Phosphonioethylation. Michael Addition to Vinylphosphonium Salts[1]

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The base-catalyzed reaction of vinylphosphonium salts with compounds containing replaceable hydrogen introduces a 2-substituted ethylphosphonium group. This reaction is called phosphonioethylation. Addition to tributylvinylphosphonium bromide of compounds containing –CH, –NH, –PH, –OH, and –SH has been carried out. Other vinylphosphonium salts react similarly. Diels–Alder addition of cyclopentadiene and bromination also have been observed. The adduct with isobutyrophenone undergoes intramolecular cyclization in the presence of base to give a cyclobutenylphosphonium salt. Michael addition to allylphosphonium salts has been investigated.

Although vinylphosphonium salts have been known for over a century,[3] their reactions have remained virtually unexplored. Doering and Schreiber,[4] have demonstrated that vinylsulfonium salts undergo anionic addition to give ylids stabilized by expansion of the octet of sulfur through $p\pi - d\pi$ overlap involving the vacant 3d orbital. Since this type of stabilization has been amply demonstrated with alkyl phosphonium compounds through the chemistry of the corresponding conjugate bases, the methylenephosphoranes,[5] we undertook a study of the chemistry of vinylphosphonium salts with particular emphasis on their electrophilic reactivity toward compounds containing replaceable hydrogen.

Some preliminary work in this area indicated that vinylphosphonium salts might be excellent alkylating agents. In 1959, in the course of our study of the elimination reactions of 2-cyanoethylphosphonium salts,[6] we observed that, in the presence of methanolic sodium methoxide, allyltris(2-cyanoethyl)phosphonium iodide reacted to give exclusively bis(2-cyanoethyl)-methoxypropylphosphine and none of the allylbis(2-cyanoethyl)phosphine. At that time, we speculated that the addition of methoxide occurred rapidly before

$$[CH_2{=}CHCH_2P(CH_2CH_2CN)_3]^+I^- \xrightarrow[CH_3OH]{CH_3ONa} (CH_3OC_3H_6)P(CH_2CH_2CN)_2 + CH_3OCH_2CH_2CN + NaI$$

the elimination reaction as a result of isomerization of the double bond and the activation provided by the phosphonium group. More recently, Kabachnik and co-workers[7] have described the addition of halogens, amines, alcohols, malonic esters, etc., to vinyldiphenylphosphine oxide.

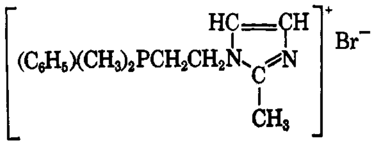
Tributylvinylphosphonium bromide prepared by basic elimination of acetate ion from tributyl-2-acetoxyethylphosphonium bromide was chosen as a model compound for this study.[8] We have found that this compound alkylates compounds containing replaceable hydrogen (Z–H) to yield 2-substituted ethylphosphonium salts. We call these reactions "phosphonioethylations."

$$[(C_4H_9)_3PCH{=}CH_2]^+Br^- + Z\text{–}H \longrightarrow [(C_4H_9)_3PCH_2CH_2Z]^+Br^-$$

Phosphonioethylation reactions of tributylvinylphosphonium bromide have been carried out with C–H compounds (*i.e.* isobutyrophenone, ethyl acetoacetate), with N–H compounds (*i.e.*, diethylamine, N-methylimidazole, benzimidazole), with an O–H compound (ethanol), and S–H compound (thiophenol), and with a P–H compound [bis(2-cyanoethyl)phosphine oxide] to give normal 1–1 Michael addition products. Reactions of tributylvinylphosphonium bromide with diethyl malonate, fluorene, and ethylene glycol gave the 2:1 diphosphonioethylated product. Finally, the addition of acetophenone to tributylvinylphosphonium bromide gave a high melting crystalline solid which is most probably the 3:1 adduct. However, since good molecular weight or n.m.r. data could not be obtained, the 2:1 adduct cannot be rigorously excluded.

All of these phosphonioethylations required gentle heating (53–137°) for 2–24 hr. and, with the exception of the amine and thiophenol additions, required catalysis by small amounts of inorganic or organic bases. The resulting products were obtained in yields of 69–95%. Specific reaction conditions and products are listed in Table I. In those cases where the phosphonium bromide was a syrup, it was converted to a crystalline tetraphenylborate derivative and is listed as such in Table I.

