

A Nuclear Magnetic Resonance Study of the Formaldehyde-Induced Exchange of Methylol Groups in Tetrakis(hydroxymethyl)phosphonium Chloride and Tris(hydroxymethyl)phosphine¹

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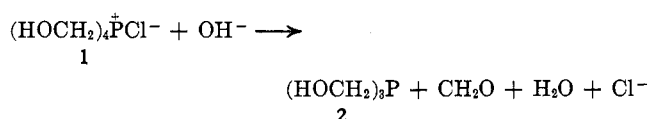
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¹H nmr spectra of solutions of tetrakis(hydroxymethyl)phosphonium chloride (1) to which less than 1 mol of NaOD was added exhibited signals due to the phosphonium salt and tris(hydroxymethyl)phosphine (2). At higher temperatures the separate signals coalesced to one singlet in a reversible manner. ³¹P nmr spectra indicated at least one other major phosphorus-containing species to be formed in addition to 2. At elevated temperature all ³¹P signals reversibly broadened. Upon removal of solvent and formaldehyde from fully neutralized solutions of the salt, the phosphine and a trace of the corresponding oxide (3) were isolated. The nmr results are interpreted as involving chemical exchange of methylol groups between the phosphonium salt and the phosphine, accomplished by reversible attack of the phosphine phosphorus on formaldehyde. A second pathway, equilibration of the phosphine with its O-methylolated adduct, is invoked to account for the second phosphorus-containing product, present in solution, but not isolated.

Neutralization of tetrakis(hydroxymethyl)phosphonium chloride (1) with aqueous sodium hydroxide to furnish tris(hydroxymethyl)phosphine (2)³ has become



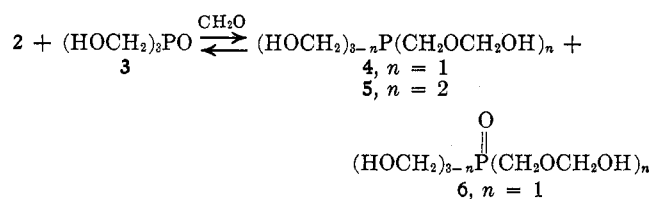
important as the basis for several useful flame retardants⁴ and the related reaction of 1 with fluorinated amines has been suggested⁵ as a way to impart oil repellency to textile fabrics. Because of these practical applications, the reaction of 1 and base has been the subject of an extensive scrutiny by ¹H and ³¹P nmr spectroscopy in these laboratories as a means to a better understanding of the role played by the various components of solutions of neutralized 1. During the course of our investigations, Vullo^{6a} interpreted ¹H and ³¹P nmr data obtained upon neutralization of 1 as indicative of reversible reaction of the product formaldehyde both with the phosphine 2 and the corresponding by-product³ phosphine oxide 3 to yield mono-, di-, and trihemiformals of 2 and 3^{6b} (Scheme I). While our

early data were, for the most part, in agreement with that of Vullo, the nmr study of the system 1 + NaOH has been extended significantly. Evidence is now reported for what may be interpreted as a temperature-dependent chemical exchange of methylol groups between 1 and 2, brought about by reversible attack of the phosphorus in 2 on the carbon of formaldehyde.⁷ Although a somewhat analogous case of averaging in which reversibly formed P-P bonds are involved has been recently reported,⁸ reorganizations involving P-C bonds at quadruply bound phosphorus are apparently rare.⁹ The present nmr study also leads to a better understanding of the part played by formaldehyde in certain reactions of the phosphine 2.

Results

Evidence of a reversible, temperature-dependent process involving the methylol groups of 2 developed during synthesis of the phosphine by a novel method which averted certain difficulties encountered in Gordon's procedure.¹⁰ Fairly pure 2 was obtained in good yield by the simple expedient of adding Dowex-1 anion-exchange resin in the OH form to a nitrogen-blanketed aqueous or methanolic solution of the salt 1 until the equivalence point (pH 8.3¹¹ in water, apparent pH 7.3^{11a} in methanol) was reached, followed by removal of solvent and formaldehyde *in vacuo* at 50–70°. An excess of the resin resulted, instead, in the formation of the oxide 3 in good yield, together with a copious evolution of hydrogen. Only the oxide could be recrystallized; the phosphine was used as the waxy solid obtained after cooling the syrupy product to –30°. Elemental analyses for both compounds were quite satisfactory, and peaks in their mass spectra above

SCHEME I



(1) Presented in part at the Southeast-Southwest Regional ACS Meeting, New Orleans, La., Dec. 2–4, 1970.

