

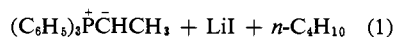
# Studies in Phosphinemethylene Chemistry. X. The Reaction of Organolithium Reagents with Alkyltriphenylphosphonium Halides. The Mechanism of Phosphinemethylene Formation<sup>1</sup>

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When organolithium reagents attack  $[(C_6H_5)_3P^+R]X^-$  ( $R = \text{ethyl or higher alkyl}$ ) it appears that simple proton abstraction by the organometallic base from the alkyl carbon atom adjacent to the phosphorus atom occurs. However, when  $R = \text{methyl}$ , ca. 25% of the organolithium reagent is consumed in a competing attack at the phosphorus atom. In the case of methyl-lithium, this attack at phosphorus was shown to lead to formation of  $(C_6H_5)_2(CH_3)\overset{+}{P}CH_2$ . In the case of ethyllithium, this attack at phosphorus gave  $(C_6H_5)_2(C_2H_5)\overset{+}{P}CH_2$ . Deuteration experiments showed that in the latter instance a mixture of this phosphinemethylene and of  $(C_6H_5)_2(CH_3)\overset{+}{P}CHCH_3$  was formed originally, but that subsequent transylidation reactions consumed the phosphineethylidene and formed the phosphine-methylene reagent.

The reaction of organometallic bases with alkyltriphenylphosphonium halides was reported first by Coffman and Marvel,<sup>3</sup> who prepared triphenylphosphonium salts  $[(C_6H_5)_3PCH_2CH_3]I + n-C_4H_9Li \longrightarrow$



phinemethylene, -ethylidene, -isopropylidene, and -diphenylmethylene by the action of *n*-butyllithium or tritylsodium on the appropriate phosphonium salt. These reactions were formulated as shown in eq. 1. The view that such reactions merely involved abstraction of the relatively acidic  $\alpha$ -proton of the alkyl group attached to phosphorus by the organometallic base was not questioned by subsequent investigators in the phosphinealkylidene area. The renewed and very active interest in phosphinealkylidenes as synthetic reagents, following the discovery of their application in a general olefin synthesis by Wittig and co-workers,<sup>4</sup> has resulted in many new and interesting reactions of these reagents with organic substrates.<sup>5</sup> Although a number of mechanistic studies have been carried out on phosphinemethylene reactions, none were devoted

(1) (a) Part IX: D. Seyferth, M. A. Eisert, and J. K. Heeren, *J. Organometal. Chem.*, **2**, 101 (1964). (b) Preliminary communication: D. Seyferth, J. K. Heeren, and W. B. Hughes, *J. Am. Chem. Soc.*, **84**, 1764 (1962). (c) Presented in part at the symposium "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.

(3) D. D. Coffman and C. S. Marvel, *J. Am. Chem. Soc.*, **51**, 3496 (1929).

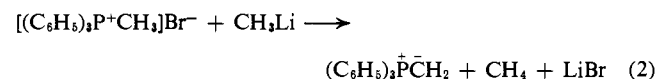
(4) (a) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953); (b) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

(5) For reviews see: (a) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959); (b) S. Trippett, "Advances in Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 83-102; (c) S. Trippett, *Quart. Rev.*, **17**, 406 (1963).

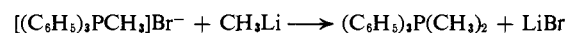
to the question of the mechanism of phosphinealkylidene generation by the organolithium route.

If one considers an alkyltriphenylphosphonium halide, e.g.,  $[(C_6H_5)_3P^+CH_2R]Br^-$ , it is readily apparent that there are two possible sites in the molecule where the highly nucleophilic organolithium reagent could attack: at the  $\alpha$ -hydrogen atoms of the alkyl group, whose acidity has been enhanced by the adjacent positive charge (as had been assumed by the previous workers in this field), but also at the positively charged phosphorus atom itself. It was the purpose of this research to elucidate in as much detail as possible the mechanism of the reaction of organolithium reagents with alkyltriphenylphosphonium salts and, more specifically, to determine whether or not attack at the phosphorus atom occurs.

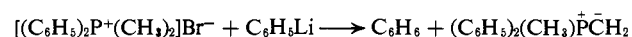
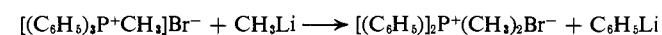
We considered first the reaction of methylithium in diethyl ether with methyltriphenylphosphonium bromide. If a simple proton abstraction were occurring in the generation of the phosphinemethylene reagent by this method, then eq. 2 would describe this reaction.



When this reaction was carried out, a yellow ether solution, characteristic of a phosphinemethylene reagent, was formed. One such reaction mixture was quenched with concentrated hydrobromic acid (reaction A), another with cyclohexanone, using the usual Wittig reaction procedure<sup>4b</sup> (reaction B). The organic layers from both reactions were examined by gas liquid-chromatography (g.l.c.), and it was found that both contained a significant amount of benzene (24-26% in reaction A, 21-25% in reaction B). Since this benzene could only derive from phenyl groups originally attached to phosphorus, this observation was taken to indicate that ca. 25% of the methylithium was being consumed by attack at the phosphorus atom. Two possible mechanisms were considered for such attack at phosphorus: (a) one in which benzene is lost intramolecularly from a P(V) intermediate



and (b) one in which the benzene is formed in a bimolecular metalation reaction



It is important to note that either mechanism predicts that  $(C_6H_5)_2(CH_3)\overset{+}{P}CH_2$  will be produced by attack

at phosphorus. Thus, assuming *ca.* 25% attack at phosphorus and 75% attack at the methyl protons in the  $[(C_6H_5)_3P^+CH_3]Br^-CH_3Li$  reaction, one is led to expect the formation of  $(C_6H_5)_2(CH_3)P^+CH_2^-$  and  $(C_6H_5)_3P^+CH_2^-$  in 1:3 molar ratio. The HBr quench would then give a 1:3 mixture of  $[(C_6H_5)_2P^+(CH_3)_2]Br^-$  and  $[(C_6H_5)_3P^+CH_3]Br^-$ , and the Wittig reaction a 1:3 mixture of methyldiphenylphosphine oxide and triphenylphosphine oxide. This important point was examined experimentally in several ways, quantitatively in the case of the reaction with hydrobromic acid, qualitatively in the case of the Wittig reaction. It was shown by quantitative infrared spectroscopy that a mixture of  $[(C_6H_5)_2P^+(CH_3)_2]Br^-$  and  $[(C_6H_5)_3P^+CH_3]Br^-$  had been formed in a ratio of approximately 1:3 when the reaction mixture was treated with HBr, and in the reaction with cyclohexanone the formation of methyldiphenylphosphine oxide was verified.

