gem-Diphosphinoalkanes. Preparation and Characterization

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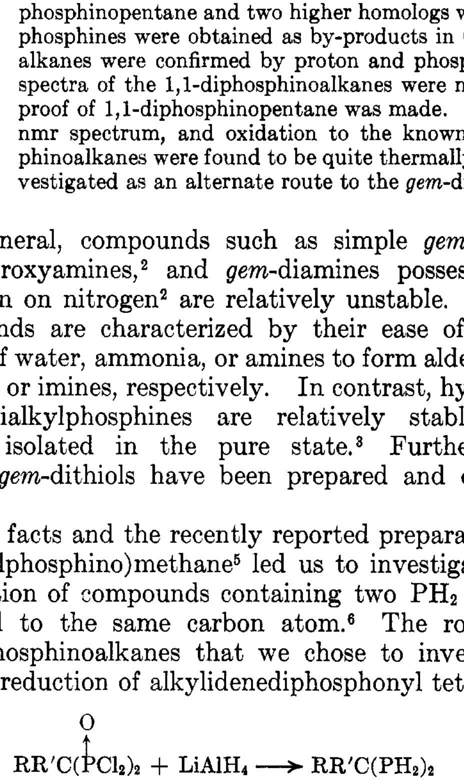
The preparation of several members of a new class of organophosphorus compounds, *gem*-diphosphinoalkanes, by the lithium aluminum hydride reduction of the corresponding alkylidenediphosphonyl tetrachlorides, is described. Although the parent compound, diphosphinomethane, was obtained in low yields (1–6%), 1,1-diphosphinopentane and two higher homologs were obtained in moderately good yields (28–52%). Mono primary phosphines were obtained as by-products in 6–13% yields. In general the structures of the *gem*-diphosphinoalkanes were confirmed by proton and phosphorus nmr spectral analysis. However, because the proton nmr spectra of the 1,1-diphosphinoalkanes were more complex than was originally anticipated, a rigorous structure proof of 1,1-diphosphinopentane was made. This was accomplished by mass spectral analysis, the phosphorus nmr spectrum, and oxidation to the known 1,1-pentylidenediphosphonic acid. In general, the *gem*-diphosphinoalkanes were found to be quite thermally stable. The reduction of two *gem*-diphosphonates was briefly investigated as an alternate route to the *gem*-diphosphines.

In general, compounds such as simple *gem*-diols,[1] *gem*-hydroxyamines,[2] and *gem*-diamines possessing a hydrogen on nitrogen[2] are relatively unstable. These compounds are characterized by their ease of elimination of water, ammonia, or amines to form aldehydes, ketones, or imines, respectively. In contrast, hydroxymethyldialkylphosphines are relatively stable and readily isolated in the pure state.[3] Furthermore, certain *gem*-dithiols have been prepared and characterized.[4]

These facts and the recently reported preparation of bis(ethylphosphino)methane[5] led us to investigate the preparation of compounds containing two PH_2 groups attached to the same carbon atom.[6] The route to *gem*-diphosphinoalkanes that we chose to investigate was the reduction of alkylidenediphosphonyl tetrachlorides with lithuim aluminum hydride. The *gem*-diphosphonyl tetrachlorides were selected over the *gem*-diphosphonates because carboxylic acid chlorides are more readily reduced with metal hydrides in general than are esters[7] and because *gem*-diphosphonates possessing an α-hydrogen atom are rapidly metalated with sodium hydride (see Experimental Section). We hoped to avoid the possibility of this complicating side reaction with lithium aluminum hydride. Subsequently, the reduction of two *gem*-diphosphonates was briefly investigated and the results are summarized in Table I along with the properties of the *gem*-diphosphinoalkanes.



$$RR'C(\overset{\overset{O}{\uparrow}}{P}Cl_2)_2 + LiAlH_4 \longrightarrow RR'C(PH_2)_2$$

The parent compound diphosphinomethane (I)[6] was obtained in low yields from the reduction of solid methylenediphosphonyl tetrachloride with lithium aluminum hydride in dibutyl ether at 0–5°.[8] The structure of I was confirmed by phosphorus (Table I) and proton nmr spectral analyses. In the latter the PH region of the spectrum consisted of two triplets centered at τ 7.13 (J_{PH} = 202 cps, J_{PHCH} = 7.2 cps).[9] The gas phase infrared spectrum of a sample of I collected from the gas chromatograph is given in Table I. Possible reasons for the low yields of I are discussed in a later portion of this paper.

