684 cm^{-1}; nmr signals ($DCCl_3$) at δ 7.15–8.16 (nine protons), 4.73 (quartet, one proton), and 1.76 ppm (doublet, three protons).

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.48; H, 4.88.

2-Hydroxy-3-(1′-methyl-1′-phenylethyl)-1,4-naphthoquinone was recrystallized from cyclohexane as pale, yellow needles: mp 137–137.5°; infrared absorptions (KBr) at 3308, 1648, 1590, 772, 732, and 704 cm^{-1}; nmr signals ($DCCl_3$) at δ 7.39–8.04 (four protons), 7.23 (five protons), and 1.82 ppm (singlet six protons).

Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.51; Found C, 78.13; H, 5.62.

2-Hydroxy-3-(diphenylmethyl)-1,4-naphthoquinone was recrystallized from cyclohexane: mp 188–188.5° (lit.[6] mp 186.5°); infrared absorptions (KBr) at 3355, 1652, 1589, 1492, 744, 724, and 698 cm^{-1}; nmr signals (DMSO) at δ 7.92 (four protons), 7.27 (ten protons), and 5.95 ppm (singlet, one proton).

2-Hydroxy-3-cyclohexyl-1,4-naphthoquinone was recrystallized from cyclohexane: mp 136–137.5° (lit.[3] mp 136.5–137.5°; infrared absorptions at 3355, 1661, 1589, 726, and 675 cm^{-1}; nmr signals ($DCCl_3$) at δ 7.60–8.04 (*ca.* four protons), 3.08 (multiplet, *ca.* one proton), 1.15–2.12 ppm (multiplet, *ca.* ten protons).

Kinetic Measurements. *t*-Butyl Peroxide Determinations.—Solutions containing *t*-butyl peroxide and I in ethylbenzene (molar ratio of I to ethylbenzene about 1:50, the limit of solubility of the quinone at 125°) were placed in a 100-ml round-bottom flask with an 8-in. neck. The flask was sealed with a rubber septum and suspended in a constant-temperature oil bath set at 125°. Samples (1.0–1.5 ml) were withdrawn at various time intervals with a syringe equipped with a 10-in. needle. The peroxide content of the withdrawn sample was determined by gas chromatographic analysis of a mixture consisting of an accurately weighed quantity of the sample and benzene which served as an internal standard. A correction factor relating the mole ratios of *t*-butyl peroxide and benzene to the ratios of their chromatographic peak areas was determined from mixtures containing known amounts of each. The gas chromatographic analysis were performed with an F & M Model 5750 instrument equipped with a hydrogen flame detector using a 6 ft × 1/8 in. column packed with 2% DEGS and 8% SF-96 on 60/80 mesh Chromosorb W. The chromatograms were traced with a Mosely recorder equipped with a disk intergrator.

Acetyl Peroxide Determinations.—Solutions consisting of acetyl peroxide (dissolved in dimethyl phthalate) and I in acetic acid were placed in a 100-ml round-bottom flask equipped with an 8-in. neck. The flask was sealed with a rubber septum and placed in a constant-temperature bath set at 70°. Samples were withdrawn at various time intervals and their peroxide content was determined by the iodometric method outlined by Silbert and Swern.[7]

Registry No.—I, 83-72-7.

[7] L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

1,4-Diphosphoniacyclooctene and Diene Salts. Their Formation, Hydrolysis, and Attempted Conversion to 1,4-Diphosphacyclooctatetraenes

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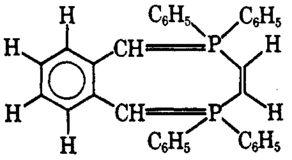
Received June 22, 1967

Our interest in the 1,4-diphosphorus cyclohexanes[1–3] led us to prepare 1,4-diphosphorus derivatives of benzocyclooctene and diene in order to obtain the diylide tetraene (A).



