Anal. Calcd for $C_{14}F_{18}S_4$: C, 26.34; F, 53.57; S, 20.09; mol wt, 638. Found: C, 26.49; F, 53.83; S, 20.09; mol wt, 638 (mass spectrometry).

Infrared absorptions (KBr wafer) were at 6.18 and 6.54 (C=C) and 7.5–9 μ (C—F). Ultraviolet absorption occurred at $\lambda_{max}^{isooctane}$ 296 mμ (ϵ 21,100). F^{19} nmr resonances are an A_3B_3 group centered at +56.2 ppm for CF_3—C=C (area 2) and a singlet at +61.6 ppm for CF_3 (area 1).

B.—A mixture of 27.5 g (0.25 mol) of potassium sulfide, 30 ml (38 g, 0.50 mol) of carbon disulfide, and 150 ml of distilled dimethylformamide was stirred at 25° for 2 hr. Then 58.2 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene was added, and the reaction was continued for 3 days at 25°. The resulting mixture of solid and orange liquid was diluted with 1.5 l. of water and extracted with two 100-ml portions of petroleum ether. The combined organic layers were dried and distilled to give 23.1 g (34%) of **10**, bp 82° (20 mm), identified by comparison of the infrared and nmr spectra with those of a known sample (see above).

This synthesis was also carried out using sodium sulfide nonahydrate, carbon disulfide, and 2,3-dichlorohexafluoro-2-butene in methanol, but the yield was only 13%.

An attempt to form a sulfonium salt with boiling benzyl bromide failed.

Bis(trifluoromethyl)thioketene Dimer (14).—Powdered potassium sulfide (44 g, 0.4 mol) and 100 ml of dimethylformamide were stirred and cooled in a −80° bath while 40 g (0.2 mol) of octafluoroisobutylene was added as a gas. When addition was complete, the mixture was stirred at 0° for 0.5 hr. Vacuum was then applied and volatile material was collected in a −80° trap while the reaction mixture was heated to 100°. The solid product was isolated by filtration, washed with water, and dried to give 19.5 g (62%) of crystalline bis(trifluoromethyl)thioketene dimer, **14**. Recrystallization from chloroform gave product, mp 85–86°, shown by mixture melting point and infrared spectrum to be identical with an authentic sample.[4]

Yields in this reaction were much lower at higher reaction temperature, presumably because the product is sensitive to attack by potassium sulfide in dimethylformamide. With hydrated sodium sulfide in dimethyformamide, a 44% yield was obtained.

Bis(perfluoro-1,1-dimethylethyl) Trisulfide (15) and Tetrasulfide (16). A.—The dimethylformamide filtrate above, from which thioketene dimer **14** had been separated, was diluted with water to cause separation of about 3 g of oil. The principal component, separated by gas chromatography, was the trisulfide **15**, mp 44–44.5° after recrystallization from chloroform. No functional groups were detected by infrared analysis and no proton by nmr analysis. The F^{19} nmr was a singlet at +63.3 ppm.

Anal. Calcd for $C_8F_{18}S_3$: C, 17.99; S, 18.01. Found: C, 18.18; S, 18.10.

B.—The assumption that trisulfide **15** is formed from a reaction initiated by fluoride ion was confirmed by the greatly increased yields obtained with sulfur plus potassium or cesium fluoride in place of potassium sulfide.

A mixture of 152 g (1.0 mol) of cesium fluoride, 64 g (2.0 g-atoms) of sulfur, and 250 ml of dimethylformamide was stirred while 700 g (3.5 mol) of octafluoroisobutylene was added as a gas. The exothermic reaction was maintained at 60–70° by controlling the rate of addition. When the sulfur was consumed during the addition, more was added to give a total of 112 g (3.5 g-atoms) of sulfur used. The mixture was then poured into water in a hood (caution; toxic gas evolved), and the mixture was extracted with petroleum ether. The organic extract was washed with water, dried, and cooled to −80° to precipitate 142 g (21%) of thioketene dimer **14**. Distillation of the filtrate gave 326 g (35% based on olefin, 52% based on sulfur) of trisulfide **15**, bp 96–100° (50 mm), which solidified on cooling and was shown to be identical with the earlier sample. A 20-g fraction boiling up to 123° (50 mm) probably contained the tetrasulfide **16**.

A similar run carried out with potassium fluoride in place of cesium fluoride gave a low yield of tetrasulfide **16** in a solid fraction with bp 123–138° (45 mm). Recrystallization at −80° from petroleum ether and then from chloroform gave **16**, mp 74–77°. F^{19} nmr showed a singlet at +63.3 ppm.

Anal. Calcd for $C_8F_{18}S_4$: C, 16.98; S, 22.66. Found: C, 17.36; S, 22.04.

Registry No.—**1**, 2342-08-7; **3**, 2924-06-3; **4**, 2924-05-2; **6**, 16005-65-5; **9**, 16005-61-1; **10**, 16005-62-2; **11**, 16031-09-7; **14**, 7445-61-6; **15**, 16005-64-4; **16**, 16065-65-9.

Fluoro Olefins. II. Isomerization of β-Substituted Perfluoro Olefins. Kinetic *vs.* Equilibrium Control[1]

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The scope of the synthetic sequence for the preparation of β-substituted perfluoro olefins from triphenylphosphine, sodium chlorodifluoroacetate, and polyfluorinated ketones has been extended to the polyfluorinated ketone, 1-phenylpentafluoropropanone. The product mixture consisted of 2-phenylheptafluoro-1-butene and *cis*- and *trans*-2-phenylheptafluoro-2-butene. The latter arises by a fluoride ion catalyzed isomerization of 2-phenylheptafluoro-1-butene to the isomeric internal fluoro olefin. The product ratio of external olefin to internal olefin and the *trans/cis* ratio of the internal olefin were found to be highly dependent upon the choice of alkali metal chlorodifluoroacetate and reaction time. With sodium and potassium chlorodifluoroacetate, the isomerization yielded an initial *trans/cis* (k_2/k_1) kinetic ratio of 1.2 and 2.0, respectively, which is markedly different from the equilibrium ratio of ~6.7. The effect of added alkali metal fluoride salts greatly accelerated the decomposition of the alkali metal chlorodifluoroacetates in the Wittig reaction and enhanced the equilibration of the *trans–cis* isomers in the order Cs ≫ Rb > K ≫ Na. Two mechanisms are suggested to explain the initial kinetic ratio of *trans/cis* isomers. The first mechanism involves a linear transition state with or without the intermediacy of a "discrete" fluoro carbanion. The second mechanism involves a six-membered cyclic transition state consisting of fluoro olefin and alkali metal fluoride.

