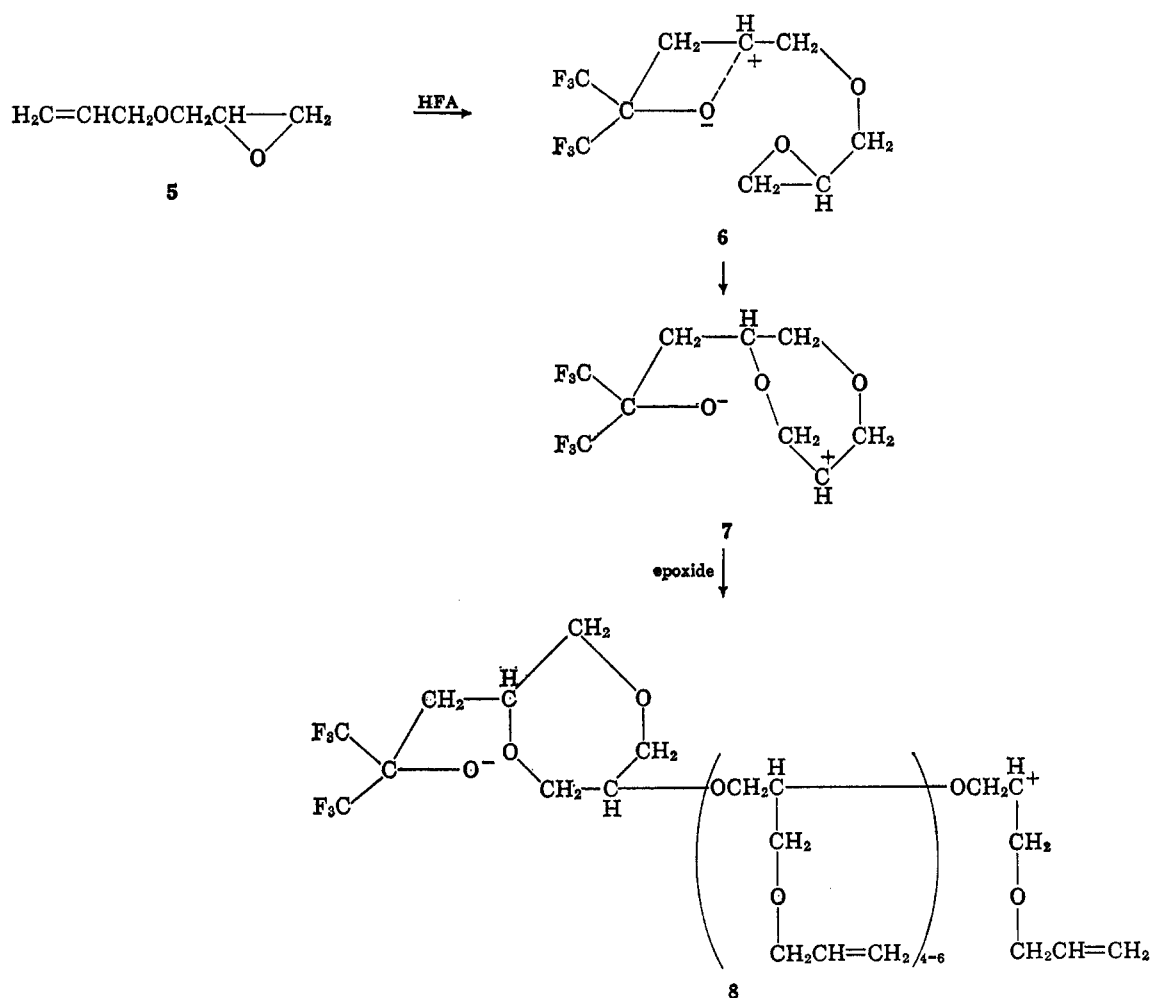


Figure 2.—Reaction of allyl glycidyl ether with hexafluoroacetone, suggested route.

ether. This polymer did not arise from direct reaction of epoxide with the HFA nor by reaction of epoxide with the usual bis(trifluoromethyl)carbinol adduct. Therefore the polymer probably resulted by trapping of an intermediate.

(B) From the trapping reaction conditions and the character of the polymeric product, the intermediate should have appreciable ionic character.

(C) Support for the ionic character of the intermediate is also given by (1) the electrophilicity of the HFA in the reaction, (2) the strong dependence of rate on electron-donating capacity of the substituents, (3) the high reaction rate with some olefins, compared with "concerted" 1,5-hydrogen-shift reactions, and (4) an appreciable solvent effect.

(D) Evidence that the intermediate is cyclic is seen (1) in the reaction characteristics (C1-C3) above, which are also characteristic of certain 1,2-cycloaddition reactions of olefins and which apparently pass through a four-membered cyclic intermediate, (2) by granting the ionic character of the intermediate, the absence of a Wagner-Meerwein type of rearrangement in formation of the HFA- β -pinene adduct, and (3) by assuming an equilibrium between the reactants and the intermediate, the lack of rearrangement of unreacted *cis*-butene-2⁹ or 3,3-dimethylbutene-1.

A detailed discussion follows.

A. Interception of a Reaction Intermediate.—HFA reacted readily with allyl glycidyl ether (AGE) (5,

Figure 2) in the presence of a trace of antioxidant, under mild conditions, in the dark, to give low polymers. With a 2:1 AGE/HFA mole ratio, heating at 75–100° for 3 hr, and an autogenous pressure of 40 psi, 95% of the AGE and about 28% of the HFA were converted into a viscous liquid product, mol wt 1085, which contained six to eight AGE units and one HFA unit. Ir and nmr spectral data indicated almost complete loss of carbonyl and epoxy groups, low terminal double-bond content, formation of some associated hydroxyl and internal double bonds, and that the high aliphatic ether content was maintained (see Experimental Section, part K).

With a lower initial AGE/HFA ratio (1:1), polymer in lower conversion was again formed, mol wt 919, which had an AGE/HFA ratio of 3:2 (see Experimental Section, part K).

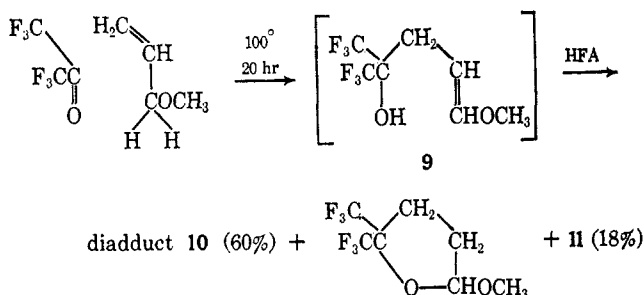
The polymers would not have resulted by direct reaction of the fluoro ketone on the epoxide group, for HFA does not react with phenyl glycidyl ether ($\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$) under these reaction conditions.

Also, the polyethers would not have resulted from an initial 1,5-hydrogen-shift reaction, followed by a secondary reaction of the *gem*-perfluorodimethylcarbinol group with the epoxide group (an $\text{S}_{\text{N}}1$ substitution of the epoxide by a neutral species¹⁷), for reaction of such

(17) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, 1953, pp 343, 344.

an alcohol (the isobutylene-HFA adduct) with allyl glycidyl ether does not take place under these conditions. Also, in the reaction of HFA with octene-1 in the presence of phenyl glycidyl ether, the adduct of HFA and octene-1 was formed by a 1,5-hydrogen shift as usual, but no product involving the phenyl glycidyl ether was found (see Experimental Section, part N). This experiment also shows that the first epoxy ring opening in the HFA-AGE reaction was intramolecular.

