140–144°). β-(α-Methylstyryl)phosphonic acid is reported to melt at 95°.[26]

Reaction of Triethyl Phosphite wth Methylphenylacetylene. A. Formation of Diethyl β-(β-Methylstyryl)phosphonate (14).—A mixture of 11.6 g. (0.10 mole) of methylphenylacetylene and 33.2 g. (0.20 mole) of triethyl phosphite was refluxed (150°) for 4 days. Distillation under reduced pressure gave triethyl phosphite, 9.6 g. of methylphenylacetylene (83.5% recovery), 10.2 g. of a mixture of triethyl phosphate and diethyl ethylphosphonate,[24] and 1.1 g. (24% based on unrecovered acetylene) of **14**, b.p. 128° (0.5 mm.), 144–145° (1.0 mm.).

Anal. Calcd. for $C_{13}H_{19}O_3P$: C, 61.41; H, 7.53; P, 12.18. Found: C, 61.18, 61.27; H, 7.74, 7.68; P, 12.00, 11.91.

The infrared spectrum was quite similar to that of **5**; the p.m.r. spectral data have been reported in the text.

B. Formation of 1,2-Bis(diethylphosphono)-1-phenylpropane (15).—A repetition of the above reaction with an increase in reaction time to 9 days led to the recovery (65.5%) of the acetylene and the isolation of **14** (22.8% based on unrecovered acetylene) and 1.43 g. of **15**, b.p. 195–196° (1.0 mm.). The p.m.r. spectrum of this fraction indicated slight contamination by **14**. This was purified by chromatography through a silicic acid column (70 g., 2.5-cm. diameter); elution with chloroform gave **15**, 1.17 g.

Anal. Calcd. for $C_{17}H_{30}O_6P_2$: C, 52.03; H, 7.70; P, 15.80; mol. wt., 392. Found: C, 51.86, 52.09; H, 7.63, 7.81; P, 15.97, 16.13; mol. wt., 407, 411.[27]

The infrared spectrum of **15** confirmed the presence of diethylphosphono and monosubstituted benzene functions. The p.m.r. spectrum of **15** showed a group of four broad complex multiplets centered at τ = 2.47 (5.0H aromatic), 4.00 (7.9H, -O-CH_2-), 7.75 (1.8H, methine), and 8.85 p.p.m. (15.3H, methyl).

Reaction of Tri-*n*-butyl Phosphite with Diphenylacetylene.—A mixture of 17.8 g. (0.10 mole) of diphenylacetylene and 50.0 g. (0.20 mole) of tri-*n*-butyl phosphite was refluxed at 190° for 8 days. Distillation of the reaction mixture gave a low-boiling fraction consisting of tri-*n*-butyl phosphate, di-*n*-butyl *n*-butylphosphonate, and unreacted acetylene[24] and 6.82 g. of **1,2-bis(di-*n*-butylphosphono)-1,2-diphenylethane (18)**, b.p. 152–154° (0.2 mm.). G.l.c. analysis indicated this fraction to be contaminated with tri-*n*-butyl phosphate. A solution of 2.0 g. of this material was chromatographed through a silicic acid column (100 g., 2.5-cm. diameter); elution with chloroform gave 1.57 g. of **18**.

Anal. Calcd. for $C_{30}H_{58}O_6P_2$: C, 63.59; H, 8.54; P, 10.93; mol. wt., 577. Found: C, 63.24, 63.30; H, 8.38, 8.35; P, 11.17, 11.10; mol. wt., 553, 557.[27]

The infrared spectrum showed bands at 1241 (P→O) and 754 and 698 cm.$^{-1}$ (monosubstituted phenyl) and the absence of olefinic absorption. The p.m.r. spectrum showed signals at τ = 2.8, multiplet, 10.2H (aromatic); 6.15, multiplet, 10.1H (-O-CH_2- + methine); 8.5, multiplet, 14.9H (methylene); and 9.07 p.p.m., triplet, 12.7H (methyl, $J_{HH} \cong 7.0$ c.p.s.). The p.m.r. spectrum is consistent in all respects with the postulated structure.

