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STUDIES IN PHOSPHINEMETHYLENE CHEMISTRY

XIV[a]. THE REACTION OF VINYLIC PHOSPHONIUM BROMIDES WITH ORGANOLITHIUM REAGENTS[b]

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In connection with an investigation concerning the reaction of vinylic lithium reagents with tetraphenylphosphonium bromide[2] we became interested in studying the action of phenyllithium and other organolithium reagents on vinyltriphenylphosphonium bromide. Of main interest was the possibility that organolithiums might add to the vinylic double bond to produce new phosphinealkylidene reagents (eqn. 1).

$$[(C_6H_5)_3PCH{=}CH_2]Br + RLi \rightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2R + LiBr \qquad (1)$$

The first vinylphosphonium halide, $[(C_2H_5)_3PCH{=}CH_2]Br$, was reported by A. W. Hofmann in 1861[3], but reactions of vinylphosphonium salts were not studied until nearly 100 years later. Wittig, Eggers and Duffner prepared (β-piperidinoethyl)-triphenylphosphonium iodide by a route which must have involved *in situ* formation of vinyltriphenylphosphonium bromide and nucleophilic addition of lithium piperidide to the latter [giving $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2NC_5H_{10}$][4]. However, it was the recent work of Keough and Grayson[5] which produced a detailed knowledge of the chemistry of vinylic phosphonium salts and showed the β-addition of nucleophiles to the vinyl group to be a very facile and synthetically very useful reaction ("phosphonioethylation") (eqn. 2). Later work by Schweizer and co-workers made elegant use of this

$$[R_3PCH{=}CH_2]X + Z^- \xrightarrow{ZH} [R_3PCH_2CH_2Z]X \qquad (2)$$

reactivity of vinylphosphonium salts in organic synthesis[6-9]. However, none of these workers studied the action of organolithium reagents on vinylphosphonium salts. This prior art would lead one to predict that RLi addition as shown in eqn. (1) should occur very readily, but the complexity of RLi/phosphonium halide interactions as demonstrated in our previous studies[10-13] suggested the possibility of other modes of

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[a] For Part XII see ref. 1.

[b] For a preliminary communication see ref. 2; presented in part at the IUPAC Symposium on Organophosphorus Compounds, Heidelberg, May 20–22, 1964.

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attack as well, such as α proton abstraction from the vinyl group, *ortho*-proton abstraction from phenyl groups and direct attack at phosphorus.

The action of phenyllithium on vinyltriphenylphosphonium bromide was studied first, since this system was of particular interest to our study of the vinyllithium/tetraphenylphosphonium bromide reaction[13].

When a stirred, ethereal suspension of the vinylphosphonium salt was treated with an equivalent quantity of ethereal phenyllithium solution, a deep red, almost homogeneous solution resulted, typical of solutions of triphenylphosphinealkylidenes. When the solution was treated with either hydrobromic acid (to form the phosphonium bromide) or water (to form the phosphine oxide by benzene loss) only noncrystallizable oils could be obtained as products. When the solution was treated with acetone, benzene (56 %) and 2-methyl-4-phenyl-2-butene (41 %) were obtained as products. The reactions leading to the olefinic product are summarized by eqns. (3) and (4):

$$[(C_6H_5)_3PCH{=}CH_2]Br + C_6H_5Li \rightarrow (C_6H_5)_2\overset{+}{P}{-}\overset{-}{C}HCH_2C_6H_5 + C_6H_6 + LiBr \qquad (3)$$

$$(C_6H_5)_2\overset{+}{P}{-}\overset{-}{C}HCH_2C_6H_5 + (CH_3)_2C{=}O \rightarrow C_6H_5CH_2CH{=}C(CH_3)_2 + (C_6H_5)_3PO \qquad (4)$$

Thus phenyllithium addition to the vinylphosphonium salt had occurred, but the interaction between these reactants obviously was complicated, with alternate modes of attack by phenyllithium being quite important. The formation of oils in the reactions quenched with hydrobromic acid was indicative of the presence of a mixture of phosphonium salts.

The positive charge on phosphorus in the vinylphosphonium salt would enhance the acidity of protons attached to nearby carbon atoms and the observed benzene formation could be rationalized in terms of abstraction of the α proton of the vinyl group* or an *ortho*-proton of a phenyl substituent by phenyllithium. In agreement with this idea was the finding that phenyllithium added to isopropenyltriphenylphosphonium bromide in high yield without concomitant formation of benzene (eqn. 5):

$$[(C_6H_5)_3PC(CH_3){=}CH_2]Br + C_6H_5Li \rightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}(CH_3)CH_2C_6H_5 \xrightarrow{C_6H_5CHO} C_6H_5CH{=}C(CH_3)CH_2C_6H_5 \quad (86\%) \qquad (5)$$

If β-proton abstraction, leading to $(C_6H_5)_2\overset{+}{P}{-}CH{=}\overset{-}{C}H$, were to occur, facile β-elimination to give triphenylphosphine and acetylene might be expected. However, as noted below, triphenylphosphine was not a direct reaction product.

Further experiments with (α-deuteriovinyl)triphenylphosphonium bromide shed more light on this question. Treatment of this compound with phenyllithium in ether, followed by Wittig reaction of the phosphinealkylidene with acetone, gave benzene (38 %) and pure 2-methyl-3-deuterio-4-phenyl-2-butene (36 %). Mass spectral analysis of the benzene formed showed it to consist of 45 % C_6H_5D and 55 % C_6H_6. Thus it appears that α proton abstraction from the vinyl group by the organometallic base is in-

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* In this connection it may be noted that treatment of $[(C_6H_5)_3PCH{=}C(C_6H_5)_2]Br$ with phenyllithium gave $(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}{=}C(C_6H_5)_2$, characterized by its Wittig reaction with benzophenone to give tetraphenylallene[14].

volved only to the extent of 45% in the benzene-producing reaction. The source of the C_6H_6 in this experiment remains unknown. The most likely possibility is *ortho*-proton abstraction from phenyl groups, a reaction which was found to occur when organolithium reagents attack tetraphenylphosphonium bromide[11], but experimental verification for such conjecture is lacking. If such a process were indeed occurring, organophosphorus products whose isolation would be difficult would be expected.

In a preliminary communication[2] we reported that styrene and triphenylphosphine also were produced in quite low yield in the vinyltriphenylphosphonium bromide–phenyllithium reaction. We now believe that this statement is not correct. In many subsequent experiments we were unable to find evidence for the formation of styrene. The previous "identification" of styrene was based on GLC retention time alone. If styrene had been formed, either by direct attack of phenyllithium at the phosphorus atom of $[(C_6H_5)_3PCH{=}CH_2]Br$ or by partial decomposition of $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2C_6H_5$ in an olefin-forming decomposition of the type described by Bestmann *et al.*[15] for certain other phosphinealkylidenes, then it should have been possible to verify this experimentally, since styrene would have survived the reaction conditions. [In one experiment styrene (60 mole %) was added to the suspension of vinyltriphenylphosphonium bromide in ether before phenyllithium was added; the resulting mixture was quenched with acetone and subsequent work-up showed a 77% recovery of styrene.] Other experiments showed that triphenylphosphine was not a direct product of the reaction. However, heating of a distillation residue from a vinyltriphenylphosphonium bromide/phenyllithium/acetone reaction sequence to rather high temperature resulted in distillation of triphenylphosphine and its isolation in 29% yield. The source of the phosphine is not known. We suggest that it most likely is formed in the thermal decomposition of a proton abstraction product. Thus abstraction of the α proton of the vinyl group of the vinylphosphonium salt would give the phosphinealkylidene, $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}{=}CH_2$ (II). If this species reacted normally with ketones [as does $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}{=}C(C_6H_5)_2$][14], then 1,1-disubstituted allenes would be expected as products. Several experiments carried out with benzophenone and diethyl ketone as Wittig reaction carbonyl components failed to produce evidence for formation of the expected allenes*. Thus decomposition of (II) or of a product derived from it could be responsible for the appearance of triphenylphosphine at higher temperatures.

Since the preparation of vinyltriphenylphosphonium bromide is time-consuming and tedious, its generation *in situ* from two different precursors was examined and found to be quite satisfactory for preparative purposes. (β-Bromoethyl)triphenylphosphonium bromide was treated with two molar equivalents of phenyllithium in ether and the resulting mixture was allowed to undergo Wittig reaction with acetone. 2-Methyl-4-phenyl-2-butene was produced in 38% yield, in addition to benzene [51% yield after correction for the benzene formed in the initial reaction occurring (eqn. 6)].

$$[(C_6H_5)_3PCH_2CH_2Br]Br + C_6H_5Li \rightarrow [(C_6H_5)_3PCH{=}CH_2]Br + C_6H_6 + LiBr \qquad (6)$$

Here dehydrobromination by phenyllithium (eqn. 6) was followed by eqns. (3) and

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* Wittig and Haag[16] report that *terminal* allenes do not appear to be accessible by the Wittig reaction route.

