the series). These combined fractions contained 60% cis isomer and 40% trans isomer. Fractions 17 through 35 were combined: 179 g, boiling range 71.5–75°, $n^{25}$D 1.3974 (varied from 1.3966 to 1.3979 for the series). These combined fractions contained about 38% cis isomer and 62% trans isomer. Fractions 36 through 39 were combined: 35 g, boiling range 75–75.5°, $n^{25}$D 1.3982. The latter combination contained less than 1% cis isomer and more than 99% trans-1-methoxy-1-butene. In a further attempt to obtain the pure cis isomer, fractions 2–16 were refractionated. This was unsuccessful and the best fraction contained only 80% cis isomer: bp 69–70°, $n^{25}$D 1.3930.

The cis and trans isomers have been prepared by the distillation of butyraldehyde dimethyl acetal containing sodium acid sulfate.[26] The reported yield of the mixture of isomers was 70% and the isomer ratio was 1.5 parts trans to 1 part cis. The reported physical constants were for trans (98%), bp 76° (754 mm), $n^{20}$D 1.4021; for cis (94%), bp 71° (749 mm), $n^{20}$D 1.4020.

Further evidence for the assigned structures was obtained from their infrared spectra and by their hydrogenation to methyl butyl ether. The fraction enriched in the cis isomer (80%) had a C=C stretch at 1640, the C—O—C stretch at 1260, and a strong, broad band characteristic of cis out-of-plane C—H bending at 730 cm$^{-1}$ as well as some absorption frequencies characteristic of the trans isomer. The trans isomer exhibited a doublet at 1670 and 1650 characteristic of the C=C stretch of vinyl ethers,[27] along with a medium band at 973, and a strong band at 933 cm$^{-1}$ characteristic of the out-of-plane bending of the trans C—H.

*trans*-1-**Methoxy-2-butene**.—Crotyl alcohol was prepared by the sodium borohydride (60 g, 1.6 moles) reduction of water-saturated crotonaldehyde (90% crotonaldehyde, 334 g, 4.8 moles contained) in 400 ml of water containing 1 pellet of sodium hydroxide. The aqueous layer was removed and extracted three times with 200-ml portions of ether. The extracts and the alcohol layer were combined and dried over magnesium sulfate. Distillation provided 163 g (48%) of crotyl alcohol, bp 70–78° (100 mm),

$n^{25}$D 1.4224. The alcohol was converted into crotyl chloride by reaction with 425 ml of concentrated hydrochloric acid. The mixture was shaken vigorously in a separatory funnel at 10-min intervals over a period of 1 hr. The organic layer was extracted with water and dried over calcium chloride. The mixture was first distilled through a short helices-packed column and then redistilled on a spinning-band column to obtain 79 g (39%) of crotyl chloride, bp 53–55° (290 mm), $n^{25}$D 1.4281.[28]

The crotyl chloride (79 g) was converted into 1-methoxy-2-butene by the procedure of Roberts[29] using 32 g of sodium and 1300 ml of methanol. There was obtained 36 g (48%) of predominantly trans-1-methoxy-2-butene having bp 76–77°, $n^{25}$D 1.3965. Analysis by glpc indicated a composition of 95% trans, 4.5% cis, and 0.5% consisting of two other substances. Infrared showed the absorption frequencies expected for the trans-1-methoxy-2-butene (3005, 2880, 2800, 1675, 1450, 1150, 968, and 905 cm$^{-1}$) with the 968-cm$^{-1}$ band being the C–H out-of-plane deformation for the trans configuration. The material also showed a weak and broad band at 725 cm$^{-1}$ which is probably due to the cis isomer. The 905-cm$^{-1}$ band could be due to the presence of 3-methoxy-1-butene formed by allylic rearrangement during the preparation of crotyl chloride and/or the ether. However, we do not believe this is true because there was not a concomitant band at 990 cm$^{-1}$ and this 905-cm$^{-1}$ band of the same relative intensity also was present in the infrared spectrum of the trans isomer trapped from glpc of both the synthetic ether and from the hydrogenation of methoxybutadiene.

**Registry No.**—*trans*-1-Methoxy-1,3-butadiene, 10034-09-0; methyl butyl ether, 628-28-4; 4-methoxy-1-butene, 4696-30-4; cis-1-methoxy-1-butene, 10034-12-5; trans-1-methoxy-1-butene, 10034-13-6; trans-1-methoxy-2-butene, 10034-14-7; crotyl chloride, 591-97-9; cis-1-methoxy-2-butene, 10034-16-9.

(26) M. Farine, M. Peraldo, and G. Bressan, *Chim. Ind.* (Milan), **42**, 967 (1960); *Chem. Abstr.*, **55**, 11,284 (1961).

(27) G. J. Dege, R. L. Harris, and J. S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 3374 (1959).

(28) L. F. Hatch and S. S. Nesbitt [*ibid.*, **72**, 729 (1950)] reported bp 84.1°, $n^{20}$D 1.4390, for the cis isomer and bp 84.8°, $n^{25}$D 1.4327, for the trans isomer.

(29) J. D. Roberts, W. G. Young, and S. Winstein, *ibid.*, **64**, 2163 (1942).

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# Fluoro Olefins. I. The Synthesis of β-Substituted Perfluoro Olefins[1]

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The reaction of polyfluorinated ketones with difluoromethylenetriphenylphosphorane, $(C_6H_5)_3P=CF_2$, generated *in situ* from sodium chlorodifluoroacetate and triphenylphosphine, provides a general, one-step route to β-substituted perfluoro olefins. Olefins containing a β-alkyl, alicyclic, phenyl, or substituted phenyl substituent were obtained in 16–78% yields. Trapping experiments with tetramethylethylene and isopropyl alcohol failed to trap any difluorocarbene in these reactions suggesting that the mechanism does not involve the trapping of difluorocarbene by triphenylphosphine. An alternative mechanism involving decomposition of an intermediate phosphobetaine salt is proposed as a route to the difluoromethylene ylid.

No simple general route to perfluoro olefins containing a β substituent, other than halogen, hydrogen, or perhaloalkyl group, has been reported. Middleton and co-workers[3] have observed the formation of 2-phenylpentafluoropropene by the pyrolysis of 7,7-bis-(trifluoromethyl)-1,3,5-cycloheptatriene at 500°. The perfluorinated analog, decafluoro-α-methylstyrene, has been prepared by the defluorination of perfluoroisopropylcyclohexane over nickel gauzes at 750°.[4] A few

other perfluoro olefins containing simple alkyl β substituents have also been prepared;[5] however, the reaction sequence was generally long and the yields were generally low.

Owing to the unique reactivity of fluoro olefins in fluorocarbon chemistry, we were interested in preparing perfluoro olefins containing β substituents for synthetic and mechanistic studies and required a facile route to these compounds. Previous attempts by other workers to prepare fluoro olefins containing a β substituent utilizing either free-radical[6] or ionic reactions[7] have met with little or no success. In the ionic

(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. Herkes, The University of Iowa, Aug 1966; (c) preliminary report, D. J. Burton and F. E. Herkes, *Tetrahedron Letters*, No. 23, 1883 (1965).

(2) National Aeronautics and Space Administration Trainee, 1964–1966.

(3) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965).

(4) B. R. Letchford, C. R. Patrick, and J. C. Talow, *Tetrahedron*, **20**, 1381 (1964).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 3565 (1953).

(6) P. Tarrant and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 3640 (1955).

(7) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956); I. L. Knunyants, L. S. German, and B. L. Dyatkin, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, 221 (1960); P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).
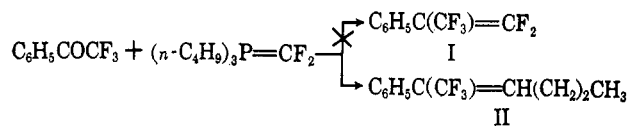
reactions previously investigated, the only product found was that derived from a nucleophilic displacement reaction at the α-carbon atom to yield α-substituted internal olefins.

