Table I

Pmr Data

Compd	δ^a		J, cps	
	CH_2	$C(CH_3)_3$	Pb^{207}, H-α	Pb^{207}, H-γ
$[(H_3C)_3CCH_2]_3PbCl$	2.45	1.12	30.0 ± 0.2	8.0 ± 0.1
$[(H_3C)_3CCH_2]_3PbBr$	2.53	1.11	28.0 ± 0.2	8.0 ± 0.1
$[(H_3C)_3CCH_2]_3Pb\text{–}Pb[CH_2C(CH_3)_3]_3$[b,c]	2.01	1.03	19.8 ± 0.2	5.0 ± 0.1

[a] Chemical shifts are in parts per million downfield from an internal standard of tetramethylsilane and are accurate to 0.01 ppm. [b] Coupling between protons and lead through three bonds ($Pb^{207}\text{–}Pb\text{–}C\text{–}H^1$) was 12.0 ± 0.2 cps. [c] A low-intensity quartet expected from the system $Pb^{207}\text{–}Pb^{207}\text{–}CH_2$ could not be observed because of the poor signal-to-noise ratio.

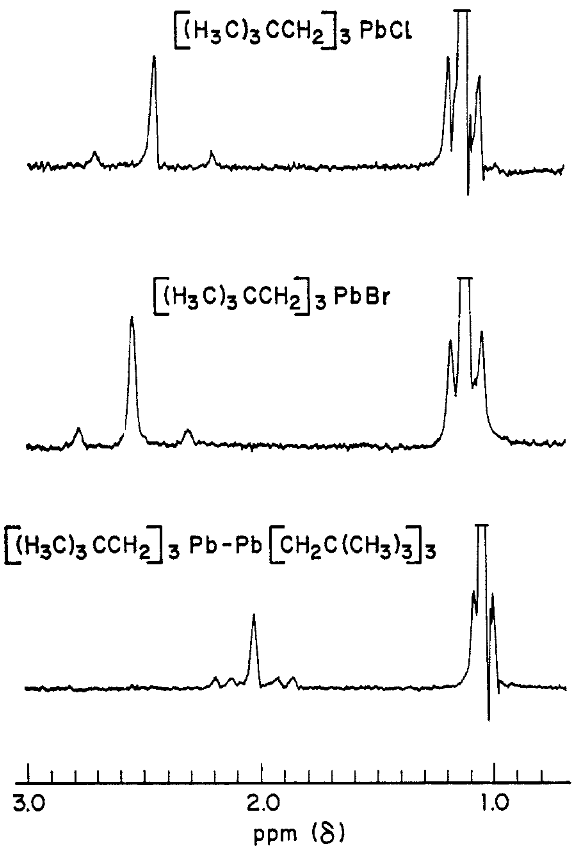

Figure 1.—Pmr spectra of trineopentyllead chloride, trineopentyllead bromide, and hexaneopentyldilead in deuteriochloroform solutions.

Experimental Section

Melting points are uncorrected. The proton magnetic resonance spectra were recorded on 0.2 *M* solutions in deuteriochloroform, using a Varian Associates A-60 spectrometer. Tetrahydrofuran was distilled from calcium hydride before use. Experiments involving preparation and reaction of neopentylmagnesium chloride were carried out under an atmosphere of prepurified nitrogen.

Reaction of Neopentylmagnesium Chloride with Lead Chloride.—To a stirred solution of 13.90 g (0.05 mole) of lead chloride in 200 ml of tetrahydrofuran at 0° was added dropwise over a period of 30 min a solution of neopentylmagnesium chloride, prepared from 2.92 g (0.12 g-atom) of magnesium and 10.66 g (0.1 mole) of neopentyl chloride in 100 ml of tetrahydrofuran. The resulting dark black mixture was refluxed for 1 hr and then filtered while hot. Tetrahydrofuran was removed from the filtrate *in vacuo* and the residue was extracted with 600 ml of boiling 95% aqueous ethanol. On cooling the extract a yellow crystalline solid, 4.5 g, separated.

The yellow solid was stirred with 100 ml of petroleum ether (bp 30–60°). Filtration gave 2.7 g of a white solid which was identified as trineopentyllead chloride. Removal of solvent from the filtrate *in vacuo* gave 1.8 g of hexaneopentyldilead as shiny yellow crystals.

Trineopentyllead Chloride.—Recrystallization of trineopentyllead chloride from absolute ethanol furnished an analytically pure sample, mp 207–208°.

Anal. Calcd for $C_{15}H_{33}ClPb$: C, 39.51; H, 7.24; Cl, 7.80. Found: C, 39.47; H, 7.16; Cl, 7.88.

Hexaneopentyldilead.—Hexaneopentyldilead obtained above was analytically pure, mp 202–203° dec.

Anal. Calcd for $C_{30}H_{66}Pb_2$: C, 42.84; H, 7.85. Found: C, 42.83; H, 7.64.

Its infrared spectrum (KBr pellet), determined using a Perkin-Elmer 221 spectrometer equipped with sodium chloride optics, showed absorptions at 2950 (s), 2902 (s), 2865 (s), 1440 (m), 1350 (m), 1230 (s), 1092 (s), 995 (w), and 700 (s) cm^{-1}.

