The residue (0.82 g) was spectrally identical with ozonolysis-derived VIII, and was somewhat purer than comparable ozonolysis residues.

Vpc Analysis. Neat residual samples of VIII (secured from different sources and contaminated with VII) gave chromatograms consisting of four substances with retention time less than 1 min, plus VII and methyl benzoate in about a 35:65 molar ratio. Previous investigation of the methanolic ozonolysis of *trans*-stilbene[47] indicated that gas chromatography of VIII at 150° did not give methyl benzoate as the exclusive aromatic degradative product, but a significant amount of VII as well. Apparently the hydroperoxide undergoes hydrolytic as well as thermal decomposition.

The different VII:VIII ratios resulting from ozonolyses of IV and V were reflected in vpc data obtained from injection of the respective reaction mixtures. The peak area of VII relative to that of methyl benzoate was found to be, in the single experiments performed, 50:50 in the case of IV and 88:12 for V. Calculations assuming the retention of the 35:65 ratio mentioned above from component VIII of each mixture[48] gave the following approximations for molar proportions of VII:VIII in these reactions: IV, 34:66; V, 85:15. Although these ratios were not in quantitative agreement with those based on direct isolation, they at least faithfully mirrored the degree of difference between the systems.

α,α'-Dimethoxybenzyl Peroxide (XVIII). Ozonolysis of *trans*-Stilbene.—*trans*-Stilbene (3.61 g, 20 mmoles), in 45 ml each of methanol and reagent grade methylene chloride, was ozonated at −66 to −69°, to the appearance of a blue color. A work-up similar to that used in the styrene series was carried out, except that no active oxygen determinations were performed. The distilled reaction solvent contained 2.1 mmoles of VII (DNPH assay). The vacuum distillate from the pentane extract weighed only 0.97 g; infrared analysis revealed it to be VII accompanied by a larger amount of an extraneous material having strong ν_{CO} absorption (9.05 and 9.5 mμ). Independent synthesis[49] and nmr spectra proved this new compound to be the dimethyl acetal of VII. The pot residue from this same extract weighed 2.91 g; infrared and nmr spectra showed very little VIII, mostly a structurally similar, nonhydroxylic condensation product later shown to be XVIII (see next paragraph). The ether extract gave virtually no vacuum distillate (*ca.* 0.03 g), and a pot residue weighing 1.09 g which was VIII containing a little XVIII.

Extended refrigeration of the pentane pot residue gave a low-melting (below 40°) solid which proved to be pure XVIII. This peroxide, whose spectra (Table II) coincided with the assigned structure, was almost inert to sodium iodide in refluxing isopropyl alcohol.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 6.63; mol wt, 274. Found: C, 70.12; H, 6.22; mol wt (vapor pressure osmometry), 258.

Reaction of XVIII with Triethylamine.—An ice-cooled solution of 0.65 g (2.4 mmoles) of XVIII in 2 ml of methanol was treated with 2 drops of triethylamine. After overnight standing, infrared spectra showed that bands characteristic of both VII and methyl benzoate were in evidence, and that absorption due to XVIII (notably the very strong ν_{CO} at 9.05 μ) had completely disappeared. Exactly one-third by weight of the total solution was added to an excess of DNPH test solution; filtration and drying left 0.225 g of the benzaldehyde derivative, equivalent to 0.8 mmole. The yield of VII in the total solution was therefore quantitiative. Vpc analysis of the balance showed that the yield of methyl benzoate, by comparison of its peak area with that due to VII, was about 92%.

Registry No.—IV, 100-42-5; V, 873-66-5; VI, 768-49-0; VII, 100-52-7; VIII, 10027-71-1; X, 10027-72-2; XII, 10027-73-3; IX, 50-00-0; XI, 75-07-0; XIV, 10027-74-4; XVIII, 10027-75-5.

Acknowledgments.—We wish to thank Dr. A. M. Fusco and Mr. W. M. Arnheim for determining and aiding in the interpretation of the nmr spectra, and Professor N. Kornblum for a number of helpful discussions.

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[47] C. D. Johnson and P. S. Bailey, *J. Org. Chem.*, **29**, 703 (1964). (*Cf.* Table II in this paper.)

[48] We concur with a referee's statement that such an assumption is quantitatively invalid. The obvious great difference in aldehyde/ester ratios, however, agreed sufficiently well with what one would expect from our other results that this vpc data was felt to be worthy of inclusion.

[49] T. Langvad, *Acta Chem. Scand.*, **8**, 336 (1954); *Chem. Abstr.*, **49**, 5277c (1955).

