9.8 min (~7%). The various fractions, except the first higher boiling fraction, were collected by preparative glpc.

The infrared spectrum of the 2-butanol, derived from the reduction of 0.73 g (0.01 mole) of *trans*-2-butene oxide in 10 ml of 1.01 *M* borane-d_3 in tetrahydrofuran, was identical with the spectrum of authentic *erythro*-3-deuterio-2-butanol. Spin decoupling of the high-field methyl signal produced a broadened doublet for the methylene hydrogen identical in position with that observed under identical spin-decoupling conditions with *erythro*-3-deuterio-2-butanol.

The second high-boiling fraction (retention time of 1.80 min) was purified by molecular distillation at 55–57° (0.5 mm). The infrared spectrum showed intense O–H and C–O absorption peaks. The nmr spectrum of the sample displayed a triplet at −62.9 cps (*J* of 8 cps) and two overlapping doublets at −67.3 and 68.9 cps (*J*'s of 7 cps each) in the methyl region corresponding to nine hydrogens, a multiplet in the unsubstituted methylene region at −88 cps corresponding to 3.6 hydrogens, and a broad multiplet at −203 cps corresponding to 5.1 hydrogens.

The highest boiling fraction (retention time of 9.8 min) was purified by molecular distillation at 100° (0.2 mm). The infrared spectrum displayed intense O–H and C–O absorption peaks. The nmr spectrum displayed a triplet at −62 cps (*J* of 7 cps) and two overlapping doublets at −65 and −67 cps (*J*'s of 6 cps each) in the methyl region corresponding to 9.0 hydrogens, a broad multiplet in the unsubstituted methylene region at −94 cps, corresponding to 7.7 hydrogens, and a broad multiplet at −206 cps corresponding to 9.1 hydrogens.

Reduction of Styrene Oxide. To a solution of 7.0 g (0.058 mole) of styrene oxide in 55 ml of tetrahydrofuran was added 56.1 ml of 1.04 *M* borane in tetrahydrofuran. No exothermic reaction was noted. The reaction mixture was allowed to stand at room temperature for 12 days in a sealed flask and was then worked up as described for the reduction of *cis*-2-butene oxide. Analysis of the residue by glpc on a 5-ft 20% Carbowax 20M column on Chromosorb W at 180° with a helium flow rate of 1 ml/sec showed seven peaks with retention times of 1.27 (unidentified, <1%), 1.76 (styrene oxide, 8%), 2.58 (1-phenylethanol, 1%), 3.6 (2-phenylethanol, 41%), and three higher boiling fractions at 5.6 (~0.7%), 7.4 (~24%), and 9.6 min (~3.2%). The 2-phenylethanol and 7.4-min fractions were collected by preparative glpc.

The nmr spectrum of the 2-phenylethanol, derived by reduction of styrene oxide (0.61 g, 0.005 mole) with 5.0 ml of 1.01 *M* borane-d_3 in tetrahydrofuran for 9 days, displayed a broadened doublet at −158 cps ($C_6H_5CH_2$, relative intensity of 1.76 hydrogens), a singlet at −198 cps (assigned to the hydroxyl hydrogen), a barely resolved triplet at −212 cps (CH_2OH, relative intensity of 1.24), with aromatic hydrogen absorption appearing at −437 cps.

The 7.4-min fraction was purified by molecular distillation at approximately 75° at 0.2 mm. The nmr spectrum displayed a triplet at −53 cps (*J* of 7 cps) with a relative intensity of three hydrogens, a broad multiplet at −84 cps (intensity of four hydrogens), a singlet at −139 cps (intensity of one hydrogen), a multiplet at −203 (intensity of four hydrogen), an apparent triplet at −255 cps (intensity of one hydrogen), and aromatic hydrogen absorption at −421 cps.

Reduction of *trans*-Stilbene Oxide with Borane-d_3 in Tetrahydrofuran. A mixture of 1.00 g (0.005 mole) of *trans*-stilbene oxide and 5.0 ml of 1.01 *M* borane-d_3 in tetrahydrofuran was placed in a sealed ampoule and allowed to stand at room temperature for 19 days, during which time the reaction mixture became gelatinous. The reaction mixture was worked up as described above. Analysis of the reaction mixture on a 5.5-ft 20% Carbowax 20 M on firebrick column showed the presence of diphenylacetaldehyde, *trans*-stilbene oxide, 1,2-diphenylethanol, and 2,2-diphenylethanol (approximately equal amounts of the 1,2- and 2,2-diphenylethanols were present). The mixture was partially separated by column chromatography on Florisil, the 1,2-diphenylethanol, 2,2-diphenylethanol, and apparent polymeric material fraction (approximately 0.22 g) being finally separated by preparative gas–liquid partition chromatography. Infrared analysis of the 1,2-diphenylethanol fraction thus derived indicated a mixture of *threo*- and *erythro*-2-deuterio-1,2-diphenylethanol of 2.2 to 1.0. The presence of 1-deuterio-1,2-diphenylethanol was quite low and could not be unambiguously determined.

Reduction of *cis*-Stilbene Oxide with Borane-d_3 in Tetrahydrofuran. Reduction of 1.00 g (0.005 mole) of *cis*-stilbene with 5.0 ml of 1.01 *M* borane-d_3 in tetrahydrofuran was carried out as described for *trans*-stilbene. Analysis and separation by column chromatography on Florisil gave 4% diphenylacetaldehyde, 17% 1,2-diphenylethanol, 17% 2,2-diphenylethanol, and 25% unidentified product, apparently polymeric material. Analysis of the nmr spectrum of the benzoate prepared from the 1,2-diphenylethanol fraction showed the presence of 6% 1-deuterio-1,2-diphenylethanol, 65% *threo*-2-deuterio-1,2-diphenylethanol, and 29% *erythro*-2-deuterio-1,2-diphenylethanol.

