Anal. Calcd. for $C_8H_{14}O_2$: C, 67.61; H, 9.86. Found: C, 67.53; H, 10.05.

***t*-Butyl Methacrylate.**—To a solution of 11.5 g. (0.12 mole) of sodium *t*-butoxide in dry tetrahydrofuran under nitrogen was slowly added 10.4 g. (0.10 mole) of methacrylyl chloride with cooling. After addition of the acid chloride was complete, the solution was stirred for 30 min. and then poured into 100 ml. of ice–water. The organic layer was extracted with ether, and the ether layer then washed with dilute sodium bicarbonate solution and dried with magnesium sulfate. Distillation yielded 4.5 g. (26%) of pure *t*-butyl methacrylate, b.p. 134–136° [lit.[32] b.p. 135.8–136.3° (762 mm.), 72–74° (93 mm.)], $n^{20.5}_{\text{D}}$ 1.4169.

***t*-Butyl acrylate** was prepared by a procedure similar to that used for *t*-butyl crotonate. It was purified by evaporative distillation at about 100 mm., $n^{20.5}_{\text{D}}$ 1.4100 (lit.[33] $n^{19.4}_{\text{D}}$ 1.4074).

Methyl β-vinylacrylate was prepared by the method of Kohler and Butler,[34] b.p. 78–79° (24 mm.) [lit.[34] b.p. 77–80° (25 mm.)].

Spectra.—All spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 0.01- and 0.1-cm. quartz cells. The details of the technique have been described previously.[1b]

Acknowledgment.—The authors wish to thank Professors Raymond Disch, Martin Karplus, and E. M. Kosower for interesting and valuable discussion and Mr. Melvyn Kassenoff for the preparation of some of the esters used in this work. We also wish to thank Mr. S. Goodman and Mr. James Halper for help with computer programming.

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[33] K. W. F. Kohlrausch and R. Skrabal, *Monatsh.*, **70**, 377 (1937).

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The Thermal Stability of (2-Substituted ethyl)diphenylphosphines. The Potent Neighboring Group Effect of the Trivalent Phosphorus Atom[1]

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Received May 10, 1965

(2-Hydroxyethyl)diphenylphosphine (Ib) underwent thermal decomposition to give *s*-ethylenebis(diphenylphosphine oxide). Similar cleavages were observed for its acetate (Ic) and benzoate (Id) derivatives with the formation of *s*-ethylenebis(diphenylphosphine). A common mechanism is proposed for these decompositions, involving the initial formation of a 1,1-diphenylphosphoniacyclopropane salt intermediate, owing to the anchimeric effect of the trivalent phosphorus atom.

Neighboring group participation by the nitrogen, oxygen, and sulfur atoms in promoting certain nucleophilic displacements is well documented,[2] but only recently has evidence emerged supporting such an anchimeric effect occurring in the case of a trivalent phosphorus atom.[3–6] The powerful nucleophilic properties of trivalent phosphorus compounds are well known,[7] and it was on this basis that a study of the chemical properties of several (2-substituted ethyl)diphenylphosphines was initiated to determine the feasibility of synthesizing potential antineoplastic phosphines.

Mann and Hitchcock[3] have reported the self-quaternization of (2-bromoethyl)ethylphenylphosphine at room temperature with the formation of 1,4-diethyl-1,4-diphosphoniacyclohexane dibromide. Rauhut, *et al.*,[4] have demonstrated the exothermic self-quaternization of dialkyl-2-acetoxyethylphosphines to give 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane diacetates at temperatures in excess of 80°, and in a number of examples, when a strict temperature control was imposed during the exothermic reaction, poly(dialkyl)ethylenephosphonium acetates were isolated. The analogous 3-acetoxypropylphosphines did not undergo a similar self-quaternization reaction even when heated to 300°.[4] Recently, Schweizer and Bach[8] have shown the unexpected formation of 1,2-ethylenebis(triphenylphosphonium bromide) from triphenyl phosphorus and 2-bromophenetole. A vinyl phosphonium salt was indicated as a reactive intermediate in the sequence of this reaction. The results which we have obtained with several (2-substituted ethyl)diphenylphosphines corroborates the observations of these researchers as to the unusual properties of the trivalent phosphorus atom and its interaction with potential phosphoniaethylation agents, generated from phosphonium salts.