Fuqua and co-workers have recently reported the preparation of terminal difluoro olefins by the reaction of aldehydes[8] with difluoromethylenetriphenylphosphorane. Under similar conditions, ketones did not yield the corresponding terminal fluoro olefins. However, by employing the difluoromethylenetri-n-butylphosphorane these workers were successful in converting simple ketones[9] into terminal difluoro olefins in moderate yields. Trifluoroacetophenone, however, did not yield any fluoro olefin under these "ketone" conditions.[9]
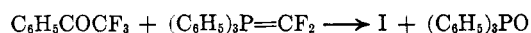
Although simple ketones such as cyclohexanone and acetophenone were found to be inert to difluoromethylenetriphenylphosphorane by Fuqua, we have observed that ketones containing an α-perfluoroalkyl group react readily with this ylid to yield β-substituted perfluoro olefins in excellent yields. This paper presents the general synthetic scope of this reaction and some mechanistic details of the ylid formation. Subsequent publications in this series will deal with an extension of this reaction to diene formation and with the isomerization of the initially formed β-substituted fluoro olefin.

### Results and Discussion

The attempted preparation of 2-phenylpentafluoropropene (I) by Fuqua, *et al.*, employing difluoromethylenetri-n-butylphosphorane and trifluoroacetophenone failed to give the expected olefin (I), but yielded only 1,1,1-trifluoro-2-phenyl-2-hexene (II).[9] Similar results have been obtained in our laboratory employing these

$$C_6H_5COCF_3 + (n\text{-}C_4H_9)_3P{=}CF_2 \underset{\text{II}}{\overset{\text{I}}{\underset{\displaystyle C_6H_5C(CF_3){=}CH(CH_2)_2CH_3}{\overset{\displaystyle C_6H_5C(CF_3){=}CF_2}{\Bigg\langle}}}}$$

conditions. However, by employing the difluoromethylenetriphenylphosphorane, we have successfully prepared I in a 68% yield. The reaction could be conveniently carried out on a small scale by simply heating a mixture of the ketone, phosphine, and sodium chlorodifluoroacetate in diglyme at 100°. For larger scale

$$C_6H_5COCF_3 + (C_6H_5)_3P{=}CF_2 \longrightarrow I + (C_6H_5)_3PO$$

preparative reactions, a saturated solution[10] of the sodium chlorodifluoroacetate is added dropwise to a mixture of the ketone and triphenylphosphine in diglyme at 140–150°. As pointed out by the earlier

(8) S. A. Fuqua, G. W. Duncan, and R. M. Silverstein, *Tetrahedron Letters*, No. 23, 1461 (1964); S. A. Fuqua, G. W. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965).

(9) S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *Tetrahedron Letters*, No. 9, 521 (1965); S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 2543 (1965).

(10) In contrast to the report by Fuqua, *et al.*,[8] who noted the apparent low solubility of the sodium chlorodifluoroacetate in diglyme and employed heated dropping funnels to overcome this difficulty, we have found this salt to be fairly soluble in diglyme (0.60 g/ml) and have employed saturated solutions at room temperature successfully. In fact, in some of our initial work, we also encountered some solubility problems and associated this with either incomplete drying of the salt or partial decarboxylation of the salt in the drying step. When the salt is properly prepared and dried, no solubility problem was encountered. It was also noted that when incomplete solubility was observed, the yields were generally lower and a longer induction period for the decarboxylation reaction was observed.

workers, this mode of addition prevents any violent exothermic decomposition in the decarboxylation of the salt. This reaction scheme has been applied to a variety of polyfluorinated ketones and has been found to be a general route to β-substituted perfluoro olefins containing a β-alkyl (n-butyl), alicyclic (cyclohexyl), or aromatic (phenyl or substituted phenyl) substituent. The results of these reactions and their physical properties are summarized in Table I.

The polyfluorinated ketones, with the exception of p-dimethylaminotrifluoroacetophenone, can be conveniently prepared from the appropriate Grignard reagent and a perfluoro acid *via* the method of Dishart and Levine.[11] Thus, by the proper choice of the alkyl

$$3RMgBr + R_fCO_2H \longrightarrow RCOR_f \xrightarrow{(C_6H_5)_3P{=}CF_2} RC(R_f){=}CF_2$$

or aryl group in the Grignard reagent and the selection of the appropriate perfluoro acid, almost any β substituent can be introduced by this reaction sequence.

The yields of the resulting olefins, with the exception of the p-dimethylamino compound, were generally good. This is in contrast to the hydrocarbon analog and is attributed in most part to the greater inductive effect of the α-perfluoroalkyl group rendering the carbonyl carbon more electrophilic and thereby more susceptible to attack by the ylid. In the case of the p-dimethylaminotrifluoroacetophenone, the electron-donating ability of the p-dimethylamino group almost completely cancels the effect of the perfluoro group. Consequently, this compound behaves more like the hydrocarbon analogs and gives only a low yield of the terminal olefin (16%). In an earlier report[1c] it was speculated that the failure to obtain the terminal difluoro olefins under these conditions with cyclohexanone and acetophenone may have been due to the reaction of the α hydrogens in the ketones undergoing side reactions with the fluoride ion generated in these reactions. However, the successful reaction of the benzyltrifluoromethyl ketone and the n-butyltrifluoromethyl ketone under these conditions (*cf.* Table I) preclude this hypothesis and give additional support that only activation of the carbonyl was required for a successful Wittig-type reaction under these conditions.

Concentration studies employing trifluoroacetophenone as a model ketone indicated that the best yield of the fluoro olefins could be obtained employing a 2:2:1 mole ratio of triphenylphosphine, sodium chlorodifluoroacetate, and ketone, respectively. Diglyme was the solvent choice in most of the Wittig reactions employing triphenylphosphine and sodium chlorodifluoroacetate with the polyfluorinated ketones. The reaction was conveniently carried out by heating a mixture of the phosphine, salt, and appropriate ketone in diglyme at 100° for 20 hr, followed by steam distillation of the reaction mixture and fractional distillation of the organic layer. In cases where fractional distillation could not be used to separate the fluoro olefins, preparative gas chromatography was employed.

Initial experiments in product isolation using an extraction method and steam distillation gave comparable results. The extraction method consisted of quenching the reaction mixture in n-hexane and filtering off the insoluble triphenylphosphine oxide. The

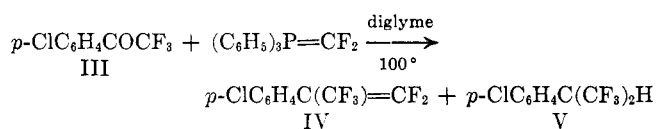(11) K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956).