A

Reaction of *o*-bis(bromomethyl)benzene (I) with ethylenebis(diphenylphosphine) (II)[4] or *cis*-vinylenebis(diphenylphosphine) (III)[5] (in refluxing benzene) gave 1,1,4,4-tetraphenyl-1,4-diphosphonia-6,7-benzocyclooctene-6 dibromide (IV) and 1,1,4,4-tetraphenyl-1,4-diphosphonia-6,7-benzocyclooctadiene-2,6 dibromide (V), respectively, in quantitative yields (Scheme I).

Infrared spectral analysis of both IV and V showed bands at 1430–1440 and 1105–1110 cm^{-1}, expected of a phenylphosphonium salt. Solubilities and titration with aqueous silver nitrate confirmed this conclusion. Elemental analysis showed IV to be a 1:1 adduct of I and II and V to be a 1:1 adduct of I and III. Preparation of picrates of both IV and V by treatment with aqueous sodium picrate followed by elemental analysis of these materials showed that all of the halogen in IV and V was ionic. Both IV and V are, therefore, cyclic. The solubilities and melting points also make it unlikely that IV or V are very long polymeric phosphonium salts.

Molecular weight data obtained for methanolic solutions of V employing an osmometer show it to be associated and effectively a 1:1 electrolyte at concentrations above 0.01 *M* (with an effective mol wt = 1/2 mol wt) but to dissociate at decreasing concentrations (Table I). Extrapolation to infinite dilution proved to be impossible owing to lack of reliability of the instrument at very low concentrations. Conductance mea-

Table I

Molecular Weight Determinations of V in Methanol Solution by Osmometric Method

Concn, moles/l.	Mol wt
0.0137	323
0.0272	332
0.0530	337

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[1] A. M. Aguiar, H. J. Aguiar, and D. J. Daigle, *J. Am. Chem. Soc.*, **87**, 671 (1965).

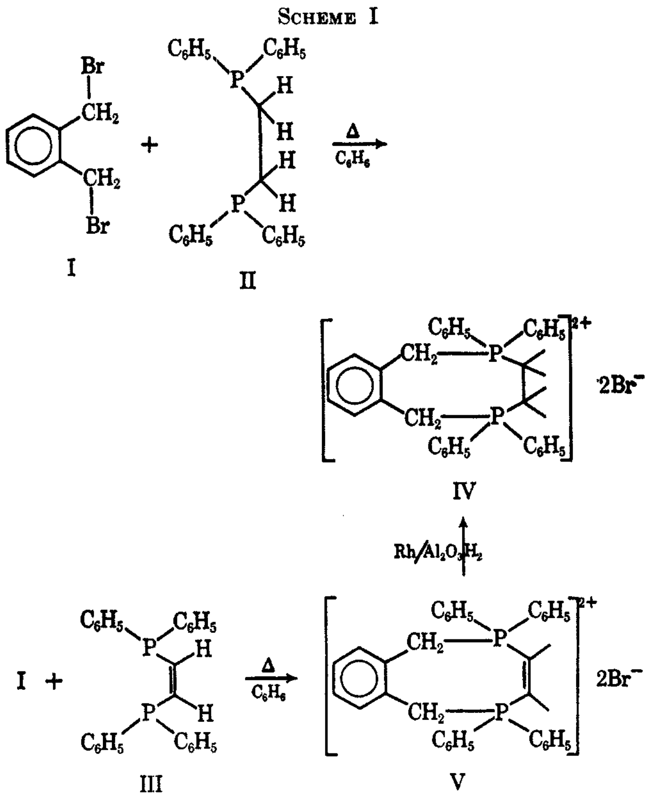
[2] A. M. Aguiar and H. J. Aguiar, *ibid.*, **88**, 4090 (1966).

[3] A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *ibid.*, **89**, 3067 (1967). The rhodium catalyst was suggested by Professor A. I. Meyers of Louisiana State University in New Orleans.

[4] A. M. Aguiar and J. Beisler, *J. Org. Chem.*, **29**, 1660 (1964).