Variation of the vinylphosphonium salt substituents indicate that the reaction proceeds well with cycloaliphatic and mixed alkylaryl groups attached to phosphorus. When dimethylphenylvinylphosphonium bro-



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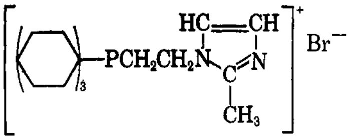

II

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(1) Phosphonium Compounds. IV. Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) To whom inquiries should be addressed.

(3) A. W. Hofmann, *Ann. Suppl.*, **1**, 145, 275 (1861).

(4) W. von E. Doering and K. C. Schreiber, *J. Am. Chem. Soc.*, **77**, 514 (1955).

(5) U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

(6) M. Grayson, P. T. Keough, and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959).

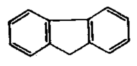
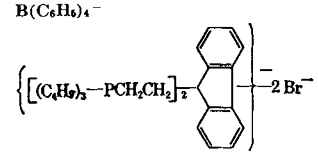
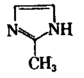
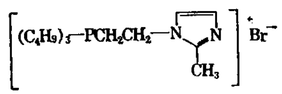
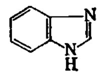
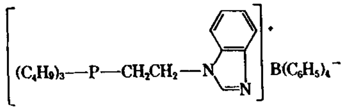
(7) M. I. Kabachnik, T. Ya Medved, Ya. M. Polikarpov, and K. S. Yudena, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk*, **9**, 1584 (1962).

(8) M. M. Rauhut, G. B. Borowitz, and H. C. Gillham [*J. Org. Chem.* **28**, 2565 (1963)] report the preparation of tributyl-2-acetoxyethylphosphonium bromide. The sodium carbonate-promoted elimination to give tributylvinylphosphonium bromide, m.p. 152–153°, was carried out in refluxing dimethoxyethane; *cf.* M. M. Rauhut, G. B. Borowitz, and M. Grayson, to be published.

(9) Prepared by R. Rabinowitz and R. Marcus, unpublished results, Central Research Division, American Cyanamid Co., Stamford, Conn.