Studies in Phosphinemethylene Chemistry. XV. The Reaction of Tetraarylphosphonium Bromides with Vinylic Organolithium Reagents[1]

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Abstract: The reaction of vinyllithium with tetraphenylphosphonium bromide was found to give styrene (65%) and triphenylphosphine (80%). Further studies suggested that these are formed *via* intermediate vinyltetraphenylphosphorane. When isopropenyllithium was used, α-methylstyrene was produced in 70% yield, but analogous reactions of *cis*- and *trans*-1-propenyllithium gave only low yields of *cis*- and *trans*-propenylbenzene, respectively. The reaction of vinyllithium with tetra-*p*-tolylphosphonium bromide resulted in formation of *p*-methylstyrene (61%).

In a previous paper of this series,[5] we showed that the major reaction occurring between alkyllithium reagents and tetraphenylphosphonium bromide can be summarized by eq 1. A mechanism involving formation of an intermediate pentacovalent phosphorane,

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[1] (a) Part XIV: D. Seyferth and J. Fogel, *J. Organometal. Chem.*, in press; (b) preliminary communication: D. Seyferth, J. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, **86**, 307 (1964); (c) presented in part at the IUPAC Symposium on Organophosphorus Compounds, Heidelberg, May 20–22, 1964.

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[3] National Science Foundation Predoctoral Fellow, 1960–1963; National Institutes of Health Predoctoral Fellow, 1963–1965.

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[5] D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3467 (1965).

$$[(C_6H_5)_4P]Br + RCH_2Li \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HR + C_6H_6 + LiBr \quad (1)$$

$(C_6H_5)_4PCH_2R$, and concerted decomposition of the latter to give benzene and a triphenylphosphinealkylidene was favored. However, the evidence for such a mechanism was only circumstantial in nature, and such a pentacovalent intermediate could not be isolated. On the other hand, pentaphenylphosphorane[6] was stable up to its melting point of 124°, and at 130° underwent decomposition to give benzene (81%), triphenylphosphine (22%), biphenyl (22%), and 9-phenyl-9-phosphafluorene (10%).[7] The stability of pentaphenylphosphorane suggested that a vinyltetraphenylphosphorane might be sufficiently stable to permit isolation. If that were indeed possible, then hydrogenation of the latter should lead to formation of ethyltetraphenylphosphorane, the suspected intermediate in the tetraphenylphosphonium bromide–ethyllithium reaction. This product should (if the postulates cited above were to be correct) not be isolable and should decompose to benzene and triphenylphosphineethylidene (eq 2 and 3). Such a reaction sequence,

$$[(C_6H_5)_4P]Br + CH_2{=}CHLi \longrightarrow (C_6H_5)_4PCH{=}CH_2 + LiBr \quad (2)$$

$$(C_6H_5)_4PCH{=}CH_2 + H_2 \xrightarrow{\text{catalyst}} (C_6H_5)_4PCH_2CH_3 \longrightarrow C_6H_6 + (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_3 \quad (3)$$

if observed, would provide more direct evidence in favor of the postulated pentavalent phosphorus intermediate.

For these reasons the action of vinyllithium on tetraphenylphosphonium bromide was studied. The results were best described by eq 4, rather than by eq 2. This

$$[(C_6H_5)_4P]Br + CH_2{=}CHLi \longrightarrow (C_6H_5)_3P + C_6H_5CH{=}CH_2 + LiBr \quad (4)$$

result was of considerable interest for two reasons: (a) it suggested the possibility of a new and perhaps useful arylolefin synthesis based on organophosphorus chemistry, and (b) it was reminiscent of one mode of pentaphenylphosphorane decomposition, that which yields $(C_6H_5)_3P$ and biphenyl, and hence provided a suggestion that perhaps the reaction of vinyllithium with tetraphenylphosphonium bromide did lead initially to a $(C_6H_5)_4PCH{=}CH_2$ intermediate. Accordingly, it was decided to study this reaction and its various ramifications in greater detail.

When an ethereal suspension of tetraphenylphosphonium bromide was treated at room temperature with an ethereal solution of vinyllithium, an exothermic reaction which was accompanied by development of a deep red color commenced immediately. At −78° no reaction occurred, and at −15 to −30° the reaction proceeded at a measurable rate. The organic phase of the hydrolyzed reaction mixture was distilled *in vacuo* into a receiver at −78° and analyzed by glpc. The yield of styrene was 65%. The distillation residue was extracted to give triphenylphosphine (80%). Proton nmr studies of such tetraphenylphosphonium bromide–vinyllithium reaction mixtures showed that only vinyllithium was present in solution at −55°, but that only styrene was present in solution at room temperature. Glpc analysis of a crude reaction mixture (without work-up) showed the reaction to be complete within 25 min at room temperature.

Experiments were also performed in which aliquots of the supernatant liquid of the reaction mixture were removed at various time intervals. The samples were injected into water in such a way that the ethylene (formed from vinyllithium and water) was trapped as 1,2-dibromoethane in a bromine solution. Styrene and 1,2-dibromoethane were determined by quantitative gas–liquid chromatography. It was seen that at −78° no reaction occurred, that at *ca.* −30° styrene was slowly formed, and that at room temperature the reaction was rapid.

