ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Phosphinemethylenes.' I. Triphenylphosphoniumcyclopentadienylide

BY FAUSTO RAMIREZ AND STEPHEN LEVY[1]

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Triphenylphosphoniumcyclopentadienylide (V), a remarkably stable phosphinemethylene, has been prepared. The ultraviolet and infrared absorption spectra and the electric dipole moment are recorded. V is stable in boiling alkali and fails to react with ketones, unlike other triphenylphosphinemethylenes known.

The phosphinemethylenes[2] or phosphorus "ylides" (I) have been known for many years,[3] but their potential value in organic synthesis was not appreciated until very recently.[4] Wittig and coworkers[4] discovered the reaction of triphenylphosphinemethylenes (I, R = C_6H_5) with aldehydes and ketones and, thus, developed a new and valuable olefin synthesis.

$$\underset{\text{Ia}}{(R_3P{=}CXY} \longleftrightarrow \underset{\text{Ib}}{R_3\overset{(+)}{P}{-}\overset{(-)}{C}XY)} + \underset{\text{II}}{R'R''C{=}O} \longrightarrow$$

$$\underset{\text{III}}{R_3PO} + \underset{\text{IV}}{R'R''C{=}CXY}$$

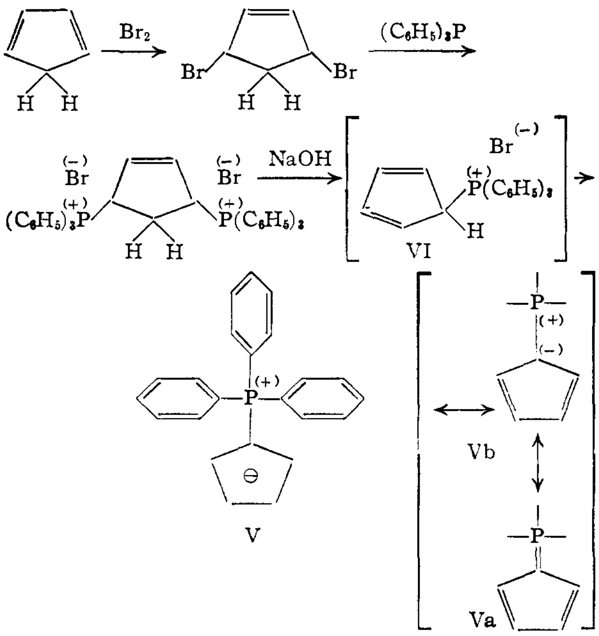
The phosphinemethylenes are usually prepared by the reaction of an organolithium on a quaternary phosphonium halide, $(R_3P{-}CHXY)^{(+)}\,Br^{(-)}$. Ordinarily, they are not isolated since they are unstable, affording under hydrolytic conditions the tertiary phosphine oxide and a hydrocarbon portion. Consequently, data bearing on their structure—such as ultraviolet and infrared absorption spectra and electric dipole moments—are lacking.

$$R_3P{=}CXY + H_2O \longrightarrow$$
$$R_2(YXHC)PO + RH \text{ or } R_3PO + CH_2XY$$

The evidence in the literature suggests that the color[5] of the phosphinemethylenes, their stability and their ability to react with carbonyl functions depend markedly on the distribution of the negative charge in the molecule. For example, in the triphenylphosphine series, the red-orange[5] monophenyl derivative[4] (I, X = H, Y = C_6H_5) is somewhat more stable and considerably less reactive toward carbonyl functions than the yellow[5] parent compound (I, X = Y = H). The red[5] diphenyl derivative[3b,d] (I, X = Y = C_6H_5) and the yellow[5] fluorenyl derivative[3e] have been isolated in the solid state. The bright red *p*-nitrophenyl compound[3g] (I, X = H, Y = *p*-NO_2-C_6H_4) could be prepared by the action of dilute aqueous alkali on *p*-nitrobenzyltriphenylphosphonium bromide at low temperature.

Our search for correlations between structure and physical and chemical properties of the phosphinemethylenes has led to the preparation of triphenylphosphoniumcyclopentadienylide (V). The distribution of the negative charge over the cyclopentadienide ring should confer on this structure a high degree of stability, in line with recent views on non-benzenoid aromatic systems.[6] The reaction sequence shown in Chart I was followed. The bromination and the reaction with triphenylphosphine were carried out in chloroform solution. The intermediates were not isolated and an over-all yield of 41% was realized.[6d]

CHART I



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(1) From part of the Ph.D. Thesis of S. Levy.