The importance of fluoride ion has been well demonstrated in a wide variety of ionic reactions of perfluoro- and polyfluorinated olefins.[3] Owing to its unique reactivity as a strong nucleophile in unsaturated fluorine systems, it has been employed as a catalyst for anionic polymerizations, condensation and addition reactions, and rearrangements of polyfluorinated olefins. The major part of its applicability in these cases is to form

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[1] (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 9K; (b) taken in part from the Doctoral Dissertation of F. E. H., the University of Iowa, Aug 1966; (c) preliminary report, D. J. Burton and F. E. Herkes, *Tetrahedron Lett.*, No. 50, 4509 (1965).

[2] National Aeronautics and Space Administration Trainee, 1964–1966.

[3] For an excellent review, see R. D. Chambers and R. H. Mobbs, *Advan. Flourine Chem.*, **4**, 50 (1965).

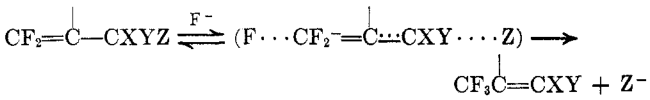
in situ perfluoro- and polyfluorinated carbanions which can then react further to give other products.

Although much is known concerning the stability[4,5] and reactivity[3] of these fluoro carbanions, little is known

$$R_fCF{=}CF_2 \underset{}{\overset{F^-}{\rightleftharpoons}} (R_fCFCF_3)^-$$

as to their intermediacy in fluoride-catalyzed fluoroolefin rearrangements.

The earliest report of fluoride-catalyzed isomerization of perfluoro- and polyfluorinated olefins was by Miller and coworkers.[6-8] They found that addition of fluoride ion to fluoropropenes in formamide brought about rearrangement of the double bond with the subsequent elimination of halide ion.



$$CF_2{=}\overset{|}{C}{-}CXYZ \overset{F^-}{\rightleftharpoons} (F\cdots CF_2{}^-{=}\overset{|}{C}{\cdots}CXY\cdots\cdots Z) \longrightarrow CF_3\overset{|}{C}{=}CXY + Z^-$$

They postulated a rearrangement which proceeded through a low-energy SN2′ transition state with or without the intermediacy of a "discrete" carbanion (*i.e.*, having a finite lifetime). Similarly, Dresdner[9] and Gibbs[10] have carried out reactions of perfluoro olefins in the vapor phase utilizing both alkali metal and alkaline earth fluorides as catalysts to give highly substituted isomeric perfluoro olefins. Gens and coworkers[11] have used exchange techniques employing F^{18} to demonstrate equilibration of perfluoro olefins with metallic fluorides. Finally, Miller[12] and Dresdner[9] have carried out the isomerization of perfluorodienes to perfluorodialkylacetylenes *via* a series of fluoride ion catalyzed substitutions and rearrangement reactions.

These rearrangement reactions provided excellent models for demonstrating the allylic SN2′ nature of the isomerization reaction, but they gave no information as to the stability and structural configuration of the transistion state of this rearrangement process. The simplest model for this type of rearrangement involves a bimolecular rate determining attack of fluoride ion on the fluoro olefin followed by the concerted[13] expulsion of halide ion in the same step. It thus seems necessary that more information is needed to demonstrate the mode of this rearrangement and its scope with regard to steric factors, stability of a possible transient fluoro carbanion, and geometrical requirements for stereochemical products which might arise in several different mechanisms.

Results and Discussion

In an attempt to extend the synthetic sequence of the preparation of β-substituted perfluoro olefins[14] to higher homologous fluoro olefins, we have observed the formation of the desired 2-phenylheptafluoro-1-butene (IV), formed by the reaction of triphenylphosphine (I), sodium chlorodifluoroacetate (II), and 1-phenylpentafluoropropanone (III) in diglyme at 100°, and the more stable isomeric internal 2-phenylheptafluoro-2-butene (V) formed by the fluoride ion catalyzed rearrangement of IV. The fact that the rearrangement proceeded to a considerable extent during the Wittig reaction[15] led us to investigate this reaction in more detail.

$$\underset{\text{I}}{(C_6H_5)_3P} + \underset{\text{II}}{CF_2ClCO_2Na} + \underset{\text{III}}{C_6H_5COC_2F_5} \xrightarrow[100°]{\text{diglyme}} \underset{\text{IV}}{C_6H_5C(C_2F_5){=}CF_2} \xrightarrow{F^-} \underset{\text{V }(\textit{cis–trans})}{C_6H_5C(CF_3){=}CFCF_3}$$

When the Wittig reaction was carried out using equimolar quantities of I, II, and III in dry diglyme at 100°, a 60% yield of a mixture of isomeric olefins was obtained after 20 hr. The three isomers were readily separated on a 10 ft × 0.25 in. β,β-oxidipropionitrile column at 65° in the following order: *trans* V, IV, and *cis* V. The structure of the isomeric olefins was determined by elemental analysis, infrared, ultraviolet, and H^1 and F^{19} nmr spectroscopy. The structure of *cis* and *trans* V was further confirmed by independent synthesis employing phenyllithium and perfluoro-2-butene at −78°.[16]

The olefinic mixture obtained when equimolar amounts of I, II, and III were employed in diglyme at 100° was composed of 90% V in a *trans/cis* ratio of 1.9. Support for a fluoride ion catalyzed rearrangement of the initially produced IV was found when the same ylide reaction was quenched after 70% of the theoretical amount of carbon dioxide had evolved (6.5 hr). In this case, 95% of the olefinic products consisted of IV. The remaining 5% was composed of V in a ratio of 1.2, *trans/cis*. By varying the concentration of ylide, little change in the yield of products and isomer ratio was observed after 20 hr (*cf.* Table I).