(2) One of the Laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) M. Grayson, *J. Amer. Chem. Soc.*, **85**, 79 (1963).

(4) J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Amer. Dyest. Rep.*, **57**, 981 (1968).

(5) S. E. Ellzey, Jr., W. J. Connick, Jr., G. L. Drake, Jr., and W. A. Reeves, *Text. Res. J.*, **39**, 809 (1969).

(6) (a) W. J. Vullo, *J. Org. Chem.*, **33**, 3665 (1968). (b) Other evidence for the reversible nature of the reaction of 2 and formaldehyde was recently reported by R. H. Carlson, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13–17, 1971.

(7) A report of less extensive evidence of averaging of the CH₂OH environments of 1 and 2 in pyridine or triethylamine has appeared: S. E. Ellzey, Jr., W. J. Connick, Jr., and G. J. Boudreaux, *Can. J. Chem.*, **49**, 3581 (1971).

(8) F. Ramirez and E. A. Tsolis, *J. Amer. Chem. Soc.*, **92**, 7553 (1970).

(9) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 169 (1967).

(10) I. Gordon and G. M. Wagner, U. S. Patent 3,257,460 (1966); *Chem. Abstr.*, **65**, 8962 (1966).

(11) (a) Values obtained from titration of 1 with NaOH in the respective solvents. (b) L. M. Fodor, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1963.

TABLE I
¹H NMR DATA FOR SOLUTIONS OF (HOCH₂)₄P⁺Cl⁻ (1) AND NaOD IN D₂O

Mol of NaOD/mol of 1	Temp, °C	δ , ppm (<i>J</i> , Hz) vs. DSS					
		1	2	1-2 composite		3	Other
				Found	Calcd ^a		
0.25	-13	4.77 (1.5)	4.14 (5.5)			<i>b</i>	4.85, 4.91
0.25	80			4.65	4.65	4.18 (3.0)	4.83
0.5	-7	4.80	4.15 (5.0)			<i>c</i>	<i>d</i>
0.5	65			4.52	4.50	4.22 (3.0)	4.87
0.85	-10	<i>d</i>	4.16 (5.4)			<i>c</i>	<i>d</i>
0.85	60			4.31	4.27	<i>c</i>	4.87
1.0	3		4.14 (5.5)			<i>b</i>	4.81, 4.83, 4.90
1.0	37			4.15	4.15	<i>c</i>	4.82

^a Position of the composite singlet calculated from the relation $\delta = 4.77p_1 + 4.15p_2$, where p_1 and p_2 are the fractional CH₂ populations in 1 and 2, respectively. ^b One line under 2. ^c Not seen, under 2. ^d Under HOD.

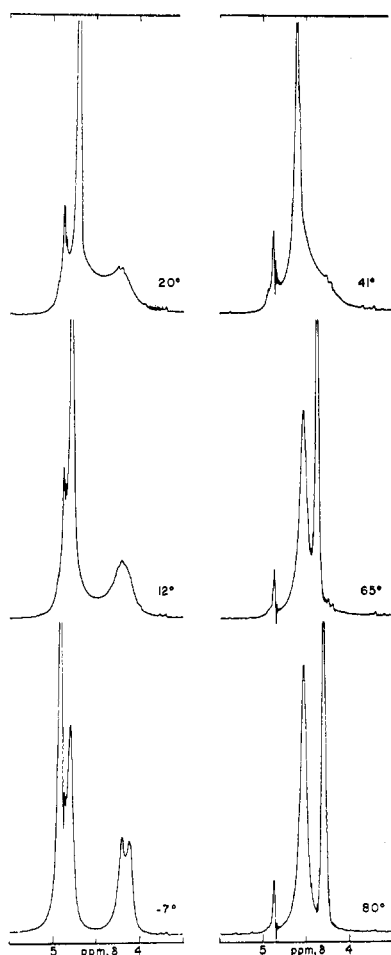


Figure 1.—Variable temperature ¹H nmr spectra for solution of 1 + 0.5 mol of NaOD in D₂O (DSS reference). The tallest peak is due to HOD.

