The Methanethiol Adduct[8] from Methyl Malvalate (8).—A sample of homogeneous methyl malvalate (0.333 g or 1.13 mmol) was allowed to stand away from air for 8 days at room temperature with 15 ml of a 10% benzene solution of methyl mercaptan. After volatiles were blown off in a stream of pure nitrogen, the residue was pumped in a high vacuum to a constant weight of 0.389 g (100.5%). This methyl mercaptan adduct was colorless though faintly milky. It showed the same single spot on thin layer chromatography and the same single peak on gas–liquid chromatography as the sample obtained after further purification. Preparative gas–liquid chromatography, using an 8-ft 10% silicone oil (SE-30) column at 230° with helium as the carrier, provided approximately 0.3 ml of water-white product.

Anal. Calcd for $C_{20}H_{38}O_2S$: C, 70.12; H, 11.18. Found: C, 70.12; H, 11.32.

The adduct gave one spot on thin layer chromatography on a silica plate with 8:1 hexane–ether as developing solvent. Gas–liquid chromatography through a 6-ft silicone oil (SF-96) column at 230° produced a single symmetrical peak. The adduct showed $n^{25}D$ 1.4702; ir (neat) 3060 (cyclopropane), but no peaks at 1875 or 1005 cm^{-1}; nmr (20% in CCl_4) δ 0.3–0.85 (complex, cyclopropane H's), 0.90 (distorted t, CH_3 at position 17), 1.1–1.8 (complex), 2.0 (s, SCH_3), 2.2 (distorted t, CH_2COOCH_3), 3.60 (s, OCH_3). The ratio of the area under the 3.60-ppm signal to all others was very close to the expected 3:35.

Registry No.—**2**, 24471-13-4; **3**, 24471-14-5; **6**, 24471-15-6; **7**, 24471-16-7; **8**, 5026-66-4; **9**, 24471-18-9; **10**, 24471-19-0; **11**, 24471-20-3; **12**, 24471-23-6; 1-chloro-4,5-(ethoxycarbonylmethano)-4-decene, 24471-24-7; 1-chloro-4,5-carboxymethano-4-decene, 24471-25-8; 1-chloro-4,5-(chlorocarbonylmethano)-4-decene, 24471-26-9; 1-chloro-4,5-methano-4-decene, 24471-27-0; methyl 5,6-methano-5-undecenoate, 24471-28-1; 1-cyano-4,5-methano-4-decene, 24471-29-2.

Acknowledgment.—We gratefully acknowledge the help of Southern Regional Research Laboratory, U. S. Department of Agriculture [Research Grant No. 12-14-100-7992 (72)], that made this work possible.

Compounds Derived from 1-Methyl-4-phosphoraninone. A Wittig Reaction with Retention of Phosphorus

DANIEL LEDNICER

Research Laboratories of The Upjohn Company, Kalamazoo, Michigan 49001

Recieved December 23, 1969

1-Methyl-4-phosphoraninone was condensed with a series of arylmagnesium bromides. The resulting alcohols were converted to a series of derivatives including 1,2,3,6-tetrahydro-4-aryl-1,1-dimethylphosphorinium iodides. These latter were allowed to react *via* their ylides with aromatic aldehydes to afford 3,6-diaryl-3,5-hexadienyldimethylphosphine oxides. The reaction of these ylides with ketones also gave the corresponding dienes.

Though innumerable nitrogen heterocyclic compounds have been prepared as potential medicinal agents, their phosphorus counterparts remain largely unknown. Recent reports on the preparation and biological activity of the phosphorus analogs of a series of phenothiazines[1] and the finding that 4-phosphoraninones[2] prepared from bis(2-cyanoethylalkyl)phosphines[3] readily add Grignard reagents[4] led us to use 1-methyl-4-phosphoraninone (**1**) as the key intermediate for the present work.