Trineopentyllead Bromide.—To a stirred solution of 0.8404 g (0.001 mole) of hexaneopentyldilead in 20 ml of benzene was added 1% bromine solution in benzene till the yellow color of the lead compound was discharged. Benzene was then removed *in vacuo*. Trineopentyllead bromide was left behind as white solid in almost quantitative yield. Its analytical sample was prepared by recrystallization from absolute ethanol, mp 166°.

Anal. Calcd for $C_{15}H_{33}BrPb$: C, 36.00; H, 6.60; Br, 16.00. Found: C, 36.32; H, 6.42; Br, 15.58.

Acknowledgment.—The author is grateful to Professor Dietmar Seyferth of Massachusetts Institute of Technology for advice and encouragement.

3d-Orbital Resonance in Trivalent Organophosphines. II. Additions of Organolithium Compounds to Vinylphosphines[1]

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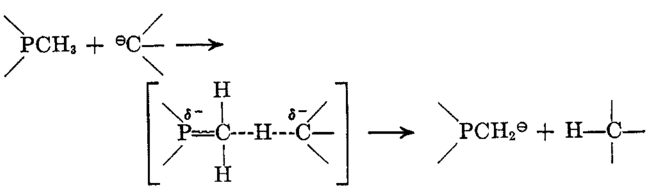
Received September 22, 1965

In the first paper of this series, the selective methyl metalations of methyldiphenylphosphine, dimethylphenylphosphine, and di-*n*-hexylmethylphosphine were described.[1b] Also, it was reported that dimethyldodecylphosphine was metalated approximately 15 times as rapidly as dimethyldodecylamine. The selective methyl metalation of the methylphenylphosphines and the enhanced rate of metalation of dimethyldodecylphosphine, relative to the analogous amine, were regarded as evidence for d-orbital resonance stabilization of the incipient α-carbanions by trivalent phosphorus in the transition state.



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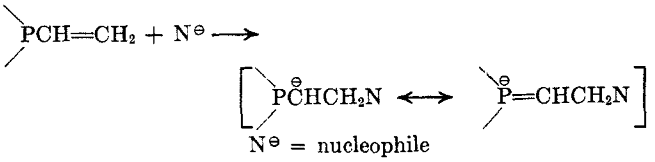
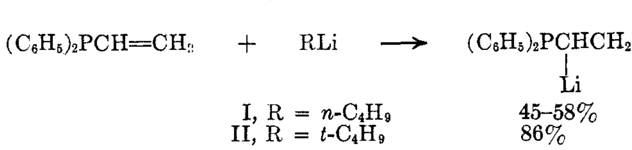
[1] (a) Presented in part at the 149th Meeting of the American Chemical Society, April 1965, Detroit, Mich. (b) Part I: D. J. Peterson and H. R. Hays, *J. Org. Chem.*, **30**, 1939 (1965).

In accord with this proposal of electron delocalization by trivalent phosphorus atoms, it has now been established that the unsaturated linkages of vinylphosphines are subject to Michael-type addition reactions.



Specifically, *n*-butyllithium and *t*-butyllithium add to the terminal carbon atom of diphenylvinylphosphine to give (α-lithio-*n*-hexyl)diphenylphosphine (I) and (α-lithio-γ,γ-dimethylbutyl)diphenylphosphine (II), respectively.

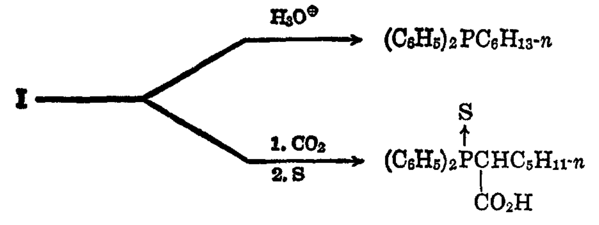


$$(C_6H_5)_2PCH{=}CH_2 + RLi \longrightarrow (C_6H_5)_2P\underset{\displaystyle Li}{C}HCH_2R$$

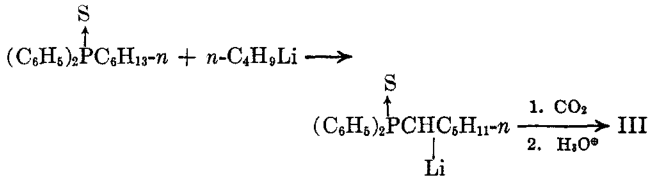
I, R = n-C_4H_9 45–58%
II, R = t-C_4H_9 86%

The reaction of *n*-butyllithium with di-*n*-butylvinylphosphine results in the formation of a telomer.