## TABLE I

### β-SUBSTITUTED PERFLUORO OLEFINS

$$\begin{array}{c} R \\ \backslash \\ C{=}CF_2 \\ / \\ R_f \end{array}$$

| R | $R_f$ | Registry no. | Yield,[a] % | Bp (mm), °C | $n^{20}D$ | $\nu C{=}CF_2$, $\mu$ | C, % Calcd | C, % Found | H, % Calcd | H, % Found |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $CF_3$ | 1979-51-7 | 68 | 51–52 (44) | 1.4216 | 5.75 | 51.92 | 51.91 | 2.43 | 2.61 |
| $C_6H_5CH_2$ | $CF_3$ | 7781-82-0 | 61 | 63–64 (26) | 1.4305 | 5.68 | 54.05 | 54.04 | 3.15 | 3.22[b] |
| $C_6H_{11}$ | $CF_3$ | 7781-83-1 | 65 | 131–132 (748) | 1.3839 | 5.75 | 50.70 | 50.74 | 4.70 | 4.85 |
| $p$-$ClC_6H_4$ | $CF_3$ | 7785-11-7 | 64 | 62 (13) | 1.4485 | 5.76 | 44.53 | 44.38 | 1.65 | 1.85 |
| $p$-$FC_6H_4$ | $CF_3$ | 1979-54-0 | 66 | 62–63 (57) | 1.4107 | 5.74 | 47.78 | 47.89 | 1.77 | 2.06[c] |
| $p$-$CH_3C_6H_4$ | $CF_3$ | 1979-52-8 | 72 | 155–156 | 1.4298 | 5.75 | 53.03 | 53.71 | 3.18 | 3.23[d] |
| $p$-$CH_3OC_6H_4$ | $CF_3$ | 1979-53-9 | 78 | 73–74 (12) | 1.4459 | 5.75 | 50.42 | 50.42 | 2.94 | 2.95 |
| $p$-$(CH_3)_2NC_6H_4$ | $CF_3$ | 7781-86-4 | 16 | e | ... | 5.75 | 52.79 | 52.70 | 3.98 | 4.28[f] |
| $n$-$C_4H_9$ | $CF_3$ | 7781-87-5 | 59 | 82.5–83.5 | 1.3360 | 5.73 | 44.68 | 44.48 | 4.79 | 4.94 |
| $C_6H_5$ | $C_2F_5$ | 5300-25-4 | 48 | 138–139 (737) | 1.4032 | 5.77 | 46.51 | 46.27 | 1.94 | 1.94 |
| $C_6H_5$ | $C_3F_7$ | 7781-89-7 | 42 | 62–63 (22) | 1.3916 | 5.78 | 42.85 | 42.73 | 1.62 | 1.98 |

[a] Glpc yield based on starting ketone.   [b] Calcd for F: 42.79. Found: 42.76.   [c] Calcd for F: 50.44. Found: 50.20.   [d] Calcd for F: 39.91. Found: 39.92.   [e] Mp 42.5–43.0°.   [f] Calcd for N: 5.58. Found: 5.74.

diglyme was then removed by thoroughly washing the $n$-hexane extract with water. The yield of 2-phenyl-pentafluoropropene obtained in this way was 74% compared to 68% yield by the steam distillation procedure. The advantage of the steam distillation technique was the ease of separation of the olefin and ketone from the triphenylphosphine oxide and unreacted triphenylphosphine.

In the reaction using $p$-chlorotrifluoroacetophenone (III), there was observed, in addition to a 32% yield of the expected 2-($p$-chlorophenyl)pentafluoropropene (IV), a 37% yield of the hydrogen fluoride addition product, 2-($p$-chlorophenyl)-2-H-hexafluoropropane (V).

$$p\text{-}ClC_6H_4COCF_3 + (C_6H_5)_3P{=}CF_2 \xrightarrow[100°]{\text{diglyme}}$$
III

$$p\text{-}ClC_6H_4C(CF_3){=}CF_2 + p\text{-}ClC_6H_4C(CF_3)_2H$$
$$\qquad\qquad IV \qquad\qquad\qquad\qquad V$$

The saturated product presumably arises by the attack of fluoride ion[12] on the terminal difluoromethylene group of the initially formed fluoro olefin (IV) and subsequent abstraction of a proton from the solvent (diglyme). Although diglyme is generally considered to be a nonprotic solvent, the presence of a basic moiety can and has been shown to remove $\alpha$ protons from diglyme.[13] In the absence of a proton-donating solvent (i.e., dimethylformamide), the intermediate carbanion readily eliminates fluoride ion in a reversible[14] process to produce the initial $\beta$-substituted perfluoro olefin. Since each of the intermediate fluoro carbanions has as its stabilizing factor a negative hyperconjugative effect[16] in the trifluoromethyl group, the controlling factor in the formation and collapse (i.e., loss of fluoride ion) of this carbanion, is in most part dependent upon the

(12) Under the conditions of the reaction, a moderate amount of fluoride ion is generated by decomposition of the difluoromethylene ylid or in the decarboxylation of sodium chlorodifluoroacetate.
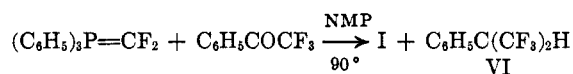
(13) W. H. Snyder, J. Parascandola, and M. Wolfinger, *J. Org. Chem.*, **31**, 2037 (1966).

(14) In the case of $\beta$-substituted fluoropropenes, the process is reversible; however, when the butene and pentene analogs are employed, the fluoro carbanion collapses via a $S_N2'$ irreversible process to produce the internal fluoro olefin.[15]

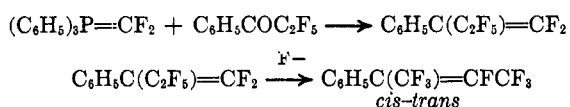(15) D. J. Burton and F. E. Herkes, *Tetrahedron Letters*, No. 50, 4509 (1965).

(16) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 68.

stabilization by the $\beta$ substituent. In the case of the $p$-chlorophenyl derivative, the carbanion can be stabilized by d-orbital resonance through the delocalization of electrons by the $p$-chloro substituent. In contrast then, $\beta$ substituents which are electron releasing either by resonance or induction should show poor stabilization of an intermediate carbanion and subsequently produce little, if any, of the saturated products. In the case of the $\beta$-alkyl, alicyclic, and *para*-substituted methyl, methoxyl, fluoro, hydro, and dimethylamino derivatives, the expected $\beta$-substituted perfluoro olefins were the only products observed. Using a modified procedure, the 2-($p$-chlorophenyl)pentafluoropropene was obtained in a 67% yield of substituting the lithium salt of chlorodifluoroacetic acid[17] in dimethylformamide for the sodium salt in diglyme.

To determine what effect the solvent had on the reaction conditions and yield of fluoro olefin, a study using trifluoroacetophenone as a model ketone was carried out using a variety of dipolar aprotic solvents. The results of this study are summarized in Table II.

## TABLE II

### EFFECT OF SOLVENTS ON THE REACTION OF TRIPHENYLPHOSPHINE, SODIUM CHLORODIFLUOROACETATE, AND TRIFLUOROACETOPHENONE

$$C_6H_5COCF_3 \xrightarrow[2CF_2ClCO_2Na]{(C_6H_5)_3P} C_6H_5C(CF_3){=}CF_2$$

| Solvent | Time, hr[a] | Temp, °C | Olefin, %[b] |
|---|---|---|---|
| Diglyme | 3.2 | 100 | 57 |
| Dimethylformamide | 0.5 | 90 | 84 |
| N-Methyl-2-pyrrolidone | 0.5 | 90 | 44[c] |
| Dimethyl sulfoxide | 0.5 | 90 | 26 |

[a] The time required for >70% of the amount of carbon dioxide to evolve (based on a 100% excess of salt).   [b] Glpc yield based on starting ketone.   [c] A 38% yield of 2H,2-phenylhexafluoropropane was also obtained.

