Reactions of Phosphorus Compounds. XXI.[1a] Preparation and Reactions of 5-Benzoyl-2,2,2,5-tetraphenyl-1-oxa-2-phospholane

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Received June 27, 1969

The title compound (9a) was prepared from benzoin (1) and vinyl triphenylphosphonium bromide (4) in a variety of solvents. A number of reactions and spectra of 9a were examined to confirm its structure and investigate its synthetic utility.

In an earlier publication[1b] we reported a product ($C_{34}H_{29}O_2P$) from the reaction of vinyl triphenylphosphonium bromide (**4**) and the sodium salt of benzoin (**2**) whose structure had escaped elucidation. We now wish to report the chemical and physical data which have led us to identify this compound as 5-benzoyl-2,2,2,5-tetraphenyl-1-oxa-2-phospholane (**9a**).

Recent interest in phosphoranes with only one P–O covalent bond has resulted in the preparation and identification of species with four[2,3] and five[4-7] atoms in the heterocyclic ring. All of the compounds prepared have ^{31}P nmr absorption (relative to 85% H_3PO_4) at δ 36–59 ppm, which is characteristic of pentacovalent phosphorus compounds[2] and not of phosphonium salts.[8] Compound **9a** absorbs at 49.5 ppm in chloroform.

These data initially led to the postulation that the phosphepin (**7**) had been obtained (Scheme I), since **5** most probably was the intermediate on the pathway to the 2,3-diphenyl-2,5-dihydrofuran (**6**). However, the chemical and physical data indicated that **5** must be in ready equilibrium with **2** (and/or **3**) and that the carbanionic site of **3** must react (undoubtedly irreversibly) to form **8**, which then gives the phospholane (**9**) as shown in Scheme II. The ^{31}P data shows that **9** exists predominantly in form **9a** in chloroform.

The 60-MHz proton nmr in $CDCl_3$ of **9a** consists of a complex pattern of multiplets which collapse on warming of the $CDCl_3$ solution to two sharp four-line patterns, attesting to the ready equilibrium of **9a** with **8** and thus allowing for a deuterium–proton exchange. The same effect may be observed by the addition of D_2O to the sample. The initial integration [δ 1.6–2.3 (m, 1, H_B) and 2.6–3.9 ppm (m, 3, $CH_BH_ACH_2P$)] contracts from four protons to two [δ 1.85 (dd, 1, H_B, $J_{H_BP} = 12$ Hz, $J_{AB} = 13$ Hz) and 3.33 ppm (dd, 1, H_A, $J_{H_AP} = 38$ Hz)], indicating the sequence shown in Scheme III.

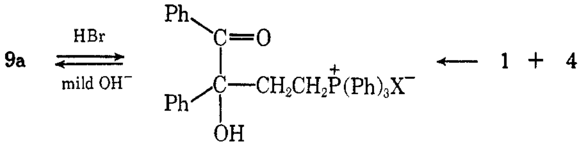
Table I shows the yields of the dihydrofuran, **6**, the phospholane, **9a**, and the phosphonioethylated salt, **10a**, obtained in a variety of solvents. The 3,4-diphenyl-3-hydroxy-4-oxobutyltriphenylphosphonium bromide (**10a**) may also be formed by the acidification of **9a** (quantitative) or by the fusion at 150° (47%) of an excess of benzoin with vinyl triphenylphosphonium bromide (**4**).

Table I

Solvent Effects on Yields of **6**, **9a**, and **10**

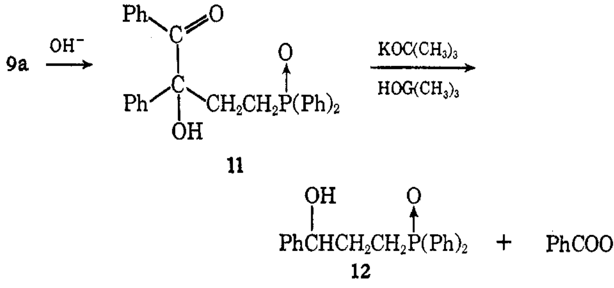
Solvent[a]	Yield, % **6**	**9a**	**10**
DMF[b,c]	35	12	
DMF[d]	50	0	
DMSO[b]	1	66	0
Acetonitrile[b]	77	0	0
t-Butyl alcohol[b]	21	0	46
THF[b]	0	0	59
THF[e]	5	0	80

[a] Benzoin, NaH, and vinyl salt in equimolar amounts. [b] Room temperature. [c] Reference 1. [d] 65°. [e] Room temperature (4 days), reflux temperature (2 days).



10a, X = Br
b, X = Cl

The phospholane may be recovered from the salt **10** (93% yield) by mild basification. Similar reversible conversions of pentavalent phosphorus species have been observed.[6,9] Prolonged treatment of **9a** with aqueous base yields 3,4-diphenyl-3-hydroxy-4-oxobutyldiphenylphosphine oxide (**11**). When **11** was refluxed with alcoholic potassium *t*-butylate, 3-phenyl-3-hydroxypropyldiphenylphosphine oxide (**12**) was recovered.



Treatment of **9** with aqueous ethanolic sodium hydroxide also gave **12**, but in addition yielded 31% carboxy phosphine oxide **13** and benzhydrol. A

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[1] (a) Paper XX in this series: E. E. Schweizer, W. S. Creasy, K. K. Light, and E. T. Shaffer, *J. Org. Chem.*, **34**, 212 (1969). (b) E. E. Schweizer and J. G. Liehr, *ibid.*, **33**, 583 (1968).