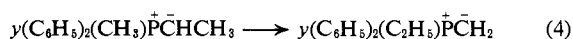
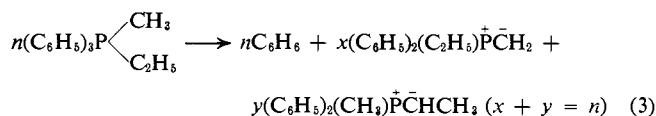
Further proof for partial attack at phosphorus in the  $[(C_6H_5)_3P^+CH_3]Br^-RLi$  system was given by a study of the action of *p*-deuteriophenyllithium on the phosphonium halide. If only methyl proton abstraction were occurring, then the benzene produced in this reaction would be 100% monodeuteriobenzene. Two such reaction mixtures were quenched with concentrated hydrobromic acid and cyclohexanone, respectively, and in both cases the benzene produced was isolated by g.l.c. Analysis of the latter (mass spectrometry and falling drop method) showed that in the HBr reaction the benzene was composed of 31%  $C_6H_6$  and 69%  $C_6H_5D$ , in the cyclohexanone reaction, of 28%  $C_6H_6$  and 72%  $C_6H_5D$ . Thus in the present case it appears that significant attack occurs also at the phosphorus atom, although the major reaction again is abstraction of a methyl group proton by the lithium reagent.

In this phase of the study no experimental evidence is available concerning the relative merits of mechanism a or b for the RLi attack at phosphorus. We favor the former mechanism, but will defer discussion of this point until the next paper of this series.

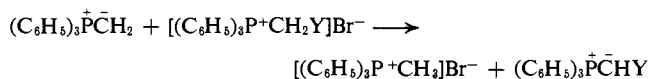
Having shown that RLi attacks at the phosphorus atom as well as the methyl protons of a methyltriphenylphosphonium halide, it became of interest to us to relate the relative importance of the two possible routes to phosphinealkylidene formation to structural factors in the phosphonium salt and in the organolithium reagent. Experiments in which other alkyl lithium reagents were allowed to react with methyltriphenylphosphonium bromide demonstrated that partial attack by RLi at phosphorus in this phosphonium halide appears to be general behavior. The extent of such attack does not appear to vary much for different primary alkyl lithium reagents. Thus, the per cent yields of benzene obtained in these reactions with ethyl- and *n*-butyllithium were 24 and 29%, respectively. In both cases the phosphinealkylidenes formed were characterized by their reactions with cyclohexanone; in both cases methylenecyclohexane was the sole olefinic product. The yield of the latter was high with all lithium reagents:  $CH_3Li$ , 82%;  $C_2H_5Li$ , 81%; and  $n-C_4H_9Li$ , 86%. In view of our belief that phosphine-methylene formation *via* RLi attack at phosphorus occurred through intramolecular loss of benzene from a

P(V) intermediate, these results were at first sight somewhat surprising. It might have been expected that such benzene loss from the ethyllithium-derived P(V) intermediate,  $(C_6H_5)_3P^+CH_3^-$ , would lead to a

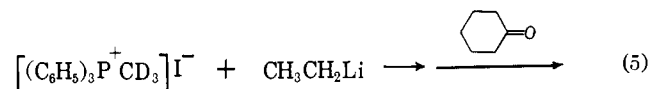
mixture of  $(C_6H_5)_2(C_2H_5)P^+CH_2^-$  and  $(C_6H_5)_2(CH_3)P^+CHCH_3^-$ , hence to a mixture of methylene- and ethylidene-cyclohexane on reaction with cyclohexanone. Such specificity, *i.e.*, the apparent formation of only  $(C_6H_5)_2(C_2H_5)P^+CH_2^-$  by ethyllithium attack at phosphorus, could result from (a) specific formation of this phosphinemethylene from the  $(C_6H_5)_3P(C_2H_5)CH_3$  intermediate (not considered to be very likely), or (b) a "transylidation" reaction involving  $(C_6H_5)_2(CH_3)P^+CHCH_3^-$  formed in the nonselective decomposition of this P(V) intermediate, *i.e.*



Although such intermolecular proton transfer between (or intramolecular proton transfer within) phosphine-methylene reagents has not been demonstrated previously, transylidations of the type







(where Y is a stabilizing substituent) have been reported by Bestmann.<sup>6</sup> The following reaction (5) was carried out in order to differentiate between the two possibilities a and b. The results of three separate runs are



given in Table I. That the much higher (35% total)

**Table I.** Reaction of  $[(C_6H_5)_3P^+CD_3]I^-$  with Ethyllithium (Cyclohexanone Quench)

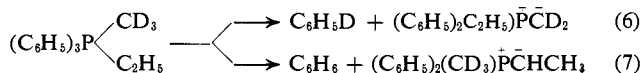
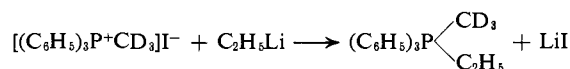
Run no.	Reaction time, hr.	Yield, % <sup>a</sup>			Isotopic composition, % <sup>a</sup>			
		$C_6H_5Y$		$C_6H_6$	$C_6H_5D$			
1	2.5	35	67	60	40	Not determined		
2	2.5	34	62	56	44	3	12	85
3	1.5	35.5	66	53	47	4	17	79

<sup>a</sup> Y = H or D.

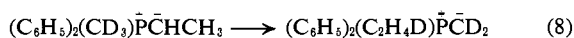
benzene yield (as compared to the  $[(C_6H_5)_3P^+CH_3]Br^-C_2H_5Li$  reaction) was not due to a change in the halide ion was shown by the fact that benzene in only 25% yield was obtained when ethyllithium was allowed to react with methyltriphenylphosphonium iodide under the same conditions. Several aspects of these last two experiments merit discussion.

(6) H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).

The results of reaction 5 demonstrate that case b mentioned above obtains. The fact that  $C_6H_6$  as well as  $C_6H_5D$  was obtained is explicable by the reaction scheme listed below (eq. 6 and 7) for that portion (35%) of the attack which occurs at phosphorus.