those of the molecular ions were of insignificant intensity. When the 60-MHz ¹H nmr spectrum of the initially isolated phosphine 2 was run as the neat supercooled liquid at ambient temperature, the CH₂ protons gave a very broad signal (almost a singlet) at 4.38 ppm (TMS = 0 ppm). Examination at elevated temperature resulted in a sharpened *singlet* and not the doublet expected from coupling to phosphorus. In acetone-*d*₆ the CH₂ signal was a doublet at 4.24 ppm, *J* = 6.3 Hz, and impurity peaks occurred at 4.80 (singlet) and near 4.12 ppm (possibly a doublet), in good agreement with Vullo.^{6a} In D₂O a "filled-in" doublet was at 4.15 ppm, *J* = 5.5 Hz (DSS as reference), at room temperature and reversibly became a singlet at higher temperatures.

Operation of a temperature-dependent process is strikingly illustrated by the nmr spectra of a solution of the salt 1 in D₂O to which 0.5 mol of NaOD was added (Figure 1). At the lowest temperature of observation, -27°, the broad singlet at 4.81 ppm,¹² due to 1, nearly obliterates signals due to OCH₂O near 4.9 ppm, although a broad doublet due to phosphine CH₂ is seen at 4.17 ppm, *J* = 5.5 Hz. As the temperature is raised to about 5°, the HOD signal moves upfield to cover the signals near 4.8–4.9 ppm, and the PCH₂ signal at 4.17 ppm is no longer a doublet. With a further temperature increase the signal due to 1 is broadened (under HOD) and the broadened signal at 4.17 ppm is surmounted by the small doublet at 4.22 ppm, *J* = 3.0 Hz, due to the oxide 3 (or a related structure). Between 20 and 40°, the signals due to 1 and 2 merge, and at 65° there results a sharper *singlet* ($w_{1/2} \sim 6$ Hz) at 4.52 ppm. (In a solution to which only 0.25 mol of NaOD was added, the *doublets* due to 1 and 2 may still be seen at 3°.) The effects observed with varying ratios of NaOD to 1 are reversible with temperature changes. From Table I it may be seen that the positions of the composite PCH₂ *singlet* at four different ratios of NaOD to 1 agree quite well with values (δ) calculated by weight averaging the eight protons of 1 with the six of 2, according to the relation $\delta = p_1\delta_1 + p_2\delta_2$, where p_1 and p_2 are the fractional CH₂ populations in the 1 and 2 environments.¹³

In a solution of a synthetic mixture (1:1 molar) of 1 and 2 at slightly below ambient temperature, *doublets* for the CH₂ signals of the phosphonium salt and the phosphine were at their normal positions, but at 70° these were already reversibly coalesced to a broad *singlet* at an averaged chemical shift, 4.57 ppm (calcd 4.50 ppm).

In a solution of 2 and an equimolar amount of formaldehyde (from thermal depolymerization of paraformaldehyde) in D₂O at 20° or below, the phosphine *doublet* was seen at 4.13 ppm, but, when observed at 60°, the doublet had been reversibly coalesced into a *singlet* at 4.18 ppm.

Information on the composition of solutions of neutralized 1 not obtainable from the ¹H spectra, and further evidence to support chemical exchange averaging of CH₂OH groups was given by variable temperature ³¹P spectra obtained at 40.5 MHz on several of these solutions. The chemical shifts observed at room temperature are summarized in Table II. In many

(12) M. J. Gallagher, *Aust. J. Chem.*, **21**, 1197 (1968).

(13) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 219.