[2] G. Wittig and A. Haag, *Chem. Ber.*, **96**, 1535 (1963). ^{31}P nmr supports a cyclic structure with pentacovalent phosphorus—not a zwitterion as reported.

[3] G. H. Birum and C. N. Matthews, *Chem. Commun.*, 137 (1967).

[4] R. Huisgen and J. Wolff, *Tetrahedron Lett.*, 917 (1967).

[5] J. Wolff and R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **6**, 457 (1967).

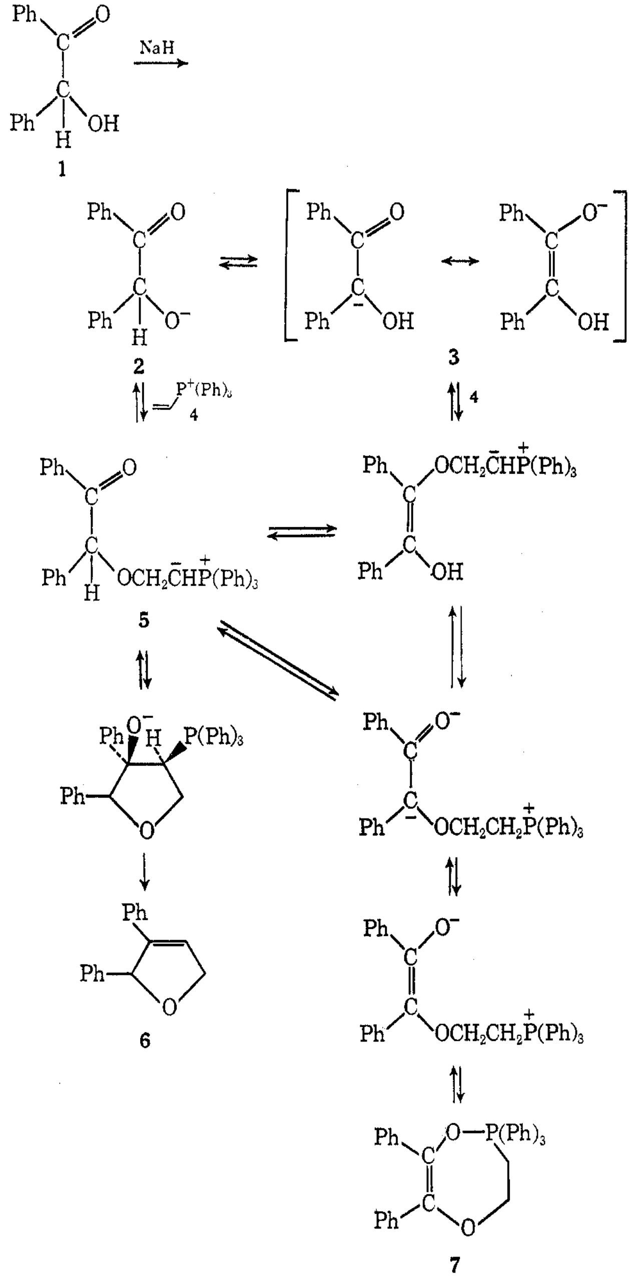
[6] H. J. Bestmann, T. Denzel, R. Kunstman, and J. Lengyel, *Tetrahedron Lett.*, 2895 (1968).

[7] A. R. Hands and A. J. H. Mercer, *J. Chem. Soc.*, 1099 (1967).

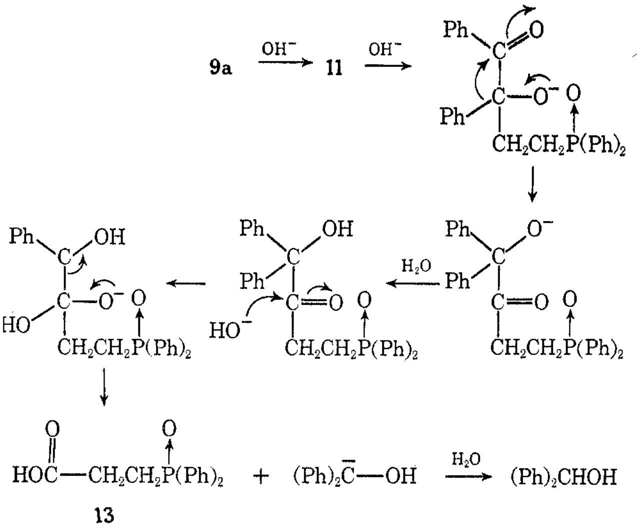
[8] J. R. Van Wazer and J. H. Letcher in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 169.

[9] M. Masaki, F. Fukini, and M. Ohta, *J. Org. Chem.*, **32**, 3564 (1969).

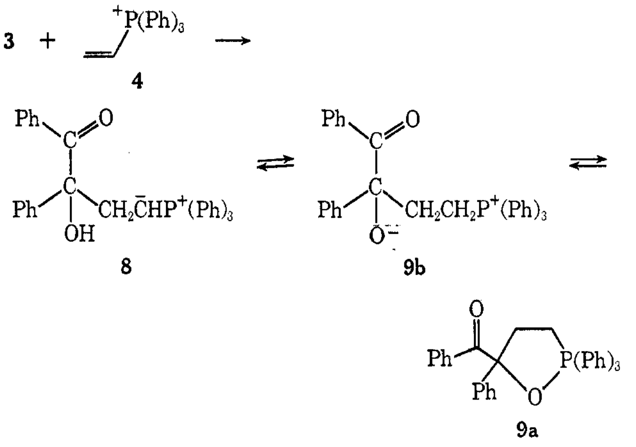
SCHEME I



reasonable mechanism for the formation of the latter products may be written as follows.