TABLE I

PHOSPHONIOETHYLATION REACTIONS WITH TRIBUTYLVINYLPHOSPHONIUM BROMIDE

								Analysis, %									
								Calcd.						Found			
Addendum	Solvent	Catalyst	Temp., °C.	Time, hr.	Product	% yield[a]	M.p., °C.	C	H	P	N	S	Br	C	H	P	N	S	Br
$CH_3\overset{\overset{O}{\|}}{C}C_6H_5$	$CH_3\overset{\overset{O}{\|}}{C}C_6H_5$	$R_4N^+OH^-$ [b]	120	3.0	$\{[(C_4H_9)_3P\text{—}CH_2CH_2]_3C\overset{\overset{O}{\|}}{C}C_6H_5\}^{+3}3Br^-$ [c]	80	203-204	57.30	9.43	8.86			22.87	57.00	8.81	8.52			22.77
$(CH_3)_2CH\overset{\overset{O}{\|}}{C}C_6H_5$	C_6H_6	30% KOH-CH_3OH	80	3.0	$[(C_4H_9)_3PCH_2CH_2C(CH_3)_2\overset{\overset{O}{\|}}{C}C_6H_5]^+B(C_6H_5)_4^-$	95	152-153	82.73	8.97	4.44				82.66	8.83	4.55			
$CH_3\overset{\overset{O}{\|}}{C}CH_2\text{-}COOC_2H_5$	$CH_3\overset{\overset{O}{\|}}{C}CH_2\text{-}COOOC_2H_5$	10% NaOH	70	3.0	$[(C_4H_9)_3PCH_2CH_2CH(COOC_2H_5)\overset{\overset{O}{\|}}{C}CH_3]^+\text{-}B(C_6H_5)_4^-$	90	163-165	77.86	8.91	4.56				77.81	8.93	4.83			
$CH_2(\overset{\overset{O}{\|}}{C}OC_2H_5)_2$	$CH_2(\overset{\overset{O}{\|}}{C}C_2H_5)_2$	10% NaOH	137	3.0	$\{(C_4H_9)_3P\text{-}CH_2CH_2]_2C(COOC_2H_5)_2\}^{+2}2B(C_6H_5)_4^-$	77	137-139	79.28	8.98	4.93				79.19	8.94	5.11			
	CH_3CN	$R_4N^+OH^-$ [b]	82	9.0		92	225-226	62.77	8.99	7.89			20.36	62.50	9.25	7.66			20.48
	$CH_3OCH_2CH_2OCH_3$		80	2.5		85	165-166	55.23	9.27	7.91	7.15			55.25	9.00	8.15	7.45		
	$CH_3OCH_2CH_2OCH_3$		80	8.0		80	155	81.06	8.46	4.65	4.20			81.14	8.41	4.34	4.53		
$(C_2H_5)_2NH$	$(C_2H_5)_2NH$		53	0.5	$[(C_4H_9)_3\text{-}PCH_2CH_2N(C_2H_5)_2]^+B(C_6H_5)_4^-$	63	155-156	81.14	9.89	4.98	2.25			81.35	9.59	5.05	2.21		
C_2H_5OH	C_2H_5OH	$NaOC_2H_5$	78	8.0	$[(C_4H_9)_3PCH_2CH_2OC_2H_5]^+B(C_6H_5)_4^-$	87	174-175	80.78	9.49	5.20				80.25	9.12	5.00			
$HOCH_2CH_2OH$	*d*	10% NaOH	100	8.0	$\{(C_4H_9)_3PCH_2CH_2OCH_2CH_2OCH_2CH_2\text{-}P(C_4H_9)_3\}^{+2}2B(C_6H_5)_4^-$	85	155-156	80.81	9.22	5.34				80.83	9.26	5.06			
C_6H_5SH	CH_3CN		82	3.0	$[(C_4H_9)_3PCH_2CH_2SC_6H_5]^+B(C_6H_5)_4^-$	74	165-166	80.23	8.56	4.70		4.87		80.49	8.71	4.81		5.01	
$(NCCH_2CH_2)_2\overset{\overset{O}{\|}}{P}H$	CH_3CN	$R_4N^+OH^-$ [b]	82	24.0	$[(C_4H_9)_3PCH_2CH_2\overset{\overset{O}{\|}}{P}(CH_2CH_2CN)_2]^+B(C_6H_5)_4^-$	69	176-178	74.99	8.44	8.79	3.98			75.27	8.67	8.82	4.22		

[a] Yields are reported for the phosphonioethylated bromide. They are based on the mole quantity of tributylvinylphosphonium bromide in each experiment. [b] 40% benzyltrimethylammonium hydroxide in CH_3OH. [c] Most probably the 3:1 adduct. However, the calculated microanalytical values for the 2:1 adduct (C, 58.56; H, 9.29, 8.39; Br, 21.56) are sufficiently close to leave some doubt about the structure. No successful molecular weight determination could be made for this compound because of variable solution ionization. Furthermore, proton n.m.r. was inconclusive. [d] No solvent was used in this reaction and the stoichiometry was 0.05 mole of tributylvinylphosphonium bromide to 0.025 mole of ethylene glycol.

mide and tricyclohexylvinylphosphonium bromide[9] were allowed to react with 2-methylimidazole, I and II were obtained in 99 and 85% yields, respectively.

Other reactions of the vinyl group of tributylvinylphosphonium bromide have been carried out including bromination and Diels–Alder addition of cyclopentadiene. For example, bromine reacts with tributylvinylphosphonium bromide in carbon tetrachloride to give the oily product (III) which forms a low

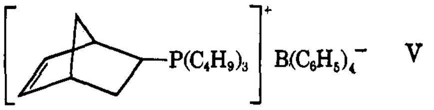
$$[(C_4H_9)_3PCHBrCH_2Br]^+Br^-$$
III

melting hygroscopic tetraphenylborate. Treatment of III with an equimolar amount of triethylamine yields triethylaminehydrobromide plus the sirup (IV), which