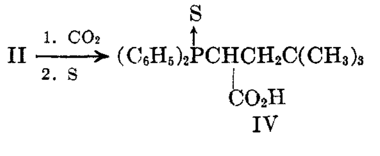
The reaction of *n*-butyllithium with diphenylvinylphosphine in ether was mildly exothermic and proceeded quite rapidly, even at 0°. The addition product I was characterized by protonation and by carbonation followed by sulfurization. An nmr spectrum of III showed a singlet at τ −1.05 (area 1), multiplets at τ 1.8–2.3 (area 4.2), 2.3–2.72 (area 6.2), 5.96–6.46 (area 1), and 7.5–8.9 (area 8.7), and a triplet at τ 9.08 (area 2.3), characteristic of an acid proton, *ortho* hydrogens (eight-line pattern), *meta* and *para* hydrogens, methine proton attached to a diphenylthiophosphoryl group, methylene protons, and a terminal methyl group, respectively. The structure assignment of III was confirmed by an alternate synthesis.[2] The compounds from the two sources were shown to be identical by a comparison of their infrared spectra and a mixture melting point determination.



III



$$(C_6H_5)_2\overset{\displaystyle S\atop\uparrow}{P}C_6H_{13}\text{-}n + n\text{-}C_4H_9Li \longrightarrow (C_6H_5)_2\overset{\displaystyle S\atop\uparrow}{P}\underset{\displaystyle Li}{C}HC_5H_{11}\text{-}n \xrightarrow[2.\ H_3O^{\oplus}]{1.\ CO_2} \text{III}$$



$$\text{II} \xrightarrow[2.\ S]{1.\ CO_2} (C_6H_5)_2\overset{\displaystyle S\atop\uparrow}{P}\underset{\displaystyle CO_2H}{C}HCH_2C(CH_3)_3$$

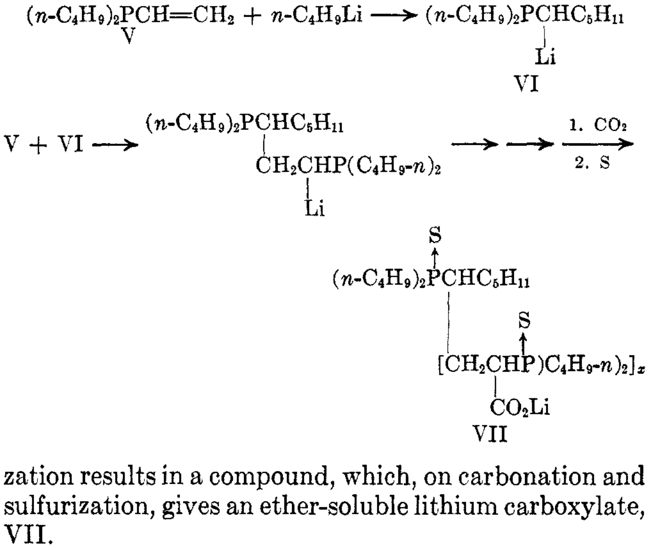
IV

The adduct II was characterized by carbonation and subsequent sulfurization.

The 100-Mc nmr spectrum of IV is shown in Figure 1. In $CDCl_3$, the spectrum consists of a broad peak at τ −0.24 corresponding to the carboxyl proton (area 1), two aromatic multiplets at τ 2.05 and 2.52 (area 9.8), a multiplet due to the methine proton at τ 6.23 (area 1), multiplets due to the methylene protons at τ 7.86 and 8.22 (area 2), and a singlet at τ 9.13 arising from the *t*-butyl protons (area 8). The spectral resolution in $CDCl_3$ was not sufficient for an accurate assignment of the coupling constants. However, an analysis of the spectrum of IV in pyridine at 70° was obtained (Figure 2). Using the principle of spectral superposition,[3] considering the P–CH–CH_2 fragment as an ABMX system (where M and X refer to the methine proton and phosphorus atom, respectively), the following chemical shifts (τ) and coupling constants (cycles per second) were obtained: ν_A 8.30, ν_B 7.77, and ν_M 6.25; J_{AP} = 19.0, J_{BP} = 2.5, J_{MP} = 16.2, J_{AB} = 14.2, J_{AM} = 1.5, and J_{BM} = 10.5. The assignment of the phosphorus–proton couplings was confirmed by a separate decoupling experiment in which the phosphorus resonance was irradiated while observing the proton resonances. It is of interest to note the large difference in coupling of the methylene protons with the phosphorus atom (J_{AP}, J_{BP}).

The molecular weight of IV was shown to be 346 by mass spectral analysis. The mass spectrum of IV, like its isomer III, exhibts a base peak of 218, presumably owing to the $[(C_6H_5)_2PSH]^+$ ion.

The reaction of *n*-butyllithium with di-*n*-butylvinylphosphine (V) was more complex. Apparently, the organolithium compound adds in Michael fashion to give (α-lithio-*n*-hexyl)di-*n*-butylphosphine (VI), but this compound undergoes subsequent addition to another molecule of vinylphosphine. Further telomerization results in a compound, which, on carbonation and sulfurization, gives an ether-soluble lithium carboxylate, VII.



Since Michael-type addition reactions usually occur only under normal conditions with conjugated olefins,[4] it seems reasonable to conclude that the phosphino

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(2) D. Seyferth and D. E. Welch, *J. Organometal. Chem.*, **2**, 1 (1964).

(3) J. A. Pople and T. Schaefer, *Mol. Phys.*, **3**, 547 (1960).