2-(Butoxyethyl)diphenylphosphine (Ia), synthesized from diphenylphosphine and *t*-butoxyethyl chloride,[6] was stable at least to 350° without any apparent decomposition. Cleavage[9] of the ether gave (2-hydroxyethyl)diphenylphosphine (Ib) and, contrary to recent reports,[10] it was readily distilled under reduced pressure without decomposing into diphenylvinylphosphine. However, at elevated temperatures (305°) a violent exothermic reaction occurred with the formation of III[11] (55%) and diphenylvinylphosphine[10] (12%). Both the acetate Ic and the benzoate Id, prepared from the alcohol Ib were also thermally labile, decomposing into *s*-ethylenebis(diphenylphosphine) (IV),[12,13] diphenylvinylphosphine, and the appropriate acid. While Ib and Ic were stable at normal temperature, Id slowly underwent self-quaternization

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[1] This investigation was supported by the U. S. Public Health Service, Research Grants No. CA-06605 and CA-07368 from the National Cancer Institute.

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[6] T. P. Abbiss, A. H. Soloway, and V. H. Mark, *J. Med. Chem.*, **7**, 763 (1964).

[7] M. Grayson, *Chem. Eng. News*, **40** (49), 90 (1962).

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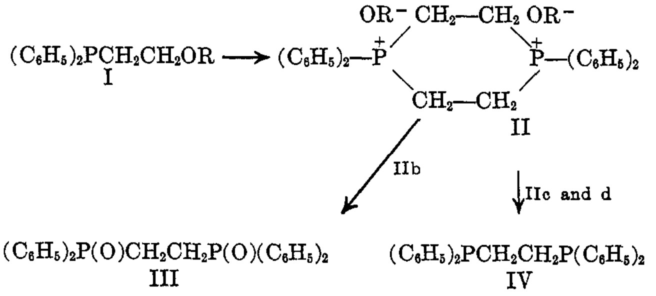
[12] W. Hewertson and H. R. Watson, *ibid.*, 1490 (1960).

[13] K. Issleib and D. Muller, *Chem. Ber.*, **92**, 3175 (1959).

to yield 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibenzoate (IId) which was isolated as the diiodide. The acetate, Ic, in the presence of catalytic amounts of its own methiodide underwent a similar type of self-quaternization.



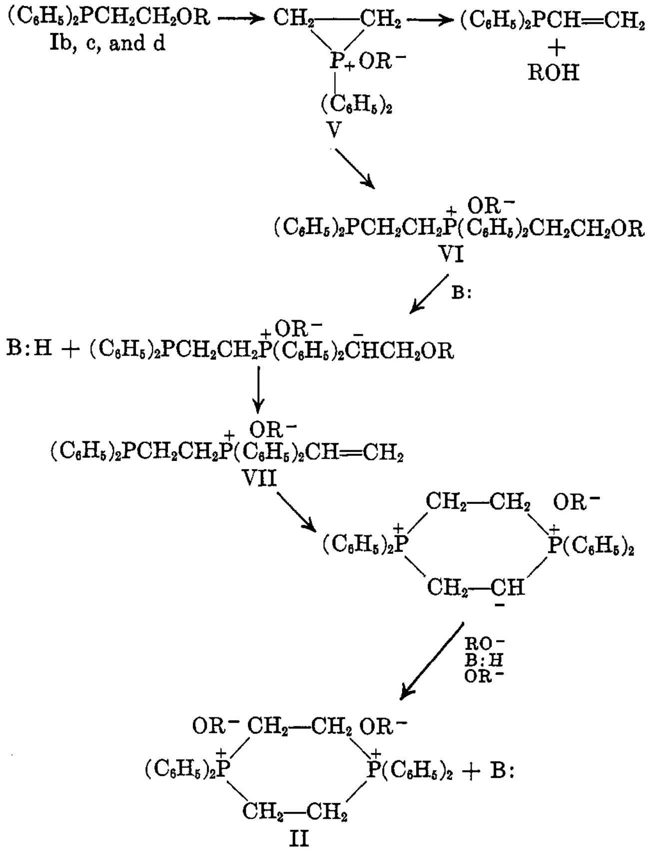
a, R = $C(CH_3)_3$
b, R = H
c, R = $COCH_3$
d, R = COC_6H_5