Reaction of Tri-*n*-butyl Phosphite with Nonyne-1.—A mixture of 16.2 g. (0.10 mole) of nonyne-1 and 50.0 g. (0.20 mole) of tri-*n*-butyl phosphite was refluxed at 190° for 5 days. Distillation of the reaction mixture gave a series of low-boiling fractions identified as nonyne-1 (51.2% recovery), tri-*n*-butyl phosphite, di-*n*-butyl *n*-butylphosphonate (37.3%), and tri-*n*-butyl phosphate (17.3%),[24] and 5.8 g. of material with b.p. 175–176° (0.5 mm.). G.l.c. analysis of the material indicated contamination by both tri-*n*-butyl phosphate and di-*n*-butyl *n*-butylphosphonate. A 2.0-g. sample of this material was chromatographed on silicic acid (100 g., 2.5-cm. diameter column); elution with chloroform gave 1.48 g. of **1,2-bis(di-*n*-butylphosphono)nonane (20)**.

Anal. Calcd. for $C_{25}H_{54}O_6P_2$: C, 58.78; H, 10.60; P, 12.09; mol. wt., 512. Found: C, 58.81, 58.74; H, 10.79, 10.88; P, 12.13, 12.27; mol. wt., 493, 497, 504.[27]

The compound showed a strong phosphoryl absorption at 1242 cm.$^{-1}$. The p.m.r. spectrum of **20** showed multiplets centered at τ = 6.0 (8.0H, -O-CH_2-) and 8.3 (33.5H, methylene + mehtine) and a triplet at 9.07 p.p.m. (14.9H, methyl, J_{HH} = 7.0–7.2 c.p.s.).

Acknowledgment.—The authors are indebted to the Victor Chemical Division, Stauffer Chemical Company, for generous gifts of starting materials.

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[26] E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930).

[27] Molecular weight determinations were carried out with a Mechrolab Model 301A vapor pressure osmometer, using dilute solutions in benzene at 37°. We are indebted to Mr. M. Bollinger for carrying out these determinations.

3d-Orbital Resonance in Trivalent Organophosphines. I. Metalation of Methylphosphines

DONALD J. PETERSON AND HUGH R. HAYS

The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio

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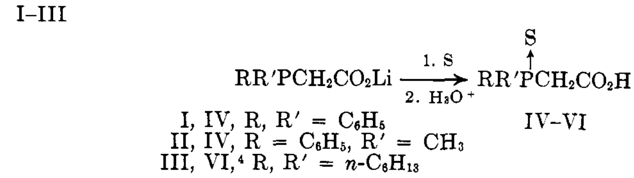
Alkyllithium compounds selectively metalate methyldiphenylphosphine, dimethylphenylphosphine, and di-*n*-hexylmethylphosphine on a methyl carbon atom to give the corresponding phosphino carbanions in yields ranging from 14–54%. The relative rates of metalation of dimethyldodecylphosphine to dimethyldodecylamine have been found to be *ca.* 15:1. The enhanced rates of metalation of the methylphosphines provide evidence for 3d-orbital resonance stabilization of the incipient α-phosphino carbanion by trivalent phosphorus.

Although the hydrogen–metal interchange reaction (metalation) has been used extensively as a method for the preparation of heteroatom-substituted organometallic compounds,[1] little is known about the metalation of tertiary organophosphines. In 1945 Gilman and Brown reported[2] that triphenylphosphine was metalated in the *meta* position by *n*-butyllithium to the extent of 6%. More recently, Aguiar and coworkers[3] have demonstrated that benzyldiphenylphosphine is metalated at the benzyl position by phenyllithium.

We now wish to report the results of a study of the metalation of some methylphosphines. We find that *t*-butyllithium selectively metalates methyldiphenylphosphine (I), dimethylphenylphosphine (II), and di-*n*-hexylmethylphosphine (III) on a methyl carbon atom. The yields of the phosphino carbanions, based on the weights of the derivatives obtained from carbonation and subsequent sulfurization, vary from 14 to 54% (see Table I).



$$\underset{\text{I–III}}{RR'PCH_3} + t\text{-}C_4H_9Li \longrightarrow RR'PCH_2Li + t\text{-}C_4H_{10} \xrightarrow{CO_2}$$

$$RR'PCH_2CO_2Li \xrightarrow[2.\ H_3O^+]{1.\ S} \underset{\text{IV–VI}}{RR'\overset{\overset{S}{\uparrow}}{P}CH_2CO_2H}$$

I, IV, R, R′ = C_6H_5
II, IV, R = C_6H_5, R′ = CH_3
III, VI,[4] R, R′ = *n*-C_6H_{13}

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[1] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

[2] H. Gilman and G. E. Brown, *J. Am. Chem. Soc.*, **67**, 824 (1945).