These results are quite different from that obtained by reaction of HFA with allyl methyl ether. Thus Gambaryan, *et al.*,⁶ under roughly equivalent conditions obtained, at a somewhat lower rate, the products 10 and 11, expected from the usual adduct 9 resulting from a 1,5-hydrogen shift.



B. Ionic Character of the Intermediate from the Trapping Reaction.—In the HFA-AGE reaction, it appears that a cationically initiated polymerization took place. Thus, with anionic initiation the 1:1 copolymer with HFA would have formed.^{18a} Also, the low nucleophilicity of the *gem*-perfluorodimethyl carbinol anion has been demonstrated.^{18a}

Free-radical polymerizations of epoxides to form low polymers are known, but are difficult to initiate.^{18b,19} Thus, with di-*t*-butyl peroxide initiator, phenyl glycidyl ether at 145–155° for 4 hr formed a low molecular weight polymer in 8% conversion, with 92% recovered ether.^{18b} Also, if free-radical propagation was involved, some HFA would be expected to be incorporated along the polymer chain.¹⁰ Further, hydroquinone inhibitor was present.

Under these conditions a biradical intermediate appears too unreactive²⁰ to initiate epoxy polymerizations.

The suggested reaction course is shown in Figure 2. After initiation to form the cyclic dipolar intermediate 6, reaction proceeds by intramolecular attack of the carbonium ionic center on the epoxy oxygen. (Perhaps the six-membered cyclic transition state for this step encourages this reaction course rather than the 1,5-hydrogen shift.) Epoxy ring opening then may lead to the more stable (secondary) carbonium ion 7. This mode of attack predominates in acid-catalyzed ring openings of substituted epoxides.^{21,17} The latter carbonium ion then reacts with other epoxide groups available in the solution. The increased incorporation of HFA in the second example may have resulted from

secondary reaction of excess HFA with the pendant allyl groups in the polymer 8 (Figure 2). However, further work is necessary to determine the polymer structure in detail.

In the propagation, step, it appears that a conventional cationic step is involved. This is suggested by the reaction of HFA with a mixture of AGE and phenyl glycidyl ether. In this case, some phenyl glycidyl ether was incorporated in the polymer. When the AGE, phenyl glycidyl ether, and HFA were present in the reactant mixture in a 1:1:1 mole ratio, the resulting ratio in the polymer was 4:1:2.4 (see Experimental Section, part L). This further supports the view that the reaction is stepwise, and that the initial intermediate has ionic character, and against the view that the epoxy group in AGE participates in the HFA-allyl group reaction in a concerted fashion.

The difference in activity of the epoxy groups in AGE and in phenyl glycidyl ether may also involve the former being within the "solvation sphere," and perhaps more advantageously oriented for reaction with the dipolar cyclic intermediate.

These results, then, may be considered as supporting evidence that "intimate" ion pairs²² resulting from *cis* additions can exist as intermediates^{2c} with the attached epoxy group intercepting the intimate ion pair before the latter reaches the solvent-separated, ion-pair stage.

In any case, the utility of this type of trapping agent for detecting an intermediate as well as demonstrating its ionic character is shown.

C. Substituent Effects and Ionic Character of the Intermediate.—It was previously mentioned that the effects of substituents on the rate of formation of the HFA adducts show typical electrophilic behavior for the HFA. This usually suggests a carbonium ion mechanism.⁷ However, such substituent effects are also qualitatively similar to those in 1,2-cycloadditions of 1,1,2,2-dichlorodifluoroethylene to olefins,^{20,23} which are believed to proceed *via* a two-step mechanism through a cyclic "biradical" intermediate²³ (thus resembling at least geometrically the four-membered dipolar ion intermediate postulated for the HFA-olefin reactions).

A biradical intermediate does not appear to be involved in the HFA-olefin reactions, based on (a) the interception of the intermediate with an epoxy group (as mentioned above), (b) the slower reaction of HFA with 2-chloropropene than with propylene (the reverse would be expected for a biradical intermediate, for the chlorine atom, by electron delocalization, should stabilize the biradical²⁰), and (c) the lack of ring-opened products (which have been observed in peroxide-catalyzed reactions of β -pinene with chloroalkanes^{24,25}).

The great differences in rate of adduct formation for olefins with electron-donating *vs.* electron-withdrawing substituents (see Chart I) are characteristic of reactions involving carbonium ion intermediates.⁷

The high reaction rate for many of the olefins with HFA has not been observed for previously described

(18) (a) N. L. Madison, *Polymer Preprints*, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 1099; (b) A. Otu, M. Okano, and R. Oda, *Bull. Chem. Soc. Jap.*, **37**, 570 (1964).

(19) A. E. Gurgiolio, "Reviews in Macromolecular Chemistry," Vol. I, 1966, pp 39–193; see p 124.

(20) P. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.*, **86**, 628 (1964), and references quoted therein.

(21) H. C. Chitwood and B. T. Freure, *ibid.*, **68**, 680 (1946).

(22) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(23) P. D. Bartlett, G. Wallbillick, and L. K. Montgomery, *J. Org. Chem.*, **32**, 1290 (1967), and earlier references.

(24) D. M. Olroyd, G. S. Fisher, and L. A. Goldblatt, *J. Am. Chem. Soc.*, **72**, 2407 (1950).

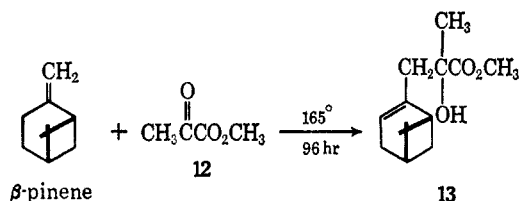
(25) G. Du Pont, R. Dulon, and G. Clement, *Bull. Soc. Chim. Fr.*, 257 (1951).

TABLE II
 EFFECTS OF SOLVENTS ON REACTION RATES

Solvent	Dielectric constant (20°)	TCNE ^a + <i>p</i> -MS, <i>k</i> ₂ (10 ⁴)	BTFMDCNE + TBVS, ^b % convn	Diels-Alder reactions, ^c % convn	DCTFA ^d + DIB	
					% convn ^e	<i>k</i> ₂ (10 ⁸) ^f
CH ₂ Cl ₂	9.08	1600	55.0		18	290 + 40
EtOAc	6.40	330	83.0		10	160
Et ₂ O	4.34	2.8			2	30
CCl ₄	2.24		2.3			
Cyclohexane	2.07	0.04			~0.5	~8
CH ₂ Cl ₂ /C ₆ H ₆		40,000		<7	~30	
CH ₂ Cl ₂ /Et ₂ O		570			6	
CH ₂ Cl ₂ /CCl ₄			24			