Reaction of ketone **1** with a series of arylmagnesium bromides afforded the corresponding alcohols (Scheme I). Because of the conformational stability of trivalent phosphorus,[5] these products would be expected to be mixtures of the geometrical isomers about phosphorus and C-4. Indeed, each of the oily alcohols exhibited a pair of P–CH_3 doublets in the nmr in a roughly 1:1 ratio. Reaction of these phosphines with methyl iodide afforded the quaternary salts; since this last reaction removes one of the centers of isomerism by symmetrizing the phosphorus, each alcohol mixture gave a single crystalline methiodide (**2–7**) (Table I).

Alternately, the center of isomerism at C-4 was removed by conversion of the alcohol to the olefin. These last products, though often crystalline, proved too labile to air to characterize as the free bases. Conversion to either the *p*-toluenesulfonate (**8, 9**) or methiodide (**10–13**) gave a series of stable, easily characterized compounds. In the case of the *m*-trifluoromethylphenyl derivative, one of the isomers of the alcohol was isolated as its *p*-toluenesulfonate salt (**14**); attempts to dehydrate this last compound were unavailing.

The Wittig reaction has come to be one of the most versatile of methods for the elaboration of carbon chains; modifications of the reaction are legion.[6,7] Since this reaction involves in its first stages the generation of a carbanionoid center, the phosphonium salt chosen usually contains but one group with hydrogens α to phosphorus. In the course of the reaction reorganization of the bonding in the intermediate betaine results in the loss of phosphorus as a phosphine oxide.[8,9]

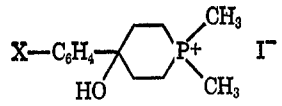
The quaternary salts **10–13** contain structural features which suggest a novel modification of the Wittig reaction: first, though there are three sets of α hydrogens, the allylic ring proton should be removed in preference to the others; and, second, collapse of the betaine (Scheme II), as in the generally accepted mechanism, should lead to a product in which the phosphorus is retained.

Treatment of a suspension of the quaternary salt **11** in THF with butyllithium followed by benzaldehyde gave upon work-up and chromatography a crystalline compound (**15**). The nmr spectrum of this material showed the presence of two aromatic rings (multiplets from δ 6.9 to 7.7; 9 H), the three vinyl protons as multi-

(1) R. A. Wiley and J. H. Collins, *J. Med. Chem.*, **12**, 146 (1969).
(2) R. P. Welcher, G. A. Johnson, and V. P. Wystrach, *J. Amer. Chem. Soc.*, **82**, 4437 (1960).
(3) M. Grayson, P. T. Keough, and G. A. Johnson, *ibid.*, **81**, 4803 (1959).
(4) H. E. Shook, Jr., and L. D. Quin, *ibid.*, **89**, 1841 (1967).
(5) L. D. Quin and H. E. Shook, Jr., *Tetrahedron Lett.*, 2193 (1965).
(6) S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).
(7) H. J. Bestman, *Angew. Chem. Int. Ed. Engl.*, **4**, 583 (1965).
(8) A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.*, **85**, 2790 (1963).
(9) M. E. Jones and S. Trippett, *J. Chem. Soc., C*, 1090 (1966).