The fact that only methylenecyclohexane is obtained requires that the phosphineethylidene reagent formed in reaction 7 undergo inter- or intramolecular transylidation (eq. 8). The methylenecyclohexane formed,



however, consisted of 82%  $c-C_6H_{10}=CD_2$ , 14.5%  $c-C_6H_{10}=CHD$ , and 3.5%  $c-C_6H_{10}=CH_2$  (average of runs 2 and 3). This is not surprising, since such transylidations are equilibrium processes. The possi-

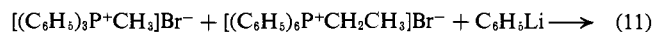
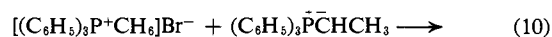
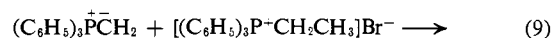
bility of proton abstraction by  $(C_6H_5)_2(C_2H_4D)\overset{+}{P}\overset{-}{C}D_2$  to give a  $CD_2H$ -substituted species, etc., will result in some scrambling of H and D, so that at the time of the cyclohexanone quench some  $\geq \overset{+}{P}\overset{-}{C}H_2$  and  $\geq \overset{+}{P}\overset{-}{C}HD$

reagents, as well as  $\geq \overset{+}{P}\overset{-}{C}D_2$ , will be present. The reproducibly different benzene yields when ethyllithium attacked  $[(C_6H_5)_3P^+CH_3]I^-$  (25%) and  $[(C_6H_5)_3P^+CD_3]I^-$  (35%) are best explained in terms of an isotope effect. Substitution of D for H results in a diminished rate of attack at the methyl group, hence attack at the phosphorus atom is more favorable. The magnitude of this effect,  $35/25 = 1.4$ , is in line with this reasoning. The high ratio of benzene to deuteriobenzene (1.3:1) obtained in the reactions of Table I suggests that an isotope effect is also operative in the decomposition of the P(V) intermediate. The yields of methylenecyclohexane in Table I (average = 65%) are low compared to those obtained in the case of the undeuterated salt (average = 77%). The increase in attack at phosphorus in the deuterated salt, reflected in the higher benzene yields, leads to a larger portion of alkylidene-triphenylphosphinemethylene. As phenyl groups are replaced by alkyl groups, the yield of olefins in the Wittig reaction is known to decrease. For example, trimethylphosphinemethylene with cyclohexanone in refluxing tetrahydrofuran gave no olefin at all, while in ethylene glycol dimethyl ether at 100° only a 15% yield of methylenecyclohexane was obtained.<sup>7</sup>

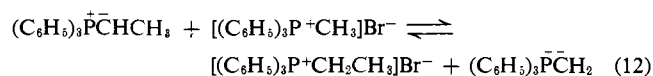
A relatively clear picture of the attack of an organolithium reagent ( $C_2H_5Li$  or higher alkyl lithium) on a methyltriphenylphosphonium halide thus has emerged. The major attack occurs at a methyl proton, but a significant amount of attack also occurs at the phosphorus atom. When attack at phosphorus occurs, benzene is lost, and a mixture of phosphinealkylidenes,  $(C_6H_5)_2(RCH_2)\overset{+}{P}\overset{-}{C}H_2$  and  $(C_6H_5)_2(CH_3)\overset{+}{P}\overset{-}{C}HR$ , is formed initially. Subsequent transylidations produce the thermodynamically more stable phosphinemethylene ( $\geq \overset{+}{P}\overset{-}{C}H_2$ ) reagent at the expense of the  $(C_6H_5)_2(CH_3)\overset{+}{P}\overset{-}{C}HR$  formed initially.

(7) S. Trippett and D. Walker, *J. Chem. Soc.*, 1266 (1961).

That triphenylphosphinemethylene is thermodynamically more stable than triphenylphosphineethylidene was demonstrated by carrying out reactions 9, 10, and 11. These reaction mixtures then were quenched



with cyclohexanone. If a true equilibrium situation (eq. 12) obtains, then these reactions should give at



equilibrium the same relative concentrations of phosphinealkylidenes, and after the Wittig reaction, the same relative yields of methylene- and ethylidenecyclohexane. These reactions were carried out in an identical manner, and the results in Table II were ob-

Table II. The Transylidation Reaction (12), Cyclohexanone Quench

Reaction	Yield, %		$c-C_6H_{10}=CHCH_3$
	$c-C_6H_{10}=CH_2$	$c-C_6H_{10}=CHCH_3$	$c-C_6H_{10}=CH_2$
9	85	3	0.04
10	86	5	0.06
11	85	5	0.06

tained. In the reactions of Table II the olefin yields are taken as a measure of the relative concentrations of the corresponding phosphinealkylidenes. Inherent in this is the assumption that both phosphinealkylidenes react at the same rate with cyclohexanone. That this assumption is reasonably valid in the methyl-ethyl phosphonium salt system was demonstrated by treating a 1:1 molar ratio of methyl- and ethyltriphenylphosphonium bromide with 2 equiv. of phenyllithium and then quenching the mixture of the two reagents with 1 molar equiv. of cyclohexanone. The yields of olefinic products were ethylidenecyclohexane, 41%, and methylenecyclohexane, 54%, a ratio of 0.71:1 (as compared with 0.05:1 in Table II).

The results of this transylidation study indicate that the triphenylphosphinealkylidene having the fewer alkyl groups on the  $\alpha$ -carbon atom is greatly favored. This is in agreement with the decrease in ability of an alkyl group (as compared with a hydrogen atom) to stabilize the charge-separated resonance form,  $(C_6H_5)_3\overset{+}{P}\overset{-}{C}RR'$ , because of its electron-donating (+I) inductive effect. Deuteration experiments showed that in reaction 11 the equilibrium mixture of the methyl- and ethylphosphonium salt-derived ylides did not result directly from the attack of phenyllithium on the phosphonium halides, but rather that subsequent transylidation reactions led to the observed equilibrium mixture. Thus treatment of an equimolar mixture of  $[(C_6H_5)_3P^+CH_2CH_3]I^-$  and  $[(C_6H_5)_3P^+CD_3]I^-$  with 1 molar equiv. of phenyllithium, followed by a Wittig reaction with cyclohexanone, gave benzene in 96% yield and methylenecyclohexane in 82% yield. Of significance was the fact that the benzene contained