TABLE I

REACTION OF 1-PHENYLPENTAFLUOROPROPANONE WITH TRIPHENYLPHOSPHINE AND SODIUM CHLORODIFLUOROACETATE IN DIGLYME AT 100°

Molar ratio			Time,	Olefin,[a]	IV,[b]	V,[b] %		
I	II	III	hr	%	%	*cis*	*trans*	*trans/cis*
1	1	2	20	29	31.3	27.2	42.8	1.2
1	1	1	6.5	44	94.9	2.4	2.8	1.2
1	1	1	20	60	10.6	30.9	58.6	1.9
2	2	1	20	65	9.7	33.7	56.6	1.7
3	3	1	20	65	19.2	30.6	49.8	1.6
1	2	1	0.5[c]	48	100	...	...	...

[a] Glpc yield of net olefin based on ketone. [b] Mole per cent of total olefin. [c] Lithium chlorodifluoroacetate employed at 90°.

Owing to the fact that lithium fluoride is a poor fluoride ion source in fluoro-olefin reactions, we carried out the Wittig reaction using lithium chlorodifluoroacetate (VI) in place of II. Employing diglyme as the solvent, the time required for 75% of the theoretical amount of carbon dioxide to evolve was 48 hr compared to 6.5 hr using II. The isolated olefin, however, con-

[4] A. Streitwieser and D. Holtz, *J. Amer. Chem. Soc.*, **89**, 692 (1967).

[5] S. Andreades, *ibid.*, **86**, 2003 (1964).

[6] W. T. Miller, Jr., U. S. Patent 2,842,603.

[7] J. H. Fried and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **81**, 2078 (1959).

[8] W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

[9] R. D. Dresdner, F. N. Tiumac, and J. A. Young, *J. Org. Chem.*, **30**, 3524 (1965).

[10] H. H. Gibbs, U. S. Patent 3,000,979 (1962).

[11] T. A. Gens, U. S. Atomic Energy Commission, ORNL-2306, 1957, p 117; T. A. Gens, J. A. Wethington, A. R. Brose, and E. R. Van Artsdalen, *J. Amer. Chem. Soc.*, **79**, 1001 (1956).

[12] W. T. Miller, Jr., W. Frass, and P. R. Resnick, *ibid.*, **83**, 1767 (1961).

[13] Although the mechanism implies a concerted rearrangement, the possible formation of an intermediate anion must also be considered.[7]

[14] F. E. Herkes and D. J. Burton, *J. Org. Chem.*, **32**, 1311 (1967).

[15] The source of fluoride ion arises mainly in the decomposition of II and/or the intermediate ylide, $(C_6H_5)_3P{=}CF_2$.

[16] S. Andreades, *J. Amer. Chem. Soc.*, **84**, 864 (1962).

sisted only of IV. By employing dimethylformamide[17,18] (DMF) as the solvent instead of diglyme, the time of decarboxylation of VI was decreased approximately 100-fold (0.5 hr *vs.* 48 hr). This route was subsequently used as an alternate route to the preparation

$$\mathrm{I} + \mathrm{III} + \mathrm{CF_2ClCO_2Li} \xrightarrow{\mathrm{DMF}} \underset{\mathrm{IV}}{\mathrm{C_6H_5C(CF_2CF_3){=}CF_2}}$$

of terminal perfluoro olefins containing more than three carbon atoms.

Surprisingly, the *in situ* formation of fluoride ion in this Wittig reaction (as sodium fluoride) serves as a good source of catalyst for this rearrangement in contrast to other fluoro olefin reactions[19] with sodium fluoride which conversely are almost nil. The importance of this *in situ* formation of fluoride ion was further demonstrated by allowing IV to react with finely ground sodium fluoride in diglyme at 100° (Table II). After 45 hr, which was twice the time employed for the Wittig reaction, no isomerization to V occurred and only after 720 hr did any appreciable rearrangement take place (25%).

TABLE II

REACTION OF 2-PHENYLHEPTAFLUORO-1-BUTENE WITH ALKALI METAL FLUORIDES IN DIGLYME AT 100°

IV (MF) Molar ratio	Time, hr	V,[a] % *cis*	V,[a] % *trans*	IV,[a] %	*trans/cis*
1:2 (NaF)	45	0	0	100	...
1:2 (NaF)	72	1.9	2.8	95	1.5
1:2 (NaF)	720	12.2	13.6	74.3	1.2
1:2 (KF)[b]	47	18.8	81.2	0	4.3
1:2 (KF)	48	18.6	81.4	0	4.4
1:2 (KF)	720	14.5	84.5	0	6.0
1:2 (KF)[c]	20	30.3	68.3	0	2.2
1:2 (KF)[d]	20	0	0	100	...
1:2 (RbF)	24	13.7	86.4	0	6.4
1:2 (CsF)	31	11.5	88.5	0	7.7
1:2 (CsF)	45	12.3	87.7	0	7.3
1:0.13 (CsF)	23	19.8	80.2	0	4.1

[a] Mole per cent in total olefin mixture. [b] The ratio of *trans* to *cis* was 1.9 after 4.0 hr and 2.1 after 24 hr. [c] Sixfold excess of water added to the reaction mixture. [d] Threefold excess of perfluoropropionic acid added to the initial reaction mixture.

From the fact that the relative nucleophilic reactivities of the alkali metal fluorides decreases in the order Cs ≫ Rb > K > Na ≫ Li, one might predict that an increase in the extent of rearrangement would occur employing other salts of chlorodifluoroacetic acid. Potassium chlorodifluoroacetate (VII) was subsequently prepared and the ylide reaction repeated in an analogous fashion as that described for the sodium salt. This resulted in all cases in essentially complete conversion (>98%) into V. In addition to the complete rearrangement of IV to V by potassium fluoride, the *trans/cis* ratio increased to 2.0 after >70% of the theoretical amount of carbon dioxide had evolved (4 hr) compared to 1.2 which was observed under similar conditions with II (Table III).

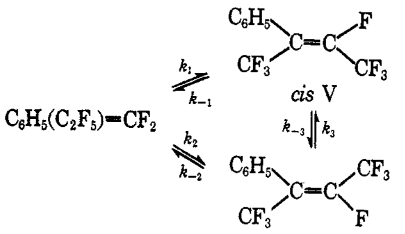
TABLE III

REACTION OF 1-PHENYLPENTAFLUOROPROPANONE WITH TRIPHENYLPHOSPHINE AND POTASSIUM CHLORODIFLUOROACETATE IN DIGLYME AT 100°

Molar ratio I	Molar ratio III	Molar ratio VII	Time, hr	Olefin,[a] %	IV,[b] %	V,[b] % *cis*	V,[b] % *trans*	*trans/ cis*
1	1	1	4	31	0	32.9	67.2	2.0
1	1	1	20	44	1.0	30.8	69.2	2.2
1	1	1	20	37	0	29.8	70.3	2.3
2	1	2	20	82	2.1	27.3	70.6	2.6

[a] Glpc yield of net olefin based on ketone. [b] Mole per cent of total olefin.