(2) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 28, 355.

(3) (a) A. Michaelis and E. Kohler, *Ber.*, **32**, 1566 (1899); (b) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919); (c) H. Staudinger and W. Braunholtz, *ibid.*, **4**, 897 (1921); (d) C. Coffman and C. Marvel, THIS JOURNAL, **51**, 3496 (1929); (e) L. Pinck and G. Hilbert, *ibid.*, **69**, 723 (1947); (f) G. Wittig and M. Rieber, *Ann.*, **562**, 177 (1949); (g) F. Krönhke, *Chem. Ber.*, **83**, 253 (1950).

(4) (a) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953); (b) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954); (c) G. Wittig and W. Haag, *ibid.*, **88**, 1654 (1955); (d) G. Wittig, *Experientia*, **12**, 41 (1956).

(5) With perhaps some exceptions,[3d,e] the few solid phosphinemethylenes described are of unknown degree of purity. Only qualitative observations on the color of ether or chloroform solutions of the phosphinemethylenes have been recorded.

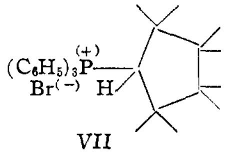
(6) (a) W. von E. Doering and C. H. DePuy, THIS JOURNAL, **75**, 5955 (1953); (b) D. Lloyd and J. Sneezum, *Chemistry & Industry*, 1221 (1953); (c) *cf.* W. Baker and J. McOmie in J. W. Cook, "Progress in Organic Chemistry," Academic Press, Inc., New York, N. Y., Vol. III, 1955, p. 58.

(6d) ADDED IN PROOF: The structural and stereochemical problems arising in the bromination of cyclopentadiene have been discussed recently (W. G. Young, H. K. Hall, Jr., and S. Winstein, THIS JOURNAL, **78**, 4338 (1956)). In the present work no attempt was made to effect the reaction of triphenylphosphine with pure isomers of dibromocyclopentene. The formation of a bis-triphenylphosphonium bromide was suggested by observations relating the yield of V to the moleratio of triphenylphosphine dibromocyclopentene used. These points, as well as the formation of some triphenylphosphine *oxide*, are being scrutinized further.

The phosphinemethylene V was obtained as pale yellow crystals of m.p. 229–231°. It formed a rather unstable picrate of m.p. 155–156°. V was readily soluble in dilute aqueous mineral acids and from these solutions it was reprecipitated, unchanged, upon addition of alkali. *It was not affected by prolonged boiling with concentrated aqueous alcoholic potassium hydroxide.* All attempts to effect reaction with ketones (benzophenone, fluorenone, cyclohexanone) failed. Some evidence for reaction with benzaldehyde was noted, but no pure product could be isolated.

Molecular weight determination showed V to be monomeric. Proof of its structure was obtained by catalytic hydrogenation of a solution in hydrobromic acid (*i.e.*, of VI or a tautomer thereof). The triphenylcyclopentylphosphonium bromide (VII) so obtained was identical with an authentic sample prepared from cyclopentyl bromide and triphenylphosphine.

The ultraviolet absorption spectrum of V in a hydroxylic and in an aprotic solvent is shown in Fig. 1. Considerable degree of conjugation is in evidence.



VII

The electric dipole moment of V, measured[7] in benzene solution at 25°, is 7.0 *D*. This corresponds to roughly equal contributions from the pentacovalent structure Va (calculated moment nearly zero) and the tetracovalent structure Vb (and its resonance forms, summarized in V; calculated moment 14.0 *D*).

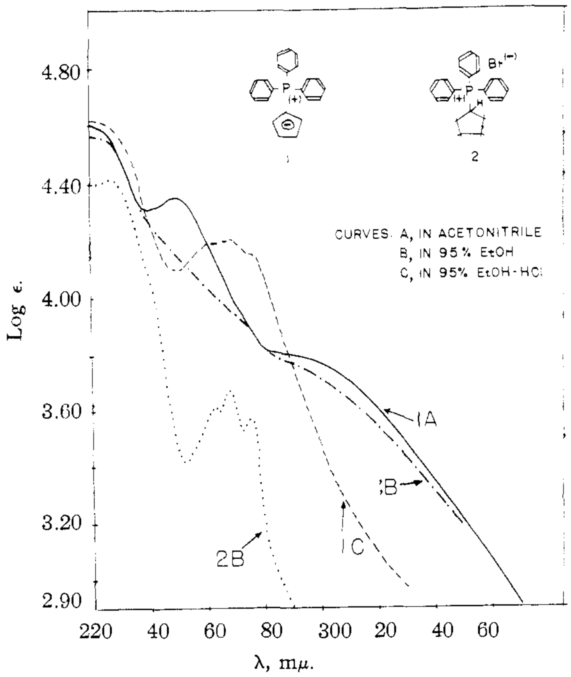


Fig. 1.