TABLE II
³¹P NMR CHEMICAL SHIFTS FOR SOLUTIONS OF
 (HOCH₂)₃P⁺Cl⁻ (1) AND BASE

Solution (D ₂ O)	δ (³¹ P), ppm, vs. external 85% H ₃ PO ₄
1 ^a	-25.8 ^b
1 + 0.5 mol of NaOD	-26.6, +24.8, +29.1 ^c
1 + 0.85 mol of NaOD	-48.7, -47.9, -27.5, +24.3, +28.4, +33.0
1 + 1.0 mol of NaOH ^d	+24.6, ^e +28.8
2	-49.0, ^f +24.5 ^g
2 + 1.0 mol of CH ₂ O	-49.3, -48.6, -47.7, +24.9, +29.1, +33.6
3 ^a	-48.7

^a Solvent H₂O. ^b Seven of the expected nine lines seen, $J \sim 2$ Hz. ^c In another sample observed at 24.3 MHz, an additional weak signal was seen at +32.9 ppm. Its presence or absence may depend on the age of the solution. ^d Solvent 80:20 MeOH-H₂O. ^e The value of $J \sim 5$ Hz could be easily determined from the low-field signal, but the high-field signal was rather broad and its splitting pattern was not evident. The latter comprised $\sim 20\%$ of the mixture. ^f Trace. ^g Five of the expected seven lines seen, $J \sim 5$ Hz.

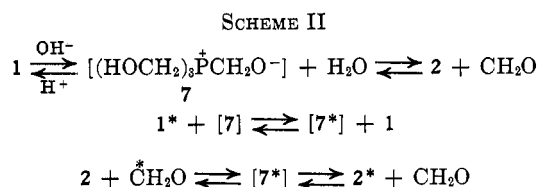
cases the noise levels precluded observation of spin coupling patterns and electronic integration. For the solution of 85% neutralized 1 the estimated (planimeter) relative areas of the three signals at positive field were 46:42:12 (low to high field). An interesting feature of this solution was that in the temperature range 5–35° all ³¹P signals (except the H₃PO₄ lock) were sharper at low temperature and broadened reversibly with increasing temperature (at 35° the weakest signals at -47.9, -48.7, and +33.0 ppm were lost in the noise), although the relative areas of the three highest field signals appeared to be rather temperature independent. Reversible broadening of all signals at elevated temperatures was also characteristic of solutions of half-neutralized 1 and a mixture of 2 and formaldehyde. The operation of such reversible temperature dependence in both the ¹H and ³¹P nmr spectra is indicative of an exchange process involving CH₂OH groups attached to phosphorus.

Although the role played in the exchange process by the various phosphorus compounds is subject to some speculation, it seems apparent that formaldehyde is involved in the exchange of CH₂OH groups between the phosphonium salt 1 and the phosphine 2, and also plays a part in the temperature-dependent coalescence of the PCH₂ doublet of 2 either in fully neutralized solutions of 1 or in solutions of 2 and formaldehyde. Comparison of the integrals of the room temperature ¹H spectra of 2 in D₂O before and after heating the dry solid at 70° *in vacuo* (the odor of formaldehyde was noted in the pump exhaust) revealed a decrease in the impurity peak near 4.80 ppm as the CH₂ doublet at 4.15 ppm, $J = 5.5$ Hz, became sharper. The report¹⁴ that singlets for the hydrates of the monomer and dimer of formaldehyde appear near 4.8 ppm in D₂O renders plausible the possible presence of these compounds in solutions of either 1 treated with base or of 2 prepared from 1. A sample of 2 in D₂O was treated overnight with dimedone (to remove formaldehyde as the water-insoluble dimethone derivative) and filtered; its nmr spectrum contained no signal at 4.8 ppm and the CH₂ doublet of 2 persisted even at 84° (other signals were present, apparently due to reaction between 2 and

dimedone). A sample of the phosphine 2 (kindly supplied by Dr. A. W. Frank of SRRL) prepared from formaldehyde and excess PH₃¹⁵ gave the expected *doublet* even at 80° in D₂O, but addition of 1 drop of formaldehyde solution caused almost complete coalescence at this temperature. Similarly, treatment with dimedone of an equimolar mixture of 1 and 2 effectively prevented coalescence and the separate CH₂ doublets for the salt 1 and phosphine 2 were seen at their normal positions at elevated temperature.