^a Tetracyanoethylene with *p*-methoxystyrene. Data of Wiley,³³ 0.10 *M* in *p*-MS, 0.006 *M* in TCNE, 25°. ^b *cis*-1,2-Bis(trifluoromethyl)-1,2-dicyanoethylene with *t*-butyl vinyl sulfide (data of Proskow, *et al.*³⁴). Reactant concentration was 10% (w/v) of solution, 25°. Reaction rate estimated by disappearance of the charge-transfer complex. ^c See ref 33. ^d *sym*-Dichlorotetrafluoroacetone with 2,4,4-trimethylpentene-1: 0.6 *M* DCTFA, 1.0 *M* DIB, 25 ± 2° (see also Experimental Section, part F). ^e Conversion into adduct at 20 hr. ^f Calculated as second-order rate constant.

uncatalyzed 1,5-hydrogen-shift reactions believed to proceed in concerted fashion.^{14b,26-29}



As examples, the reaction of β-pinene with a ketone containing a reactive carbonyl group (methyl pyruvate 12) to form the 3,4-unsaturated alcohol 13 was reported to require 96 hr at 165° to reach equilibrium (55% conversion).^{14b} Also, the reaction of β-pinene with acrylonitrile took 4 hr at 235° to attain 42% conversion into the adduct.²⁶ On the other hand, the β-pinene-HFA reaction proceeded in high conversions in a few minutes at 25°. (The reaction of acetylene dicarboxylic ester with isopropylideneamine to give a diene amine by a 1,5-hydrogen shift proceeded under mild conditions, and a 1,4 dipolar intermediate was postulated. No direct evidence for the mechanism was presented.)³⁰

Apparently, the HFA-olefin reactions proceed as readily as the analogous Diels-Alder reactions (HFA with isobutylene *vs.* HFA with isoprene³¹). This is unusual in other systems when relative rates of 1,5-hydrogen shifts *vs.* Diels-Alder cyclization are compared.^{23,29}

The carbonyl group of HFA is electron deficient because of the electron-withdrawing effect of the trifluoromethyl groups, and so would resemble a weakly polarized olefinic group. This is supported by the low nucleophilic activity of HFA.^{10,12} Thus, 1,5-hydrogen shifts in HFA-allylic olefin reactions would be expected to occur with similar difficulty to the above-described "concerted" rearrangements.

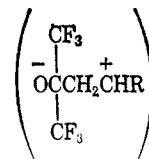
The reaction of DCTFA with 2,4,4-trimethylpentene-1 (diisobutylene) proceeded slowly enough to readily follow the reaction at room temperature. It was

observed, qualitatively, that an appreciable solvent effect existed, probably larger than that expected for concerted reactions.

Thus, Diels-Alder reactions are reported to show very small solvent effects, with rates slower in the more polar solvents (acetone, acetic acid) than in chloroform or carbon tetrachloride and with maximum differences in reaction rate in these solvents being *ca.* sevenfold.^{32,33}

On the other hand, the reaction of DCTFA with diisobutylene (DIB) in various solvents led to the results shown in Table II (see Experimental Section, part F). The solvent effects on the rate through this representative group differed by about 30-fold, and rates increased with increased polarity of the medium. The relative effects of methylene chloride, ethyl acetate, and diethyl ether on reaction rate were considerably smaller than those observed in the 1,2-cycloaddition reactions of *p*-methoxystyrene (*p*-MS) with tetracyanoethylene, by a factor of about 100. On the other hand, the relative effects of these solvents on the DCTFA-DIB reaction were about the same as those found in the 1,2-cycloaddition reaction of *cis*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene with *t*-butylvinyl sulfide.³⁴ In the latter, strong evidence existed for a four-membered cyclic zwitterion intermediate.³⁴

D. Evidence for a Cyclic Intermediate.—If an intermediate with considerable ionic character of the



type described above existed in extended form, skeletal rearrangements would be expected for molecules capable of Wagner-Meerwein rearrangements, such as β-pinene, camphene, or neohexene-1.

In the reaction of DCTFA with β-pinene, high conversions and essentially quantitative yields of a monoadduct were obtained under mild conditions.

The nmr and ir spectra of the high boiling fraction indicated only one product, the 3,4 internally double-bonded adduct having only one vinylic hydrogen (see Experimental Section, parts G and H). That

(26) C. J. Albisetti, N. G. Fisher, M. J. Hogsed, and R. M. Joyce, *J. Amer. Chem. Soc.*, **78**, 2637 (1956).

(27) A. G. Smith and B. L. Yates, *J. Org. Chem.*, **30**, 2067 (1965).

(28) J. Wolensky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962).

(29) J. Ross, A. I. Gebhart, and J. F. Gerecht, *ibid.*, **68**, 1373 (1946).

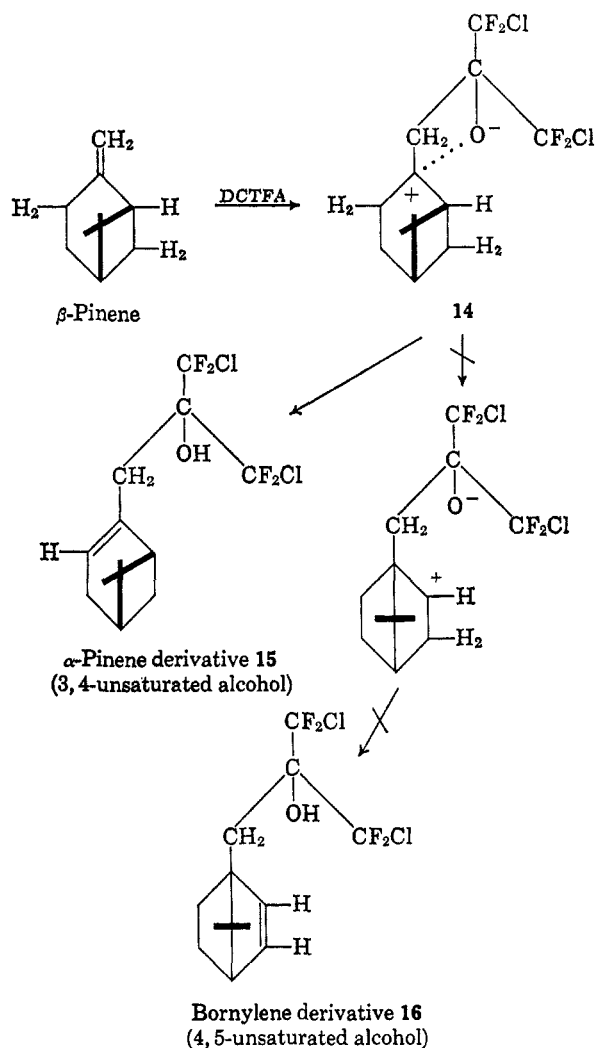
(30) R. Huisgen and K. Herbig, *Ann. Chem.*, **688**, 98 (1965); see also R. Huisgen, M. Morikawa, D. Breslow, and R. Grashey, *Chem. Ber.*, **100**, 1602 (1967).

(31) W. Linn, *J. Org. Chem.*, **29**, 3111 (1964).

(32) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **77**, 6287 (1955).

(33) D. W. Wiley, to be published.

(34) S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966).

Figure 3.—Reaction of β -pinene with DCTFA.

is, the adduct was the one expected from β -pinene by a 1,5-hydrogen shift *without* skeletal rearrangement 15 (Figure 3).

