Reactions of Triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane, Synthesized from a Cyclic Ylide–Ketone Adduct

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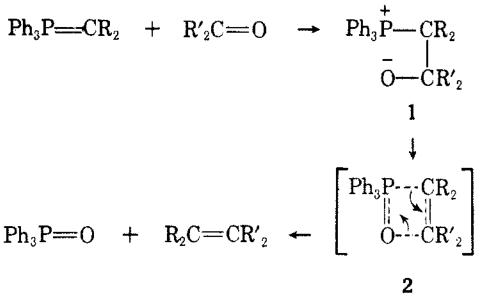
The first characterized example of a stable, cyclic ylide–ketone adduct (**4a**) has been synthesized from hexaphenylcarbodiphosphorane and hexafluoroacetone. Nmr spectroscopy (P^{31}, H^1, and F^{19}), X-ray crystallography, and chemical activity were used in establishing the structure. Cleavage of the adduct by warming above 110° in inert solvents yielded triphenylphosphine oxide and triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane (**8**), a new chemically versatile ylide. With strong acids, **8** gave bis(trifluoromethyl)vinylphosphonium salts, while with malononitrile a phosphonium inner salt was obtained. Alcohols and phenols cleaved **8**, giving bis(trifluoromethyl)vinyl ethers and triphenylphosphine. Mercaptans and amines similarly gave bis(trifluoromethyl)vinyl sulfides and amines. A dimer of bis(trifluoromethyl)thioketene was obtained from sulfur and **8**. Diphenylketene and **8** underwent a Wittig reaction to give 1,1-diphenyl-4,4-bis(trifluoromethyl)butatriene.

The few intermediates that have previously been isolated in the extensively investigated Wittig olefin synthesis have generally been assumed to have noncyclic betaine structures **1**, a cyclic state **2** being transient during cleavage to phosphine oxide and olefin products.[1-3] A stable adduct, mp 157–158°, that we have synthesized from hexafluoroacetone and hexaphenylcarbodiphosphorane (**3**),[4-6] however, has the unusual cyclic structure 4,4-bis(trifluoromethyl)-2,-2,2-triphenyl-3-(triphenylphosphoranylidene)-1,2-oxaphosphetane (**4a**) rather than the expected betaine structure (**4b**).[7] In this synthesis gaseous hexafluoroacetone could be used directly or it could be formed *in situ* from 2,2,2-triphenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholane (**5**) obtained by reaction of triphenylphosphine with hexafluoroacetone.[8]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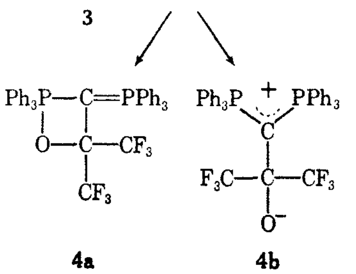
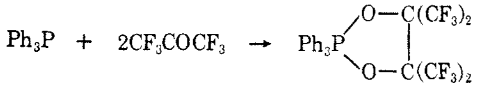

3

4a 4b

(none formed)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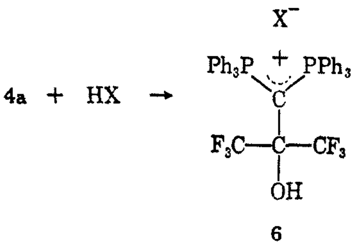
Nmr measurements were important in determining the structure of **4a**. Most significant was the P^{31} spectrum which contained two doublets of equal areas and coupling constants at -7.3 and at $+54.0$ ppm. Two doublets would be expected from spin–spin coupling of the two nonequivalent phosphorus atoms of **4a**, the doublet at -7.3 ppm being within the phosphorus ylide range and the doublet at $+54.0$ ppm being characteristic of cyclic structures having phosphorus covalently bonded to five substituents.[9,10] The two equivalent phosphorus atoms of the mesomeric phosphonium structure **4b** would be expected to have only a single P^{31} resonance at about -20 to -25 ppm.[6] The H^1 spectrum had a multipeak aryl hydrogen region at -6.5 to -8.0 ppm, a comparatively broad absorption which is consistent with the unsymmetrical structure of **4a** but not with **4b** in which all of the phenyl groups would have equivalent environments. The F^{19} spectrum contained a poorly resolved doublet at $+71.2$, the slight splitting (~0.8 cps) probably resulting from preferential spin–spin coupling of the six equivalent fluorine atoms with one of the phosphorus atoms of **4a**.

Acid treatment of **4a** resulted in narrowing of the H^1 nmr aryl hydrogen region to about 1 ppm and re-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$X = PF_6$, BF_4, and $[CF_3CO_2]_2H$

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(1) G. Wittig and G. Geisler, *Ann.*, **580**, 44 (1953).

(2) S. Trippett, *Quart. Rev.* (London), **17**, (1963).

(3) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York N. Y., 1966.

(4) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

(5) (a) C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, **84**, 4349 (1962); (b) C. N. Matthews, U. S. Patent 3,262,971 (July 26, 1966).

(6) G. H. Birum and C. N. Matthews, *J. Am. Chem. Soc.*, **88**, 4198 (1966).

(7) (a) G. H. Birum and C. N. Matthews, *Chem. Commun.*, 137 (1967); (b) G. H. Birum and C. N. Matthews, Abstracts, 153rd National Meeting of the ACS, Miami Beach, Fla., April 1967, p 0-31.

(8) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan [*Tetrahedron Letters*, 2151 (1966)], and R. F. Stockel [*ibid.*, 2833 (1966)] have also reported the synthesis of **5**.

(9) G. H. Birum and J. L. Dever, Abstracts, 135th National Meeting of the ACS, Chicago, Ill., Sept. 1958, p 101-P.

(10) F. Ramirez, Symposium on Organo-Phosphorus Compounds, Heidelberg, Germany, May 1964, p 337.

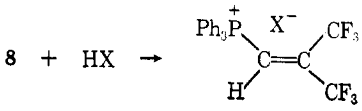
placement of the two P^{31} doublets by a moderately broad singlet at about -22 ppm. This is consistent with ring-opening of **4a** and formation of symmetrical mesomeric phosphonium salts **6**.