Reactions of 2,3-Dichlorotetrafluoropropene with Nucleophiles Containing Phosphorus[1]

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A series of novel 2-chlorotetrafluoroallylphosphorus compounds has been prepared by reaction between 2,3-dichlorotetrafluoropropene and nucleophiles containing phosphorus, including phosphites, phosphinide ions, and phosphines. The spectral properties of these compounds are discussed.

The chemistry of polyfluoroalkyl derivatives of phosphorus is of considerable interest, in that the strongly electron-withdrawing polyfluoroalkyl groups profoundly modify the normal chemical behavior of the phosphorus atom and attached groups. This area of chemistry has been the subject of some attention in recent years.[2] However one restriction on the types of molecules available for study in this area has been the fact that the main preparative routes have been free-radical reactions either of polyfluoroalkyl iodides,[3,4] *e.g.*, as in eq 1, or of fluoro olefins,[5,6] *e.g.*, as in eq 2.

$$CF_3I + P \longrightarrow CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P \qquad (1)$$

$$CF_2{:}CF_2 + PH_3 \longrightarrow CHF_2CF_2PH_2 + (CHF_2CF_2)_2PH + H_2PCF_2CF_2PH_2 \qquad (2)$$

In the present work a new approach to the synthesis of phosphorus compounds bearing an unsaturated polyfluoroalkyl group has been developed. This depends on the susceptibility of a polyfluoroallylic chloride to nucleophilic attack.

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[1] This work was supported by Grant GP-3887 from the National Science Foundation.

[2] For a review, see R. E. Banks and R. N. Haszeldine in *Advan. Inorg. Chem. Radiochem.*, **3**, 367 (1961).

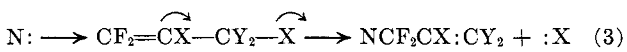
[3] F. W. Bennett, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

[4] H. J. Emeleus and J. D. Smith, *ibid.*, 375 (1959).

[5] G. W. Parshall, D. C. England, and R. V. Lindsey, *J. Am. Chem. Soc.*, **81**, 4801 (1959).

[6] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1083 (1963).

The high reactivity of certain fluorinated allylic chlorides toward nucleophiles has been pointed out by Miller and his co-workers.[7] The reaction proceeds by an SN2′ mechanism (eq 3). Fluorinated allylic chlorides of this kind have been relatively inaccessible, but the current availability of 1,3-dichloro-1,1,3,3-tetrafluoro-2-propanone[8] makes a simple route to a fluorinated allylic chloride of this type now feasible. Reaction of 1,3-dichloro-1,1,3,3-tetrafluoro-2-propanone with phosphorus pentachloride gives 1,2,2,3-tetrachlorotetrafluoropropane[9] which is dechlorinated by zinc in ethanol to 2,3-dichlorotetrafluoropropene[7a] (eq 4).



$$\mathrm{N}\colon \longrightarrow \mathrm{CF_2}\!=\!\overset{\curvearrowright}{\mathrm{C}}\mathrm{X}\!-\!\mathrm{CY_2}\!-\!\overset{\curvearrowright}{\mathrm{X}} \longrightarrow \mathrm{NCF_2CX{:}CY_2} + {:}\mathrm{X} \quad (3)$$

$$\mathrm{CClF_2COCClF_2} \xrightarrow{\mathrm{PCl_5}} \mathrm{CClF_2CCl_2CClF_2} \xrightarrow{\mathrm{Zn}} \mathrm{CF_2{:}CClCClF_2} \quad (4)$$

The Arbuzov reaction of a phosphorus(III) ester with an alkyl halide is one of the most widely used methods of forming carbon–phosphorus bonds. This reaction has now been applied to 2,3-dichlorotetrafluoropropene. Reaction of this olefin with trimethyl phosphite is rapid and vigorous. Methyl chloride is evolved, and distillation of the residue gives a good yield of dimethyl 2-chlorotetrafluoroallylphosphonate which has been characterized by elemental analysis, infrared spectroscopy, and ^{1}H and ^{19}F nmr spectroscopy (see Tables I–III and eq 5). The ester has been further characterized by its conversion, by a standard reaction, into the corresponding acid chloride which, in turn, can be hydrolyzed to 2-chlorotetrafluoroallylphosphonic acid. This latter is a hygroscopic solid and, like other polyfluoroalkylphosphonic acids,[2] is a strong, dibasic acid (eq 6).