The same result was obtained on examining the undistilled reaction product. Therefore this adduct did not arise by secondary thermal reactions. Also equivalent results were obtained in reaction of β -pinene with HFA (see Table I and the Experimental Section, part G). The vpc and nmr spectral data indicate that less than 1% of the rearranged product is present.

We presume that β -pinene-HFA reaction proceeds by the same mechanism as that for the AGE-HFA reaction. This assumption is supported by the high reactivity of β -pinene toward adduct formation. The product expected if skeletal rearrangement had occurred, 16, would be the one expected if reaction occurred either by "nonclassical" carbonium ion mechanism or by rapidly equilibrating "classical" ions.³⁵ The lack of skeletal rearrangement indicates neither of these.

β -Pinene has been used frequently as a probe for carbonium ion intermediates^{14b,15,16} for Wagner-Meerwein-type rearrangements or ring-opening reactions occur overwhelmingly with this reactant under solvolytic conditions or with most acid catalysts which ordinarily lead to carbonium ions.³⁶

Although it is recognized that occurrence or nonoccurrence of skeletal rearrangement in reaction of bicyclic compounds is *per se* not a criterion for the presence or absence of mesomeric or classical cation intermediates,³⁷ usually the extent of rearrangement can be accounted for by considering the degree of kinetic control of the reaction rate. In the β -pinene systems, however, the reported rearranged products are those expected with either thermodynamic or kinetic control. As a result, lack of skeletal rearrangement in β -pinene reactions has been taken as practically conclusive evidence for a concerted mechanism.

On the other hand, hydrogen chloride may be added to the double bond of either α - or β -pinene in nonpolar or weakly polar nonsolvolyzing solvents (hydrocarbons, diethyl ether) at reduced temperatures (-70 to -15°), to give the same "pinene hydrochloride," with very little skeletal rearrangement.³⁸ This reaction has long been considered to involve carbonium ions as intermediates.⁸

Brown and Liu, in additions of HCl or DCl to α -fenchene, apobornylene, or camphene also observed a very low level of rearrangement ($\leq 10\%$), in ethyl

(36) J. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 186.

(37) See ref 36, pp 136-137.

(38) J. L. Simonsen, "The Terpenes," Vol. II, Cambridge University Press, London, 1940, pp 172, 202.

(35) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965).

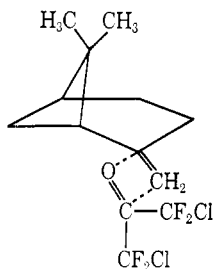
ether or methylene chloride solvents at 0 to -78° .³⁹ Additions were also shown to be *cis*.³⁹

Other olefin addition reactions in which rearrangements do not occur are hydroborations,^{40,41} oxymercuration,^{42,43} sulfenyl halide additions,⁴⁴ and acid-catalyzed hydrations.^{45,7d} In all of these cases intermediates obtained by *cis* additions have been suggested.⁸

The addition of chlorine in common solvents to strained bicyclic olefins also appears to proceed by a *cis* addition.⁴⁶ De La Mare and Bolton suggest that such reactions proceed through a transition state or intermediate with considerable carbonium ionic character, with a structure similar to that suggested above the HFA-olefin reactions. They also suggest that such a transition state or intermediate lies earlier on the reaction path than the carbonium ion intermediate, and that each intermediate may react directly to form a product.^{5b,c}

The lack of rearrangement with such intermediates may be related to geometrical limitations to orbital interpretation. In the case of HFA-olefins, the carbonyl group and the double bond of the olefin approach in parallel planes, orthogonal to the direction of the covalent bond to be formed, to get π -orbital overlap, and the substituents on the olefin remain essentially coplanar through the transition state and in the intermediate **4** (Figure 1). This is shown in **17** for DCTFA with β -pinene. Drieding models indicate (for either *exo* or *endo* addition) that the resulting orientation for the potentially migrating C—C bond is certainly not coplanar, let alone coaxial, with the C⁺—O⁻-directed bond in the intermediate.

Therefore orbital penetration is very low, and the rate of skeletal rearrangement in the β -pinene moiety is small compared with the 1,5-hydrogen shift.



17

Winstein and coworkers^{47,48} have shown that even in the presence of ionizing solvents and bases at least as strong as H₂O (solvolyzing systems), if the geometry is unfavorable for bond delocalization in the carbonium ion, then rearrangement occurs after the rate-determining ionization step. Note that the β -pinene-HFA reaction was carried out neat, in a low polarity medium,⁴⁹

(39) H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967), and also earlier references.

(40) G. Zweifel and H. C. Brown, *ibid.*, **86**, 393 (1964).

(41) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(42) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

(43) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(44) See ref 36, pp 161-162.

(45) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **82**, 4729 (1960).

(46) S. J. Cristol, F. R. Stermitz, and P. S. Ramsey, *ibid.*, **78**, 4939 (1956).

(47) S. Winstein and D. Trifan, *ibid.*, **74**, 1151 (1952).

(48) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952).

(49) Carl Brock of the Orchem Department, Du Pont, has found the apparent dielectric constant of 20% HFA-H₂O in toluene to be 2.47 at 25°.

in which intimate ion pairs would be encouraged and with relatively high-directed bond character.²²

Discussion

A.—If the above-described mechanism has validity, noncatalyzed reactions of HFA with *nonallylic* olefins could proceed through the same intermediate. This view appears to have support in the reaction of HFA with styrene, in which low molecular weight polystyrene is rather slowly formed and most of the polymer contains no HFA end group (Experimental Section, part N).

Thus the cyclic dipolar intermediate may be formed first, followed by polymerization *via* cationic initiation. Support for the cationic mechanism is (1) propagation in the presence of hydroquinone (not biradical)^{50a} and (2) the rather sluggish rate coupled with low molecular weight (high chain transfer to monomer).^{50a}

Another example is the reaction of HFA and DCTFA with dienes in the Diels-Alder reaction. These occurred extremely readily below 0°.³¹ Therefore they may be considered two-step reactions in which the first step involves the formation of the four-centered dipolar ion (the ion stabilized by allylic resonance), followed by ring closure through ion-pair collapse.

A similar situation probably exists for the vinyl ethers, with the formation of oxetanes.^{12b,50b}

B.—The cyclic intermediates to the adducts formed from HFA and allylic olefins (like those of 1,2-bis(trifluoromethyl)-1,2-dicyanoethylene and electron-rich alkenes³⁴), would be formed in accordance with the Hoffmann-Woodward selection rules, which predict that noncatalyzed concerted four-membered cycloadditions (no intermediate) are disfavored thermal processes, and, on the other hand, discrete four-membered cyclic intermediates are permitted.⁵¹

Previous workers showed that addition of electrophilic polar reagents to strained bicyclic systems (HCl, oxymercuration) proceed in an *exo* fashion, even with *gem*-dimethyl groups in the 7 position of bornene systems.^{39,43} In the addition of HFA to β -pinene, molecular models (Drieding) show no appreciable steric problems with either an *exo* or an *endo* approach. With an *exo* addition in this case, support is offered for the view that a nonclassical ion is not necessary to explain the *exo* addition in these systems.³⁹

General Conclusions

A.—A four-centered cyclic dipolar intermediate is present in addition reactions of HFA or DCTFA with unhindered olefins, including strained bicyclic olefins, and this intermediate can directly participate in reactions with nucleophilic groups.