Dimethylformamide and N-methyl-2-pyrrolidone proved to be excellent solvents in these reactions as indicated by the increased yield of olefin and milder reaction conditions compared to diglyme. This can

(17) The lithium salt was employed because of the decreased reactivity of lithium fluoride with perfluoro olefins.

best be rationalized on the basis of decreased solvation of the chlorodifluoroacetate anion, and increased solvation of the sodium cation by the dipolar aprotic solvent.[18] With N-methyl-2-pyrrolidone, there was obtained, in addition to a 44% yield of the expected 2-phenylpentafluoropropene (I), a 30% yield of the hydrogen fluoride addition product, 2-phenyl-2-H-hexafluoropropane (VI). Stringent drying of the solvent gave similar results demonstrating that the solvent, N-methyl-2-pyrrolidone, caused protonation of the intermediate carbanion.

$$(C_6H_5)_3P{=}CF_2 + C_6H_5COCF_3 \xrightarrow[90°]{NMP} I + C_6H_5C(CF_3)_2H$$
$$\phantom{(C_6H_5)_3P{=}CF_2 + C_6H_5COCF_3 \xrightarrow[90°]{NMP} I + }VI$$

The low yield of olefin using dimethyl sulfoxide as the solvent was presumably due to a competing side reaction with either sodium chlorodifluoroacetate or the triphenylphosphinedifluoromethylene ylid, since at 90° an exothermic reaction occurred with the evolution of dimethyl sulfide.[19] Support for this hypothesis was obtained by carrying out several control experiments. The first experiment involved heating a mixture of triphenylphosphine and dimethyl sulfoxide in a neutral medium (diglyme) at 100°. No formation of dimethyl sulfide was observed after 20 hr. However, upon dropwise addition of sodium chlorodifluoroacetate to this same reaction mixture, a slightly exothermic reaction occurred and an 84% yield of dimethyl sulfide was isolated.[20] Presumably there was reaction between the difluoromethylene ylid and dimethyl sulfoxide to produce dimethyl sulfide.[22] This type of behavior of ylids with sulfoxides has been reported by Szmant[23] using dichloromethylenetriphenylphosphorane as a means of converting sulfoxides to sulfides.

With ketones containing perfluoroalkyl groups of more than one carbon atom, a modified procedure had to be employed since a fluoride ion catalyzed isomerization of the initially formed terminal fluoro olefin occurred to give mixtures of the cis and trans internal perfluoro olefins.[15] The procedure used to obtain the pure ter-

$$(C_6H_5)_3P{=}CF_2 + C_6H_5COC_2F_5 \longrightarrow C_6H_5C(C_2F_5){=}CF_2$$

$$C_6H_5C(C_2F_5){=}CF_2 \xrightarrow{F^-} \underset{cis\text{-}trans}{C_6H_5C(CF_3){=}CFCF_3}$$

minal olefin in these cases consisted in substituting the lithium salt of the acid in dimethylformamide for the sodium salt in diglyme. Using this modification 48 and 42% yields of 2-phenylheptafluorobutene-1 and 2-phenylnonafluoropentene-1 were obtained, respectively. The identification of the β-substituted perfluoro olefins was based primarily on elemental analysis, infrared, ultraviolet, and H[1] and F[19] nmr spectroscopy. The carbon–fluorine double-bond stretch was quite

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

(19) In contrast to our results using dimethyl sulfoxide, Fuqua[9] has reported that dimethyl sulfoxide is a satisfactory solvent in the Wittig reaction using tri-*n*-butylphosphine, sodium chlorodifluoroacetate, and cyclohexanone.

(20) Determined as 2(CH₃)₂S·3HgCl₂.[21]

(21) W. F. Faragher, J. C. Morrell, and S. Conroy, *J. Am. Chem. Soc.*, **51**, 2774 (1929).

(22) This is the most reasonable mechanism based on this control reaction; however, when a mixture of sodium chlorodifluoroacetate and dimethyl sulfoxide was heated in diglyme at 100°, a 70% yield of dimethyl sulfide was also produced. In the latter case, there seems to be a different mechanism taking place to form the sulfide.

(23) J. P. Castrillon and H. H. Szmant, *J. Org. Chem.*, **30**, 1338 (1965).

characteristic of the terminal fluoro olefins appearing at 5.74–5.78 μ and was in good agreement with the infrared spectra of similar types of 1,1-difluoro olefins.[24]

The ultraviolet spectra of the β-phenyl-substituted pentafluoropropenes (*cf.* Table III) showed a noticeable

TABLE III

ULTRAVIOLET DATA OF β-PHENYL-SUBSTITUTED PERFLUORO OLEFINS



| X | Y | λmax, mμ | 95% ethanol | Cyclohexane |
|---|---|---|---|---|
| CF₃ | C₆H₅ | 218 | 4,970 | 5,740 |
| CF₃ | p-CH₃C₆H₄ | 222 | 7,060 | 7,490 |
| CF₃ | p-ClC₆H₄ | 224 | 10,200 | 11,000 |
| CF₃ | p-CH₃OC₆H₄ | 230 | 8,870 | 9,030 |
| CF₃ | p-FC₆H₄ | 217 | 4,590 | 4,710 |
| CF₃ | p-(CH₃)₂NC₆H₄ | 267 | 14,200 | ... |
| C₂F₅ | C₆H₅ | 216 | 5,460 | 5,800 |
| C₃F₇ | C₆H₅ | 216 | 5,650 | 6,240 |

solvent effect in 95% ethanol and cyclohexane. In the case of the α-substituted perfluorostyrenes, the extinction coefficient increased with increasing α substitution, $\alpha\text{-}n\text{-}C_3F_7 > \alpha\text{-}C_2F_5 > \alpha\text{-}CF_3$, compared with the hydrocarbon series in which a notable decrease occurs with increasing α substitution.[25] This is no doubt due to the greater inductive effect in the case of the fluorocarbon analogs.

The F[19] nmr spectra of the β-substituted perfluoropropenes were also consistent with the assigned structures. Table IV summarizes the chemical shifts and

TABLE IV

F[19] NMR[a] SPECTRAL DATA OF β-SUBSTITUTED PERFLUORO OLEFINS



| X | δ₁ | δ₂ | δ₃ | J₁,₂ | J₂,₃ | J₁,₃ |
|---|---|---|---|---|---|---|
| C₆H₅CH₂ | 61.2 | 78.2 | 82.4 | 10.6 | 19.5 | 20.8 |
| p-CH₃C₆H₄ | 60.8 | 76.7 | 78.4 | 11.5 | 10.8 | 24.5 |
| p-ClC₆H₄ | 61.6 | 78.9 | 80.6 | 11.7 | 9.1 | 24.4 |

[a] The chemical shifts are expressed in φ* values upfield from CCl₃F (0.0 ppm) and the coupling constants are in cycles per second.

coupling constants of several of the perfluoro olefins. The chemical shift for the CF₃ group appeared as a doublet of doublets centered at φ* +60 to +62
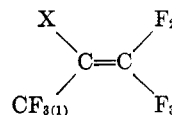


caused by the splitting of the two vinyl fluorines and was in agreement with earlier reports.[26] On the basis of the coupling constants $J_{1,2}$ and $J_{1,3}$, the vinyl fluorine (3) was assigned the *cis* configuration and the vinyl fluorine (2) was given the *trans* configuration. Both

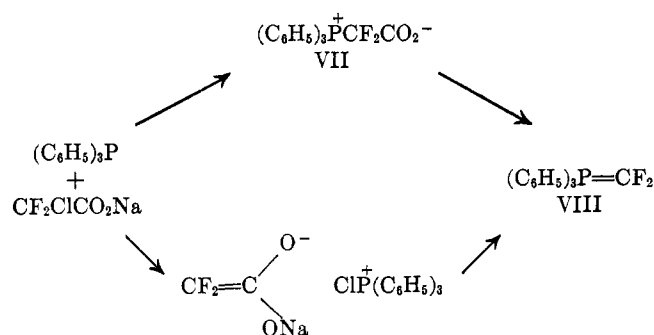(24) J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1954.

(25) C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, **77**, 369 (1955).

(26) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961).

Stone[26] and Swalen[27] have reported coupling constants of 9–12 cps and 21–24 cps for the respective *trans* and *cis* coupling of the $CF_3$ group in $\alpha$-substituted perfluoropropenes. Andreades[28] has reported similar coupling constants in the *cis*- and *trans*-2-phenylheptafluoro-2-butenes. In all three instances the chemical shift of the fluorine *trans* to the $CF_3$ group occurred at a lower applied field than one *cis* to this group.