The infrared spectrum of V in KBr is described in the Experimental section. The bands present[8] at 6.75, 6.98 and 9.05 μ also have been found in a number of structures of type $(C_6H_5)_3\overset{(+)}{P}$–R, including triphenylphosphine oxide.

Experimental[9]

Triphenylphosphoniumcyclopentadienylide (V).—A solution of cyclopentadiene (9.08 g., b.p. 39–40°, $n^{19}D$ 1.4449; by cracking of dimer and distillation through a 12″ Vigreux column, under nitrogen) in chloroform (10 ml.) was treated with a solution of bromine (22 g.) in chloroform (10 ml.). The bromination was carried out under a nitrogen atmosphere at −50 to −40°. The solution was diluted with 30 ml. of chloroform and was treated at −40° with a solution of triphenylphosphine (72.1 g.) in chloroform (220 ml.). The solution was heated slowly and was maintained at its reflux temperature for 6 hours and at room temperature overnight. The cooled mixture was shaken with 302 ml. of 1.3 *N* aqueous sodium hydroxide. The aqueous layer was extracted with chloroform and the combined chloroform extracts and layer were dried and distilled. The residue was stirred with methanol (100 ml.) and the crude triphenylphosphoniumcyclopentadienylide (V) was collected, washed with methanol and dried; yield 18.2 g. (41%), m.p. 213–219°. After one recrystallization from chloroform–ethanol, 15.7 g. of V, m.p. 228–231°, was obtained; analytical sample pale yellow crystals, m.p. 229–231° (from chloroform–ethanol or toluene); $\lambda_{max}^{acetonitrile}$ 222 mμ (ε 38,200), 250 mμ (ε 21,600) and *ca.* 295 mμ (ε 5,900), with tailing into longer wave lengths (ϵ_{375} <100); bands in KBr at 6.75 (m), 6.98 (s), 7.42 (m), 7.65 (w), 8.22 (m), 8.50 (w), 9.05 (s), 9.55 (m), 9.70 (m-s) and 10.05 (w) μ.

Anal. Calcd. for $C_{23}H_{19}P$: C, 84.6; H, 5.9; P, 9.5; mol. wt., 326. Found: C, 84.7; H, 6.1; P, 9.5; mol. wt. (Rast), 338.

The phosphinemethylene V was readily soluble in 5% aqueous hydrochloric acid. Compound V was recovered unchanged upon addition of alkali to the acid solution.

V was recovered unchanged after prolonged reflux with aqueous alcoholic potassium hydroxide of various concentrations.

Triphenylphosphoniumcyclopentadienylide Picrate.—A solution of V (0.489 g.) in carbon disulfide (100 ml.) was treated with a solution of picric acid (0.378 g.) in carbon disulfide (350 ml.). The crude yellow picrate (0.608 g., m.p. 155–156°) which separated was dried at 68° (0.3 mm.) and analyzed as such since recrystallization from methanol or ethyl acetate led to some decomposition; λ_{max}^{EtOH} 220 mμ (ε 44,600), 267 mμ (ε 14,400), 275 mμ (ε 12,400) and 360 mμ (ε 15,800); shoulder at 260 mμ (ε 14,900).

Anal. Calcd. for $C_{29}H_{22}N_3PO_7$: C, 62.7; H, 4.0. Found: C, 62.8; H, 4.3.

No pure picrate could be obtained in chloroform, benzene or ethanol solutions.

Attempted Reaction of Triphenylphosphoniumcyclopentadienylide (V) with Carbonyl Compounds.—The reaction of V with benzophenone, fluorenone and cyclohexanone was explored in ether, chloroform, ethanol and tetrahydrofuran at reflux temperatures and at room temperature for periods as long as 120 hours. In all cases most of V was recovered. At elevated temperatures in the absence of solvent some decomposition was noted, but no pure substance could be isolated. Some interaction between V and benzaldehyde was noted in chloroform and tetrahydrofuran but no pure substance could be isolated.