B.—Attempts are often made to determine the existence of a reaction intermediate by "trapping" the intermediate. Results may be negative, however, if the potentially reactive group is present only in the solvation sphere. Positive results may be obtained by using appropriate polyfunctional reagents. Allyl glycidyl ether appears to be particularly useful in noncatalyzed reactions, and also indicates the polarity of the intermediate.

(50) (a) C. Walling, *ibid.*, **66**, 1602 (1944); (b) H. R. Davis, U. S. Patent 3,164,610 (1965).

(51) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

C.—A reaction is often considered concerted by a demonstration of lack of skeletal rearrangement in the reaction products. This has been considered particularly strong evidence if the alternative mechanism involves a "carbonium ion" intermediate for which rearrangement is the rule.

This work indicates, however, that in reactions which appear to involve *cis* additions no skeletal rearrangement need be expected. This also implies that an intermediate is formed which is cyclic and had existed for a negligible period in the open-chain form.^{20,34}

D.—As the above conclusions pertain specifically to 1,5-hydrogen shift (thermal addition) reactions of olefins with asymmetric dienophiles (such as formaldehyde, sulfur trioxide, chloral), these reactions, previously considered concerted,^{14b} should be reexamined, using appropriate polyfunctional trapping reagents.

Experimental Section⁵²

A. Preparation of the Adduct of HFA with Propylene [$\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)_2\text{OH}$].—Hydroquinone (0.1 g) was placed in a dry 300-cc stainless steel shaker tube, which was flushed with nitrogen and cooled to -70° , and HFA (83 g, 0.5 mol, Orchem Department, E. I. du Pont de Nemours and Co., used without further purification) and propylene were introduced (21 g, 0.5 mol). The tube was then sealed, shaking was started, and the temperature was brought up in stages. Thus, at 50° , the autogeneous pressure was 250 psi, with no pressure drop or exotherm observed over a 1-hr period. The temperature was then raised to 75° , and pressure reached 310 psi; at 130° it was 375 psi, and at 125° it was 400 psi. At 150° a slow pressure drop was observed (440 \rightarrow 435 psi), and so the tube was shaken at this temperature for 2.5 hr. The tube was then cooled and vented, and 18 g (17% conversion) of the adduct was obtained (see Table I).

B. Preparation of the Adduct of HFA with 2-Chloropropene-1 [$\text{CH}_2=\text{C}(\text{Cl})\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$].—2-Chloropropene-1 (38 g, 0.5 mol, Columbia Organic Chemicals Co., used directly), hydroquinone (0.1 g), and HFA (83 g, 0.5 mol) were allowed to react as in part A (see also Table I). No pressure drop was observed until the internal temperature reached 164° , whereupon it was held at this temperature for 4 hr. The rather steady rate of pressure drop at 164° of about 20 psi/hr indicates that the reaction is not appreciably reversible at these temperatures.

About 60 g of liquid products were obtained which on a single distillation through a 24-in. platinum gauze spinning-band column gave ca. 12.0 g (10%) composed principally of the adduct; infrared absorption (CCl_4) included bands at 2.9 (sharp, $-\text{OH}$) and at 6.1μ ($-\text{C}=\text{CH}_2$); nmr peaks were at δ 5.48 (1.9 H, multiplet, $>\text{C}=\text{CH}_2$), 3.86 (1 H, broad, $\text{O}-\text{H}$), and 2.98 (1.9 H, singlet, $-\text{CH}_2-$).

Anal. Calcd for $\text{C}_6\text{H}_5\text{ClF}_6\text{O}$: C, 29.70; H, 2.07; Cl, 14.64; F, 47.00. Found: C, 30.41; H, 2.57; Cl, 14.06; F, 45.51.

C. Preparation of the Adduct of HFA with Allyl Chloride [$\text{CHCl}=\text{CHCH}_2\text{C}(\text{CF}_3)_2\text{OH}$].—Allyl chloride (38 g, 0.5 mol, Eastman White Label), HFA (83 g, 0.5 mol), and hydroquinone (0.01 g) reacted as in part A with no pressure drop observed even at 165° for 4 hr (600 psi developed). The tube was then cooled, and 40 g of nonviscous liquid was obtained. Distillation gave 3 g (3%) of the adduct; infrared absorption (CCl_4) showed bands at 2.8 (OH), 8.1, 8.6, 9.3, 13.9 ($\text{C}-\text{F}$), and 6.0μ ($\text{C}=\text{C}$).

Anal. Calcd for $\text{C}_6\text{H}_5\text{ClF}_6\text{O}$: C, 29.70; H, 2.07; Cl, 14.64. Found: C, 29.72; H, 2.18; Cl, 14.35.

D. Preparation of the Adduct of 2,4,4-Trimethylpentene-1 (Diisobutylene) and Dichlorotetrafluoroacetone (DCTFA) [$(\text{CH}_3)_2\text{CCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$] $\text{C}(\text{CF}_2\text{Cl})_2\text{OH}$].—DCTFA (28 g, 0.14 mol, Allied Chemical Co.), cooled in ice, was mixed with 11 g (0.10 mol) of diisobutylene (Phillips Chemical Co., pure grade).

(52) Boiling points are uncorrected. The proton nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 nmr spectrometer, and chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Spectra were determined on 10% solutions in carbon tetrachloride unless otherwise indicated. Infrared spectra were obtained on a Perkin-Elmer Infracord and calibrated with polystyrene. The 3,3-dimethylbutene-1 was obtained from Sinclair Chemical Co. and the methacrylonitrile was obtained from the Vistron Corp.

The solution was then heated to reflux in a flask fitted with a magnetic stirrer, reflux condenser, and thermometer. The internal temperature rose from 57 to 70° over a 5-hr period. On one distillation, 16 g (50%) of essentially the adduct was obtained (see Table I); the infrared absorption (CCl_4) included a peak at 2.9μ (OH); the nmr peaks (neat) were at δ 5.15 (2 H, singlet, $=\text{C}=\text{CH}_2$), 3.65 (1 H, singlet, $-\text{OH}$), 2.80 (2.0 H, singlet, $-\text{CH}_2-\text{C}(\text{CF}_3)_2-$), 2.05 (2.3 H, singlet, $-\text{CH}_2-$), and 0.90 (9.1 H, singlet, $-\text{C}(\text{CH}_3)_3$); the nmr peaks (CCl_4) of diisobutylene starting material were at δ 4.80, 4.60 (2 H, two broad singlets, $=\text{C}=\text{CH}_2$), 1.90 (2 H, singlet, $-\text{CH}_2$), 1.76 (3 H, multiplet, $-\text{CH}_3$), and 0.90 (9 H, singlet, $-\text{C}(\text{CH}_3)_3$).

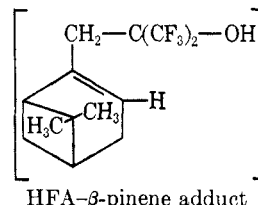
The nmr spectra of the product corresponded with the externally double-bonded structure. The peak intensity ratio for the external double-bond structure was calculated to be 1:2:2:2:9, and that for the internal double-bond structure was calculated to be 1:1:2:3:9. (The ratio actually found was 1:2:2:2:9.1.)