## Mechanism

As stated earlier, the proposed mechanism for the formation of the difluoromethylene ylid involved the trapping of difluorocarbene, generated in the decarboxylation of sodium chlorodifluoroacetate, by triphenylphosphine. However, two other plausible mechanisms, either of which may be instrumental in the Wittig sequence, have been suggested.[8]

$$(C_6H_5)_3\overset{+}{P}CF_2CO_2^-$$
$$VII$$

$$(C_6H_5)_3P + CF_2ClCO_2Na$$

$$(C_6H_5)_3P=CF_2$$
$$VIII$$

$$CF_2=C \overset{O^-}{\underset{ONa}{}} \quad Cl\overset{+}{P}(C_6H_5)_3$$

The fact that several reagents have been reported to trap difluorocarbene in both basic[29–31] and nonbasic media[32] suggested that trapping experiments with these compounds would lend some credence as to the possible formation of difluorocarbene. Seyferth[32] has claimed success in trapping the difluorocarbene generated from trimethyl(trifluoromethyl)tin in a nonbasic medium at 80° using tetramethylethylene. Similarly, Hine[30] and DeCat[31] have reported the formation of difluoromethyl ethers when difluorocarbene is generated from chlorodifluoromethane with base in the presence of alcohols. Speziale[29] attempted to trap the difluorocarbene, prepared by the action of potassium *t*-butoxide on chlorodifluoromethane, with triphenylphosphine, but recovered only unreacted phosphine. These authors proposed a preferential reaction of the difluorocarbene with the *t*-butyl alcohol similar to that reported by Hine and DeCat.

Our attempts to trap the difluorocarbene, generated by decomposition of sodium chlorodifluoroacetate, with tetramethylethylene in the presence of triphenylphosphine and trifluoroacetophenone failed to yield any of the cyclopropane derivative and instead, produced the expected 2-phenylpentafluoropropene in a 78% yield.[33]

(27) J. D. Swalen and C. A. Reily, *J. Chem. Phys.*, **34**, 2122 (1961).
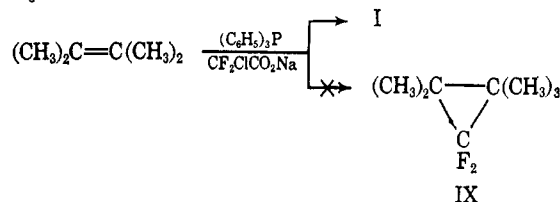(28) S. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962).
(29) A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962).
(30) J. Hine and K. Tanabe, *ibid.*, **80**, 3002 (1958), and references cited therein.
(31) A. DeCat, R. V. Poucke, R. Pollet, and P. Schatts, *Bull. Soc. Chim. Belges.*, **74**, 270 (1965).
(32) D. Seyferth, J. Yick-Pui Mui, M. E. Gordon, and J. M. Burlitch, *J. Am. Chem. Soc.*, **87**, 681 (1965).
(33) A control experiment using only sodium chlorodifluoroacetate and tetramethylethylene in diglyme at 100° for 20 hr, yielded the 1,1-difluorotetramethylcyclopropane[32] (IX) in a 12% yield.

$$C_6H_5COCF_3 +$$

$$(CH_3)_2C=C(CH_3)_2 \xrightarrow[CF_2ClCO_2Na]{(C_6H_5)_3P}$$

I

$$(CH_3)_2C\!-\!\!-\!\!C(CH_3)_2$$
$$\underset{F_2}{\overset{C}{\diagdown\diagup}}$$
$$IX$$

Apparently little, if any, of the free difluorocarbene was produced, since no cyclopropane derivative was obtained and an excellent yield of the fluoro olefin was isolated.

When isopropyl alcohol was substituted for tetramethylethylene and the reaction was carried out in a similar fashion, none of the isopropyldifluoromethyl ether or isopropyl orthoformate was detected and a 61% yield of the 2-phenylpentafluoropropene was produced. In addition, an 85% recovery of alcohol and a 10% yield of isopropyl chlorodifluoroacetate were observed. However, a control experiment, using isopropyl alcohol and sodium chlorodifluoroacetate, produced none of the ether or orthoformate and resulted in a 16% yield of the ester indicating again that under the reaction conditions (100°, 20 hr, diglyme as solvent) very little of the free difluorocarbene was generated. If difluorocarbene was present in any appreciable quantity, it should have been trapped by tetramethylethylene or isopropyl alcohol even in the presence of triphenylphosphine and trifluoroacetophenone.

A reasonable explanation for this behavior is perhaps due to the intermediate formation of the phosphobetaine salt (VII). This salt, if formed, could readily eliminate carbon dioxide by a concerted reaction to give the difluoromethylene ylid (VIII). Further support for this hypothesis was demonstrated by the rate of decarboxylation of the salt with added triphenylphosphine compared with that of the salt alone.

In the presence of triphenylphosphine, the decomposition of the salt was greatly accelerated and required only 4 to 6 hr for 70% of the theoretical amount of carbon dioxide to be evolved. In the absence of triphenylphosphine, the decomposition of the salt was very slow and required 17 hr. Evidence for the formation of similar phosphobetaine salts have been observed by Denney[34] in the corresponding hydrocarbon analogs, $(C_6H_5)_3P^+(CH_2)_nCO_2^-$. They could not, however, isolate the salt when $n = 1$. Our attempts, using his method, also failed to produce the phosphobetaine salt (VII).

Although the *in situ* formation of the difluoromethylenetriphenylphosphorane is not a new reaction, its preparation utilizing triphenylphosphine and sodium chlorodifluoroacetate in an essentially nonbasic medium[35] is an attractive route to fluoro olefins, since the presence of bases would cause undesirable side reactions with the polyfluorinated ketones and ylid products. Other preparations of the difluoromethylenetriphenylphosphorane for the synthesis of 1,1-difluoro

(34) D. B. Denney and L. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962).
(35) Rabinowitz[36] has also claimed success in generating the difluoromethylene ylid in a nonbasic medium from dibromo and dichlorodifluoromethane and triphenylphosphine.
(36) R. Rabinowitz and R. Marcus, *J. Am. Chem. Soc.*, **84**, 1312 (1962).

TABLE V

PHYSICAL PROPERTIES OF POLYFLUORINATED KETONES

$$R_fCO_2H + 3RMgX \longrightarrow R_fCOR_f$$

| R | $R_f$ | Registry no. | Yield, % | Bp (mm), °C | $n^{20}D$ | $\nu_{C=O}, \mu$ | C, % Calcd | C, % Found | H, % Calcd | H, % Found |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $CF_3$ | 434-45-7 | 71 | 64-65 (33) | 1.4586 | 5.82 | 55.18 | 54.98 | 2.90 | 3.17 |
| $p\text{-}CH_3C_6H_4$ | $CF_3$ | 394-59-2 | 47 | 79-80 (22) | 1.4708 | 5.83 | 57.44 | 57.48 | 3.76 | 4.03 |
| $p\text{-}FC_6H_4$ | $CF_3$ | 655-32-3 | 57 | 66-67 (34) | 1.4477 | 5.84 | 50.00 | 49.92 | 2.08 | 1.76 |
| $p\text{-}CH_3OC_6H_4$ | $CF_3$ | 711-38-6 | 58 | 72-73 (2) | 1.5005 | 5.85 | 52.94 | 52.92 | 3.72 | 3.91 |
| $C_6H_{11}$ | $CF_3$ | 6302-04-1 | 69 | 53-54 (30) | 1.3919 | 5.68 | 53.33 | 53.40 | 6.11 | 6.04 |
| $C_6H_5CH_2$ | $CF_3$ | 350-92-5 | 65 | 66 (16) | 1.4468 | 5.63 | 57.44 | 57.29 | 3.72 | 4.01 |
| $p\text{-}ClC_6H_4$ | $CF_3$ | 321-37-9 | 42 | 83-84 (24) | 1.4908 | 5.80 | 46.04 | 45.70 | 1.92 | 1.92 |
| $C_6H_5$ | $C_2F_5$ | 394-52-5 | 64 | 62-63 (22) | 1.4319 | 5.85 | 48.21 | 47.98 | 2.26 | 2.37 |
| $C_6H_5$ | $C_3F_7$ | 559-91-1 | 70 | 69-70 (18) | 1.4169 | 5.85 | 43.79 | 43.56 | 1.82 | 2.08 |

olefins have been shown to involve the use of bases such as ammonia[37] and alkyllithiums.[38]

Initially it was anticipated that the ylid could be generated in a nonbasic medium followed by the addition of the polyfluorinated ketone. However, this possibility was ruled out when an attempt to generate the ylid, using triphenylphosphine and sodium chlorodifluoroacetate, followed by the addition of trifluoroacetophenone at 100° gave a 95% recovery of the starting ketone. Furthermore, by generating this ylid at 100° and cooling the reaction mixture to room temperature under nitrogen followed by the addition of benzaldehyde, none of the desired 1,1-difluorostyrene was found. Apparently, the difluoromethylenetriphenylphosphorane is not stable under the reaction conditions and decomposes rapidly in the absence of a carbonyl moiety.