Two paths for the reaction, both involving initial attack at the phosphorus atom, seemed most likely. The first (mechanism A) involved attack by vinyllithium at the phosphorus atom to form vinyltetraphenylphosphorane as an unstable intermediate (eq 2), followed by decomposition of the latter to styrene and triphenylphosphine (eq 5). The second possibility considered

$$(C_6H_5)_4PCH{=}CH_2 \longrightarrow (C_6H_5)_3P + C_6H_5CH{=}CH_2 \quad (5)$$

(mechanism B) is illustrated by eq 6–9.

$$[(C_6H_5)_4P]Br + CH_2{=}CHLi \longrightarrow [(C_6H_5)_3PCH{=}CH_2]Br + C_6H_5Li \quad (6)$$

$$[(C_6H_5)_3PCH{=}CH_2]Br + C_6H_5Li \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2C_6H_5 + LiBr \quad (7)$$

$$(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2C_6H_5 \longrightarrow (C_6H_5)_3P + C_6H_5CH{=}CH_2 \quad (8)$$

$$(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2C_6H_5 \longrightarrow (C_6H_5)_3\overset{+}{P}CH_2\overset{-}{C}HC_6H_5 \longrightarrow (C_6H_5)_3P + C_6H_5CH{=}CH_2 \quad (9)$$

The reactions (eq 2 and 5) involved in mechanism A, as mentioned above, are very similar to those observed in the formation and in one decomposition pathway of pentaphenylphosphorane, respectively. It did not seem unreasonable that vinyltetraphenylphosphorane would decompose at a lower temperature than pentaphenylphosphorane, and that only one mode of thermal decomposition would be observed for the vinylic phosphorane.

Mechanism B required that $(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH_2C_6H_5$ formed in eq 7 be unstable in ether at room temperature with decomposition *via* eq 8 or 9 to styrene and triphenylphosphine. As was found out in studies subsequent to our initial observation of the vinyllithium–tetraphenylphosphonium bromide reaction, phenyllithium does add to the vinylphosphonium bromide as shown in eq 6. The phosphinealkylidene reagent produced, however, is stable in ether solution and can be made to undergo the Wittig reaction with acetone.[1a] Thus mechanism B is eliminated.[8] However, mechanism A was thereby not proved and can only be considered the most probable one remaining *vis-à-vis* several less likely mechanisms.

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[6] G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949).

[7] G. Wittig and G. Geissler, *ibid.*, **580**, 44 (1953).

[8] It should be mentioned that some phosphinealkylidenes are not stable. Thus, triphenylphosphine-*n*-butoxymethylene decomposes at room temperature to give triphenylphosphine and products in principle derivable from $:CHOC_4H_9$.[9] Also, Bestmann, *et al.*,[10] have shown that certain phosphinealkylidenes decompose on being heated to give triphenylphosphine and olefin by a mechanism analogous to eq 9 above.

[9] G. Wittig and W. Böll, *Chem. Ber.*, **95**, 2526 (1962).

[10] H. J. Bestmann, H. Häberlein, and I. Pils, *Tetrahedron*, **20**, 2079 (1964).

Table I. The Reactions of 1-Propenyllithium with Tetraphenylphosphonium Bromide

Starting 1-propenyllithium, %		Volatile products, %					
		1-Propenylbenzene			1-Phenyl-1,3-butadiene[a]		Benzene, yield
cis	*trans*	Yield	*cis*	*trans*	Yield	*cis/trans*	
0	100	14	0	100	. . .	. . .	33
0	100	10	0	100	. . .	. . .	33
0	100	25	0	100	. . .	. . .	56
3	97	18	3	97	5	1.54	. . .
91	9	16	88.5	11.5	14	1.40	53
97	3	7	97	3	6	1.36	23
97	3	8.5	96.4	3.6	6.6	1.20	25

[a] Obtained when reaction mixture was quenched with benzaldehyde.

There is some evidence to suggest that the lifetime of a possibly involved vinyltetraphenylphosphorane is not long. Experiments were conducted by analyzing a reaction mixture of vinyllithium and tetraphenylphosphonium bromide for vinyllithium and styrene at timed intervals. Despite the fact that these reactions were heterogeneous, useful information could have been obtained under the proper conditions, namely, if the vinyllithium were seen to disappear much faster than the styrene appeared. This would have been good evidence for the formation of an intermediate in the reaction. However, the experiments only showed that vinyllithium disappeared from the reaction mixture in about 10 hr at −15° and that styrene appeared in about the same time interval. The experiments only showed that *if* an intermediate was involved in the reaction, it decomposed almost immediately, but not that an intermediate was involved.

When the reaction of tetraphenylphosphonium bromide and vinyllithium was carried out in a suspension of tetrahydrofuran in place of ether, the yield of styrene was not diminished (62%), although the recovery of triphenylphosphine was poorer (43%).

The reaction between tetraphenylphosphonium bromide and vinyllithium which gives styrene and triphenylphosphine does not account for the total consumption of reactants. When the usual red-brown reaction mixture was quenched with acetone, the color was discharged, but styrene (obtained in 60% yield) was the only olefinic product observed. Just what this experiment implies in terms of other species present is not known. It may be noted, however, that in the reaction of tetraphenylphosphonium bromide with methyllithium a red reaction mixture also was formed.[5] In that case the major side reaction which occurred (in addition to formation of triphenylphosphinemethylene, which is yellow in THF solution) was *ortho* proton abstraction from phenyl groups attached to phosphorus.