(4). Even more practical from the standpoint of ease of phosphonium salt preparation is the use of $[(C_6H_5)_3PCH_2CH_2P(C_6H_5)_3]Br$ as a precursor. Treatment of this salt with two molar equivalents of phenyllithium, followed by reaction of the phosphinealkylidene formed with acetone, gave 2-methyl-4-phenyl-2-butene in 51 % yield and benzene in 35 % (corrected) yield. In this case the reaction summarized by eqn. (7) precedes (3) and (4)[4], and it is this sequence of reactions which explains the difficulty experienced by Wittig *et al.*[4] in their attempted synthesis of the bisphosphinealkylidene reagent from 1,2-ethylenebis(triphenylphosphonium) dibromide.

$$[(C_6H_5)_3PCH_2CH_2P(C_6H_5)_3]Br_2 + C_6H_5Li \rightarrow [(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2P(C_6H_5)_3]Br + C_6H_6 + LiBr$$
$$\downarrow$$
$$[(C_6H_5)_3P-CH=CH_2]Br + (C_6H_5)_3P \qquad (7)$$

The addition of other organolithium reagents to vinyltriphenylphosphonium bromide proceeded much less satisfactorily for reasons unknown. The results obtained with methyl- and ethyllithium are listed in Table 1. Of particular interest is the fact that methylenecyclohexane and ethylidenecyclohexane respectively were obtained in low yield in these reactions. This suggests that to a small extent attack at phosphorus is occurring when these alkyllithiums react with vinyltriphenylphosphonium bromide (eqn. 8).

$$[(C_6H_5)_3PCH=CH_2]Br + CH_3Li \rightarrow (C_6H_5)_2(CH_2=CH)\overset{+}{P}-\overset{-}{C}H_2 + C_6H_6 + LiBr \qquad (8)$$

This study was extended to an investigation of the action of organolithium reagents on other vinylic phosphonium halides. As has been mentioned above, phenyllithium added to isopropenyltriphenylphosphonium bromide to give $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH_2C_6H_5$ in high yield (eqn. 5). Methyl-, *n*-butyl- and vinyllithium reacted in similar fashion (Table 1). In the case of the $[(C_6H_5)_3PC(CH_3)=CH_2]Br$/phenyllithium reaction the phosphinemethylene produced also was characterized by acidic and basic hydrolysis to give the corresponding phosphonium salt, $[(C_6H_5)_3PCH(CH_3)CH_2C_6H_5]Br$ and phosphine oxide, $(C_6H_5)_2P(O)CH(CH_3)CH_2C_6H_5$, respectively.

Especially noteworthy is the addition of triphenylphosphinemethylene to the isopropenylphosphonium salt (eqn. 9):

$$[(C_6H_5)_3PC(CH_3)=CH_2]Br + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2 \rightarrow [(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH_2CH_2P(C_6H_5)_3]Br \quad (9)$$

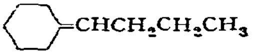
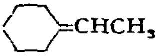
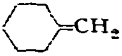
The initial product of this reaction was not characterized directly, but upon its treatment with phenyllithium with subsequent addition of benzaldehyde, 1,5-diphenyl-2-methyl-1,4-pentadiene was obtained in 37 % yield (eqns. 10 and 11).

$$[(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH_2CH_2P(C_6H_5)_3]Br + C_6H_5Li \rightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH_2\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3 + C_6H_6 + LiBr \quad (10)$$

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH_2\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3 + 2\,C_6H_5CHO \rightarrow C_6H_5CH=C(CH_3)CH_2CH=CHC_6H_5 + 2\,(C_6H_5)_3PO \quad (11)$$

TABLE I

ADDITIONS OF ORGANOMETALLIC REAGENTS TO VINYLIC PHOSPHONIUM BROMIDES

Phosphonium salt	*Addition reagent*	*Quenching agent*	*Products (% yield)*
$[(C_6H_5)_3PCH=CH_2]Br$	C_6H_5Li	acetone	$C_6H_5CH_2CH=C(CH_3)_2$ (41 %)
	CH_3CH_2Li	cyclohexanone	 (16 %)  (tr.) C_6H_6 (5 %)
	CH_3Li	cyclohexanone	 (13 %)  (6 %) C_6H_6 (17 %)
$[(C_6H_5)_3PCH=CHCH_3]Br$	C_6H_5Li	benzaldehyde	$C_6H_5CH=CHCH=CH_2$ (22, 10 %) $C_6H_5CH=CHCH(CH_3)C_6H_5$ (6 %)
$[(C_6H_5)_3PC(CH_3)=CHCH_3]Br$	C_6H_5Li	benzaldehyde	$C_6H_5CH=C(CH_3)CH(CH_3)C_6H_5$ (6 %)
$[(C_6H_5)_3PC(CH_3)=CH_2]Br$	C_6H_5Li	benzaldehyde	$C_6H_5CH=C(CH_3)CH_2C_6H_5$ (86 %)
	C_6H_5Li	hydrobromic acid	$[(C_6H_5)_3PCH(CH_3)CH_2C_6H_5]Br$ (80 %)
	C_6H_5Li	water	$(C_6H_5)_2P(O)CH(CH_3)CH_2C_6H_5$ (50 %)
	CH_3Li	benzaldehyde	$C_6H_5CH=C(CH_3)CH_2CH_3$ (59 %)
	$CH_2=CHLi$	benzaldehyde	$C_6H_5CH=C(CH_3)CH_2CH=CH_2$ (92 %)
	n-C_4H_9Li	benzaldehyde	$C_6H_5CH=C(CH_3)(CH_2)_4CH_3$ (99 %)
	$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2$[a]	benzaldehyde	$C_6H_5CH=C(CH_3)CH_2CH=CHC_6H_5$ (37 %)

[a] Followed by C_6H_5Li.

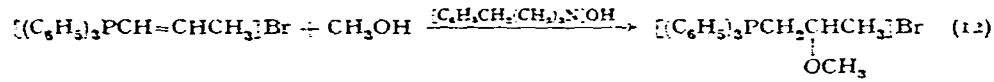
The addition of phosphinealkylidenes to the activated C=C bond of α,β-unsaturated ketones when addition to the C=O linkage is highly hindered has been reported[17], and thus phosphinemethylene addition to the activated C=C bond of the isopropenylphosphonium halide is not altogether unexpected.

Similar reactions of phenyllithium with (1-methyl-1-propenyl)triphenylphosphonium bromide and 1-propenyltriphenylphosphonium bromide were not as successful. With the former the Wittig reaction product after addition of benzaldehyde was obtained in only 6 % yield. With the 1-propenylphosphonium salt, again after treatment of the resulting phosphinealkylidene solution with benzaldehyde, the expected product, $C_6H_5(CH_3)CHCH=CHC_6H_5$, was obtained in equally low yield. Here, however, 1-phenyl-1,3-butadiene was obtained in yields of up to 22 %. Isolation of the latter suggests α proton abstraction from the propenyl group by phenyllithium, followed by isomerization of the resulting $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}=CHCH_3$ to the more stable

$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH=CH_2$. The alternate possibility, γ-proton abstraction from the propenyl group to give $(C_6H_5)_3\overset{+}{P}-CH=CH\overset{-}{C}H_2$ is considered to be less likely, and the apparent absence of $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH=CH_2$-derived products (via initial γ proton abstraction) in the reaction of (1-methyl-1-propenyl)triphenylphosphonium bromide with phenyllithium is to be noted in this connection.

It thus appears that as a synthetically useful method, the addition of organolithium reagents to vinylic phosphonium salts is strictly limited. Good yields of products are only obtained in cases where the vinylic group does not have an α proton. Otherwise yields are usually low to moderate and the reactions are complex in nature. This rather low selectivity is due mostly to the high basicity of the organolithium reagents.

As stated above, other workers have studied the addition of bases other than organometallic reagents to the double bonds of vinylic phosphonium salts and it was not our intention to duplicate their work. The unintentional finding that methanol undergoes base-catalyzed addition to 1-propenyltriphenylphosphonium bromide is, however, worth mentioning (eqn. 12).



$$[(C_6H_5)_3PCH=CHCH_3]Br + CH_3OH \xrightarrow{[C_6H_5CH_2(CH_3)_3N]OH} [(C_6H_5)_3PCH_2\underset{\underset{OCH_3}{|}}{C}HCH_3]Br \quad (12)$$

Keough and Grayson[5] found that methanolic sodium hydroxide caused isomerization of allyl- to 1-propenylphosphonium halides without concomitant addition of methanol to the C=C linkage. A change in basic catalyst to benzyltrimethylammonium hydroxide during our attempted preparative use of this isomerization reaction resulted in formation of the Michael addition product.

EXPERIMENTAL

General comments

Elemental analyses were performed by Dr. S. M. NAGY, M.I.T. Microchemical Laboratory, Galbraith Laboratories, Knoxville, Tenn., or Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.; combustion analyses for deuterium (falling drop method) by JOSEF NEMETH, Urbana, Illinois. Deuterium content is given in terms of atom % excess deuterium.

Infrared (IR) spectra were recorded using a Baird Model B or a Perkin-Elmer Infracord 237 or 337 infrared spectrophotometer*. Intensities of absorptions are recorded as strong (s), medium (m), weak (w), or shoulder (sh). Proton nuclear magnetic resonance (NMR) spectra were obtained with a Varian Associates A-60 high resolution spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane. Mass spectra were taken on a CEC Model 21-130 mass spectrometer.

Melting points were taken with a Mel-Temp or Büchi melting point apparatus and are corrected.

Gas-liquid chromatography (GLC) was carried out on 12 mm × 10 ft glass columns packed with 25% General Electric Co. SE-30 Silicone Gum (column A),

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* Infrared spectra were obtained for all compounds prepared and are given in ref. 18.

General Electric Co. XF-1150 Cyanoethylsilicone Fluid (column B) or Dow Corning Corp. 710 Silicone Fluid (column C) on Johns-Mansville Chromosorb P, utilizing thermal conductivity detectors with 10 to 20 p.s.i. of helium as carrier gas. A 12 mm × 3 ft. column packed with the 710 Fluid (column D) was also used. Gas–liquid chromatographic (GLC) analyses were carried out by comparing peak areas by planimetry to peak areas of a known amount of standard which was added to the mixture to be analyzed. Whenever possible, the relative peak responses of compounds under consideration and the standards were determined independently by comparing the peaks of weighed mixtures. All retention times of products were compared with those of authentic materials and identification was made certain by comparing their infrared spectra with those of authentic samples.

Solvents were dried by distillation from lithium aluminum hydride or calcium hydride if possible. Liquid reagents and other solvents were dried over anhydrous magnesium sulfate and purified by distillation. Solids were dried *in vacuo* over phosphorus pentoxide. All experiments involving organolithium reagents or phosphinealkylidenes were carried out in dried apparatus under an atmosphere of prepurified nitrogen.

Generally, organophosphonium bromides, chlorides and iodides were recrystallized from ethanol/ethyl acetate. The chlorides were prepared from the bromides by passing a methanolic solution of the latter through J. T. Baker Chemical Co. Dowex 1-X8 anion exchange resin (chloride form). The iodides were prepared by treating solutions of the bromides with a solution of potassium iodide, the iodide precipitating immediately. (Aqueous solutions were used if the bromides were water soluble; if not, aqueous methanolic solutions using the minimum amount of methanol necessary to dissolve the bromide.) Salts melting above 135° were dried *in vacuo* over phosphorus pentoxide at 110°.