TABLE I

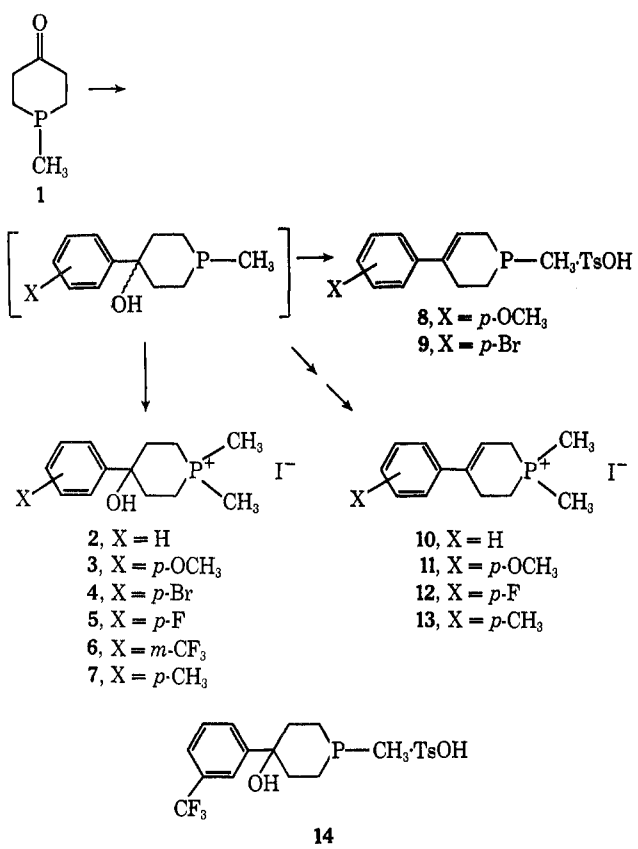
4-HYDROXY-1,1-DIMETHYL-4-ARYLPHOSPHORANINIUM IODIDES



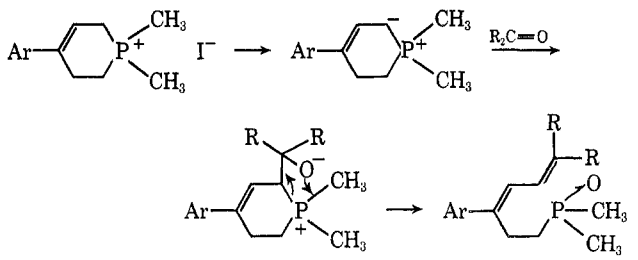
Compd no.[a]	X	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % I	Found, % C	Found, % H	Found, % I
2	H	228–230	41	44.59	5.76		44.66	5.81	
3	*p*-CH_3O	212–214	58	44.22	5.83	33.38	44.21	5.72	33.40
4[b]	*p*-Br	233–235.5	45	36.39	4.46	29.58	36.54	4.30	29.26
5	*p*-F	227.5–229	47	42.58	5.20		42.58	5.29	
6	*m*-CF_3	142–148	28	40.21	4.58		40.75	4.72	
7	*p*-CH_3	182–183	44	46.17	6.09		45.94	6.12	

[a] Compound recrystallized from acetonitrile–ether. [b] Recrystallized from acetonitrile.

SCHEME I

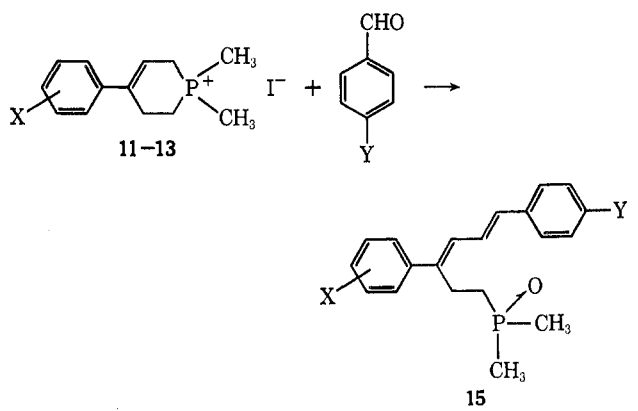


SCHEME II



quence of the purification procedure rather than a stereoselective reaction, particularly in view of the less than 50% yields. It is of note in this regard that, in the case of the tolyl compound (**15h**, **15i**) (Table II), both possible isomers were obtained in pure form.

SCHEME III



plets (δ 6.4 to 6.9), the methoxyl as a three-proton singlet at δ 4.9, the ethylene carrying the phosphorus as an A_2B_2 pattern of multiplets centered at δ 1.85 and 3.1, and finally the two methyl groups on phosphorus as a six-proton doublet (J = 13 Hz) centered at δ 1.5. The double bond adjacent to the ring has perforce the *trans* configuration; since only a single isomer was isolated, the geometry of the newly generated double bond cannot be assigned unambiguously. The uv spectrum of the product [λ_{max} 330 mμ (ϵ 53,000)] suggests it to be the *trans,trans* compound.[10] As can be seen from Table II this reaction can be applied quite generally to the preparation of substituted 3,6-diaryl-3,5-hexadienyldimethylphosphine oxides by the choice of the appropriate salt and aromatic aldehyde. Though a single isomer was isolated in most cases we consider this a conse-

The reaction of the cyclic ylides with representative ketones similarly afforded the phosphorus-containing dienes. Both benzophenone and cyclohexanone gave the condensation products in workable yields. Though the product from the condensation with acetone was obtained in good yield as a crude material, this product (**18**) proved difficult to handle; the yield of pure material was consequently quite low.