Moderate solubility of the adduct in benzene ($\sim$10%) and failure to alkylate with methyl iodide provide further evidence that it does not have the ionic structure **4b**. The failure to alkylate stands in contrast to the ready alkylations by methyl iodide which occurred with adducts of **3** and carbon dioxide or carbon disulfide[11] and with Wittig and Haag's stable adduct obtained from isopropylidenetriphenylphosphorane and diphenylketene.[12] The cyclic structure **4a** is also supported by an X-ray crystallographic study.[13]

The unexpected stability of **4a** may be due to the strengthening of the C–O bond by the inductive effect of neighboring trifluoromethyl groups[14] and to the high electron density at the phosphorus-bonded carbon atom, a condition that would not facilitate cleavage of the P–C bond.

The Wittig olefination sequence was completed by warming **4a** above 110° in inert solvents. For example, when a mixture of equal weights of **4a** and chlorobenzene was warmed at 120–125° for 5–10 min under nitrogen and the reaction mixture was chilled to 5° and filtered, an orange solid was obtained. Its weight was about half that of the starting material, **4a**, and it consisted of approximately equimolar quantities of triphenylphosphine oxide (**7**) and the new ylide, triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane (**8**), as determined by P^{31} nmr measurements and yields of derivatives. Part of the triphenylphosphine oxide (**7**) could be isolated, but **8** proved to be too similar to **7** in solubility characteristics and too reactive for ready separation. It was found convenient to use the mixture of **7** and **8**, usually dissolved in benzene, for the synthesis of derivatives. Fading of the marked orange-red color of the benzene solution frequently served as a useful indicator in determining when a stoichiometric amount of a reactant had been added.

Active hydrogen compounds react with **8** in several ways. The addition of anhydrous hydrogen chloride to a benzene solution of **7** and **8** resulted in precipitation of triphenyl-2,2-bis(trifluoromethyl)vinylphosphonium chloride (**9a**). Triphenylphosphine oxide (**7**) was isolated from the filtrate. Trifluoracetic acid and hexafluoroacetylacetone also added to **8** to give analogous phosphonium salts **9b** and **9c**, the anions apparently being hydrogen bis(trifluoracetate) and hexafluoroacetylacetonate, respectively. The hexafluorophosphate salt **9d** was obtained by metathesis of **9a** and **9c** with potassium hexafluorphosphate and the fluoroborate salt **9e** by metathesis of **9a** and **9b** with fluoroboric acid. A characteristic of the cation of these salts was an F^{19} nmr spectrum that contained two quartets of equal areas and coupling constants, one of the quartets consisting of three-peak systems. The quartets resulted from coupling of the two trifluoromethyl groups, and the three-peak systems presumably resulted from coupling of one of the trifluoromethyl groups with phosphorus and the vinyl hydrogen atom.



9a, X = Cl

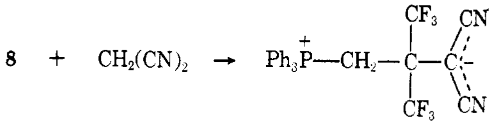
b, X = $CF_3\overset{O}{\overset{\|}{C}}O\cdots H\cdots O\overset{O}{\overset{\|}{C}}CF_3$

c, X = $(CF_3CO)_2CH$

d, X = PF_6

e, X = BF_4

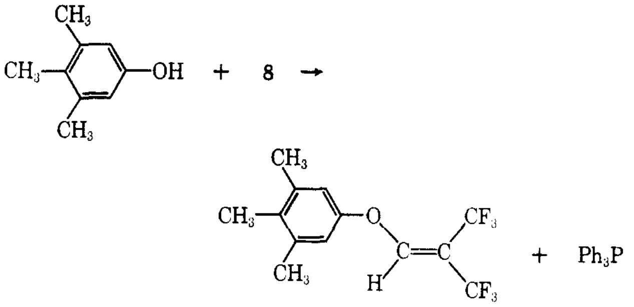
Unlike strong acids, malononitrile gave an inner salt **10** when added to a benzene solution of **7** and **8**. The



10

assignment of structure **10** was based on nmr spectra showing a P^{31} nmr chemical shift at -24.8 ppm for the phosphonium group, an H^1 nmr doublet at -3.6 ppm (J_{HP} = 13.5 cps) for the two equivalent methylene hydrogen atoms, and an F^{19} nmr doublet at $+68.3$ ppm (J_{FP} = 1.5 cps) for the six equivalent fluorine atoms and on molecular weight measurements and elemental analyses. The inner salt was recovered unchanged after treatment of a methanol solution with fluoroboric acid.

Cleavage of **8** occurred with 3,4,5-trimethylphenol, yielding 2,2-bis(trifluoromethyl)vinyl 3,4,5-trimethylphenyl ether (**11**) and triphenylphosphine. The triphenylphosphine was separated from **11** and the accompanying triphenylphosphine oxide by precipitation as methyltriphenylphosphonium iodide; **11** was then extracted from the oxide with pentane. Infrared, nmr, and mass spectra were consistent with structure **11**. The F^{19} nmr spectrum contained two quartets of doublets, the quartets having equal areas and coupling constants. The doublets had nonequivalent coupling constants resulting from unequal coupling of the vinyl hydrogen atom with the *cis*- and *trans*-trifluoromethyl groups. Similar nmr patterns were obtained for the reaction mixtures resulting from treatment of **8** with phenol, ethanol, and methanol, indicating that the reaction is general for alcohols and



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[11] C. N. Matthews, J. S. Driscoll, and G. H. Birum, *Chem. Commun.*, 736 (1966).

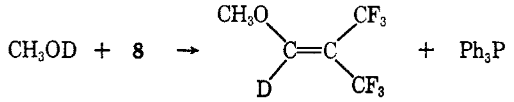
[12] G. Wittig and A. Haag, *Chem. Ber.*, **96**, 1535 (1963).

[13] We thank G. Chioccola and J. J. Daly of Monsanto Research S. A., Zurich, Switzerland, for communicating to us the results of an X-ray study to be published shortly.

[14] A. M. Lovelace, D. A. Rausch, and W. Postelnak, "Aliphatic Fluorine Compounds," Rheinhold Publishing Corp., New York, N. Y., 1958, p 106.

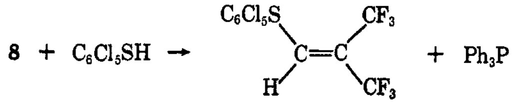
phenols. It appears to be quantitative according to P^{31} and F^{19} nmr measurements.