66.5% C<sub>6</sub>H<sub>6</sub> and 33.5% C<sub>6</sub>H<sub>5</sub>D. These results indicate that initially a *ca.* 2:1 mixture of  $\text{>P}^+\text{CHCH}_3$  and  $\text{>PCD}_2$  species was formed. However, by the time of quenching, the *phosphinemethylene* reagent predominated, in agreement with the results of reaction 11. (This makes the reasonable assumption that benzene formation is irreversible.) The high ratio of benzene to deuterio-benzene obtained in this reaction suggested that an isotope effect was operative here. This was confirmed by a study of the action of 1 molar equiv. of phenyllithium on a 1:1 mixture of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>CH<sub>3</sub>]I<sup>-</sup> and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>CD<sub>3</sub>]I<sup>-</sup>, followed by quenching with cyclohexanone. Methylenecyclohexane was obtained in 84% yield, and the benzene (95% yield) contained 60% C<sub>6</sub>H<sub>6</sub> and 40% C<sub>6</sub>H<sub>5</sub>D. The methylenecyclohexane formed in these experiments was a mixture of *c*-C<sub>6</sub>H<sub>10</sub>=CH<sub>2</sub>, *c*-C<sub>6</sub>H<sub>10</sub>=CHD, and *c*-C<sub>6</sub>H<sub>10</sub>=CD<sub>2</sub>. Thus in the case of the [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>C<sub>2</sub>H<sub>5</sub>]I<sup>-</sup> + [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>CD<sub>3</sub>]I<sup>-</sup> + C<sub>6</sub>H<sub>5</sub>Li reaction, the "methylenecyclohexane" contained 5, 29, and 66% of these species, respectively. The n.m.r. spectrum of this particular mixture in carbon tetrachloride showed absorption at 1.57 (6 H) and 2.12 p.p.m. (4 H), the same chemical shifts as found in the n.m.r. spectrum of pure methylenecyclohexane. The vinylic proton absorption at 4.6 p.p.m., however, was greatly decreased in intensity, in agreement with extensive deuteration of the molecule in the positions specified.

In another series of experiments methyllithium was allowed to react with several different alkyltriphenylphosphonium halides. These reactions were carried out in the same manner as the series discussed above, with the phosphinealkylidene reagents being quenched with cyclohexanone or *n*-heptaldehyde. The results are summarized in Table III. In the case of the ethyl-

Table III. Action of Methyllithium on [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>R]Br<sup>-</sup>

R in [(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P <sup>+</sup> R]Br <sup>-</sup>	Yield, % of C <sub>6</sub> H <sub>6</sub>	Yield, % of olefin
CH <sub>3</sub>	21.5	80 <sup>a</sup>
CH <sub>3</sub> CH <sub>2</sub>	Trace	97 <sup>a,b</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Trace	92 <sup>a,b</sup>
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	0	87 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	0	52 <sup>a</sup>

<sup>a</sup> From Wittig reaction with cyclohexanone. <sup>b</sup> Traces of methylenecyclohexane also were found. <sup>c</sup> From Wittig reaction with *n*-heptaldehyde.

triphenylphosphonium bromide-methyllithium reaction attempts were made to induce more attack at phosphorus by the following variations in reaction conditions: (a) use of the more polar solvent, tetrahydrofuran; (b) carrying out the reaction at -15° instead of at room temperature. Also, the action of ethyllithium, a more reactive reagent than methyllithium, on the ethylphosphonium salt was examined. All of these reactions gave high yields of ethylidenecyclohexane (>90%) after treatment with cyclohexanone, but no increase in the amount of benzene formed was observed.

This series of reactions demonstrates that the other extreme in behavior, attack only at the  $\alpha$ -hydrogens of an alkyltriphenylphosphonium halide, is possible. The increase in steric hindrance at phosphorus when the

methyl group in [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>CH<sub>3</sub>]Br<sup>-</sup> is replaced by an ethyl group should only be slight. However, since the lithium reagent has two possible sites of attack available, the slight increase in steric hindrance at phosphorus may be just sufficient to make it energetically more favorable to abstract a proton. That such slight changes in structure can affect so markedly the reactions observed is, however, rather surprising.

In summary, one recognizes from the results of this work that the originally proposed mechanism for the attack of organolithium reagents on alkyltriphenylphosphonium halides is the one preferred in all cases. Simple proton abstraction from the  $\alpha$ -carbon atom of the alkyl group appears to be the sole mode of attack in the case of all alkyl groups larger than methyl, and even with methyltriphenylphosphonium bromide, such attack is favored over attack at phosphorus by a factor of 3. When attack does occur at phosphorus to any extent, a rather complicated sequence of reactions ensues which ultimately leads to a phosphinemethylene reagent. The finding that attack at phosphorus can lead to the formation of phosphinealkylidene reagents leads to the prediction that the action of alkyl lithium reagents on tetraphenylphosphonium bromide should result in formation of a triphenylphosphinealkylidene. This was found to be the case,<sup>1b</sup> and this aspect of our investigations will be discussed in the next paper of this series.

## Experimental

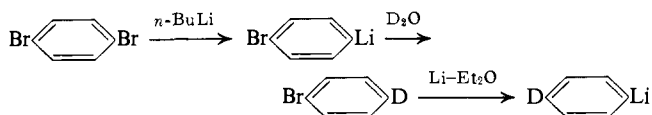
Elemental analyses were performed by Dr. S. M. Nagy (M.I.T.) or by the Galbraith Laboratories, Knoxville, Tenn. Combustion analyses for deuterium (falling drop method) were performed by J. Nemeth, Urbana, Ill. Infrared spectra were recorded using a Baird Model B or a Perkin-Elmer Infracord 337 infrared spectrophotometer. Intensities of absorptions are recorded as strong (s), medium (m), or weak (w). Proton resonance spectra were obtained with a Varian Associates A-60 high-resolution n.m.r. spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

Benzene and olefin yields were determined by quantitative gas-liquid chromatography (g.l.c.) using 8 ft.  $\times$  12 mm. (o.d.) glass columns packed with Dow Corning 550 or 710 silicone fluids or General Electric Co. SE-30 silicone grease on a support of Johns-Manville Chromosorb P or Chromosorb W. Thermal conductivity detectors were used with helium as the carrier gas.

Diethyl ether, pentane, and tetrahydrofuran were dried by distillation from LiAlH<sub>4</sub> or CaH<sub>2</sub>. All experiments involving the preparation or use of organolithium reagents and phosphinealkylidenes were carried out under an atmosphere of prepurified nitrogen.

*Preparation of Organolithium Reagents.* Methyl-, ethyl-, and phenyllithium were prepared from the corresponding bromide and lithium wire in diethyl ether. *n*-Butyllithium was prepared from either the bromide in ether or from the chloride in pentane. Ethyl- and *n*-butyllithium (in ether) were prepared at -10 to -30° and stored at -78°, but only for short times. All solutions of organolithium reagents were standardized by the double titration method using 1,2-dibromoethane in place of benzyl chloride.<sup>8</sup> *p*-

Deuteriophenyllithium was prepared by standard procedures.



