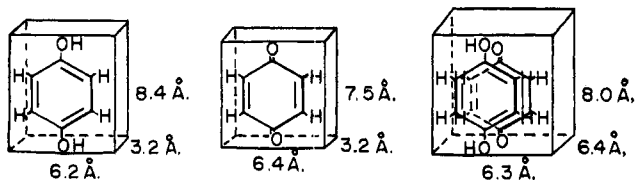kcal./mole). Extremely accurate calculations and a thorough knowledge of the specific interactions in each solvent would be required to make corrections within this narrow range.

Alternatively, an "average value" of ΔA can be determined by considering a series of *pure* single component solvents. In Figure 3, $\Delta F°$ values for quinhydrone in solution have been plotted against the surface tension of the corresponding solvents. The best line connecting these points, by the method of least squares, has been drawn. The slope of this line, -0.129×10^{10} cm.^{2}/mole, corresponds to a value of -21.4 Å.^{2} per molecule for ΔA. This value, which lies between those calculated for each aqueous solvent system, suggests that solvation effects may vary throughout the ranges of aqueous composition.

Figure 3. Standard free energy of quinhydrone formation in pure organic solvents *vs.* surface tension of the solvent; line fitted by the method of least squares.

Another value for ΔA may be estimated from the dimensions of "solvent cages" around molecular models of quinhydrone and its components assuming no specific solvent–solute interactions. For the purpose of these calculations, the solvent cages were estimated to be rectangular boxes with dimensions determined from van der Waals radii. The predicted loss in surface area in going from isolated components to the complex
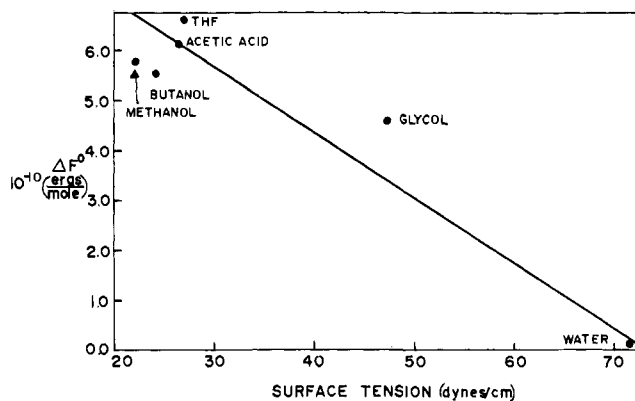
is 89 Å.^{2}. (Note that the volume is assumed not to change.)

Studies in Phosphinemethylene Chemistry. XI. The Reaction of Alkyllithium Reagents with Tetraphenylphosphonium Bromide[1]

Dietmar Seyferth,[2a] William B. Hughes, and James K. Heeren[2b]
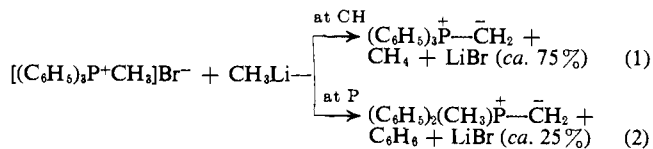
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received April 5, 1965

The reaction of methyllithium with tetraphenylphosphonium bromide in THF–ether medium has been studied in some detail. The principal attack occurs at phosphorus and results in formation of triphenylphosphinemethylene, benzene, and lithium bromide. A portion (<20%) of the attack by the lithium reagent involves abstraction of an ortho proton and leads to formation of 9-phenyl-9-phosphafluorene. Triphenylphosphineethylidene and triphenylphosphine-n-butylidene were prepared by the action of ethyllithium and n-butyllithium, respectively, on tetraphenylphosphonium bromide, again via RLi attack at phosphorus.

(1) (a) Part X: D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, in press. (b) Preliminary communication: D. Seyferth, J. K. Heeren, and W. B. Hughes, *ibid.*, 84, 1764 (1962). (c) Presented in part at the symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 12–15, 1963.
(2) (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) Fellow of the M. I. T. School for Advanced Study, 1961–1962.

In the previous paper of this series[1a] we showed that methyl-, ethyl-, and *n*-butyllithium attacked methyltriphenylphosphonium halides at phosphorus as well as at the methyl protons (eq. 1 and 2). This observa-

$$[(C_6H_5)_3P^+CH_3]Br^- + CH_3Li \longrightarrow \begin{cases} \overset{\text{at CH}}{\longrightarrow} (C_6H_5)_3P\text{---}\overset{+}{C}\overset{-}{H_2} + \\ CH_4 + LiBr \,(ca.\,75\%) \quad (1) \\ \overset{\text{at P}}{\longrightarrow} (C_6H_5)_2(CH_3)P\text{---}\overset{+}{C}\overset{-}{H_2} + \\ C_6H_6 + LiBr \,(ca.\,25\%) \quad (2) \end{cases}$$

tion led to the prediction that the reaction of an alkyllithium compound with tetraphenylphosphonium bromide, in which there are no aliphatic C–H bonds adjacent to phosphorus, should result in formation of a triphenylphosphinealkylidene *via* attack at phosphorus (eq. 3). It was the purpose of this study to test this prediction.

The action of methyllithium on tetraphenylphosphonium bromide had been investigated previously by

$$[(C_6H_5)_4P^+]Br^- \; RCH_2Li \longrightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HR + C_6H_6 + LiBr \tag{3}$$

Wittig and Geissler[3] in an attempt to prepare methyltetraphenylphosphorane, $(C_6H_5)_4PCH_3$. When these reactants in diethyl ether were shaken in a sealed Schlenk tube under nitrogen for 4 months and the resulting reaction mixture then was hydrolyzed, no products derivable from triphenylphosphinemethylene were isolated. Several phosphorus-containing compounds were, however, found: dimethyldiphenylphosphonium cation (as the iodide, 20% yield), 9-phenyl-9-phosphafluorene (I, 37%), and triphenylphosphine (2%). Only much later[4] was an explanation for the isolation of one of these, the dimethyldiphenylphosphonium cation, given in terms of possible formation of the $[(C_6H_5)_4P(CH_3)_2]^-$ anion, and, from this, of $(C_6H_5)_3P(CH_3)_2$. Hydrolysis of either of these was then assumed to give the observed $[(C_6H_5)_2P(CH_3)_2]^+$.