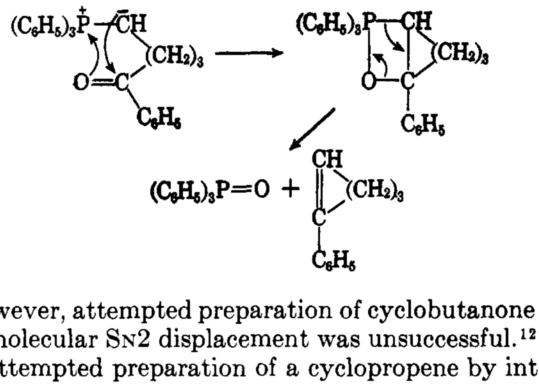
$$[(C_4H_9)_3PCBr{=}CH_2]^+Br^-$$
IV

can be converted to a crystalline tetraphenylborate. The position of the vinyl bromine in IV has not been positively determined, although elimination of the terminal bromine from III is anticipated on the basis of the acidity of the proton on carbon next to phosphorus, as well as analogy with the elimination chemistry of 1,2-dibromoethyldiphenylphosphine oxide[7] and 2-bromoethyltriethylphosphonium bromide.[3] Adequate resolution of the vinyl H region by n.m.r. could not be obtained for unambiguous isomer differentiation.

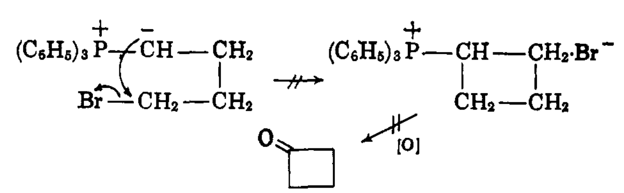
Kabachnik[7] also reported the Diels–Alder reaction of diphenylvinylphosphine oxide with cyclopentadiene obtained *in situ* by the thermal cracking of dicyclopentadiene. Under analogous conditions, tributylvinylphosphonium bromide reacted with cyclopentadiene to give a sirupy Diels–Alder adduct in 59% yield. This was converted to a crystalline tetraphenyl borate, presumably of the substituted norbornene structure indicated (V).


V

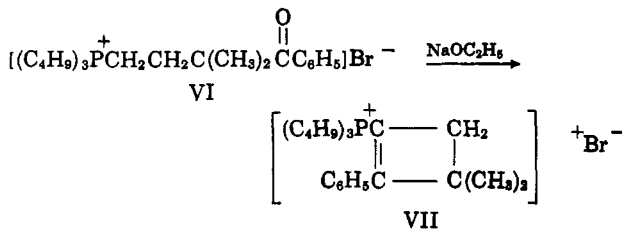
The use of methylenephosphoranes in the preparation of small ring olefins by intramolecular Wittig and other reactions has been reported recently by a number of groups.[10-14] For example, 1-phenylcyclopentene was prepared by Bieber and Eisman as follows.[10]



However, attempted preparation of cyclobutanone by intramolecular SN2 displacement was unsuccessful.[12-14] The attempted preparation of a cyclopropene by intramolecular Wittig reaction gave only a 1,4-cyclohexadiene.[11]

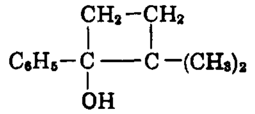


We have found that four-membered rings can be prepared by intramolecular reaction of the methylenephosphorane derived from VI prepared by the phosphonioethylation of isobutyrophenone. A 6% yield of tributyl-3,3-dimethyl-2-phenyl-1-cyclobutenylphosphonium bromide (VII) was isolated from treatment of VI with an equivalent of sodium ethoxide. The structure of VII is based on infrared, ultraviolet, n.m.r., and elementary analytical data. In a separate experiment, distillation of the sirup containing VII gave tributylphosphine, tributylphosphine oxide, and a compound of mass peak 176. The latter corresponds to a formula $C_{12}H_{16}O$, possibly VIII. The formation of VII and VIII can be rationalized most readily on the basis of intramolecular cyclization of VI followed by loss of water and base-promoted phosphorus–carbon bond cleavage, respectively.

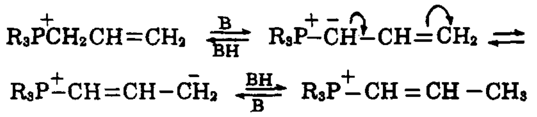


$$[(C_4H_9)_3\overset{+}{P}CH_2CH_2C(CH_3)_2\overset{O}{\overset{\|}{C}}C_6H_5]Br^- \xrightarrow{NaOC_2H_5}$$
VI

VII


VIII

As an extension of the study of the chemistry of vinylphosphonium salts, the possibility of isomerization of allyphosphonium salts in the presence of bases[5,6,15] led us to consider these readily available compounds as substituted phosphonioethylation reagents.