The F^{19} nmr spectrum for the vinyl ether **12**, resulting from the use of methanol-*d*, contained two identical quartets without any of the additional peak splitting that occurred from coupling of fluorine with hydrogen when ordinary methanol was used.



12

Vinyl sulfides were obtained by cleavage of **8** with aryl and alkyl mercaptans, again in quantitative yields according to P^{31} and F^{19} nmr measurements. For example, pentachlorothiophenol and **8** gave pentachlorophenyl 2,2-bis(trifluoromethyl)vinyl sulfide (**13**) and triphenylphosphine. The F^{19} nmr spectrum of **13** contained two quartets, one of them consisting of doublets having a coupling constant equivalent to that of a well-resolved H^1 nmr quartet that represented the single hydrogen atom in the molecule. Apparently, only one of the two trifluoromethyl groups coupled measurably with the vinyl hydrogen in this case.



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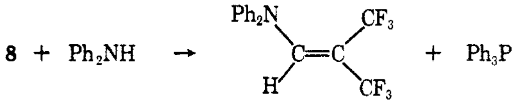
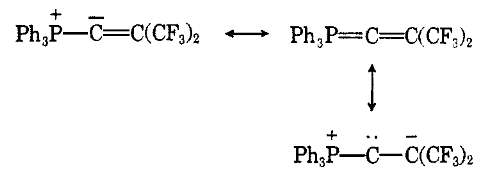
Diphenylamine and **8** gave N,N-diphenyl-N-[2,2-bis(trifluoromethyl)vinyl]amine (**14**) and triphenylphosphine. Two F^{19} nmr quartets of doublets as well as infrared and mass spectra were in agreement with structure **14**.



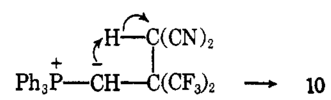
14

The formation of three types of products—vinylphosphonium salts, phosphonium inner salts, and olefins—from active hydrogen compounds and **8** is, perhaps, best explained by assuming possible carbenoid as well as ylide character for the phosphorane. A typical ylide reaction would be addition of acids to yield vinylphosphonium salts (**9**). In the malononitrile case the initially formed salt is unstable because it has a nucleophilic anion. This apparently attacks the β-carbon atom of the cation, giving **15** which rearranges by intramolecular proton transfer to the stable inner salt (**10**). With alcohols, phenols, mercaptans, and amines, however, carbenoid insertion of **8** seems preferable since the resulting inner salts (**16**) could readily eliminate triphenylphosphine to give olefinic products (**17**).



$$\mathrm{Ph_3\overset{+}{P}{-}\overset{-}{C}{=}C(CF_3)_2} \longleftrightarrow \mathrm{Ph_3P{=}C{=}C(CF_3)_2} \updownarrow \mathrm{Ph_3\overset{+}{P}{-}\ddot{C}{-}\overset{-}{C}(CF_3)_2}$$

8



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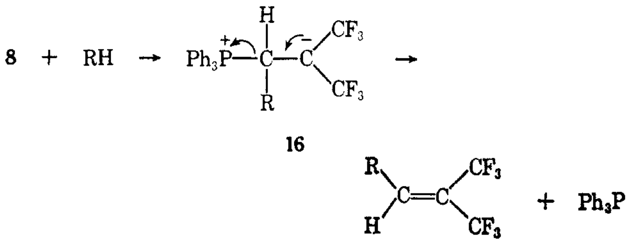
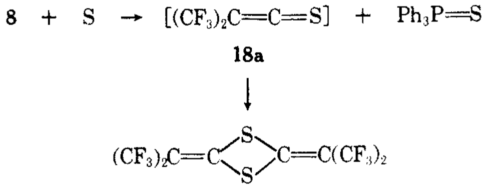


16 **17**

RH = alcohols, phenols, mercaptans, and amines

In another type of reaction, **8** was readily cleaved by sulfur, giving triphenylphosphine sulfide and 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane (**18**) which has been synthesized recently by another method.[15] The precursor for **18** was, no doubt, bis(trifluoromethyl)thioketene[15] (**18a**).



18a **18**

The chemical versatility of **8** was further demonstrated by a Wittig-type reaction with diphenylketene, giving 1,1-diphenyl-4,4-bis(trifluoromethyl)butatriene (**19**) and triphenylphosphine oxide. The infrared spectrum of **19** contained an absorption band of medium intensity at 4.82 μ for the cumulated system. Mass spectra fragmentation data, nmr spectra, molecular weight results, and elemental analyses were also in agreement with structure **19**.

$$\mathbf{8} + \mathrm{Ph_2C{=}C{=}O} \longrightarrow \mathrm{Ph_2C{=}C{=}C{=}C(CF_3)_2} + \mathrm{Ph_3P{=}O}$$

19

Experimental Section

Melting points were obtained in a Thomas-Hoover Unimelt instrument and are corrected. Infrared spectra were determined in potassium bromide disks (unless otherwise noted) on a Beckman IR-4 spectrophotometer. Proton nuclear magnetic resonance (nmr) spectra were obtained at 60.0 or 100.0 Mc on Varian A-60 or HR-100 spectrometers with tetramethylsilane as an internal standard. Phosphorus nmr spectra were determined at 24.3 or 40.5 Mc on Varian HR-60 or HR-100 instruments and are reported with respect to 85% H_3PO_4 contained in a capillary. Fluorine nmr spectra were measured at 56.4 Mc on a Varian A-56/60 instrument and are reported with respect to trichlorofluoromethane. The nmr measurements were generally made on saturated solutions. Mass spectra were obtained on a Consolidated Engineering Corp. Type 21-103C spectrometer. Elemental analyses and molecular weights were determined by Galbraith Laboratories, Knoxville, Tenn.

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[15] M. S. Raasch, *Chem. Commun.*, 577 (1966).