Other experiments were carried out in order to establish the scope of the 1-alkenyllithium–tetraarylphosphonium halide reaction, and to determine whether or not this reaction was stereospecific in terms of the geometry of the vinylic lithium reagents, as well as in terms of the structure of the aryl group transferred from phosphorus.

When tetra-*p*-tolylphosphonium bromide was treated with vinyllithium, *p*-methylstyrene (61%) was the only olefinic product obtained. This showed that the carbon atom of the aromatic ring originally attached to phosphorus in the phosphonium salt is the carbon atom of the aromatic ring that is attached to the vinyl group in the product. When tetraphenylphosphonium bromide was treated with isopropenyllithium, the only volatile product was α-methylstyrene (isopropenylbenzene) (70%). Specifically, neither 1-propenylbenzene nor allylbenzene was present. In experiments employing the same phosphonium salt and 1-propenyllithium, 1-propenylbenzene was the only C-9 hydrocarbon obtained (see below), no α-methylstyrene or allylbenzene being obtained.

The experiments conducted with 1-propenyllithium and tetraphenylphosphonium bromide were instructive in another manner. It was found that the starting 1-propenyllithium and the 1-propenylbenzene produced in the reaction contained the same *cis/trans* ratio, whether starting with material that was 100% *trans*, 97% *cis*, or of intermediate isomeric composition. The data are summarized in Table I. Thus, no geometric isomerization occurs in the reaction under discussion.

As can be seen in Table I, there were products other than 1-propenylbenzene and triphenylphosphine from the reaction of 1-propenyllithium and tetraphenylphosphonium bromide. Benzene was a product of every reaction and 1-phenyl-1,3-butadiene was a product when the reaction mixture was quenched with benzaldehyde. The two compounds are undoubtedly produced by the following reaction sequence (eq 10 and 11).

$$[(C_6H_5)_4P]Br + CH_3CH{=}CHLi \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH{=}CH_2 + C_6H_6 + LiBr \qquad (10)$$

$$(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH{=}CH_2 + C_6H_5CHO \longrightarrow (C_6H_5)_3PO + C_6H_5CH{=}CHCH{=}CH_2 \qquad (11)$$

These results are of interest in connection with some previous work in these laboratories. In our study of that portion of the reaction occurring between tetraphenylphosphonium bromide and methyllithium which leads to triphenylphosphinemethylene,[5] it was not possible to determine with certainty if a pentacovalent organophosphorus intermediate was involved or whether an exchange–proton abstraction sequence prevailed. In the present study, the part of the reaction of 1-propenyllithium and tetraphenylphosphonium bromide that leads to triphenylphosphinevinylmethylene (eq 10) could either involve a P(V) intermediate (eq 12 and 13)

$$[(C_6H_5)_4P]Br + CH_3CH{=}CHLi \longrightarrow (C_6H_5)_4PCH{=}CHCH_3 + LiBr \qquad (12)$$

$$(C_6H_5)_4PCH{=}CHCH_3 \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH{=}CH_2 + C_6H_6 \qquad (13)$$

or an exchange–proton abstraction sequence (eq 14 and 15).

$$[(C_6H_5)_4P]Br + CH_3CH{=}CHLi \longrightarrow [(C_6H_5)_3PCH{=}CHCH_3]Br + C_6H_5Li \quad (14)$$

$$[(C_6H_5)_3PCH{=}CHCH_3]Br + C_6H_5Li \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH{=}CH_2 + C_6H_6 + LiBr \quad (15)$$

One step (eq 15) of the exchange–metalation mechanism involves the reaction of phenyllithium and 1-propenyltriphenylphosphonium bromide. Thus, if the exchange–proton abstraction mechanism is operative, all the products of the 1-propenyltriphenylphosphonium bromide–phenyllithium reaction should be obtained in the reaction of 1-propenyllithium with tetraphenylphosphonium bromide. It has been found[1a] that when 1-propenyltriphenylphosphonium bromide is treated with phenyllithium, not only is the species $(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH{=}CH_2$ formed (eq 15), but also addition of phenyllithium to the double bond occurs (eq 16).

$$[(C_6H_5)_3PCH{=}CHCH_3]Br + C_6H_5Li \longrightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH(CH_3)C_6H_5 + LiBr \quad (16)$$

The phosphinealkylidene produced was characterized as 1,3-diphenyl-1-butene (6%) by its Wittig reaction with benzaldehyde. The absence of 1,3-diphenyl-1-butene from among the products of the reaction of 1-propenyllithium and tetraphenylphosphonium bromide suggests that no $(C_6H_5)_3\overset{+}{P}\overset{-}{C}HCH(CH_3)C_6H_5$ is formed in the reaction, and therefore that an exchange (eq 14) is not occurring. However, the failure to detect a product that would constitute at most a 6% yield cannot be considered as providing conclusive evidence concerning this question.

In summary, the reaction of vinylic lithium reagents with tetraarylphosphonium salts has been shown to give good yields of arylolefins in the case of vinyl- and isopropenyllithium, but not with 1-propenyllithium. It is possible that this reaction may have preparative utility when applied to other vinylic lithium reagents (*e.g.*, α- and β-styryllithium, α-stilbenyllithium, etc.), but further studies are required to establish the possible generality of this reaction.

Experimental Section

General Comments. Elemental analyses were performed by Dr. S. M. Nagy, Massachusetts Institute of Technology Microchemical Laboratory, Cambridge, Mass., Galbraith Laboratories, Knoxville, Tenn., or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Infrared 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.