In our study we chose to carry out the reaction of methyllithium with tetraphenylphosphonium bromide in a solvent medium in which tetrahydrofuran (THF) was the major component (4:1 THF–diethyl ether). We were prompted to do this by our own experience and that of others which showed greatly enhanced reactivity of methyllithium in THF over methyllithium in ether. When a suspension of tetraphenylphosphonium bromide in THF was treated with 1 molar equiv. of ethereal methyllithium, the phosphonium salt dissolved, and a reddish brown solution was formed. Cyclohexanone was added and the resulting mixture was heated at reflux for 6 hr. Distillation of volatile materials and their analysis by gas–liquid chromatography (g.l.c.) showed that methylenecyclohexane had been produced in 70% yield and benzene in 95% yield. The formation of methylenecyclohexane provided clear indication for the formation of triphenylphosphinemethylene in at least 70% yield. This apparently is a general reaction, since similar results were obtained with other alkyllithium reagents. Thus ethyllithium gave ethylidenecyclohexane in 67% yield and benzene in 92% yield, and n-butyllithium gave n-butylidenecyclohexane in 40% yield and benzene in 93% yield.

In all of these reactions the yields of benzene were nearly quantitative. In terms of eq. 3, this would imply nearly quantitative formation of the respective phosphinealkylidene. However, the olefin yields in the subsequent Wittig reaction with cyclohexanone were surprisingly low in view of the high yields obtained when these phosphinealkylidenes were generated from the corresponding alkyltriphenylphosphonium halide.[1a] In addition, when triphenylphosphinemethylene was prepared by the $[(C_6H_5)_3P^+CH_3]Br^- + C_6H_5Li$ reaction, a yellow solution was obtained in both diethyl ether and THF medium. In the $[(C_6H_5)_4P^+]Br^- + CH_3Li$ reaction, as mentioned above, a dark, reddish brown solution was obtained. These observations suggested that other reactions, in addition to reaction 3, were occurring in the case of tetraphenylphosphonium bromide, and we were prompted to examine the $[(C_6H_5)_4P^+]Br^-$–RLi system in more detail.

(3) G. Wittig and G. Geissler, Ann., 580, 44 (1953).
(4) G. Wittig and W. Böll, Chem. Ber., 95, 2526 (1962), footnote 12.

Quenching of the red-brown solution obtained in the tetraphenylphosphonium bromide–methyllithium reaction with hydrogen bromide gas resulted in immediate discharge of the color. Work-up of the reaction mixture led to the isolation in 18% crude yield of 9-phenyl-9-phosphafluorene (I). Another such red-brown solu-
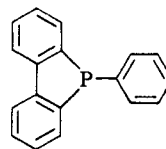
I

tion was quenched with cyclohexanone. The residue remaining after removal of volatile materials was worked up to give phosphine (I) in 9% yield as its methylphosphonium tetraphenylborate. Table I gives the yields of I or of a derivative of I from several such reactions.

Table I. Formation of 9-Phenyl-9-phosphafluorene in the Reaction of Methyllithium with Tetraphenylphosphonium Bromide

Quenching reagent	Product isolated	Yield, %
HBr(g)		18
HBr(g)		11
HBr(g)		10
		9

9-Phenyl-9-phosphafluorene was first reported as a decomposition product of pentaphenylphosphorane.[3] It was later obtained in 60% yield when the decomposition of pentaphenylphosphorane was carried out by shaking the latter in pyridine for 150 hr. at room temperature.[5] Its formation when the $[(C_6H_5)_4P^+]Br^- + CH_3Li$ reaction was carried out in ether already has been mentioned.
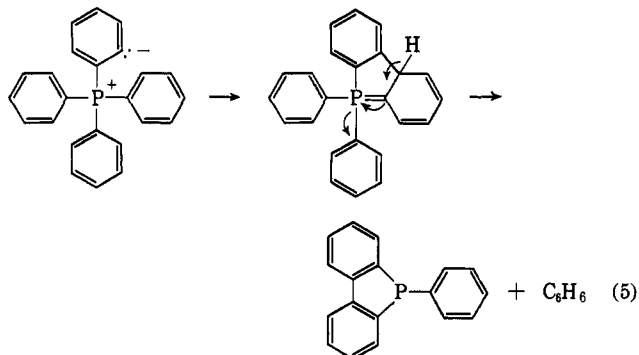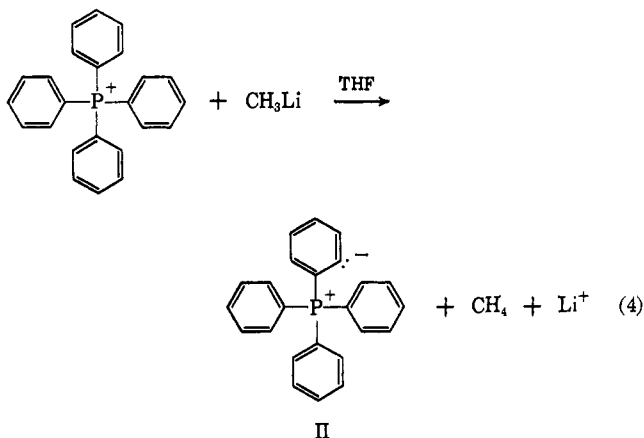
The formation of 9-phenyl-9-phosphafluorene in the methyllithium–tetraphenylphosphonium bromide reaction is best rationalized as occurring as a result of the abstraction of an *ortho* proton from the phosphonium salt by the organometallic base (eq. 4).

ortho metalation of triphenylphospine by phenylsodium with resulting formation of I in low yield has been reported,[3] and *ortho*-proton abstraction in the present case should be even more favorable because of the enhancement of the acidity of the *ortho* protons by

(5) G. A. Razuvaev and N. A. Osanova, Dokl. Akad. Nauk SSSR, 104, 552 (1955).

