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A STUDY OF THE REACTION COURSE OF TRIPHENYLPHOSPHINE WITH BROMOMETHYLTRIPHENYLPHOSPHONIUM BROMIDE

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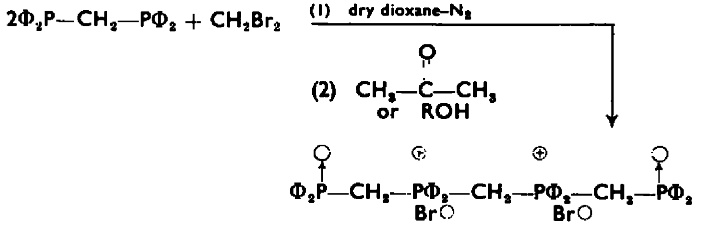
Abstract—A mechanism for the reaction of triphenylphosphine with bromomethyltriphenylphosphonium bromide is proposed to explain the different reaction products in (1) aprotic solvents and (2) in the presence of oxygenated protic compounds.

In an investigation designed to yield phosphonium polymers with alternating phosphorus-carbon bonds in the backbone, dibromomethane was reacted with methylenebis(diphenylphosphine) under a variety of conditions. Instead of high polymer formation, complex mixtures of low-molecular weight products were obtained. One of the products isolated in this series of experiments was I.



$$2\Phi_2P{-}CH_2{-}P\Phi_2 + CH_2Br_2 \xrightarrow[(2)\ CH_3{-}\overset{O}{C}{-}CH_3\ \text{or}\ ROH]{(1)\ \text{dry dioxane-}N_2} \Phi_2\overset{O}{\overset{\uparrow}{P}}{-}CH_2{-}\overset{\oplus}{P}\Phi_2{-}CH_2{-}\overset{\oplus}{P}\Phi_2{-}CH_2{-}\overset{O}{\overset{\uparrow}{P}}\Phi_2 \quad 2Br^{\ominus}$$

I

In order to elucidate the sequence of reactions leading to the formation of I, a monomeric "model" reaction of triphenylphosphine (II) with bromomethyltriphenylphosphonium bromide (III) was studied.

It was found that II reacted with III in an aprotic solvent such as benzonitrile to yield a mixture of products, IV, V, VI. On treating the mixture with methanol, VII, V, VIII, and IX were obtained.

The existence of methylenetriphenylphosphorane as a long-lived intermediate in the reaction of II with III was ruled out by the nonreactivity of benzonitrile[2a] and also by the fact that added benzophenone failed to undergo a Wittig reaction.[3] Methylenetriphenylphosphorane (X), however, reacted, although in low yield, with dibromotriphenylphosphorane under comparable conditions to yield methylenebis(triphenylphosphonium bromide) VII.[2b]