$$\mathrm{CF_2{:}CClCClF_2} + \mathrm{(CH_3O)_3P} = \mathrm{CH_3Cl} + \mathrm{CF_2{:}CClCF_2P(O)(OCH_3)_2} \quad (5)$$

$$\mathrm{CF_2{:}CClCF_2P(O)(OCH_3)_2} + \mathrm{PCl_5} \longrightarrow \mathrm{CF_2{:}CClCF_2POCl_2} \xrightarrow{\mathrm{H_2O}} \mathrm{CF_2{:}CClCF_2PO_3H_2} \quad (6)$$

$$\mathrm{p}K_{\mathrm{a}_1}{}' = 2.1,\ \mathrm{p}K_{\mathrm{a}_1}{}' = 5.2$$

TABLE I

INFRARED SPECTRA OF $\mathrm{CF_2{:}CCl{\cdot}CF_2G}$ COMPOUNDS

G	$\nu_{\mathrm{C=C}}$, cm^{-1}	$\nu_{\mathrm{C-F}}$, cm^{-1}	Other bands (ν, cm^{-1})	Registry no.
Cl	1730	1340, 1045		684-04-8
$\mathrm{P(O)(OCH_3)_2}$	1728	1325, 1040–1050[a]	P═O, 1285 POC, 1040–1050[a]	10075-13-5
$\mathrm{POCl_2}$	1720	1332, 1040	P═O, 1295	10075-14-6
$\mathrm{P(O)(C_6H_5)_2}$	1715	1320, 1030	P═O, 1215	10075-15-5
$\mathrm{PHCH_3}$	1730	1322, 1030	PH, 2315	10103-00-1
$\mathrm{PHC_2H_5}$	1725	1334, 1045	PH, 2315	10103-01-2
$\mathrm{PHC_6H_5}$	1725	1312, 1035	PH, 2320	10103-02-3
$\mathrm{P(CH_3)_2}$	1730	1320, 1020		10103-03-4
$\mathrm{P(C_6H_5)_2}$	1725	1310, 1015		10075-16-8

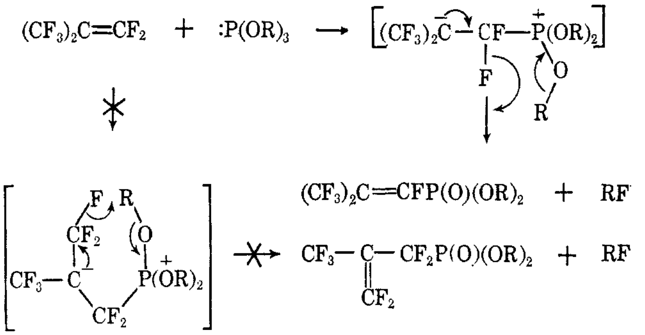
[a] Bands overlap.

Reaction of 2,3-dichlorotetrafluoropropene with methyl diphenylphosphinite leads, in an analogous Arbuzov reaction, to the crystalline 2-chlorotetrafluoroallyldiphenylphosphine oxide (eq 7).

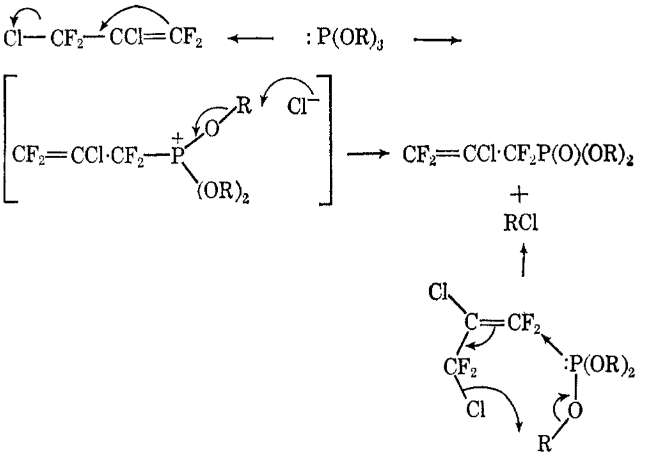
$$\mathrm{CF_2{:}CClCClF_2} + \mathrm{(C_6H_5)_2POCH_3} = \mathrm{CH_3Cl} + \mathrm{CF_2{:}CClCF_2P(O)(C_6H_5)_2} \quad (7)$$

These Arbuzov reactions may be contrasted, mechanistically, with reactions reported[10] between trialkyl phosphites and perfluoro olefins in which displacement of a vinyl fluorine was noted (*e.g.*, Scheme I). It is possible to write reasonable cyclic transition states for this reaction which would lead to either vinylic or allylic fluorine elimination. The observed vinylic displacement suggests that the seven-membered transition state for allylic elimination is less favorable than the five-membered one leading to vinyl elimination; there may also be a minor amount of conjugation between the double bond and the phosphonyl group in the vinyl ester which could help stabilize it. In the much more facile reactions of 2,3-dichloropropene reported here, the presence of a more easily displaced γ chlorine swings the reaction over to allylic displacement *via* either a quasi-phosphonium intermediate or a concerted reaction (Scheme II).