**Preparation of Alkyltriphenylphosphonium Halides.** These were prepared by the reaction of the alkyl halide with triphenylphosphine (M & T Chemicals, Inc.), usually in benzene solution. Alkyltriphenylphosphonium bromides and iodides were in general conveniently purified by recrystallization from a mixture of chloroform-ethyl acetate or methanol-ethyl acetate. Well-formed crystals also were obtained by recrystallization from water. The addition of some drops of saturated aqueous KBr will induce crystallization. Phosphonium tetraphenylborates were recrystallized from boiling methanol or a methanol-nitromethane mixture. The phosphonium salts were dried at 110° *in vacuo* (0.5 mm.) over P<sub>2</sub>O<sub>5</sub> prior to their reaction with RLi.

**Dimethyldiphenylphosphonium bromide** was prepared as follows. A solution of 0.058 mole of methyldiphenylphosphine in 50 ml. of benzene was treated with excess of methyl bromide and stirred under nitrogen for several hours. The resulting white precipitate was filtered, washed with benzene and ether, and dried to give 14.3 g. (85%), m.p. 216–219°. Three recrystallizations from chloroform-ethyl acetate gave m.p. 217–218°. *Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>BrP: C, 56.94; H, 5.46. Found: C, 56.49; H, 5.59. Derivatives: iodide, m.p. 251–252° (*Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>I<sub>2</sub>P: C, 49.14; H, 4.71. Found: C, 49.08; H, 4.57); picrate, m.p. 117–118° (from ether-ethyl acetate) (*Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>3</sub>O<sub>7</sub>P: C, 54.18; H, 4.09. Found: C, 54.05; H, 3.65).

**Ethylmethyldiphenylphosphonium bromide** was prepared similarly by reaction of methyldiphenylphosphine with ethyl bromide, m.p. 170–171° (from chloroform-ethyl acetate) (*Anal.* Calcd. for C<sub>15</sub>H<sub>18</sub>BrP: C, 58.28; H, 5.87. Found: C, 58.02; H, 5.80; n.m.r. (30% in CDCl<sub>3</sub>): two triplets (3 H) at 1.13 and 1.47, a doublet (3 H) at 2.92 (*J*<sub>PC<sub>H</sub></sub> = 13.8 c.p.s.), a sextet (2 H) at 3.37 (*J* = 7.5 c.p.s.), and complex phenyl absorption at 7.83 p.p.m. (10 H). The tetraphenylborate had m.p. 144.5–145.5° (from methanol) (*Anal.* Calcd. for C<sub>39</sub>H<sub>38</sub>BP: C, 85.40; H, 6.98. Found: C, 85.73; H, 7.17); iodide, m.p. 183–184° (*Anal.* Calcd. for C<sub>15</sub>H<sub>18</sub>I<sub>2</sub>P: C, 50.58; H, 5.09. Found: C, 50.69; H, 4.99).

**Trideuteriomethyltriphenylphosphonium Iodide.** Fully deuterated methyl iodide was prepared by the method of Cotton, *et al.*<sup>9</sup> A solution of 0.1 mole of CD<sub>3</sub>I and 0.1 mole of triphenylphosphine in 50 ml. of benzene was stirred under nitrogen for 2 hr. using a Dry Ice condenser. The solid precipitate was filtered, washed with benzene, and dried to give 36 g. (90%), m.p. 185–186° (lit.<sup>4a</sup> m.p. for [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>-CH<sub>3</sub>]<sup>-</sup> 184–186°). *Anal.* (deuterium, by the falling drop method) Calcd. for C<sub>19</sub>H<sub>15</sub>D<sub>3</sub>IP: atom %

excess deuterium, 16.67. Found: atom % excess deuterium, 16.50 (99% deuterated). A second preparation was carried out in the same manner, giving material with m.p. 185–187°. *Anal.* Found: atom % excess deuterium, 16.60.

**The Reaction of Methylithium with Methyltriphenylphosphonium Bromide.** **A. Cyclohexanone Quench.** In a 300-ml., three-necked flask equipped with reflux condenser and magnetic stirrer and maintained under 1 atm. of nitrogen was placed 11.4 mmoles of methyltriphenylphosphonium bromide and 50 ml. of ether. To this mixture was added rapidly 7.95 ml. of 1.26 *N* (10 mmoles) of methylithium in ether. The reaction mixture was stirred for 2.5 hr., after which the yellow solution was quenched with 20 mmoles of cyclohexanone and heated under reflux for 15 hr. The volatile products were removed by reduced pressure trap-to-trap distillation. The distillate was analyzed by g.l.c. at 100° using excess cyclohexanone as the standard. In this method the millimoles of cyclohexanone in the distillate was determined by quantitative precipitation<sup>10</sup> as the 2,4-dinitrophenylhydrazone. The analysis indicated that 2.1 mmoles (21%) of benzene and 8.0 mmoles (80%) of methylenecyclohexane had been formed. The products were isolated and identified by means of their infrared spectra. Methylenecyclohexane was fully characterized (*Anal.* Calcd. for C<sub>7</sub>H<sub>12</sub>: C, 87.42; H, 12.58. Found: C, 87.73; H, 12.55); n.m.r. (CCl<sub>4</sub> solution): absorptions at 1.53 (6 H), 2.08 (4 H), and vinyl proton absorption at 4.52 p.p.m. (2 H); the Varian Associates NMR Spectra Catalogue (spectrum No. 180) gives absorptions at 1.5, 2.1, and 4.55 p.p.m.; the infrared spectrum (pure liquid): 3060(m), 2880(s), 2640(w), 1776(m), 1672(w), 1644(s), 1440(s), 1392(m), 1338(m), 1316(w), 1274(w), 1140(m), 1100(w), 1022(m), 984(m), 880(s), 852(s), and 756(m) cm.<sup>-1</sup>.

A separate reaction mixture was worked up for phosphine oxides in the following manner. Solvent and volatile products were removed at reduced pressure. The solid residue was hydrolyzed and extracted with hot benzene. After the extracts had been dried, the benzene was removed. This left an off-white, crystalline solid, 4.67 g., m.p. 124–145°. The infrared spectrum of methyldiphenylphosphine oxide in CHCl<sub>3</sub> in the fingerprint region shows a very strong band at 888, with a somewhat weaker associated band at 877 and a medium band at 1300 cm.<sup>-1</sup>. All three of these bands are absent in the spectrum of triphenylphosphine oxide in chloroform solution. However, triphenylphosphine oxide does exhibit a very strong band at 545 cm.<sup>-1</sup> which is absent in the spectrum of methyldiphenylphosphine oxide. An authentic mixture of both phosphine oxides exhibits all four bands. The phosphine oxide residue from the above reaction had an infrared spectrum identical with that of the authentic mixture and in particular showed the three bands characteristic of methyldiphenylphosphine oxide mentioned above.