Preparation of phosphonium salts

(*1*) *1-Propenyltriphenylphosphonium bromide* was prepared by base-catalyzed rearrangement of allyltriphenylphosphonium bromide[5] in 82 % yield; white crystals, m.p. 217–219° (lit.[5] m.p. 213–214°).

The NMR spectrum ($CDCl_3$) showed a doublet ($J = 6.5$ cps) with each peak split into a quartet (J *ca.* 1 cps) at 2.37 ppm (lit.[5] 2.36 ppm) for the methyl group, a multiplet for the vinyl protons from 6.57 to 8.43 ppm partly obscured by the phenyl protons, and the phenyl protons at 7.82 ppm. Coupling constants of 6.5, 18 and 22 cps could be discerned for the vinyl protons. Assuming coupling constants analogous to those found for vinyl- and isopropenyltriphenylphosphonium bromide (see below) the following coupling constants were assigned: H–H, 18 cps; P–H, 22 cps; 2-vinyl–methyl, 6.5 cps. These values indicate that the configuration of the double bond is *trans*, since values of 18 cps and 25 cps were found for the *trans*-H–H and the *cis*-P–H coupling constants respectively in the vinyl- and isopropenyl salts [*vs.* 12.5 cps for the *cis*-J(H–H) and 50 cps for *trans*-J(P–H)]. This was in contrast to the spectrum of the allyl salt which showed no peak upfield (toward tetramethylsilane) of 4.4 ppm, nor between 5.8 and 7.5 ppm, but showed all its non-aromatic protons between 4.4 and 5.8 ppm.

The IR spectrum ($CHCl_3$) showed bands at 3050 (w), 2925 (s), 2670 (w), 2440 (m), 1965 (w), 1895 (w), 1815 (w), 1640 (m), 1615 (m), 1590 (m), 1485 (m), 1440 (s), 1335 (w), 1315 (m), 1115 (s), 998 (m), 960 (m) and 815 (m) cm^{-1}. In contrast, the allyl salt (starting material) showed bands at 2750, 1385 and 925 cm^{-1}, but not the bands at 1615 or 960 cm^{-1}. Moreover, the bands from 1600 to 1700 cm^{-1} were much more intense in the spectrum of the propenyl salt than in that of the allyl salt.

(2) *Ethylene-1,2-bis(triphenylphosphonium) dibromide.* 1,2-Dibromoethane and 2 equivalents of triphenylphosphine in benzene solution were stirred and heated at reflux overnight. Crystals, m.p. 313–314° (lit.[4] m.p. 308–315°), of white solid precipitated in quantitative yield.

(3) *(β-Hydroxyethyl)triphenylphosphonium bromide.* (β-Hydroxyethyl)triphenylphosphonium bromide was prepared from 2-bromoethanol and triphenylphosphine in refluxing benzene solution. The product, white crystals, m.p. 217–218.5° (lit.* m.p. 214°), precipitated in over 90% yield. (Found: C, 61.71; H, 5.27; Br, 20.93. $C_{20}H_{20}BrOP$ calcd.: C, 62.03; H, 5.21; Br, 20.64%.)

The NMR spectrum ($CDCl_3$) showed a complex multiplet for the methylene protons, with a triplet ($J = 6$ cps) at 3.68 ppm, a sharp singlet at 3.89 ppm and another triplet ($J = 6$ cps) at 4.22 ppm. The hydroxyl proton appeared as a singlet at 5.05 ppm, which disappeared upon the addition of hydrochloric acid and reappeared as a very broad singlet at 6.33 ppm. The phenyl protons appeared centered at 7.75 ppm. The integration was 7:13:7:7:115 for the triplet:singlet:triplet:hydroxyl:phenyl respectively.

The chloride melted at 240–242° [lit. mp. 233° (ref. 20), 233–236° (ref. 21)]. The iodide melted at 188–189° (lit.[19] m.p. 185–186°).

(4) *(β-Bromoethyl)triphenylphosphonium bromide.* (β-Bromoethyl)triphenylphosphonium bromide was prepared by refluxing 35 g of (β-hydroxyethyl)triphenylphosphonium bromide in 300 ml of 48% hydrobromic acid for 3 weeks. (The reaction is incomplete in 2 weeks.) The reaction mixture was diluted with an equal volume of water and then extracted with chloroform. After the chloroform layer had been water-washed and dried, the salt was precipitated in *ca.* 75% yield by boiling off the chloroform while adding ethyl acetate.

The NMR spectrum ($CDCl_3$) of a sample of the white crystals, m.p. 198–200°**, showed a six line multiplet at 3.71 ppm for the β-methylene protons split by the phosphorus ($J = 17.5$ cps) and the adjacent methylene protons ($J = 6$ cps), a five line multiplet at 4.58 ppm for the α-methylene protons split by the phosphorus ($J = 12$ cps) and the adjacent methylene protons ($J = 6$ cps), and the phenyl peak centered at 7.87 ppm. The integration was 20:20:160 respectively. (Found: C, 53.67; H, 4.44; Br, 35.84. $C_{20}H_{19}Br_2P$ calcd.: C, 53.36; H, 4.25; Br, 35.51%.)

The reineckate, $[(C_6H_5)_3PCH_2CH_2Br]^+[Cr(NH_3)_2(SCN)_4]^-$, had m.p. 136–137° d. (from acetone/water). (Found: C, 41.54; H, 3.81. $C_{24}H_{25}BrN_6PS_4$ calcd.: C, 41.86; H, 3.66%.)

(5) *Deuterated (β-bromoethyl)triphenylphosphonium bromide.* Deuteriobromic acid was prepared by adding 40 g (2.22 moles) of deuterium oxide (General Dynamics Corp., Liquid Carbonic Division, 99.7% D_2O) to 200 g (2.30 equivs.) of phosphorus

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* Michaelis and Von Gimborn[19] report 114° for the m.p. of the bromide and 129–130° for the m.p. of the chloride, but these figures were probably reported incorrectly and should be 214° and 229–230°.

** Friedrich and Henning[22] report 288° and 298° for samples of this compound prepared from triphenylphosphine and 1,2-dibromoethane, but these are undoubtedly impure samples of ethylene-1,2-bis(triphenylphosphonium) dibromide.

tribromide in 200 ml of carbon tetrachloride, and permitting the evolved deuterium bromide gas to condense in 160 g of deuterium oxide. The entire operation was carried out under nitrogen with well-dried apparatus.

(α,α-Dideuterio-β-bromoethyl)triphenylphosphonium bromide was obtained by refluxing for 14 days a solution of 28.8 g of vinyltriphenylphosphonium bromide in the deuteriobromic acid prepared as described above. The workup procedure used was the same as that described above for the preparation of (β-bromoethyl)triphenylphosphonium bromide. White crystals, m.p. 198–200°, were obtained in 80% yield. (Found: C, 52.77; H + D, 4.28; atom% deuterium, 10.20. $C_{20}H_{17}Br_2D_2P$ calcd.: C, 53.12; H + D, 4.68%; atom % deuterium, 10.50%. Atom % deuterium of 10.20 would indicate 1.94 atoms of deuterium per molecule.)

The NMR spectrum ($CDCl_3$) showed a doublet (J = 18 cps) at 3.80 ppm for the β-methylene protons and the aromatic protons at 7.85 ppm.

The possibility that deuterium atoms are incorporated in the β-position instead of or in addition to the α-position is refuted by the following. (*a*) Addition of deuteriobromic acid to the vinylphosphonium salt must lead initially to the (α-deuterio-β-bromoethyl)phosphonium salt. (*b*) The NMR spectra of the nondeuterated and deuterated salts clearly show that both deuterium atoms are incorporated on the same carbon atom: For the hydrogen atoms assigned to the α proton, the same five-peak multiplet occurs in the spectrum of the monodeuterated salt (see below) as is observed in the spectrum of the nondeuterated salt, but the peak area for the former was one-half that of the latter, *vis-à-vis* the peaks assigned to the β protons. There was no peak in that position in the spectrum of the dideuterated salt. For the β protons there was a sextet in the spectrum of the nondeuterated salt (see below), a quartet in the spectrum of the monodeuterated salt (see below) and a doublet in the spectrum of the dideuterated salt, showing the change in the number of adjacent (splitting) protons from two to one to zero.

(α-Deuterio-β-bromoethyl)triphenylphosphonium bromide was prepared in exactly the same way as was (α,α-dideuterio-β-bromoethyl)triphenylphosphonium bromide. There is no obvious difference in the procedures used that could account for the difference in degree of deuteration in different experiments that otherwise seemed identical. It is possible that enough carbon tetrachloride was mixed with the deuteriobromic acid to lower its boiling point*. In this experiment there was obtained a 35% yield of white, crystalline (α-deuterio-β-bromoethyl)triphenylphosphonium bromide, m.p. 198–200°. (Found: C, 53.51; H + D, 4.57; atom % deuterium, 4.65. $C_{20}H_{18}Br_2DP$: calcd.: C, 53.24; H + D, 4.47%; atom % deuterium, 5.25. Atom % deuterium 4.65 would indicate 0.89 atom of deuterium per molecule.)

The NMR spectrum ($CDCl_3$) showed a doublet of a doublet (J = 6 cps, J = 18 cps) at 3.80 ppm for the β-methylene protons, the 5-peak multiplet for the doublet of a triplet (J = 12 cps, J = 6 cps respectively) at 4.85 ppm for the α-methylene proton and the phenyl protons at 7.85 ppm. The integration was 14:7:115 respectively.