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{Cl}_2\text{F}_4\text{O}$: Cl, 23.66. Found: Cl, 23.08.

E. Reaction of Diisobutylene (DIB) and DCTFA at Room Temperature. Search for Biproducts, Intermediates by Nmr.—Reaction was carried out by dissolving 0.2 g of the olefin in 0.3 g of DCTFA at -70° in an nmr tube and quickly bringing the tube in the spectrometer to room temperature. The nmr data for the DIB and the adduct were identical with the higher temperature case. If the cyclic ether adduct is formed to any extent, the peak due to $-\text{C}(\text{CH}_3)_3$ compared to that due to $\text{H}_2\text{C}=\text{C}<$ should increase from the initial 9:2 ratio. Also the ratio of peaks due to $-\text{CH}_2-\text{C}(\text{CF}_2\text{Cl})_2/\text{H}_2\text{C}=\text{C}<$ should become >1 . The initial ratio of the 0.9- to 4.7-ppm band was 4.8 (theory 4.5). The 2.9- to 5.2-ppm band ratio was 1.08 (theory 1.0). These ratios remained essentially constant over a period of 48 hr at room temperature, with conversion into the adduct rising to 55%. Also, there was no evidence of complex formation between the DIB and the DCTFA by band splitting, chemical shift, or solution color.

F. Reaction of DIB with DCTFA. Effect of Solvent on Reaction Rate.—Qualitative comparisons were obtained by observing the intensity of the infrared absorption band associated with the $-\text{C}(\text{CF}_2\text{Cl})_2-\text{OH}$ group in the adduct (2.82μ in cyclohexane and methylene chloride, 2.90μ in ethyl acetate, 3.05μ in diethyl ether). The band intensity was related to adduct concentration by comparison with solutions of known concentration. The reactions were carried out in the following way. DCTFA (1.19 g) was added to 1.12 g of DIB in the solvent tested so as to give 10.0 ml of solution (0.6 M DCTFA, 1.0 M DIB). Mixing was carried out below -70° in the presence of 0.001 g of hydroquinone. The solvents were reagent grade, dried with Linde Molecular Sieve 5A, and duplicate runs were made. After mixing, samples were withdrawn with a syringe and compared in the same infrared cell. Initial data were taken 5 min after the mixing operation. Conversion differences between duplicates were less than 10%.

G. Preparation of the Adduct of HFA and β -Pinene.— β -Pinene [bp $65-66^\circ$ (23 mm), 13.8 g, 0.1 mol, containing 10% α -



pinene by nmr⁵³), hydroquinone (0.1 g), and HFA (17 g, 0.1 mol) reacted as in A. The tube was brought up to room temperature with shaking for 2 hr. Ca. 25 g of colorless, nonviscous liquid was obtained. On standing, large crystals (~ 3 g) slowly formed. About 18 g of the liquid phase was distilled to give 9 g of the adduct which crystallized on standing, mp $33-34^\circ$, the same value as that of the crystals which originally separated (see Table I). Infrared absorptions (CCl_4) were found at 2.9 (sharp, $-\text{OH}$), 7.8-9.0, 9.8, 13.9, 14.8 ($\text{C}-\text{F}$), 6.1 (vw, $\text{C}=\text{C}$), and 12.3μ (w, $\text{HR}_1\text{C}=\text{CR}_2$).⁵⁴ No peak was found near 14.3μ , characteristic

(53) "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, entries no. 274 and 272.

(54) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 51, 52.

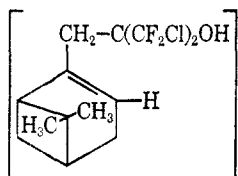
of C—H stretching in *cis* —CH=CH— structures of the norbornene type.⁵⁴ The nmr peaks (CCl₄) at δ 2.97 (1 H, broad, —OH), 5.60 (1 H, broad, —CH=C—), 2.64 [2 H, singlet, —CH₂—C(CF₃)₂—], 1.30, (3.1 H, sharp singlet, —CH₃), and 0.84 (3 H, sharp singlet, —CH₃) indicate only a single product, the simple adduct without rearrangement.

Thus the peak at δ of 2.97 ppm was proved due to the —OH group, as it disappeared on shaking with D₂O. The peak at δ 5.60 ppm had an area equivalent to one vinylic proton, and is the only peak downfield of the 2.97-ppm peak. The magnitude and shift direction is as expected for a product with an α -pinene skeleton (see also discussion on reaction of β -pinene with DCTFA). The peaks at δ 0.84 and 1.30 ppm, attributed to the *gem*-methyl groups, are essentially at the same positions as the *gem*-dimethyl groups of α -pinene, supporting further the location of the double bond in the adduct (the *gem*-dimethyl peaks in β -pinene are at δ 0.70 and 1.20 ppm and in *p*-anisyl bornylene are at δ 0.80 and 0.92).⁵⁵ Vpc indicated purity of over 98% based on relative area of the peaks and total volume of collected products. This indicates that negligible reaction or dissociation of the adduct occurs on the vpc column.⁵⁶

With this information about the product stability in hand, examination of the vpc of the undistilled, unheated crude product (and correcting for the separated crystals) indicated the unrearranged adduct to be present in about 81% conversion, 99% yield, with four more volatile impurities present in about 1% total concentration.

Anal. Calcd for C₁₃H₁₆F₆O: C, 51.66; H, 5.30; F, 37.75. Found: C, 51.31; H, 5.32; F, 37.46.

H. Reaction of β -Pinene with DCTFA.—Mixing 14 g (0.10 mol) of β -pinene with an excess of DCTFA (35 g, 0.17 mole) at



—70° and warming slowly resulted in an exothermic reaction, and the temperature rose to 0° within a few minutes. After 1 day at room temperature the solution was distilled, giving 21 g (66%) of the adduct (see Table I).

The infrared spectrum indicated the presence of an internal double bond similar to that in α -pinene derivatives, *i.e.*, absorption (CCl₄) at 6.05 (vw, C=C) and 12.6 μ (w) (CH out-of-plane deformation of trisubstituted ethylenes).⁵⁴ Also there was no peak near 14.3 μ which is characteristic of norbornene [CH stretching of *cis* CH=CH⁵⁴]. Other peaks were at 2.95 (OH), 8.3–9.8 (s), and 14.6 μ (w) [—C(CF₃)₂—OH]. The nmr analysis (CCl₄) supported this conclusion; *i.e.*, only one methynyl proton was present [δ 5.7 (1 H, broad)], with the chemical-shift magnitude and direction expected on substituting a —C(CF₃)₂—OH group for H (δ 5.7 for the adduct compared to δ 5.15 for α -pinene, *vs.* δ 6.0 for norbornene).⁵⁷ Other nmr peaks were at δ 3.3 (1 H, broad, —OH), 2.8 (1.8 H, multiplet, —CH₂ *exo*), 1.31 (2.8 H, singlet, —CH₃), and 0.86 (2.9 H, singlet, —CH₃). The position of the *gem*-dimethyl groups support the α -pinene structure in the product.

The column holdup and residue was identical with the distilled adduct in viscosity and infrared spectrum. No unexpected infrared peaks were observed for the forerun.