Triphenylcyclopentylphosphonium Bromide (VII).—A mixture of triphenylphosphine (2.62 g.) and cyclopentyl bromide (1.49 g.) was heated for 12 hours at 200° (nitrogen atmosphere). The cooled crystalline mixture was stirred with benzene affording 2.84 g. of crude bromide (m.p. 254–256°). Recrystallization from ethyl acetate–methanol afforded 1.75 g. of VII, m.p. 261–263°; analytical sample

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[7] We thank Dr. M. T. Rogers of Michigan State University for measuring and interpreting the electric dipole moment. These results will be published shortly by Dr. Rogers.

[8] The 7.0 μ band is known to be due to phosphorus–phenyl vibrations (*cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Ch. 18.

[9] Analyses by Micro-Tech Laboratories, Skokie, Ill., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

white needles, m.p. 261–263° (water); λ_{max}^{EtOH} 226 mμ (ε 25,200), 262 mμ (ε 4,000), 268 mμ (ε 4,700) and 271 mμ (ε 3,900).

Anal. Calcd. for $C_{23}H_{24}PBr$: C, 67.2; H, 5.9; P, 7.5; Br, 19.4. Found: C, 67.0; H, 5.8; P, 7.7; Br, 20.1.

Triphenylcyclopentylphosphonium Bromide (VII) from Triphenylphosphoniumcyclopentadienylide (V).—A solution of the phosphinemethylene (V, 0.245 g.) in 30 ml. of water containing 5 ml. of 20% hydrobromic acid was hydrogenated at atmospheric pressure using 109 mg. of PtO_2 catalyst. After 24 hours, a 43-mg. portion of fresh catalyst was added. Two additional portions of fresh catalyst had to be added before reduction was complete; total volume of hydrogen absorbed, 41.7 ml.; calculated, 37.7 ml. Removal of the water and recrystallization of the colorless residue from the minimum amount of water gave a substance, m.p. 259–261°, shown to be identical with authentic triphenylcyclopentylphosphonium bromide (VII) (infrared spectra and mixed m.p.).

The phosphinemethylene (V) was recovered unchanged when thiophene-free benzene solutions were shaken with hydrogen in the presence of PtO_2 catalyst at atmospheric pressure or at 50 pounds pressure.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

A New Synthesis of Simple Fluorocarbon Tertiary Amines[1]

BY RICHARD DRESDNER

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Both $(CF_3)_3N$, tris-(trifluoromethyl)-amine and bis-(trifluoromethyl)-pentafluoroethylamine, have been synthesized by the reaction of $CF_3N{=}CF_2$, perfluoro-2-azapropene, with CF_3SF_5, trifluoromethylsulfur pentafluoride, and $C_2F_5SF_5$, perfluoroethylsulfur pentafluoride, respectively. The preparation of both $C_2F_5SF_5$ and $(C_2F_5)_2SF_4$, bis-(perfluoroethyl)-sulfur tetrafluoride, and their simple physical properties are described. A simple vapor pressure equation, the heat of vaporization, boiling point, freezing point and Trouton's constant for $(CF_3)_3N$ have been measured or calculated.

Introduction

Preparations for both $(CF_3)_3N$[2] and $(CF_3)_2N$-C_2F_5[3] are described in the chemical literature. This paper describes their preparation using perfluorinated reactants, namely, $CF_3N{=}CF_2$, perfluoro-2-azapropene[4,5] and CF_3SF_5, trifluoromethylsulfur pentafluoride and $C_2F_5SF_5$, pentafluoroethylsulfur pentafluoride.

The thermal reaction of CF_3SF_5 with the fluorocarbon olefin $CF_3CF{=}CF_2$, perfluoropropene, produced C_4- to C_8-fluorocarbons with the elimination of SF_4.[6] It has been demonstrated in this work that when CF_3SF_5 and $C_2F_5SF_5$ are allowed to react thermally with $CF_3N{=}CF_2$, $(CF_3)_3N$ and $(CF_3)_2$-NC_2F_5 result in reasonable yields. Uniquely, the fluorocarbon portions of the fluorocarbon sulfur compounds attach themselves to the nitrogen atom while one atom of fluorine, in each case, adds to the existing $=CF_2$ group of $CF_3N{=}CF_2$. Neither reaction occurs appreciably until the decomposition temperatures of the fluorocarbon sulfur compounds are reached or exceeded. For example, CF_3SF_5 decomposes 20% by weight at 500° in a flow system at atmospheric pressure,[6] while $C_2F_5SF_5$ decomposes 100% under the same conditions forming C_4F_{10}, SF_4 and other low boiling sulfur fluorides. In a closed system under pressure, CF_3SF_5 and $C_2F_5SF_5$ decompose completely at 423 and 380°, respectively.