[5] A. M. Aguiar and D. J. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

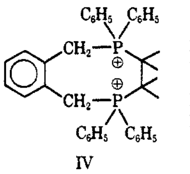
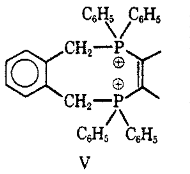
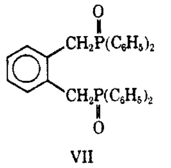
SCHEME I



surements, however, show that V is indeed a 2:1 electrolyte (Figure 1). This behavior is similar to that observed in other cyclic diphosphonium salts.[6]

Proton magnetic resonance spectra of trifluoroacetic acid solutions of IV and V at 60 MHz also support the assigned structures (Table II).

TABLE II

Compound	Nmr assignment[a]	τ, ppm	Multiplicity	J_{PH}, cps	Area ratio	Solvent
 IV	P-phenyl	2.18	Complex	...	10	TFA[b]
	Phenyl protons	2.68	Complex	...	1	
		2.96	Complex	...	1	
	Benzyl	4.95	Doublet	14	2	
	PCH_2CH_2P	6.40	Doublet	7	2	
 V	P-phenyl	2.2	Complex	...	10	TFA[b]
	Phenyl protons	2.85	Complex	...	1	
		3.3	Complex	...	1	
	Benzyl	4.95	Doublet	13.0	2	
	Vinyl	1.20 1.54 1.87	"Pseudo-triplet"	...	1	
 VII	P-phenyl	2.12 2.4	Complex	...	5	$CDCl_3$
	Phenyl	3.05	Singlet	...	1	
	Benzyl	5.95	Doublet	12	1	

[a] Proton nmr shifts at 60 MHz employing tetramethylsilane as an internal standard. [b] TFA = trifluoroacetic acid.

The spectrum of V shows the 20 P-phenyl protons as a split complex centered at τ 2.2 ppm, the other four phenyl protons as two broad multiplets centered at τ 2.85 and 3.3 ppm, while the four benzyl protons appear as a doublet centered at τ 4.95 ppm (J_{PH} = 13.0 cps). Roughly the same pattern is observed for compound IV.

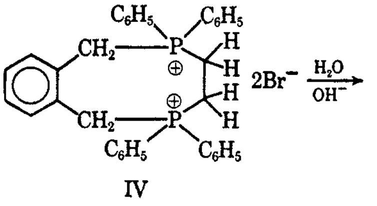
The two vinyl protons in V appear as two peaks with a shallow broad complex in the center appearing at lower field strength than the P-phenyl protons. The upfield peak overlaps to some extent with the P-phenyl proton complex at 60 MHz. This is the pattern observed for bisphosphonium salts of *cis*-vinylenebis(diphenylphosphine).[2,3] The low-field peak is at τ 12. ppm and the upfield peak is a *ca.* 40 cps away.

The ethylene protons of IV show up as a doublet at τ 6.40 (J_{PH} = 7 cps) which is the usual second-order spectra observed[1,4] for quaternized derivatives of ethylenebis(diphenylphosphine).

Conversion of V into IV was accomplished at 45 psi of hydrogen by employing 5% rhodium on alumina catalyst (Scheme I).[3]

Basic hydrolysis of IV gave ethylenebis(diphenylphosphine) dioxide (VI) (Scheme II).