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

Gas–liquid partition chromatography (glpc) was carried out on 12 mm × 10 ft glass columns packed with 25% General Electric Co. SE 30 Silicone Gum (column A), 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 psi of helium as carrier gas. A 12 mm × 3 ft column packed with the 710 fluid (column D) was also used. Gas–liquid partition chromatographic (glpc) 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 were compared with those of authentic materials and identification of products 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.

Preparation of Phosphonium Halides. Tetraphenylphosphonium bromide was prepared by the method of Horner and Hoffmann.[11] **Tetra-*p*-tolylphosphonium bromide** was prepared by a method adapted from the preparation of tetraphenylphosphonium bromide of Hirusawa, *et al.*[12] In a sealed tube under a nitrogen atmosphere were placed 3.40 g of tri-*p*-tolylphosphine, 1.91 g of *p*-bromotoluene, 0.04 g of nickel(II) bromide (anhydrous), and 5 g of methanol. The mixture was heated at 170° for 3 hr. After solvent and unconverted *p*-bromotoluene had been removed under reduced pressure, the residue was treated with 30 ml of water. Filtration gave 3.67 g of yellow solid, and another 0.38 g was precipitated from the filtrate by addition of potassium bromide. Recrystallization gave white solid, mp 325–327°, in 32% yield.

Anal. Calcd for $C_{28}H_{28}PBr$: C, 70.74; H, 5.94; Br, 16.81. Found: C, 70.51; H, 5.91; Br, 17.12.

The iodide melted at 267–269° (lit.[13] mp 260–264°).

Organolithium Reagents. Vinyllithium was prepared by treating a pentane solution of tetravinyltin with *n*-butyllithium and then dissolving the resulting solid vinyllithium in ether.[14]

The purity of various isomers of chloro- and bromopropenes was determined by quantitative glpc using column B at 40° and 10 psi for the chlorides and 80° and 10 psi for the bromides. *trans*-1-Propenyllithium and 2-propenyllithium were prepared from the corresponding bromide and lithium wire in ether.[15] Both *cis*- and *trans*-1-propenyllithium were prepared from the corresponding 1-chloropropene and lithium wire (containing 1.1% sodium).[16] In both cases it has been shown that isomeric purity is retained. Solutions of organolithium reagents were standardized by the double titration method using 1,2-dibromoethane in place of benzyl chloride.[17]

Reaction of Vinyllithium and Tetraphenylphosphonium Bromide. A. In Diethyl Ether. In a 300-ml, three-necked flask fitted with a magnetic stirrer and an efficient reflux condenser were placed 10.76 g (25.7 mmoles) of tetraphenylphosphonium bromide and 50 ml of ether. To the stirred suspension was added in one portion (under nitrogen) 127 ml of 0.20 *M* vinyllithium (25.4 mmoles). The mixture was refluxed gently and quickly became deep red-brown. After 8 min the Gilman Color Test I was negative. When, after 3 hr, 1 ml of water was added, the mixture turned lighter in color and a small amount of solid formed. The mixture was filtered to yield a clear, yellow filtrate and a tan, solid residue. The volatile materials were distilled directly from the filtrate (pot temperature to 100° (0.5 mm)) into a Dry Ice cooled receiver, leaving behind an orange, glassy residue. Analysis of the distillate by glpc (column C, 130°, 10 psi, toluene standard) showed that styrene had been formed in 65% yield. A sample of styrene was collected by glpc and had an infrared spectrum (pure liquid) identical with that of an authentic sample. A sample of the styrene thus isolated also was converted to 1,2-dibromo-1-phenylethane, which had a melting point and mixture melting point identical with a sample prepared from authentic styrene.

The orange residue from the distillation was triturated with ether, then filtered. To the ether extracts was added 20 g of methyl iodide, and the mixture thus formed was stirred at room temperature overnight with protection from light. Methyltriphenylphosphonium

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[11] L. Horner and H. Hoffmann, *Chem. Ber.*, **91**, 45 (1958).

[12] Y. Hirusawa, M. Oku, and K. Yamamoto, *Bull. Chem. Soc. Japan*, **30**, 667 (1957).

[13] D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 666 (1942).

[14] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

[15] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

[16] D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, **86**, 883 (1964).

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

odide (8.44 g) was obtained; this represents an 82% yield of triphenylphosphine. (In an independent experiment it was shown that triphenylphosphine is precipitated quantitatively as methyltriphenylphosphonium iodide under these conditions.) A recrystallized sample of the above methyltriphenylphosphonium iodide melted at 187–189° and showed no melting point depression with an authentic sample. The infrared spectrum (KBr) was identical with that of an authentic sample.

The tan residue from the filtration of the original reaction mixture was treated with 1 *N* hydrochloric acid and filtered to yield a clear, colorless filtrate. A filtered solution of 3 g of sodium tetraphenylborate and 0.1 g of aluminum chloride in water was added dropwise to this solution to precipitate 1.72 g of tetraphenylphosphonium tetraphenylborate. This is equivalent to a 10% recovery of tetraphenylphosphonium bromide. It was shown in a separate experiment that the tetraphenylphosphonium cation is precipitated by sodium tetraphenylborate from aqueous acid solution quantitatively as tetraphenylphosphonium tetraphenylborate under these conditions. A recrystallized (from pyridine) sample of tetraphenylphosphonium tetraphenylborate melted at 304–306° and its mixture melting point was not depressed. The infrared spectrum (Nujol mull) of the tetraphenylborate was identical with that of authentic material.