(6) *Vinyltriphenylphosphonium bromide.* Vinyltriphenylphosphonium bromide was prepared by a method adapted from that of Doering and Schreiber[23] for the

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[*] In subsequent preparations care was taken to remove all carbon tetrachloride from the deuteriobromic acid. It was then found that after 8 days a mixture of mono- and dideuterated material was produced, but after 16 days the product was pure (α,α-dideuterio-β-bromoethyl)-triphenylphosphonium bromide.

preparation of vinyldimethylsulfonium bromide from (β-bromoethyl)dimethylsulfonium bromide as follows. To a solution of 3.5 g of (β-bromoethyl)triphenylphosphonium bromide, 75 ml of water and 3 drops of a 1 % phenolphthalein solution was added moist silver oxide[24] prepared from 2.0 g of silver nitrate. The mixture was stirred (about 5 min) until most of the dark brown silver oxide had been converted to light tan silver bromide, acetic acid being added any time the indicator turned red. [If the solution was permitted to remain basic for a short time, the product was converted to (β-hydroxyethyl)triphenylphosphonium bromide.] White crystals, m.p. 188.5–190° (lit.[6–9] m.p. 189–190°), were obtained in yields of up to 85 % by extraction with chloroform and then precipitation from the dried chloroform extracts with ethyl acetate. (Found: C, 65.08; H, 5.12; Br, 21.60. $C_{20}H_{18}PBr$ calcd.: C, 65.01; H, 4.91; Br, 21.65 %.)

Titration according to Ross and Denney[25] showed a molecular weight of 362 and 376 (calcd. 369.2).

The NMR spectrum ($CDCl_3$) showed the phenyl protons from 7.9 to 8.3 ppm with the vinyl protons showing a complex set of peaks from 6.05 to 9.1 ppm. The terminal vinyl proton *trans* to the phosphorus atom was centered at 7.21 ppm, and the terminal vinyl proton *cis* to the phosphorus atom at 6.24 ppm. The following coupling constants can be assigned: *trans* P–H, 50 cps; *cis* P–H, 25 cps; *trans* H–H, 18 cps; *cis* H–H, 12.5 cps. The nonterminal vinyl proton is obscured by the phenyl peaks. The NMR spectra of $[(C_6H_5)_3PCD{=}CH_2]Br$ and $[(C_6H_5)_3PC(CH_3){=}CH_2]Br$ (see below) were essential to these assignments. For the CH_2 protons of the α-deuteriovinyl salt, two doublets were observed with coupling constants of 25 and 50 cps, and the same pattern was observed for isopropenylphosphonium bromide with coupling constants of 22 and 48 cps. With the above information the spectrum of the vinyl salt was examined. It appeared that the β proton that was split by 25 cps by phosphorus was split by 18 cps by the α proton, while the β proton that was split by 50 cps by the phosphorus was split by 12.5 cps by the α proton. If these values for the coupling constants are considered valid, then geometric assignments may be made. Assuming that *trans* coupling constants are greater than *cis*, then the proton with coupling constants of 50 and 12.5 cps is *trans* to the phosphorus and *cis* to the α proton.

The IR spectrum ($CHCl_3$) showed bands at 3050 (w), 2940 (s), 2450 (m), 1980 (sh), 1925 (w), 1890 (w), 1775 (w), 1660 (w), 1620 (w), 1600 (w), 1590 (m), 1480 (m), 1440 (s), 1395 (m), 1340 (m), 1320 (m), 1120 (s), 1000 (s), and 980 (m) cm^{-1}.

(7) *(α-Deuteriovinyl)triphenylphosphonium bromide.* (α-Deuteriovinyl)triphenylphosphonium bromide, m.p. 186–187.5°, was prepared from (α,α-dideuterio-β-bromoethyl) triphenylphosphonium bromide by the procedure described above for the synthesis of the nondeuterated material. (Found: C, 64.74; H, 4.92; atom % deuterium, 5.37. $C_{20}H_{17}BrDP$: C, 64.88; H, 5.12 %; atom % deuterium, 5.55. Atom % deuterium of 5.37 would indicate 0.97 atom of deuterium per molecule.)

The NMR spectrum ($CDCl_3$) showed two doublets, one at 6.24 ppm ($J = 25$ cps) and the other at 7.21 ppm ($J = 50$ cps), in place of the complex multiplet observed for the vinylic protons in the nondeuterated compound.

The IR spectrum ($CHCl_3$) showed bands at 3050 (m), 2925 (s), 2670 (w), 2440 (m), 2240 (w), 2190 (m), 1960 (w), 1890 (w), 1815 (w), 1610 (w), 1580 (m), 1500 (m), 1480 (m), 1440 (s), 1380 (m), 1330 (w), 1305 (m), 1110 (s), 1040 (w), 1020 (sh), 995 (m), 980 (sh), 920 (m), and 845 (m) cm^{-1}.

(8) *(1-Hydroxy-2-propyl)triphenylphosphonium bromide* was prepared from equivalent quantities of 2-bromo-1-propanol and triphenylphosphine in refluxing benzene. The white solid precipitated after several days in yields up to 25 %. Continuation of the reaction only led to the precipitation of side products, but no more of the desired salt precipitated. The yield could not be improved by changing the solvent or the mole ratios of the reactants. After repeated recrystallization, the salt melted between 156° and 162°. (Found: C, 62.84; H, 5.67; Br, 20.40; mol. wt. 415[25]. $C_{21}H_{22}BrOP$ calcd.: C, 62.85; H, 5.53; Br, 19.92 %; mol. wt. 401.)

The NMR spectrum ($CDCl_3$) showed a doublet of a doublet ($J = 7$ cps, $J = 19$ cps) at 1.40 ppm for the methyl protons, a doublet ($J = 6$ cps) of a triplet ($J = 16$ cps) at 3.90 ppm for the methylene protons, a multiplet at 4.52 ppm for the methinyl proton, a triplet ($J = 6$ cps) at 5.39 ppm for the hydroxyl proton, and aromatic protons from 7.4 to 8.5 ppm. The hydroxyl triplet disappeared upon the addition of hydrochloric acid and a singlet appeared at 4.12 ppm. The integration was 22:15:7.5:7:110 respectively.

The iodide melted at 172–173.5°. (Found: C, 56.48; H, 5.27. $C_{21}H_{22}IOP$: C, 56.26; H, 4.95 %.)

(9) *Isopropenyltriphenylphosphonium bromide.* Isopropenyltriphenylphosphonium bromide was prepared directly by refluxing (1-hydroxy-2-propyl)triphenylphosphonium bromide in 48 % hydrobromic acid for 2 weeks. The workup procedure used was the same as described above in the preparation of (β-bromoethyl)triphenylphosphonium bromide. White crystals, m.p. 196.5–197.5°, were obtained in 93 % yield. (Found: C, 65.72; H, 5.15; Br, 21.07; mol. wt.[25], 388. $C_{21}H_{20}BrP$ calcd.: C, 65.80; H, 5.26; Br, 20.85 %; mol. wt. 383.)

The NMR spectrum ($CDCl_3$) showed a doublet ($J = 14$ cps) at 2.31 ppm for the methyl protons, a doublet ($J = 22$ cps) centered at 6.08 ppm for the vinyl proton *cis* to the phosphorus atom, a doublet ($J = 48$ cps) centered at 6.92 ppm for the vinyl proton *trans* to the P atom, and the aromatic protons from 7.4 to 7.9 ppm.

The IR spectrum ($CHCl_3$) showed bands at 3050 (w), 2925 (s), 2440 (m), 1975 (w), 1900 (w), 1810 (w), 1600 (w), 1580 (m), 1480 (m), 1430 (s), 1330 (w), 1310 (w), 1105 (s), 990 (m), 955 (m), and 920 (w) cm^{-1}.

The chloride melted 234–236°. (Found: C, 74.41; H, 6.09; Cl, 10.54. $C_{21}H_{20}PCl$ calcd.: C, 74.44; H, 5.95; Cl, 10.47 %.)

(10) *(3-Oxo-2-butyl)triphenylphosphonium bromide.* A solution of 3-bromo-2-butanone and triphenylphosphine in benzene was permitted to stand at room temperature. After several days a white solid mixture of the desired product and 2-butenoxytriphenylphosphonium bromide had precipitated. (The butenoxy compound is formed by attack of triphenylphosphine at the oxygen with expulsion of bromide ion. This type of behavior is typical for the reactions of tertiary phosphines and α-halogenocarbonyl compound[26]. For instance, bromoacetophenone leads to either a quaternary phosphonium salt or to the enoxyphosphonium salts, depending on the solvent. Moreover, triphenylphosphine oxide and acid, known hydrolysis products of enoxyphosphonium salts, are formed upon treatment of the mixture with water.) The precipitate was treated with water in order to hydrolyze the 2-butenoxytriphenylphosphonium bromide to triphenylphosphine oxide, 2-butanone and hydrobromic acid. Extraction of the solid thus formed with more water led to a solution of the desired phosphonium salt. Crystals, m.p. 185–187°, of white (3-oxo-2-butyl)triphenyl-

phosphonium bromide were obtained by precipitation from the water with potassium bromide. A 22 % yield was obtained by repeated collection from the benzene mixture over a 3 week period. (Found: C, 64.10; H, 5.62; Br, 19.50. $C_{22}H_{22}BrOP$ calcd.: C, 63.93; H, 5.37; Br, 19.39 %.)

The NMR spectrum ($CDCl_3$) showed a doublet of a doublet ($J = 7.5$ cps, $J = 18$ cps) at 1.73 ppm for the 1-methyl protons, a singlet at 2.58 ppm for the 4-methyl protons, a multiplet for the methinyl proton from 7.1 ppm into the phenyl peaks, and phenyl protons from 7.6 to 8.2 ppm.

The IR spectrum ($CHCl_3$) showed bands at: 3060 (m), 2945 (s), 2790 (m), 2450 (m), 1950 (w), 1900 (w), 1815 (w), 1710 (s), 1615 (w), 1588 (m), 1480 (m), 1440 (s), 1378 (w), 1360 (m), 1300 (w), 1165 (m), 1110 (s), 1040 (m), 998 (m), 965 (w), 685 (s) cm^{-1}.

The iodide melted 155.5–157°. (Found: C, 57.26, 57.48; H, 5.21, 5.23. $C_{22}H_{22}IOP$ calcd.: C, 57.40; H, 4.82 %.)