Anal. Calcd for C₁₃H₁₆Cl₂F₄O: F, 22.68. Found: F, 22.29.

I. Treatment of α -Pinene with DCTFA.—On mixing α -pinene with DCTFA at room temperature for 20 hr, only a slight reaction occurred. That is, traces of absorption in the infrared (CCl₄) at 5.75, 6.05, 7.95, 8.1 (shoulder), 11.45, and 11.65 μ indi-

(55) W. F. Erman and T. J. Flaunt, *J. Org. Chem.*, **27**, 1526 (1962).

(56) Runs were carried out on the Perkin-Elmer Model 154 with a stainless steel column length of 2 m, 0.25-in. o.d., packed with 20% fluoroalkyl pyromellitate on Gas Chrom R, 60–80 mesh. The helium flow rate was 10 cc/7.4 min; the vaporizer temperature was 210° and the column temperature 150°. Similar patterns were seen on silicone gum nitrile XL-60 on Gas Chrom R at a column temperature of 125° and a vaporizer temperature of 175°. The retention time, under the former conditions, was 10.45 min (98.0% of total) with the impurity at 8.3 min (1.5% of total).

(57) In the series CH₂=CHCH₂C₇H₁₅, CH₂=CHCH₂OH, CH₂=CHCH₂NH₂, and CH₂=CHCH₂Br, the chemical-shift values for the methynyl hydrogens are, respectively, δ 5.80, 6.0, 5.92, and 6.05 ppm.⁵⁴

cate presence of small amounts of an externally double-bonded adduct, particularly in the residue after distillation.

J. The Adduct of HFA and α -methylvinyl methyl ether [CH₃OC(=CH₂)CH₂C(CF₃)₂OH] was obtained by using reaction conditions given in part A (see Table I). Infrared analysis (CCl₄) showed absorptions at 2.95 (mod.,⁵⁸ associated OH), 6.0 (H₂C=C=), and 7.8 (s), 8.0 (s), 8.3 (s), 8.7 (s), 9.3 (s), and 9.7 μ (s) (C—F). Bands at 10.1 μ (mod.), 10.7 (mod.) were present in the original ether but were of low intensity. New bands were also found at 13.7 μ (mod.) and 14.9 μ (mod.). Missing from the original ether were the bands that appeared at 6.2 (mod.), 9.2 (s), and 12.7 μ (s). No appreciable differences in spectra were observed whether the analysis was run neat or as a 1% solution in CCl₄ (association by internal hydrogen bonding). The nmr peaks (neat) were at δ 5.15 (1 H, broad, —OH), 4.3 (2.1 H, multiplet, >C=CH₂), 3.7 (3.2 H, singlet, CH₃—O), and 2.85 [2.1 H, singlet, —CH₂—C(CF₃)₂—].

Anal. Calcd for C₇H₈F₆O₂: C, 35.30; H, 3.36; F, 47.90. Found: C, 35.79; H, 3.54; F, 47.22.

K. The Reaction of HFA with allyl glycidyl ether (AGE) was carried out according to the procedure in part A using 23 g (0.2 mol) of AGE [Shell Chemical Co., bp 76° (53 mm)], 0.2 g of hydroquinone, and 17 g (0.1 mol) of HFA. At 75–79°, a slow pressure drop was observed (pressure fell from 40 psi to 35 psi in 1 hr). The rate of pressure drop was slightly greater at 100°; after 3 hr the pressure was 15 psi. The clear viscous product was placed in a spinning-band column under vacuum to constant weight to remove unreacted material.

The residue after removing volatiles (HFA, AGE) was a viscous liquid (27 g) with bp >150° (1 mm) and mol wt 1085 (boiling point elevation in benzene). The elemental analyses indicate a minimum HFA content of 14, 16, and 13 mol %, respectively, or 1 mol of HFA/6.1–6.7 mol of AGE (minimum mol wt 862–897).

Anal. Calcd for 1 mol of (C₃H₆O)/6.5 mol of (C₆H₁₀O₂) or C₄₂H₆₆O₁₄F₅: C, 55.6; H, 7.15; F, 12.6. Found: C, 55.33; H, 6.98; F, 12.64.

By ebulliometry the mole ratio would be 1 mol of HFA/8 mol of AGE. The infrared spectrum (neat and in carbon tetrachloride) indicated the loss of some double bond (3.2 μ) and epoxy content (11.8 μ) from the AGE and loss of the carbonyl group of the HFA (5.4 μ). Also, hydroxyl groups, intermolecularly associated, were formed (2.9–3.1 μ). The product was not soluble in 5% aqueous sodium hydroxide. This information, coupled with the high aliphatic ether content which was maintained (9.0 μ), and increased —CH— absorption (7.2 μ), suggests the formation of dioxane and/or polyethylene glycol units associated with the hydroxyl groups.

A new absorption at 14.0 μ supports the idea of chains containing at least three aliphatic carbon atoms, expected if the HFA added to the allyl double bond (also phenyl glycidyl ether did not react with HFA under these conditions).

Stronger absorption at 5.9 μ (still weak) suggests the formation of new internal double bonds. These double bonds could arise in a termination step.

The nmr spectrum also indicated the complete loss of the epoxide group by loss of a multiplet (relative area 2) at δ 2.5

(>C—CH₂—O) and by loss of a multiplet (relative area 1)

at δ 3.0 (—CH—C(O)<).

Also, the nmr analysis indicated formation of ethylene glycol ether groups and some disappearance of the terminal allylic double bond [ratios of band areas of δ 5.7 (multiplet, >C—

CH=C<), 5.2 (multiplet, >CH₂=C—C<), 3.95 (multiplet, C=C—CH₂—O—), and 3.5 (multiplet, —O—CH₂—C—O—) were

1.1:2.2:1:4.9, whereas initial ratios for AGE were 1:2:2.1:2.2, respectively].

In the run in which the AGE/HFA mole ratio was 1:1, and which gave a polymer with AGE/HFA ratio of 3:2, the loss of allylic and epoxy groups and formation of internal olefin were also indicated in the nmr. The relative band areas for δ 5.7, 5.2, 3.95, 3.5 were 1.4:2:2.6:4.9. The nmr spectrum also exhibited a broad multiplet, δ 2.4–3.0 (relative area *ca.* 1), which suggests

>C=CH structures.

Other characteristics of the latter run were 13 g of product obtained, mol wt 919 (ebullioscopic), and product insoluble in 5% NaOH. From the elemental analyses, the polymer contained 41, 42, and 38 mol % of HFA, respectively. Thus the product had an equivalent weight of 330–356, with an AGE/HFA mole ratio of 1.67–1.44 (3:2). The ir spectrum indicated relatively more OH (3.0 μ) and C–F (8.0 μ) content than in the first run.

Anal. Calcd for 3 mol of AGE/2 mol of HFA ($C_{24}H_{30}F_{12}O_8$): C, 42.7; H, 4.35; F, 33.8. Found: C, 42.54; H, 4.47; F, 31.98.