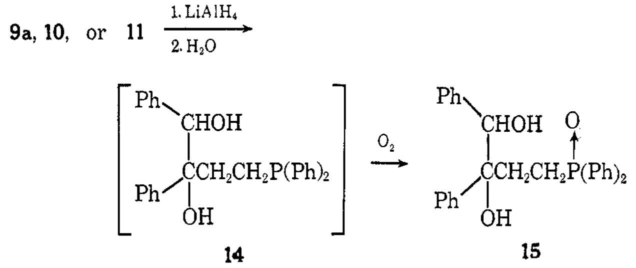


SCHEME II

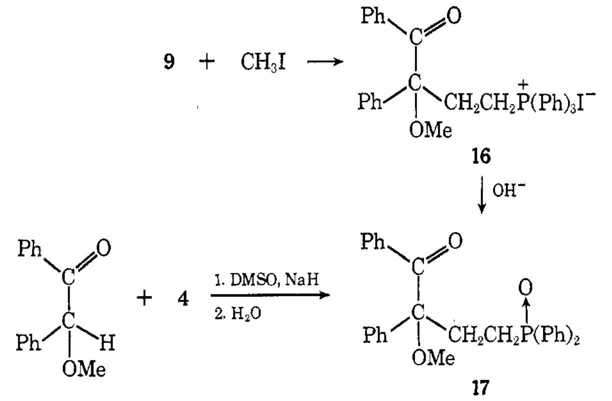


Initial conversion into the phosphine oxide **11** is supported by a further experiment in which **11**, treated under identical conditions, gave the same results.

Reduction of **9a**, **10**, or **11** with lithium aluminum hydride would be expected to produce 3,4-diphenyl-3,4-dihydroxybutyldiphenylphosphine (**14**); however, the phosphine was readily oxidized on recovery and was isolated as the corresponding phosphine oxide, **15**.

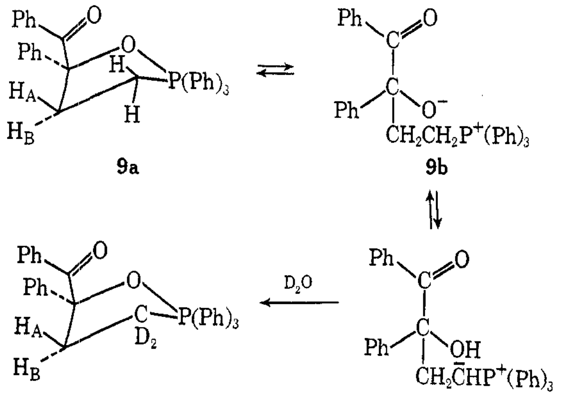


Compound **9** reacts with methyl iodide, in a manner expected in view of the known reactions of phospholanes,[6] to give 3,4-diphenyl-3-methoxy-4-oxobutyltriphenylphosphonium iodide (**16**), which may be hydrolyzed with aqueous base to 3,4-diphenyl-3-methoxy-4-oxobutyldiphenylphosphine oxide (**17**). This latter product is identical with that prepared by allowing the sodium salt of benzoin methyl ether to react with **4** in DMSO, followed by aqueous work-up (97% yield), a phosphonioethylation identical with that required in the formation of **9**.

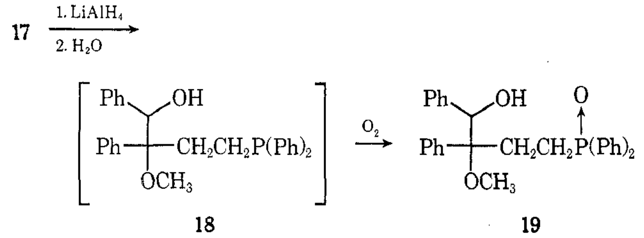


The phosphine oxide **17** may be reduced with $LiAlH_4$ to give (after hydrolysis) 3,4-diphenyl-4-hydroxy-3-

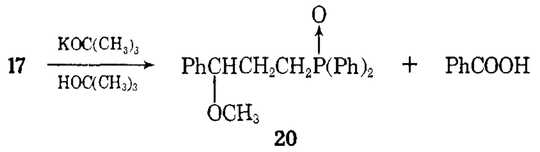
SCHEME III



methoxybutyldiphenylphosphine (**18**), which is oxidized on work-up to the corresponding phosphine oxide (**19**).

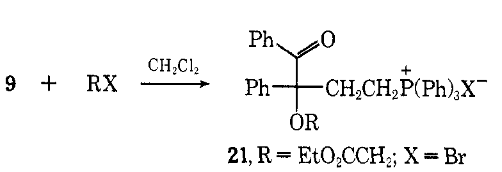


Treatment of **17** with potassium *t*-butylate in *t*-butyl alcohol gave 3-phenyl-3-methoxypropyldiphenylphosphine oxide (**20**).



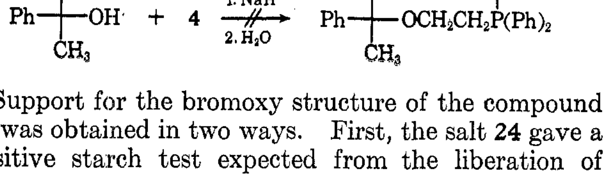
This last series of reactions serve uniquely to identify the site of attachment of the Michael-type adduct at carbon and not oxygen, thus demonstrating the correctness of the structure assignment of the new pentavalent phosphorus species as the phospholane, **9a**, and not the phosphepin, **7**.