(4) At least one important exception has been reported. The highly reactive *t*-butyllithium adds to ethylene [P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953)]. Consequently, the addition of *t*-butyllithium to a vinylphosphine does not in itself constitute proof of activation of an olefinic linkage by a phosphino group.

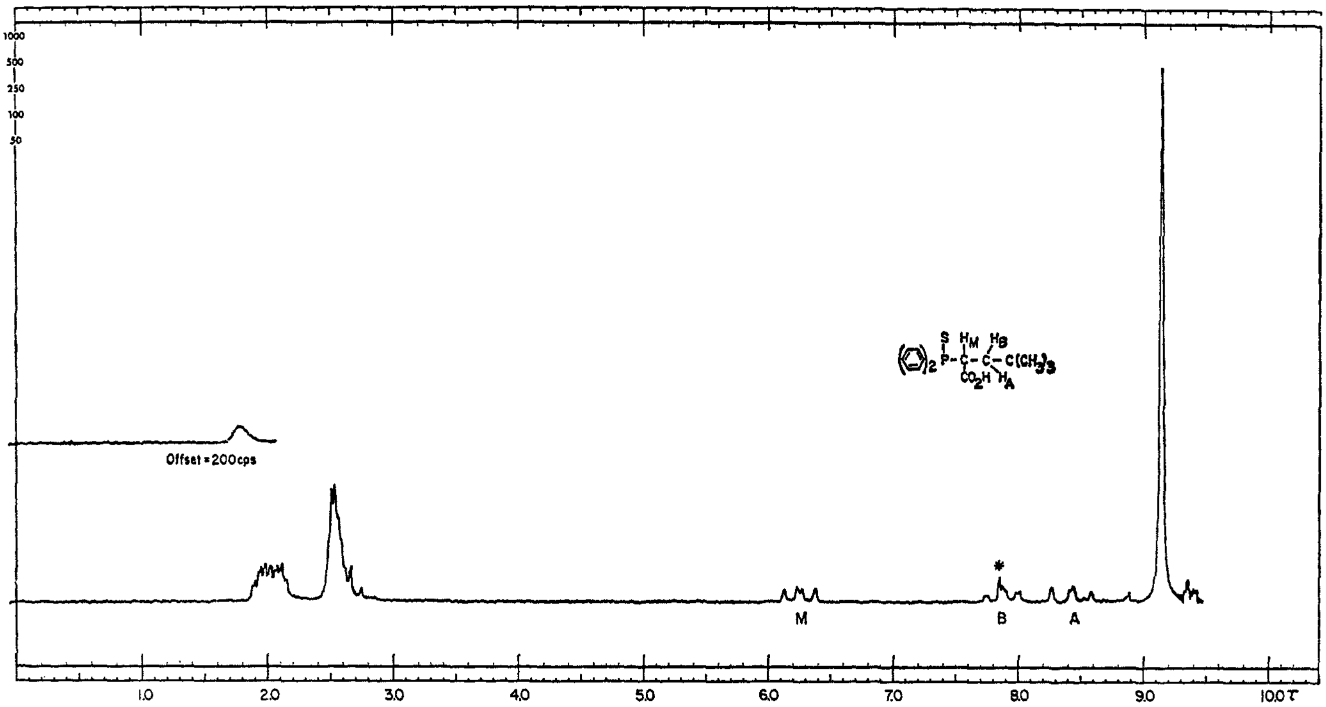


Figure 1.—The 100-Mc spectrum of IV in $CDCl_3$ solution. The asterisk indicates a peak due to impurity.

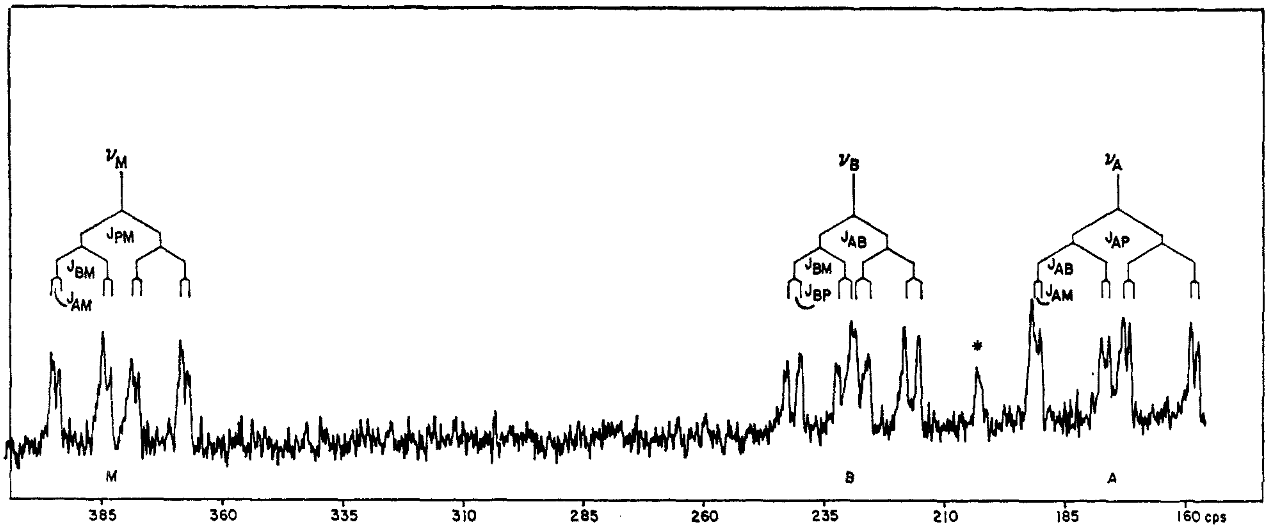
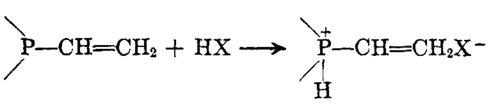