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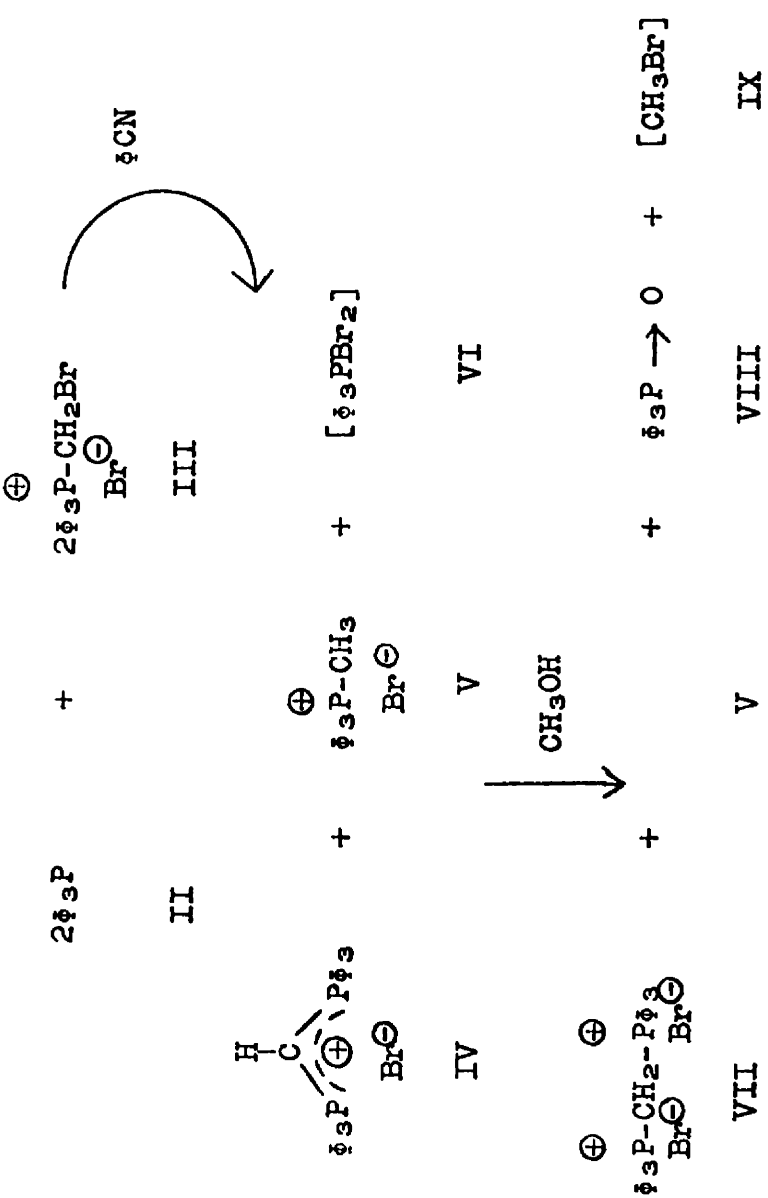
[1] This work was sponsored in part by the Air Force Systems Command, United States Air Force, under contract AF 33(616)–7853.

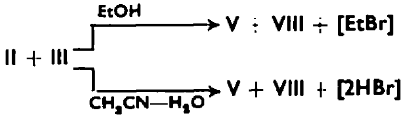
[2a] The reaction of benzonitrile with an ylide at 25° has been reported, vis. A. Bladé-Font, W. McEwen and C. VanderWerf, *J. Amer. Chem. Soc.* **82**, 2646 (1960); [b] Also, the very low yield of VII in the reaction of X with VI is probably due to the reaction of X with benzonitrile.

[3] G. Wittig and G. Geissler, *Liebigs Ann.* **680**, 44 (1963).

(1)


2Φ₃P
II
+
2Φ₃P⊕-CH₂Br Br⊖
III
ΦCN
Φ₃P⊕ H-C⊕ PΦ₃ Br⊖
IV
+
Φ₃P⊕-CH₃ Br⊖
V
+
[Φ₃PBr₂]
VI
CH₃OH
Φ₃P⊕-CH₂-⊕PΦ₃ Br⊖ Br⊖
VII
+
V
+
Φ₃P → O
VIII
+
[CH₃Br]
IX

The reaction of II with III, in the presence of oxygen-containing, protic compounds leads to a different reaction course.[4]



(2)

$$\mathrm{II}+\mathrm{III}\begin{cases}\xrightarrow{\mathrm{EtOH}} \mathrm{V} : \mathrm{VIII} + [\mathrm{EtBr}]\\ \xrightarrow[\mathrm{CH_3CN{-}H_2O}]{} \mathrm{V}+\mathrm{VIII}+[2\mathrm{HBr}]\end{cases}$$

(3) $2\,\mathrm{II} + \mathrm{III} \xrightarrow{\mathrm{CH_3OH}} 2\mathrm{V} + \mathrm{VIII}$

Under these conditions, neither of the methylenebis(phosphonium) salts IV or VII was formed.

A reaction scheme to accommodate the preceding data is proposed (see p. 4).