[3] A. M. Aguiar, J. Giacin, and A. Mills, *J. Org. Chem.* **27**, 674 (1962).

TABLE I

METALATION OF METHYLPHOSPHINES[a]

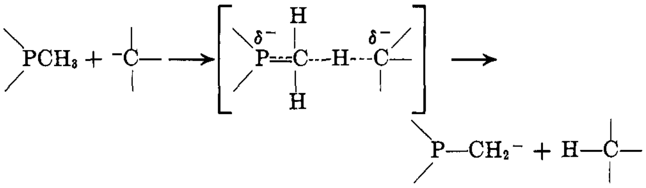
Expt.	Phosphine	Alkyllithium compound	Solvent	Time, hr.	Yield of acid (%)	Recovered phosphine (as sulfide), %
1	I[b]	n-C_4H_9Li	Ether	16	IV (14.3)	56
2		n-C_4H_9Li	Ether	48	(20.6)	38
3		n-C_4H_9Li	Pentane	48	(0)	85.5
4		t-C_4H_9Li	Pentane	40	(24[c])	74
5		t-C_4H_9Li	Pentane	120	(20)	59
6		t-C_4H_9Li	Pentane	168	(31.6)	*d*
7		t-C_4H_9Li	Pentane	192	(26)	51
8		t-C_4H_9Li	Pentane	312	(35.8)	35
9	II[b]	n-C_4H_9Li	Pentane	168	V (0)	81
10		t-C_4H_9Li	Pentane	48	(43)	43
11		t-C_4H_9Li	Pentane	120	(54)	23
12		*e*	Pentane	144	(49.5)	25
13		t-C_4H_9Li	Pentane	168	(43)	25
14	III[f]	t-C_4H_9Li	Pentane	70	VI (40.1)	24
15		t-C_4H_9Li	Pentane	41	(45.1[g])	35.8[g]
16		t-C_4H_9Li	Pentane	72	VI (46.2)	35
17		t-C_4H_9Li	Pentane	114	(30.9[h])	17.5
18	VII	t-C_4H_9Li	Pentane	120	VI (0)	80[i]
19		t-C_4H_9Li	Pentane	144	Trace[j]	78.5

[a] Unless stated otherwise, approximately a 10% excess of organolithium compound was used. [b] Yellow precipitate, presumably the metalated phosphine, forms during the reaction. [c] Yield of crude product. [d] No attempt was made to determine the yield of recovered starting phosphine. [e] Two moles of alkyllithium used per mole of phosphine. [f] See ref. 4. [g] After carbonation, the reaction mixture was treated with hydrogen peroxide to give phosphine oxides. [h] The crude acid obtained was subjected to distillation resulting in decomposition to di-*n*-hexylmethylphosphine oxide (18%) and di-*n*-hexylmethylphosphine sulfide (12.9%). [i] Isolated as tributylphosphine oxide. [j] Tentatively identified as (α-carboxy-*n*-butyl)di-*n*-butylphosphine sulfide.

In addition to the failure to isolate any isomers of IV–VI on work-up, the absence of significant amounts of metalated isomers in these reactions, *i.e.*, ring metalation in the phenylphosphines (I and II) and hexyl metalation in di-*n*-hexylmethylphosphine, is indicated by P^{31} n.m.r. spectral analysis. Thus, the crude acids obtained from carbonation and sulfurization give rise to only single signals, suggesting the preponderance of a single isomer.[5,6] See Table II for n.m.r. data.