Experimental Section[11]

1-Methyl-4-(*p*-methoxyphenyl)-4-phosphoraninol.—To the ice-cooled Grignard reagent prepared from 11.0 g (0.059 mol) of

(10) The corresponding uv spectra for *trans,trans*- and *cis,trans*-1,4-diphenylbutadiene are λ_{max} 330 mμ (ϵ 50,000) and λ_{max} 312 mμ (ϵ 30,000): J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957).

(11) All melting points are uncorrected and reported as obtained on a Thomas–Hoover capillary melting point apparatus. Nmr spectra were obtained in deuteriochloroform on a Varian A-60A spectrometer. The author is indebted to the Department of Physical and Analytical Chemistry of The Upjon Co. for spectral determinations and elemental analyses.

TABLE II

3,6-DIARYL-3,5-HEXADIENYLDIMETHYLPHOSPHINE OXIDES

$$p\text{-}XC_6H_4C(CH_2CH_2PO(CH_3)_2)=CHCH=CH-(p\text{-}C_6H_4Y)$$

Compd no.	X	Y	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
15a	CH_3O	H	135–137	50	74.09	7.40	73.72	7.49
15b	CH_3O	CH_3O	147–149	50[a]	70.67[b]	7.57	70.73	7.67
15c	F	CH_3O	167–169	41[a]	70.38	6.75	70.26	6.77
15d	F	F	122–125	21	69.35	6.11	69.02	6.51
15e	F	CH_3[c]	141–143	51	73.66	7.07	73.41	7.05
15f	F	CH_3[d]	117–119.5	20	73.66	7.07	73.42	7.68
15g	F	NO_2[e]	177–179	13	64.33	5.67	63.97	5.91
15h	CH_3	H	130–132	45	77.77	7.77	77.27	8.21
15i	CH_3	F	129–131	43	73.66	7.07	73.44	7.15

[a] Isolated without chromatography. [b] Nmr shows presence of 0.5 mol of acetone; calcd for $C_{22}H_{27}O_3P \cdot 0.5Me_2CO$. [c] *trans,trans*, λ_{max} 323 (ϵ 37,950). [d] *trans,cis*, λ_{max} 323 (ϵ 36,000). [e] Recrystallized from aqueous methanol.

anisyl bromide and 1.45 g (0.06 g-atom) of magnesium in 50 ml of THF (tetrahydrofuran) there was added 5.0 g (0.036 mol) of 1-methyl-4-phosphoraninone in 50 ml of THF. The mixture was allowed to stand overnight at room temperature, cooled in ice, and treated with 50 ml of saturated ammonium chloride. Ether was then added and the organic layer was washed with water. The ether was extracted several times with 2.5 *N* hydrochloric acid. The gum which precipitated when the acid extracts were made basic was taken up in ether. This last extract was washed with water and brine, percolated through sodium sulfate, and taken to dryness. There was obtained 7.73 g (98%) of the crude alcohols as a viscous syrup.

Proceeding exactly as above, but using the Grignard reagents from *p*-dibromobenzene, *p*-fluorobromobenzene, and *p*-bromotoluene, respectively, there was obtained 1-methyl-4-(*p*-bromophenyl)-4-phosphoraninol (98%), 1-methyl-4-(*p*-fluorophenyl)-4-phosphoraninol (98%), and 1-methyl-4-(*p*-tolyl)-4-phosphoraninol. All these products were obtained as viscous oils and were not characterized.

1-Methyl-4-(*m*-trifluoromethyl)-4-phosphoraninol *p*-Toluenesulfonate (14).—To the Grignard reagent prepared from 22.5 g (0.10 mol) of *m*-trifluorobromobenzene and 2.45 g of magnesium in 250 ml of THF there was added 5.20 g of the ketone in 50 ml of THF. The alcohol was obtained in the same manner as those above. A solution of that oil in 200 ml of xylene was treated with 8.40 g of *p*-toluenesulfonic acid and the precipitated solid was collected on a filter. A small sample was recrystallized from acetonitrile–ether to mp 201–205°.