SCHEME I



The extent of this kinetically controlled isomerization by sodium and potassium fluoride to the initial *trans/cis* ratio is not readily apparent since a slow equilibration by sodium and potassium fluoride competes favorably with this isomerization. From Scheme I, it can be seen that at zero time after rearrangement has occurred, the ratio of k_2 to k_1 is simply the initial kinetic ratio.[20] In the case where II was employed in the Wittig reaction, the initial k_2/k_1 ratio is, or very nearly

$$\mathrm{d}(trans\ \mathrm{V})/\mathrm{d}(cis\ \mathrm{V}) = k_2/k_1\ (t = 0)$$

equals, 1.2 and increases with time to 1.9 after 20 hr. With VII, complete rearrangement to V was observed if the reaction is quenched after >70% of the theoretical amount of carbon dioxide had evolved (4 hr). The observed kinetic ratio is approximately 2.0 and changes only 10% over a 16-hr period. This ratio is appreciably larger than 1.2 which was obtained using II. The isomerization of IV by potassium fluoride to V is apparently very fast at 100° and the equilibration of *cis* and *trans* V is very slow and thus makes the value of 2.0 a valid number for the initial kinetic ratio (k_2/k_1). On the other hand, the isomerization of IV by sodium fluoride is much slower compared to that of potassium fluoride since only 5% rearrangement to V occurs after 6 hr and increases to 90% only after 20 hr have elapsed. Thus it becomes necessary to determine some of the underlying factors which effect the extent of the kinetic reaction control when II and VII are employed in the Wittig reaction. Since both salts, sodium and potassium fluoride, are generated *in situ*, a solubility difference and hence a concentration dependence could account for the increased amount of *trans* olefin in the case of potassium chlorodifluoroacetate. However, evidence in the case of II seems to infer a leveling off after 20 hr at a *trans/cis* ratio of 1.6. Miller[7] has stated that the rates of reaction of halide ions with chlorofluoroallyl chlorides show a prominent dependence upon the concentration of nucleophile, and Graham[21] has observed a direct dependence on the reaction velocity with the amount of cesium fluoride

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[17] This effect can best be rationalized by the decreased solvation of the chlorodifluoroacetate anion and the increased solvation of the lithium cation by the dipolar aprotic solvent.[18]

[18] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[19] C. G. Krespan, *J. Org. Chem.*, **27**, 1813 (1962).

[20] W. O. Haag and H. Pines, *J. Amer. Chem. Soc.*, **82**, 387 (1960).

[21] D. P. Graham, *J. Org. Chem.*, **31**, 955 (1966).

added in the anionic polymerization of perfluoroethylene. In the latter case, a surface reaction with the cesium fluoride was suggested in which the "cesium atom of the ion pair retain its position in the lattice of the cesium fluoride crystal."

The equilibration of *cis* and *trans* V to the thermodynamic ratio was demonstrated by heating IV with a twofold excess of finely ground potassium fluoride in diglyme at 100° (Table II). After 4 hr, the rearrangement was complete. The *trans/cis* ratio of 1.9 after 4.0 hr increased to only 2.1 after 24 hr, again indicating a slow equilibration by potassium fluoride. These values agree well with the results obtained in the Wittig reaction employing VII. By allowing this reaction to continue, the respective *trans/cis* isomers slowly equilibrated and was maximized at 6.0 after 720 hr.

The isomerization of IV was also carried out with rubidium fluoride and cesium fluoride (Table II) to compare their relative reactivities with that of sodium and potassium fluoride. With rubidium fluoride, the *trans/cis* ratio was 6.4 after 24 hr and that of cesium fluoride was 7.3–7.7 after 31 hr. Thus the relative rate of approach to equilibrium of V by alkali metal fluorides is CsF ≫ RbF > KF ≫ NaF.

This equilibrium was further demonstrated by allowing the pure *cis* and *trans* isomers of V to react under similar conditions with finely ground potassium, rubidium, and cesium fluoride thereby enabling equilibrium to proceed from either side. The rate of equilibration was much faster with the *trans* isomer (Table IV) than that of the *cis* isomer (Table V). With cesium fluoride, the equilibrium ratio of 7.8 was reached after 24 hr compared to 82 hr for both potassium and rubidium fluoride. The equilibrium constant of approximately 6.7 for this fluoride ion catalyzed isomerization thus corresponds to a difference in free energy of formation ($\Delta F°$) of the *cis* and *trans* isomers of ~ -1.41 kcal/mol at 100° in favor of the *trans* isomer of V. The apparent discrepancy in the equilibrium constant comparing potassium and rubidium fluoride to cesium fluoride for this isomerization at 100° is not clear at this time. A possible explanation for this phenomenon is a preferential fluoride ion catalyzed dimerization or telomerization of the *cis* isomer in the case using cesium fluoride, since only 85–91% of the total olefin mixture was accounted for in this equilibration.[22] This, however, could only occur if the rate of dimerization of the *cis* olefin was faster than equilibration by cesium fluoride. A similar trend in this predominance of a *cis* isomer to react preferently with cesium fluoride was recently reported by Dresdner.[9] They observed in the vapor phase dimerization of perfluoropropene catalyzed by cesium fluoride that more *cis*-$(CF_3)_2CFCF{=}CFCF_3$ is formed relative to the *trans* isomer at 100°, and by increasing the temperature to 150° this *cis/trans* ratio decreased by a factor greater than 10. In addition, a tenfold increase in $(CF_3)_2C{=}CFCF_2CF_3$ was also observed with this temperature rise. In the equilibrium study using potassium and rubidium fluoride, 97–100% total recovery of olefin was usually observed.

TABLE IV

REACTION OF *cis*-2-PHENYLHEPTAFLUORO-2-BUTENE WITH ALKALI METAL FLUORIDES IN DIGLYME AT 100°

MF^a	Time, hr	*cis* V,^{b} %	*trans* V,^{b} %	*trans/cis*
KF	65	16.0	84.00	5.2
KF	102	13.3	86.7	6.5
RbF	79	12.1	97.9	7.3
RbF	96	12.7	87.2	6.8
CsF	55	11.5	88.5	7.6
CsF	65	11.3	88.7	7.9

^{a} Salt in twofold excess. ^{b} Mole per cent in olefin mixture.