Figure 2.—The ABM portion of IV in pyridine solution. The asterisk indicates a peak due to impurity.

group has activated the alkene linkage of the vinylphosphine toward nucleophilic addition. The activating effect is apparently a result of the ability of trivalent phosphorus atoms to stabilize the transition state for the addition reaction by delocalization of the negative charge on the α carbon atom into its vacant d-orbitals.[5] A similar behavior has been observed for vinylsilicon[6a] and vinylsulfur[6b] compounds, which, like phosphorus, have d-orbitals available for bonding.

It is of interest to note that Kabachnik and co-workers have reported[7] that di-*n*-butylvinylphosphine is inert to piperidine at 160°. However, the desired addition reaction was realized when run in the presence of an acid catalyst. As suggested by Kabachnik,[7] this finding would appear to be consistent with the addition reaction being preceded by a conversion of the vinyl phosphine to the more reactive vinylphosphonium salt. Additions of nucleophiles to vinylphosphorus compounds in which the central atom has positive character are well known.[6a]



$$>P{-}CH{=}CH_2 + HX \longrightarrow >\overset{+}{P}(H){-}CH{=}CH_2X^-$$

Experimental Section

All reactions and manipulations involving phosphines and organolithium compounds were performed under an atmosphere of oxygen-free argon. Nmr spectra were obtained on Varian Associates HR-60 (phosphorus), A-60 (proton), and HA-100

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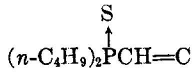
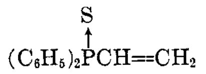
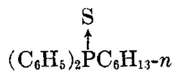
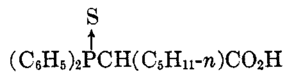
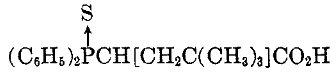
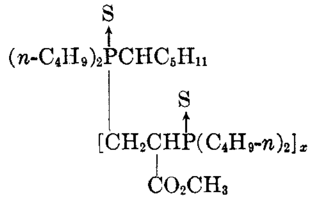
[5] After this manuscript was submitted for publication, a report on the addition of lithium diphenylphosphide to β-styryldiphenylphosphine appeared: A. M. Aguiar and D. Diagle, *J. Org. Chem.*, **30**, 3527 (1965). As a referee has pointed out, this finding aids the argument that the 3d-orbitals of the phosphorus do act as electron acceptors, even when in competition with an aromatic nucleus.

[6] (a) D. Seyferth, *Progr. Inorg. Chem.*, **3**, 137 (1962); (b) W. E. Parham and R. F. Motter, *J. Am. Chem. Soc.*, **81**, 2146 (1959).

[7] M. I. Kabachnik, E. N. Tsvetkov, and C. C. Yu, *Tetrahedron Letters*, **No. 1**, 5 (1962).

TABLE I

PHOSPHORUS NMR DATA

No.	Phosphine sulfide	Chem shift,[a] ppm
1	 $(n\text{-}C_4H_9)_2\overset{S}{\overset{\uparrow}{P}}CH{=}CH_2$	−44[b]
2	 $(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}CH{=}CH_2$	−37.5[b]
3	 $(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}C_6H_{13}\text{-}n$	−42.0[b]
4	 $(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}CH(C_5H_{11}\text{-}n)CO_2H$	−46[b]
5	 $(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}CH[CH_2C(CH_3)_3]CO_2H$	−48.3[c]
6	 $(n\text{-}C_4H_9)_2\overset{S}{\overset{\uparrow}{P}}CHC_5H_{11}$ / $[CH_2CH(CO_2CH_3)\overset{S}{\overset{\uparrow}{P}}(C_4H_9\text{-}n)_2]_x$	−58[b]

[a] Relative to 85% H_3PO_4. [b] Run in $CHCl_3$. [c] Run in acetone.

(proton) spectrometers. The phosphorus nmr data are summarized in Table I.

The molecular weight determinations were run on an Atlas CH-4 mass spectrometer. The compounds were introduced directly into the ion source (*ca.* 70°) to avoid thermal decomposition.

The addition reactions, sulfurizations, and carbonations were carried out as previously described.[1b]

Diphenylvinylphosphine (VIII) and diphenyl-*n*-hexylphosphine (IX) were prepared by the reaction of chlorodiphenylphosphine with the corresponding Grignard reagents: VIII, bp 116–118° (0.5 mm), $n^{25}D$ 1.6215 [lit.[8] bp 104° (0.25 mm), $n^{24.5}D$ 1.6260]; IX, bp 138° (0.09 mm), $n^{20}D$ 1.5760 [lit.[9] bp 136–141 (0.2 mm), $n^{20}D$ 1.5766].