It is proposed that the first step of the reaction is a nucleophilic attack of phosphorus on "positive" bromine to form the ion-pair (A). Analogous ion-pair formation probably occurs during the course of the reaction of tertiary phosphines with other active halogen compounds such as α-dihalomethylphosphonium salts,[5] α-haloketones,[6] α-haloaldehydes,[7] α-haloamides,[8] α-haloacids,[9] α-halonitriles,[10] α-halonitroalkanes,[11] α-halosulfones,[12] tetrahalomethanes[5,13] and others.[14,15] In several of the foregoing cases, ion-pairs of this type have been suggested as intermediates.[13,15]

In the absence of facile proton donors, the negatively charged carbon of the anion would be expected to displace bromide from the phosphorus-containing cation of the ion pair to form VII. Since VII is acidic,[16] a rapid proton exchange of VII with anion of the ion pair would yield the observed products IV, V, VI.

Treatment of this mixture with methanol yields the final products, VII, V, VIII and IX (Eq. [1]). The formation of VII undoubtedly occurs by addition of hydrogen bromide (generated by the methanolysis of dibromotriphenylphosphorane to triphenylphosphine oxide[17]) to IV.[16]

[4] D. W. Grisley, Jr., *Tetrahedron Letters* 435 (1963).

[5] F. Ramirez, N. Desai and N. McKelvie, *J. Amer. Chem. Soc.* **84**, 1745 (1962).

[6] I. Borowitz and L. Grossman, *Tetrahedron Letters* 471 (1962).

[7] H. Hoffman and H. J. Diehr, *Tetrahedron Letters* 583 (1962).

[8a] A. Speziale and L. Smith, *J. Amer. Chem. Soc.* **84**, 1868 (1962);

[b] A. Speziale and R. Freeman, *Ibid.* **82**, 903 (1960).

[9] D. Denney and L. C. Smith, *J. Org. Chem.* **27**, 3404 (1962).

[10] P. Schiemenz and H. Engelhard, *Chem. Ber.* **94**, 578 (1961).

[11] S. Trippett and D. Walker, *J. Chem. Soc.* 2976 (1960).

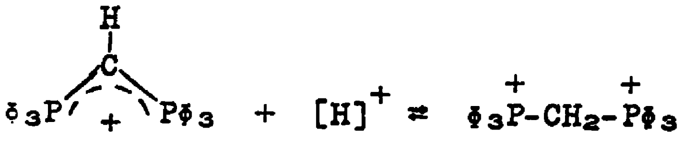
[12] H. Hoffmann and H. Förster, *Tetrahedron Letters* 1547 (1963).

[13] R. Rabinowitz and R. Marcus, *J. Amer. Chem. Soc.* **84**, 1312 (1962).

[14] H. Hoffman, *Angew. Chem.* (int. Ed.) **1**, 605 (1962).

[15] S. Trippett, *Quart. Revs.* 406 (1963).