(*11*) *(3-Hydroxy-2-butyl)triphenylphosphonium bromide.* (3-Hydroxy-2-butyl)-triphenylphosphonium bromide was prepared in 54 % recrystallized yield by adding solid sodium borohydride portionwise to 5.5 g of (3-oxo-2-butyl)triphenylphosphonium bromide solution in 150 ml of methanol, which was rapidly stirred and cooled by ice-water. The addition required about 5 min and was continued until further addition caused no more fizzing (about 2 equivalents of sodium borohydride being necessary). The mixture then was acidified immediately with hydrobromic acid and the solvent was removed at reduced pressure. The residue was treated with water and the aqueous mixture extracted with chloroform. After the chloroform layer was dried, white crystals, m.p. 244–246°, were precipitated by boiling off the chloroform as ethyl acetate was added. (Found: C, 63.28; H, 5.90; Br, 19.51. $C_{22}H_{24}BrOP$ calcd.: C, 63.62; H, 5.82; Br, 19.24 %.)

The NMR spectrum ($CDCl_3$) showed a doublet ($J = 6$ cps) for the 4-methyl protons at 1.41 ppm overlapping a doublet of a doublet ($J = 7$ cps, $J = 20$ cps) for the 1-methyl protons at 1.34 ppm a quartet ($J = 7$ cps) with much fine splitting at 3.83 ppm for the 3-methinyl proton, a multiplet from 4.25 to 4.80 ppm for the 2-methinyl proton, a doublet ($J = 5$ cps) at 5.35 ppm for the hydroxyl proton, and the phenyl protons from 7.7 to 8.3 ppm. The hydroxyl doublet disappeared and was replaced by a broad singlet at 6.9 ppm upon the addition of hydrochloric acid.

The iodide melted 234–235°. (Found: C, 57.08; H, 5.65. $C_{22}H_{24}IOP$ calcd.: C, 57.15; H, 5.23 %.)

(*12*) *(1-Methyl-1-propenyl)triphenylphosphonium bromide.* (1-Methyl-1-propenyl)-triphenylphosphonium bromide was prepared by heating 6.0 g of (3-hydroxy-2-butyl)-triphenylphosphonium bromide at reflux in 85 ml of 48 % hydrobromic acid for 21 days. The reaction mixture was worked up in the manner described above for the preparation of (β-bromoethyl)triphenylphosphonium bromide. White crystals, m.p. 204–204.5, were obtained in 81 % yield. (Found: C, 66.31; H, 5.87; Br, 20.20. $C_{22}H_{22}BrP$ calcd.: C, 66.50; H, 5.58; Br, 20.12 %.)

The NMR spectrum ($CDCl_3$) showed a multiplet from 2.04 to 2.37 ppm for the methyl protons, a doublet ($J = 24$ cps*) of a quartet ($J = 7$ cps) at 6.60 ppm for

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* A value of 24 cps, based on the above tentative conclusions, would indicate that the phosphorus was *cis* to the vinyl proton. Since the bulky triphenylphosphorus group would be expected to assume a configuration *trans* to the terminal methyl group, the assumption that the *trans* coupling constant would be larger than the *cis*, as stated above, is somewhat strengthened.

the vinyl proton, and the phenyl protons centered at 7.94 ppm. The integration was 36:6:100 respectively.

The IR spectrum ($CHCl_3$) showed bands at 3050 (sh), 2940 (s), 2450 (m), 1960 (w), 1900 (w), 1820 (w), 1625 (m), 1588 (m), 1580 (sh), 1483 (m), 1440 (s), 1380 (w), 1340 (w), 1320 (w), 1115 (s), 1080 (sh), 1000 (m), 930 (sh), 924 (w), 685 (m), and 660 (m) cm^{-1}.

The chloride melted 165–167°. (Found: C, 74.63; H, 6.36. $C_{22}H_{22}ClP$: calcd. C, 74.87; H, 6.29%.)

(13) 2-Butyltriphenylphosphonium bromide. In a sealed, thick-walled glass tube were heated at 155° for 4 days 12.6 g (48 mmoles) of triphenylphosphine, 17 g (124 mmoles) of 2-bromobutane and 7 g of acetonitrile. Yellow solid, 22.3 g, m.p. 160–196°, and a small quantity of liquid were obtained when the mixture was cooled. The solid was dissolved in chloroform. The acidic chloroform solution so formed was washed with aqueous potassium bromide solution until neutral, then dried. Boiling off the chloroform while adding ethyl acetate led to isolation of 15.1 g (79% yield) of product, m.p. 230–232°. (Found: C, 65.84; H, 6.01; Br, 20.30. $C_{22}H_{24}BrP$ calcd.: C, 66.17; H, 6.06; Br, 20.03%.)

The NMR spectrum ($CDCl_3$) of the compound showed a doublet of a doublet ($J = 7$ cps, $J = 13$ cps) at 1.40 ppm for the 1-methyl protons, a triplet ($J = 7$ cps) with each peak slightly split into a doublet ($J = 1$ cps) at 1.30 ppm for the 4-methyl protons, a multiplet from 1.7 to 2.3 ppm for the methylene protons, a multiplet from 4.8 to 5.4 ppm for the methinyl proton, and a multiplet from 7.5 to 8.3 for the phenyl protons.

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 1-bromobutane and lithium wire in pentane. Ethyllithium was prepared at below 0° and stored at −78°. Vinyllithium was prepared by treating a pentane solution of tetravinyltin with *n*-butyllithium, and then dissolving the resulting solid vinyllithium in ether[27]. All solutions of organolithium reagents were standardized by the double titration method using 1,2-dibromoethane in place of benzyl chloride[28].

Reaction of phenyllithium and vinyltriphenylphosphonium bromide

(a) Acetone quench. To a stirred suspension of 5.09 g (13.8 mmoles) of vinyltriphenylphosphonium bromide and 90 ml of ether was added 12.4 ml of 1.11 M (13.8 mmoles) of phenyllithium. After 5 min the mixture was deep red and almost homogeneous, and the Gilman Color Test I was negative. After 40 min, 5 ml of acetone was added to the mixture. A light tan, thick slurry resulted. After the mixture had been stirred and heated at reflux overnight, the volatile components were distilled directly (pot temperature to 150°/0.5 mm) into a Dry Ice-cooled receiver. GLC analysis (column A, 116°, 10 p.s.i., *n*-bromobutane standard; 180°, 20 p.s.i., bromobenzene standard) of the distillate showed that 2-methyl-4-phenyl-2-butene (41%) and benzene (56%) were present. Styrene was not observed as a product. Samples of both compounds were collected by GLC, and had IR spectra identical to those of corresponding authentic samples. The NMR spectrum of 2-methyl-4-phenyl-2-butene was identical to that of an authentic sample.

(*b*) *In the presence of styrene.* To a stirred suspension of 11.1 mmoles of vinyltriphenylphosphonium bromide, 0.68 g (6.54 mmoles) of styrene and 75 ml of ether was added over 5 min 11.1 mmoles of phenyllithium. When, after 10 min, the Gilman Color Test I was negative, acetone (5 ml) was added to the mixture. The resulting yellow slurry was stirred and heated at reflux overnight, then was filtered. The volatile compounds were distilled directly (pot temperature to 155°/0.5 mm) from the filtrate into a Dry Ice-cooled receiver. GLC analysis (column A, 115°, 20 p.s.i., mesitylene standard) showed the presence of 2-methyl-4-phenyl-2-butene (14 %), benzene (44 %) and styrene (77 % recovery).

(*c*) *Treatment with iodomethane.* The mixture resulting from the reaction of vinyltriphenylphosphonium bromide and phenyllithium (11.4 mmoles of each) was quenched with acetone (5 ml) as described above. After the resulting mixture had been stirred for 3 days at room temperature, it was filtered. To the filtrate was added 10 g of iodomethane, and the resulting solution was let stand overnight with protection from light. No methyltriphenylphosphonium iodide precipitated, indicating the absence of triphenylphosphine.

(*d*) *Triphenylphosphine as a product.* The reaction of vinyltriphenylphosphonium and phenyllithium (14.1 mmoles of each) followed by treatment of the resulting mixture with acetone (5 ml) was carried out as described above under "acetone quench". However, the pot temperature in the distillation rose to 175°/0.5 mm, and triphenylphosphine, m.p. 78.5–80° (mixed m.p. undepressed), distilled into the connector between the pot and receiver. GLC analysis of the distillate as described above showed the presence of benzene (54 %) and 2-methyl-4-phenyl-2-butene (41 %).

Another experiment was run in the same way as described above for the acetone quench reaction, the pot temperature in the distillation rising to 150°/0.5 mm GLC analysis of the distillate showed the presence of benzene (56 %) and 2-methyl-4-phenyl-2-butene (41 %). The distillation of the pot residue was then continued with a fresh receiver up to a pot temperature of 185°/0.5 mm. The oily distillate thus obtained was dissolved in ether and the resulting solution of triphenylphosphine was treated overnight with iodomethane. The triphenylphosphine was converted to methyltriphenylphosphonium iodide (1.62 g, 29 %). A recrystallized sample melted at 186–188° and showed no mixture m.p. depression.

Preparation of authentic 2-methyl-4-phenyl-2-butene

To a stirred suspension of 19.2 g (50 mmoles) of isopropyltriphenylphosphonium bromide and 700 ml of ether was added 51 mmoles of phenyllithium. The deep red mixture was stirred for 1 h and then treated with 9.2 g (76 mmoles) of phenylacetaldehyde. (Eastman Organic Chemicals phenylacetaldehyde, 50 % solution in ethanol, was purified by stripping off the ethanol and then fractionally distilling.) The resulting thick, white mixture was stirred and heated at reflux for 40 h, cooled and filtered. The filtrate was distilled through a 10 in. Vigreux column to give 2.16 g (29 % yield) of clear, colorless liquid, b.p. 86–90°/16 mm (lit.[29] b.p. 92°/15 mm), n_D^{25} 1.5119, $n_D^{18.3}$ 1.5152, n_D^{17} 1.5156 (lit. $n_D^{18.3}$ 1.5125[29], n_D^{17} 1.5158[30]). (Found: C, 90.17; H, 9.76. $C_{11}H_{14}$ calcd.: C, 90.35; H, 9.65 %.)