Discussion

The thermal decomposition of the (2-substituted ethyl)diphenylphosphines Ib, Ic, and Id and the self-quaternization of the dialkyl-2-acetoxy-ethylphosphines[4] would appear to involve a common mechanism. Such a mechanism must explain two important observations. The first one is the catalysis of the quaternization of (2-acetoxyethyl)diphenylphosphine at room temperature by its own methiodide. Small amounts of poly(dialkyl)ethylenephosphonium acetates caused a similar catalytic effect on the self-quaternizations of dialkyl-2-acetoxyethylphosphines,[4] while the 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane salts were without effect. The second observation is the difference in the thermal stability of the four (2-substituted ethyl)diphenylphosphines described above.

The possibility of a neighboring group participation by a trivalent phosphorus atom has been proposed[5] to account for the high lability of groups on the β position to trivalent phosphorus.[4–6] This is corroborated by the fact that dialkyl-3-acetoxypropylphosphines do not undergo similar self-quaternizations.[4] The nucleophilicity of trivalent phosphorus is convincingly demonstrated by its transannular interaction with a carbonyl function.[14] The following mechanism is suggested which is entirely consistent with this and other observed facts (see col. 2, top).

In the initial step a highly labile 1,1-diphenylphosphoniacyclopropane salt (V) is formed as a consequence of the neighboring group effect of the trivalent phosphorus atom. This hypothesis is supported by the observation that the thermal stability of the phosphine Ia, Ib, Ic, and Id decreased as the potential of the function as a leaving agent increases. This active intermediate (V) can undergo two competing reactions: one, a base-initiated ring opening would give diphenylvinylphosphine, which occurred to some extent in all of the pyrolytic reactions; second, the reaction of the cyclopropane salt with another molecule of the tertiary phosphine would give the phosphonium salt VI. This latter step, essentially a phosphinylethylation reaction, is analogous to the reaction of nucleophiles with a vinyl phosphonium salt.[8] The phosphine-



phosphonium dimer (VI) can undergo a base, autocatalyzed reaction, *via* ylid formation, to give the vinylphosphonium salt VII. The base could be the dimer itself or a molecule of the initial tertiary phosphine.[8] Cyclization of this intermediate VII would result in the preparation of the observed 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane salts (II). A similar intermolecular reaction of the vinylphosphonium salt with another molecule of phosphine I would lead to poly(disubstituted)ethylenephosphonium salts. These have been observed by others.[4] The above base-catalyzed mechanism is in all essentials similar to that proposed by Schweizer and Bach[8] to explain the formation of *s*-ethylenebis(triphenylphosphonium bromide) from 2-phenoxyethyltriphenylphosphonium bromide and triphenylphosphorus.

At elevated temperatures the cyclic compounds, 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane diacetate and dibenzoate, would be expected to decompose to give *s*-ethylenebis(diphenylphosphine). This reaction is anticipated by analogy with the thermal decomposition of 1,4-diethyl-1,4-diphenyl-1,4-diphosphoniacyclohexane dibromide to form *s*-ethylenebis(ethylphenylphosphine).[3] Similarly, cleavage of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dihydroxide, on heating, into *s*-ethylenebis(diphenylphosphine oxide) would be expected. The pyrolysis of quaternary phosphonium hydroxides to tertiary phosphine oxides has been well established.[15,16] Especially pertinent to this work is the very interesting observation of Aguiar, *et al.*,[17] in synthesizing 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide from ethylene-

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(14) N. J. Leonard, S. E. Cremer, and A. L. Ternay, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