4,4-Bis(trifluoromethyl)-2,2,2-triphenyl-3-(triphenylphosphoranylidene)-1,2-oxaphosphetane (4a).—Gaseous hexafluoroacetone was dispersed in a stirred mixture of hexaphenylcarbodiphosphorane (**3**)[4-6] (21.4 g, 0.04 mole) and dry diglyme (65 g) under nitrogen at 40–50°. The flow of hexafluoroacetone was continued for 0.5 hr after the yellow color of **3** disappeared. The reaction mixture was then cooled at 5° for 3 hr and filtered under nitrogen. The resulting product was washed with diglyme and diethyl ether to give a white solid (21.5 g, 76% yield): mp 155–157° dec (157–158° from diglyme–diethyl ether); molecular weight by vapor pressure osmometry in benzene, 706 and 700 (theoretical for a 1:1 adduct, 702.6). The P^{31} nmr spectrum exhibited doublets of equal area at -7.3 and at $+54.0$ ppm, $J_{PP'} = 47 \pm 7$ cps (measured in a saturated methylene chloride solution at both 24.3 and 40.5 Mc); the F^{19} spectrum contained a poorly resolved doublet at $+71.2$ ppm ($J_{FP} \sim 0.8$ cps), and the H^1 spectrum had a multipeak aryl hydrogen region at -6.5 to -8.0 ppm.

Anal. Calcd for $C_{40}H_{30}F_6OP_2$: C, 68.37; H, 4.30; F, 16.22; P, 8.82. Found: C, 68.02; H, 4.24; F, 16.19; P, 8.86.

A solution of **4a** (2.0 g) in benzene (5 g) and methyl iodide (1.5 g) was stirred at room temperature for 20 hr. Evaporation of the solvent in nitrogen followed by washing of the residue with ether and drying, gave recovered **4a** (2.0 g), mp 155–157°, having infrared and P^{31} and F^{19} nmr spectra identical with those of the starting material. The results were the same when **4a** was warmed in a solution of methanol and methyl iodide.

2,2,2-Triphenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholane (5).—Triphenylphosphine (26.2 g, 0.10 mole) and dry diglyme (26 g) were stirred under nitrogen in a flask equipped with a Dry Ice condenser as gaseous hexafluoroacetone was dispersed below the surface at ambient temperature until the reaction mixture was saturated with the ketone. Filtration and washing of the product with heptane gave 40.3 g (68% yield) of a white solid, **5**, mp 118–119° dec (from ether), having a P^{31} nmr singlet at $+22.2$ ppm (in $CDCl_3$) and an F^{19} nmr singlet at $+67.7$ ppm and molecular weight in $CHCl_3$, 595 and 600 (theoretical, 594).

Anal. Calcd for $C_{24}H_{15}F_{12}O_2P$: C, 48.50; H, 2.54; F, 38.35; P, 5.22. Found: C, 48.31; H, 2.61; F, 38.40; P, 5.03.

A rapid-scan mass spectrometer–gas chromatographic analysis of the off-gas at the melting point showed that it was over 99% hexafluoroacetone. The residue was triphenylphosphine, mp 79–80°, having a characteristic P^{31} nmr chemical shift at $+6.2$ ppm.

A portion of the hexafluoroacetone–triphenylphosphine adduct (**5**) (5.9 g, 0.01 mole) and hexaphenylcarbodiphosphorane (5.4 g, 0.01 mole) were added to dry diglyme (15 g) and the mixture was stirred under nitrogen and warmed at 65–75° for 0.5 hr. After cooling, the reaction mixture was filtered and washed with ether to give 5.3 g (72% yield) of a white powder, mp 153–154°, which was shown by infrared and nmr (P^{31} and F^{19}) spectra to be the same compound, **4a**, that was obtained when hexaphenylcarbodiphosphorane was treated with gaseous hexafluoroacetone.

[2-Hydroxy-2-trifluoromethyl-3,3,3-trifluoro-1-(triphenylphosphoranylidene)propyl]triphenylphosphonium Hexafluorophosphate (6).—A solution of the hexaphenylcarbodiphosphorane–hexafluoroacetone adduct (**4a**) (1.0 g) in diglyme was stirred as 65% hexafluorophosphoric acid (1.5 g) was added dropwise. Heat of reaction raised the temperature to 45°. The reaction mixture was stirred for 2 hr and then diluted with ether to precipitate 1.1 g of a white powder. Recrystallization from diglyme–ether gave 1.0 g (83% yield) of white solid (**6**) ($X = PF_6$), mp 213–213.5° dec. The P^{31} nmr spectrum (in acetonitrile) contained a moderately broad peak at -21.6 ppm and a heptet at $+144.8$ ppm ($J_{PF} = 706$ cps); the F^{19} spectrum contained a singlet at $+71.6$ ppm and a doublet at $+72.5$ ppm ($J_{FP} = 709$ cps), the area ratio of singlet to doublet being 1:1; and the H^1 spectrum contained an aryl proton region at -7.1 to -8.0 ppm and a broad hydroxylic proton signal at -6.3 ppm, the areas approximating the theoretical 30:1 ratio.

Anal. Calcd for $C_{40}H_{31}F_{12}OP_3$: C, 56.65; H, 3.68; F, 26.88; P, 10.96. Found: C, 56.62; H, 3.79; F, 27.12; P, 11.17.

The same hexafluorophosphate salt was also prepared by first treating a benzene solution of **4a** with anhydrous HCl and then treating the resulting chloride salt with KPF_6 in methanol.

[2-Hydroxy-2-trifluoromethyl-3,3,3-trifluoro-1-(triphenylphosphoranylidene)propyl]triphenylphosphonium Hydrogen Bis(trifluoroacetate) (6).—A solution of the hexaphenylcarbodiphosphorane–hexafluoroacetone adduct (**4a**) (2 g) in methylene chloride was treated with trifluoroacetic acid (2 g). The reaction mixture was then evaporated to dryness under nitrogen and the residue was recrystallized from benzene–acetonitrile to give 1.8 g of white powder (**6**) [$X = (CF_3CO_2)_2H$], mp 153–154° dec. The P^{31} nmr spectrum (in $CDCl_3$) had a moderately broad signal at -21.2 ppm; the F^{19} spectrum contained singlets of equal areas at $+71.4$ and at $+76.2$ ppm; and the H^1 spectrum contained an aryl hydrogen region centered at -7.5 ppm and a singlet at -9.9 ppm, the areas approximating a 15:1 ratio.

Anal. Calcd for $C_{44}H_{32}F_{12}O_5P_2$: C, 56.76; H, 3.46; F, 24.49; P, 6.65. Found: C, 56.55; H, 3.66; F, 24.11; P, 6.64.