$$\text{(structure)} + \text{CH}_3\text{Li} \xrightarrow{\text{THF}}$$

$$\text{(structure II)} + \text{CH}_4 + \text{Li}^+ \quad (4)$$

II

$$\text{(structure)} \rightarrow \text{(structure)} \rightarrow$$

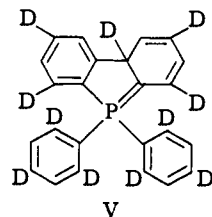$$\text{(structure)} + \text{C}_6\text{H}_6 \quad (5)$$

the positively charged phosphorus atom. A precedent for eq. 5 exists in the literature. Wittig and Benz[6] reported that 9-phenyl-9-phosphafluorene results when benzyne is generated (from the o-bromofluorobenzene + Mg reaction in THF) in the presence of triphenylphosphine. They postulated a mechanism in which the first step is reaction of benzyne with triphenylphosphine to give the betaine II; a cyclization followed by loss of benzene as shown in eq. 5 was postulated to follow. Strong evidence for the occurrence of II as an intermediate was provided by the isolation in low yield of an adduct of II with triphenylborane, III. Novel application of the triarylphosphine–benzyne reaction to preparative organophosphorus chemistry was made recently by Wittig and Matzura.[7]

$$\text{(structure III)}$$

III
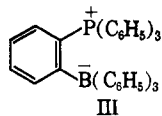
We have carried out experiments, the results of which are compatible with the mechanism [reactions 4 and 5] postulated for formation of 9-phenyl-9-phosphafluorene in the $[(\text{C}_6\text{H}_5)_4\text{P}^+]\text{Br}^- + \text{CH}_3\text{Li}$ reaction. A suspension of tetra(phenyl-2,4,6-d_3)phosphonium bromide in THF was treated with an ethereal solution of methyllithium. The resulting dark red solution was treated with excess of cyclohexanone. The postulated mechanism for forming 9-phenyl-9-phosphafluorene would involve the following steps: (1) attack by methyllithium at the ortho-deuterium atom of a phenyl group to give the betaine IV; (2) nucleophilic attack by the anionic center at the ortho position of an adjacent phenyl group to give the intermediate phosphorane V;

(6) G. Wittig and E. Benz, Chem. Ber., **92**, 1999 (1959).
(7) G. Wittig and H. Matzura, Angew. Chem., **76**, 187 (1964).

$$\text{(C}_6\text{H}_2\text{D}_3)_3\text{P}^+\text{—(structure)—D}$$

IV
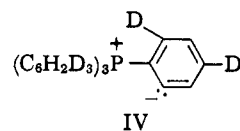
and (3) subsequent decomposition of V, with loss in

$$\text{(structure V)}$$

V

this case of tetradeuteriobenzene, to the heterocyclic phosphine VI. Thus the benzene formed would be

$$\text{(structure VI)}$$

VI
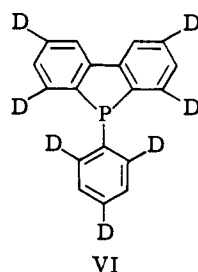
tetradeuterated and the 9-phenyl-9-phosphafluorene heptadeuterated. Gas chromatographic analysis of the volatile products of this reaction showed that benzene (95%) and methylenecyclohexane (70%) had been formed. The benzene was collected by g.l.c. and examined by mass spectrometry. Its mass spectrum indicated that it contained 12% $\text{C}_6\text{H}_2\text{D}_4$, 86% $\text{C}_6\text{H}_3\text{D}_3$, and 2% $\text{C}_6\text{H}_4\text{D}_2$.[8] The trideuteriobenzene arises from methyllithium attack at phosphorus with subsequent loss of $\text{C}_6\text{H}_3\text{D}_3$ (a trideuteriophenyl anion and a proton from the methyl group) and phosphinemethylene formation (eq. 3). Work-up of the solid reaction products resulted in isolation of 9-phenyl-9-phosphafluorene (as its methyl tetraphenylborate) in 9% yield. The 12% yield of tetradeuteriobenzene in this reaction is in good agreement with the yields of the heterocyclic phosphine in this system (this result and Table I).

This work thus has shown that in the $[(\text{C}_6\text{H}_5)_4\text{P}^+]$-$\text{Br}^-\text{–CH}_3\text{Li}$ system there are two competitive reactions: (a) attack at phosphorus leading to triphenylphosphinemethylene and benzene, and (b) attack at an ortho-hydrogen atom of a phenyl group, giving a betaine (II) which rearranges with loss of benzene to 9-phenyl-9-phosphafluorene. It is noteworthy that in systems where phosphinealkylidene formation is not possible, high yields of the latter heterocycle are obtained. For example, in the reaction of tetraphenylphosphonium bromide with lithium diethylamide, a 60% yield of I was obtained.[9] The reaction of t-butyltri-

(8) The mass spectrum of the bromobenzene-2,4,6-d_3 used in the synthesis of the deuterated phosphonium salt also showed the presence of 2% dideuterated material which would be retained in the subsequent synthesis reactions.
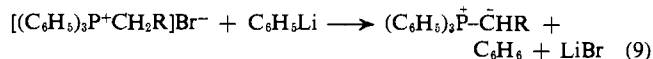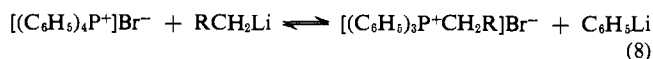(9) H. Hoffmann, Chem. Ber., **95**, 2563 (1962).

phenylphosphonium bromide with lithium piperidide also gave I as the major product.[10]

Two possible mechanisms may be envisioned for phosphinealkylidene formation involving attack at phosphorus: (a) formation of a pentacovalent phosphorus intermediate (eq. 6), followed by its decomposition to the observed products (eq. 7); and (b) an exchange reaction giving an alkyltriphenylphosphonium
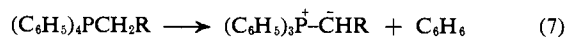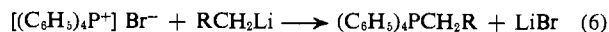
$$[(C_6H_5)_4P^+] \ Br^- + RCH_2Li \longrightarrow (C_6H_5)_4PCH_2R + LiBr \quad (6)$$

$$(C_6H_5)_4PCH_2R \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HR + C_6H_6 \quad (7)$$

ion (eq. 8), followed by α-hydrogen abstraction from the latter (eq. 9). Wittig and Rieber[11] have demonstrated

$$[(C_6H_5)_4P^+]Br^- + RCH_2Li \rightleftharpoons [(C_6H_5)_3P^+CH_2R]Br^- + C_6H_5Li \quad (8)$$

$$[(C_6H_5)_3P^+CH_2R]Br^- + C_6H_5Li \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HR + C_6H_6 + LiBr \quad (9)$$

the easy formation of pentaphenylphosphorane by the reaction of tetraphenylphosphonium bromide with phenyllithium in ether. More recently, Hellwinkel[12] has prepared the stable methyl- and n-butylbisbiphenylenephosphoranes (VIIa and VIIb) by treating bisbiphenylenephosphonium iodide with methyl- and n-butyllithium. These results show that a pentacovalent