Di-*n*-butylvinylphosphine (V) was prepared in a similar manner from di-*n*-butylchlorophosphine and vinylmagnesium bromide: bp 120–125° (*ca.* 10 mm) [lit.[10] bp 64° (3.5 mm)].

The phosphines, VIII, IX, and V, were further characterized by conversion to the corresponding phosphine sulfides: diphenylvinylphosphine sulfide, mp 53–56° (lit.[8] mp 53.3–54.9°); diphenyl-*n*-hexylphosphine sulfide, mp 48–49° (lit.[9] mp 51–52°); and di-*n*-butylvinylphosphine sulfide, bp 95–100° (1 mm), $n^{27}D$ 1.5107. The proton and phosphorus nmr spectra of di-*n*-butylvinylphosphine sulfide were consistent with the structure assignment.

Anal. Calcd for $C_{10}H_{21}PS$: C, 58.8; H, 10.3. Found: C, 58.0; H, 10.3.

Reactions of Diphenylvinylphosphine with *n*-Butyllithium. A. Acid Hydrolysis and Sulfurization.—To 8.5 g (0.04 mole) of diphenylvinylphosphine dissolved in 25 ml of ether there was slowly added 32 ml (15% hexane solution, 0.05 mole) of *n*-butyllithium. Subsequent to the complete addition and 1 hr of stirring at room temperature, the reaction mixture was hydrolyzed with a dilute ammonium chloride solution. The organic layer was separated and treated with 1.28 g (0.04 mole) of sulfur (exothermic reaction). Distillation of the reaction mixture gave the following fractions (per cent by glpc) composed of diphenyl-*n*-hexylphosphine sulfide and diphenylvinylphosphine sulfide, respectively: (1) 3.52 g., 80/20%, bp 205–212° (0.01 mm); (2) 2.16 g, 88/12%, bp 205–212° (0.01 mm); (3) 0.98 g, 95/5%, bp 212–219° (0.01 mm). Fraction 3 crystallized, mp 43–45°. A crystallization from absolute ethanol raised the melting point of the diphenyl-*n*-hexylphosphine sulfide to 46.5–48.5°. A mixture melting point determination with an authentic sample gave no depression. A proton nmr spectrum of the phosphine sulfide in $CDCl_3$ was consistent with the structure assignment: aromatic protons (10) at τ 1.85–2.7, P–CH_2– (2) at τ 7.2–7.8, methylene protons (8) at τ 8–8.9, and methyl protons (2.9) at τ 9.15. The total yield of diphenyl-*n*-hexylphosphine sulfide was 5.65 g (47%). The tarry distillation residue, which partially crystallized on standing, was triturated with hexane and filtered to give 0.62 g of compound melting over the range 109–112.5°. Two crystallizations from an ethyl acetate–hexane mixture (40:60) afforded 0.6 g (5%) of compound, mp 114–116°, tentatively identified as 1,3-bis(diphenylthiophosphinyl)octane.

Anal. Calcd for $C_{32}H_{36}P_2S_2$: C, 70.33; H, 6.60. Found: C, 70.4; H, 7.0.

A P^{31} nmr spectrum of the phosphine sulfide in benzene exhibited two resonance signals of approximately equal intensity at −40.4 and −47.7 ppm presumably due to the two nonequivalent phosphorus atoms. The proton nmr spectrum was also in accord with the proposed structure; *ortho* protons (8) centered at τ 2.3, *meta* and *para* protons (12) centered at τ 2.7, a complex pattern at τ 7.0–8.7 (7), methylene protons (6) [$-CH_2(CH_2)_3CH_3$] centered at τ 8.9, and methyl protons (2.6) at τ 9.14.

B. Acid Hydrolysis.—To 7.0 g (0.033 mole) of diphenylvinylphosphine dissolved in 35 ml of ether and cooled to −10°, 38.6 ml (15% hexane solutions, 0.06 mole) of *n*-butyllithium was added over 0.5 hr. After standing for 6 hr at −10°, the reaction mixture was allowed to warm to room temperature and hydrolyzed with a dilute aqueous ammonium chloride solution. The organic layer was separated, concentrated, and distilled to give 5.15 g (57.6%) of diphenyl-*n*-hexylphosphine, bp 112–117° (0.03 mm). An infrared spectrum of the compound was superimposable on that of an authentic sample.

The distillation residue, 1.5 g, which contained some additional diphenyl-*n*-hexylphosphine, as evidenced by gas chromatography, was not further worked up.