SCHEME II



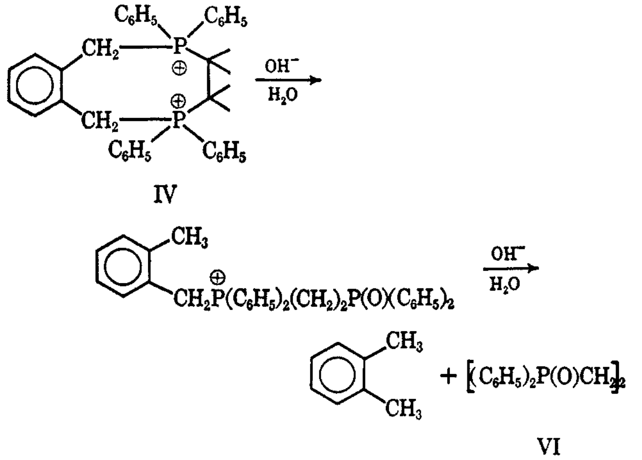
$(C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2$

VI

The exact fate of the *o*-xylene moiety in the basic hydrolysis of IV has not been conclusively established, but it appears to be *o*-xylene. These results can be rationalized by assuming a normal stepwise hydrolytic mechanism (Scheme III).

This is analogous to the hydrolysis of the dibenzyl bromide salt of ethylenebis(diphenylphosphine)[7] (Scheme IV).

SCHEME III



VI

SCHEME IV

$$[(C_6H_5)_2P(CH_2C_6H_5)CH_2]_2Br_2 \xrightarrow[H_2O]{OH^-} [(C_6H_5)_2P(O)CH_2]_2$$

VI

On the other hand, similar hydrolysis of V leads to preferential cleavage of the vinylene bridge (Scheme V).

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(6) A. M. Aguiar, K. C. Hansen, and J. Mague, *J. Org. Chem.*, **32**, 2383 (1967).

(7) A. M. Aguiar and Erwyn Freeman, unpublished results.

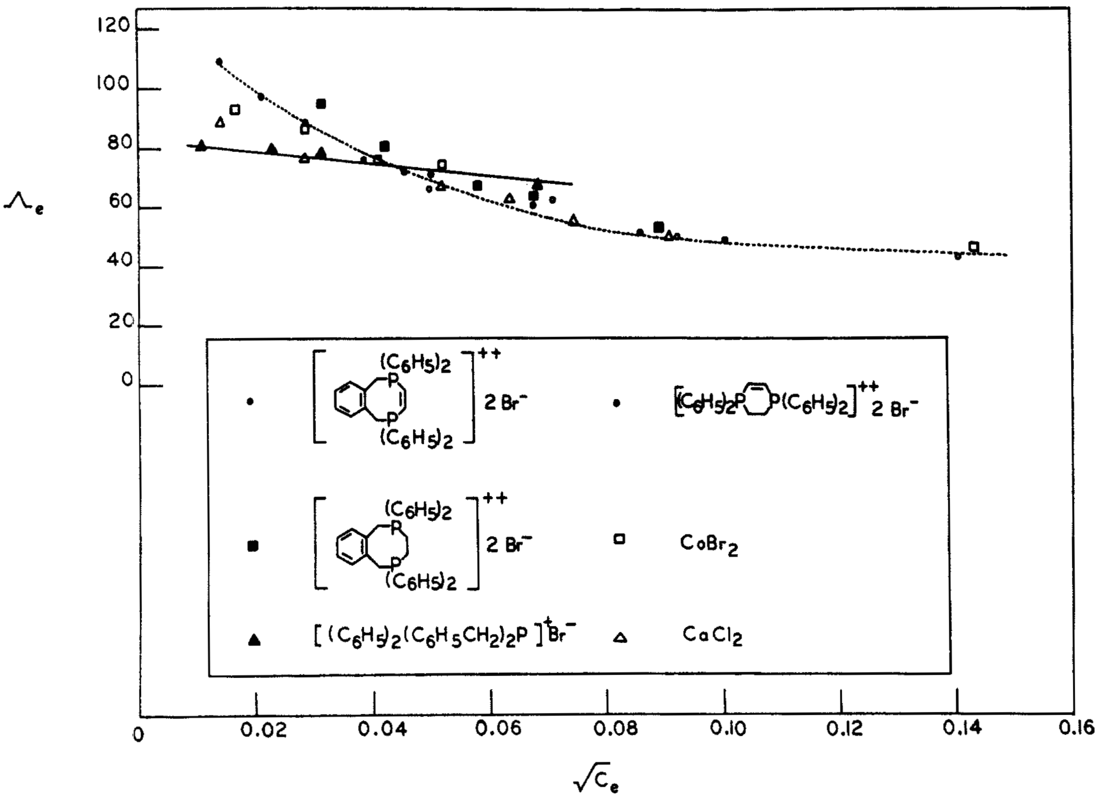
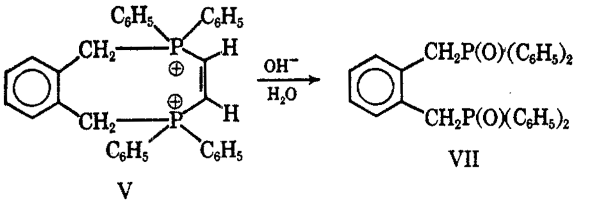