The reaction of methyltriphenylphosphonium bromide with methylithium followed by treatment with cyclohexanone was carried out several times, benzene being obtained in yields of 21, 18, 19, 26, 23, and 22%

(8) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

(9) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

(10) H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart, *Anal. Chem.*, **11**, 1021 (1939).

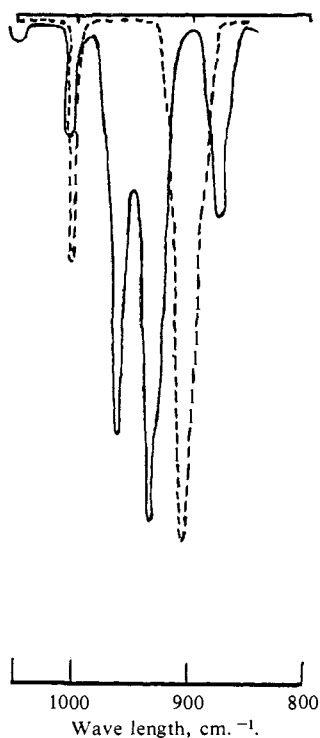


Figure 1. Infrared spectra (in  $\text{CHCl}_3$ ) of  $[(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_3]\text{Br}^-$  and of  $[(\text{C}_6\text{H}_5)_2\text{P}^+(\text{CH}_3)_2]\text{Br}^-$  in the  $1100\text{--}800\text{-cm.}^{-1}$  region: —,  $[(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_3]\text{Br}^-$ ; ---,  $[(\text{C}_6\text{H}_5)_2\text{P}^+(\text{CH}_3)_2]\text{Br}^-$ .

and methylenecyclohexane in yields of 80, 77, 82, 80, 82, and 74%, respectively.

In another experiment in which the Wittig reagents present were quenched with benzophenone, crystallization of the phosphine oxides and sublimation gave a small amount of methyldiphenylphosphine oxide, whose melting point ( $110\text{--}111^\circ$ ), mixture melting point, and infrared spectrum established its identity.

**B. HBr Quench.** The reaction of methyl lithium (10 mmoles) with methyltriphenylphosphonium bromide (11 mmoles) in ether was carried out as described above. The resulting yellow solution was quenched after 2.5 hr. with 5.0 ml. of 48% hydrobromic acid. The ether layer was separated and washed once with 25 ml. of water and dried. After a trap-to-trap distillation *in vacuo* the volatile products were analyzed by g.l.c. at  $88^\circ$  using toluene as the internal standard. The distillate was found to contain 2.4 mmoles (24%) of benzene, which was identified by means of its g.l.c. retention time and its infrared spectrum. The aqueous layer was saturated with KBr and extracted with chloroform. Crystallization of the regenerated phosphonium salts was induced by adding ethyl acetate and evaporating the mixture. The first crop, 2.95 g., m.p.  $226\text{--}229^\circ$ , was essentially pure methyltriphenylphosphonium bromide. The second crop, 0.405 g., had m.p.  $172\text{--}180^\circ$ . Total weight recovery was 84%. A duplicate experiment gave benzene in 25% yield and two crops of recovered phosphonium salts: I, 2.77 g., m.p.  $228\text{--}230^\circ$ ; II, 0.48 g., m.p.  $170\text{--}180^\circ$ ; total weight recovery 81%.

The recovered phosphonium salts of melting range  $170\text{--}180^\circ$  from both experiments were combined and treated with lithium aluminum hydride by the method of Gough and Trippett.<sup>11</sup> The resulting mixture of pos-

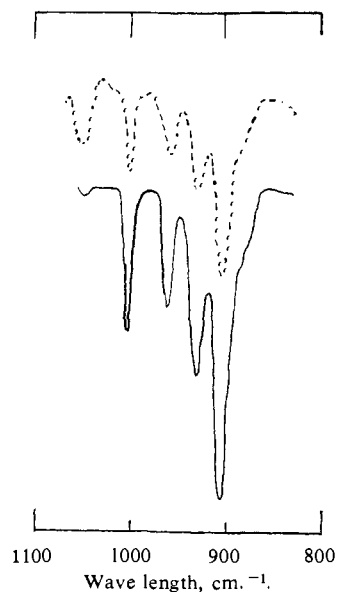


Figure 2. Infrared spectra of  $[(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_3]\text{Br}^- + [(\text{C}_6\text{H}_5)_2\text{P}^+(\text{CH}_3)_2]\text{Br}^-$  mixtures in the  $1100\text{--}800\text{-cm.}^{-1}$  region: ---, III-60-R; —, authentic mixture of  $[(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_3]\text{Br}^-$  and  $[(\text{C}_6\text{H}_5)_2\text{P}^+(\text{CH}_3)_2]\text{Br}^-$ .

phines was analyzed by g.l.c. (SE 30 silicone grease at  $240^\circ$ ), and it was shown that methyldiphenyl- and dimethylphenylphosphine were present in a mole ratio of 1:9 (comparison of g.l.c. retention times and infrared spectra). A sample of dimethylphenylphosphine was collected using a Dow-Corning 550 silicone oil column, the active sites of which had been saturated with *N,N*-dimethylaniline. The phosphine was treated with excess of methyl iodide. The resulting trimethylphenylphosphonium iodide, m.p.  $234\text{--}235^\circ$  (from MeOH-EtOAc), was identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample prepared by the reaction of phenyldichlorophosphine with methyl lithium, followed by treatment with methyl iodide.

In other experiments the phosphonium salts obtained in the HBr quench were analyzed by infrared spectrometric techniques. The phosphinemethylene reagents formed by reaction of 25 mmoles each of methyl lithium and methyltriphenylphosphonium bromide in 75 ml. of ether were quenched with anhydrous, gaseous hydrogen bromide. The infrared spectrum of the product phosphonium salts (sample III-60-R), along with the spectra of several authentic  $[(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_3]\text{Br}^- + [(\text{C}_6\text{H}_5)_2\text{P}^+(\text{CH}_3)_2]\text{Br}^-$  mixtures (samples III-60-A, B, and C) were taken in the  $800\text{--}1100\text{-cm.}^{-1}$  region (in which these halides show appreciable differences (*cf.* Figure 1)).<sup>12</sup> Figure 2 shows the spectra of the product phosphonium salt and of an authentic mixture of the two phosphonium salts under consideration in this region. The results are summarized in Table IV, where *A* is the absorbance measured from the infrared spectrum,  $\lambda$  is the molar extinction coefficient, and *C* is the molar concentration.<sup>13</sup> The

(11) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 4263 (1961).