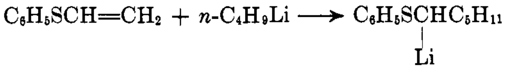
The high degree of selectivity exhibited by the methylphenylphosphines for methyl metalation is of considerable interest since it has been demonstrated[7] that methyldiphenylamine undergoes ring metalation. It is of additional interest to note that dimethyldodecylamine[8] is metalated only to the extent of 7.2% by *t*-butyllithium under conditions that give rise to essentially quantitative metalation of dimethyldodecylphosphine. This significant rate difference has been demonstrated by subjecting the metalation products resulting from the reaction of *t*-butyllithium with the phosphine and the amine in pentane over a 4-day period to deuteration and mass spectral analyses. The amine spectrum reveals 7.2% monodeuterium incorporation. The phosphine mass spectrum showed 21.8% dimethyldodecylphosphine-d_0, 54.9% -d_1, 20.4% -d_2, and 2.9% -d_3. A competitive metalation reaction, in which the molar ratios of dimethyldodecylphosphine, dimethyldodecylamine, and *t*-butyllithium were 1:1:1, and subsequent deuteration after 4 days at 25° resulted in 5% dimethyldodecylamine-d_1 and 33% dimethyldodecylphosphine-d_0, 51% -d_1, and 13% -d_2. We are currently investigating the reason for the multiple deuterium incorporation.

These apparent differences in the acidities of the aminomethyl and the phosphinomethyl hydrogens are contrary to that expected from a consideration of the electronegativities of nitrogen (3.0) and phosphorus (2.1). The selective methyl metalation of the methylphenylphosphines and the differences in rates of metalation of dimethyldodecylamine and dimethyldodecylphosphine can best be rationalized by invoking the concept of d-orbital resonance stabilization of the incipient α carbanion by trivalent phosphorus.[9]



This stabilization would, of course, lower the energy of activation for methyl metalation, and, consequently, increase the rate of this reaction relative to either ring metalation in the methylphenylphosphines, or methyl metalation in the amine.

Differences of this nature have been observed between various sulfur and oxygen compounds. Thus, it has been reported[10] that methyl phenyl sulfide is metalated on the methyl carbon atom, and not on the ring, as is anisole. Furthermore, *n*-butyllithium is reported[11] to add to the terminal carbon of phenyl vinyl sulfide, a reaction not shown by the analogous vinyl ether. The driving force for this Michael-type addition appears to be due, at least in part, to d-orbital stabilization of the carbanion by sulfur.[11]



$$C_6H_5SCH{=}CH_2 + n\text{-}C_4H_9Li \longrightarrow C_6H_5S\underset{\displaystyle Li}{\underset{|}{C}}HC_5H_{11}$$

In conjunction with the present work on the metalation of methylphosphines, which afforded only the

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[4] Isolated as the methyl ester. The yields of this ester are probably poor indications of the yield of metalated III, since considerable decomposition occurred during isolation.

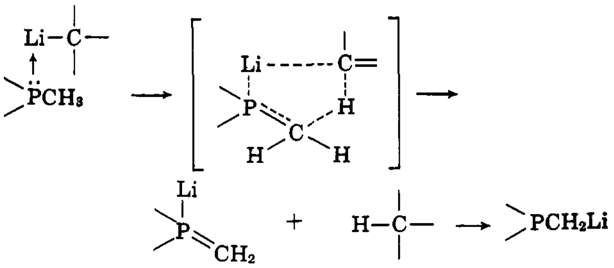
[5] The absence of more than one signal in the P^{31} n.m.r. spectra of the crude acids cannot be regarded as proof for the existence of only one isomer, since it is possible, although not probable, that the isomeric acids of each pair have identical chemical shifts.

[6] The chemical shifts of the acids (IV–VI) were found to be influenced by the presence of pivalic acid, arising from carbonation of *t*-butyllithium. Pure V, for example, has a chemical shift of −37.7 p.p.m., while a 2:1 ratio of V–pivalic acid has a chemical shift of −33.9 p.p.m.

(7) H. Gilman and S. M. Spatz, *J. Org. Chem.*, **17**, 860 (1952).

(8) R. A. Damico, unpublished results from this laboratory.

(9) The transition state for the metalation reaction could conceivably involve coordination of the lithium ion with the nonbonding electrons of phosphorus. This coordination would create a partial positive charge



on phosphorus, and, consequently, contract the d-orbitals resulting in a more favorable overlap with the incipient carbanion. For a discussion of the utilization of d-orbitals in chemical bonding, see D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(10) H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **62**, 987 (1940).

(11) W. E. Parham and R. F. Motter, *ibid.*, **81**, 2146 (1959).