$$R_3\overset{+}{P}CH_2CH{=}CH_2 \underset{BH}{\overset{B}{\rightleftharpoons}} R_3\overset{+}{P}{-}\overset{-}{C}H{-}CH{=}CH_2 \rightleftharpoons R_3\overset{+}{P}{-}CH{=}CH{-}\overset{-}{C}H_2 \underset{B}{\overset{BH}{\rightleftharpoons}} R_3\overset{+}{P}{-}CH{=}CH{-}CH_3$$

Allyltributylphosphonium bromide (IX), allyltriphenylphosphonium bromide (X), and chloride (XI) were prepared in high yield by the reaction of the appropriate tertiary phosphine with the appropriate allyl halide. The reactivity of these salts towards conventional Michael addendums was investigated. In individual experiments, when both X and XI were dissolved in acetonitrile, treated with benzyltrimethylammonium hydroxide, and heated on a steam bath for 30 min., they isomerized to give the triphenylpropenylphosphonium salt (XII).

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(10) T. I. Bieber and E. H. Eisman, *J. Org. Chem.*, **27**, 678 (1962).

(11) C. E. Griffin and G. Witschard, *ibid.*, **27**, 3334 (1962).

(12) G. Märkl, *Angew. Chem.*, **74**, 696 (1962).

(13) A. Mondon, *Liebigs Ann. Chem.*, **603**, 115 (1957).

(14) H. J. Bestmann and H. Haberlein, *Z. naturforsch*, **17B**, 787 (1962).

(15) H. J. Bestmann, O. Kratzer, and H. Simon, *Chem. Ber.*, **95**, 2750 (1962).

$$[(C_6H_5)_3PCH{=}CHCH_3]^+X^-$$
$$\text{XII, } X = \text{Cl or Br}$$

The structure of these compounds was confirmed by infrared, n.m.r., and microanalysis. Attempted base-catalyzed additions of acetophenone, isobutrophenone, diethyl malonate, methanol, and 2-methylimidazole to X yielded only the isomerized derivative (XII).

In contrast, allyltributylphosphonium bromide (IX) does not isomerize under the conditions described but readily gives 1:1 adducts with ethanol and diethyl malonate in 60 and 48% yields, respectively. These compounds are presumably 2-substituted propylphosphonium salts formed by rapid addition to a small equilibrium concentration of the reactive, rearranged propenylphosphonium salt. From these results, it would appear that the substituents attached to phosphorus exert a pronounced effect on the stability of the propenylphosphonium group.

Experimental[16]

General Procedure for Phosphonioethylation Reactions with Tributylvinylphosphonium Bromide.—In general all of the phosphonioethylation reactions with tributylvinylphosphonium bromide[8] were carried out by mixing 0.05 mole (15.4 g.) of tributylvinylphosphonium bromide with 0.05 mole of the addendum in 50–100 ml. of appropriate solvent and heating the resulting mixture under nitrogen at reflux for several hours. The exact conditions for each of these reactions are given in Table I. With a number of relatively volatile compounds (*e.g.* acetophenone, ethyl acetoacetate, diethyl malonate, diethylamine, and ethanol), an excess of addendum was used as the reaction solvent. At the end of the reaction period the solvent was removed *in vacuo,* and the remaining reaction sirup was washed with anhydrous diethyl ether until it either crystallized to yield the product as a solid bromide, or a clean sirup remained having a good infrared spectrum for the desired compound. In those cases where sirups were obtained, they were converted to crystalline derivatives by treatment with 1 *N* solutions of sodium tetraphenylboron in either acetone, ethyl acetate, or tetrahydrofuran. The resulting products (bromides or tetraphenylborates) were recrystallized several times from either acetone, ethyl acetate, benzene, or tetrahydrofuran prior to microanalysis. The individual microanalytical results for these compounds also are given in Table I.

Reaction of Tricyclohexylvinylphosphonium Bromide with 2-Methylimidazole.—Tricyclohexylvinylphosphonium bromide (3.8 g., 0.01 mole) was mixed with 0.8 g.(0.01 mole) of 2-methylimidazole in 50 ml. of acetonitrile and heated at reflux under nitrogen for 2 hr. The mixture then was cooled to room temperature and filtered to yield 4.0 g. (85%) of crystalline product, m.p. 240–242°, which was identified by infrared analysis as the desired addition compound (especially 1535-cm.$^{-1}$ absorption).