SCHEME I



SCHEME II



Reactions of 2,3-dichlorotetrafluoropropene with anions containing phosphorus have, so far, proved to be generally too vigorous to be useful synthetically. Thus reactions with the sodium derivative of dimethyl phosphite, $\mathrm{(CH_3O)_2PONa}$, or with sodium phosphinide, $\mathrm{NaPH_2}$, have led to destruction of the olefin with extensive formation of tarry materials. Reaction with lithium diphenylphosphinide in tetrahydrofuran is, however, somewhat more controllable and gives 2-

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[7] (a) W. T. Miller, Jr., and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 4164 (1957); (b) W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

[8] Produced by the General Chemical Division of Allied Chemical Corp.

[9] B. S. Farah and E. E. Gilbert, *J. Org. Chem.*, **30**, 1241 (1965).

[10] I. L. Knunyants, E. Y. Pervova, and V. V. Tyuleneva, *Dokl. Akad. Nauk SSSR*, **129**, 576 (1959).

TABLE II

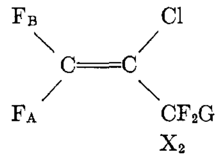
^{1}H NMR SPECTRA OF CF_2:$CClF_2G$ COMPOUNDS[a]

G	δ_{PH}	J_{PH}, cps	$\delta_{C_6H_5}$	δ_{CH_3}	J_{CH_3P}, cps	J_{HCPH}, cps	J_{HPCF}, cps
$PHCH_3$	3.97	207	...	1.25	4.3	7.9	15–18
PHC_2H_5	3.87	207	...	m, 1.0–2.2 (includes CH_2)	...	~7	~18
PHC_6H_5	4.13	219	m, 6.5–7.1	...	...	...	~17
$P(O)(OCH_3)_2$				3.85	11.0		
$P(C_6H_5)_2$			m, 7.4–8.1				
$P(O)(C_6H_5)_2$			m, 6.5–7.5				

[a] Determined at 60 Mc. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal tetramethylsilane; m = multiplet.

TABLE III

^{19}F NMR SPECTRA OF STARTING PROPENE AND PHOSPHONYL COMPOUNDS[a]



G	X				A			B	
	δ_X, ppm	J_{AX}, cps	J_{BX}, cps	J_{PX}, cps	δ_A, ppm	J_{AB}, cps	J_{PA}, cps	δ_B, ppm	J_{PB}, cps
Cl	53.2	33.8	7.8	...	78.2	14.6	...	80.0	...
$P(O)(OCH_3)_2$	108.0	27.3	7.4	109	77.0	19.0	6.9	74.8	9.8
$POCl_2$	104.7	28.4	7.2	146	72.1	6.6	11.6	69.3	16.2
$P(O)(C_6H_5)_2$	105.9	27.9	7.5	88	76.4	14.8	5.5	74.8	7.5
F[b]	64.97	23.4	9.4	...	77.67	17.2	...	77.37	...

[a] Spectra were determined at 56.4 Mc. Chemical shifts (δ) are reported in parts per million (ppm) upfield from internal CCl_3F.
[b] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **34,** 2122 (1961).

chlorotetrafluoroallyldiphenylphosphine, though in low yield (eq 8).

$$CF_2{:}CClCClF_2 + (C_6H_5)_2PLi = LiCl + CF_2{:}CClCF_2P(C_6H_5)_2 \quad (8)$$

The only reactions between primary or secondary phosphines and fluoro olefins so far reported have been free-radical addition reactions yielding saturated polyfluoroalkylphosphines.[5] It has now been found that all classes of phosphines are sufficiently nucleophilic to react with 2,3-dichlorotetrafluoropropene. The present discussion will be limited to the reactions of some primary and secondary phosphines. Diphenylphosphine yields 2-chlorotetrafluoroallyldiphenylphosphine, $CF_2{:}CCl{\cdot}CF_2P(C_6H_5)_2$, identical with the compound prepared by the reaction between the olefin and lithium diphenylphosphinide described above. This phosphine undergoes fairly rapid autoxidation in solution at room temperature to yield the corresponding phosphine oxide, identical with the compound prepared by reaction between the olefin and methyl diphenylphosphinite (eq 9). In analogous reactions the

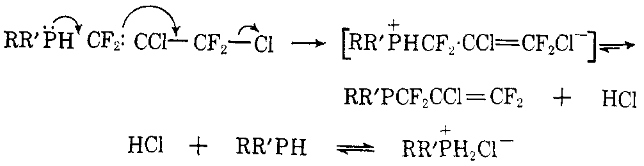
$$CF_2{:}CCl{\cdot}CF_2P(C_6H_5)_2 \xrightarrow{O_2} CF_2{:}CCl{\cdot}CF_2P(O)(C_6H_5)_2 \quad (9)$$

primary phosphines, methyl- and ethylphosphine, yield the secondary phosphines, 2-chlorotetrafluoroallylmethylphosphine and 2-chlorotetrafluoroallylethylphosphine.