TABLE II

PROTON AND PHOSPHORUS N.M.R. DATA

Phosphorus n.m.r.			Proton[a] n.m.r., τ (no. of protons)				
Phosphine	Solvent	Chemical shift,[b] p.p.m.	Solvent	Aromatic *H*	P-CH_2CO_2H	P-CH_3	-$CO_2H(CH_3)$
$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}CH_3$	$CHCl_3$	−35.2[c]	$CDCl_3$	2.32 m (9.3)		7.78 d (3) $J = 13$	
$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}CH_2CO_2H$	DMSO	−37.3	DMSO	2.35 m (10)	6.16 d (2) $J = 15$		
$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}CH_2CO_2H$			$CDCl_3$	2.35 m (10)	6.5 d (2) $J = 14.5$		−2.08 s (1)
$C_6H_5\overset{\overset{S}{\uparrow}}{P}(CH_3)_2$	$CHCl_3$	−32.5					
$C_6H_5(CH_3)\overset{\overset{S}{\uparrow}}{P}CH_2CO_2H$	Acetone	−37.7	$CDCl_3$[d]	2.2 m (5.1)	6.67 d (2) $J = 13.9$	7.8 d (3) $J = 13.2$	−0.1 (1.1)
			$CD_3\overset{\overset{O}{\|}}{C}CD_3$	2.15 m	6.65 m	7.8 d	−0.1
$(n\text{-}C_6H_{13})_2\overset{\overset{S}{\uparrow}}{P}CH_3$	$CHCl_3$	−42.7	$CDCl_3$			8.35 d $J = 12$	
$(n\text{-}C_6H_{13})_2\overset{\overset{O}{\uparrow}}{P}CH_3$	$CHCl_3$	−43.6	$CDCl_3$			8.54 d $J = 12$	
$(n\text{-}C_6H_{13})_2\overset{\overset{S}{\uparrow}}{P}CH_2CO_2CH_3$	$CHCl_3$	−47	$CDCl_3$		6.94 d (2) $J = 13.8$		6.25 s (3)
$(n\text{-}C_6H_{13})_2\overset{\overset{O}{\uparrow}}{P}CH_2CO_2CH_3$	$CHCl_3$	−45	$CDCl_3$		6.97 d (2) $J = 15$		6.24 s (3)

[a] Data recorded: chemical shift is in τ units (relative to tetramethylsilane), relative number of protons in parentheses, coupling constant *J* (c.p.s.), splitting pattern (s = singlet, d = doublet, m = multiplet). [b] Relative to 85% H_3PO_4. [c] L. Maier [*Helv. Chim. Acta*, **47**, 120 (1964)] reported −35.5 p.p.m. [d] Sample at 55°.

corresponding primary phosphinomethyllithium compounds, we have found that *n*-butyllithium adds readily to diphenylvinylphosphine to give the secondary organometallic compound, α-diphenylphosphinohexyllithium. This reaction will be discussed in greater detail in a future publication pertaining to the additions of nucleophiles to vinylphosphines.

In hydrocarbon solvents, *t*-butyllithium was found to be superior to *n*-butyllithium as a metalating agent for I. Thus, in pentane, I was converted to diphenylphosphinomethyllithium in *ca.* 20% yield during 40 hr. (Table I, 4), while, in contrast, I was inert to *n*-butyllithium during a 48-hr. (Table I, 3) reaction time.

The data obtained from this study also show qualitatively that the rate of metalation of I by *n*-butyllithium is considerably faster in diethyl ether than in pentane. Under identical reaction conditions, I is metalated to the extent of 21% by *n*-butyllithium in ether (Table I, 2), while, in pentane, I is inert (Table I, 3) to the organolithium compound. This solvent effect is in accord with the findings of others.[12]

Relative to the three methylphosphines studied, tributylphosphine (VII) was found to be essentially inert to *t*-butyllithium in pentane. Apparently, the substitution of an alkyl group for an α hydrogen atom raises the energy requirements for the formation of the phosphino carbanion to such an extent that the rate of metalation is negligible under the conditions employed. The formation of a single metalated phosphine, di-*n*-hexylphosphinomethyllithium, from the reaction of *t*-butyllithium with III, can be explained similarly.