Experimental

Materials.—CF_3SF_5 and $(CF_3)_2SF_4$, bis-(trifluoromethyl)-sulfur tetrafluoride, were prepared electrochemically in an anhydrous HF solution of methyl sulfide.[7,8] The respective yields of the sulfur compounds are 50 and 8% based on the current passed.

$CF_3N{=}CF_2$ (b.p. −33°, mol. wt. 133) was prepared by pyrolysis of $(CF_3)_2NCOF$, bis-(trifluoromethyl)-carbamyl fluoride, at 615°.[5]

$C_2F_5SF_5$ was prepared electrochemically in an anhydrous HF solution of ethyl sulfide. The co-product $(C_2F_5)_2SF_4$ was also isolated in small yields. These two substances are unreported compounds. They were carried over in the gas stream from an electrochemical (Simon's) cell and were trapped in a Dry-Ice cooled condenser after the gas stream from the cell had been passed over lime and bubbled through NaOH solution. An attempt was made to retain the cell solution at a mole ratio of about 0.005 sulfide/HF. About 3 moles of ethyl sulfide was used in preparing 0.84 mole of $C_2F_5SF_5$ and 0.087 mole of $(C_2F_5)_2SF_4$. One hundred and twenty-five grams of other fluorine-containing substances boiling above −54° was collected. No attempt was made to trap products boiling below this.

These two materials were identified by molecular weight and elemental analyses. The elemental analyses were performed similarly to those reported by Silvey and Cady[9] with the exceptions that the fusions were done in a sealed glass tube at 640° and the $S^{=}$ ion was removed with an exact quantity of Ag^+ before titration for F^-. At least two fusions were made with each compound and three aliquots of each fusion analyzed.

Anal. Calcd. for C_2SF_{10}: F, 77.3; S, 13.0; mol. wt., 246. Found: F, 77.3 ± 0.4; S, 12.8 ± 0.10; mol. wt., 244–247; b.p. 11.3°. Calcd. for C_4SF_{14}: F, 76.9; S, 9.25; mol. wt., 346. Found: F, 76.5 ± 0.3; S, 9.22 ± 0.12; mol. wt., 344–347; b.p. 68.0°; $n^{25}\text{D}$ 1.2753; d_{25} 1.878$_5$; $MR\text{D}$ 31.81.

It is of interest to note that $(CF_3)_2SF_4$, isomeric with $C_2F_5SF_5$, has a reported b.p. of 20.5°.[8] Also $C_4F_9SF_5$, isomeric with $(C_2F_5)_2SF_4$, has the properties b.p. 70.0°, $n^{25}\text{D}$ 1.2710, d_{25} 1.8451 and $MR\text{D}$ 31.92.[10]

Reaction of $CF_3N{=}CF_2$ with CF_3SF_5.—The equipment for the reaction between CF_3SF_5 (b.p. −20.5°) and $CF_3N{=}CF_2$ (b.p. −33°) has been described.[1] The reactor was filled

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[1] This work was supported by the Chemistry Branch of the Office of Naval Research and reproduction of all or any part of this paper for purposes of the United States Government is permitted.

[2] E. A. Kauck and J. H. Simons, U. S. Patent 2,616,927 (1952).

[3] R. N. Haszeldine, *J. Chem. Soc.*, 102 (1951).

[4] D. A. Barr and R. N. Haszeldine, *ibid.*, 2532 (1955).

[5] J. A. Young, Division Ind. & Eng. Chem., Fluorine Chemistry Subdivision, 118th Meeting A.C.S., Minneapolis, Minn., Sept. 11–16, 1955.

[6] R. Diesdner, THIS JOURNAL, **77**, 6633 (1955).

[7] J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).

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[9] G. A. Silvey and G. H. Cady, THIS JOURNAL, **72**, 3624 (1950).

[10] W. A. Severson, T. J. Brice and R. I. Coon, Minnesota Mining and Manufacturing Co., St. Paul, Minn., 128th Meeting American Chemical Society, Minneapolis, Minn., Sept. 11–16, 1955. Division of Industrial and Engineering Chemistry, Fluorine Chemistry Sub division.