The net result of these reactions is the production of 2-chlorotetrafluoroallylphosphines, as summarized in eq 10, but the reactions appear to involve various equilibria. If stoichiometrically equivalent amounts of phosphine and olefin are used, the reaction appears to go rapidly at first, and a solid product (presumably a phosphonium chloride) deposits. Reaction then slows down. The presumed reaction sequence is as shown in eq 11. The intermediate, 2-chlorotetrafluoroallyl phosphonium chloride probably dissociates almost completely to give the very weakly basic 2-chlorotetrafluoroallylphosphine, and the hydrogen chloride thus generated produces the rather insoluble phosphonium chloride of the starting phosphine. The components of the reaction mixture have limited mutual solubilities, and the reaction passes through various heterogeneous stages. The actual reaction conditions given in the Experimental Section are probably not the best achievable; it is noteworthy that in reaction mixtures left for relatively long periods, of the order of 1 week at room temperature, yields of products were high.

$$CF_2{:}CCl{\cdot}CClF_2 + RR'PH = CF_2{:}CCl{\cdot}CF_2PRR' + HCl \quad (10)$$

R = alkyl, aryl; R′ = alkyl, aryl, H

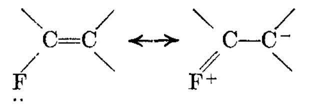


$$RR'\ddot{P}H\ CF_2{:}CCl{-}CF_2{-}Cl \longrightarrow [RR'\overset{+}{P}HCF_2{\cdot}CCl{=}CF_2Cl^-] \rightleftharpoons RR'PCF_2CCl{=}CF_2 + HCl$$
$$HCl + RR'PH \rightleftharpoons RR'\overset{+}{P}H_2Cl^- \quad (11)$$

Phosphine itself does not appear to be a sufficiently powerful nucleophile to react with the propene in like fashion. When the two compounds are heated together a slow reaction does take place, but the product is a saturated polyfluoroalkylphosphine. Presumably the thermal addition of phosphine to fluoro olefins[5] is faster, in this case, than any nucleophilic displacement which could occur. The reaction product is tentatively identified, by infrared spectroscopy and by ^{1}H nmr spectroscopy, as 2,3-dichloro-1,1,3,3,tetrafluoropropylphosphine (eq 12).

$$PH_3 + CF_2{:}CClCClF_2 = H_2PCF_2CHClCClF_2 \qquad (12)$$

The main features of the infrared spectra of the 2-chlorotetrafluoroallyl phosphorus compounds are given in Table I. The most prominent feature in the spectra is the intense band at 1715–1730 cm^{-1} associated with the double-bond stretching of the $CF_2{=}CClCF_2$ portion of the molecules. This band is relatively invariant in these compounds, since the structural changes are occurring at positions relatively remote from the double bond, and it has proved to be diagnostically useful in following reactions. Two other intense bands, one in the region 1310–1340 cm^{-1}, and one in the region 1015–1050 cm^{-1}, appear to be associated with CF stretching frequencies. The lower frequency band is assignable to the stretching of a fluorine atom attached to a saturated carbon atom, by analogy with assignments made for many fluorocarbons and their derivatives.[11] The higher frequency band is present in all the compounds studied and, in addition, a band in a very similar position is apparent in the spectra of a large number of olefins containing a $CF_2{=}CXY$ group.[12] The band is, however, absent in some compounds containing a $CClF{=}CXY$ group.[13] It seems reasonable to assign this band to a CF vibration in molecules which contain a $CF_2{=}CXY$ group. It occurs at higher frequencies than those observed for a CF vibration in saturated compounds, and this is in agreement with the frequently postulated[14] mesomeric interaction of vinylic fluorine atoms with adjacent double bonds (eq 13). The diagnostic value of the correlation of this 1310–1340-cm^{-1} band with a vinyl CF vibration in a $CF_2{=}CXY$ group is, however, somewhat doubtful since it is reported[15] that some compounds lacking this feature have marked absorption in this region.