B. In Tetrahydrofuran. In a similar experiment (10-mmole scale) employing tetrahydrofuran in place of ether as the solvent, a 62% yield of styrene was obtained. In this experiment the residue from the distillation was triturated with ether and filtered. From the ethereal filtrate was obtained a 43% yield of triphenylphosphine, whose melting point (80–81.5°) was not depressed by admixture with an authentic sample.

In another experiment on a 10-mmole scale, samples of the supernatant liquid of the reaction mixture were examined by glpc. After 25 min styrene was present in 43% yield, and the quantity did not increase thereafter.

C. Acetone Quench. In another experiment (17-mmole scale) the ethereal reaction mixture was treated with 2 ml of dry acetone instead of water. The mixture became light tan and solid formed. Much of the ether was distilled from the mixture through a Widmer column, and then the remaining volatile components of the mixture were distilled directly (pot temperature to 155° (0.2 mm)) into a Dry Ice cooled receiver. Glpc analysis (column A, 130°, 20 psi, bromobenzene standard) showed that styrene was present in 60% yield, but no product with the retention time (16 min) of 2-methyl-4-phenyl-2-butene was observed.

D. At −78°. In a side-arm test tube (nitrogen inlet by way of the side arm) were placed 0.50 g (1.2 mmoles) of tetraphenylphosphonium bromide and 1.5 ml of ether, and the tube was placed in a Dry Ice–acetone bath. After 15 min, 1.37 ml (0.6 mmole) of 0.44 *M* vinyllithium was added under nitrogen at such a rate (over 5 min) as to keep the temperature below −55°. Efficient shaking was provided. After 3 hr at −78°, no apparent change had occurred. A sample of the supernatant liquid was withdrawn by pipet and placed in an nmr tube maintained at −78°.

The nmr spectrum of the sample (at −50 to −54°) was identical from 4.0 to 8.0 ppm with the spectrum of vinyllithium in ether.[18]

Another experiment was run in the same way, except that the 1.5 ml of ether was replaced by 1.5 ml of tetrahydrofuran. Again the nmr spectrum between 4.0 and 8.0 ppm was identical with that of vinyllithium in ether.

Reaction of *trans*-1-Propenyllithium with Tetraphenylphosphonium Bromide. A. Benzaldehyde Quench. To a stirred suspension of 25.8 mmoles of tetraphenylphosphonium bromide and 125 ml of ether was added 44 ml of 0.57 *M* (25.0 mmoles) *trans*-1-propenyllithium (prepared from 97% *trans*-1-chloropropene). The mixture slowly turned red. After 4 hr, the now deep red, almost homogeneous mixture was treated with 2.6 g (24.5 mmoles) of benzaldehyde. After the resulting yellow slurry was stirred and heated at reflux overnight, it was filtered. The volatile compounds were distilled directly from the filtrate (pot temperature to 150° (0.5 mm)) into a Dry Ice cooled receiver. Analysis of the distillate by glpc (column A, 105 and 210°, 20 psi; column B, 110°, 20 psi, ethylbenzene standard) showed the presence of 1-propenylbenzene (18% yield, 97% *trans*, and 3% *cis*) and 1-phenyl-1,3-butadiene (5% yield, *cis*/*trans* ratio, 1.54). 1,3-Diphenyl-1-butene, a comparison sample of which was available from the benzaldehyde-quenched reaction of phenyllithium and 1-propenyltriphenylphosphonium bromide,[1a] could not be detected. Samples of *trans*-1-propenylbenzene and both *cis*- and *trans*-1-phenyl-1,3-butadiene were collected by glpc. Each sample had an infrared spectrum (CCl_4) identical with that of the corresponding authentic sample.

B. Water Quench. Tetraphenylphosphonium bromide (21.1 mmoles) was treated with 21 mmoles (150 ml) of ethereal *trans*-1-propenyllithium and the mixture was stirred. After 10 min, the color of the mixture was red-brown and the Gilman Color Test I was negative. After it had been stirred overnight the dark red-brown mixture was treated with 1 ml of water. The resulting light orange mixture was filtered. Distillation of the volatile components from the filtrate (pot temperature to 100° (0.5 mm)) directly into a Dry Ice cooled receiver followed. Glpc analysis of the distillate (column C, 160°, 15 psi, toluene standard) showed the presence of *trans*-1-propenylbenzene (14% yield) and benzene (33% yield), but no *cis*-1-propenylbenzene. Benzene was collected by glpc and identified by its infrared spectrum (pure liquid). A sample of *trans*-1-propenylbenzene was collected by glpc and had an nmr spectrum (CCl_4) identical with that of an authentic sample. The ultraviolet spectrum ($CHCl_3$, Applied Physics Corp. Cary Model 14 recording spectrophotometer) showed λ_{max} 253 mμ (log ϵ 4.22), 285 (3.10), and 293 (2.94) (lit.[19] λ_{max} 249 mμ (log ϵ 4.16), 2.84 (3.01), and 293 (2.80).

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.36; H, 8.74.

The oily residue from the distillation was extracted with ether and to the ether was added 6.5 g of methyl iodide. The triphenylphosphine (9% yield) was precipitated as 0.705 g of methyltriphenylphosphonium bromide as described for the reaction between the phosphonium salt and vinyllithium in diethyl ether.