(15) G. F. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

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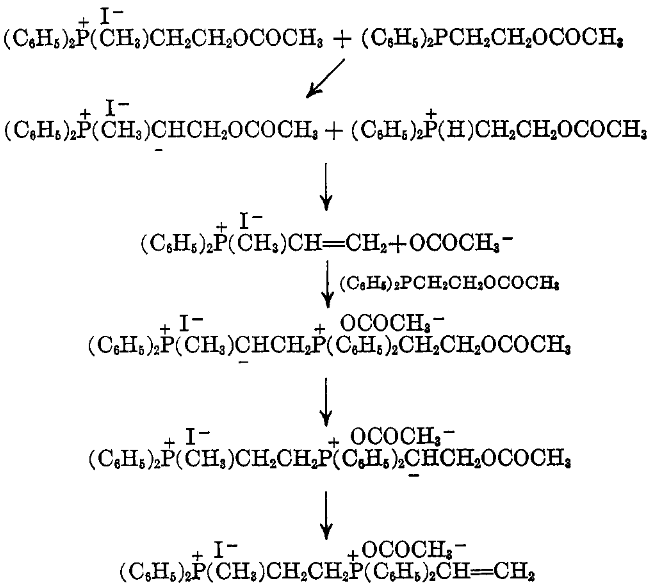
(17) A. M. Aguiar, H. Aguiar, and D. Daigle, *J. Am. Chem. Soc.*, **87**, 671 (1965).

bis(diphenylphosphine) and 1,2-dibromoethane and the mechanism proposed by these authors to account for its conversion by strong aqueous base to ethylenebis(diphenylphosphine)monoxide. The preceding work supports their contention that a base-initiated vinylphosphonium salt is a possible intermediate in the formation of the phosphine oxide.

The catalytic effect of (2-acetoxyethyl)methyldiphenylphosphonium iodide in promoting the quaternization of (2-acetoxyethyl)diphenylphosphine can be explained also by a similar base-catalyzed mechanism outlined below. The failure of 1,1,4,4-tetraalkyl-1,4-diphosphoniacyclohexane salts to promote such quaternizations[4] can be attributed to the fact that thermodynamically the formation of vinyl phosphonium salts from such cyclic structures is not favored except possibly under strongly alkaline conditions.[16]



$$(C_6H_5)_2\overset{+}{P}(CH_3)CH_2CH_2OCOCH_3\ I^- + (C_6H_5)_2PCH_2CH_2OCOCH_3 \longrightarrow (C_6H_5)_2\overset{+}{P}(CH_3)\underset{-}{C}HCH_2OCOCH_3\ I^- + (C_6H_5)_2\overset{+}{P}(H)CH_2CH_2OCOCH_3$$

$$\longrightarrow (C_6H_5)_2\overset{+}{P}(CH_3)CH{=}CH_2\ I^- + OCOCH_3^- \xrightarrow{(C_6H_5)_2PCH_2CH_2OCOCH_3} (C_6H_5)_2\overset{+}{P}(CH_3)\underset{-}{C}HCH_2\overset{+}{P}(C_6H_5)_2CH_2CH_2OCOCH_3\ I^-\ OCOCH_3^-$$

$$\longrightarrow (C_6H_5)_2\overset{+}{P}(CH_3)CH_2CH_2\overset{+}{P}(C_6H_5)_2\underset{-}{C}HCH_2OCOCH_3\ I^-\ OCOCH_3^- \longrightarrow (C_6H_5)_2\overset{+}{P}(CH_3)CH_2CH_2\overset{+}{P}(C_6H_5)_2CH{=}CH_2\ I^-\ OCOCH_3^-$$

In summary this mechanism accounts for the instability of certain, β-substituted ethylphosphines, the catalytic effect of potential vinyl phosphonium salts in promoting the quaternization of several tertiary phosphines, and the products obtained by the pyrolysis of such compounds. Further work is currently underway on the synthesis of functionally substituted trialkylphosphines to determine the validity of this postulated mechanism.

Experimental Section

All manipulations were carried out under nitrogen unless otherwise stated. Melting points were taken on a Fisher-Johns apparatus and are as observed.

(2-t-Butoxyethyl)diphenylphosphine (Ia).—To a suspension of diphenylphosphine (18.8 g.) in 150 ml. of liquid ammonia, cooled to −75°, was added with stirring small pieces of sodium (2.34-g. total amount). The total time of addition was 2 hr., and, upon completion, the solution became tan colored. To this mixture was added with stirring a solution of 2-*t*-butoxyethyl chloride (14.0 g.),[18] in 35 ml. of anhydrous ethyl ether. The addition time was 2 hr., and at the conclusion of this period the ammonia was allowed to evaporate. Dry ethyl ether (200 ml.) was added and the mixture was stirred for an additional 0.5 hr. Oxygen-free water (150 ml.) was introduced, and the ether phase was separated and dried. Evaporation of the ether furnished a colorless oil which upon fractional distillation yielded 24.2 g. of (2-*t*-butoxyethyl)diphenylphosphine (84.5%), b.p. 146–148° (1.0 mm.). *Anal.* Calcd. for $C_{18}H_{23}OP$: C, 75.52; H, 8.04; P, 10.84. Found: C, 75.72; H, 8.30; P, 11.03.