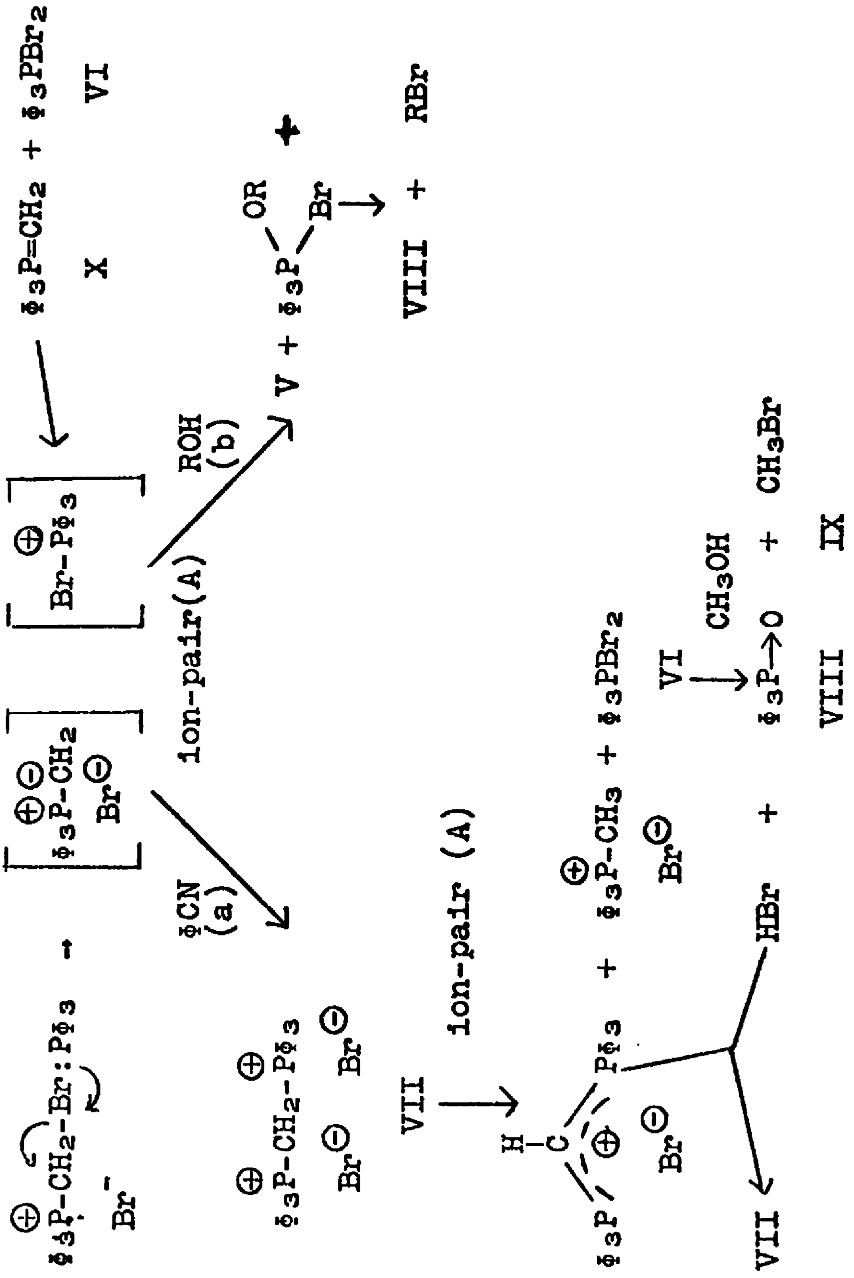
[16] PK_a for the equilibrium



$$\Phi_3\mathrm{P}\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}{}^{-}\overset{+}{}\mathrm{P}\Phi_3 + [\mathrm{H}]^+ \rightleftharpoons \Phi_3\overset{+}{\mathrm{P}}{-}\mathrm{CH_2}{-}\overset{+}{\mathrm{P}}\Phi_3$$

is 5·4 ± 0·1. See F. Ramirez, N. Desai, B. Hansen and N. McKelvie, *J. Amer. Chem. Soc.* **83**, 3539 (1961).

[17] G. Wiley, R. Hershkowitz, B. Rein and B. Chung, *J. Amer. Chem. Soc.* **86**, 964 (1964).

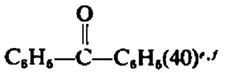

Ion-pair(A)
ΦCN (a)
ROH (b)
X
VI
V
RBr
VIII
VII
Ion-pair (A)
CH₃OH
IX
CH₃Br
HBr

In the presence of oxygen-containing protic compounds a rapid proton-transfer occurs between ROH and *A* which precludes path (a) so that the major products are V, VIII, and the bromide derived from R (Eqs. [2] and [3]).

The nonparticipation of benzophenone and benzonitrile in the reaction can be explained by a kinetic preference of ion pair A for path (a).

From the foregoing study of the model reaction, it is evident that a similar mechanism can account for the production of I in the reaction of methylenediphenylphosphine with dibromomethane. The lack of high-polymer formation can be attributed to a chain termination involving rapid proton-transfer analogous to the reaction between intermediate VII and ion-pair A.