C. Carbonation and Sulfurization.—To 8.5 g (0.04 mole) of diphenylvinylphosphine dissolved in 25 ml of ether and cooled to 0°, 28.8 ml (15% hexane solution, 0.045 mole) of *n*-butyllithium was added dropwise. Subsequent to the complete addition, the reaction mixture was allowed to warm to room temperature and then carbonated and treated with sulfur as previously described.[1b] There was obtained on work-up 6.1 g (45%) of crude (α-carboxy-*n*-hexyl)diphenylphosphine sulfide (III), melting over the range 109–114°. Crystallizations from benzene-hexane (60:40) mixtures afforded 3.60 g (26%) of product, mp 129–131°, and 0.39 g (2.5%) of product, mp 125–129°. A proton nmr spectrum of the product was consistent with the structure assignment: aromatic at τ 1.8–2.7, methine at τ 5.98–6.46, methylene centered at τ 8.68, methyl at τ 9.18, and an acidic proton at τ 1.05 in the ratio of 10:1:8.2:3.1:1. An infrared spectrum of the product was superimposable on that of an authentic sample. Also, a mixture melting point determination gave no depression.

Preparation of (α-Carboxy-*n*-hexyl)diphenylphosphine Sulfide.—To 12.8 g (0.045 mole) of diphenyl-*n*-hexylphosphine sulfide dissolved in 20 ml of ether was slowly added 32 ml (15% hexane solution, 0.05 mole) of *n*-butyllithium. After 1.5 hr, the reaction mixture was carbonated and worked up as previously described[1b] to give 7.3 g (57%) of recovered diphenyl-*n*-hexylphosphine sulfide and 1.93 g (12.4%) of acid (III) (after two crystallizations from a benzene–hexane mixture), mp 130–132°.

Anal. Calcd for $C_{19}H_{23}O_2PS$: C, 65.89; H, 6.65; P, 8.95; S, 9.24; mol wt, 346. Found: C, 65.9; H, 7.3; P, 8.7; S, 10.5; mol wt, 346.

Reaction of Diphenylvinylphosphine with *t*-Butyllithium.—To 1.5 g (0.007 mole) of diphenylvinylphosphine dissolved in 20 ml of pentane, 10 ml (1.88 *M* in pentane, 0.019 mole) of *t*-butyllithium was added dropwise, resulting in a mildly exothermic reaction. The orange solution was then stirred for 2.5 hr, carbonated,[1b] treated with 0.32 g (0.01 mole) of sulfur, and extracted with water. The organic layer was separated, dried over sodium sulfate, and concentrated to give 0.48 g of neutral material.

The aqueous layer was acidified with dilute sulfuric acid and extracted thoroughly with ether. Concentration of the ether extracts afforded an oil that crystallized on standing. The solid was washed free of 0.35 g of pivalic acid with cold hexane. The residual acid, 2.03 g (86%), melted over the range 172–190°. A crystallization from a benzene–hexane (70:30) solvent gave 1.2 g of (α-carboxy-γ,γ-dimethylbutyl)diphenyl-

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[8] K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **26**, 2537 (1961).

[9] C. Stuebe, W. M. LeSuer, and G. R. Norman, *J. Am. Chem. Soc.*, **77**, 3526 (1955).

[10] M. I. Kabachnik, C. C. Yu, and E. N. Tsvetkov, *Dokl. Akad. Nauk. SSSR*, **135**, 603 (1960).

phosphine sulfide (IV), mp 194.5–197°. A second crystallization from benzene afforded 0.98 g (38.6%) of acid, mp 196.5–198.5°. Work-up of the mother liquors gave an additional 0.52 g (21%) of product, mp 190–196°.

Anal. Calcd for $C_{13}H_{23}O_2PS$: C, 65.89; H, 6.65; mol wt, 346. Found: C, 66.4; H, 7.5; mol wt, 346.

The Reaction of *n*-Butyllithium with Di-*n*-Butylvinylphosphine.—To 4.5 g (0.026 mole) of di-*n*-butylvinylphosphine dissolved in 25 ml of ether, and contained in a metalation tube,[1b] 30 ml (1.6 *M* in hexane, 0.05 mole) of *n*-butyllithium was added rapidly. After stirring for 24 hr at room temperature, the reaction mixture was carbonated,[1b] treated with 1.28 g (0.04 mole) of sulfur, and extracted thoroughly with water. The organic layer was concentrated and distilled, bp 30–85° (0.5 mm), to give 0.57 g of a mixture of di-*n*-butyl ketone and tri-*n*-butyl alcohol, as evidenced by gas phase chromatographic retention times and infrared spectral analysis. An infrared spectrum of the distillation residue had an absorption band at 6.2 μ characteristic of a carboxylic acid salt.[11] The residue was dissolved in ether and acidified with dilute sulfuric acid. The organic layer was separated, dried over sodium sulfate, and concentrated. An infrared spectrum of the concentrate, 4.6 g, did not exhibit the 6.2-μ band and did have an absorption band at 5.87 μ characteristic of a carboxylic acid.[11] A portion of the amorphous acid, 2.5 g, was esterified with diazomethane in the usual manner. An infrared spectrum of the ester had a carbonyl absorption at 5.77 μ. An nmr spectrum of the material in $CDCl_3$ exhibited proton absorptions at τ 6.26 (3), 8.56 (65), and 9.04 (26), assigned to methoxy, methylene, and methyl groups, respectively. The polymeric acid contained 59.3% carbon and 10.4% hydrogen by analysis.