Phospholane **9** was found to react with a number of active halides to give salts (**21**–**24**) in good yields.



21, R = EtO_2CCH_2; X = Br
22, R = EtO_2C; X = Cl
23, R = PhCH=O; X = Cl
24, R = Br^-; X = Br

Attempts to carry out the phosphonioethylation of methyl benzoin with **4** were unsuccessful.



Support for the bromoxy structure of the compound **24** was obtained in two ways. First, the salt **24** gave a positive starch test expected from the liberation of iodine from aqueous iodide solution owing to oxidation by Br^+. Second, salt **24** reacted with acetone to yield salt **10** (quantitatively) and bromoacetone.

The salt **21** was obtained in 71% yield on allowing **9** to react with ethyl bromoacetate in solution (CH_2Cl_2). However, in a solvent-free reaction a possible carbenoid reaction might be occurring, since the only products recovered were **10** (86%) and traces of diethylfumarate.

The salts **22** and **23** were obtained in yields of 82 and 94%, respectively.

A new synthesis of the unique pentavalent phosphorus species (phospholane) has been uncovered. A few reactions of the phospholane **9a** have been examined. Further examination of the reactions of vinyl (and substituted vinyl) triphenylphosphonium salts to give pentacovalent phosphorus heterocyclic systems, and their reactions, is under way.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord 137, proton nmr spectra on a Varian A-60A analytical nmr spectrometer using tetramethylsilane as the standard, and ^{-31}P nmr spectra on a Varian HA-100 nmr spectrometer using 85% H_3PO_4 as the external standard. Melting points are uncorrected and were obtained on a Fisher-Johns melting point apparatus. Analyses were run by Microanalysis, Inc., Wilmington, Del., and M-H-W Laboratories, Garden City, Mich.

Unless otherwise indicated, all the reactions were undertaken in anhydrous conditions under a blanket of dry nitrogen. The sodium hydride used was a 55% dispersion in mineral oil obtained from Metal Hydrides, Inc., Beverly, Mass.

3,4-Diphenyl-3-hydroxy-4-oxobutyltriphenylphosphonium Chloride (10b).—Vinyl triphenylphosphonium bromide (**4**,[10] 3 g, 0.008 mol) and benzoin (**1**, 10 g, 0.047 mol) were blended intimately and heated to 140° (oil-bath temperature) for 3 days. After the mixture had been cooled and dissolved in methylene chloride, the solution was added dropwise to 0.5 l. of vigorously stirred anhydrous ether. The resulting precipitate was dissolved and reprecipitated as above. The white crystals were washed with water and acetone, extracted into methylene chloride, dried ($CaCl_2$), and precipitated to give **10b**[11] (2.2 g, 47%), mp 247–249°. Tlc of the original product mixture showed three spots only, identified (by comparison) as starting materials and salt **10b**. Spectral data for **10b** follow: ir (KBr) 1115 (s, CP), 1240 (s, COC), 1680 (s, C=O), and 3200 cm^{-1} (m, OH); uv (MeOH) 232 mμ (ϵ 26,800) and 253 (14,000); nmr ($CDCl_3$) δ 2.2–2.9 (m, 2, $\mathbf{CH_2}CH_2P$), 3.3–4.1 (m, 2, $CH_2\mathbf{CH_2}P$), 5.2 (s, 1, HC), and 7.0–8.1 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{34}H_{30}PO_2Cl$: C, 75.47; H, 5.33; P, 5.73. Found: C, 75.51; H, 5.60; P, 5.42.

Preparation of 5-Benzoyl-2,2,2,5-tetraphenyl-1-oxa-2-phospholane (9). A. From Salt 10a.—The salt **10a** (0.7 g, 0.0013) was placed in 20 ml of 20% aqueous sodium hydroxide solution. The mixture was heated to boiling and then immediately allowed to cool to room temperature. The resulting green-yellow crystals of **9** were washed consecutively with water, methanol, acetonitrile, and ether, dissolved in methylene chloride, and dried (K_2CO_3). Hexane was added slowly, with stirring, to the dried, concentrated methylene chloride solution, yielding 0.6 g (93%) of the phospholane **9**: mp 216–218°; ir (KBr) 1105 (s, CP), 1160 (m, POC), 1220 (s, POC), and 1665 (s, C=O) cm^{-1}; uv (CH_3OH) 228 mμ (ϵ 33,300), 253 (17,400), and 275 (8030); mol wt (cryoscopic, camphor) 566 (theory 500); mass spectrum *m/e* 423, 395, 262, 188, 105, and 77; ^{31}P nmr[12] (CH_2Cl_2) 49.5 ppm (br s); proton nmr ($CDCl_3$) δ 1.6–2.3 (m, 1, $CH_A\mathbf{H_B}CH_2P$), 2.6–3.9 (m, 3, $\mathbf{CH_A}H_B\mathbf{CH_2}P$), and 6.9–7.9 ppm (m, 25, C_6H_5); after shaking this sample with D_2O, two sharp four-line patterns were observed, 3.33 (dd, 1, $CH_AH_BCD_2P$, J_{H_AP} = 38 Hz) and 1.85 ppm (dd, 1, $CH_AH_BCD_2P$, J_{H_BP} = 12 Hz, J_{AB} = 13 Hz); integrity of the patterns was confirmed by spin decoupling.

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(10) E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**, 1746 (1964).