Anal. Calcd for $C_{20}H_{24}F_3O_4PS$: C, 53.56; H, 5.34. Found: C, 53.86; H, 5.07.

The remaining solid was reconverted to the free base to afford 8.47 g (86%) of oil.

1-Methyl-1,2,3,6-tetrahydro-4-(*p*-methoxyphenyl)phosphorin Tosylate (8).—A mixture of the crude alcohol obtained from 5 g of the phosphoraninone and 8.0 g of *p*-toluenesulfonic acid in 200 ml of benzene was heated at reflux under a Dean–Stark trap overnight. The mixture was then extracted in turn with water and two portions of 2.5 *N* hydrochloric acid. The aqueous layer was then made basic under a blanket of nitrogen. The precipitated oil was taken up in ether and washed with water and brine. A solution of 6.4 g of *p*-toluenesulfonic acid in 10 ml of acetone was then added and the precipitated solid was collected on a filter. The solid was recrystallized several times from acetonitrile–ether to afford 6.25 g (48%) of solid, mp 161–162°.

Anal. Calcd for $C_{20}H_{25}O_4PS$: C, 61.21; H, 6.42. Found: C, 61.00; H, 6.69.

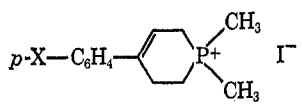
1-Methyl-1,2,3,6-tetrahydro-4-(*p*-bromophenyl)phosphorin Tosylate (9).—A mixture of 4.79 g of the crude alcohol obtained above and 3.40 g of *p*-toluenesulfonic acid in 100 ml of xylene was heated under a Dean–Stark trap overnight. The mixture was allowed to cool and the solvent was decanted from the oily solid. The latter was washed with ether and recrystallized twice from methanol. There was obtained 1.92 g (25.5%) of the salt, mp 210–215°.

Anal. Calcd for $C_{19}H_{22}BrO_3PS$: C, 51.71; H, 5.03. Found: C, 51.99; H, 5.27.

1,2,3,6-Tetrahydro-1,1-dimethyl-4-arylphosphorinium Iodides (Table III).—A solution of the crude alcohol and 2 equiv of *p*-toluenesulfonic acid in 200 ml of xylene was heated at reflux under a Dean–Stark trap for 8 hr. The mixture was allowed to cool and extracted thoroughly with water. The aqueous layer was made strongly basic (under nitrogen) and extracted with ether. The extracts were worked up in the normal way and converted to their methiodides.

TABLE III

1,2,3,6-TETRAHYDRO-1,1-DIMETHYL-4-ARYLPHOSPHORINIUM IODIDES



Compd no.	X	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
10	H	186–189	81	47.00	5.46	47.44	5.68
11	CH_3O	217–219	48	46.42	5.57	46.58	5.67
12	F	222–224	72	44.54	4.89	44.85	4.95
13	CH_3	184–185.5	43	48.57	5.82	48.63	5.87

3,6-Diaryl-3,5-hexadienyldimethylphosphine Oxides (Table II).—In a typical experiment, 6.4 ml of 1.6 *N* butyllithium in pentane was added to a well-stirred ice-cooled suspension of 0.01 mol of the appropriate finely powder quaternary salt in 60 ml of THF. At the end of 10–15 min a solution of 0.011 mol of the appropriate aldehyde in 20 ml of THF was added to this. The mixture was then stirred for 30 min at room temperature and 5 hr at reflux. After cooling, 50 ml of saturated ammonium chloride in ether was added. The organic layer was separated, washed in turn with water and brine, and taken to dryness under vacuum. The residue (except when crystalline; see Table II) was chromatographed on Florisil[12] (elution with 1 l. of 20% acetone–Skellysolve B,[13] then 100% acetone). The crystalline fractions were combined and recrystallized from acetone–Skellysolve B.