(13)

The ^1H nmr spectra of relevant compounds are presented in Table II. Most of the spectral features reported are quite normal for organophosphorous compounds. The PH signal in the three secondary phosphines is split by coupling to ^{31}P and, for the methyl and ethyl phosphines, to the α-CH of the alkyl group. In addition a substantial coupling of some 15–18 cps to the CF_2 group adjacent to phosphorus is apparent, and there is a small further coupling, of about 1–2 cps, which may be due to a long-range coupling to one of the vinyl fluorines, *i.e.* a $J_{FC:CCPH}$ over five bonds.

In Table III the ^{19}F nmr spectra of the starting propene and of the phosphonyl compounds are presented. In these compounds there are large enough chemical shift differences between the A, B, and X_2 fluorine nuclei to make an adequate analysis of the $ABPX_2$ system possible by first-order methods. The assignment of coupling constants and chemical shifts to the *cis*- and *trans*-vinylic fluorines has been made by analogy with those determined for $CF_2{:}CCl\cdot CF_3$.[16]

Table IV gives the chemical shift ranges for the three-coordinate phosphorus compounds prepared. In these compounds the chemical shift differences are smaller and first-order methods can no longer be applied. A detailed analysis of the spectra of these compounds is currently underway.

TABLE IV

^{19}F NMR SPECTRA OF 3-COORDINATE PHOSPHORUS COMPOUNDS

$CF_2{:}CCl{\cdot}CF_2G^a$

(AB) (X_2)

G	δ_A–δ_B[b]	δ_X[c]
$PHCH_3$	79.0–80.7	91.6
PHC_2H_5	79.0–80.6	89.4
PHC_6H_5	79.4–80.8	90.6
$P(C_6H_5)_2$	78.0–79.8	94.7

[a] Spectra were determined at 56.4 Mc. Chemical shifts (δ) are given in parts per million (ppm) upfield from internal CCl_3F. [b] Estimated limits for chemical shifts. [c] Midpoint of multiplet.

Experimental Section

Volatile materials were handled in a conventional vacuum line. Involatile three-coordinate phosphorus compounds were handled in a nitrogen-filled glove bag. Molecular weights of volatile compounds were determined by vapor density methods. Infrared spectra were recorded on Beckman IR-12 and IR-5 spectrophotometers; ^1H nmr spectra were recorded on a Varian A-60 spectrometer, and ^{19}F nmr spectra were recorded on a Varian A-56/60 spectrometer.

Phenylphosphine was prepared by lithium aluminum hydride reduction of phenylphosphonous dichloride, and diphenylphosphine by hydrolysis of sodium diphenylphosphinide, prepared by sodium cleavage of triphenylphosphine.

Methylphosphine.—Lithium aluminum hydride (15 g) was added to diethylene glycol diethyl ether (250 cc) in a 1-l., three-neck flask fitted with a dropping funnel and connected to the vacuum system. The apparatus was evacuated and the flask was cooled to −10°. A solution of methylphosphonic dichloride (25 g, 188 mmoles) in diethylene glycol diethyl ether (100 cc) was slowly added *via* the dropping funnel. The volatile material produced was condensed in a trap cooled to −196°. Purification was effected by fractional condensation through a trap at −80°, the methylphosphine condensing at −196°, yielding 5.0 g (104 mmoles, 55%). *Anal.* Calcd for CH_5P: mol wt, 48. Found: mol wt, 49. The identity of the product was confirmed by infrared spectroscopy.

Dimethylphosphine.—Lithium aluminum hydride (4 g) was added to 100 cc of diethyleneglycol diethyl ether in a 500-cc, three-necked flask fitted with a dropping funnel and stirrer and connected to two traps cooled in liquid nitrogen. The solution was blanketed with nitrogen and cooled to −20°. A solution of 10.3 g (90 mmoles) of dimethylphosphinic chloride in 50 cc of diethylene glycol diethyl ether was added dropwise to the hydride slurry, which was held at −20°. Materials condensing in the traps were transferred to the vacuum line and fractionated; dimethylphosphine condensed at −196°, yielding 1.92 g (30 mmoles, 34%). *Anal.* Calcd for C_2H_7P: mol wt, 62. Found: mol wt, 61.1.

2,3-Dichlorotetrafluoropropene.—1,3-Dichlorotetrafluoro-2-propanone (100 g, 0.50 mole) and phosphorus pentachloride (150 g) were added to a 500-ml steel autoclave and heated at 275–285° for 24 hr. After cooling, the liquid product was slowly added, with vigorous stirring, to water (250 cc) at 20–25°. The lower layer was separated and washed with 10% sodium hydroxide solution (100 cc), and water (100 cc). The product was distilled to give 1,2,2,3-tetrachlorotetrafluoropropane (103 g, 0.41 mole, 82%), bp 110–112°.