VIIa, R = CH_3
b, R = n-C_4H_9
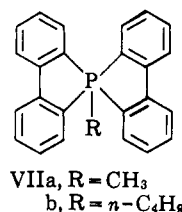
phosphorus species can result from the action of an organolithium reagent on a tetraarylphosphonium salt, although this P(V) product need not be stable in all cases. Stable pentavalent phosphorus compounds appear to be limited to cases where the attached groups are rather electronegative, the alkylbisbiphenylenephosphoranes representing a unique system where other factors appear to be important.

The thermal decomposition of VIIa was reported[12]
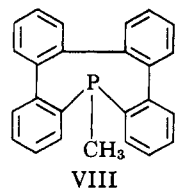
VIII

to give VIII. This observation, however, does not exclude from consideration an alkyltetraphenylphosphorane intermediate in our case, since an alternate mode of decomposition of alkyltetraarylphosphoranes to triarylphosphinealkylidenes and arene is possible. An analogous alkylbisbiphenylenearsorane has been prepared and its decomposition, summarized by eq. 10, was noted.[13] Formation of IX possibly resulted by
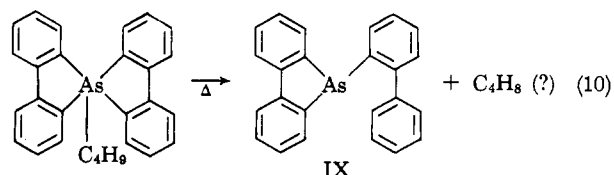

decomposition of an intermediate arsinebutylidene (X). In any case, removal of a phenyl anion from a P(V) intermediate appears to be relatively easily accomplished, as demonstrated by the reaction of pentaphenyl-

X
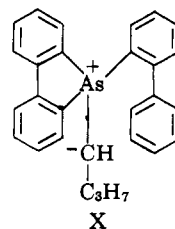
phosphorane with triphenylborane.[14] A concerted

$$(C_6H_5)_5P + (C_6H_5)_3B \xrightarrow{Et_2O} [(C_6H_5)_4P] [B(C_6H_5)_4]$$
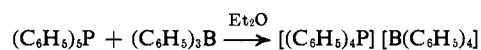
loss of benzene from a trigonal bipyramidal methyltetraphenylphosphorane[15] intermediate by a cyclic mechanism thus seems easily possible, especially in the polar solvent medium used.
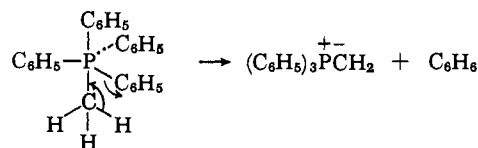
This evidence, admittedly only circumstantial in nature, leads us to favor mechanism a, above.

It will be noted that the main difference between mechanism a and mechanism b is that in the latter phenyllithium is involved as an intermediate, while in mechanism a it is not. Accordingly, some experiments designed to show the presence or absence of phenyllithium were performed. These, however, did not provide conclusive evidence for or against either mechanism because of the unassessable possibility of the intervention of anionic hexaorganophosphorus intermediates. In one such experiment tetraphenylphosphonium bromide was added to a tenfold excess of methyllithium in THF. If phenyllithium were involved in this reaction, then some portion of it should remain in solution after consumption of the phosphonium salt, owing to its unsuccessful competition in step 9 with the large excess of methyllithium. The deep red-brown solution obtained was quenched with trimethylchlorosilane, and g.l.c. analysis subsequently showed that trimethylphenylsilane has been formed in 31% yield. In another experiment, in which only a threefold excess of methyllithium was used, trimethylphenylsilane was obtained in 7.6% yield. These results indicate that phenyllithium was indeed present in the above reaction systems and at first sight appear to sup-

(10) D. Seyferth, M. A. Eisert, and J. K. Heeren, J. Organometal. Chem. (Amsterdam), 2, 101 (1964). In this system attack at a β-proton of the t-butyl group, resulting in β-elimination to triphenylphosphine and isobutylene, was observed as a minor reaction.
(11) G. Wittig and M. Rieber, Ann., 562, 187 (1949).
(12) D. Hellwinkel, Chem. Ber., 98, 576 (1965).
(13) D. Hellwinkel, Angew. Chem., 76, 382 (1964).

(14) G. Wittig and P. Raff, Ann., 573, 197 (1951).
(15) A three-dimensional X-ray study has shown the phenyl groups in pentaphenylphosphorane to be arranged about phosphorus in a trigonal bipyramidal configuration[16] and it seems reasonable that this configuration would be adopted by the proposed P(V) intermediate.
(16) P. J. Wheatley, J. Chem. Soc., 2206 (1964).

port the exchange–metalation mechanism (b). However, there is an alternate pathway for the generation of phenyllithium; initially a pentaorganophosphorus species may be formed, which then reacts with additional methyllithium to give a hexavalent, anionic phosphorus species. The latter could dissociate reversibly as shown

$$(C_6H_5)_4PCH_3 + CH_3Li \rightleftharpoons Li^+[(C_6H_5)_4P^-(CH_3)_2] \quad (11)$$
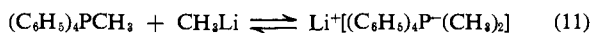
in eq. 11, or it could dissociate to give phenyllithium and dimethyltriphenylphosphorane.[17] Such complexing of

$$Li^+ [(C_6H_5)_4P^-(CH_3)_2] \rightleftharpoons (C_6H_5)_3P(CH_3)_2 + C_6H_5Li \quad (12)$$
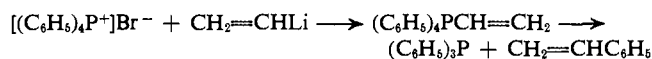
a P(V) species by excess lithium reagent, followed by dissociation in part as shown in eq. 12, could result in the buildup of phenyllithium in the reaction medium.