(11) A chlorine–bromine exchange occurred during the drying ($CaCl_2$) stage.

(12) We wish to thank Dr. G. S. Reddy and Mr. D. Nickerson of the E. I. du Pont de Nemours and Co. for this spectrum.

Anal. Calcd for $C_{34}H_{29}PO_2$: C, 81.57; H, 5.84; P, 6.19. Found: C, 81.44; H, 5.84; P, 6.36.

B. From Benzoin (1) and Vinyl Triphenylphosphonium Bromide (4) in DMSO.—Benzoin (0.1 mol) was added to a prereacted mixture of sodium hydride (0.1 mol) and 50 ml of DMSO at room temperature. Immediately 0.1 mol of the salt **4** in 100 ml of DMSO was added dropwise to the mixture, and the solution was stirred at room temperature for 6 hr. The precipitate which formed was filtered off, recrystallized from chloroform, filtered, and washed with acetonitrile to give 33 g (66%) of phospholane, **9**, melting point and mixture melting point identical with the sample obtained above in A.

C. From 1 and 4 in Acetonitrile.—The sodium salt was prepared by adding benzoin (**1**, 0.042 mol) and sodium hydride (0.041 mol) in 50 ml of ether and stirring for 0.5 hr. The salt **4** (0.042 mol) was added all at once and 100 ml of acetonitrile was distilled into the mixture. The solution was allowed to stir at room temperature for 2 days and subsequently quenched with 300 ml of water. Extraction with ether, drying ($CaCl_2$), concentration, and precipitation with cold methanol gave 6.7 g (77%) of 2,5-dihydro-2,3-diphenylfuran (**6**), mp 79–80°. The furan was shown to be identical with that obtained previously.[15] The phospholane **9** could not be detected by examination of a methylene chloride extract of the reaction mixture.

D. From 1 and 4 in THF.—The reaction was undertaken at room temperature for 4 days as described above (C), except for the substitution of THF for acetonitrile. The reaction was then heated under reflux for 2 days. Working up the solution as above yielded triphenylphosphine oxide (0.5 g, 5%), and the furan **6** was identified by tlc and presumed to match (in yield) the triphenylphosphine oxide found. Methylene chloride extract of the aqueous solution (after ether extraction), drying ($CaCl_2$), and concentration gave, on ether precipitation, 21.5 g (80%) of salt **10a**, melting point and mixture melting point identical with those reported in a previous experiment.

3,4-Diphenyl-3-hydroxy-4-oxobutyltriphenylphosphonium Bromide (10b).—Phospholane **9** (0.002 mol) was added to 20 ml of ethanol which was saturated with hydrogen bromide and refluxed for 24 hr. The solution was cooled and neutralized with dilute sodium hydroxide, during which time the salt **10b** precipitated; 1.1 g (95%) of **10b** was recovered by filtration. After crystallization from methylene chloride–ether and drying, an analytically pure sample was obtained, mp 257.5–259.5°. The ir and nmr spectra were identical with those found for the chloride salt **8a**. The mixture melting point of **10a** and **10b** was 240–245°.

Anal. Calcd for $C_{34}H_{30}PO_2Br$: C, 70.23; H, 5.20; Br, 13.74. Found: C, 70.01; H, 5.37; Br, 13.82.

3,4-Diphenyl-3-hydroxy-4-oxobutyldiphenylphosphine Oxide (11).—Phospholane **9** (0.0064 mol) was heated under reflux for 96 hr in 20 ml of a 20% aqueous sodium hydroxide solution. Filtering of the cooled mixture gave 2.8 g (99%) of **11**. An analytically pure sample was obtained by dissolving the product in methylene chloride, drying ($CaCl_2$), and precipitating with ether: mp 202–204°; ir (KBr) 1110 (s, CP), 1170 (s, PO), 1260 (s, COC), 1680 (s, C=O), and 3400 cm^{-1} (m, OH); nmr ($AsCl_3$) δ 2.3–3.1 (m, 4, CH_2CH_2P), 6.9 (m, 1, OH), and 7.1–8.1 ppm (m, 20, C_6H_5).

Anal. Calcd for $C_{28}H_{25}PO_3$: C, 76.34; H, 5.72; P, 7.03. Found: C, 76.22; H, 5.78; P, 7.28.

3-Phenyl-3-hydroxypropyldiphenylphosphine Oxide (12).—Potassium *t*-butoxide (1.1 g, 0.01 mol) was added to a solution of **11** (0.3 g, 0.0007 mol) in 25 ml of *t*-butyl alcohol; the solution was refluxed under nitrogen for 72 hr. Dilution with 200 ml of water, extraction with chloroform, drying ($MgSO_4$), concentrating, and precipitating with hexane afforded white crystals of **12** (0.14 g, 60%), mp 144–146°.

Acidification of the water solution (48% HBr) followed by extraction with chloroform, drying ($MgSO_4$), and concentrating gave benzoic acid (*ca.* 0.05 g), presumably formed *via* acidic hydrolysis of *t*-butyl benzoate: ir ($CHCl_3$) 1115 (s, CP), 1170 (s, PO), and 3250 cm^{-1} (m, OH); nmr ($CDCl_3$) δ 1.6–2.6 (m, 4, CH_2CH_2P), 3.0–4.2 (m, 1, OH), 4.77 (t, 1, CH), and 7.0–7.9 ppm (m, 15, C_6H_5). On addition of D_2O to the sample the δ 4.2–3.0 multiplet disappeared.

Anal. Calcd for $C_{21}H_{21}O_2P$: C, 74.98; H, 6.29; P, 9.21. Found: C, 74.88; H, 6.29; P, 9.06.