A methiodide was prepared by treating this phosphine ether with methyl iodide in anhydrous methanol. The white solid obtained afforded colorless prisms of (2-*t*-butoxyethyl)methyldiphenylphosphonium iodide from ethanol–ether, m.p. 212–214°. *Anal.* Calcd. for $C_{19}H_{26}IOP$: C, 53.27; H, 6.08; I, 29.27; P, 7.24. Found: C, 53.24; H, 6.19; I, 29.66; P, 7.27.

(2-Hydroxyethyl)diphenylphosphine (Ib).—To 5.0 g. of (2-*t*-butoxyethyl)diphenylphosphine was added 20 ml. of concentrated hydrochloric acid. An exothermic reaction occurred rapidly with the formation of two layers. *t*-Butyl chloride separated as the upper layer and this was evaporated by a stream of nitrogen. The remaining colorless, aqueous phase was kept at room temperature for 2 hr. prior to its evaporation under reduced pressure at a temperature of 45–50°. A colorless oil was obtained. This crude hydrochloride was then dissolved in 10 ml. of oxygen-free water, and the solution was made alkaline by treatment with an oxygen-free 10% sodium hydroxide solution. The resultant oil was extracted with three 50-ml. portions of ethyl ether, and the combined extracts were dried over anhydrous sodium sulfate. The ether phase was separated and evaporated, and distillation of the residual oil gave 2.8 g. of (2-hydroxyethyl)diphenylphosphine (69.5%), b.p. 178–180° (3.0 mm.), 204–206° (15 mm.), 3320 cm.$^{-1}$ (OH). *Anal.* Calcd. for $C_{14}H_{15}OP$: C, 73.04; H, 6.52; P, 13.48. Found: C, 72.84; H, 6.52; P, 13.45.

This compound was also characterized as its methiodide, (2-hydroxyethyl)methyldiphenylphosphonium iodide, which afforded feathery, colorless needles, m.p. 186–188°.[10] *Anal.* Calcd. for $C_{15}H_{18}IOP$: C, 48.39; H, 4.84; I, 34.14; P, 8.66. Found: C, 48.40; H, 4.84; I, 33.89; P, 8.39.

Pyrolysis of (2-Hydroxyethyl)diphenylphosphine.—(2-Hydroxyethyl)diphenylphosphine (3.0 g.) was heated on an oil bath at 290° under an air condenser. The phosphine began to boil with the evolution of a gas. The temperature was gradually raised to 330° over a period of 10 min. and heating was discontinued with the cessation of the reaction. Upon cooling, the residual oil solidified. Recrystallization from benzene–ether yielded *s*-ethylenebis(diphenylphosphine oxide) (1.50 g.) as colorless prisms, m.p. 270–272°. *Anal.* Calcd. for $C_{26}H_{24}O_2P_2$: C, 72.56; H, 5.58; P, 14.42. Found: C, 72.71; H, 5.70; P, 14.38.

A cold trap (solid carbon dioxide–acetone) attached to the reaction system contained a colorless oil, which, on distillation, afforded diphenylvinylphosphine (0.4 g.), b.p. 110° (0.2 mm.). This compound was characterized as its methiodide, which was recrystallized from ethanol–ether as colorless prisms, m.p. 124–125°. *Anal.* Calcd. for $C_{15}H_{16}IP$: C, 50.88; H, 4.52; P, 8.76. Found: C, 50.61, H, 4.93; P, 8.26.

(2-Benzoxyethyl)diphenylphosphine (Id).—A 20% solution of butyllithium in *n*-hexane (5 ml.) was added slowly with stirring to a solution of (2-hydroxyethyl)diphenylphosphine (2.3 g.) in anhydrous ether (50 ml.). When the addition was complete, the mixture was stirred for 10 min. prior to the introduction of 1.4 g. of benzoyl chloride in 20 ml. of ethyl ether. The time of addition was 15 min. The mixture was then stirred for 0.5 hr. and oxygen-free water (30 ml.) was added. The ether layer was separated and dried over anhydrous sodium sulfate. Evaporation of the liquid phase gave 3.0 g. of (2-benzoxyethyl)diphenylphosphine (89.6%) as a pale, yellow, viscous oil, 1710 cm.$^{-1}$ (C=O).