Anal. Calcd. for $C_{24}H_{42}BrN_2P$: C, 61.39; H, 9.02; Br, 17.02; N, 5.97; P, 6.60. Found: C, 60.61; H, 9.22; Br, 17.32; N, 5.98; P, 6.53.

Reaction of Dimethylphenylvinylphosphonium Bromide with 2-Methylimidazole.—Dimethylphenylvinylphosphonium bromide (2.5 g., 0.01 mole) was mixed with 0.8 g. (0.01 mole) of 2-methylimidazole in 50 ml. of a 50 vol. % dimethoxyethane–acetonitrile mixture and heated at reflux for 5.0 hr. Upon cooling to room temperature, 3.0 g. (99% yield) of a tan crystalline solid, m.p. 183–185°, was obtained which was identified by infrared as the 1:1 addition compound (1535 cm.$^{-1}$).

Anal. Calcd. for $C_{14}H_{20}BrN_2P$: C, 51.39; H, 6.16; N, 8.56; P, 9.47. Found: C, 51.05; H, 7.23; N, 8.27; P, 9.58.

Reaction of Tributylvinylphosphonium Bromide with Bromine.—Tributylvinylphosphonium bromide (15.4 g., 0.05 mole) was mixed with 150 ml. of carbon tetrachloride and heated to 65° to facilitate solution. Bromine (9.6 g., 0.06 mole) was mixed with an additional 50 ml. of carbon tetrachloride and slowly added to the refluxing phosphonium salt solution over a 3-hr. period under nitrogen. At the end of this time the excess carbon tetrachloride was removed *in vacuo* and the remaining orange-yellow sirup was divided into two equal portions.

The first portion of this sirup was mixed with 100 ml. of anhydrous benzene and 1.8 g. (0.025 mole) of triethylamine and was heated at reflux for 2 hr. At the end of this time the reaction mixture was cooled to room temperature and filtered to remove a quantitative yield of triethylamine hydrobromide. The filtrate was concentrated *in vacuo* to a brown sirup which was taken up in a mixture of ethyl acetate and acetone and treated with 8.5 g. (0.025 mole) of sodium tetraphenylboron in ethyl acetate. The mixture was filtered to remove sodium bromide, the filtrate was concentrated *in vacuo,* and the residue was recrystallized from ethyl acetate to yield 3.2 g. (22% yield) of a white solid, m.p. 148–149°. Infrared analysis of this solid showed a sharp band at 960 cm.$^{-1}$ indicative of *trans* C=C but no band at 1230 cm.$^{-1}$ ($-CH_2Br$). The spectrum also showed the presence of butyl groups on phosphorus and the phenyl groups of tetraphenylboron but none of the characteristic vinyl absorption of tributylvinylphosphonium bromide. N.m.r. analysis in deuteriochloroform and acetone did not shed further light on the structure of this compound although a weak vinyl hydrogen structure was observed at about 3 τ.

Anal. Calcd. for $C_{38}H_{45}BBrP$: C, 73.20; H, 7.28; Br, 12.82; P, 4.97. Found: C, 73.20; H, 7.46; Br, 12.81; P, 4.91.

The second portion of crude material was taken up in chloroform and 8.5 g. (0.025 mole) of sodium tetraphenylboron in ethyl acetate was added to the chloroform solution. This solution was filtered to remove sodium bromide, and the brown sirup which remained after concentration of the filtrate was taken up in acetone. After standing for several days tan crystals slowly deposited from the acetone solution. In a sealed capillary these crystals melted at 62–63°, but upon standing in air this material appeared to be very hygroscopic and immediately reverted to a brown sirup. Infrared analysis of this tan material indicated that it was the tetraphenylborate of the desired dibromide; however, this compound was too unstable for microanalysis.

Reaction of Tributylvinylphosphonium Bromide with Cyclopentadiene.—Tributylvinylphosphonium bromide (15.4 g., 0.05 mole) was mixed with 50 ml. of dicyclopentadiene and heated at 150 to 180° for 6.0 hr. When the reaction mixture cooled to room temperature a heavy oil separated from solution. The oil was taken up in benzene and purified by passage through a 30-cm. neutral alumina column. A 59% yield of the desired bromide was obtained as a clear sirup and converted to the crystalline tetraphenylborate (dec. >170°).