The formation of hexavalent, anionic species is known to occur in the chemistry of the group V elements. Lithium hexaphenylantimonate has been prepared by treating pentaphenylantimony with phenyllithium.[18] This compound dissociates reversibly at a slow rate and has been used as a reagent for the slow generation of phenyllithium.[19] Recently Hellwinkel[12] isolated a hexavalent, anionic organophosphorus compound, bisbiphenylenephosphonium trisbiphenylenephosphate. Thus, the trimethylphenylsilane isolated in the reactions described above resulted from the reaction of trimethylchlorosilane with phenyllithium, but the latter could have been formed either by reaction 8 or by reaction 12. The decrease in yield of trimethylphenylsilane in the 3:1 reaction would be expected in either case, since in mechanism b the phenyllithium formed then could compete more favorably in step 12, and, alternatively, there would be less complexing of a P(V) species because of the decrease in methyllithium concentration. Thus we cannot distinguish between a P(V) intermediate being involved and an exchange–metalation mechanism on the basis of the trimethylchlorosilane trapping experiments. However, we tend to favor the mechanism in which a P(V) intermediate is formed.

The results of this study are of interest to the general problem of quaternary phosphonium halide–organolithium reactions, and it seems appropriate at this point to place the present work in context with some other recent work in this area.

(1) When organolithium reagents react with tetraphenylphosphonium bromide, attack can occur at the phosphorus atom or at an *ortho* aromatic proton. (a) An aryllithium reagent reacts at phosphorus to form a stable pentaarylphosphorane.[11] (b) With alkyllithium reagents, attack at phosphorus (which ultimately results in a triphenylphosphinealkylidene, eq. 3) predominates over attack at *ortho* protons (eq. 4 and 5). (c) With vinylic lithium reagents there occurs attack at phosphorus, as shown below.[20] The P(V) intermediate,

$$[(C_6H_5)_4P^+]Br^- + CH_2{=}CHLi \longrightarrow (C_6H_5)_4PCH{=}CH_2 \longrightarrow$$
$$(C_6H_5)_3P + CH_2{=}CHC_6H_5$$

however, is not stable and decomposes as shown. (d)

With dialkylamidolithium compounds, attack at *ortho* C–H results in high yields of 9-phenyl-9-phosphafluorene *via* intermediate II.[9]

(2) When organolithium reagents react with an alkyltriphenylphosphonium halide of type $[(C_6H_5)_3P^+CH_2R]X^-$ or $[(C_6H_5)_3P^+CHRR']X^-$, attack can occur at the phosphorus atom or at an alkyl proton adjacent to the phosphorus atom.[1a] (a) When R = alkyl or when the phosphonium salt is of the type $[(C_6H_5)_3P^+CHRR']X^-$, attack at the α-proton is highly favored; only trace amounts of products resulting from attack at phosphorus are found. A triphenylphosphinealkylidene reagent is formed. (b) When R = H (*i.e.*, a methylphosphonium salt), about 25–30% of the attack occurs at phosphorus, the remainder at the methyl protons. That portion of the attack occurring at phosphorus is described by eq. 2. (c) When a dialkylamidolithium reagent reacts with an alkyltriphenylphosphonium halide, only attack at the α-protons of the alkyl group is observed, even in the case of methyltriphenylphosphonium bromide.

(3) When organolithium reagents react with *t*-butyltriphenylphosphonium bromide, attack can occur at phosphorus, at an *ortho* aromatic proton, or at a β-alkyl proton.[10] (a) In the case of methyllithium, about 50% of the reagent was consumed in attack at phosphorus; with ethyllithium, about 30%. No products due to attack at the *ortho* or the β-protons could be identified. (b) With lithium piperidide, 9-phenyl-9-phosphafluorene was isolated in 42% yield, and 16% of isobutylene also was obtained. The latter possibly, but not necessarily, resulted from attack at a *t*-butyl proton.

(4) When organolithium reagents react with vinyltriphenylphosphonium bromide, attack occurs principally at the β-carbon atom and at the α-proton of the vinyl group.[20]

$$[(C_6H_5)_3P^+CH{=}CH_2]Br^- + C_6H_5Li$$
$$\longrightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HCH_2C_6H_5 + LiBr$$
$$\longrightarrow C_6H_6 + LiBr + (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}{=}CH_2 \quad (?)$$

The above discussion shows that in quite similar reaction systems, the reaction of a phosphonium salt with an organolithium reagent may actually take quite different courses. The actual mode of interaction when several pathways are available is quite sensitive to slight changes in electronic and steric characteristics of the phosphonium salt and of the organolithium reagent. Our studies in this general area are continuing.

Experimental

General Comments. The general comments of part X[1a] apply here as well and need not be repeated. It should be emphasized that all experiments involving the preparation or use of organolithium reagents and phosphinealkylidenes were carried out under an atmosphere of prepurified nitrogen.

Organolithium reagents were prepared and analyzed as described in part X. Tetraphenylphosphonium bromide was prepared by the method of Horner and Hoffman.[21]

(17) See ref. 4. The intervention of anionic [R₄P]⁻ species in those cases where an organolithium reagent attacks at the phosphorus atom of a phosphonium salt was suggested by Professor G. Wittig, IUPAC Symposium on Organophosphorus Compounds, Heidelberg, May 20–22, 1964.

(18) G. Wittig and K. Clauss, *Ann.*, 577, 26 (1952).
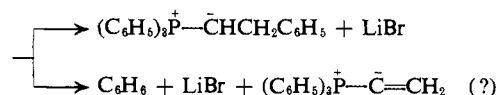
(19) G. Wittig and E. Benz, *Tetrahedron*, 10, 37 (1960).

(20) D. Seyferth, J. S. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, 86, 307 (1964).

(21) L. Horner and H. Hoffmann, *Chem. Ber.*, 91, 45 (1958).