Hydrolysis of 9a in Aqueous Ethanolic Sodium Hydroxide.—The phospholane **9a** (2.5 g, 0.005 mol) was added to a mixture of 25 ml of 20% aqueous sodium hydroxide and 25 ml of ethanol and stirred under reflux for 96 hr. The mixture was diluted with 250 ml of water, extracted with two 100-ml portions of chloroform, dried ($MgSO_4$), and concentrated to dryness, yielding a mixture which was shown to be benzhydrol (0.30 g, 32%, soluble in cold ether) and 3-phenyl-3-hydroxypropyldiphenylphosphine oxide (**12**, insoluble in cold ether, soluble in hot ether 1.24 g, 74%) by nmr and melting point.

Acidification of the aqueous layer (above) followed by extraction with two 100-ml portions of chloroform and treatment as above gave benzoic acid (0.44 g, 72%) and 2-carboxyethyldiphenylphosphine oxide (**13**, 0.43 g, 31%). Compound **13** was recrystallized from ether–hexane: mp 133–135° (lit.[13] mp 138°); ir ($CHCl_3$) 1715 (s, C=O), 1170 (s, PO), and 1120 cm^{-1} (s, CP); nmr ($CDCl_3$) δ 2.2–2.9 (m, 4, CH_2CH_2), 7.2–8.1 (m, 10, C_6H_5), and 10.5–10.6 ppm (s, 1, COOH).

Hydrolysis of 11 in Aqueous Ethanolic Sodium Hydroxide.—Treatment of a 2.2-g (0.005 mol) sample of the oxide **11** as above afforded the following yields of products: benzhydrol, 0.25 g (27%); **12**, 1.23 g (73%); benzoic acid, 0.46 g (75%); and **13**, 0.33 g (24%).

3,4-Diphenyl-3-methoxy-4-oxobutyltriphenylphosphonium Iodide (16).—Phospholane **9** (0.01 mol) and 25 ml of methyl iodide were refluxed for 2 days. On cooling and adding ether, 6.2 g (97%) of analytically pure salt **16** was obtained: mp 230–232°; ir (KBr) 1115 (s, CP), 1240 (m, COC), and 1680 cm^{-1} (s, C=O); uv (CH_3OH) 238 mμ (ϵ 34,000) and 255 (15,100); nmr ($CDCl_3$) δ 1.6–3.0 (m, 4, CH_2CH_2P), 3.2 (s, 3, OCH_3), and 7.1–8.1 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{35}H_{32}PO_2I$: C, 65.45; H, 5.02; P, 4.82; I, 19.75. Found: C, 65.36; H, 5.05; P, 4.79; I, 19.74.

3,4-Diphenyl-3-methoxy-4-oxobutyldiphenylphosphine Oxide (17).—The phosphonium salt **16** (0.0081 mol) was refluxed for 48 hr in 20 ml of 20% aqueous potassium hydroxide. After cooling, extracting with methylene chloride, drying (K_2CO_3), and concentrating, the oxide **17** was precipitated by addition of ether. The phosphine oxide **17** obtained (3.5 g, 95%) was recrystallized from methylene chloride–ether to give an analytically pure sample: mp 177–179°; ir (KBr) 1120 (s, CP), 1190 (s, P=O), 1240 (s, COC), and 1680 cm^{-1} (s, C=O); nmr ($AsCl_3$) δ 1.6–3.1 (m, 4, CH_2CH_2P), 3.2 (s, 3, OCH_3), and 7.1–8.1 ppm (m, 20, C_6H_5).

Anal. Calcd for $C_{29}H_{27}PO_3$: C, 76.63; H, 5.99; P, 6.81. Found: C, 76.56; H, 6.23; P, 6.62.

Phosphonioethylation of Benzoin Methyl Ether.—To a suspension of NaH (0.44 g, 0.01 mol) of 50 ml of dry DMSO was added benzoin methyl ether (4.5 g, 0.02 mol). After having been stirred for 0.5 hr at 25°, the solution was deep green. A solution of **4** (3.7 g, 0.01 mol) in 100 ml of DMSO was then added dropwise and the solution was allowed to stir for 2 hr, after which time it had become medium red and was then poured into 500 ml of water and extracted with two 200-ml portions of warm ether. The ether extracts were combined, dried ($MgSO_4$), and concentrated. Cooling at 0° for 1 hr, followed by filtration, gave 4.4 g (97%) of white crystals of **17**, mp 174–175°, mmp 173–176° with an authentic sample, ir and nmr identical with those reported above.

3-Phenyl-3-methoxypropyldiphenylphosphine Oxide (20).—Potassium *t*-butoxide (2.25 g, 0.02 mol) was added to a solution of **17** (6.0 g, 0.013 mol) in 100 ml of dry *t*-butyl alcohol; the solution was allowed to reflux for 5 days. After having been cooled and added to 500 ml of water, the suspension was extracted with chloroform, dried ($MgSO_4$), and concentrated to give 2.9 g (63%) of **20**.

Acidification of the water solution, extraction with chloroform, drying, and concentrating afforded 0.67 g of benzoic acid (44%).

An analytical sample of **20** was obtained by chromatography on Florisil (ethyl acetate eluent). Recovery of **20** was 2.1 g (46%): mp 128–130°; ir ($CHCl_3$) 1100 (s, COC), 1110 (s, CP), and 1190 cm^{-1} (s, P=O); nmr ($CDCl_3$) δ 1.7–2.6 (m, 4, CH_2CH_2P), 3.15 (s, 3, OCH_3), 4.18 (t, 1, CH), and 7.0–7.9 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{22}H_{23}O_2P$: C, 75.42; H, 6.62. Found: C, 75.80; H, 6.60.