TABLE V

REACTION OF *trans*-2-PHENYLHEPTAFLUORO-2-BUTENE WITH ALKALI METAL FLUORIDES IN DIGLYME AT 100°

MF^a	Time, hr	*cis* V,^{b} %	*trans* V,^{b} %	*trans/cis*
KF	24	7.0	93.0	13.3
KF	82	13.3	86.7	6.5
KF	102	13.6	86.4	6.4
RbF	24	13.4	86.6	6.4
RbF	82	12.8	87.2	6.8
RbF	102	12.8	87.2	6.8
CsF	24	11.4	88.6	7.8
CsF	82	11.2	88.8	7.9
CsF	102	11.3	88.7	7.8

^{a} Salt in twofold excess. ^{b} Mole per cent in total olefin mixture.

To test further the catalytic activity of other alkali metal fluorides in the Wittig reaction, a series of experiments were carried out employing the usual reagents (I, II, and III) and a twofold excess of potassium, rubidium, and cesium fluoride. The results of these experiments are shown in Table VI.

TABLE VI

REACTIONS OF 1-PHENYLPENTAFLUOROPROPANONE WITH TRIPHENYLPHOSPHINE AND SODIUM CHLORODIFLUOROACETATE IN THE PRESENCE OF ALKALI METAL FLUORIDES IN DIGLYME AT 100°

Molar ratio				Time,	Olefin,^{a}	IV,^{b}	V,^{b} %		*trans/*
I	II	III	MF	hr	%	%	*cis*	*trans*	*cis*
1	1	1	2 (KF)	6.5^c	51	84.4	4.9	10.7	2.2
2	2	1	4 (KF)	20	58	0	31.4	68.7	2.2
1	1	1	2 (RbF)	3.5^c	54	85.8	4.8	9.4	2.0
1	1	1	2 (RbF)	2.8^c	54	75.5	8.9	15.6	1.7
1	1	1	2 (RbF)	20	48	0	13.4	86.6	6.4
1	1	1	2 (CsF)	1.0^c	35	0	15.6	84.4	5.4
1	1	1	2 (CsF)	20	48	0	12.5	87.5	7.0

^{a} Glpc yield of total olefin based on starting ketone. ^{b} Mole per cent of total olefin. ^{c} Time required for 70% of the theoretical amount of carbon dioxide to evolve.

If the reaction employing potassium fluoride is quenched after all the carbon dioxide had evolved (6.5 hr), the amount of IV in the olefinic mixture is 84%. The *trans/cis* ratio was 2.2 and appears to be similar to the initial kinetic ratio (k_2/k_1) obtained employing I, III, and VII (Table II). By allowing this reaction to continue for 20 hr, total rearrangement of IV occurred to give a *trans/cis* ratio of 2.2 similar to that obtained after 6.5 hr. This ratio also compares well with that found using potassium fluoride and IV alone in diglyme at 100° for 20 hr (Table III). This further supports the fact that with added potassium fluoride as the source of fluoride ion, the rearrangement of IV is very fast compared with the subsequent equilibration of the *cis* and *trans* isomers of V. The assumption that the value of 1.9–2.2 is the initial kinetic ratio in the isomer-

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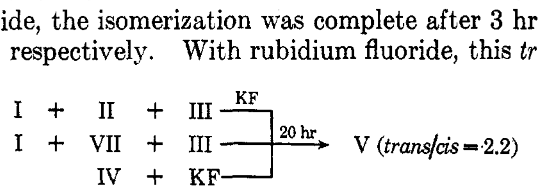
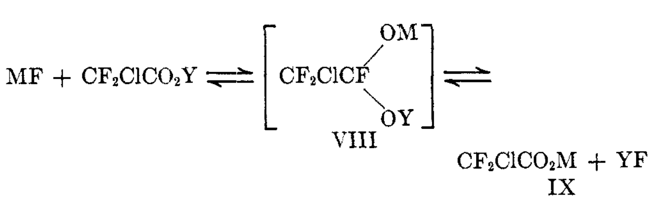
(22) A control experiment employing only the respective *cis* and *trans* isomers of V in diglyme at 100° failed to produce any thermal isomerization.

ization of IV by potassium fluoride is thus justified in light of these results. With added rubidium and cesium fluoride, the isomerization was complete after 3 hr and 1 hr, respectively. With rubidium fluoride, this *trans*/*cis* isomer ratio was approximately 2.0 after 3 hr and increased to the equilibrium value of 6.4 after 20 hr. The greater reactivity of cesium fluoride was shown in the *trans*/*cis* ratio of 5.4 after only 1 hr.



The rate of carbon dioxide evolution also increases with the addition of rubidium and cesium fluoride. This enhanced decarboxylation is due most probably to a direct reaction of the fluoride salt with II to produce a new alkali metal chlorodifluoroacetate *in situ*.[23]



Y = Na, Li
M = Na, K, Rb, Cs

This equilibrium to form IX from II is greater for the rubidium and cesium cation than that for the potassium cation as indicated in the rate of decarboxylation with these added alkali metal fluorides. This observation was further demonstrated when VI was used instead of II (Table VII). As pointed out earlier, the total time required for the decarboxylation of VI in diglyme was 48 hr. With added lithium fluoride, no change in this rate occurred as expected. However, with added sodium, potassium, rubidium, and cesium fluoride, the rate was vastly increased, indicating a greater equilibrium toward IX in favor of the larger cation. The fact[18] that inorganic lithium salts (*i.e.*, lithium chloride and lithium fluoride) are quite insoluble and tend to form solvates, and some cases form ion pairs, in dipolar aprotic solvents could be the driving force in this equilibrium. Haszeldine[24] has postulated a similar type of equilibrium in the solid state when sodium perfluorovalerate was decarboxylated in the presence of added potassium fluoride. He observed formation of perfluoro-1-butene and perfluoro-2-butene in a 1:1 ratio. He further observed no isomerization when a mixture of perfluoro-1-butene and potassium fluoride was heated alone and also in the dry decarboxylation of sodium perfluorovalerate alone.