(12) All spectra were obtained on 4–5 wt. % chloroform solutions on a Perkin-Elmer Model 337 Infracord using 0.1-mm. sodium chloride cells.

(13) Since all samples contained the same volume of solvent (250  $\mu\text{l.}$ ), the molar concentration is directly proportional to the number of moles, and this figure alone has been used.

**Table IV.** Analysis of Mixtures of  $[(C_6H_5)_3P^+CH_3]Br^-$  and  $[(C_6H_5)_2P^+(CH_3)_2]Br^-$  by Infrared Spectroscopy

Sample no.	$[(C_6H_5)_3P^+CH_3]Br^-$ mmoles $\times 10^{-5}$	$[(C_6H_5)_2P^+(CH_3)_2]Br^-$ mmoles $\times 10^{-5}$	$C_1/C_2$	$A_1$	$A_2$	$\lambda_1$	$\lambda_2$	$A_1/A_2$	$\lambda_1/\lambda_2$
III-60-A	2.38	1.09	2.18	0.257	0.094	108	862	2.84	1.25
III-60-B	1.88	1.56	1.20	0.178	0.127	95	814	1.40	1.17
III-60-C	2.24	0.815	2.75	0.241	0.071	107	870	3.40	1.23
III-60-R (sample 1)				0.166	0.045			3.70	
(sample 2)				0.182	0.046			3.96	
III-61-A <sup>a</sup>	2.72	1.05	2.59	0.235	0.075	864	715	3.13	1.21
III-61-B <sup>a</sup>	3.11	0.88	3.54	0.269	0.057	865	648	4.73	1.33
III-61-C <sup>a</sup>	2.30	1.59	1.44	0.171	0.111	744	698	1.54	1.07
III-61-R <sup>a</sup> (sample 1)				0.155	0.058			2.68	
(sample 2)				0.158	0.056			2.82	
(sample 3)				0.144	0.047			3.06	

<sup>a</sup> Duplicate runs.

subscripts 1 and 2 refer to the methyltriphenyl- and the dimethyldiphenylphosphonium salts, respectively. The absorption at  $905\text{ cm}^{-1}$  ( $A_1$ ) is present only in the spectrum of the methyltriphenylphosphonium salt, while that at  $960\text{ cm}^{-1}$  ( $A_2$ ) is present only in the spectrum of the dimethyldiphenylphosphonium salt (cf. Figure 1). The data obtained in a duplicate experiment are summarized in Table IV also.

From the authentic mixtures of phosphonium salts a value for the ratio of the molar extinction coefficients ( $\lambda_1/\lambda_2$ ) can be obtained by application of Beer's law:  $A_1/A_2 = \lambda_1/\lambda_2 \times C_1/C_2$ . The data from Table IV give an over-all average value of  $\lambda_1/\lambda_2 = 1.20$ . Using this value and the experimentally determined absorbancies, the mole ratio ( $C_1/C_2$ ) of methyltriphenyl- and dimethyldiphenylphosphonium bromide in the reaction residues was calculated. The results are given in Table V for all runs, together with the benzene yields as determined by g.l.c.

**Table V.** Analysis of Phosphonium Salts from the Reaction

Reaction	$C_6H_6$ , %	Calcd. ratio <sup>a</sup>	$[(C_6H_5)_3P^+CH_3]Br^- + CH_3Li \xrightarrow{HB} [(C_6H_5)_2P^+(CH_3)_2]Br^-$	
			Infrared ratio	mole % of $[(C_6H_5)_2P^+(CH_3)_2]Br^-$
III-60	23	3.4	3.08	24 (av.)
III-61	27	2.7	3.28	29 (av.)
			2.21	
			2.33	
			2.53	

<sup>a</sup>  $[(C_6H_5)_3P^+CH_3]Br^- / [(C_6H_5)_2P^+(CH_3)_2]Br^-$ . Calculation based on assumption of complete reaction and that the amount of  $C_6H_6$  formed is the same as the amount of the  $[(C_6H_5)_2P^+(CH_3)_2]Br^-$  formed.

**Wittig Reactions.** All other Wittig reactions mentioned in the Discussion were carried out essentially as described above for the  $[(C_6H_5)_3P^+CH_3]Br^- + CH_3Li$ , cyclohexanone quench procedure, and details may be found in the Ph.D. Thesis of W. B. H.<sup>14</sup>

The olefins, other than methylenecyclohexane, produced in these reactions were characterized as follows.

(14) W. B. Hughes, Ph.D. Thesis, Massachusetts Institute of Technology, Jan. 1965.

**Ethylidenecyclohexane** (Anal. Calcd. for  $C_8H_{14}$ : C, 87.19; H, 12.81. Found: C, 87.17; H, 12.75) n.m.r. ( $CCl_4$ ) showed a quartet at 5.06 ( $J = 7$  c.p.s., 1 H, vinyl proton), broad absorptions centered at 2.07 and 1.55 p.p.m. (13 H); infrared spectrum (pure liquid): 2940(s), 2860(s), 1675(m), 1450(s), 1380(m), 1350(m), 1310(w), 1270(w), 1235(m), 1220(w), 1140(w), 1115(m), 1010(s), 940(m), 895(m), 855(m), and 815(s)  $cm^{-1}$ ).

**n-Propylidenecyclohexane** (Anal. Calcd. for  $C_9H_{16}$ : C, 87.03; H, 12.97. Found: C, 87.05; H, 12.93) infrared spectrum (20% in  $CCl_4$ ) showed 2900(s), 1660(m), 1440(s) with shoulders at 1456 and 1432, 1368(m), 1362(m), 1310(w), 1294(m), 1260(w), 1232(m), 1140(m), 1114(m), 1068(m), 1030(m), 984(m), 936(m), 910(w), 890(m), and 840(s)  $cm^{-1}$ ).

**n-Butylidenecyclohexane** had  $n^{25D}$  1.4618 (Anal. Calcd. for  $C_{10}H_{18}$ : C, 86.88; H, 13.12. Found: C, 86.90; H, 13.06); n.m.r. ( $CCl_4$ ): triplet at 5.06 ( $J = 7$  c.p.s., 1 H, vinyl proton), complex absorption at 2.23–0.67 p.p.m.; infrared spectrum (pure liquid) 3050(w), 2960(s), 2930(s), 2860(s), 2665(w), 1720(w), 1675(m), 1460(s), 1380(m), 1300(m), 1270(m), 1230(m), 1154(w), 1120(w), 1022(m), 1005(m), 940(m), 892(m), 857(m), 825(w), 730(w), and 700(w)  $cm^{-1}$ ).