The NMR spectrum (CCl_4) showed a singlet slightly split into a doublet (J = 1 cps) at 1.71 ppm for the six methyl protons, a doublet (J = 7 cps) at 3.29 ppm for the methylene protons, a triplet (J = 7 cps) with much fine splitting (J *ca.* 1 cps) at

5.29 ppm for the methinyl proton, and the aromatic protons centered at 7.16 ppm. The integration was 50:16:7.5:45, respectively.

Reaction of phenyllithium and (α-deuteriovinyl)triphenylphosphonium bromide

A 10 ml sample of phenyllithium (8.4 mmoles) was treated with 1.0 g (9.1 mmoles) of freshly distilled chlorotrimethylsilane. GLC analysis of the resulting mixture (column A, 100°, 15 p.s.i., toluene standard) showed the presence of benzene (0.28 mmole) and phenyltrimethylsilane (94 %).

To a stirred suspension of 3.10 g (8.4 mmoles) of (α-deuteriovinyl)triphenylphosphonium bromide and 80 ml of ether was added 8.4 mmoles of phenyllithium (containing 0.28 mmole of benzene, see above). After 1 h, 5 ml of acetone was added to the red solution. The resulting yellow slurry was stirred and heated at reflux overnight, then was filtered. The volatile components were distilled directly from the filtrate (pot temperature to 135°/0.2 mm) into a Dry Ice-cooled receiver. GLC analysis of the distillate (column A, 125°, 20 p.s.i.; 75°, 10 p.s.i.; toluene and *n*-decane standards) showed the presence of benzene (38 %) and 2-methyl-4-phenyl-2-butene (36 %). A sample of benzene, collected by GLC, was shown to contain 42 % C_6H_5D and 58 % C_6H_6 by mass spectrometric analysis (Consolidated Electrodynamics Corporation Model 21-130 mass spectrometer) at a sample pressure of 40 μ, a filament current of 40 μa and a voltage setting of 400. (Several traces were obtained and the results are based on averaged intensities.) Since the total yield of benzene was 3.20 mmoles, there were 1.85 mmoles of C_6H_6 and 1.34 mmoles of C_6H_5D. However, 0.28 mmoles of benzene ($0.28 \times 0.938 = 0.26$ mmoles of C_6H_6 and $0.28 \times 0.062 = 0.02$ mmoles of C_6H_5D) was added with the phenyllithium, so that only 1.59 mmoles (55 %) of C_6H_6 and 1.32 mmoles (45 %) of C_6H_5D were actually produced in the reaction.

Reaction of phenyllithium and ethylene-1,2-bis(triphenylphosphonium) dibromide

To a stirred suspension of 10 mmoles of ethylene-1,2-bis(triphenylphosphonium)-dibromide and 85 ml of ether was added 20 mmoles of phenyllithium. The mixture became deep red and the Gilman Color Test I was negative after 50 min. When, after another 40 min, 4 ml of acetone was added, the mixture refluxed and a thick, light tan slurry resulted. After the mixture was stirred and heated at reflux overnight, the volatile components were distilled directly (pot temperature to 135°/0.8 mm) from the reaction mixture into a Dry Ice-cooled receiver. GLC analysis (column A, 114°, 10 p.s.i., *n*-heptane standard; 180°, 20 p.s.i., bromobenzene standard) showed the presence of 2-methyl-4-phenyl-2-butene (51 %) and benzene (35 % over the amount formed in the initial elimination step.)

Reaction of phenyllithium and (β-bromoethyl)triphenylphosphonium bromide

To a stirred suspension of 15.7 mmoles of (β-bromoethyl)triphenylphosphonium bromide and 75 ml of ether was added 30.2 mmoles of phenyllithium. When 2 ml of acetone was added to the red solution, an exothermic reaction ensued. After the light tan slurry was stirred and heated at reflux for 3 days, the volatile materials were distilled directly (pot temperature to 175°/0.4 mm) into a Dry Ice-cooled receiver. GLC analysis of the distillate showed that 2-methyl-4-phenyl-2-butene (38 %) and benzene (51 % over the amount formed in the initial dehydrobromination step) were present.

Reaction of ethyllithium and vinyltriphenylphosphonium bromide

To a stirred suspension of 10.6 mmoles of vinyltriphenylphosphonium bromide and 70 ml of ether was added 9.8 mmoles of ethyllithium. The mixture quickly became deep red-brown and almost homogeneous. After 6 h, 3 ml of cyclohexanone was added, the mixture becoming lighter in color and thick with solid. After the mixture was stirred and heated at reflux overnight, the volatile components were distilled directly (pot temperature to 100°/0.5 mm) into a Dry Ice-cooled receiver. GLC analysis of the distillate (column A, 162°, 17 p.s.i., toluene standard) showed the presence of *n*-butylidenecyclohexane (16%) and benzene (5%). In addition there was a trace of material with the GLC retention time of ethylidenecyclohexane. A sample of *n*-butylidenecyclohexane was collected by GLC. (Found: C, 86.89; H, 13.09. $C_{10}H_{18}$ calcd.: C, 86.88; H, 13.12%.)

The IR spectrum (CCl_4) of *n*-butylidenecyclohexane was identical to that of an authentic sample prepared from triphenylphosphine-*n*-butylidene and cyclohexanone.

Reaction of methyllithium and vinyltriphenylphosphonium bromide

To a stirred suspension of 14.3 mmoles of vinyltriphenylphosphonium bromide and 75 ml of tetrahydrofuran was added 14.3 mmoles of methyllithium. When 2 ml of cyclohexanone was added to the red solution, an exothermic reaction ensued, and a thick, tan slurry formed which was stirred and heated at reflux overnight. All the volatile components were distilled directly (pot temperature to 200°/0.15 mm) into a Dry Ice-cooled receiver. GLC analysis of the distillate (column A, 60°, 10 p.s.i.; 140°, 15 p.s.i., *n*-heptane and *n*-octane standards) showed the presence of benzene (17%), *n*-propylidenecyclohexane (13%) and a compound with the retention time (5 min) of methylenecyclohexane (6%).

A sample of *n*-propylidenecyclohexane was collected by GLC. The IR spectrum (CCl_4) was identical to that of an authentic sample[10]. The NMR spectrum (CCl_4) showed a triplet ($J = 7$ cps) at 0.95 ppm for the methyl protons, a multiplet from 1.4 to 2.3 ppm for the methylene protons, and a triplet ($J = 7$ cps) at 5.07 ppm for the vinyl proton.

Reaction of phenyllithium and 1-propenyltriphenylphosphonium bromide

To a stirred suspension of 25.5 mmoles of 1-propenyltriphenylphosphonium bromide and 150 ml of ether was added 25.5 mmoles of phenyllithium. Benzaldehyde (31.5 mmoles) was added. The resulting yellow, thick slurry was stirred and heated at reflux overnight, then filtered. The volatile materials were distilled directly from the filtrate (pot temperature to 160°/0.4 mm) into a Dry Ice-cooled receiver. GLC analysis of the distillate (column C, 223°, 20 p.s.i., bibenzyl standard) showed the presence of 1,3-diphenyl-1-butene (6% yield; ratio isomer B/isomer A, 0.26) (retention times; isomer A, 11 min; isomer B, 15 min) and (145°, 20 p.s.i.) 1-phenyl-1,3-butadiene (10% yield; *cis/trans* ratio, 1.43). In a similar reaction run on a 10.4 mmole scale, there was obtained 22% of 1-phenyl-1,3-butadiene, but the yield of 1,3-diphenyl-1-butene was not determined. Samples of both isomers of 1-phenyl-1,3-butadiene, collected by GLC, showed IR spectra identical to those of the corresponding authentic material.

Samples of each isomer of 1,3-diphenyl-1-butene were collected by GLC and identified by their IR and NMR spectra and the analysis of the isomer A. (Found: C, 92.15; H, 7.94. $C_{16}H_{16}$ calcd.: C, 92.26; H, 7.74%.)

The NMR spectrum (CCl_4) of isomer A showed a doublet ($J = 7$ cps) at 1.31 ppm for the methyl protons, a doublet ($J = 10$ cps) of a quartet ($J = 7$ cps) at 3.94 ppm for the methinyl proton, a doublet of a doublet ($J = 10$ cps, $J = 11.5$ cps, center peaks partly overlap) at 5.71 ppm for the 2-vinyl proton, a doublet ($J = 11.5$ cps) at 6.41 ppm for the 1-vinyl proton, and the phenyl protons in a singlet at 7.17 ppm. The integration was 30:10:10:10:110 respectively.

The NMR spectrum (CCl_4) of isomer B showed a doublet ($J = 6.5$ cps) at 1.40 ppm for the methyl protons, a multiplet at 3.5 ppm for the methinyl protons, a multiplet at 5.7 ppm for the 2-vinyl protons, a doublet ($J = 2$ cps) at 6.28 ppm for the 1-vinyl proton, and a singlet at 7.18 ppm for the phenyl protons. Due to lack of a sufficient quantity of material, the splitting of the multiplets at 3.5 and 5.7 ppm could not be seen.

Tentative assignment of the structures of the isomers on the basis of the NMR coupling constants between the adjacent vinylic protons would indicate that isomer A is the *trans* and isomer B the *cis* compound. In general, the *trans* coupling constant is larger than the *cis*, and although 2 cps is a slightly low value for the *cis* coupling constant, 10 cps is within the range observed for *trans* coupling constants.