Anal. Calcd. for $C_{43}H_{56}BP$: C, 84.02; H, 9.18; P, 5.04. Found: C, 83.00; H, 8.79; P, 5.14.

Reaction of 3-Benzoyl-3-methylbutyltributylphosphonium Bromide with Sodium Ethoxide.—3-Benzoyl-3-methylbutyltributylphosphonium bromide (22.9 g., 0.05 mole) dissolved in 25 ml. of absolute ethanol was added to a freshly prepared solution of sodium ethoxide (0.05 mole) in 50 ml. of absolute ethanol, under nitrogen. The resulting mixture was heated at ethanol reflux, then cooled and filtered to remove sodium bromide. The excess solvent was distilled from the reaction mixture at atmospheric pressure, and the remaining pot residue, a brown semisolid sirup, was distilled under reduced pressure. A few milliliters of volatile forecut was obtained (mainly ethyl alcohol). Then a small quantity of yellow oil was collected, b.p. 115–170° (12 mm.), before the pot residue completely pyrolyzed to a black tar, and solid tributylphosphine oxide began to collect in the distillation receiver. Analysis of this oil by gas–liquid chromatography and mass spectrometry indicated that it was mainly tributylphosphine and tributylphosphine oxide with an unknown peak at mass 176 corresponding to the empirical formula $C_{12}H_{16}O$.

This experiment was repeated using the same conditions and quantities as above. After removal of the ethanol, the remaining brown semisolid sirup was filtered, and a white crystalline solid was collected, m.p. 225–226°, which weighed 1.2 g. and represented a 6% yield based on the starting phosphonium salt. The infrared spectrum of this material did not show any of the carbonyl bands characteristic of the starting material, but did show phenyl bands and two new bands at 940 and 920 cm.$^{-1}$ indicative of C=C but different from the vinyl band of the tributylphosphonium salt (925 cm.$^{-1}$). N.m.r. proton analysis in deuteriochloroform also showed that there were no protons on carbon bearing an oxygen. Basing a proton count on one phenyl group, n.m.r. analysis estimated that there were 37 remaining protons or a total of 42 (±3) protons. Ultraviolet analysis of this solid in

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[16] Melting points are uncorrected.

methanol showed an absorption maximum at 241 mμ which is the absorption region for styrene and 1-phenyl cycloalkenes, and microanalysis indicated an empirical formula of $C_{24}H_{40}BrP$ for this compound.

Anal. Calcd. for $C_{24}H_{40}BrP$: C, 65.59; H, 9.18; Br, 18.19; P, 7.05. Found: C, 65.04; H, 9.53; Br, 18.22; P, 7.10.

Preparation of Allyltributylphosphonium Bromide.—Tributylphosphine (95 g., 0.47 mole) was mixed with 250 ml. of acetonitrile and 121 g. (1.0 mole) of allyl bromide was added dropwise at such a rate as to keep the acetonitrile refluxing. The resulting mixture was kept at room temperature for 2.0 hr. and then the acetonitrile was removed *in vacuo*. The remaining sirup was treated with diethyl ether to yield 148 g. (97%) of the desired phosphonium salt as a white crystalline solid, m.p. 78–80°. Infrared analysis of this compound showed that it was definitely the allyl and not the propenyl salt.

Anal. Calcd. for $C_{15}H_{32}BrP$: C, 55.72; H, 9.98; Br, 24.72; P, 9.58. Found: C, 55.23; H, 9.35; Br, 25.13; P, 9.49.

Preparation of Allyltriphenylphosphonium Chloride and Bromide.—Allyltriphenylphosphonium chloride and bromide were prepared by a procedure previously described.[17] A 50% yield of the crystalline chloride was obtained, m.p. 234–235°, and a 62% yield of pure bromide, m.p. 225–227°. Infrared analysis of both salts showed strong allyl absorption at 960 cm.$^{-1}$.

Base-Catalyzed Isomerization of Allyltriphenylphosphonium Halides.—Allyltriphenylphosphonium bromide (3 g.) was dissolved in acetonitrile and treated with 3 drops of 40% methanolic benzyltrimethylammonium hydroxide. The mixture was heated on a steam bath for 30 min. and then the acetonitrile was removed under reduced pressure leaving a solid white residue. This residue was recrystallized from a benzene–hexane mixture, m.p. 213–214°. The infrared spectrum of this material showed a band at 1620 cm.$^{-1}$ (vinyl C=C), but the terminal allyl band at 960 cm.$^{-1}$ was missing. Microanalysis found that this material had the same empirical formula as the allyltriphenylphosphonium bromide.