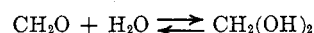
Discussion

Methylol Group Exchange.—Based on the ¹H nmr data, it is feasible to explain the temperature-dependent coalescence of the doublets of 1 and 2 during neutralization of 1 as involving the exchange of CH₂OH groups between the salt and the phosphine, through the zwitterion 7 as an intermediate or transition state, as in Scheme II. The salt 1 yields water in its irreversible,



complete neutralization to 2 and formaldehyde through 7. As long as some 1 is present, an exchange of CH₂OH groups between 1 and 2 may take place by means of the virtual reactions between 1 and 7, and between 2 and formaldehyde. Thus, as the rate of P–C bond making or breaking (in times/second) in the $1 \rightleftharpoons 2 + \text{CH}_2\text{O}$ exchange exceeds the value of J_{PCH} (in hertz) for one of the components, splitting in this signal will be lost and a *singlet* will result for that component. As the rate increases beyond the separation (in hertz) of the separate signals for the two components, the two singlets will coalesce into *one singlet* at a weighted-average position determined by the relative numbers of protons in the two environments. It should be noted that, if the exchange process took place somehow without breaking all P–C bonds, then the resulting averaged signal would be expected to be a *doublet* with a J_{PCH} which is the weighted average of the J values for 1 and 2. Arguments similar to the above based on the virtual reaction of 2 and formaldehyde through 7 may be used to explain absence of splitting in the CH₂ signal in solutions of the phosphine and formaldehyde.

The above discussion has apparently neglected the possibility of coalescence of the CH₂ signals from formaldehyde since these protons are also exchanging with those of 1 and 2. Whereas it is CH₂O which is involved in the reaction with 2, it is the signals for the hydrates of the monomer and dimer of formaldehyde which are actually observed in the nmr spectra.¹⁴ If, *e.g.*, the dehydration of formaldehyde hydrate is the rate determining step in the reversible sequence of events by which the CH₂ protons of 1, 2, and formaldehyde hydrate exchange, then it is within the realm of possibility



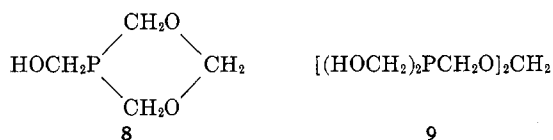
(14) J. Hine and F. C. Kokesh, *J. Amer. Chem. Soc.*, **92**, 4383 (1970).

(15) M. Reuter and L. Orthner, German Patent 1,035,135 (1958); *Chem. Abstr.*, **54**, 14124 (1960).

that, although the reactions relating **1** and **2** (Scheme I) may proceed at a rate exceeding that required for coalescence of the CH₂ signals of **1** and **2** ($\Delta\nu = 37$ Hz), the dehydration may proceed at a rate inferior to that required for coalescence of the three signals and the signal for formaldehyde hydrate will therefore persist.^{14,16} Calculations show that the positions found for the **1-2** composite (Table I) agree better with values based on **1** and **2** only than with those based on **1**, **2**, and formaldehyde hydrate, particularly for the higher degrees of neutralization.