Table VII

Reactions of 1-Phenylpentafluoropropanone with Triphenylphosphine and Lithium Chlorodifluoroacetate in the Presence of Alkali Metal Fluorides in Diglyme at 100°

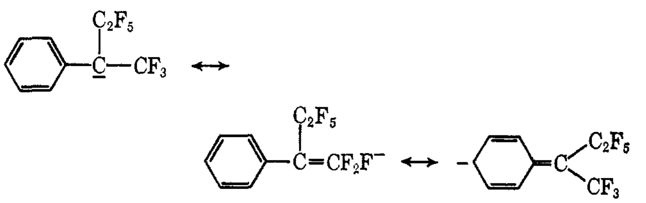
Molar ratio				Time, hr	Olefin,[a] %	IV,[b] %	V,[b] %		trans/cis
I	VI	III	MF				cis	trans	
1	1	1	2 (LiF)	47	31	100	0	0	...
1	1	1	2 (NaF)	20	43	40.7	23.4	35.9	1.8
1	1	1	2 (KF)	3.2	78	0	31.0	69.0	2.2
1	1	1	2 (RbF)	1.8	63	0	23.0	77.0	3.4
1	1	1	2 (RbF)	20	22	0	12.5	87.5	7.0
1	1	1	2 (CsF)	20	32	0	11.4	88.6	7.8

[a] Glpc yield of total olefin based on starting ketone. [b] Mole per cent of total olefin.

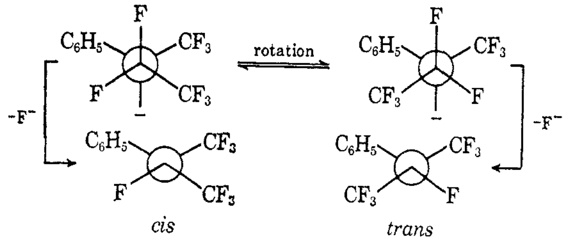
$$KF + C_4F_9CO_2Na \rightleftharpoons C_4F_9CO_2K + NaF$$

Up to this point, little has been said concerning the mechanism of this isomerization. Unfortunately the fact that a slow equilibration of the *cis*/*trans* olefins occurs in the presence of fluoride ion does not lend any definitive information as to the *exact* kinetic distribution of V. The isomerization presumably proceeds through a bimolecular S_N2' type of rearrangement involving the attack of fluoride at the terminal difluoromethylene group rather than that at the saturated carbon atom holding the group displaced since no 2H,2-phenyloctafluorobutane was obtained upon quenching with water.

This facile addition of fluoride ion to the difluoromethylene group has as its driving force, a negatively charged transistion state in which both β-phenyl substitutent and β-perfluoroalkyl groups contribute largely to its stabilization by induction and electron delocalization.



Once this intermediate carbanion is formed, the loss of a β fluorine can occur either *cis* or *trans* to the attacking fluoride ion. An equal probability of *trans* or *cis* elimination will take place if the intermediate carbanion attains a planar configuration or inverts faster than it loses a β-fluorine ion. However, a *cis* elimination of fluoride ion is energetically unfavorable since this would put the two trifluoromethyl groups and also a phenyl and a trifluoromethyl group in an unfavorable eclipsed position. A *trans* elimination which allows free carbon–carbon bond rotation is more reasonable as there are energetically no unfavorable barriers, and hence a nonstereospecific formation of products.



Miller[7] and Park[25] have found that the order of leaving groups in a variety of S_N2' reactions involving fluoro olefins is in the order I > Br > Cl > F > OR > H. That is, if an intermediate carbanion is formed, the departing moiety will depend upon its polar and leaving group character. This presupposes a transient carbanion which can invert or rotate before elimination in a fast

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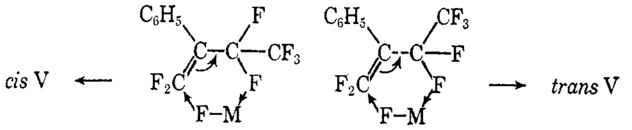
(23) A. N. Nesmeyanov, K. A. Pecherskaya, and G. Ya. Uretskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 240 (1948); *Chem. Abstr.*, **42**, 4924*g* (1948).

(24) R. N. Haszeldine, *J. Chem. Soc.*, **61** (1956).

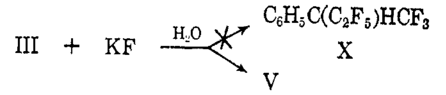
(25) J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, **31**, 1116 (1966).

step. A "free" fluoro-carbanion intermediate does not seem plausible since a greater amount of the *cis* isomer is formed with sodium and potassium fluoride in the initial kinetic ratio compared with the equilibrium ratio.

An additional mechanism which can adequately explain the observed low initial ratio of *trans* to *cis* with different alkali metal fluorides is that of a six-membered cyclic transistion state involving a *cis* removal of fluoride ion by the alkali metal cation to give stereospecific products. The character of the alkali fluoride now becomes important since the more electropositive (greater polarizability) the alkali metal cation, the greater the rate of reaction to produce the isomeric olefins. This is the case in which the series of reactivity of the alkali metal fluorides would be in the order Cs ≫ Rb > K > Na. The cyclic transistion state of S_N2'-type reactions is not without precedent. Miller[26] has suggested that a cyclic intermediate may be involved in the reaction of polyfluorinated propenes with monohalogen iodides. This type of mechanism also adequately explains Miller's results employing sodium iodide and other alkali metal halides with acyclic polyfluorinated propenes. The transition state will thus involve the concerted removal of the least basic β substituent.



Trapping Experiments.—In an attempt to demonstrate the existence of a possible carbanion intermediate, trapping experiments were carried out employing water as a source of labile protons. In the reaction of IV with potassium fluoride in diglyme using a sixfold excess of water, no formation of 2H,2-phenyloctafluorobutane (X) was observed. The isomerization was complete after 20 hr to give V in a *trans/cis* ratio of 2.2 similar to that obtained in the absence of water. When a stronger proton source such as perfluoropropionic acid was employed, no rearrangement took place. This was due to the formation of the relatively unreactive HF_2^- which is poor nucleophile for fluoro-olefin systems.[7]



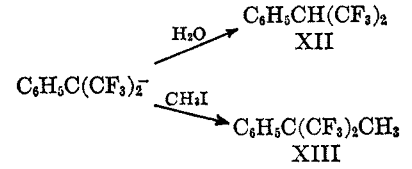
$$\text{III} + \text{KF} \xrightarrow{H_2O} \begin{cases} C_6H_5C(C_2F_5)HCF_3 \ (\text{X}) \\ \text{V} \end{cases}$$

Graham[27] has observed a similar trend in attempts to trap perfluoro carbanions formed from long-chain terminal perfluoro olefins and cesium fluoride with carbon dioxide at low temperatures. The rearrangement observed by Graham proceeded faster than the addition of carbon dioxide, even at −25°.