Anal. Calcd. for $C_{21}H_{20}BrP$: C, 65.81; H, 5.26; Br, 20.85; P, 8.08. Found: C, 66.14; H, 5.35; Br, 21.11; P, 8.08.

When this experiment was repeated with the allyltriphenylphosphonium chloride, a phosphonium salt was recovered having the same melting point as the starting material (235–236°) but an infrared spectrum which again showed the presence of a band at 1620 cm.$^{-1}$ and the loss of a band at 960 cm.$^{-1}$. N.m.r. proton analysis of this compound further confirmed that this was the propenyl salt. A-CH_3 considerably split was seen at 7.64 τ and there were olefinic hydrogens near 3 τ although weak and obscured by the phenyls.

Attempted Phosphonioethylation Reactions with Allyltriphenylphosphonium Chloride.—Three 1-g. samples of allyltriphenylphosphonium chloride were mixed individually with 15-ml. portions of acetophenone, isobutyrophenone, and diethyl malonate and 3 drops of benzyltrimethylammonium hydroxide solution was added to each reaction flask. The resulting reaction mixtures were heated on a steam bath for 1 hr. and then cooled and worked up. In all three cases a phosphonium salt was quantitatively recovered and identified by infrared analysis as the isomerized propenyl compound.

In a fourth experiment 5 g. of allyltriphenylphosphonium chloride was mixed with 25 ml. of absolute methanol containing a catalytic amount of sodium methoxide and was heated at the reflux temperature of methanol for 1 hr. Upon working up the reaction mixture, the isomerized propenyl salt was again obtained.

A fifth experiment in which 16.9 g. (0.05 mole) of allyltriphenylphosphonium chloride was refluxed overnight with 3.4 g. (0.05 mole) of 2-methylimidazole gave the same results as the latter four experiments.

Attempted Base-Catalyzed Isomerization of Allyltributylphosphonium Bromide.—Allyltributylphosphonium bromide (3 g. 0.01 mole) dissolved in 50 ml. of acetonitrile with 3 drops of benzyltrimethylammonium hydroxide solution was refluxed for 30 min. At the end of this time the crystalline solid which was recovered from this mixture had the identical infrared spectrum and melting point as the starting material.

Reaction of Allyltributylphosphonium Bromide with Ethanol.—Allyltributylphosphonium bromide (16.0 g., 0.05 mole) was mixed with 50 ml. of absolute ethanol, and a small piece of sodium about the size of a pea was added to the clear solution. When the sodium had dissolved, the mixture was refluxed under nitrogen for 10 hr. The reaction mixture was cooled, neutralized with a few drops of 48 % hydrobromic acid, filtered, and the excess ethanol was removed. The remaining sirup was washed with diethyl ether and dried under vacuum; it weighed 12.5 g. (60% yield) and the infrared spectrum indicated that it was pure product. This sirup was taken up in ethanol and converted to the crystalline tetraphenylborate, m.p. 112–113°.

Anal. Calcd. for $C_{41}H_{58}BOP$: C, 80.90; H, 9.60; P, 5.09. Found: C, 80.79; H, 10.22; P, 4.97.

Reaction of Allyltributylphosphonium Bromide with Diethylmalonate.—Allyltributylphosphonium bromide (12.5 g., 0.038 mole) was mixed with 50 ml. of diethyl malonate containing 5 drops of benzyltrimethylammonium hydroxide and heated at 130–135° overnight. The mixture was then cooled and washed three times with diethyl ether. The remaining sirup was dried to a constant weight (8.0 g., 48% yield) and examined by infrared analysis. Its spectrum was consistent with the structure of the expected malonate adduct. This sirup was taken up in acetonitrile and converted to a crystalline tetraphenylborate which gave fine white needles from ethyl acetate, m.p. 134–136°.

Anal. Calcd. for $C_{46}H_{64}BO_4P$: C, 76.44; H, 8.93; P, 4.29. Found: C, 76.11; H, 9.08; P, 4.53.

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[17] M. Grayson and P. T. Keough, *J. Am. Chem. Soc.*, **82**, 3919 (1960).