The original aqueous layer was acidified with dilute sulfuric acid and thoroughly extracted with ether. Concentration afforded 0.76 g of material that was distilled under reduced pressure to give 0.12 g of valeric acid, bp 30–50° (0.5 mm), n^{20}_D 1.4094. The distillation residue was esterified in the usual manner. An nmr spectrum of the esterified material was essentially identical with the spectrum of the ester described above.

Acknowledgment.—The author is indebted to Dr. J. McLeskey for the detailed proton nmr analysis of one of the compounds.

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(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, New York, N. Y., 1958, p. 174.

The Reaction of Aryl Chloroformates with Silver Nitrate

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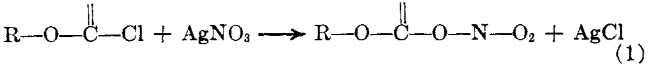
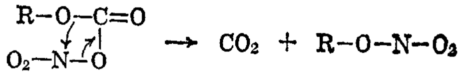
Received October 28, 1965

The reaction of silver nitrate with chloroformates has not been extensively investigated. However, during the past several years a few publications have emerged. Boschan[1] and, slightly later, Mortimer[2] reported on the reactions of alkyl chloroformates and presented a facile synthesis of alkyl nitrate esters. Each gave evidence that the major reaction pathway involved initial formation of an alkyl nitratoformate.



$$R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl + AgNO_3 \longrightarrow R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}N{-}O_2 + AgCl \quad (1)$$

More recently, confirming kinetic proof has been presented by Kevill and Johnson.[3] Boschan suggested that the next step was a concerted SNi rearrangement with loss of carbon dioxide to form the product nitrate.



(2)

At about the same time, Chaney and Wolfrom[4] reported that the reaction of phenyl chloroformate with silver nitrate yields *o*-nitrophenol. By analogy with the above reactions, they suggested that phenyl nitrate might be a primary intermediate which subsequently rearranged internally to the more stable isolated product.

We have repeated and extended the latter work and have obtained results that lead to further speculation with regard to some of these mechanisms. Experiments were carried out in essentially the same manner used by previous workers. An acetonitrile solution of silver nitrate and aryl chloroformate was stirred at 0–10° for several hours. After removing silver chloride precipitate by filtration, the reaction mixture was examined by vpc and the products were isolated and identified by standard methods. A summary of pertinent experiments and results are presented in Table I.

TABLE I

REACTIONS BETWEEN ARYL CHLOROFORMATES AND SILVER NITRATE

Substrate	Moles of $AgNO_3$	Product(s) (%)
p-Cresyl chloroformate[a]	2.0	*o*-Nitro-*p*-cresol (44)
Phenyl chloroformate[a,b]	1.0	*o*-Nitrophenol (34) *p*-Nitrophenol (28)
Phenyl chloroformate and *p*-cresol[c]	1.3	*o*-Nitrophenol (3.6) *p*-Nitrophenol (2.9) *o*-Nitro-*p*-cresol (43)

[a] Isolated yields. [b] In a similar reaction, vpc analysis of the crude reaction product showed 19% *o*-nitrophenol, 33% *p*-nitrophenol, and less than 0.01% *m*-nitrophenol. [c] Values shown were obtained by vpc. Because of difficulty with tailing, the analysis for *p*-nitrophenol is inaccurate. However, the values shown are qualitatively correct.

As shown, the reaction of phenyl chloroformate with silver nitrate yields not only *o*-nitrophenol but also large amounts of the *para* isomer. This mixture does not result from secondary rearrangement of a primarily formed *o*-nitrophenol as shown by the stability of that material under the reaction conditions (see Experimental Section). In addition, the exchange experiment wherein *p*-cresol was extensively nitrated in the presence of reacting phenyl chloroformate and silver nitrate suggests that the reaction is intermolecular.[5]

The lack of positional specificity and the intermolecular nature of the reaction are consistent with the following sequence (3). The first step is identical with that suggested by previous workers[1–4] and is predicated on their work and on the known reaction of silver nitrate with benzoyl chloride to form benzoyl nitrate.[6] We have described the subsequent ionization as yielding nitronium and phenolate ions that recombine to the

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(1) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

(2) G. A. Mortimer, *J. Org. Chem.*, **27**, 1876 (1962).

(3) D. N. Kevill and G. H. Johnson, *J. Am. Chem. Soc.*, **87**, 928 (1965).

(4) A. Chaney and M. L. Wolfrom, *J. Org. Chem.*, **26**, 2998 (1961).

(5) This result might also be explained by transesterification of the *p*-cresol and subsequent intramolecular reaction of the *p*-cresyl chloroformate with silver nitrate. However, when 1 mole of *p*-cresol and 1 mole of phenyl chloroformate were treated with a deficiency (0.5 mole) of silver nitrate, the product mixture contained 0.5 mole of phenyl chloroformate and no *p*-cresyl chloroformate, suggesting that there was little or no transesterification under the reaction conditions.

(6) (a) A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press Ltd., London, 1959, Chapter 6; (b) F. Francis, *J. Chem. Soc.*, **89**, 1 (1906).