Treatment with methyl iodide yielded colorless prisms (ethyl acetate–chloroform) of the methiodide, m.p. 130–131°. *Anal.* Calcd. for $C_{22}H_{22}IO_2P$: C, 55.46; H, 4.62; I, 26.68; P, 6.51. Found: C, 55.20; H, 4.74; I, 26.35; P, 6.26.

Oxidation of the tertiary phosphine with hydrogen peroxide in acetone solution produced the phosphine oxide. This compound gave colorless prisms from ethyl acetate, m.p. 122°. *Anal.* Calcd. for $C_{21}H_{19}O_3P$: C, 72.00; H, 5.43; P, 8.86. Found: C, 71.80; H, 5.39; P, 8.97.

Pyrolysis of (2-benzoxyethyl)diphenylphosphine.—Attempted distillation of (2-benzoxyethyl)diphenylphosphine (3.0 g.) at 0.4 mm. resulted in a violent exothermic reaction when the bath temperature reached 156°, and a pale yellow oil distilled which solidified in the air condenser. The bath temperature was gradually raised to 200°, but no further reaction occurred. The dark brown residue solidified on cooling and yielded after recrystallization from methanol *s*-ethylenebis(diphenylphosphine) (1.05 g.) as colorless prisms, m.p. 141–142°. *Anal.* Calcd. for

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(18) H. C. Beyerman and J. B. Bontekoe, *Rec. trav. chim.*, **81**, 691 (1962).

$C_{26}H_{24}P_2$: C, 78.39; H, 6.03; P, 15.58. Found: C, 78.29; H, 5.63; P, 15.68.

The pale yellow distillate was partitioned between oxygen-free 10% sodium bicarbonate solution and ethyl ether. The aqueous phase on acidification gave benzoic acid (0.65 g.). The ether phase was dried over anhydrous sodium sulfate and upon evaporation yielded diphenylvinylphosphine (0.25 g.), characterized as its methiodide.

(2-Acetoxyethyl)diphenylphosphine (Ic).—(2-Acetoxyethyl)diphenylphosphine (2.8 g.), a colorless oil, 1720 cm.$^{-1}$ (C=O), was obtained from 2.3 g. of (2-hydroxyethyl)diphenylphosphine in an entirely similar manner to the procedure described for the synthesis of Id. This compound was characterized as its methiodide, colorless prisms (ethanol-ether), m.p. 107–108°. *Anal.* Calcd. for $C_{17}H_{20}IO_2P$: C, 49.27; H, 4.83; I, 30.68; P, 7.49. Found: C, 49.04; H, 5.00; I, 30.91; P, 7.33.

Pyrolysis of (2-Acetoxyethyl)diphenylphosphine.—Attempted distillation of Ic (4.2 g.) at 0.35 mm. produced similar results to those obtained with Id. When the bath temperature reached 147°, a violent exothermic reaction occurred with the distillation of a colorless oil. The bath temperature was raised slowly to 180°, but no further reaction occurred. The brown residue yielded *s*-ethylenebis(diphenylphosphine) (1.9 g.) as colorless prisms, m.p. 141–142°, and from the colorless distillate diphenylvinylphosphine (0.4 g.), b.p. 110° (0.22 mm.), and acetic acid (0.61 g.) were obtained.

1,1,4,4-Tetraphenyl-1,4-diphosphoniacyclohexane Diiodide.—(2-Benzoxyethyl)diphenylphosphine (2.1 g.) was left at room temperature under nitrogen for 15 days. During the course of this period it had changed to a pale yellow, opaque solid. This mixture was partitioned between ethyl ether (40 ml.) and 2 *N* hydrochloric acid (15 ml.). From the ether phase 0.31 g. of benzoic acid was isolated. To the filtered aqueous solution a 10% sodium iodide solution (10 ml.) was added. The precipitated 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane diiodide was removed, washed well with distilled water, and dried. A white insoluble amorphous powder remained, m.p. 316–318°. *Anal.* Calcd. for $C_{28}H_{28}I_2P_2$: C, 49.00; H, 4.21; P, 9.25; mol. wt. (on dichloride), 497. Found: C, 49.34; H, 4.77; P, 9.13; mol. wt. (isomometric molecular weight determination), 403.