[2-Hydroxy-2-trifluoromethyl-3,3,3-trifluoro-1-(triphenylphosphoranylidene)propyl]triphenylphosphonium Tetrafluoroborate (6).—A solution of the hexaphenylcarbodiphosphorane–hexafluoroacetone adduct (**4a**) (1.0 g) in diglyme was stirred as 48% fluoroboric acid (0.5 g) was added dropwise. After 1.5 hr, 1.1 g of white solid was precipitated by addition of ether. Recrystallization from diglyme–acetonitrile by addition of ether gave 0.9 g (80% yield) of white solid (**6**, $X = BF_4$), mp 215–215.5° dec. The P^{31} nmr spectrum (in acetonitrile) contained a moderately broad signal at -22.0 ppm; the F^{19} spectrum contained a singlet at $+70.3$ ppm for the cation and a multiplet at $+150.3$ ppm for the anion in a 3:2 area ratio; and the H^1 spectrum contained an aryl proton region at -7.1 to -8.0 ppm and a broad hydroxylic signal at -6.2 ppm, approximating a 30:1 area ratio.

Anal. Calcd for $C_{40}H_{31}BF_{10}OP_2$: C, 60.75; H, 3.96; B, 1.37; F, 24.05; P, 7.84. Found: C, 60.67; H, 4.20; B, 1.20; F, 23.81; P, 7.74.

Triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane (8).—A mixture of the hexaphenylcarbodiphosphorane–hexafluoroacetone addust (**4a**) (38.0 g) and dry chlorobenzene (35 g) was stirred under nitrogen and warmed at 120–126° for 5 min. The resulting dark red-brown solution was cooled at 5° for 20 hr and then filtered under nitrogen. The solid product was washed with ether to give 18.7 g of an orange solid mixture, mp 110–155°, having a P^{31} nmr singlet (in benzene) at -24.5 ppm for triphenylphosphine oxide and another P^{31} singlet at -4.1 ppm, the latter singlet and an F^{19} doublet at $+61.4$ ppm ($J_{FP} = 3.5$ cps) being attributed to **8**. The area ratio of the P^{31} singlet at -24.5 ppm to that at -4.1 ppm was approximately 4:3 (for some batches the area ratio was about 1:1). No other P^{31} or F^{19} nmr signals were observed. Attempts to separate the two components by recrystallization resulted in isolation of some triphenylphosphine oxide, but pure **8** was not obtained. The mixture was used in the preparation of derivatives of **8**.

Triphenyl-2,2-bis(trifluoromethyl)vinylphosphonium Chloride (9a).—A portion of the mixture (5.0 g) of **8** and triphenylphosphine oxide (**7**) was dissolved in dry benzene (20 ml). The solution was stirred under nitrogen as anhydrous hydrogen chloride was dispersed below the surface until the last trace of the initial orange-red color disappeared. The reaction mixture was filtered and the solid product was washed with benzene and ether and then recrystallized from diglyme–acetonitrile to give 1.6 g of white solid (**9a**), mp 153–154° dec. The P^{31} nmr spectrum (in $CDCl_3$) had a singlet at -17.3 ppm; the H^1 spectrum had a doublet at -9.1 ppm ($J_{HP} = 8.5$ cps) and aryl hydrogen multiplets at -7.5 to -8.3 ppm, the areas approximating a 1:15 ratio; and the F^{19} spectrum contained a quartet at $+58.1$ ppm ($J_{CF_3CF_3} = 7.5$ cps) and a quartet of triplets at $+63.2$ ppm ($J_{CF_3CF_3} = 7.5$ cps; $J_{CF_3HP} \sim 0.5$ cps), the quartets having equal areas.

Anal. Calcd for $C_{22}H_{16}ClF_6P$: C, 57.34; H, 3.50; Cl, 7.69; F, 24.74; P, 6.72. Found: C, 57.24; H, 3.69; Cl, 7.93; F, 24.68; P, 6.73.

Triphenylphosphine oxide (2.2 g), having infrared and P^{31} nmr spectra that were essentially identical with those of an authentic sample, was isolated from the filtrate obtained after the hydrogen chloride treatment.

Triphenyl-2,2-bis(trifluoromethyl)vinylphosphonium Hydrogen Bis(trifluoroacetate) (9b).—A solution of the mixture (2.3 g) of **8** and triphenylphosphine oxide in benzene (6.5 g) was stirred as trifluoroacetic acid (1.0 g) was added rapidly, causing the initial orange-red color to change to light yellow. After standing at room temperature for 20 hr, the reaction mixture was diluted with ether and filtered and the solid product recrystallized from diglyme–ether to give 1.2 g of white crystals (**9b**), mp 119–121° dec. The P^{31} nmr spectrum (in $CDCl_3$) had a singlet at −17.5 ppm; the H^1 spectrum contained a doublet at −8.5 ppm (J_{HP} = 9 cps) for the vinyl hydrogen atom and an aryl hydrogen region at −7.6 to −8.1 ppm (an nmr signal was not observed for the hydrogen atom in the anion); and the F^{19} spectrum contained a singlet at +76.0 ppm for the anion, a quartet at +58.6 ppm ($J_{CF_3CF_3}$ = 7.6 cps), and a quartet of triplets at +64.4 ppm ($J_{CF_3CF_3}$ = 7.6 cps; J_{CF_3HP} = 1.2 cps), the areas of the singlet and two quartets having the theoretical 2:1:1 ratio.

Anal. Calcd for $C_{26}H_{17}F_{12}O_4P$: C, 47.84; H, 2.63; F, 34.93; P, 4.75. Found: C, 47.69; H, 2.81; F, 34.20; P, 4.84.

Triphenyl-2,2-bis(trifluoromethyl)vinylphosphonium Hexafluoracetylacetonate (9c).—A benzene solution of the mixture (4.0 g) of **8** and triphenylphosphine oxide was stirred under nitrogen as hexafluoroacetylacetone was added dropwise until the initial orange-red color faded to light yellow. After 1 hr the reaction mixture was filtered and the solid product was washed with benzene and ether to give 2.05 g of slightly yellow powder, mp 153–154° dec. Recrystallization from carbon tetrachloride–diglyme gave 1.2 g of light yellow solid, mp 154–155° dec. The P^{31} nmr spectrum (in $CDCl_3$) had a singlet at −18.1 ppm; the H^1 spectrum contained a doublet at −9.4 ppm (J_{HP} = 8.4 cps) for the vinyl hydrogen atom, an aryl hydrogen multiplet at −7.5 to −8.1 ppm, and a singlet at −5.3 ppm for the hydrogen atom in the anion, the areas approximating the theoretical 1:15:1 area ratio; and the F^{19} spectrum contained a singlet at +76.7 ppm for the anion and quartets at +58.6 and +63.8 ppm ($J_{CF_3CF_3}$ = 7.6 cps), the areas having the theoretical 2:1:1 ratio.