L. Terpolymerization of HFA with AGE and Phenyl Glycidyl Ether.—AGE (11.0 g, 0.1 mol), phenyl glycidyl ether (15.0 g, 0.1 mol), hydroquinone (0.01 g), and HFA (17 g, 0.1 mol) were allowed to react according to the procedure given in part A. The temperature was raised to 100° for 2 hr. A slow pressure drop was observed over this time period (40 psi \rightarrow 30 psi). The temperature was raised to 115° for 3 hr more. This was accompanied by a further pressure drop to 15 psi. The tube was cooled and vented. Approximately 37 g of slightly viscous, light-colored liquid was obtained, which on distillation under nitrogen at reduced pressures in a platinum gauze-filled spinning-band still gave the following fractions: (1) 2.4 g, bp 40–70° (1.5–2.0 mm) (pot 90–100°, bath 120–140°); (2) 12.1 g, bp 70–78° (1 mm) (pot 120–150°, bath 150–158°); and (3) residue 15.5 g, very viscous, light amber liquid.

The residue was further heated in a rotating evaporator at 150° (1 mm) for 30 min. This residue (13 g) was still light amber, but was now a rather hard solid at room temperature. Its cryoscopic molecular weight (in benzene) was 1063. The infrared spectrum (5% in CCl_4) showed a weak, broad absorption band at 2.9–3.0 (associated —OH), a strong band at 8.1 (C—F), and moderately strong bands at 6.15, 6.60, 9.4 and 14.6 μ characteristic of the phenyl group. The band intensities of the latter corresponded to a 15% concentration by weight of phenyl glycidyl ether in the residue. Bands at 8.6 and 8.8 (strong) and 10.6 μ (weak, ether groups) were also present.

From the analyses, an average of 2.4 mol of HFA/1 mol of phenyl glycidyl ether/4 mol of AGE is present in the polymeric residue. The calculations from the elemental analyses alone, or per cent of fluorine plus infrared estimates of phenyl glycidyl ether content give minimum molecular weights which agree very well with each other and with the observed molecular weight (996 vs. 1006 vs. 1063).

Anal. Calcd for 2.5 mol of HFA/1 mol of PGE/4 mol of AGE ($C_{81}H_{100}F_{30}O_{25}$): C, 47.6; H, 4.9; F, 27.95. Found: C, 48.26; H, 4.74; F, 27.23.

M. Reaction of HFA with Octene-1 in the Presence of Phenyl Glycidyl Ether.—Octene-1 (11 g, 0.1 mol, Phillips Chemical Co., pure grade), phenyl glycidyl ether (distilled, 30 g, 0.2 mol), hydroquinone (0.01 g), and HFA (17 g, 0.1 mol) were allowed to react according to procedure A. The tube was held at 75° for 1 hr. The internal pressure reached 15 psi, and there was no pressure drop. The inside temperature was then raised to 100° for 2 hr. The gauge pressure fell to zero (atmospheric) within 1 hr. The tube was cooled and vented. The product was a clear, nonviscous liquid (51 g). The infrared spectrum of the crude product (5% in CCl_4) greatly resembled straight phenyl glycidyl ether, but with increased absorption at 2.9–3.0 and at 7.7 μ , indicating that some adduct was formed.

On distillation, the fractions were (1) 12.1 g, bp 35–53° (0.7 mm), almost all at 52–53° (0.7 mm); (2) 7.5 g, bp 53–71° (0.7 mm); (3) 20.7 g, bp 71–73° (0.6 mm); and (4) 1.6 g of residue, clear, nonviscous liquid.

The infrared spectrum of fraction 1 showed the bands expected for the HFA–octene adduct, *i.e.*, 2.8 (fairly weak, OH), 6.6, and doublets at 6.7, 6.8 (fairly weak, C=C), 8.0 8.6 (very strong, C—F), and 10.1, 10.6 (mod., —CH=CH—), and 14.1 μ (moderate, C—F). This fraction, although not redistilled to remove small amounts of low boiling material, gave an elemental

analysis which supported this structure. The boiling point was in the expected range from the literature value for the 1-nonene–HFA adduct.³

Anal. Calcd for $C_{11}H_{16}F_6O$: C, 45.37; H, 5.99; F, 42.70. Found: C, 49.50; H, 5.90; F, 38.0.

The infrared spectra of fractions 3 and 4 were exactly those of phenyl glycidyl ether. Fraction 2 was a mixture of the adduct and phenyl glycidyl ether.

Thus about 27 of the original 30 g of phenyl glycidyl ether were recovered, and about 50% of the octene and HFA were converted into adduct. There was no evidence for secondary products which might result from reaction of the adduct with phenyl glycidyl ether.

N. Reaction of HFA with Styrene.—Styrene (64 g, 0.5 mol, Eastman White Label) and hydroquinone (0.01 g) were placed in the 300-cc bomb, and HFA (99 g, 0.6 mol) was added under nitrogen as in procedure A. Shaking was started below 0°, and the tube was then heated at 130° for 1 hr. An appreciable exotherm was observed during this period indicating a slow reaction, and the pressure rose to 370 psi. However, there was no pressure drop, which indicated a negligible reaction of the HFA. The internal temperature was then raised to 150° for 1 hr. Again an exotherm was evident, but again no pressure drop was observed (415 psi). The internal temperature was raised to 165° for 4 hr, and again the exotherm, but no pressure drop, was observed (450 psi). The tube was cooled, and 72 g of a stiff gel were removed. This gel was soluble in benzene, and slightly soluble in acetone. The product was treated with three successive 250-ml portions of acetone in an Osterizer, and the extracts were combined and distilled at 40–50 mm. About 10 g of styrene were recovered, bp 25° (40–50 mm). The distillation residue was dried in a vacuum oven at 70° for 14 hr. It was a gummy, tacky solid (2 g) with mol wt 629 (cryoscopic, benzene). The inherent viscosity (0.25% in benzene) was 0.023. The elemental analyses indicate 83–86 wt % styrene, or eight to nine molecules of styrene present for every molecule of HFA, and a formula weight of 894. The infrared spectrum showed bands at 2.8 (weak, —OH), 5.95 (C=C), and 8.2 and 8.6 μ (strong, C—F).

Anal. Calcd for $(C_8H_8)_8(C_8F_8O)$ or $C_{67}H_{54}F_8O$: C, 80.5; H, 6.5; F, 11.5. Found: C, 80.48; H, 6.58; F, 10.79.

The acetone-insoluble residue (59 g) was a stiff, brittle plastic. *Anal.* Calcd (for polystyrene) C_8H_8 : C, 92.3, H, 7.7. Found: C, 90.0; H, 7.6; F, 2.3.

After reprecipitation out of benzene with acetone in an Osterizer, the infrared spectrum was that of polystyrene, and the F content dropped to less than 0.4%. The ebullioscopic molecular weight in benzene was 6700 ± 700 . Thus both fractions exhibited a lower molecular weight than calculated for one HFA end group (0.4% by weight of HFA per chain in the higher molecular weight fraction would lead to a molecular weight of *ca.* 25,000). This is a much higher chain-transfer level than is found in free-radical-initiated styrene polymerizations.

Registry No.—Adduct A, 646-97-9; adduct B, 15735-54-3; adduct C, 15735-55-4; adduct D, 15735-56-5; adduct G, 15735-57-6; adduct H, 15816-02-1; adduct J, 15735-58-7; HFA, 684-16-2; AGE, 106-92-3; phenyl glycidyl ether, 122-60-1; octene-1, 111-66-0; styrene, 100-42-5.

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