Experimental

All reactions and manipulations involving phosphines and organolithium compounds were performed under an atmosphere of oxygen-free argon. The organolithium compounds used in this work were obtained from commercial sources. Gas chromatographic analyses were performed with a column composed of 10% Apiezon L on Fluoropak and with helium as the carrier gas. N.m.r. spectra were obtained on Varian Associates HR-60 (phosphorus) and A-60 (proton) spectrometers. The molecular weight determinations and deuterium incorporation analyses were made on an Atlas CH-4 mass spectrometer. The samples were introduced directly into the ion source (*ca.* 70°) to avoid thermal decomposition.

The metalation reactions were most conveniently carried out in the following way. To a 180-ml. cylindrical tube, which was connected to an argon source by means of rubber tubing fitted tightly over the tapered neck, there were introduced, by means of a calibrated syringe, the phosphine (0.02–0.05 mole), the organolithium compound (0.02–0.07 mole), and the solvent (20–50 ml.). The solution was then agitated by means of a magnetic stirrer for the desired length of time. Subsequently, the rubber tubing was clamped off between the metalation tube and the argon source and was connected to a three-necked flask containing a Dry Ice–solvent (ether or hydrocarbon) mixture. The three-necked flask was joined to an argon source and a gas bubbler (filled with mineral oil) by means of a three-way stopcock. A glass stopper, which functioned as a gas release value, was fitted *loosely* into the third neck of the flask. The mixture of organometallic compounds was then carbonated by inverting the tube (the flow was controlled by a pinch clamp)

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(12) G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 12.

and slowly releasing the contents into the carbonation vessel. The argon flow was turned on following the complete evolution of the carbon dioxide. Elemental sulfur was then introduced into the reaction mixture in three or four portions (exothermic reaction). After 0.5 hr. of stirring at room temperature, water was added; the organic layer was separated, dried over sodium sulfate, concentrated, and distilled under reduced pressure to give the recovered phosphine (as the corresponding sulfide). The aqueous layer was acidified with hydrochloric acid and extracted thoroughly with ether. The ether extracts were combined, dried, and concentrated. The residue consisted of a mixture of either valeric acid or pivalic acid (if considerable amounts of these acids are present, it is necessary to remove them by high-vacuum distillation so that IV and V can be purified by crystallization), and IV–VI. The acids, IV and V, were purified by crystallization from a benzene–acetone mixture and a benzene–hexane mixture, respectively: IV, m.p. 195–198°[13]; and V, m.p. 120–122°. VI was esterified with methanol and distilled: b.p. 177–185° (0.2–0.25 mm.).

The organophosphines, I–III, were prepared by the reaction of chlorodiphenylphosphine, dichlorophenylphosphine, or dichloromethylphosphine with the corresponding Grignard reagents: I, b.p. 125–128° (0.5 mm.) [lit.[13] b.p. 108–110° (0.15 mm.)]; II, b.p. 85° (15 mm.) [lit.[14] b.p. 83–84° (13.5 mm.)]; and III, b.p. 110–120° (0.01–0.02 mm.), n^{26}_{D} 1.4602. The dimethyldodecylphosphine, b.p. 107° (0.8 mm.), was prepared according to a described procedure.[15]

The organophosphine sulfides were prepared by the dropwise addition of the phosphines to a suspension of sulfur in benzene: methyldiphenylphosphine sulfide, b.p. 145° (0.015 mm.), n^{27}_{D} 1.6506 [lit.[13] b.p. 162–163° (0.4 mm.), n^{25}_{D} 1.6503]; dimethylphenylphosphine sulfide, m.p. 42.5–44.5° (lit.[16] m.p. 42°); and di-*n*-hexylmethylphosphine sulfide, b.p. 135–140° (0.02–0.03 mm.), n^{26}_{D} 1.4967.

Di-*n*-hexylmethylphosphine oxide (very hygroscopic) was prepared by the oxidation of the corresponding phosphine with a slight excess of 15% hydrogen peroxide in benzene: b.p. 115–120° (0.04 mm.) [lit.[17] b.p. 130–135° (0.2 mm.)], m.p. 43–45° (sealed capillary).