In contrast to the carbanion formed from IV and potassium fluoride, 2-phenylpentafluoropropene (XI) readily reacted with water and methyl iodide in the presence of cesium fluoride to give the respective protonated (XII) and alkylated (XIII) products. In this case, the intermediate carbanion is formed in a reversible process which can then react further to form new products, whereas in the former example the intermediate carbanion collapses irreversibly to form the more stable and unreactive V.

$$C_6H_5C(CF_3){=}CF_2 + CsF \rightleftharpoons C_6H_5C(CF_3)_2^-$$

XI



$$C_6H_5C(CF_3)_2^- \begin{cases} \xrightarrow{H_2O} C_6H_5CH(CF_3)_2 \ (\text{XII}) \\ \xrightarrow{CH_3I} C_6H_5C(CF_3)_2CH_3 \ (\text{XIII}) \end{cases}$$

In conclusion, it should be pointed out that no suitable mechanism explains *all* the results. The pros and cons of the most reasonable interpretations are given for both linear and cyclic transition states involving a certain degree of carbanion character. Additional work is thus required in addition to trapping of intermediate species. Work is in progress to determine some of these limiting variables in this rearrangement reaction.

Experimental Section

All boiling points are corrected. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using a neat film calibrated *vs.* polystyrene. Ultraviolet spectra were obtained on a Cary Model 11 recording spectrophotometer using both 95% ethanol and purified cyclohexane. Glpc analysis of the isomeric fluoroolefin mixtures were performed on a F & M Model 720 dual-programmed gas chromatograph using helium as the carrier gas. Quantitative analyses were determined from the relative areas under the peaks using external standards of both olefin and ketone. Column A was a 10 ft × 0.25 in. o.d. copper column packed with 10% w/w β,β-oxidipropionitrile on 100–120 mesh Gas Chrom P. Column B was a 10 ft × 0.25 in. o.d. copper column packed with 20% w/w Carbowax 20M supported on 100–120 mesh Gas Chrom P.

Materials.—Triphenylphosphine was obtained from Eastman Organic Chemicals and used without further purification. Diglyme (Ansul Ether 141) was purified by predrying over calcium hydride and finally distilled from lithium aluminum hydride under reduced pressure.[28] Dimethylformamide was purified by predrying over calcium hydride followed by distillation from barium oxide at reduced pressure. 1-Phenylpentafluoropropanone was prepared in 64% yield according to the method of Dishart and Levine.[29] 2-Phenylpentafluoropropene was prepared according to the procedure previously described.[14] The inorganic fluorides, sodium (Mallinckrodt reagent), potassium (Baker and Adamson), rubidium (Ozark Mahoning), and cesium (American Potash), were dried by grinding the salts to a fine powder and heating *in vacuo* (30 mm) at 105–110° for 70 hr in a vacuum oven. Sodium, potassium, and lithium chlorodifluoroacetate were prepared from chlorodifluoroacetic acid (Allied Chemical) and the corresponding alkali metal carbonates in ether following the earlier described procedure.[14]

1-Phenylpentafluoropropanone, with Sodium Chlorodifluoroacetate and Triphenylphosphine.—A mixture consisting of triphenylphosphine, sodium chlorodifluoroacetate, and 1-phenylpentafluoropropanone in 70 ml of dry diglyme was heated at 100° for 20 hr or until the theoretical amount of carbon dioxide had evolved (6.5 hr). The mixture was steam distilled to give 1 l. of distillate. The organic layer was separated and diluted to a volume of 50 ml with *n*-pentane. Glpc analysis of the product mixture was obtained on columns A and B using external standards of 2-phenylheptafluoro-1-butene and 1-phenylpentafluoropropanone. These results are summarized in Table I. Similar results obtained employing potassium chlorodifluoroacetate, sodium chlorodifluoroacetate and added inorganic fluorides, and lithium chlorodifluoroacetate and added inorganic fluorides are summarized in Tables III, VI, and VII, respectively.

Preparation of 2-Phenylheptafluoro-1-butene (IV).—A mixture of 65.6 g (0.250 mol) of triphenylphosphine, 65.0 g (0.472 mol)

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[26] A. H. Fainberg and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **79**, 4170 (1957).

[27] D. P. Graham and W. B. McCormack, *J. Org. Chem.*, **31**, 958 (1966).

[28] G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 28 (1963).

[29] K. T. Dishart and R. Levine, *J. Amer. Chem. Soc.*, **78**, 2268 (1956).

of lithium chlorodifluoroacetate, and 50.0 g (0.236 mol) of 1-phenylpentafluoropropanone in 300 ml of dry dimethylformamide was heated at 80° for 0.5 hr under a nitrogen atmosphere. After the theoretical amount of carbon dioxide had evolved, the mixture was steamed distilled to give 1 l. of distillate, and the organic layer separated. The organic layer was washed with ten 50-ml portions of water and dried over calcium sulfate.

Fractional distillation on an 18-in. spinning-band column yielded 29.2 g (48%) of pure 2-phenylheptafluoro-1-butene: bp 138–139° (737 mm); $n^{20}\mathrm{D}$ 1.4032; $\nu_{\max}$ ($C{=}CF_2$) at 5.77 μ; $\lambda_{\max}^{\text{cyclohexane}}$ 216 μ (ε 5800) and $\lambda_{\max}^{95\%\ \text{ethanol}}$ 216 mμ (ε 5460). Glpc analysis on column A of the distilled liquid showed only one peak.

Anal. Calcd for $C_{10}H_5F_7$: C, 46.51; H, 1.94. Found: C, 46.27; H, 1.94.