Anal. Calcd for $C_{27}H_{17}F_{12}O_2P$: C, 51.27; H, 2.71; F, 36.05; P, 4.90. Found: C, 51.21; H, 2.86; F, 36.26; P, 5.04.

Triphenyl-2,2-bis(trifluoromethyl)vinylphosphonium Hexafluorophosphate (9d).—An ethanol solution of the phosphonium chloride **9a** (1.0 g) was stirred as potassium hexafluorophosphate (0.5 g) was added. The reaction mixture was warmed to reflux, cooled, filtered, and the solid product washed with distilled water. Recrystallization twice from ethanol gave 0.4 g of white solid, **9d**, mp 174–176°. The P^{31} nmr spectrum (in $CDCl_3$) contained a singlet at −17.8 ppm for the cation and a heptet at +150.0 ppm (J_{PF} ~ 730 cps) for the anion; the F^{19} spectrum contained a doublet at +72.9 ppm (J_{PF} = 714 cps) and quartets at +59.3 and +65.3 ppm ($J_{CF_3CF_3}$ = 7.5 cps), the areas having the theoretical 2:1:1 ratio; the H^1 spectrum contained an aryl multiplet at −7.5 to −8.3 ppm (a signal for the vinyl hydrogen could not be seen, probably because of masking by the aryl multiplet).

Anal. Calcd for $C_{22}H_{16}F_{12}P_2$: C, 46.32; H, 2.83; F, 39.97; P, 10.86. Found: C, 46.40; H, 2.54; F, 40.44; P, 10.66.

The same hexafluorophosphate salt, **9d**, was prepared by treatment of the hexafluoroacetylacetonate salt, **9c**, with potassium hexafluorophosphate.

Triphenyl-2,2-bis(trifluoromethyl)vinylphosphonium Tetrafluoroborate (9e).—A methanol solution of the hydrogen bis(trifluoroacetate)salt (**9b**) (0.4 g) was stirred as 48% fluoroboric acid (0.5 g) was added dropwise. After 0.2 hr distilled water was added, causing a white solid to separate. This was dissolved in methanol, again treated with fluoroboric acid, and then precipitated with water and dried to give 0.3 g of white solid (**9e**), mp 112–114°. The P^{31} nmr spectrum (in $CDCl_3$) had a singlet at −17.3 ppm; the H^1 spectrum contained a doublet for the vinyl hydrogen atom at −8.05 ppm (J_{HP} = 9.2 cps) and an aryl hydrogen region at −7.5 to −8.0 ppm, the areas approximating a 1:15 ratio; and the F^{19} spectrum contained a BF_4^- multiplet at +151.7 ppm, a quartet at +58.4 ppm ($J_{CF_3CF_3}$ = 7.4 cps), and a quartet of triplets at +64.3 ppm ($J_{CF_3CF_3}$ = 7.4 cps; J_{CF_3HP} = 1.1 cps).

Anal. Calcd for $C_{22}H_{16}BF_{10}P$: C, 51.58; H, 3.15; B, 2.11; F, 37.09; P, 6.05. Found: C, 51.37; H, 3.10; B, 2.50; F, 36.62; P, 6.15.

Treatment of the chloride salt (**9a**) with fluoroboric acid in a similar manner gave the same tetrafluoroborate salt (**9e**), as shown by melting points and infrared and nmr (P^{31}, F^{19}, and H^1) spectra.

Inner Salt of 8 and Malononitrile (10).—A benzene solution of the mixture (1.0 g) of **7** and **8** was stirred under nitrogen as malononitrile (0.2 g) was added in portions. After a few minutes the orange-red color faded to yellow and a solid separated. The reaction mixture was warmed to reflux, cooled, and filtered to give 0.6 g of light tan powder, mp 164–169°. Recrystallization of a portion from ethanol gave light tan crystals, mp 167–169° dec. The P^{31} nmr spectrum (in $CDCl_3$) contained a moderately broad singlet at −24.8 ppm; the H^1 spectrum had a doublet at −3.6 ppm (J_{HP} = 13.5 cps) and aryl hydrogen multiplets at −7.4 to −8.0 ppm, the areas approximating the theoretical 2:15 ratio; and the F^{19} spectrum had a doublet at +68.3 ppm (J_{FP} = 1.5 cps). The infrared spectrum contained nitrile absorption at 4.6 (m) and at 4.7 μ (s). The molecular weight in acetone was 494 (theoretical, 490).

Anal. Calcd for $C_{25}H_{17}F_6N_2P$: C, 61.23; H, 3.49; F, 23.24; N, 5.71; P, 6.32. Found: C, 60.89; H, 3.59; F, 23.24; N, 5.51; P, 6.08.

A solution of **10** (0.3 g) in methanol was stirred as 48% fluoroboric acid (0.5 g) was added. Dilution of the solution with distilled water resulted in precipitation of 0.2 g of light tan solid, mp 173–174° dec, having infrared and nmr (H^1, F^{19}, and P^{31}) essentially identical with those of the starting material.

3,4,5-Trimethylphenyl 2,2-Bis(trifluoromethyl)vinyl Ether (11).—A benzene solution of a mixture (5.0 g) of **7** and **8** was stirred under nitrogen as 3,4,5-trimethylphenol was added until the initial orange-red color faded to light yellow. The P^{31} nmr spectrum of the reaction mixture contained a peak at −24.4 ppm for triphenylphosphine oxide and a peak of slightly larger area at +5.8 ppm for triphenylphosphine. Methyl iodide (3 g) was added and the mixture was stirred for 2 hr and then filtered to give 2.7 g of methyltriphenylphosphonium iodide (identified by its infrared and P^{31} and H^1 nmr spectra). Evaporation of the filtrate to dryness and extraction with pentane and ether gave 2.1 g of insoluble triphenylphosphine oxide. Evaporation of the combined pentane and ether solutions gave 1.8 g of white solid, mp 43–45°. Recrystallization of a portion from aqueous ethanol gave white crystals, mp 45–46°. The infrared spectrum contained a band at 5.96 μ (m) (C═C). The H_1 nmr spectrum (in $CDCl_3$) contained peaks at −7.55 (br), −6.81, −2.28, and −2.15 ppm in the theoretical 1:2:6:3 area ratio; and the F^{19} spectrum contained quartets of doublets at +59.4 ppm ($J_{CF_3CF_3}$ = 6.4 cps; J_{CF_3H} = 0.9 cps) and at +61.8 ppm ($J_{CF_3CF_3}$ = 6.4 cps; J_{CF_3H} = 1.5 cps), the two quartets having equal areas. The mass spectrum (at 70 and 8.2 ev) showed the parent ion (*m/e* 298) to be present in greatest abundance and the isotopic abundance ratio (with *m/e* 299) and fragmentation data in agreement with structure **11**.