TABLE 1. REACTIONS OF TRIPHENYLPHOSPHINE WITH BROMOMETHYLTRIPHENYLPHOSPHONIUM BROMIDE

	REACTANTS (mmoles)						PRODUCTS (mmoles)			
Run	II	III	Additive	Solvent	Temp	Time(hr)	IV	V	VII	VIII
1	20	20	None	C_6H_5CN	142°	4·5	—	7·3[a,b]	7·3[a,c]	6·8[a]
2	20	20	None	C_6H_5CN	142°	3·0	8·1[d]	7·9[d]	—	—
3	20	20	None	CH_3CN	82°	22·0	—	9·5[a,b]	4·8[a,c]	—
4	20	20	 $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$(40)[e,f]	CH_3CN	82°	22·0	—	6·7[a,b]	5·4[a,c]	2·5
5	20	20	H_2O (20)	CH_3CN	82°	22·0	—	15·0	[g]	11·0
6	20	20	None	CH_3CH_2OH	78°	22·0	—	17·0	[g]	17·0
7	40	20	None	CH_3OH	65°	24·0	—	31·0	[g]	13·0

[a] Isolated after methanol workup of reaction mixture.

[b] Amount determined by quantitative NMR analysis of the crude salt.

[c] Isolated as the monohydrate.

[d] Amount determined by quantitative NMR spectrum of the reaction mixture.

[e] 34 mmoles recovered from the reaction mixture.

[f] Amount determined by quantitative VPC analysis.

[g] Unable to be detected by IR spectra.

EXPERIMENTAL[18]

Materials. Triphenylphosphine, purchased from Metal and Thermit Corporation, was dissolved in toluene, the solution was filtered, and the clear filtrate was evaporated *in vacuo* to yield the dried material, m.p. 81·5–84°. Bromomethyltriphenylphosphonium bromide m.p. 236·5–241·5°, was prepared by the method of Driscoll.[19] Before use, the salt was dried at 110°/0·1 mm over P_2O_5, and transferred to the reaction mixture in a dry N_2 atm. Dibromotriphenylphosphorane[20] was prepared by the addition of an equimolar amount of bromine to triphenylphosphine in benzonitrile.

Dibromomethane (Eastman White Label) was dried ($MgSO_4$) and purged with N_2 before use. Methylenebis(diphenylphosphine) m.p. 118–122° was prepared by the method of Issleib.[21]

Triphenylphosphonium methylenetriphenylphosphorane bromide, m.p. 272–274° was prepared by the method of Ramirez.[14]

Authentic samples. Methyltriphenylphosphonium bromide (Aldrich Chemical Company) had a m.p. 224–228°. The preparation of methylenebis(triphenylphosphonium bromide)monohydrate, m.p. 301·5–304·5° has been reported.[19] Triphenylphosphine oxide, m.p. 150–151° was purchased from the Metal and Thermit Corporation.

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[18] M.ps are uncorrected.

[19] J. S. Driscoll, D. W. Grisley, Jr., J. V. Pustinger, J. E. Harris and C. N. Matthews, *J. Org. Chem.* **29**, 2427 (1964).

[20] L. Horner, H. Oediger and H. Hoffmann, *Liebigs Ann.* **626**, 26 (1959).

[21] K. Issleib and D. Müller, *Chem. Ber.* **92**, 3175 (1959).

Solvents. Benzonitrile (Matheson) was dried over molecular sieves, then distilled, b.p. 79–80°/20 mm under N_2 before use. Acetonitrile (Eastman, Spectro grade) was distilled under N_2 over P_2O_5 directly into the reaction mixture. Other solvents, of the highest purity, were dried and purified by distillation before use.

General procedures. All reactions were performed under an atm. of dry N_2. Dried reagents and solvents were transferred to the reaction mixtures in an atm. of dry N_2. Reaction products, methyltriphenylphosphonium bromide, methylenebis(triphenylphosphonium bromide), monohydrate, and triphenylphosphine oxide were identified by comparison of their m.ps and IR spectra with those of authentic samples.

Proton NMR spectra. The spectra were determined with a Varian Associates Model A-60 NMR spectrometer having a fixed magnetic field of 14,092 gauss and a rotating r.f. field of 60 Mc. All chemical shifts (δ in ppm) were measured from tetramethylsilane as internal standard.