Reaction of phenyllithium and (1-methyl-1-propenyl)triphenylphosphonium bromide

To a stirred suspension of 7.74 mmoles of (1-methyl-1-propenyl)triphenylphosphonium bromide and 150 ml of ether was added 7.0 ml of 1.11 *M* phenyllithium. Benzaldehyde (7.74 mmoles) was added to the deep red solution; a thick, white slurry resulted. Hydroquinone (0.1 g) was added and the mixture was stirred and heated at reflux overnight. It then was filtered and the volatile compounds were distilled directly from the filtrate (pot temperature to 160°/0.2 mm) into a Dry Ice-cooled receiver. GLC analysis (column D, 200°, 16 p.s.i., 1,3-diphenoxypropane standard) showed the presence of 1,3-diphenyl-2-methyl-1-butene (6 %). Analysis (column A, 170°, 20 p.s.i.) showed no peak of a retention time between that of benzaldehyde (3 min) and diphenylmethane (14 min), or (column A, 230°, 20 p.s.i.) between that of benzaldehyde (1.5 min) and 1,3-diphenyl-2-methyl-1-butene (12.5 min) (diphenylmethane, 4.5 min.) as would be expected for 1-phenyl-2-methyl-1,3-butadiene. Analysis (column A, 110°, 20 p.s.i.) showed the presence of benzene (17 %). A sample of 1,3-diphenyl-2-methyl-1-butene was collected by GLC and was characterized by means of its IR and NMR spectra. (Found: C, 91.17; H, 8.76. $C_{17}H_{18}$ calcd.: C, 91.84; H, 8.16 %.)

The NMR spectrum (CCl_4) showed a doublet ($J = 7$ cps) at 1.40 ppm for the 4-methyl protons, a doublet ($J = 1.5$ cps) at 1.62 ppm for the 2-methyl protons, a quartet ($J = 7$ cps) at 4.23 ppm for the 3-methinyl proton, a singlet with fine splitting at 6.37 ppm for the vinyl proton, and the aromatic protons in a doublet ($J = 4$ cps) at 7.18 ppm. The integration was 27:28:8:8.5:90, respectively.

Reaction of methyllithium and isopropenyltriphenylphosphonium bromide

To a stirred suspension of 4.0 g (10.4 mmoles) of isopropenyltriphenylphosphonium bromide and 125 ml of ether was added dropwise over 5 min 10.4 mmoles of methyllithium. The mixture became deep red and after 2 h most of the solid had been consumed. Benzaldehyde (2.2 g, 20 mmoles) was added. The resulting light tan slurry was stirred and heated at reflux overnight, then filtered. The volatile materials were distilled directly from the filtrate (pot temperature to 135°/0.5 mm) into a Dry Ice-cooled receiver. GLC analysis (column A, 140°, 20 p.s.i., acetophenone standard) of the distillate showed the presence of 1-phenyl-2-methyl-1-butene (59 %). The compound consisted of two isomers whose GLC retention times were so close together (12 and 12.7 min) that their yield ratio could not be determined, nor could they be collected separately. A sample of the mixed isomers collected using GLC had an IR spectrum identical to that of an authentic sample.

Preparation of authentic 1-phenyl-2-methyl-1-butene

To a stirred suspension of 10.9 g (27.3 mmoles) of 2-butyltriphenylphosphonium bromide and 350 ml of ether was added 27.3 mmoles of phenyllithium. After 1 h 35.0 mmoles of benzaldehyde was added to the red solution and the light tan slurry thus formed was stirred and heated at reflux overnight. The mixture was filtered, and the filtrate was distilled (after the ether was stripped) through an 8 inch Vigreux column. There was obtained 2.50 g (63 % yield) of clear, colorless liquid, b.p. 87°/11 mm. GLC analysis ((column A, 140°, 20 p.s.i.) showed that the 1-phenyl-2-methyl-1-butene was 99 % pure and consisted of two isomers whose retention times were too close for the isomers to be separated. A sample of the mixed isomers was collected by GLC. (Found: C, 90.20; H, 9.81. $C_{11}H_{14}$ calcd.: C, 90.35; H, 9.65 %.)

The NMR spectrum (CCl_4) of the mixture of isomers showed two overlapping triplets (looking like a triplet with each peak slightly split into a doublet) at 1.00 and 1.05 ppm (both $J = 7$ cps) for the 4-methyl protons, two overlapping doublets (looking like a triplet of $J = 1.3$ cps) at 1.74 and 1.79 ppm for the protons of the methyl group attached to C-2, an eight peak multilpet for the two overlapping quartets ($J = 7$ cps) at 2.09 and 2.15 ppm for the methylene protons, a broad singlet at 6.16 ppm for the vinyl protons, and a singlet at 7.08 ppm for the phenyl protons. The integration was 24:41:8:40 for the 4-methyl/the methyl attached at C-2 plus the methylene/the vinyl/the phenyl protons, respectively.

Reaction of vinyllithium and isopropenyltriphenylphosphonium bromide

Essentially the same procedure as described above was used in the reaction of 11 mmoles of the phosphonium salt with an equimolar amount of vinyllithium, followed by Wittig reaction with benzaldehyde (15 mmoles). GLC analysis of the distillate (column A, 142°, 20 p.s.i., acetophenone standard) showed the presence of two isomers (present in equal amounts) of 1-phenyl-2-methyl-1,4-pentadiene (92 % yield). Samples of both were collected by GLC. For the isomer with the shorter retention time (16.5 min) an analysis was carried out. (Found: C, 91.17; H, 8.84. $C_{12}H_{14}$ calcd.: C, 91.08; H, 8.92 %.)

The NMR spectrum (CCl_4) showed a singlet split slightly into a doublet ($J =$ 1.25 cps) at 1.76 ppm for the methyl protons, a doublet ($J = 6.5$ cps) at 2.79 ppm for the methylene protons, two broad singlets with much fine splitting at 4.89 and 5.13 ppm for the 5-vinyl protons, a multiplet from 5.47 to 6.05 ppm for the 4-vinyl proton, a broad singlet with much fine splitting (a $J = 1.25$ cps could be seen) at 6.21 ppm for the 1-vinyl proton, and a singlet at 7.12 ppm for the phenyl protons. The integration was 32:21:21:20:52 for the methyl/methylene/5-vinyl/4-vinyl and 1-vinyl/phenyl peaks respectively.

For the isomer with the longer GLC retention time (19 min) an analysis was carried out. (Found: C, 91.17; H, 8.84. $C_{12}H_{14}$ calcd.: C, 91.08; H, 8.92 %.)

The NMR spectrum (CCl_4) showed a singlet slightly split into a doublet (J = 1.25 cps) at 1.82 ppm for the methyl protons, a doublet (J = 6 cps) at 2.89 ppm for the methylene protons, two broad singlets with much fine splitting at 4.91 and 5.14 ppm for the two 5-vinyl protons, a multiplet from 5.50 to 6.08 ppm for the 4-vinyl proton, a broad singlet at 6.30 ppm for the 1-vinyl proton, and a singlet at 7.14 ppm for the phenyl protons. The integration was 33:22:21:11:11:56, respectively.

Reaction of n-butyllithium and isopropenyltriphenylphosphonium bromide

The same procedure (11.7 mmoles each of phosphonium salt and *n*-butyllithium, 15 mmoles of benzaldehyde) was followed. GLC analysis of the distillate (column A, 175°, 20 p.s.i., *n*-dodecane standard) showed the presence of two isomers of 1-phenyl-2-methyl-1-heptene (99 % yield). The isomer of longer retention time (15 min), isomer B, was present in larger amount (60 %), than the other isomer (12 min retention time), isomer A. Samples of both isomers were collected by GLC. (Found for isomer A: C, 89.37; H, 10.68. Found for isomer B: C, 89.26; H, 10.60. $C_{14}H_{20}$ calcd.: C, 89.29; H, 10.71 %.)

The NMR spectra (CCl_4) of both isomers showed a multiplet from 0.69 to 1.00 ppm for the 7-methyl and part of the methylene protons, a multiplet from 1.00 to 1.58 ppm for most of the 4-methylene, 5-methylene and 6-methylene protons, a singlet slightly split into a doublet (J = 1.25 cps) at 1.78 ppm for the 2-methyl protons, a triplet (J = 7 cps) at 2.10 ppm for the 3-methylene protons, a broad singlet at 6.04 ppm for the vinyl proton, and a singlet at 6.92 ppm for the phenyl protons. The integration was 53:19:12:6:30 for the (7-methyl and 4-, 5- and 6-methylene)/2-methyl/3-methylene/vinyl/phenyl peaks, respectively. In the spectrum for isomer B, the peak at 1.25 ppm was slightly split into a triplet (J = 2 cps).

Reaction of phenyllithium and isopropenyltriphenylphosphonium bromide

(*a*) *Benzaldehyde quench.* To a stirred suspension of 8.9 mmoles of isopropenyltriphenylphosphonium bromide and 90 ml of ether was added 8.9 mmoles of phenyllithium. To the resulting deep red mixture was added 0.92 g (8.7 mmoles) of benzaldehyde. The resulting white slurry was stirred and heated at reflux overnight. It then was filtered and the volatile materials were distilled directly from the filtrate (pot temperature to 155°/0.4 mm) into a Dry Ice-cooled receiver. GLC analysis of the distillate (column A, 194°, 20 p.s.i.) showed the presence of two isomers of 1,3-diphenyl-2-methylpropene (86 % yield) (isomer A, retention time 26 min, 58 %; isomer B, retention time 30 min, 42 %). Samples of each isomer were collected by GLC. (Found for isomer A: C, 92.48; H, 7.72. Found for isomer B: C, 92.47; H, 8.05. $C_{16}H_{16}$ calcd.: C, 92.26; H, 7.74 %.)

The NMR spectrum (CCl_4) of isomer A showed a singlet slightly split into a doublet (J = 1.4 cps) at 1.77 ppm for the methyl protons, a singlet at 3.58 ppm for the methylene protons, a singlet at 6.52 ppm for the vinyl proton, and a doublet (J = 2 cps) at 7.21 ppm for the aromatic protons. The integration was 24:16.5:8:81, respectively.

The NMR spectrum (CCl_4) of isomer B showed a singlet slightly split into a doublet (J = 1.0 cps) at 1.76 ppm for the methyl protons, a singlet at 3.39 ppm for the methylene protons, a singlet at 6.34 ppm for the vinyl protons, and a singlet at

7.18 ppm for the phenyl protons. The integration was 27:18:10:92, respectively.