## Experimental Section

All melting and micro boiling points are corrected. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using a neat film calibrated vs. a 0.07-mm polystyrene film. Ultraviolet spectra were obtained on a Cary Model 11 recording spectrophotometer using both 95% ethanol and cyclohexane. The F[19] spectra of the β-substituted pentafluoropropenes were obtained using a Varian nmr spectrometer at 56.4 Mcps and are reported in $\phi^*$ values upfield from an external standard of $CFCl_3$. The H[1] nmr spectra were obtained on a Varian A-60 spectrometer, and are reported in δ values downfield from an internal standard of tetramethylsilane. Glpc analyses 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 the olefin and the ketone. Column A was a 2 ft × 0.25 in. o.d copper column packed with 10% w/w silicon rubber supported on 100–120 mesh Gas Chrom P. Column B was a 10 ft × 0.25 in. o.d. copper column packed with 10% w/w Carbowax 20 M supported on 100–120 mesh Gas Chrom P. Column C was a 10 ft × 0.5 in. o.d. copper column packed with 10% w/w silicon rubber supported on 100–120 mesh Gas Chrom P. Column D was a 10 ft × 0.5 in. o.d. copper column packed with 10% w/w Carbowax 20 M supported on 100–120 mesh Gas Chrom P. Triphenylphosphine was obtained from the Eastman Organic Chemical Co. 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.[39] N-Methyl-2-pyrrolidone, dimethylformamide, and dimethyl sulfoxide were purified by predrying over calcium hydride, followed by distillation from barium oxide at reduced pressure. Fluorine and chlorine microanalyses were carried out by the Galbraith Laboratories, Knoxville, Tenn.

Carbon and hydrogen microanalyses were carried out in this laboratory by Messrs. J. Empen and F. Mettille.

**Sodium Chlorodifluoroacetate.**—Sodium chlorodifluoroacetate was quantitatively prepared by carefully neutralizing 130.5 g (1.00 mole) of chlorodifluoroacetic acid (Allied Chemical Co.) with 52.9 g (0.500 mole) of solid, anhydrous sodium carbonate in 300 ml of ethyl ether, removing the solvent and water under reduced pressure, and drying over phosphorus pentoxide in a vacuum desiccator.

**Lithium Chlorodifluoroacetate.**—Lithium chlorodifluoroacetate was prepared in a fashion similar to that of the sodium salt using 130.5 g (1.00 mole) of chlorodifluoroacetic acid and 36.9 g (0.500 mole) of solid lithium carbonate in 300 ml of ether. After removal of the solvent and water under reduced pressure, the salt, being highly hygroscopic, was dried in an oven at 120–130° for 72 hr prior to use.

**Trifluoromethylcyclohexyl Ketone.**—The polyfluorinated ketones used in this study were prepared by the method of Dishart and Levine[11] and their properties are summarized in Table V. A typical procedure for trifluoromethylcyclohexyl ketone is given below.

Cyclohexylmagnesium bromide was prepared in the usual way[40] under nitrogen using 146 g (0.900 mole) of cyclohexyl bromide and 24.3 g (1.00 g-atom) of magnesium turnings in 250 ml of anhydrous ether. The Grignard reagent was filtered under nitrogen into a 1-l., three-necked, round-bottomed flask equipped with a Trubore stirrer, a reflux condenser with a gas inlet tube for nitrogen, and a pressure-equalized dropping funnel containing 34.2 g (0.300 mole) of trifluoroacetic acid (Halocarbon Chemical Co.) in 25 ml of ether. The acid was added dropwise over a 1-hr period and the reaction mixture was heated at reflux for 1 additional hr. The reaction mixture was cooled and poured onto 1000 g of crushed ice containing 100 ml of concentrated hydrochloric acid, and the layers were allowed to separate. The layers were separated, the aqueous layer was extracted three times with 100-ml portions of ether, and the combined extracts were added to the organic layer. The organic mixture was washed three times with a saturated (50-ml portions) solution of sodium bicarbonate followed by washing with (three 50-ml portions) water and finally drying over anhydrous magnesium sulfate.

The drying agent was removed and the combined filtrates were concentrated to a volume of 100 ml. Subsequent fractional distillation yielded 37.2 g (69%) of the trifluoromethylcyclohexyl ketone.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from 95% ethanol, mp 121.0–122.5°. Anal. Calcd for $C_{14}H_{15}F_3N_4O_4$: C, 46.67; H, 4.17; N, 15.55. Found: C, 46.79; H, 4.40; H, 15.97.

**General Method for the Synthesis of β-Substituted Perfluoro Olefins.**—The apparatus consisted of a 300-ml, three-necked, round-bottomed flask equipped with a thermometer, a gas inlet tube for nitrogen, and a reflux condenser backed up in series by a Dry Ice–trichloroethylene trap and a carbon dioxide–water trap.[41] Stirring was accomplished by means of a magnetic stirrer. A typical procedure is given below for 2-phenylpentafluoropropene.

(37) S. P. Markanov, A. Ya. Yakubovich, V. A. Ginsburg, A. S. Filotov, M. A. Englin, N. R. Privezentserviz, and T. Ya. Nikoforava, Dokl. Akad. Nauk. SSSR, **141**, 357 (1961).

(38) V. Franzen, Angew. Chem., **72**, 566 (1960).

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

(40) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 188.

(41) The rate of decarboxylation can be qualitatively followed by collecting the liberated carbon dioxide over water saturated with carbon dioxide.

A mixture of 52.5 g (0.200 mole) of triphenylphosphine, 30.5 g (0.200 mole) of sodium chlorodifluoroacetate, and 17.4 g (0.100 mole) of trifluoroacetophenone in 100 ml of dry diglyme was heated at a bath temperature of 100–105° for 20 hr. Carbon dioxide was evolved throughout the reaction and, after 20 hr, 65–75% (STP) of the theoretical amount of the carbon dioxide had been evolved. The reaction mixture was cooled under a nitrogen atmosphere and steam distilled to give 1 l. of distillate, and the organic layer was separated. Glpc analysis on column B indicated 68% of 2-phenylpentafluoropropene based on starting ketone. Subsequent fractionation gave 12.3 g (59%) of the fluoro olefin: bp 51–52° (44 mm), $n^{20}$D 1.4226. The H[1] nmr spectrum showed only a phenyl singlet at δ 7.30.

Additional proof that the product was the 2-phenylpentafluoropropene was obtained by irradiating a mixture consisting of 7.2 mmoles of 2-phenylpentafluoropropene with excess chlorine in a Pyrex ampoule for 24 hr with ultraviolet light. The mixture was subjected to preparative gas chromatography on column C to give 0.76 g (38%) of 1,2-dichloro-1,1,3,3,3-pentafluoro-2-phenylpropane: bp 192–193° (742 mm, microcapillary), $n^{20}$D 1.4544. *Anal.* Calcd for $C_9H_5Cl_2F_5$: C, 38.75; H, 1.81. Found: C, 38.73; H, 1.96.