3,4-Diphenyl-3,4-dihydroxybutyldiphenylphosphine Oxide (15).—Lithium aluminum hydride (0.0048 mol) and 3,4-diphenyl-3-hydroxy-4-oxobutyl-1-diphenylphosphine oxide (**11**, 0.0052 mol) were stirred for 2 days at room temperature in 30 ml of THF. The mixture was poured into cracked ice, extracted

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[13] H. Hoffmann, *Chem. Ber.*, **94**, 1331 (1961).

with methylene chloride, dried (K_2CO_3), and concentrated. The product was purified by column chromatography (Florisil) using ethyl acetate and then methanol as the eluent. White crystals of the phosphine oxide **15** (1.7 g, 80%) were recovered: mp 196–198°; ir (KBr) 1120 (s, CP), 1180 (s, P=O), 3300 (s, OH), and 3100 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 1.8–2.6 (m, 4, CH_2CH_2P), 3.4–3.9 (m, 2, OH), 4.70 (s, 1, HC), and 7.0–8.0 ppm (m, 20, C_6H_5).

Anal. Calcd for $C_{28}H_{27}PO_3$: C, 76.00; H, 6.15; P, 7.00. Found: C, 76.18; H, 6.35; P, 6.90.

The $LiAlH_4$ reductions reported in Table II were performed in essentially the same manner as listed above.

TABLE II

LITHIUM ALUMINUM HYDRIDE REDUCTIONS

Reactant (mol)	$LiAlH_4$, mol	Time, hr	Product (yield, %)
11 (0.0052)	0.0048	48	**15** (80)
9 (0.0103)	0.0105	120	**15** (41)
10a (0.0093)	0.0105	96	**15** (34)
17 (0.0075)	0.0079	96	**19** (12)

3,4-Diphenyl-3-methoxy-4-hydroxybutyldiphenylphosphine Oxide (**19**).—For experimental details and amounts of reagents see the preparation of **15** and Table II, respectively. The diphenylphosphine oxide **19** had the following data: mp 174–176°; ir (KBr) 1070 (s, COC), 1130 (s, CP), 1190 (s, P=O), and 3200 cm^{-1} (s, OH); nmr ($CDCl_3$) δ 1.8–2.6 (m, 4, CH_2CH_2P), 3.1 (s, 1, OH), 3.2 (s, 3, OCH_3), 5.0 (s, broad, 1, HC), and 6.6–8.0 ppm (m, 20, C_6H_5).

Anal. Calcd for $C_{29}H_{29}PO_3$: C, 76.29; H, 6.40; P, 6.79. Found: C, 76.61; H, 6.45; P, 6.35.

Attempted Phosphonioethylation of Methyl Benzoin with Vinyl Triphenylphosphonium Bromide (**4**).—Methyl benzoin (4.5 g, 0.02 mol) was added to a slurry of NaH (0.44 g, 52% oil dispersion, 0.01 mol) in 50 ml of dry DMSO under nitrogen. The solution was stirred for 5 min until gas evolution abated, and **4** (3.7 g in 100 ml DMSO, 0.01 mol) was added slowly. After having been stirred at 25° for 2 hr, the reaction mixture was diluted with water and extracted with ether and chloroform. The combined extracts were dried ($MgSO_4$) and concentrated. Dilution with hexane precipitated 1.9 g (68%) of triphenylphosphine oxide and concentration of the remaining hexane solution afforded 4.4 g (91%) of methyl benzoin. Ir, nmr, and tlc showed no trace of products arising from phosphonioethylation of the methyl benzoin.

3,4-Diphenyl-4-oxo-3-oxy(ethyl acetate)butyltriphenylphosphonium Bromide (**21**).—The phospholane **9** (5.0 g, 0.01 mol) was dissolved in 25 ml of dry methylene chloride and brought to vigorous reflux. Dry, distilled ethyl bromoacetate (4.0 g, 0.02 mol) in 25 ml of methylene chloride was dropped in very slowly, the addition requiring *ca.* 4 hr. The solution was refluxed for an additional 6 hr, cooled, and added to 500 ml of anhydrous ether. After filtration the residue was extracted into methylene chloride and reprecipitated in ether. After filtration, the salt was recrystallized from methylene chloride–ether four times to give 4.7 g of light pink salt, **21** (71%): mp 223–226°; ir ($CHCl_3$) 1115 (s, CP), 1220 (s, COC ester), 1230 (s, COC ether), 1680 (s, C=O ketone), and 1745 cm^{-1} (s, C=O ester); nmr ($CDCl_3$) δ 1.1 (t, 3, CH_3), 2.2–2.8 (m, 2, CH_2), 3.0–4.8 (m, 8) (4.0, s, OCH_2 superimposed on m, CH_2P and $O{=}COCH_2$), and 7.0–8.0 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{38}H_{36}O_4PBr$: C, 68.36; H, 5.44; Br, 11.97. Found: C, 68.30; H, 5.49; Br, 12.39.