Benzonitrile, the reaction solvent, was transparent in the region, 0–6·0 ppm. Authentic standards in benzonitrile gave shifts for the aliphatic protons:

triphenylphosphonium methylenetriphenylphosphorane bromide = 2·3 ppm (triplet; J_{HP} = 6 c/s)
methyltriphenylphosphonium bromide = 3·3 ppm (doublet; J_{HP} = 13 c/s)
methylenebis(triphenylphosphonium bromide) no absorption from 0–6·0
(in CH_3OH) = 6·8 ppm
(triplet, J = 16 c/s)

Reaction of methylenebis(diphenylphosphine) with dibromomethane (2:1)

A mixture of dibromomethane (8·7 g, 0·05 mole) and methylenebis(diphenylphosphine) (38·4 g, 0·1 mole) in dioxane (250 ml) was refluxed for 26 hr. The mixture was cooled and filtered to yield a white solid. The solid was washed with acetone to yield *a*, 10·9 g, m.p. 180–210°. The IR spectrum of *a* had absorptions at 1430 cm^{-1} (aromatic), and 1080–1110 cm^{-1} (phosphonium). A suspension of *a* in acetone was refluxed for several hr. The solution changed from colorless to deep orange. The mixture was filtered to yield a white solid which was washed with ether to yield *b*, 6·9 g, m.p. 176–179°. A small sample of *b* was dissolved in warm chloroform, and ether was added. Crystals separated, m.p. 160–164°. The procedure was repeated to yield I, m.p. 159–163°. (Found: C, 61·10; H, 5·03; Br, 15·49; O, 6·51; P, 12·50. MW 1025 (CH_2Br_2); Calc. for $C_{51}H_{46}Br_2O_2P_4 \cdot 2H_2O$: C, 60·58; H, 4.98; Br, 15·81; O, 6·33; P, 12·26%; MW 1010·6).

The IR spectrum of I had peaks at 3600 cm^{-1} (-OH), 1430 cm^{-1} (aromatic), 1180–1210 cm^{-1} $\left(\rangle P \rightarrow O\right)$, and 1080–1110 cm^{-1}(phosphonium).

Reaction of triphenylphosphine with bromomethyltriphenylphosphonium bromide in benzonitrile

A mixture of II (5·24 g, 20 mmoles) and III (8·72 g, 20 mmoles) in benzonitrile (25 ml) was heated at 142° for 4½ hr. The dark amber-red solution was evaporated at 60°/0·5 mm to yield a viscous oil. The oil was dissolved in methanol (40 ml) and ethyl acetate (150 ml) added. The amorphous solid that separated upon scratching was dried at 120°/20 mm to yield *d*, 5·5 g. The filtrate from *d* was evaporated to yield an orange oil *e*, 9·4 g, *e* was stirred with hot benzene (3 × 200 ml) to yield a solid *e-1*, 4·7 g, m.p. 192–213°. The solid *e-1* was dissolved in methanol (10 ml), ethyl acetate (50 ml) was added and an amorphous solid *f*, 0·9 g separated. Solids *d* and *f* were combined and recrystallized from methanol–ethyl acetate to yield VII (5·2 g, 7·3 mmoles), m.p. 302·4–304°. The filtrate from *f* was evaporated to yield a tan solid, which was washed with ethyl acetate to yield *g*, 3·2 g, m.p. 210–217°. Analysis of *g* by means of a quantitive proton NMR spectrum[22] indicated that *g* contained V (82 ± 2%, 2·6 g, 7·3 mmoles). The benzene triturates from *e* were evaporated to yield a greasy solid *e-2*, 4·0 g. Solid *e-2* was dissolved in benzene; hexane was added to separate VIII (1·9 g, 6·8 mmoles), m.p. 150–153°.