The olefin was further characterized by oxidation to the starting ketone, trifluoroacetophenone. To a mixture consisting of 9.6 mmoles 2-phenylpentafluoropropene in 20 ml of a 75% sulfuric acid solution was added 14.0 mmoles of powdered potassium dichromate over a 15-min period. After 30 hr at 25°, the reaction mixture was quenched with ice water and the layers were separated. Glpc analysis on column A indicated a 32% yield of trifluoroacetophenone. The 2,4-dinitrophenylhydrazone was prepared and recrystallized from 95% ethanol, mp 172–173° (lit.[11] mp 173.0–173.6°).

**2-Phenylpentafluoropropene. Preparative-Size Reaction.**—Into a 1-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, a gas inlet tube for nitrogen, and a reflux condenser connected to a Dry Ice–trichloroethylene trap followed by a water trap, was placed 65.2 g (0.250 mole) of triphenylphosphine and 43.5 g (0.250 mole) of trifluoroacetophenone in 200 ml of dry diglyme. The homogeneous solution was heated to 145° under a nitrogen atmosphere and the gas inlet tube was replaced with a dropping funnel containing a solution of 76.0 g (0.500 mole) of sodium chlorodifluoroacetate in 150 ml of dry diglyme. This solution was added dropwise over a 1-hr period and the reaction mixture was heated for an additional 0.5 hr to ensure complete decarboxylation of the salt. After steam distillation of the reaction mixture, the organic distillate was washed with additional water and dried over calcium sulfate. Fractional distillation of the organic mixture gave 27 g (53%) of 2-phenylpentafluoropropene: bp 59–60° (54 mm), $n^{20}$D 1.4226.

**2-(p-Chlorophenyl)pentafluoropropene. Method I.**—Using p-chlorotrifluoroacetophenone as the starting ketone, the reaction was carried out following the general procedure for the fluoro olefins. Glpc analysis, using column B, of the organic distillate after steam distillation showed three peaks. The peak with the longest retention time was observed to be unreacted ketone (2.9%). The peak with the shortest retention time was found to be the terminal fluoro olefin (36.9%) and the other component which was intermediate in retention time, was the hydrogen fluoride addition product (41.7%). The products were purified by preparative gas chromatography.

The 2-(p-chlorophenyl)-2H-hexafluoropropane had the following properties. The H[1] nmr spectrum consisted of a phenyl singlet at δ 6.99 (relative area 4) and a heptet for the tertiary hydrogen centered at 3.64 (relative area 1, $J_{HF}$ = 8.5 cps). The F[19] nmr spectrum showed a doublet at φ* +65.9 ($J_{HF}$ 8.6 cps), for the trifluoromethyl group. *Anal.* Calcd for $C_9H_5ClF_6$: C, 41.14; H, 1.91. Found: C, 41.25; H, 1.95. The properties of 2-(p-chlorophenyl)pentafluoropropene are summarized in Table I.

**2-(p-Chlorophenyl)pentafluoropropene. Method II.**—A mixture of 13.6 g (0.100 mole) of lithium chlorodifluoroacetate, 13.0 g (0.050 mole) of triphenylphosphine, and 12.1 g (0.050 mole) of p-chlorotrifluoroacetophenone in 100 ml of dry dimethylformamide was heated to 80° under a nitrogen atmosphere. At this point, carbon dioxide began to rapidly evolve and the reaction became mildly exothermic (80 → 110°). After 0.5 hr, the reaction mixture was cooled and steam distilled to give 1 l. of distillate. The organic layer was separated and analyzed by glpc on column B and shown to contain 64% of the fluoro olefin and 7.4% of the hydrogen fluoride addition product. Fractional

distillation of the mixture gave 5.4 g (45%) of pure 2-(p-chlorophenyl)perfluoropropene: bp 62° (13 mm), $n^{20}$D 1.4485. The H[1] nmr spectrum showed only a phenyl singlet at δ 7.22.

**Solvent Study.**—The apparatus and experimental procedure were the same as those used in the synthesis of the fluoro olefins. The reactants were triphenylphosphine, trifluoroacetophenone, and sodium chlorodifluoroacetate in the mole ratio 1:1:2. The time of reaction was that required for 70% of the theoretical amount of carbon dioxide to be evolved.

Diglyme and dimethylformamide gave only the expected 2-phenylpentafluoropropene in a 57 and 84% yield, respectively.

With N-methyl-2-pyrrolidine the required amount of carbon dioxide was evolved in 0.5 hr at 85–90°. Analysis of the organic products showed a 44% yield of the fluoro olefin (I) and a 38% yield of the hydrogen fluoride addition product, 2H,2-phenylhexafluoropropane (VI). A pure sample of the saturated propane was obtained by heating the mixture of olefin and hydrogen fluoride addition product with moist CsF at 75° for 20 hr in dimethylformamide. The saturated product had the following properties: bp 131.0–131.5° (743 mm, microcapillary), $n^{20}$D 1.3992. The H[1] nmr spectrum showed a phenyl singlet at δ 7.25 (relative area 5) and a heptet for the tertiary hydrogen centered at 3.90 ($J_{HF}$ = 8.5 cps).

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

**Reaction of Triphenylphosphine, Sodium Chlorodifluoroacetate, and Trifluoroacetophenone in Dimethyl Sulfoxide.**—When dimethyl sulfoxide was employed as the solvent, a mildly exothermic reaction ensued at 85° with the evolution of dimethyl sulfide. Analysis of the reaction mixture after 0.5 hr, which was the time required for the (required theoretical) amount of carbon dioxide to be evolved, showed only a 26% yield of 2-phenylpentafluoropropene (I) and a 52% recovery of starting ketone. The weight of sulfide isolated as the mercuric chloride derivative, $2(CH_3)_2 \cdot 3HgCl_2$, was 6.7 g (19.0 mmoles of dimethyl sulfide), mp 151–152°.

After steam distillation of the reaction mixture, the solid in the aqueous distillation residue was removed and recrystallized from a 1:1 mixture of benzene and n-hexane to give 4.8 g (34%) triphenylphosphine oxide, mp 154–156°.[42]

**Reaction of Triphenylphosphine and Dimethyl Sulfoxide in Diglyme.**—A control experiment was carried out by heating a mixture consisting of 49.7 mmoles of triphenylphosphine and 100 mmoles of dimethyl sulfoxide in 50 ml of dry diglyme at 100°. A trap containing a solution of 2.5% mercuric chloride was connected to the reaction vessel, and after 20 hr, no appearance of the dimethyl sulfide–mercuric chloride adduct was observed.

**Reaction of Triphenylphosphine, Dimethyl Sulfoxide, and Sodium Chlorodifluoroacetate in Diglyme.**—To the previously described reaction mixture was added dropwise a solution containing 15.2 g (100 mmoles) of sodium chlorodifluoroacetate in 30 ml of dry diglyme. Upon addition of the salt at 100°, dimethyl sulfide began to evolve as evidenced by a white precipitate in the mercuric chloride trap. The color of the reaction mixture changed from a creamy white to a creamy orange and finally to a dark brown.

The reaction mixture was heated for an additional 24 hr under a nitrogen atmosphere to remove the last traces of dimethyl sulfide. The organic mixture was cooled under nitrogen and quenched with cold water. A tan solid was precipitated and removed by filtration. To ensure complete removal of triphenylphosphine, the tan solid was washed further with cold ether to give 9.8 g (71.2% based on triphenylphosphine) of crude triphenylphosphine oxide, mp 155–156° [petroleum ether (bp 40–60°)]. The infrared spectrum was identical with that of an authentic sample.

The dimethyl sulfide–mercuric chloride complex was filtered and dried *in vacuo* over phosphorus pentoxide to give 29.8 g (84.4 mmoles of dimethyl sulfide) of $2(CH_3)_2S \cdot 3HgCl_2$, mp 151–153° (lit.[21] mp 151°).