Preparation of (Carboxymethyl)diphenylphosphine Sulfide (VI).—To a solution of 4.6 g. (0.02 mole) of methyldiphenylphosphine sulfide in 20 ml. of ether 0.022 mole of *n*-butyllithium was added dropwise. After 0.5 hr. of stirring, the reaction mixture was carbonated by pouring over an ether–Dry Ice slurry. Following the disappearance of the excess Dry Ice, the mixture was thoroughly extracted with water. Acidification of the aqueous extracts resulted in the separation of 2.35 g. (42%) of IV, melting over the range 189–193°. Two crystallizations from a benzene–acetone mixture (4:1) afforded 0.97 g. of IV, m.p. 192–195° (lit.[13] m.p. 193–195°).

Preparation of (Carboxymethyl)methylphenylphosphine Sulfide (V).—The V was prepared in the same manner as that described for IV; 6.3 g. (0.037 mole) of dimethylphenylphosphine sulfide, 0.04 mole of *n*-butyllithium, and excess carbon dioxide gave 2.01 g. (25%) of V, m.p. 120–122°, after crystallization from a benzene–hexane mixture.

Anal. Calcd.: mol. wt., 214. Found: mol. wt. (mass spectrometric), 214.

Preparation of (Carbomethoxymethyl)di-*n*-hexylphosphine Sulfide (VI).—The acid obtained from 7.4 g. (0.03 mole) of di-*n*-hexylmethylphosphine sulfide, 0.035 mole of *n*-butyllithium, and excess carbon dioxide was esterified using methyl alcohol in the usual manner to give 3.6 g. (39%) of product, n^{26}_{D} 1.4943.

Anal. Calcd.: mol. wt., 306. Found: mol. wt. (mass spectrometric), 306.

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[14] J. Meisenheimer, J. Casper, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

[15] R. G. Laughlin and J. T. Yoke, French Patent 1,317,586 (March 13, 1962).

[16] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, **8**, 226 (1963).

[17] J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963).

Studies in the Benzosilacycloalkene Series. III. Reactions of (*o*-Chlorophenyl)alkyl Derivatives with Magnesium and Lithium

HENRY GILMAN AND OREN L. MARRS

The Chemical Laboratory, Iowa State University, Ames, Iowa

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Initiation difficulties were encountered in preparing Grignard reagents in tetrahydrofuran from aryl chlorides containing an *o*-alkyl group. Lithium reacted readily with these compounds, but with silicon-containing compounds cleavage reactions apparently occur. [3-(*o*-Chlorophenyl)propyl]triphenylsilane underwent a cleavage–cyclization reaction with molten sodium to give 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene.

Previous papers[1] from this laboratory described a method for the preparation of various silicon-substituted 2:3-benzo-1-silacycloalkenes by ring closure of (*o*-chlorophenyl)alkylsilanes with molten sodium in toluene. These compounds were subsequently converted into functional derivatives[2] which should serve as precursors to larger ring systems.

However, attempts to effect ring closure of dibenzyl-[2-(*o*-chlorophenyl)ethyl]- and dibenzyl-[3-(*o*-chlorophenyl)propyl]silane with molten sodium failed. Furthermore, when *o*-chlorobenzyldiphenylsilane was similarly treated, a 55.5% recovery of the starting material was realized. We then became interested in the ease of reaction of these *o*-chloro derivatives with not only sodium, but lithium and, particularly, magnesium in tetrahydrofuran. An intramolecular cyclization reaction of the Grignard reagent of (*o*-chlorophenyl)-alkylsilanes should prove useful for the preparation of Si-H-containing benzosilacycloalkenes.[3] Having on hand various other *o*-chlorophenylalkyl derivatives, their reactivity was investigated.

Tetrahydrofuran has been found to be a useful solvent for the preparation of Grignard reagents from aryl chlorides,[4] and Ramsden and co-workers[4b] were able to prepare a Grignard reagent from every aryl chloride tried (*o*-alkyl other than methyl- and ethylpentachlorobenzene were not reported), except 2-

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[1] (a) H. Gilman and O. L. Marrs, *Chem. Ind.* (London), 208 (1961); (b) H. Gilman and O. L. Marrs, *J. Org. Chem.*, **29**, 3175 (1964).

[2] H. Gilman and O. L. Marrs, *ibid.*, **30**, 325 (1965).

[3] See H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959), for a study of the reaction of Grignard reagents with silicon hydrides.

[4] (a) H. Normant, *Compt. rend.*, **239**, 1510 (1954); (b) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957); (c) H. E. Ramsden, U. S. Patent 2,838,508 (1958).