Figure 1.—Equivalent conductances of methanolic solutions of electrolytes over a range of equivalent concentrations at 25°.

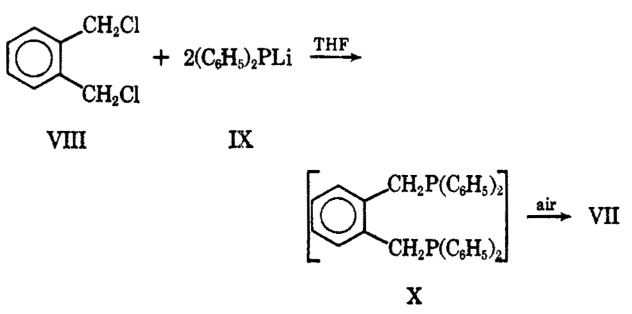
SCHEME V



It is likely that the monooxide of VII is initially formed by the same path suggested for the basic hydrolysis of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene-2 dibromide.[2] Air oxidation would lead to VII.

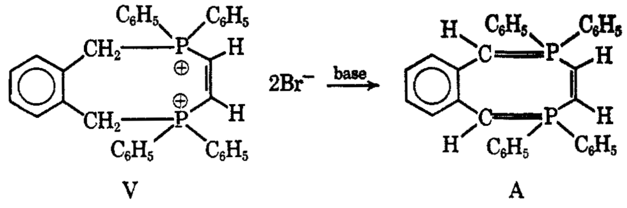
Compound VII was also produced by reaction of *o*-bis(chloromethyl)benzene (VIII) with lithium diphenylphosphide (IX) in tetrahydrofuran (Scheme VI).[8]

SCHEME VI



Formation of the cyclic diylide, 1,1,4,4-tetraphenyl-1,4-diphospha-6,7-benzocyclooctatetraene-2,4,6,8 (A), was then attempted (Scheme VII).

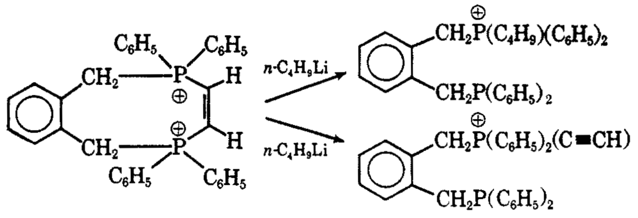
SCHEME VII



Treatment of an anhydrous methanol solution of V with 2 mole equiv of collidine, followed by concentration and cooling, precipitated collidine hydrobromide in high yield, leaving an orange-red solution. Only a red semisolid could be obtained from the solution. Treatment of this material with dilute hydrobromic acid led to recovery of a phosphonium salt of unknown structure, showing that the basic cyclic structure was probably not retained in the red semisolid. Cold, concentrated, degassed aqueous sodium hydroxide under nitrogen gave a deep red, noncrystalline solid from V (unlike from IV) which was sensitive to air. All attempts at crystallization failed. Regeneration of V with dilute hydrobromic acid failed.