Tetra(phenyl-2,4,6-d₃)phosphonium Bromide. This compound was synthesized by the sequence of reactions outlined below. This sequence of transforma-

tions preserved the isotopic purity of the final product. It was found to contain by falling drop deuterium analysis 59.2 atom % D; the calculated value is 60.0 atom % D. This corresponds to 98.7% deuteration. The *ortho–para* orientation of the deuterium atoms had been established previously in the aniline-N,N,2,4,6-d₅ hydrobromide-d[22] and in the bromobenzene-2,4,6-d₃,[23] and it is unlikely that any change in orientation would occur in any of the subsequent synthetic steps.
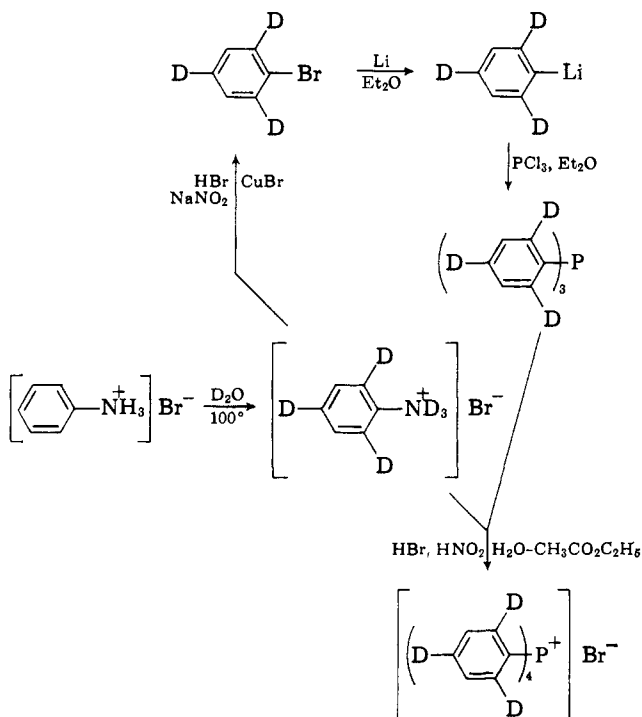
A. Aniline-N,N,2,4,6-d₅ hydrobromide-d was prepared as described by Best and Wilson.[22] A small sample of the salt after the fourth equilibration was dissolved in distilled water and 1 N NaOH added until the solution was basic. The solution then was extracted with a small amount of ether. Samples of the aniline were collected by g.l.c. (25% SE 30 on Chromosorb P, 155°, 20 p.s.i.) of the ether extracts. The infrared spectrum of this material (thin film) showed typical N–H absorption at 3425 and 3360 and strong C–D absorption at 2265 cm.$^{-1}$. The n.m.r. spectrum (CCl₄–CDCl₃) showed broad absorption centered at 3.38 (N–H) and sharp absorption at 7.18 p.p.m. (phenyl hydrogens).[24] The integrated area ratio was 1:0.9 (phenyl to nitrogen protons). The extent of deuteration of the aniline-N,N,2,4,6-d₅ hydrobromide-d was established by conversion to benzene-1,3,5-d₃ by a procedure known not to result in loss of deuterium.[22] The mass spectrum of the "benzene" isolated by g.l.c. showed it to be 97% benzene-1,3,5-d₃.

B. Bromobenzene-2,4,6-d₃ was prepared as described in the literature.[23] This product (b.p. 154–

(22) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

(23) R. I. Akawa, J. M. S. Carborough, and J. G. Burr, *J. Org. Chem.*, 24, 946 (1959).

(24) N.m.r. spectra were obtained with a Varian Associates A60 spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

157°) was obtained in 58% yield. Its mass spectrum indicated that it contained 98% bromobenzene-2,4,6-d₃ and 2% dideuterated material.

C. Tri(phenyl-2,4,6-d₃)phosphine. Lithium wire (0.4 g.-atom) was cut into small pieces and suspended in 100 ml. of ether in a 200-ml., three-necked flask fitted with condenser, pressure-equalizing dropping funnel, and magnetic stirrer. A solution of 0.197 mole of bromobenzene-2,4,6-d₃ in 25 ml. of ether was added dropwise. The reaction mixture refluxed spontaneously. After complete addition of the halide, the mixture was stirred for 1 hr. The solution was filtered under nitrogen through glass wool into a 300-ml. flask equipped as described above. The solution was cooled to 0° and 0.063 mole of PCl₃ in 15 ml. of ether was added slowly with stirring. The mixture then was brought to room temperature, refluxed for 2 hr., allowed to stand overnight, and hydrolyzed with 10% NaOH solution (with cooling). The organic layer was dried and concentrated. When chilled to −78°, this solution deposited a white solid. A second crop was obtained on further concentration and chilling. This procedure gave 10.81 g., m.p. 72.5–76°, and 3.18 g., m.p. 70–73°. a total yield of 82%. The two fractions were combined and recrystallized from reagent acetone to give 11.58 g. of tri(phenyl-2,4,6-d₃)phosphine, m.p. 75–78°. Triphenylphosphine itself has m.p. 79.5°. Sublimation of a small amount of this material at 78° (0.3 mm.) gave an analytical sample, m.p. 78.5–79.5°.

Anal. Calcd. for C₁₈H₆D₉P: C, 79.68; P, 11.42; weight of H₂O + D₂O (from a 6.367-mg. sample), 3.382 mg. Found: C, 79.90; P, 11.49; weight of H₂O + D₂O, 3.477 mg.

Direct deuterium analysis by the falling-drop method gave the following results: atom % D, calcd.: 60.0; found: 59.8.

D. Tetra(phenyl-2,4,6-d₃)phosphonium Bromide. The procedure of Horner and Hoffmann[21] was used in the reaction of benzene-2,4,6-d₃-diazonium bromide with tri(phenyl-2,4,6-d₃)phosphine. Two recrystallizations of the crude product from chloroform–ethyl acetate gave the phosphonium salt in 45% yield, m.p. 298–300°. The melting point of the undeuterated phosphonium salt prepared in this study was 296–299°. Another 1.09 g. of product, m.p. 295–299°, was obtained from the mother liquor (total yield 54%).