Still to be reconciled is the fact that the ³¹P nmr spectra of solutions of **1** and base indicate the presence of a significant amount (equal to that of **2**) of a compound with a ³¹P shift of +28.4 ppm and a lesser amount of a compound with a peak at +33.0 ppm, but neither is indicated *per se* by the ¹H spectra in D₂O at any temperature.¹⁷ It is highly possible that these compounds have PCH₂ proton signals very close to that of **2**. Furthermore, in view of the good agreement between the values found for the PCH₂ composite and those calculated on the basis of the exchange of the eight protons of **1** with the six of **2**, it is also reasonable that the two compounds having high-field ³¹P shifts may, like **2**, have three (magnetically similar) CH₂ groups about phosphorus. Reasonable structures for these two compounds are **4** and **5**, the mono- and di-hemiformals of **2** postulated by Vullo mainly on the reasonableness of the observed ³¹P chemical shifts. Intuitively one might expect **4** to be present in larger quantity. Of the two reactions of **2** and formaldehyde shown in Schemes I and II, that giving rise to **4** and **5** does not involve making and breaking of C-P bonds, and averaging of the PCH₂ protons of **2**, **4**, and **5** should lead to a composite *doublet* having an averaged chemical shift and *J*_{PCH}, with the OCH₂O protons giving rise to a signal near that of formaldehyde hydrate. As the rate of the virtual reaction of **2** and formaldehyde increases with increasing temperature, the making and breaking of C-P bonds will be the important reaction observed in the ¹H spectra but the ³¹P spectra demonstrate the continued presence of the other phosphorus species.

The observation that the addition of excess base to a fully neutralized solution of **1** in methanol-water caused disappearance of the two high-field ³¹P signals and appearance of one at -48.7 ppm (**3**) makes it appear unlikely that structures such as **8** or **9** are responsible for



the signal at +28.8 ppm, since such structures might be expected to be more stable to base.

Of the remaining ³¹P signals (those clustered near -48 ppm), it is likely that they are due to hemiformals related to the oxide **3**, such as **6** and higher homologs. The ¹H and ³¹P nmr data are compatible with averaging of the PCH₂ groups in the oxides, but in a process dis-

tinued from that involving the phosphines. Since averaging in the oxides occurs among compounds formed by attack of formaldehyde at hydroxyl oxygen (without C-P bond involvement), it should result in a composite *doublet* for the CH₂ groups on phosphorus. This is borne out in the case of solutions of **1** and base at temperatures above the coalescence point for the phosphine *doublet*; a composite doublet due to **3** and the other oxides is readily seen near the position of the signal for pure **3** (there is some indication of a slight change in both chemical shift and *J*_{PCH} of the CH₂ groups in **3** upon addition of formaldehyde).

These observations, as well as those of Vullo,^{6a} apparently rule out the presence of tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH) in solutions of **1** neutralized with base.

The Role of Formaldehyde in Some Reactions of **2**.

No compelling evidence for the existence of significant quantities of the zwitterion **7** has been obtained,¹⁸ although it seems reasonable as a transition state in the exchange reaction involving **1** and **2** and in the virtual reaction of **2** and formaldehyde. Although Grayson³ favored the zwitterion as an intermediate in the conversion of **1** to **3** with excess base, Fodor^{11b} felt that kinetic evidence favored, instead, the attack of base on hydrated **2**. Evidence has now been obtained that, even in the presence of dimedone, **2** is rapidly converted to its oxide **3** (with evolution of hydrogen) by 10% NaOD in D₂O.²⁰ Even in the presence of dimedone, the reverse transformation of **2** to **1** took place upon reaction with HCl, apparently by way of a disproportionation, since phosphine (PH₃) was identified (ir spectrum) among the several products.

In the presence of an equimolar amount of formaldehyde in D₂O, **2** was incompletely converted to its oxide (or formaldehyde adducts of the latter) during 3 months under argon at room temperature. After addition of HCl to the solution, ¹H nmr signals for **1** and the oxide **3** were observed. In a control experiment in which a sample of **2** was in D₂O in the presence of dimedone for 2 months, the final amount of **3** was about the same as initially present in the phosphine, although the amount of the phosphine was reduced, apparently by reaction with dimedone.²¹ Weak singlets at 3.67 and 3.73 ppm in a D₂O solution of **1** and 1 mol of NaOD are apparently due, respectively, to ethylene glycol and a product resulting from the latter and formaldehyde (but not 1,3-dioxolane, which absorbs at 3.92 ppm in this solution). Addition of ethylene glycol to the solution caused an increase in the signals at 3.67 and 3.73 ppm. The glycol could result from ethylene oxide, formed from **2** and formaldehyde by a sequence analogous to that reported by Mark.¹⁹

Even in the presence of dimedone, the phosphine **2** in D₂O reacted rapidly with morpholine, resulting in a complex mixture, the ¹H nmr spectrum of which suggested the presence of the known tris(morpholino-

(18) Indeed, Mark¹⁹ has reported ³¹P chemical shifts of about -30 ppm for various compounds of the type (Me₂N)₃P⁺CH(R)O⁻.