Excess pentane solution of butyllithium added to a benzene suspension of V, under nitrogen and refluxed, gave a deep red solution. Agitation of this red benzene solution with dilute hydrobromic acid led to a new phosphonium salt. This could be due to ring opening by at least two different paths (Scheme VIII).

SCHEME VIII



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[8] A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962).

Experimental Section

1,1,4,4-Tetraphenyl,1-4-diphosphonia-6,7-benzocyclooctene-6 Dibromide (IV).—Ethylenebis(diphenylphosphine)[4] (1.98 g, 5 mmoles) was dissolved in 70 ml of dry benzene under nitrogen and 1.32 g (5 mmoles) of α,α′-dibromo-*o*-xylene was added. The mixture was refluxed for 3 hr and cooled. After filtration and washing with cold benzene, the precipitate was recrystallized from methanol: yield, 3.06 g (93% yield); mp 345–347°.

Anal. Calcd for $C_{34}H_{32}P_2Br_2$: C, 61.90; H, 4.85; Br, 24.20. Found: C, 61.93; H, 4.93; Br, 23.74.

The picrate was made as was the picrate of V.

Anal. Calcd for $C_{46}H_{36}O_{14}P_2N_6$: C, 57.60; H, 3.76; N, 8.76. Found: C, 57.65; H, 4.07; N, 8.33.

1,1,4,4-Tetraphenyl-1,4-diphosphonia-6,7-benzocyclooctadiene-2,6 Dibromide (V).—*cis*-Vinylenebis(diphenylphosphine)[5] (1.98 g, 5 mmoles) was dissolved in 70 ml of anhydrous benzene under nitrogen and 1.32 g (5 mmoles) of α,α′-dibromo-*o*-xylene was added. The mixture was refluxed for 3 hr and then cooled to room temperature. Filtration of the white precipitate and recrystallization from methanol gave 3.16 g (96% yield), mp 331–334°.

Anal. Calcd for $C_{34}H_{30}P_2Br_2$: C, 61.87; H, 4.58; Br, 24.20. Found: C, 61.39; H, 4.69; Br, 23.97.

Addition of a methanolic solution of V to one of sodium picrate gave a yellow solid which was recrystallized from ethanol and water, mp 239–241°.

Anal. Calcd for $C_{46}H_{34}P_2N_6O_{14}$: C, 57.8; H, 3.58; N, 8.79. Found: C, 58.30; H, 3.43; N, 8.59.

Hydrogenation of V to IV.—A solution of 150 ml of methanol and 3.0 g of V along with 2 g of 5% rhodium on alumina was placed in a Parr apparatus. The suspension was rocked for 3.5 days, at room temperature, under 45 psi of hydrogn. After filtration, the deep yellow filtrate was concentrated. Crystallization took place. After filtration, the proton nmr spectra of these crystals in trifluoroacetic acid showed no vinyl protons and did show a doublet for the two methylenes between the phosphorus atom and was, in fact, identical with that of IV.

Basic Hydrolysis of IV.—A suspension of 1.32 g (2.0 mmoles) of IV in a solution of 50 ml of water containing 5.0 g of sodium hydroxide was refluxed for 1 hr and, after cooling to room temperature, the precipitate was filtered off, washed with water until netural, dried, and recrystallized from methanol to give ethylenebis(diphenylphosphine) dioxide (VI) identified by melting point (265°) and infrared and proton nuclear magnetic resonance spectral comparison with an authentic sample.

Basic Hydrolysis of V.—A suspension of 1.32 g (2 mmoles) of V in 60 ml of water was stirred with 5.0 g of sodium hydroxide and the mixture refluxed for 1 hr. After cooling to room temperature, the precipitate was filtered off, washed until neutral, and dried. After trituration with benzene and drying, it was recrystallized from methanol. The material was shown to be *o*-xylidenebis(diphenylphosphine) dioxide (VII) by melting point (284°), mixture melting point determination, and infrared and proton nuclear magnetic resonance spectral comparison with an authentic sample. The yield was 0.8 g (79%).