Preparation of 2-Phenylheptafluoro-2-butene (*cis–trans*). **Method I.**—2-Phenylheptafluoro-2-butene was prepared by treating a mixture of 1-phenylpentafluoropropanone and triphenylphosphine in diglyme with potassium chlorodifluoroacetate in diglyme at 125–135° similar to the procedure previously described for 2-phenylpentafluoropropene.[14] Thus, treatment of 56.0 g (0.250 mol) of 1-phenylpentafluoropropanone and 65.6 g (0.250 mol) of triphenylphosphine in 200 ml of dry diglyme with 75.7 g (0.485 mol) of potassium chlorodifluoroacetate in 200 ml of diglyme at 135° yielded, after steam distillation, 63.4 g of organic distillate. The distillate was washed with eight 50-ml portions of water and dried over calcium sulfate. Glpc analysis at this point on column B showed a mixture of *only trans-* and *cis*-2-phenylheptafluoro-2-butene in a ratio of 2.1:1.0, and unreacted ketone.

The drying agent was removed and the organic material fractionated on a Nester–Faust 24-in. Teflon spinning-band column with a reflux ratio of 40:1 to give 17.4 g (27%) of *trans*-2-phenylheptafluoro-2-butene, bp 45–46° (33 mm), $n^{20}\mathrm{D}$ 1.3995, and 7.8 g (12.1%) of *cis*-2-phenylheptafluoro-2-butene, bp 47–48° (32 mm), $n^{20}\mathrm{D}$ 1.4041. Glpc analysis of pure *cis* and *trans* isomers on column A showed each isomer to be free from contamination of starting ketone and 2-phenylheptafluoro-1-butene.

trans-2-Phenylheptafluoro-2-butene had an ir band at $\nu_{C=C}$ 5.89 μ; uv, $\lambda_{\max}^{95\%\ \text{ethanol}}$ 224 mμ (ε 2860) [lit.[16] $\lambda_{\max}^{\text{ethanol}}$ 226 mμ (ε 2840)].

Anal. Calcd for $C_{10}H_5F_7$: C, 46.51; H, 1.94. Found: C, 46.76; H, 2.13.

cis-2-Phenylheptafluoro-2-butene had an ir band at $\nu_{C=C}$ 5.93 μ; uv, $\lambda_{\max}^{95\%\ \text{ethanol}}$ 237 mμ (ε 4290) [lit.[16] $\lambda_{\max}^{\text{ethanol}}$ 238 mμ (ε 4360)].

Preparation of 2-Phenylheptafluoro-2-butene (*cis–trans*). **Method II.**—2-Phenylheptafluoro-2-butene was prepared in a manner similar to that used by Dixon[30] and Andreades[16] for the synthesis of phenyl-substituted perfluoro olefins. The procedure is given below. Into a 1-l. three-necked round-bottomed flask equipped with a Dry Ice condenser backed up to a Dry Ice–trichloroethylene trap, a mechanical stirrer, and a pressure equalized dropping funnel containing phenyllithium prepared from 39.3 g (0.250 mol) of bromobenzene and 3.9 g (0.58 g-atom) of lithium in 100 ml of dry ether, was placed 200 ml of dry ether. The flask containing the ether was cooled to −78° under nitrogen and 60.0 g (0.300 mol) of perfluoro-2-butene carefully bubbled into the ether.

The phenyllithium was added dropwise to the reaction flask such that the temperature never rose above −60°. The entire addition required 3.5 hr. After complete addition, the mixture was stirred at −60° for 3 hr and then warmed to room temperature. The excess perfluoro-2-butene was allowed to distil into a cold trap by removing the Dry Ice condenser and replacing it with a water-cooled condenser.

The reaction mixture was poured onto 400 g of crushed ice containing 30 ml of concentrated hydrochloric acid. The layers were separated and the aqueous layer was extracted with three 50-ml portions of ether and combined with the organic layer. The combined extracts were further washed with a saturated solution of sodium bicarbonate followed by water and dried over magnesium sulfate.

The ether was removed *in vacuo* to give a yellow liquid containing a white solid. The crystalline material was recrystallized from 95% ethanol, mp 170–181°, which was identified as a mixture of *cis-* and *trans*-1,2-diphenylhexafluoro-2-butene, $\nu_{C=C}$ 6.22 and 6.32 μ.

Anal. Calcd for $C_{16}H_{10}F_6$: C, 60.76; H, 3.16. Found: C, 60.49; H, 3.45.

Pure samples of the *cis-* and *trans*-2-phenylheptafluoro-2-butene were obtained using preparative gas chromatography on a 10 ft × 0.50 in. column packed with β,β-Oxidipropionitrile supported on 100–120 mesh Gas Chrom P. They were identical in all respects with the isomers obtained by method I.

Reaction of 2-Phenylpentafluoropropene with Cesium Fluoride in the Presence of Methyl Iodide.—A mixture consisting of 5.0 g (24.0 mmol) of 2-phenylpentafluoropropene, 7.6 g (50.0 mmol) of cesium fluoride, and 4.3 g (30.0 mmol) of methyl iodide in 40 ml of dry dimethylformamide was heated at 50° for 6 hr under nitrogen. The mixture was quenched by pouring onto ice–water and the organic layer separated. Glpc analysis on column B indicated a 66% yield of 2-phenyl-2-methylhexafluoropropane (XIII) and a 19.5% yield of the hydrogen fluoride addition product, 2H,2-phenylhexafluoropropane (XII).

Pure samples of XII and XIII were obtained using preparative gas chromatography on column B. XIII had bp 152.0–152.5° (735 mm, micro), $n^{20}\mathrm{D}$ 1.4158. The H^1 nmr spectrum showed a methyl singlet at δ 1.85 (area 3) and a complex multiplet centered at δ 7.52 (area 5) for the aromatic protons.

Anal. Calcd for $C_{10}H_8F_6$: C, 49.60; H, 3.31. Found: C, 49.44; H, 3.55.

Compound XII had bp 131.0–131.5° (743 mm, micro) and $n^{20}\mathrm{D}$ 1.3992. The H^1 spectrum exhibited a heptet (area 1) centered at δ 3.90 with J_{F-H} = 8.5 cps for the 2-hydrogen and a phenyl singlet at δ 7.25 (area 5) for the aromatic protons.

Anal. Calcd for $C_9H_6F_6$: C, 47.37; H, 2.63. Found: C, 47.48; H, 2.90.

Registry No.—III, 394-52-5; IV, 5300-25-4; V (*cis*), 5300-26-5; V (*trans*), 5300-27-6; *trans*-1,2-diphenylhexafluoro-2-butene, 16204-55-0; *cis*-1,2-diphenylhexafluoro-2-butene, 16204-54-9; XII, 3142-78-7; XIII, 16204-44-7.

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[30] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).