[3-(*p*-Fluorophenyl)-6,6-diphenyl-3,5-hexadienyl]dimethylphosphine Oxide (16).—The salt **12** (3.50 g) was converted to its ylide and allowed to react with 1.83 g of benzophenone. Following 18 hr of heating at reflux the mixture was worked up and chromatographed as in the general procedure. The product was recrystallized from ethyl acetate to afford 2.67 g (66%) of **16**, mp 173–176°.

Anal. Calcd for $C_{26}H_{26}FOP$: C, 77.21; H, 6.48. Found: C, 77.19; H, 6.58.

[3-(*p*-Fluorophenyl)-5-cyclohexylidene-3-pentenyl]dimethylphosphine Oxide (17).—Cyclohexanone (1 ml) in 10 ml of THF was added to a solution of the ylide prepared from 3.50 g of the salt **12**. The mixture was heated at reflux overnight and worked up as above (chromatography omitted). The product was re-

(12) A synthetic magnesia–silica gel absorbent manufactured by the Floridin Co., Warren, Pa.

(13) Skellysolve B, a petroleum fraction, bp 60–70°, sold by the Skelly Oil Co.

crystallized twice from acetone–Skellysolve B to afford 2.42 g (76%) of oxide, mp 125–127°, λ_{max} 282 (ϵ 26,200).

Anal. Calcd for $C_{19}H_{26}FOP$: C, 71.22; H, 8.18. Found: C, 71.26; H, 8.21.

[3-(*p*-Fluorophenyl)-6-methyl-3,5-heptadienyl]dimethylphosphine Oxide (18).—The ylide prepared from 3.50 g of the salt **12** was allowed to react with 0.8 ml of acetone. There was obtained on work-up 2.48 g of crude oxide, mp 81–95°. A sample was rechromatographed and recrystallized from moist Skellysolve B to give a sample (320 mg): mp 90–96°; ν_{max} 3300 cm^{-1}; nmr four aromatic protons (multiplets δ 6.8–7.6), two vinyl protons (multiplets δ 5.9–6.7), allylic methyl (three-proton singlets at δ 2.82 and 2.9), P–CH_3 (6 H, doublet about δ 1.5, J = 13 Hz).

Anal. Calcd for $C_{16}H_{22}FOP \cdot H_2O$: C, 64.48; H, 8.12. Found: C, 64.61; H, 8.00.

Registry No.—**2**, 24699-83-0; **3**, 24728-08-3; **4**, 24699-84-1; **5**, 24699-85-2; **6**, 24699-86-3; **7**, 24699-87-4; **8**, 24699-88-5; **9**, 24699-89-6; **10**, 24699-90-9; **11**, 24699-91-0; **12**, 24699-92-1; **13**, 24699-93-2; **14**, 24699-94-3; **15a**, 24691-52-9; **15b**, 24691-53-0; **15c**, 24691-54-1; **15d**, 24691-55-2; **15e**, 24691-56-3; **15f**, 24728-09-4; **15g**, 24691-57-4; **15h**, *trans,trans*, 24691-58-5; **15h**, *trans,cis*, 24691-60-9; **15i**, *trans,trans*, 24691-59-6; **15i**, *trans,cis*, 4728-00-5; **16**, 24699-95-4; **17**, 24728-96-5; **18**, 24699-96-5.

Acknowledgment.—The author wishes to express his appreciation to Mr. D. Edward Emmert of these laboratories for the preparation of sizable quantities of the various intermediates without which this work would not have been possible.

Synthesis of 2,6,7-Trioxa-4-phosphabicyclo[2.2.2]octane Systems

J. W. RATHKE,[1] J. W. GUYER, AND J. G. VERKADE

Department of Chemistry, Iowa State University, Ames, Iowa 50010

Received January 12, 1970

The formation of $P(CH_2O)_3P$ from $P(CH_2OH)_3$ and $P(OMe)_3$ is shown to be highly dependent on the manner in which the triol is prepared. Neutralization of $[P(CH_2OH)_4]Cl$ with NaOH produces 1 mol of H_2O which is difficult to remove and leads to extensive hydrolysis of the $P(OMe)_3$ when transesterification is attempted. Treating the salt with an equimolar quantity of NaOMe, although eliminating the hydrolysis problem, results in appreciable isomerization of $P(OMe)_3$ to $Me(O)P(OMe)_2$. In neither case does $P(CH_2O)_3P$ form in consistent or reasonable yields. The isomerization side reaction is shown to be due to small amounts of unneutralized phosphonium salt. A 20% molar excess of NaOMe over salt results in 20–30% yields of $P(CH_2O)_3P$ and only a trace of $Me(O)P(OMe)_2$ side product. The synthesis and characterization of the new compounds $P(CH_2O)_3As$, $OP(CH_2O)_3As$, $P(CH_2O)_3SiMe$, and $MeC(CH_2O)_3SiMe$ are also reported.