Quantitative determination of methyltriphenylphosphonium bromide and triphenylphosphonium methylenetriphenylphosphorane bromide in the reaction mixture

An identical experiment was performed with the exception that the duration was 3 hr. Upon cooling the reaction mixture to 25°, crystals separated. The mixture was heated momentarily to

[22] The IR spectrum of this mixture contained all the peaks of methyltriphenylphosphonium bromide. Attempts to purify the material resulted in excessive losses.

effect solution and then recooled to 25°. The proton NMR spectrum of the supercooled solution had the characteristic doublet of methyltriphenylphosphonium bromide at $\delta = 3{\cdot}3$ ppm and the triplet of triphenylphosphonium methylenetriphenylphosphorane bromide at $\delta = 2{\cdot}3$ ppm.

Quantitative determinations by the proton NMR spectrum of the reaction mixture yielded IV (5·1 g, 8·1 mmoles) and methyltriphenylphosphonium bromide (2·8 g, 7·9 mmoles.)

Standard mixture of triphenylphosphonium methylenetriphenylphosphorane bromide, methyltriphenylphosphonium bromide and dibromotriphenylphosphorane

A mixture of VI (2·1 g, 5 mmoles), V (1·8 g, 5 mmoles), and IV (3·1 g, 5 mmoles), and benzonitrile 15 ml, was heated to 170° in an atm. of dry N_2 to effect solution. Upon cooling the mixture to 25°, a supercooled solution was formed. The proton NMR spectrum of the solution had the doublet of V at $\delta = 3{\cdot}3$ ppm and the triplet of IV at $\delta = 2{\cdot}3$ ppm.

A portion of the original mixture (an undetermined amount) was evaporated at 60°/0·1 mm to yield a semi-solid. The semi-solid was worked up in the same manner as the reaction mixture of triphenylphosphine with bromomethyltriphenylphosphonium bromide in benzonitrile. Methylenebis-(triphenylphosphonium bromide)monohydrate was obtained (recrystallized from CH_3OH–EtOAc) (1·8 g, 2·5 mmoles) m.p. 306–309°, methyltriphenylphosphonium bromide (1·2 g, 3·2 mmoles), (determined as 82 ± 2%/wt. of a mixture [1·41 g, m.p. 211–215°] by quantitative proton NMR analysis[22]), and triphenylphosphine oxide (recrystallized from benzene–hexane) (0·72 g, 2·6 mmoles), m.p. 150–152·5°.

Reaction of hydrogen bromide with triphenylphosphonium methylenetriphenylphosphorane bromide in methanol

Hydrogen bromide was passed into a solution of triphenylphosphonium methylenetriphenylphosphorane bromide (1·24 g, 2 mmoles) in methanol (25 ml) for 30 min at room temp (ice-bath cooling). The solution was evaporated *in vacuo* to yield an oil. The oil was triturated with tetrahydrofuran to yield methylenebis(triphenylphosphonium bromide)monohydrate (1·4 g, 97% yield); m.p. 305–307°.

Reaction of methylenetriphenylphosphorane with dibromotriphenylphosphorane

n-Butyl-lithium (Foote Mineral Co.), (15 ml of 15·1% in hexane, 25 mmoles) was added to suspension of methyltriphenylphosphonium bromide (8·93 g, 25 mmoles) in benzene (50 ml).

The orange-colored suspension was added during 5 min to a stirred solution of dibromotriphenylphosphorane (~25 mmoles) in benzonitrile (90 ml) at 8°. During the addition the temp rose to 38° and the mixture turned dark. The stirred mixture was heated to 109° to distill off a liquid (25 ml) b.p. 65–80°. The reaction mixture was heated at 93–103° for 22 hr. The reaction mixture was evaporated at 50°/0·1 mm to yield a dark tar. The tar was extracted successively with hot benzene and hot chloroform. The chloroform extract was evaporated to yield a dark-brown gum. The gum was dissolved in methanol (40 ml) and ethyl acetate (150 ml) added. The resulting solution was scratched to yield a solid, *k*, 1·3 g, m.p. 295–308°. The mother liquor of *k* was heated with ethyl acetate (1000 ml) to yield a solid *l*, 0·9 g *k* and *l* were combined, dissolved in methanol and reprecipitated with ethyl acetate to yield methylenebis(triphenylphosphonium bromide)monohydrate (1·6 g, 2·2 mmoles), m.p. 308–312°.

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