Evaporation of the benzene solution gave a solid which, after recrystallization, was shown to be *cis*-vinylenebis(diphenylphosphine) dioxide by melting point (240°) and infrared spectrum. Only a 0.1-g (11.7%) yield was obtained.

***o*-Xylidenebis(diphenylphosphine) Dioxide (VII).**—To 150 ml of a solution of lithium diphenylphosphide in tetrahydrofuran (prepared from 0.1 mole (22.1 g) of diphenylphosphinous chloride and lithium[8]) was added a solution of 8.75 g (0.05 mole) of *o*-1,2-bis(chloromethyl)benzene in 50 ml of tetrahydrofuran. Addition was dropwise with rapid stirring under nitrogen. The reaction was exothermic enough to keep the solution refluxing and the red color of the phosphide solution was completely discharged toward the end of the addition.

After the tetrahydrofuran solution was concentrated by aspirator solvent stripping, the residual suspension was added to 500 ml of water containing 10 ml of 3% hydrogen peroxide and allowed to stand overnight. Filtration of the basic solution left 17.0 g of crude VII (67% yield, (mp 283°) by infrared and proton nuclear magnetic resonance spectral comparison. Acidification of the basic filtrate gave 2.33 g (10.7% yield) of diphenylphosphinic acid.

Reaction of V with *s*-Collidine in Benzene.—To a suspension of 0.99 g (1.5 mmoles) of V in 50 ml of benzene was added 0.458 g (3.78 mmoles) of *s*-collidine and the suspension was refluxed for 9 hr. There was no evidence of reaction. It was then cooled and the precipitate filtered and recrystallized from methanol.

Reaction of V with *s*-Collidine in Methanol.—To a solution of 0.66 g (1 mmole) of V in 50 ml of methanol was added 0.242 g (2 mmoles) of *s*-collidine and the solution was refluxed for 8 hr. The deep yellow solution as concentrated to a paste under aspirator vacuum and acetonitrile added. After filtration of the precipitate thus formed, it was dried to give 0.403 g of a hygroscopic solid whose proton nmr spectrum showed it to be *s*-collidine hydrobromide (theory, 0.404 g).

Treatment of the paste resulting from the evaporation of the filtrate with dilute hydrobromic acid gave 0.61 g of a solid whose ir spectrum showed it to be a phosphonium salt. Both the ir and proton nmr spectra show it to be different from the starting V.

Reaction of V with Concentrated Aqueous Sodium Hydroxide.—A concentrated aqueous sodium hydroxide solution was heated to boiling and cooled under nitrogen. To 50 ml of this solution was added 1.32 g (2 mmoles) of V under nitrogen at room temperature with rapid stirring and slight warming. A red paste was precipitated. This material was dissolved in deuteriochloroform (a small amount of white solid fell out) to give a red solution.

The ir spectrum showed that the solution contained a phosphine oxide and the nmr spectrum showed no benzyl or vinyl protons but only phenyl protons and a sharp singlet at τ 8.75 ppm in the ratio of *ca.* 24:1. The starting material could not be regenerated from the red paste by treatment with dilute hydrobromic acid.

Reaction of V with Butyllithium in Benzene.—A suspension of 1.32 g (2 mmoles) of V was suspended in 50 ml of anhydrous benzene under nitrogen. Excess butyllithium in pentane (5 mmoles) was added with stirring. It was refluxed for 2 hr to give a deep red solution. This solution was added to 15% hydrobromic acid and shaken. After the benzene had evaporated, the solid was filtered off and 1.10 g of material was obtained. The ir spectrum of a KBr disk of this material showed it to be a phosphonium salt other than the starting material.

Registry No.—IV, 15352-69-9; IV picrate, 15303-24-9; V, 15303-25-0; V picrate, 15303-26-1; VII, 15303-27-2.

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