Anal. Calcd for $C_{13}H_{12}F_6O$: C, 52.35; H, 4.06; F, 38.22. Found: C, 52.51; H, 4.18; F, 37.98.

Ethyl 2,2-Bis(trifluoromethyl)vinyl Ether.—Addition of ethanol to a mixture of **7** and **8** in benzene caused the initial orange-red color to fade to light yellow. The P^{31} nmr spectrum of the reaction mixture contained singlets at −26.2 ppm for triphenylphosphine oxide and at +6.0 ppm for triphenylphosphine; the F^{19} spectrum contained quartets of doublets at +59.0 ppm ($J_{CF_3CF_3}$ = 6.4 cps; J_{CF_3H} = 0.9 cps) and at +60.8 ppm ($J_{CF_3CF_3}$ = 6.4 cps; J_{CF_3H} = 1.6 cps), the quartets having equal areas. The product was not isolated.

Methyl 1-Deuterio-2,2-bis(trifluoromethyl)vinyl Ether (12).—Methanol-d_1, CH_3OD, was added to a benzene solution of **7** and **8** until most of the initial orange-red color had disappeared. The product and solvent were distilled at reduced pressure into a Dry Ice cooled receiver. An infrared spectrum of the colorless distillate contained an absorption band at 6.02 μ (m) (C═C). The F^{19} nmr spectrum contained quartets of equal area at +58.9 and +60.8 ppm ($J_{CF_3CF_3}$ = 6.4 cps) with no resolvable fine structure and the H^1 spectrum contained a singlet at −2.8 ppm for the methyl group. The mass spectrum showed the presence of the parent ion (*m/e* 195). Isotopic abundance at 196 and fragmentation data were in agreement with **12**. The product was not isolated from benzene. Similar decolorization of a benzene solution of **7** and **8** with methanol, CH_3OH, gave a solution having an F^{19} nmr spectrum that contained a quartet at +59.0 ppm ($J_{CF_3CF_3}$ = 6.2 cps) (fine structure unresolved) and a quartet of doublets at +60.8 ppm ($J_{CF_3CF_3}$ = 6.2 cps; J_{CF_3H} = 1.2 cps).

Pentachlorophenyl 2,2-Bis(trifluoromethyl)vinyl Sulfide (13).—A portion (1.0 g) of approximately equimolar quantities of **7** and **8** in benzene (5 ml) was stirred under nitrogen as pentachlorothiophenol was added in small portions until the initial orange-red color faded to light yellow. The P^{31} nmr spectrum of the reaction mixture showed peaks of approximately the same areas at −23.8 ppm for triphenylphosphine oxide and at +6.0 ppm for triphenylphosphine. Methyl iodide (1 g) was added, resulting in separation of a white solid after a few minutes. The mixture was stirred for 2 hr and then filtered to give 0.4 g of methyltriphenylphosphonium iodide, mp 184.5–185.5°, identified by P^{31}, H^1, and infrared spectra. The filtrate was evaporated to dryness and the residue was extracted twice with pentane, leaving 0.3 g of insoluble triphenylphosphine oxide having P^{31} nmr and infrared spectra essentially identical with those of an authentic sample. The pentane solution was evaporated to dryness; the residue was sublimed and recrystallized from aqueous ethanol and finally from methanol to give 0.2 g of white crystals, mp 91–93°. The infrared spectrum contained an absorption band at 6.15 μ (m) (C=C). The H^1 nmr spectrum (in $CDCl_3$) contained a quartet of singlets at -7.20 ppm ($J_{\mathrm{HCF_3}} = 1.6$ cps) and the F^{19} spectrum contained a quartet of singlets at $+59.9$ ppm ($J_{\mathrm{CF_3CF_3}} = 6.3$ cps) and a quartet of doublets at $+62.6$ ppm ($J_{\mathrm{CF_3CF_3}} = 6.3$ cps; $J_{\mathrm{CF_3H}} = 1.4$ cps), the quartets having equal areas. The mass spectrum showed the parent ion (*m/e* 444) in major abundance with predominant fragmentation due to loss of Cl and F.

Anal. Calcd for $C_{10}HCl_5F_6S$: C, 27.01; H, 0.23; Cl, 39.87; F, 25.64; S, 7.21. Found: C, 25.91; H, 0.25; Cl, 39.88; F, 26.04; S, 7.41.

Ethyl 2,2-Bis(trifluoromethyl)vinyl Sulfide.—A solution of **7** and **8** in benzene was treated with ethyl mercaptan until the initial orange-red color faded to light yellow. The P^{31} nmr spectrum of the reaction mixture contained singlets at -24.6 ppm for triphenylphosphine oxide and at $+6.0$ for triphenylphosphine. Distillation at reduced pressure gave a benzene solution of the product having an F^{19} nmr spectrum that contained a quartet at $+60.6$ ppm ($J_{\mathrm{CF_3CF_3}} = 6.2$ cps) and a quartet of doublets at $+62.6$ ppm ($J_{\mathrm{CF_3CF_3}} = 6.2$ cps; $J_{\mathrm{CF_3H}} = 1.3$ cps), the quartets having equal areas; the H^1 spectrum contained a triplet at -0.7 ppm ($J_{\mathrm{HH'}} = 7.4$ cps) and a quartet at -1.8 ppm ($J_{\mathrm{H'H}} = 7.4$ cps) in a 3:2 area ratio. A signal for the vinyl hydrogen atom was not observed, probably because of masking by benzene.