Anal. Calcd. for C₂₄H₈BrD₁₂P: C, 66.82; Br, 18.53; weight of H₂O + D₂O (from a 5.201-mg. sample), 2.321 mg. Found: C, 66.58; Br, 18.49; weight of H₂O + D₂O, 2.333 mg.

Direct deuterium analysis by the falling-drop method: atom % D, calcd.: 60.0; found: 59.2 (98.7% deuterated).

Reaction of Tetraphenylphosphonium Bromide with Methyllithium. A. Cyclohexanone Quench. In a 200-ml., three-necked flask equipped with reflux condenser and magnetic stirrer was placed 15 mmoles of tetraphenylphosphonium bromide in 40 ml. of THF. From a storage buret was added rapidly to the phosphonium salt 15.2 mmoles of methyllithium in diethyl ether (containing 1% nonorganometallic base). The reaction mixture became deep red-brown after several minutes. The reaction mixture was stirred at room temperature for 1 hr. and then was heated at reflux for

1 additional hr. The solution was cooled to room temperature and treated with 1.93 g. (19.6 mmoles) of cyclohexanone. The color of the reaction mixture lightened somewhat, but was not discharged. The mixture was heated at reflux for 6 hr. The volatile materials then were removed by reduced-pressure, trap-to-trap distillation (100° at 0.5 mm.). To the clear distillate was added 10.6 mmoles of n-heptane as a standard. G.l.c. analysis (25% SE 30 on Chromosorb P, 50°, 22 p.s.i.) showed the presence of benzene (95%) and methylenecyclohexane (70%). The products were identified by their g.l.c. retention times and comparison of their infrared spectra with those of authentic samples.

The pot residue after trap-to-trap distillation was treated with 50 ml. of water, which dissolved some of the solid. The mixture was extracted with benzene. The dry benzene extracts were saturated with methyl bromide, sealed, and stirred overnight. A white solid precipitated, which was filtered and washed with benzene and ether. This procedure was repeated until no more solid was precipitated by the methyl bromide treatment. The combined solids were dissolved in methanol and treated with methanolic sodium tetraphenylborate to precipitate a white solid which was filtered, washed, and dried to give 0.45 g., m.p. 172–173.5°. A mixture melting point with authentic 9-methyl-9-phenyl-9-phosphoniafluorene tetraphenylborate (m.p. 178–179°) was 173–175°. The infrared spectrum of the product in $CHCl_3$ was identical with that of an authentic sample. The crude yield was 7.8%, the recrystallized yield was 6.2%.

After methyl bromide treatment had removed all of the 9-methyl-9-phosphafluorene from the benzene extracts, the solvent was evaporated, leaving a brownish solid. Recrystallization from cyclohexane gave 1.83 g. of triphenylphosphine oxide, m.p. 150–153°; mixed melting point with authentic material (m.p. 154–156°) was 150–154°.

B. HBr Quench. Experiment (1). A slurry of 17 mmoles of tetraphenylphosphonium bromide in 75 ml. of THF was treated with 19 mmoles of methyllithium in ether. Hydrogen bromide gas was passed over the resulting red-brown solution until the color was discharged. The solvent was removed at reduced pressure and the residue treated with 500 ml. of water. Sodium hydroxide was added until the pH was ca. 6. The aqueous solution was extracted with ether. Evaporation of the dried ether extracts left an oily residue which when triturated with methanol gave white crystals (A), 0.80 g., m.p. 84–89°. On adding water to the mother liquor an additional white solid (B), 0.27 g., m.p. 69–71°, was obtained. Recrystallization of solid A from ethanol gave white plates, m.p. 91–93°. The mixture melting point with an authentic sample of 9-phenyl-9-phosphafluorene was 91–93° (lit.[3] m.p. 93–94°). The yield of crude product, based on the phosphonium salt, was 18%. The ultraviolet spectrum of the product ($CHCl_3$) showed λ_{max} at 242 mμ (ϵ 9500) and 274 mμ (ϵ 2700).

A sample of this heterocyclic phosphine from a separate but identical reaction was treated with excess of methyl iodide in ether. The resulting precipitate was filtered and dissolved in methanol. Addition of NaB-$(C_6H_5)_4$ gave 9-methyl-9-phenyl-9-phosphoniafluorene

tetraphenylborate, m.p. 177–178.5°, after two recrystallizations from methanol–acetone.

Anal. Calcd. for $C_{42}H_{36}BP$: C, 86.86; H, 6.10. Found: C, 86.35; H, 6.15.

A mixture melting point with authentic material (m.p. 178–179°) showed no depression.

Experiment (2). The same reaction was carried out on a 50-mmole scale. The resulting red-brown solution was treated with gaseous HBr as before. The volatile materials were removed by reduced-pressure, trap-to-trap distillation (to 65° at 0.3 mm.) of the reaction mixture. Analysis of the distillate by g.l.c. at 80° (toluene as standard) showed that benzene had been formed in 90% yield. When the distillation residue was treated with 500 ml. of water, a milky solution (pH about 6) resulted which contained a small amount of suspended solid. This mixture was extracted with ether. Evaporation of the ether extracts left an oily residue which could not be crystallized from methanol. Addition of bromine and then of aqueous NaOH by the method of Michaelis[25] to convert any phosphines to the phosphine oxide then was carried out. The solution was extracted with chloroform; evaporation of the extracts left a brownish solid which was recrystallized from cyclohexane to give 0.33 g. of material with m.p. 163–165° (solid C). From the mother liquor were obtained another 0.20 g. and 0.22 g., m.p. 162–165° and 158–165°, respectively. Another 0.61 g. of material, m.p. 153–160°, had been obtained from the original ether extracts prior to oxidation. Total yield was 10%. Recrystallization of solid C from benzene–cyclohexane gave material, m.p. 164–165.5° (lit.[10] m.p. 166–166.5°). Its ultraviolet spectrum (ethanol) was identical with that reported for 9-phenyl-9-phosphafluorene 9-oxide in the literature.[26]

Experiment (3). The same reaction was carried out on a 50-mmole scale and was quenched with gaseous hydrogen bromide. The reaction mixture was evaporated at reduced pressure. The residue was treated with 500 ml. of water and the pH was adjusted to 7. The aqueous solution which contained some solid was extracted with ether, and the ether extracts were treated with excess of methyl iodide. This resulted in precipitation of 4.0 g. of white solid, m.p. 186–189° (solid D). Recrystallization of D from chloroform–ethyl acetate gave white crystals, m.p. 190–192°; solid E, 2.94 g. The crude yield was 14.6%. Recrystallization of solid E from water gave slightly yellow crystals in two crops: 1.61 g., m.p. 204–205°, and 0.52 g., m.p. 202–204° (lit.[26] m.p. of 9-methyl-9-phenyl-9-phosphoniafluorene iodide is 204–205°). The total yield was 2.13 g. (11%). A sample of the iodide was converted to the tetraphenylborate which had the correct melting point and an undepressed mixture melting point.