In 1965 we reported[2] what appeared at the time to be a straightforward synthesis of $P(CH_2O)_3P$ by the transesterification of $P(CH_2OH)_3$ with trimethyl phosphite in tetrahydrofuran. Since then we have experienced little success in consistently repeating the synthesis. Moreover, it has come to our attention that several other investigators have had similar difficulties, although there is one published report[3] in which the compound was successfully prepared by our method. We thought it appropriate, therefore, to examine the synthesis more closely in an effort to elucidate the nature of the side products in the reaction of $P(CH_2OH)_3$ with $P(OMe)_3$. Moreover, it was highly desirable to determine the conditions necessary for a more reliable preparation of $P(CH_2O)_3P$ since this difunctional nonchelating ligand has been found to exhibit interesting coordination properties.[4]

It is not obvious *a priori* why the transesterification of $P(CH_2OH)_3$ with $P(OMe)_3$ should be more difficult than the analogous reaction with $RC(CH_2OH)_3$ or *cis*-1,3,5-cyclohexanetriol. These latter triols with $P(OMe)_3$ afford $P(OCH_2)_3CR$ and $P(OCH)_3(CH_2)_3$, respectively, in high yields and numerous reports in the literature from other laboratories[5] as well as ours[6] on the use of these bicyclic phosphites in other reactions attest to the reliability of our syntheses[7] of these compounds.

We show in the present report that the formation of $P(CH_2O)_3P$ is very sensitive to the manner in which the $P(CH_2OH)_3$ is prepared from the commercially available $[P(CH_2OH)_4]Cl$. It is also demonstrated that $P(OMe)_3$ undergoes deleterious hydrolysis and rearrangement reactions whereas $As(OMe)_3$ and $MeSi(OMe)_3$ are quite stable to rearrangement. The arsenic and silicon esters with $P(CH_2OH)_3$ lead to the new bicyclic compounds $P(CH_2O)_3As$ and $P(CH_2O)_3SiMe$, respectively. Also reported for the first time are $OP(CH_2O)_3As$ and $MeC(CH_2O)_3SiMe$.

Experimental Section

Elemental analyses were carried out by Chemalytics, Inc., Tempe, Ariz., or Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained on an atlas CH-4 single-focusing spectrometer at 70 eV. Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam spectrometer using sodium chloride optics. Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Melting points were taken in capillaries and are uncorrected.

$P(CH_2OH)_3$.—To a well-stirred solution of 19.05 g (0.1 mol) of $[P(CH_2OH)_4]Cl$ in 75 ml of anhydrous methanol, 65 ml of methanolic $NaOCH_3$ containing 1 g of $NaOCH_3$ in 10 ml of MeOH was added all at once, the latter being in about a 20% excess of the equimolar amount. The mixture was allowed to stir for 15 min during which time the NaCl precipitated. A small amount of dry ether (about 15 ml) was then added to precipitate the last traces of NaCl, which was subsequently removed by filtration.

(1) NSF Undergraduate Research Participant, 1969.

(2) K. J. Coskran and J. G. Verkade, *Inorg. Chem.*, **4**, 1655 (1965).

(3) W. McFarlane and J. A. Nash, *Chem. Commun.*, 127 (1969).

(4) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

(5) See, for example, F. Basolo and H. G. Schuster-Woldan, *ibid.*, **88**, 1657 (1966); C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, **7**, 1806 (1968).

(6) See, for example, A. C. Vandenbroucke, D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *ibid.*, **7**, 1825 (1968), and references therein.

(7) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).