(19) V. Mark, *J. Amer. Chem. Soc.*, **85**, 1884 (1963).

(20) S. M. Bloom, S. A. Buckler, R. F. Lambert, and E. V. Merry, *Chem. Commun.*, 870 (1970), have recently reported the formation of phosphine oxides and hydrogen upon reaction of water-soluble tertiary phosphines with aqueous sodium hydroxide.

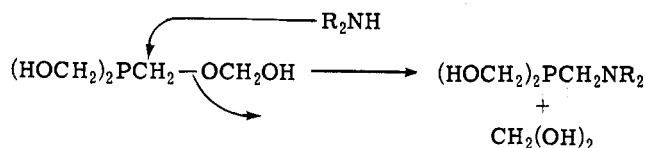
(21) The transformation of **2** to **3** under pressure at elevated temperature using a catalytic amount of formaldehyde has been reported recently: H. Haas, German Patent 1,930,521 (1970); *Chem. Abstr.*, **74**, 53987 (1971).

(16) For a discussion of the rate of dehydration of the hydrate see N. Landqvist, *Acta Chem. Scand.*, **9**, 867 (1955).

(17) Examination at 100 MHz (JEOL Model MH-100) of a solution of **1** and 1 mol of NaOD in D₂O did not reveal any new signals in the PCH₂ region that were not seen at 60 MHz.

methyl)phosphine.²² The complete absence of the phosphine **2** in the reaction mixture was readily ascertained from the spectrum; a weak doublet for the oxide **3**, originally present in the phosphine, was the only signal present at this position.

Thus, it may be seen that reactions of **2** with base, with HCl, and with morpholine, known to occur in the presence of formaldehyde, also occur under formaldehyde-free conditions. In the case of reactions of secondary amines and the phosphine **2** in the presence of formaldehyde, it is possible that the product trisubstituted aminomethylphosphines may result directly from **2**, as well as from one or all of the phosphorus species having ³¹P chemical shifts in the +28–33-ppm region. On the assumption that relative ability to act as a leaving group is inversely related to base strength, and comparing the p*K*_a of CH₂(OH)₂ (13.27²³) with that of water (15.7²⁴), it is entirely feasible that the product aminomethylphosphines could arise from hemiformals of **2** by loss of formaldehyde hydrate.



Experimental Section²⁵

Ir spectra were obtained from KBr disks, aqueous solutions between Irtran-2 plates, or a 10-cm gas cell on a Perkin-Elmer Model 137B spectrophotometer (NaCl optics).

Mass spectra of **2** and **3** were obtained at 70 eV from solid samples on a Perkin-Elmer Model 270 mass spectrometer.

All nmr spectra were obtained on samples (~20%) under nitrogen or argon. Variable temperature ¹H spectra were run on a Varian A-60A spectrometer at 60 MHz, with internal TMS or DSS at 0 ppm. The variable temperature ³¹P spectra (external 85% H₃PO₄ reference) were run on a Varian HA-100 at 40.5 MHz on portions of the same solutions; a few room temperature ³¹P spectra were run on a Varian HR-60-IL. Because

(22) H. Coates and P. A. T. Hoye, British Patent 842,593 (1960); *Chem. Abstr.*, **55**, 4363 (1961).

(23) R. P. Bell and D. P. Onwood, *Trans. Faraday Soc.*, **58**, 1557 (1962).

(24) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co. Ltd., London, 1962, p 151.

(25) Analyses and osmometric molecular weights were by Galbraith Laboratories, Inc., Knoxville, Tenn. ³¹P nmr spectra at 24.3 MHz were kindly furnished by Dr. R. H. Dinius of Auburn University, Auburn, Ala. Mass spectra were run by Dr. W. E. Franklin of SRRL. Use of the name of a company or product is not to be construed as an endorsement by the Departments of Agriculture or the Army.

of the many signals in most of the 40.5-MHz phosphorus spectra it was often necessary to use a CAT.