**Benzylidenecyclohexane** had  $n^{25D}$  1.5590 (lit.<sup>4b</sup>  $n^{25D}$  1.5604); n.m.r. spectrum ( $CCl_4$ ): phenyl absorption at 7.12 (5 H), vinyl absorption at 6.18 (1 H), and broad absorption at 2.25 and 1.58 p.p.m. (10 H).

**2-Methyl-2-nonene** had  $n^{25D}$  1.4270 (Anal. Calcd. for  $C_{10}H_{20}$ : C, 85.63; H, 14.37. Found: C, 85.65; H, 14.56); n.m.r. spectrum ( $CCl_4$ ): triplet at 5.08 ( $J = 6$  c.p.s., 1 H, vinyl proton) and complex absorption from 2.17 to 0.67 p.p.m.

**Reaction of Trideuteriomethyltriphenylphosphonium Iodide with Ethyllithium.** A suspension of 20 mmoles of trideuteriomethyltriphenylphosphonium iodide in 50 ml. of ether was treated with 15.88 ml. of 1.14 N (18 mmoles) ethyllithium in ether, and the mixture was stirred for 25 hr. at room temperature. The mixture was quenched with 40 mmoles of cyclohexanone, and the resulting mixture was heated at reflux for 18 hr. Toluene (19.2 mmoles) was added as a standard and the liquid phase analyzed by g.l.c. at  $50^\circ$ . It was found to contain "benzene" (35%) and "methylenecyclohexane" (67%). A sample of the "benzene"

was collected on the same column for mass spectral analysis. The "benzene" contained 60% C<sub>6</sub>H<sub>6</sub> and 40% C<sub>6</sub>H<sub>5</sub>D. Two other reactions gave "benzene" (56% C<sub>6</sub>H<sub>6</sub> and 44% C<sub>6</sub>H<sub>5</sub>D) in 34% yield and "benzene" (53% C<sub>6</sub>H<sub>6</sub> and 47% C<sub>6</sub>H<sub>5</sub>D) in 36% yield. The "methylenecyclohexane" yields were 62 and 66%, respectively. Samples of the "methylenecyclohexane" were collected by g.l.c. and their mass spectra obtained (cf. Table I).

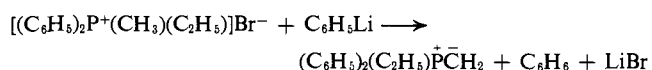
**Mass Spectrum Calculations.** Mass spectra were determined with a Consolidated Electrodynamics Corp. Model 21-130 mass spectrometer. Since the mass spectra were used only for determining the per cent isotopic composition of mixtures of deuterated species, the spectra were run at reduced voltage, under which conditions all peaks lower than the molecular ion were eliminated. Operating conditions were a sample pressure of 20 or 40  $\mu$ , filament current of 40  $\mu$ a., and voltage settings of 250–370. Several traces of each spectrum were obtained, and the results are based on averaged intensities. Examples of the type of calculations used in determining per cent isotopic composition are given in ref. 14.

**Reaction of Triphenylphosphineethylidene with Methyltriphenylphosphonium Bromide.** An ethereal solution of triphenylphosphineethylidene was prepared by treating a suspension of 11 mmoles of ethyltriphenylphosphonium bromide in 50 ml. of ether with 12.3 ml. of 0.82 *N* (10 mmoles) phenyllithium in ether. After 45 min. the bright red-orange solution gave a negative Gilman Color Test I. Methyltriphenylphosphonium bromide (11 mmoles) then was added in one portion. The resulting reaction mixture was yellow after it had been stirred at room temperature for 24 hr. It then was quenched with 20 mmoles of cyclohexanone and refluxed overnight. All volatiles were removed by reduced pressure trap-to-trap distillation (to 135° at 0.1 mm.). Toluene (8.96 mmoles) was added to the

distillate. Gas chromatographic analysis showed the presence of benzene (99%), methylenecyclohexane (85%), and ethylenecyclohexane (5%). Another reaction carried out in a similar manner gave methylenecyclohexane (78%) and ethylenecyclohexane (4%).

Essentially the same procedure was used in studying the reaction of triphenylphosphinemethylene with ethyltriphenylphosphonium bromide, and in those experiments were 1 molar equiv. each of two different phosphonium salts were treated with 1 molar equiv. of phenyllithium.

A related experiment, carried out using this general procedure, is that in which 1 molar equiv. of ethylmethyltriphenylphosphonium bromide was treated with 1 molar equiv. of phenyllithium, followed by quenching of the reaction mixture with cyclohexanone. The products obtained were benzene (91%), methylenecyclohexane (72%), and ethylenecyclohexane (ca. 1%).



In the experiment where 1 molar equiv. each of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>CD<sub>3</sub>]<sup>-</sup> and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P<sup>+</sup>C<sub>2</sub>H<sub>5</sub>]<sup>-</sup> were treated with 1 molar equiv. of phenyllithium, the isotopic composition of the resulting benzene was the item of interest. For this reason the phenyllithium solution used was checked for benzene (C<sub>6</sub>H<sub>6</sub>). Reaction of an aliquot of the C<sub>6</sub>H<sub>5</sub>Li solution with freshly distilled trimethylchlorosilane, followed by g.l.c. analysis for C<sub>6</sub>H<sub>6</sub> showed 2 mole % benzene in the phenyllithium solution. The double titration of this solution with 1,2-dibromoethane indicated the presence of 2% non-organometallic base.

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## Magnetic Resonance Spectroscopy. The Configurational Stability of Primary Grignard Reagents. 3,3-Dimethylbutylmagnesium Chloride<sup>1</sup>

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*Detailed examination of the temperature dependence of the n.m.r. spectra of 3,3-dimethylbutylmagnesium chloride and bis(3,3-dimethylbutyl)magnesium indicates that inversion of configuration at the -CH<sub>2</sub>Mg center occurs rapidly in ether solution at room temperature. Activation parameters for the inversion reactions are E<sub>a</sub> = 11 ± 2 kcal./mole, A = 10<sup>9.5 ± 1.5</sup> sec.<sup>-1</sup>, and*

*E<sub>a</sub> = 20 ± 2 kcal./mole, A = 10<sup>13.5 ± 1.5</sup> sec.<sup>-1</sup>, respectively.*

### Introduction

The configurational stability of Grignard reagents is of interest not only to the classical problems of the structure of Grignard reagents and the stereochemistry of their reactions, but also in connection with the details of carbon-metal bonding. The best explored approach

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