1,2,2,3-Tetrachlorotetrafluoropropane (100 g, 0.39 mole) was added slowly to a vigorously stirred suspension of zinc dust

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[11] J. K. Brown and K. J. Morgan in *Advan. Fluorine Chem.*, **4**, 256 (1965).

[12] D. G. Weiblen in *Fluorine Chem.*, **2**, 476 (1954).

[13] H. Goldwhite and D. G. Rowsell, unpublished observations.

[14] R. D. Chambers and R. H. Mobbs in *Advan. Fluorine Chem.*, **4**, 51 (1965).

[15] Reference 11, p 267.

[16] See Table III, footnote *b*.

(40 g) in dry ethanol (500 cc) at 70–75°. The material distilling over below 70° was collected, washed with water (50 cc), and distilled to give 2,3-dichlorotetrafluoropropene (49 g, 0.27 mole, 71%), bp 42–43°.

Reaction between 2,3-Dichlorotetrafluoropropene and Trimethyl Phosphite.—Trimethyl phosphite (2.5 g, 20 mmoles) was added to each of two heavy wall glass reaction tubes (50 cc). 2,3-Dichlorotetrafluoropropene (6.8 g, 37 mmoles) was condensed into each of the tubes from the vacuum system. The tubes were sealed and allowed to attain room temperature. After 30 min at room temperature the volatile contents were removed and fractionated in the vacuum system to give (1) methyl chloride (2.0 g, 39 mmoles) condensing at −196° and (2) 2,3-dichlorotetrafluoropropene (5.1 g, 28 mmoles) condensing at −80°. Both compounds were identified by infrared spectroscopy. The nonvolatile residue in the reaction tubes was distilled under reduced pressure through a 20-cm spinning-band column to give dimethyl 2-chlorotetrafluoroallylphosphonate (6.1 g, 24 mmoles, 60%), bp 45–48° (0.1 mm). *Anal.* Calcd for $C_5H_6ClF_4O_3P$: C, 23.4; H, 2.4. Found: C, 23.5; H, 2.7.

2-Chlorotetrafluoroallylphosphonic Dichloride.—Dimethyl 2-chlorotetrafluoroallylphosphonate (8.0 g, 31 mmoles) was added to phosphorus pentachloride (13.0 g, 62 mmoles) in a 50-ml flask fitted with a condenser set for distillation. The mixture was heated at 130–140° for 3 hr during which time methyl chloride was evolved and phosphoryl chloride was distilled over. The residue was distilled under reduced pressure to give 2-chlorotetrafluoroallylphosphonic dichloride (6.4 g, 24 mmoles, 77%), bp 37° (0.1 mm).

2-Chlorotetrafluoroallylphosphonic Acid.—2-Chlorotetrafluoroallylphosphonic dichloride (0.5534 g, 2.084 mmoles) was added to water (5 ml). The solution was evaporated under reduced pressure to give the crystalline, hygroscopic 2-chlorotetrafluoroallylphosphonic acid (0.475 g, 2.08 mmoles, 100%). *Anal.* Calcd for $C_3H_2ClF_4O_3P$: equiv wt, 114. Found: equiv wt, 114.

Reaction between 2,3-Dichlorotetrafluoropropene and Methyl Diphenylphosphinite.—2,3-Dichlorotetrafluoropropene (5.0 g, 27 mmoles) was condensed from the vacuum system into a glass reaction tube (50 cc) containing methyl diphenylphosphinite (3.1 g, 14 mmoles). A mildly exothermic reaction occurred when the reaction mixture had attained room temperature. After 30 min at room temperature, the volatile products were removed and fractionated in the vacuum system to give (1) methyl chloride (0.71 g, 14 mmoles) condensing at −196° and (2) 2,3-dichlorotetrafluoropropene (2.2 g, 12 mmoles) condensing at −80°. The solid residue remaining in the reaction tube was recrystallized from petroleum ether (bp 100–120°) to give 2-chlorotetrafluoroallyldiphenylphosphine oxide (3.9 g, 11.1 mmoles, 79%), mp 80–82°. *Anal.* Calcd for $C_{15}H_{10}ClF_4OP$: C, 51.7; H, 2.9. Found: C, 52.3; H, 3.2.

Reaction of 2,3-Dichlorotetrafluoropropene with Methylphosphine.—2,3-Dichlorotetrafluoropropene (5.0 g, 27 mmoles) and methylphosphine (2.1 g, 44 mmoles) were condensed from the vacuum system into a steel bomb (150-cc capacity). After 24 hr at room temperature the volatile material was fractionated in the vacuum system. The fraction condensing at −80° was shown by infrared spectroscopy to consist mainly of 2,3-dichlorotetrafluoropropene; methylphosphine and hydrogen chloride were also present. The fraction condensing at −24° was 2-chlorotetrafluoroallylmethylphosphine (1.8 g, 9.2 mmoles, 34%).