Decomposition of (2-Acetoxyethyl)diphenylphosphine by the Catalytic Effect of (2-Acetoxyethyl)methyldiphenylphosphonium Iodide.—(2-Acetoxyethyl)diphenylphosphine was unchanged, as assessed by its infrared spectra, on standing at room temperature for 15 days. However, the addition of 20 mg. of (2-acetoxyethyl)methyldiphenylphosphonium iodide to 500 mg. of this tertiary phosphine resulted in the polymerization of the compound to a brown solid in the same length of time. The infrared spectrum was characteristic of a quaternary phosphonium compound and could not be explained on the basis of merely the catalytic amount which had been added.

Acknowledgment.—The authors wish to thank Dr. William H. Sweet, Chief of the Neurosurgical Service, Massachusetts General Hospital, Boston, Massachusetts, and Dr. Vernon H. Mark for their assistance and encouragement, and Dr. David C. Smith for useful discussions.

The Determination of Polar Substituent Constants for the Dialkoxy- and Diarylphosphono and Trialkyl- and Triarylphosphonium Groups

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Received August 9, 1965

The syntheses of five phosphorus-substituted acetic acids have been carried out and the acidity of each has been determined. By application of a linear free energy correlation, approximate polar substituent constants (σ^*) for each of the phosphorus substituents have been determined. These studies indicate that the di-*n*-butoxyphosphono, diethoxyphosphono, and diphenylphosphono groups ($\sigma^* = 1.74$, 2.18, and 1.68) are comparable in electron-acceptor properties with carboalkoxy groups, while the tri-*n*-butyl- and triphenylphosphonium substituents ($\sigma^* = 3.75$ and 4.70) possess electron-acceptor properties comparable with those of quaternary ammonium groups.

The Hammett equation has been applied successfully to the acid dissociation constants of substituted arylphosphonic acids by Jaffé, Freedman, and Doak[1] and, more recently, to arylphosphinic acids by Quin and Dysart.[2] This relationship has been extended to arylphosphonic and arylphosphinic acids containing acidic (carboxylic, phenolic) substituents, permitting the determination of the Hammett substituent constants for the $-PO_3H^-$ ($\sigma_m = 0.25$, $\sigma_p = 0.17$),[1] $-PO_3^{2-}$ ($\sigma_m = -0.02$, $\sigma_p = -0.16$),[1] and $-PO_2H^-$ ($\sigma_p = 0.14$)[2] groups. By a similar treatment, Freedman and Jaffé have determined the substituent constants ($\sigma_m = 0.55$, $\sigma_p = 0.60$) for the diethoxyphosphono $[-P(O)(OC_2H_5)_2]$ group.[3] These substituent-constant values clearly indicate that the $-PO_3H^-$, $-PO_2H^-$, and $-P(O)(OC_2H_5)_2$ groups are moderately electron attracting, while the $-PO_3^{2-}$ group is weakly electron repelling.

In the course of studies carried out in this laboratory on the base-catalyzed reactions of organophosphorus compounds,[4] an accurate assessment of the inductive effects of certain phosphorus substituents became desirable. Presumably, inductive effects account for the magnitudes of the Hammett constants of the groups cited above, but the effects of dπ–pπ bonding cannot be completely discounted in these aromatic systems. Even though the effects of such bonding are probably quite small and possibly negligible, it was of interest to consider the application of linear free energy correlations to systems in which dπ–pπ bonding would be completely absent. Recently the Taft equation was found to apply satisfactorily to the acid dissociation constants of alkylphosphonic acids, but the attempted determination of polar (inductive) substituent constant (σ^*) values by application of this

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(1) H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953).

(2) L. D. Quin and M. R. Dysart, *J. Org. Chem.*, **27**, 1012 (1962).

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(4) (a) D. J. Martin and C. E. Griffin, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965; Abstracts, p. 58S; (b) D. J. Martin, Ph.D. Thesis, University of Pittsburgh, 1965; (c) R. H. Churi and C. E. Griffin, unpublished results.