Tetrakis(hydroxymethyl)phosphonium chloride (**1**) was obtained from Hooker Chemical Corp. and was recrystallized from absolute ethanol: ¹H nmr (D₂O) CH₂ at 4.77 ppm (*J*_{PCH} = 1.7 Hz, *J*_{13CH} ~ 153 Hz). There appeared to be little, if any, temperature (ambient–80°) or concentration effect (20–40%) on the chemical shift or couplings.

Tris(hydroxymethyl)phosphine (**2**).—To a solution of 25.0 g (0.131 mol) of **1** in 100 ml of distilled water contained in a flask fitted with a mechanical stirrer, nitrogen flush, and a combination pH electrode was added over ~45 min ~150 ml (0.21 equiv) of 20–50 mesh Dowex-1 × 8 resin in the OH⁻ form until the pH was ~8.3–8.5. After the resin was filtered, the solution was washed portionwise with 150 ml of distilled water. The filtrate was concentrated on a rotary evaporator at 65–70° under aspirator vacuum and finally under high vacuum for ~30 min. The supercooled liquid weighed 13.0 g (80%), *n*_D²⁰ 1.5497. Its neat ir spectrum between salt plates showed no bands at 1052 (1)²⁶ or 1043 or 1135 cm⁻¹ (**3**),²⁶ but had intense, broad absorption at 1010 cm⁻¹.²⁶ On further evacuation and cooling at –30°, the viscous liquid solidified to a waxy solid: ¹H nmr (D₂O) CH₂ at 4.15 ppm (*J*_{PCH} = 5.5 Hz, *J*_{13CH} ~ 148 Hz), impurity peaks at 3.67 and 4.83 ppm. The CH₂ chemical shift was little affected by temperature or concentration.

Anal. Calcd for C₃H₉O₃P: C, 29.04; H, 7.31; P, 24.96; mol wt, 124. Found: C, 28.92; H, 7.46; P, 24.79; mol wt, 130 (ethanol).

A sample of **2** prepared by addition of the resin to a methanol solution of **1** to an apparent pH of 7.3 gave essentially the same proton spectrum.

Tris(hydroxymethyl)phosphine Oxide (**3**).—Slow addition of about a 130% excess (over an equimolar amount) of the resin to an aqueous solution of 25.0 g of **1** led to vigorous evolution of hydrogen. After the mixture stood overnight and was concentrated on a rotary evaporator, 16.1 g (88%) of the oxide was obtained. Recrystallization from absolute ethanol gave 11.9 g of hygroscopic product: mp 50–52° (lit.²⁶ mp 54–55°); ir (water) strong bands at 1043 and 1134 cm⁻¹,²⁶ ¹H nmr (D₂O) CH₂ at 4.20 ppm (*J*_{PCH} = 3.1 Hz; *J*_{13CH} ~ 146 Hz).

Anal. Calcd for C₃H₉O₄P: C, 25.72; H, 6.48; P, 22.11; mol wt, 140. Found: C, 25.62; H, 6.52; P, 22.13, mol wt, 150 (ethanol).

Formaldehyde solution was prepared by bubbling the gas from thermally depolymerized paraformaldehyde into D₂O until ~24–30% was absorbed: ¹H nmr CH₂ (HOCH₂OH) at 4.83 ppm (*J*_{13CH} ~ 164 Hz), CH₂ (HOCH₂OCH₂OH) at 4.90 ppm (*J*_{13CH} ~ 166 Hz).

Solutions of **1** treated with various amounts of NaOD were prepared by addition of the calculated amount of 40% NaOD in D₂O to a solution of **1** in D₂O under nitrogen or argon with good stirring.

Registry No.—**1**, 124-64-1; **2**, 2767-80-8; **3**, 1067-12-5.

(26) M. Anteunis, M. Verzele, and G. Dacremont, *Bull. Soc. Chim. Belg.*, **74**, 622 (1965).