C. Acetone Quench. To a stirred suspension of 23 mmoles of tetraphenylphosphonium bromide and 125 ml of ether was added 23 ml of 0.98 *M* (23 mmoles) *trans*-propenyllithium (>99% yield). After 45 min the now dark red-brown mixture showed a negative Gilman Color Test I and much of the phosphonium salt had disappeared. When acetone (10 ml) was added, the mixture became lighter in color. The mixture was stirred for 2.5 hr and then was filtered. The volatile compounds were distilled directly from the filtrate (pot temperature to 130° (0.5 mm)) into a Dry Ice cooled receiver. Glpc analysis of the distillate (column C, 110°, 10 psi, mesitylene standard) showed the presence of *trans*-1-propenylbenzene (10% yield) and benzene (33% yield), but not of *cis*-1-propenylbenzene. If 4-methyl-1,3-pentadiene had been formed it would not have been detected under the conditions used.

The residue from the distillation was extracted with ether. The triphenylphosphine in these extracts was precipitated by methyl iodide (6 g) as 0.61 g of methyltriphenylphosphonium iodide (equivalent to a 7% yield of triphenylphosphine) using the procedure described for the reaction of the phosphonium salt with vinyllithium in ether.

Reaction of *cis*-1-Propenyllithium and Tetraphenylphosphonium Bromide. To a stirred suspension of 26 mmoles of tetraphenylphosphonium bromide and 150 ml of ether was added 27.6 ml of 0.94 *M* (26 mmoles) *cis*-1-propenyllithium (97% *cis*). After 7 hr, benzaldehyde (16.7 mmoles) was added to the deep red, almost homogeneous mixture. The resulting tan mixture was stirred overnight at room temperature and then filtered. The volatile materials were distilled directly from the filtrate (pot temperature to 140° (0.6 mm)) into a Dry Ice cooled receiver. Glpc analysis of the distillate (column A, 128°, 20 psi, toluene standard) showed the presence of 1-propenylbenzene (7% yield, 97% *cis* and 3% *trans*), 1-phenyl-1,3-butadiene (6% yield, *cis*/*trans* ratio, 1.36), and benzene (23% yield). In an identical experiment there were obtained 1-propenylbenzene (8.5% yield, 96.4% *cis* and 3.6% *trans*), 1-phenyl-1,3-butadiene (6.6% yield, *cis*/*trans* ratio, 1.20), and benzene (25% yield). Samples of *cis*-1-propenylbenzene and both isomers of 1-phenyl-1,3-butadiene were collected by glpc. Each had an infrared spectrum (CCl_4) identical with that of the corresponding authentic sample.

Another experiment employing 26.4 mmoles of tetraphenylphosphonium bromide and 26.4 mmoles of *cis*-1-propenyllithium (91% *cis*, 9% *trans*) was performed in the same way. The products were 1-propenylbenzene (16% yield, 88.5% *cis* and 11.5% *trans*), 1-phenyl-1,3-butadiene (14% yield, *cis*/*trans* ratio, 1.40), and benzene (53% yield). Samples of benzene and *trans*-1-phenyl-1,3-butadiene were collected by glpc and both had infrared spectra (CCl_4) identical with those of the corresponding authentic sample.

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(19) "Organic Electronic Spectral Data," Vol. I, M. J. Kamlet, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 255.

Preparation of Authentic 1-Propenylbenzene. To a stirred suspension of ethyltriphenylphosphonium bromide (83 mmoles) and 300 ml of ether was added 83 mmoles of phenyllithium solution. The resulting deep red mixture was treated with benzaldehyde (80 mmoles) and the thick mixture so formed was stirred and heated at reflux overnight. The cooled mixture was filtered and the ether was stripped from the filtrate. The rest of the filtrate then was distilled to give 3.88 g (41% yield) of 1-propenylbenzene, bp 65–67° (16 mm) (lit.[20] bp 74° (13 mm)). Glpc analysis (column A or C, 125°, 20 psi) showed a *trans/cis* ratio of 3.90 (retention times, *cis*, 11 min and *trans*, 14 min). Samples of each isomer were collected by glpc.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found for the *cis* isomer: C, 91.25; H, 8.66. Found for the *trans* isomer: C, 91.28; H, 8.75.

The refractive indices were *trans*, n^{25}D 1.5477; *cis*, n^{25}D 1.5403 (lit.[21a] *trans*, n^{25}D 1.5473; *cis*, n^{25}D 1.5400). The infrared spectrum (CCl_4) of each isomer was identical with that of the corresponding isomer recorded in the literature.[20] The high resolution of the Infracord 237 and 337 instruments permitted the observation of the following bands in the 3000-cm^{-1} region: *cis*, 3075 (m), 3050 (m), 3020 (s), 2975 (m), 2940 (m), 2910 (m), and 2850 (m) cm^{-1}; *trans*, 3075 (m), 3050 (m), 3020 (s), 2955 (m), 2920 (m), 2905 (s), and 2850 (m) cm^{-1}. The nmr spectrum (CCl_4) of each isomer was identical with that recorded in the literature.[21b]

Preparation of Authentic 1-Phenyl-1,3-butadiene.[22] To a stirred suspension of 9.41 g (24.6 mmoles) of allyltriphenylphosphonium bromide and 125 ml of ether was added 21.4 ml of 1.15 *M* (24.6 mmoles) phenyllithium. After 10 min the solution of triphenylphosphineallylidene was deep red. When 2.6 g (24.6 mmoles) of benzaldehyde was added to the mixture, an exothermic reaction commenced and a thick yellow slurry resulted. The mixture was stirred and heated at reflux for 5 hr and filtered. The volatile components of the filtrate were distilled directly (pot temperature to 120° (0.5 mm)) into a Dry Ice cooled receiver. Glpc analysis of the distillate (column A, 170°, 20 psi, toluene standard) showed that 1-phenyl-1,3-butadiene was present in 32% yield (*cis/trans* ratio, 2.13). Samples of each isomer were collected by glpc.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found for the *cis* isomer: C, 92.29; H, 7.81. Found for the *trans* isomer: C, 92.45; H, 7.67.