Reaction of 2,3-Dichlorotetrafluoropropene with Ethylphosphine.—In a similar reaction 2,3-dichlorotetrafluoropropene (5.0 g, 27 mmoles) and ethylphosphine (2.4 g, 39 mmoles) gave 2-chlorotetrafluoroallylethylphosphine (2.1 g, 10 mmoles, 37%).

Reaction of 2,3-Dichlorotetrafluoropropene with Phenylphosphine.—In a similar reaction 2,3-dichlorotetrafluoropropene (8.9 g, 35 mmoles) and phenylphosphine (1.95 g, 17.7 mmoles) gave, after 1 week at room temperature, 2-chlorotetrafluoroallylphenylphosphine (4.9 g, 17 mmoles, 96%), bp 57° (0.1 mm). *Anal.* Calcd for $C_9H_6ClF_4P$: C, 42.0; H, 2.34. Found: C, 41.2; H, 2.58.

2-Chlorotetrafluoroallyldimethylphosphine.—In a similar reaction 2,3-dichlorotetrafluoropropene (60 mmoles) and dimethylphosphine (31 mmoles) gave, after 15 hr at room temperature, 2-chlorotetrafluoroallyldimethylphosphine (10.5 mmoles, 34%) condensing in a trap at −35°.

2-Chlorotetrafluoroallyldiphenylphosphine.—A solution of diphenylphosphine (7.5 g, 40 mmoles) in 25 cc of ether was placed in a glass pressure tube (50 cc) and 2,3-dichlorotetrafluoropropene (9.2 g, 50 mmoles) was condensed in. The tube was sealed and left for 1 week at room temperature. It was then opened, volatile materials were removed, and the residue was distilled to yield 2-chlorotetrafluoroallyldiphenylphosphine (11.9 g, 89%), bp 91–95° (0.01 mm). *Anal.* Calcd for $C_{15}H_{10}ClF_4P$: C, 54.1; H, 3.03. Found: C, 54.5; H, 3.28.

A solution of 2-chlorotetrafluoroallyldiphenylphosphine (0.10 g) in trichlorofluoromethane (0.4 g) was exposed to the air at 0° for 3 days. The crystalline material which deposited in the tube was 2-chlorotetrafluoroallyldiphenylphosphine oxide (0.075 g, 74%), mp and mmp 80–81°.

Reaction between Lithium Diphenylphosphinide and 2,3-Dichlorotetrafluoropropene.—A solution of 50 mmoles of lithium diphenylphosphinide in 50 cc of tetrahydrofuran was prepared[17] and filtered under nitrogen through a medium glass frit into a dropping funnel. It was added dropwise, with stirring, to a nitrogen-blanketed solution of 2,3-dichlorotetrafluoropropene (9.2 g, 50 mmoles) in tetrahydrofuran (10 cc) held at 0°. The resulting solution was evaporated at room temperature, and the residual oil was extracted with ether (three 25-cc portions). The ethereal extract was filtered, evaporated, and distilled to yield 2-chlorotetrafluoroallyldiphenylphosphine (0.80 g, 2.9 mmoles, 6%), bp 142° (2 mm).

Reaction between Phosphine and 2,3-Dichlorotetrafluoropropene.—Phosphine (76.5 mmoles) and 2,3-dichlorotetrafluoropropene (58.0 mmoles) were placed in a steel bomb (500 cc) and heated at 160° for 96 hr. The volatile products were taken into the vacuum line and fractionated. About 0.7 cc of a liquid product condensed at −35°. It was slightly contaminated with starting olefin, but was largely 2,3-dichloro-1,1,3,3-tetrafluoropropylphosphine, as the following spectral data indicate: infrared, ν_{PH} 2325 cm^{-1} ν_{CH}, 3010 cm^{-1}; ^1H nmr, δ_{PH} = 3.62 ppm, J_{HP} = 203 cps, J_{HPCF} = 18.5 cps, J_{HPCCCF} = 2.7 cps, δ_{CH} = 4.1–4.8 ppm (v, complex).

Registry No.—Methylphosphine, 593-54-4; dimethylphosphine, 676-59-5; 2-chlorotetrafluoroallylphosphonic acid, 10103-05-6; 2,3-dichloro-1,1,3,3-tetrafluoropropylphosphine, 10075-17-9.

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[17] A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).