(*b*) *Hydrobromic acid quench.* To a stirred suspension of 4.00 g (10.4 mmoles) of isopropenyltriphenylphosphonium bromide and 120 ml of ether was added 10.4 mmoles of phenyllithium. The resulting deep red mixture was treated with 48 % hydrobromic acid (about 1.5 ml) until the color had been discharged and a thick solid formed. The mixture was filtered and the solid was dissolved in chloroform. The resulting chloroform solution was washed with aqueous potassium bromide solution until neutral. White crystals of (3-phenyl-2-propyl)triphenylphosphonium bromide (3.86 g, 80 % yield), m.p. 162–163°, were precipitated by boiling off the chloroform while adding ethyl acetate. (Found: C, 69.52; H, 6.31. $C_{27}H_{28}BrP$ calcd.: C, 70.28; H, 5.68 %.)

The NMR spectrum ($CDCl_3$) showed a doublet of a doublet ($J = 7$ cps, $J = 19$ cps) at 1.24 ppm for the methyl protons, a doublet of a doublet ($J = 12$ cps, $J = 27$ cps) at 2.35 ppm for the methylene protons, a multiplet from 3.2 to 3.8 ppm for the methinyl proton, and a complex multiplet from 7.3 to 8.4 ppm for the phenyl protons. The integration was 21:13:6:128, respectively.

The tetraphenylborate, m.p. 179–181°, was prepared by adding an aqueous methanolic solution of sodium tetraphenylborate to an aqueous methanolic solution of the bromide and was recrystallized from pyridine. (Found: C, 87.11; H, 6.90. $C_{51}H_{46}BP$ calcd.: C, 86.79; H, 7.28 %.)

(*c*) *Aqueous base quench.* To a stirred suspension of 7.8 mmoles of isopropenyltriphenylphosphonium bromide and 75 ml of ether was added 7.9 mmoles of phenyllithium. Fifty ml of water and then 0.8 g (20 mmoles) of sodium hydroxide was added. The mixture consisted of 0.54 g of tan solid, an aqueous layer and an ethereal layer; these were separated. The ether layer was evaporated to dryness, leaving 0.51 g of tan solid, m.p. 182–184°. A tan solid (0.49 g, m.p. 183–198°) precipitated when the water layer was heated at reflux overnight. The crude (3-phenyl-2-propyl)diphenylphosphine oxide (66 %) was recrystallized from ethanol/water to yield white crystals, m.p. 183.5–185° (50 % yield). (Found: C, 78.84; H, 6.88. $C_{21}H_{21}OP$ calcd.: C, 78.73; H, 6.61 %.)

The NMR spectrum ($CDCl_3$) showed a doublet of a doublet ($J = 6$ cps, $J = 16$ cps) at 1.06 ppm for the methyl protons, a multiplet from 2.14 to 3.28 ppm for the methylene and methinyl protons, a singlet at 7.18 ppm for the 3-phenyl protons, a broad singlet at 7.47 ppm for the *meta* and *para* protons of the *P*-phenyl groups, and a multiplet (symmetrical with much fine splitting) from 7.68 to 8.14 ppm for the *ortho* protons of the *P*-phenyl groups. The integration was 18:18:30:38:25, respectively.

The IR spectrum ($CDCl_3$ and $CHCl_3$) showed bands at 3070 (m), 3050 (m), 3010 (m), 2960 (m), 2930 (m), 2860 (w), 1950 (w), 1875 (w), 1800 (w), 1600 (m), 1585 (m), 1490 (m), 1480 (sh), 1455 (m), 1440 (s), 1370 (m), 1330 (w), 1300 (w), 1240 (w), 1200 (sh), 1185 (s), 1130 (s), 1105 (sh), 1075 (w), 1000 (m), 900 (w), and 860 (w) cm^{-1}.

Reaction of triphenylphosphinemethylene and isopropenyltriphenylphosphonium bromide

To a stirred suspension of 5.62 mmoles of methyltriphenylphosphonium bromide and 35 ml of tetrahydrofuran was added 5.62 mmoles of ethereal phenyllithium. To the resulting solution was added 2.14 g (5.62 mmoles) of isopropenyltriphenylphosphonium bromide. The mixture quickly became deep red and almost homogeneous. When another 5.62 mmoles of phenyllithium was added, the mixture became very dark and showed a negative Gilman Color Test I. Addition of benzaldehyde (15.4 mmoles) resulted in a vigorous reaction. The resulting dark brown solution was stirred and heated at reflux for 36 h. The volatile materials were distilled directly from the mixture (pot temperature to 175°/0.2 mm) into a Dry Ice-cooled receiver. GLC analysis (column D, 200°, 16 p.s.i.) showed the presence of four isomers of 1,5-diphenyl-2-methyl-1,4-pentadiene. Retention times and isomer percentages: isomer A, 7.3 min, 7 %; isomer B, 8.8 min, 59 %; isomer C, 12.3 min, 29 %; isomer D, 15.2 min, 6 %. The mixed isomers were collected by GLC. There was obtained 0.31 g (23 % yield) of clear colorless liquid. (Found: C, 92.21; H, 7.76. $C_{18}H_{18}$ calcd.: C, 92.26; H, 7.74 %.)

The NMR spectrum (CCl_4) of the mixture of isomers showed an unsymmetrical triplet with fine splitting at 1.70, 1.82 and 1.80 ppm for the methyl protons, a multiplet from 2.85 to 3.50 ppm for the methylene protons, a multiplet centered at 6.33 ppm for the vinyl protons and the phenyl protons centered at 7.18 ppm. The integration was 17:11:18:93, respectively.

Another experiment was run in the same way on a 10.9 mmole scale. GLC analysis of the distillate (1,3-diphenoxypropane standard) showed a total yield of 1,5-diphenyl-2-methyl-1,4-pentadiene of 37 % with isomer percentages of A, 19 %; B, 52 %; C, 26 %; D, 3 %. Samples were collected by GLC.

The IR spectrum (CCl_4) of the mixed isomers showed bands at 3075 (m), 3050 (m), 3020 (s), 2955 (m), 2920 (sh), 2900 (m), 2875 (sh), 2840 (sh), 2820 (sh), 2780 (sh), 1960 (sh), 1940 (w), 1875 (w), 1820 (sh), 1800 (w), 1740 (w), 1645 (m), 1630 (sh), 1600 (s), 1570 (w), 1495 (s), 1445 (s), 1395 (sh), 1375 (m), 1350 (w), 1170 (w), 1100 (w), 1070 (m), 1025 (m), 975 (sh), 960 (s), 920 (sh), 910 (m) and 695 (s) cm^{-1}.

Samples collected of individual isomers contained about 10 % of the other isomers. The IR spectrum (CCl_4) of isomer C did not have bands at 2955, 1740 or 1395 (sh) cm^{-1}. The spectrum was otherwise identical to that of the mixture of isomers, except that the band at 960 (s) cm^{-1} was much more intense *vis-à-vis* the bands at 1070 (m), 1025 (m) and 910 (m) cm^{-1}. The IR spectrum (CCl_4) of isomer B showed new bands at 1280 (w), 1245 (s) and 860 (s) cm^{-1}, but did not have a band at 1350 cm^{-1}. The spectrum was otherwise identical to that of the mixture of isomers except that the band at 2955 cm^{-1} was strong and the band at 960 cm^{-1} was medium.

The NMR spectrum (CCl_4) of isomer B (ignoring the peaks of the 10 % of the other isomers) showed a singlet slightly split into a doublet (J = 1.3 cps) at 1.85 ppm for the methyl protons, a doublet (J = 7.5 cps) at 3.16 ppm for the methylene protons, a doublet (J = 12 cps) of a triplet (J = 7.5 cps) at 5.79 ppm for the 4-vinyl proton, a singlet at 6.33 ppm for the 1-vinyl proton, a doublet (J = 12 cps) at 6.57 ppm for the 5-vinyl proton, and a doublet (J=4 cps) at 7.24 ppm for the phenyl protons.

Reaction of allyltriphenylphosphonium bromide and methanolic base

The methanol was boiled from a solution of 31.1 g of allyltriphenylphosphonium bromide and 10 drops of 40 % aqueous benzyltrimethylammonium hydroxide in 300 ml of methanol as ethyl acetate was being added. White solid (2-methoxypropyl)-triphenylphosphonium bromide, 19.1 g (78 %), m.p. 194.5–196°, precipitated. (The mixed m.p. with either the starting material or 1-propenyltriphenylphosphonium bromide was depressed.) (Found: C, 63.40; H, 6.02. $C_{22}H_{24}BrOP$ calcd.: C, 63.62; H, 5.82 %.)

The NMR spectrum ($CDCl_3$) showed a doublet of a doublet ($J = 5$ cps, $J = 2.5$ cps) at 1.51 ppm for the 3-methyl protons, a singlet at 2.78 ppm for the methoxyl protons, a multiplet for the methylene and methinyl protons consisting of singlets at 3.54, 3.86, 4.04, 4.23, 4.43, and 4.63 ppm and a broad peak from 3.60 to 3.80 ppm, and the phenyl protons centered at 7.78 ppm. The integration was 20:20:20:112, respectively.

The iodide melted 196–198°. (Found: C, 57.37; H, 5.67. $C_{22}H_{24}IOP$ calcd.: C, 57.15; H, 5.23%.)

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SUMMARY

The action of phenyllithium on vinyltriphenylphosphonium bromide resulted both in formation of $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2C_6H_5$ (*ca.* 45%) and in proton abstraction (in part from the α proton of the vinyl group) by the organometallic base. Even lower yields of the corresponding phosphinemethylenes were obtained when methyl- or ethyllithium are used. (β-Bromoethyl)triphenylphosphonium bromide and ethylene-1,2-bis(triphenylphosphonium) dibromide served well in the *in situ* generation of the vinylphosphonium salt in such reactions. Similar addition of phenyllithium to 1-propenyltriphenylphosphonium bromide and (1-methyl-1-propenyl)triphenylphosphonium bromide also was realized, but only in very low yield due to complicating side reactions. Organolithium reagents added to isopropenyltriphenylphosphonium bromide to give $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(CH_3)CH_2R$ in high yield. Noteworthy is the observed addition of triphenylphosphinemethylene to isopropenyltriphenylphosphonium bromide.

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