Reaction of Phospholane 9 and Pure Bromoacetic Ester at 25°.—The phospholane **9** (2.0 g, 0.005 mol) was added to 25 ml of dry, distilled ethyl bromoacetate and stirred vigorously at 25° for 12 hr. The resulting suspension was poured into 1 l. of anhydrous ether, filtered, and recrystallized from methylene chloride–ether. The white salt was filtered, was dried *in vacuo*, and was found to be nearly pure **10b**, containing a few per cent **21**: yield 2.3 g (86%); mp 242–245°; with **10b**, mmp 240–245°. Ir and nmr spectra after recrystallization from methylene chloride–ether were identical with those of the known sample of **10b**.

Investigation of the concentrated ether filtrate by nmr and vpc showed the presence of small amounts of diethyl fumarate.

3,4-Diphenyl-4-oxo-3-(ethyl carbonyldioxy)butyltriphenylphosphonium Chloride (**22**).—The phospholane **9** (5.0 g, 0.01 mol) was dissolved in 75 ml of dry CH_2Cl_2, along with 1 g of anhydrous K_2CO_3, and 7 g of dry, distilled ethyl chloroformate. The reaction was stirred at 25° for 2 days, filtered, and added to 500 ml of anhydrous ether. After filtration the residue was redissolved in CH_2Cl_2 and reprecipitated in ether. After the process had been repeated several times, 5.0 g (82%) of the pure salt **22** was recovered: mp 178–180° dec; ir ($CHCl_3$) 1115 (s, CP), 1220 (s, COC ester), 1230 (s, COC ether), 1680 (s, C=O ketone), and 1740 cm^{-1} (s, C=O ester); nmr ($CDCl_3$) δ 1.0 (t, 3, CH_3), 2.1–4.4 (m, 6) (4.1, q, OCH_2 superimposed on m, CH_2CH_2P), and 7.1–8.1 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{37}H_{34}O_4PCl$: C, 72.98; H, 5.63; Cl, 5.82. Found: C, 73.11; H, 5.48; Cl, 6.03.

3-Benzoyloxy-3,4-diphenyl-4-oxobutyltriphenylphosphonium Chloride (**23**).—Benzoyl chloride (17 g, 0.12 mol) was added slowly to a solution of **9** (20.0 g, 0.04 mol) dissolved in 100 ml of dry chloroform, during which time a slight exothermic reaction was observed. After the addition was completed, the reaction was stirred at room temperature for 1 hr and then added to 1.5 l. of anhydrous ether. Filtration of the mixture and recrystallization of the white residue from methylene chloride–ether gave 27.0 g (94%) of analytically pure **23** containing 1 mol of CH_2Cl_2 of crystallization, mp 233–236°, with softening and loss of CH_2Cl_2 at 160°.

Anal. Calcd for $C_{31}H_{34}O_3PCl \cdot CH_2Cl_2$: C, 69.47; H, 5.00; Cl, 14.65. Found: C, 69.79; H, 5.21; Cl, 15.01.

Recrystallization from acetonitrile–ether gave analytically pure **23**: mp 233–235°; ir ($CHCl_3$) 1115 (s, CP), 1270 (s, COC), 1680 (m, C=O ketone), and 1720 cm^{-1} (s, C=O ester); nmr ($CDCl_3$) δ 2.9–3.3 (m, 4, CH_2CH_2P) and 7.1–7.9 ppm (m, 30, C_6H_5).

Anal. Calcd for $C_{41}H_{34}O_3PCl$: C, 76.80; H, 5.35; Cl, 5.53. Found: C, 76.52; H, 5.68; Cl, 5.47.

3-Bromoxy-3,4-diphenyl-4-oxobutyltriphenylphosphonium Bromide (**24**).—Bromine (1.25 ml, 0.022 mol) was dropped slowly into a solution of the phospholane **9** (5.0 g, 0.01 mol) in 25 ml of methylene chloride, during which time an exothermic reaction was observed. The bromine color faded quickly after addition to the solution. The reaction mixture was stirred for 2 hr at 25°, added to 500 ml of anhydrous ether, filtered, washed with ether, and dried *in vacuo*. The yield was 6.1 g of yellow salt which crystallized from methylene chloride–ethyl acetate to give 4.33 g (65%) of analytically pure **24**: mp 214–215°; ir ($CHCl_3$) 1115 (s, CP) and 1675 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 2.1–3.0 (m, 2, CH_2), 3.0–3.8 (m, 2, CH_2P), and 7.2–8.1 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{34}H_{29}O_2PBr_2$: C, 61.83; H, 4.43; Br, 24.20. Found: C, 61.87; H, 4.62; Br, 24.48.

Shaking a chloroform solution of **24** with an aqueous NaI solution, followed by addition of starch indicator, gave the deep blue color characteristic of elemental iodine.

Reaction of 24 with Acetone.—Salt **24** (0.66 g, 0.001 mol) was dissolved in 5 ml of acetone and warmed briefly. All yellow color quickly dissipated. The solution was then dropped into 50 ml of anhydrous ether and filtered to yield 0.58 g (100%) of **10b**. Evaporation of the ether filtrate afforded 0.44 g of an oil which was shown to consist of acetone (75%) and bromoacetone (25%) by nmr and vpc. This corresponds to an 81% yield of bromoacetone.

Registry No.—**9a**, 22950-45-4; **10a**, 22946-51-6; **10b**, 22950-46-5; **11**, 22950-47-6; **12**, 22950-48-7; **15**, 22950-49-8; **16**, 22950-50-1; **17**, 22950-51-2; **19**, 22950-52-3; **20**, 22966-75-2; **21**, 22966-76-3; **22**, 22946-52-7; **23**, 22966-77-4; **24**, 22966-78-5.

Acknowledgment.—We wish to gratefully acknowledge a Public Health Service Grant from the National Cancer Institute.