**Reaction of Triphenylphosphine and Sodium Chlorodifluoroacetate Followed by the Addition of Trifluoroacetophenone at 100°.**—A homogeneous mixture consisting of 13.0 g (0.050 mole) of triphenylphosphine and 15.2 g (0.100 mole) of sodium chlorodifluoroacetate in 60 ml of diglyme was heated at 100° for *ca.* 2 hr. At this point, after 70% of the theoretical amount of carbon dioxide had been evolved, 8.7 g (0.050 mole) of trifluoroaceto-

(42) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 14.

phenone was added and the mixture was then flash distilled into a receiver cooled by Dry Ice–trichloroethylene at 80° (8 mm). Glpc analysis on column A of the distillate showed only starting ketone in a 95% recovery.

**Reaction of Triphenylphosphine and Sodium Chlorodifluoroacetate Followed by the Addition of Benzaldehyde at 25°.—** The ylid was prepared in the usual way under nitrogen by heating a mixture of 31.3 g (0.120 mole) of triphenylphosphine and 18.3 g (0.120 mole) of sodium chlorodifluoroacetate in diglyme for 18 hr at 100°. The deep brown mixture was then cooled to room temperature under nitrogen followed by the addition of 11.0 g (0.104 mole) of benzaldehyde. Continued stirring at 25° for 24 hr yielded, after work-up with $n$-pentane, a 77% recovery of unreacted benzaldehyde and none of the desired 1,1-difluorostyrene.

**Reaction of Triphenylphosphine, Sodium Chlorodifluoroacetate, Trifluoroacetophenone, and Tetramethylethylene in Diglyme at 100°.—** A mixture consisting of 50 mmoles of triphenylphosphine, 50 mmoles of sodium chlorodifluoroacetate, 50 mmoles of trifluoroacetophenone, and 100 mmoles of tetramethylethylene in 80 ml of diglyme was heated at 100° for 20 hr. Flash distillation of the organic liquids into a receiver cooled by Dry Ice–trichloroethylene followed by glpc on column B showed none of the cyclopropane derivative. The desired 2-phenylpentafluoropropene was obtained in 78% yield.

A control reaction consisting of 100 mmoles of sodium chlorodifluoroacetate and 200 mmoles of tetramethylethylene in 70 ml of diglyme at 100° for 20 hr gave the 1,1-difluorotetramethylcyclopropane in a 12% yield: bp 89.5–90.5° (740 mm, microcapillary), $n^{20}$D 1.3800. The H$^1$ nmr spectrum showed only a triplet centered at δ 1.09 ($J_{HF}$ = 2.0 cps). Reported[32] for 1,1-difluoromethylcyclopropane were $n^{25}$D 1.3772, H$^1$ nmr triplet at δ 1.08 ($J$ = 2.0 cps).

*Anal.* Calcd for $C_7H_{12}F_2$: C, 62.69; H, 8.95. Found: C, 62.45; H, 8.61.

**Reaction of Triphenylphosphine, Sodium Chlorodifluoroacetate, Trifluoroacetophenone, and Isopropyl Alcohol in Diglyme at 100°.—** Isopropyl alcohol was substituted for tetramethylethylene and the reaction was carried out in a similar manner to that previously described. After 70% of the theoretical amount of carbon dioxide had evolved (4 hr) at 100°, the reaction mixture was flash distilled into a receiver cooled by Dry Ice–trichloroethylene. Glpc analysis indicated the absence of the difluoromethylisopropyl ether and the isopropylorthoformate, and showed a 61.4% yield of the 2-phenylpentafluoropropene. In addition to an 84.5% recovery of the isopropyl alcohol, a new peak was observed (10.3% based on starting alcohol).

A control reaction using only isopropyl alcohol (100 mmoles) and sodium chlorodifluoroacetate (50 mmoles) in diglyme at 100° for 8 hr gave a peak with a retention time identical with that of the new peak observed in the former reaction in a 16% yield. A pure sample of this component was obtained by preparative gas chromatography on column D and was found to be the isopropyl ester of chlorodifluoroacetic acid. An authentic sample of this ether was obtained utilizing the method of Bergmann.[43] The isopropyl chlorodifluoroacetate had the following properties: bp 103–104° (742 mm), $n^{20}$D 1.3616. The infrared spectrum (neat) showed a peak at 5.62 μ (C=O stretch). The H$^1$ nmr spectrum showed a heptet (relative area 1) centered at δ 5.18 and a doublet centered at 1.35 (relative area 6) for the methyl protons with $J_{HH}$ = 6.0 cps.

**Registry No.—**1,2-Dichloro-1,1,3,3,3-pentafluoro-2-phenylpropane, 7785-13-9; V, 7781-96-6; VI, 3142-78-7; 1,1-difluorotetramethylcyclopropane, 823-25-6; isopropyl chlorodifluoroacetate, 7781-95-5; 2,4-dinitrophenylhydrazone of trifluoromethylcyclohexyl ketone, 7781-93-3.

(43) E. Bergmann, P. Moses, N. Neeman, S. Cohen, A. Kaluszyner, and S. Reuter, *J. Am. Chem. Soc.*, **79**, 4174 (1957).

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# Mass Spectra of Simple Exocyclic and Endocyclic Olefins

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The mass spectra of several deuterated derivatives of methylcyclohexene and methylenecyclohexane have been obtained and conclusions concerning allylic isomerization, deuterium scrambling, extent of endocyclic–exocyclic double-bond equilibration and fragmentation mechanisms have been formulated.

The use of mass spectrometry in structure elucidation of natural and synthetic materials has been adequately demonstrated,[1] and recently several applications of this technique to simple cyclic and bicyclic terpene hydrocarbons have appeared.[2] While mass spectrometry has been adapted to the quantitative analysis of hydrocarbon types,[3] it was early recognized that extensive structural rearrangement of the carbon skeleton often occurred[4] which invalidated the method for qualitative analytical purposes. Introduction of an olefinic linkage would be expected to provide some fragmentation-direction tendency,[5,6] but sufficient data is given which illustrates the inability of the olefinic linkage alone to direct clean fragmentation in straight-chain olefins.[7] Cyclic olefins might be expected to have a somewhat lessened tendency to isomerize by hydrogen transfer, and Thomas and Willhalm[8] were surprised to observe a significant, approximately equal loss of 43 mass units from both $\Delta^{4(8)}$- and $\Delta^3$-menthene (1 and 2,

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(2) (a) R. I. Reed, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 13; (b) E. von Sydow, *Acta Chem. Scand.*, **17**, 2504 (1963); (c) E. von Sydow, *ibid.*, **16**, 1791 (1964); (d) B. Willhalm, A. F. Thomas, and M. Stoll, *ibid.*, **18**, 1573 (1964).

(3) R. A. Brown, *Am. Soc. Testing Mater., Spec. Tech. Publ.*, **389**, 68 (1965).

(4) (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957; (b) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p 262.

(5) (a) See F. W. McLafferty [in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 7] for a discussion of fragmentation theory. (b) R. A. Brown and E. Gillams, ASTM E-14 Committee on Mass Spectrometry, New Orleans, La., 1954.

(6) Recently, H. D. Beckey and P. Schulze [*Z. Naturforsch.*, **20a**, 1335 (1965)] have applied the techniques of field ionization to olefins and note that the spectra show features due to the stable configuration of the allyl radical and/or the allyl ion.

(7) (a) R. Ryhage and E. Stenhagen, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 9; (b) R. I. Reed, "Ion Production by Electron Impact," Academic Press Inc., New York, N. Y., 1962, Chapter X; (c) J. A. McCloskey and M. J. McClelland, *J. Am. Chem. Soc.*, **87**, 5090 (1965).

(8) A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, **47**, 475 (1964).