The nmr spectrum (CCl_4) of the *cis* isomer showed a singlet at τ = 7.17 ppm for the phenyl protons and a complex set of peaks from 4.90 to 6.90 ppm for the vinyl protons, as follows: 4.90–5.20, multiplet; 5.34, doublet (J = 2 cps); 5.87, singlet; 6.08, singlet; 6.25, doublet (J = 2 cps); 6.47, singlet; 6.62, singlet; 6.90 ppm, singlet. The integration was 66:70 for the aromatic:vinyl protons respectively. The nmr spectrum (CCl_4) of the *trans* isomer was the same as that of the *cis* isomer except the singlets at 6.47 and 6.62 were replaced by doublets at 6.51 (J = 5 cps) and ppm 6.75 (J = 5 cps).

The infrared spectra (CCl_4) of the individual isomers were identical with those recorded in the literature.[23,24]

Reaction of Isopropenyllithium and Tetraphenylphosphonium Bromide. To a stirred suspension of 14.3 mmoles of tetraphenylphosphonium bromide and 85 ml of ether was added 25 ml of 0.58 *M* (14.3 mmoles) isopropenyllithium. The mixture was refluxed gently and turned deep red-brown. When, after 2 hr, 0.5 ml of water was added, the almost homogeneous mixture became light pink and thick with solid. After the mixture was filtered, the volatile compounds were distilled directly (pot temperature to 145° (1 mm)) into a Dry Ice cooled receiver. Glpc analysis (column A, 140°, 20 psi, toluene standard) showed that α-methylstyrene had been produced in 70% yield. A sample of α-methylstyrene collected by glpc had infrared and nmr spectra (CCl_4) identical with those of an authentic sample.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.52; H, 8.55.

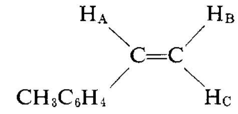
The residue from the distillation was extracted with ether; from the extracts was obtained triphenylphosphine (2.65 g after recrystallization), mp 79–81° (mixture melting point undepressed).

Reaction of Vinyllithium and Tetra-*p*-tolylphosphonium Bromide. To a stirred suspension of 1.23 g (2.6 mmoles) of tetra-*p*-tolylphosphonium bromide and 40 ml of ether was added 5.1 ml (2.6 mmoles) of 0.51 *M* vinyllithium. The resulting red-brown, almost homogeneous mixture showed a negative Gilman Color Test I after 30 min. When 0.5 ml of water was added, the red color was discharged. The clear yellow supernatant liquid was decanted from the small amount of tan gum. The volatile components in the former were distilled directly (pot temperature to 135° (0.6 mm)) into a Dry Ice cooled receiver. Glpc analysis of the distillate (column A, 115°, 20 psi, ethylbenzene standard) showed the presence of *p*-methylstyrene (61% yield). A sample was collected by glpc.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.23; H, 8.65.

The infrared spectrum (CCl_4) was identical with that recorded in the literature,[25] but differed from the spectra of *m*-methylstyrene[26] and *o*-methylstyrene[27] as follows. In the 2000- to 1650-cm^{-1} region, *p*-methylstyrene showed bands at 1895 and 1810 cm^{-1} typical of *para*-disubstituted benzenes, while *m*-methylstyrene showed a complex set of bands at 1950, 1880, 1830, 1790, and 1695 cm^{-1}, and *o*-methylstyrene showed two bands at 1830 and 1910 cm^{-1}. In the 1500–1400-cm^{-1} region, *p*-methylstyrene showed bands at 1405, 1450, and 1515 cm^{-1} while *o*-methylstyrene showed bands at 1418, 1441, 1460, and 1487 cm^{-1}. *m*-Methylstyrene showed bands at 1095 and 880 cm^{-1} unobserved with *p*-methylstyrene, but did not show a band at 1030 cm^{-1} as the latter did. *o*-Methylstyrene showed a band at 1158 cm^{-1} not observed with *p*-methylstyrene.

The nmr spectrum (CCl_4), which was identical with that recorded by Brügel, Ankel, and Krückeberg[28] (they only report the vinyl region), showed a singlet at 2.23 for the methyl protons, a doublet of a doublet (J = 17.5 cps, J = 1.5 cps) at 5.58 for the vinyl proton C (see figure below), a doublet of a doublet (J = 11 cps, J = 1.5 cps) at 5.10 for the vinyl proton B, a doublet of a doublet (J = 17.5 cps, J = 11 cps) at 6.60 for the vinyl proton A, and a symmetrical quartet with the larger center peaks (J = 5 cps) apart and the smaller outer peaks (J = 8.5 cps) further out at 7.08 ppm for the phenyl protons. The quartet for the phenyl protons is typical of a *para*-disubstituted benzene,[29] but is not observed with *ortho*-disubstituted benzenes,[30] which show singlets or a complex set of peaks, or *meta*-disubstituted benzenes,[31] which show a complex set of peaks.



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