N,N-Diphenyl-N-[2,2-bis(trifluoromethyl)vinyl]amine (14).—A benzene solution of the mixture (2.5 g) of **7** and **8** was stirred under nitrogen as diphenylamine was added in small portions until the initial orange-red color faded to yellow. After 1.5 hr a P^{31} nmr spectrum of the reaction mixture showed singlets of approximately equal areas at -24.9 ppm for triphenylphosphine oxide and at $+6.0$ ppm for triphenylphosphine. Methyl iodide (2 g) was added and the mixture was stirred for 2 hr. Filtration gave 1.5 g of methyltriphenylphosphonium iodide (identified by infrared and P^{31} and H^1 nmr spectra). Evaporation of the filtrate to dryness and extraction of the residue with pentane twice gave 1.0 g of insoluble triphenylphosphine oxide. The pentane-soluble product was recrystallized from aqueous ethanol to give 0.3 g of white needles, mp 65–66.5°. The F^{19} nmr spectrum (in $CDCl_3$) contained a quartet of doublets at $+56.0$ ppm ($J_{\mathrm{CF_3CF_3}} = 7.9$ cps; $J_{\mathrm{CF_3H}} = 1.1$ cps) and a quartet of doublets at $+58.4$ ppm ($J_{\mathrm{CF_3CF_3}} = 7.9$ cps; $J_{\mathrm{CF_3H}} = 0.8$ cps), the two quartets having equal areas; and the H^1 spectrum contained a complex aryl proton region at -7.0 to -7.7 ppm (a multiplet at -7.5 ppm appeared to be a quartet, $J_{\mathrm{HCF_3}} \sim 1.1$ cps, and could represent the vinyl proton). The infrared spectrum contained a band at 6.08 μ (m) (C=C). The mass spectrum showed the parent ion (*m/e* 331) to be present in greatest abundance with isotopic abundance at 332 and fragmentation data also being in agreement with structure **14**: molecular weight in $CHCl_3$, 320 (theoretical, 331).

Anal. Calcd for $C_{16}H_{11}F_6N$: C, 58.00; H, 3.35; F, 34.41; N, 4.23. Found: C, 57.80; H, 3.22; F, 34.29; N, 4.19.

2,4-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane (18).—A solution of the mixture (5.0 g) of **7** and **8** in benzene (10 ml) was stirred under nitrogen as powdered sulfur was added slowly until the orange-red color faded. The reaction mixture was stirred for 20 hr at room temperature and then distilled into a Dry Ice cooled receiver to a maximum pot temperature of 100° (0.1 mm). A P^{31} nmr spectrum of the residue contained singlets at -42.9 ppm for triphenylphosphine sulfide and at -24.7 ppm for triphenylphosphine oxide. An F^{19} nmr spectrum of the distillate showed a single peak at $+58.9$ ppm, indicating the presence of only one fluorine-containing product. The mass spectrum (at 70 ev) of the distillate showed the ions of greatest abundance to have masses of 388 (the molecular weight of **18**), of 194 (the molecular weight of bis(trifluoromethyl)thioketene, **18a**), and of 175 (the molecular weight of **18a** − F), the relative abundances being in the order 46:73:45. Distillation of the benzene and recrystallization of the residue from methanol gave 0.4 g of white crystals (**18**), mp 84–85°. The infrared spectrum had an absorption band at 6.19 μ (s). These properties are in agreement with those reported by Raasch[15] for **18** prepared by another route.

1,1-Diphenyl-4,4-bis(trifluoromethyl)butatriene (19).—A solution of a mixture (2.0 g) of **7** and **8** in benzene was stirred under nitrogen as diphenylketene was added dropwise until the initial orange-red color had faded to yellow. A P^{31} nmr spectrum of the reaction mixture showed only a single peak at -24.2 ppm for triphenylphosphine oxide. The mixture was evaporated to dryness and the residue was extracted with ether to separate the soluble product from insoluble triphenylphosphine oxide; evaporation and extraction was repeated with ether and then with pentane, finally giving 0.4 g of yellow solid, mp 52–60°. A portion was sublimed twice to give yellow crystals, mp 57–60°. The H^1 nmr spectrum (in $CDCl_3$) contained a simple aryl multiplet centered at -7.6 ppm; and the F^{19} nmr spectrum consisted of a singlet at $+59.9$ ppm. The infrared spectrum contained a band at 4.82 μ (m) due to the cumulated system of **19**: molecular weight in benzene, 344 (theoretical, 340); mass spectrum (at 70 ev), molecular ion at 340 (base peak); $340 - F = 321$, 17.8%; $340 - CF_3 = 271$, 10.6%; $340 - F - CF_3 = 252$, 5.4%; $340 - F - CF_3 - H = 251$, 27.2%; $340 - CF_3 - CF_2 - H = 220$, 9.1%; $340 - CF_3 - CF_3 = 202$, 31.5%; $340 - (C_6H_5)_2C + H = 175$, 4.9%; 166 $[(C_6H_5)_2C]$, 3.5%; 165 $[(C_6H_5)_2C - H]$, 23.3%; 150 $[(CF_3)_2C]$, 4.0%; $340 - (C_6H_5)_2C - CF_3 = 105$, 9%; 69 ($CF_3$), 19.1%; and 51 ($CF_2$ + H or fragmentation of the phenyl group), 24.6%.

Anal. Calcd for $C_{18}H_{10}F_6$: C, 63.52; H, 2.96; F, 33.49. Found: C, 63.44; H, 2.94; F, 33.16.

Registry No.—**4a**, 14181-19-2; **5**, 6509-85-9; **6** ($X = PF_6$), 12119-72-1; **6** ($X = BF_4$), 14264-71-2; **6** [$X = (CF_3CO_2)_2H$], 14264-72-3; **8**, 13703-34-9; **9a**, 13703-26-9; **9b**, 14264-73-4; **9c**, 14179-59-0; **9d**, 12125-44-9; **9e**, 14264-74-5; **10**, 14179-60-3; **11**, 14179-61-4; **12**, 14179-62-5; **13**, 14179-63-6; **14**, 14179-64-7; **18**, 7445-61-6; **19**, 14179-66-9; ethyl 2,2-bis(trifluoromethyl)vinyl ether, 14179-67-0; ethyl 2,2-bis(trifluoromethyl)vinyl sulfide, 14179-68-1.

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