Reaction of Tetra(phenyl-2,4,6-d_3)phosphonium Bromide with Methyllithium (Cyclohexanone Quench). Into a 200-ml., three-necked flask fitted with a magnetic stirrer and a reflux condenser was added 2.6 mmoles of the phosphonium salt, 25 ml. of THF, and 2.7 mmoles of methyllithium in 1.8 ml. of ether. The reactants were stirred together for 1 hr. at room temperature, then

(25) A. Michaelis and L. Gleichmann, *Chem. Ber.*, 15, 80 (1882).
(26) A. F. Bedford, D. M. Neinekey, I. T. Millar, and C. T. Mortimer, *J. Chem. Soc.*, 2932 (1962).

heated at reflux for 1 additional hr. The dark red-brown solution was cooled to room temperature and 3.5 mmoles of cyclohexanone was added. The mixture was heated at reflux for 6 hr. n-Heptane was added directly to the flask as an internal standard. Aliquots of the reaction mixture then were analyzed by g.l.c. (25% General Electric SE-30 on Chromosorb P, 50°, 22 p.s.i.). The analysis showed that benzene and methylenecyclohexane had been formed in yields of 93 and 71.5%, respectively. The "benzene" was identified by its g.l.c. retention time and mass spectrum (vide infra), the methylenecyclohexane by the infrared spectrum of a collected sample.

The volatile components were removed from the reaction flask by reduced-pressure, trap-to-trap distillation. Samples of the benzene were collected from the distillate by g.l.c. The mass spectrum was obtained on two separate samples, under the following operating conditions: sample pressure of 40 μ, filament current of 40 μa., voltage setting of 300; Consolidated Electrodynamics Corp. Model 21-130 mass spectrometer. The two samples showed that the benzene contained $C_6H_4D_2$ (3.6, 2.9%), $C_6H_3D_3$ (84.5, 84.7%), and C_6H_2-D_4 (11.9, 12.4%).

The residue which remained after the distillation was extracted with benzene. Treatment of the extracts with methyl bromide gave a white solid which was filtered and dissolved in methanol. Addition of NaB-$(C_6H_5)_4$ to the methanol solution gave 0.13 g. of white solid, m.p. 167–172° (crude yield 8.5%). Recrystallization from methanol–acetone raised the melting point to 173–176° (0.12 g.).

The Reaction of Tetraphenylphosphonium Bromide with Ethyllithium (Cyclohexanone Quench). The reaction of 11 mmoles of the phosphonium salt in 50 ml. of THF with 10 mmoles of ethyllithium in ether was carried out as described for the methyllithium reaction. The resulting red-brown reaction mixture was treated with 20 mmoles of cyclohexanone. A vigorous reaction ensued, and the mixture was heated at reflux for 17 hr. The work-up procedure was the same as used in the methyllithium reaction. The volatile components were analyzed by g.l.c. (Dow Corning 550 Silicone Fluid on Chromosorb P at 100° using excess cyclohexanone as standard). The distillate was found to contain benzene (92%) and ethylidenecyclohexane (67%); both were identified by comparison of their retention times and infrared spectra with those of authentic samples. For characterization of ethylidenecyclohexane, see ref. 1a.

The Reaction of Tetraphenylphosphonium Bromide

with n-Butyllithium (Cyclohexanone Quench). The reaction of 11 mmoles of the phosphonium salt in 50 ml. of THF with 10.1 mmoles of n-butyllithium in ether was performed as described above. The dark red-brown reaction mixture was treated with excess of cyclohexanone and heated at reflux for 18 hr. The reaction mixture was now a light rust color. Work-up as above gave a distillate which was shown by g.l.c. (toluene standard, 70°) to contain benzene (93% yield). G.l.c. analysis at 160° showed that n-butylidenecyclohexane (40% yield) was also present. Both products were identified by comparing their infrared spectra with those of authentic samples. For characterization of n-butylidenecyclohexane, see ref. 1a.

The Reaction of Tetraphenylphosphonium Bromide with Excess Methyllithium (Trimethylchlorosilane Quench). To 31.3 ml. of 1.60 N methyllithium in ether (50 mmoles) diluted with 50 ml. of THF was added, in one portion, 5 mmoles of tetraphenylphosphonium bromide. In ca. 10 min. the phosphonium salt had dissolved to give a dark red-brown solution. The reaction mixture was stirred for 90 min. and then was quenched with 54 mmoles of freshly distilled trimethylchlorosilane (Dow Corning Corp.) in 15 ml. of THF. The red color of the reaction mixture was not completely discharged. The volatile materials were distilled at reduced pressure (to 135° at 0.4 mm.) into a receiver cooled to −78°. Analysis of the distillate by g.l.c. showed that it contained trimethylphenylsilane (31%). A sample collected by preparative scale g.l.c. had $n^{25}D$ 1.4880 (lit.[27] $n^{25}D$ 1.4883). Its infrared spectrum was identical with that of an authentic sample of this compound prepared previously by M. A. Weiner. A separate experiment using different lots of methyllithium and phosphonium salt gave trimethylphenylsilane in 26% yield.

In another reaction the methyllithium–tetraphenylphosphonium bromide ratio was decreased to 3:1. In this case the trimethylphenylsilane yield was 7.6%. The same procedure was used in the reaction of 30 mmoles of ethyllithium with 11 mmoles of methyltriphenylphosphonium bromide. Analysis of the reaction mixture after the trimethylchlorosilane quench by g.l.c. showed no peak with the retention time of trimethylphenylsilane.

(27) A. Bygdén, Z. physik. Chem., 90, 243 (1915).