Better results were obtained when 1,1-alkylidenediphosphonyl tetrachlorides were reduced under the conditions used to prepare I. For example, 1,1-diphosphinopentane (II) was isolated in moderately good yields along with low yields of *n*-amylphosphine from the corresponding *gem*-diphosphonyl tetrachloride. The properties and identification of these products are described below.

The PH region of the proton nmr spectrum of II was more complex than was orginally anticipated.[10] For this reason the identity and purity of II were rigorously established in the following manner. Gas chromatographic analyses of II on three different columns and under a wide variety of conditions showed only one symmetrical peak.[11] The mass spectrum of II showed *m/e* peaks at 136 and 103 corresponding to the parent peak (M) of II and the $C_5H_{12}P$ fragment resulting from M − PH_2, respectively. No evidence of either higher or

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[1] D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New, York, N. Y., 1959, pp 271–272.

[2] C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co. Inc., Philadelphia, Pa., 1965, pp 233 and 826.

[3] (a) L. Maier, *Progr. Inorg. Chem.*, **5**, 185 (1963); (b) H. R. Hays, unpublished results from these laboratories.

[4] R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem. Intern. Ed. Engl.*, **3**, 277 (1964).

[5] K. Issleib and G. Doll, *Z. Anorg. Allgem. Chem.*, **324**, 259 (1963).

[6] L. Maier, *Angew. Chem. Intern. Ed. Engl.*, **4**, 984 (1965). Subsequent to our work Maier has reported the preparation of several α,ω-diphosphinoalkanes [$(CH_2)_n(PH_2)_2$, n = 1–4] by reduction of the tetraalkyl alkylenediphosphonates at the German Chemical Society Meeting in Bonn, Germany, Sept. 13–18, 1965. The reference cited is a brief abstract of this talk and the full details of the preparation of diphosphinomethane (n = 1) have not been published at this time.

[7] M. N. Rerick, "Selective Reductions of Organic Compounds with Complex Metal Hydrides," Metal Hydrides, Inc., Beverly, Mass., 1959, Table VI.

[8] Dodecylphosphine was obtained in 71% yield from dodecylphosphonyl dichloride using similar conditions (*i.e.*, 0–5°, 30-min reduction time, diethyl ether solvent). Both reductions were quite exothermic.

[9] In all but one case the yield of I was estimated by gas chromatographic analyses of the dibutyl ether solution. Distillation in one case gave a mixture of I and dibutyl ether in which the proton nmr spectrum was recorded. Consequently, the methylene protons were obscured. Subsequent distillation at atmospheric pressure gave a much purer sample of I; however, the sample of I ignited and was lost when it was inadvertently exposed to a trace of air.

[10] (a) From a first-order consideration of the proton nmr spectra of *sec*-butylphosphine and a number of other primary phosphines we had originally anticipated a pair of doublets (J_{PH} = *ca.* 200 cps, J_{CHPH} = *ca* 7 cps) for the PH portion of the spectrum of II. Subsequently, higher resolution and closer inspection of several of the spectra under consideration showed more complex patterns than could be explained by a simple first-order analysis. A detailed analysis will be presented in a later communication. (b) Proton nmr spectra obtained early in this study suggested an alternate structure, 1,2-diphosphinopentane. In addition to being highly unlikely from a chemical standpoint, this structure was excluded on the basis of the following facts. The phosphorus chemical shifts of the four isomeric butylphosphines are widely different (*i.e.*, iso- 151 ppm, *n*- 140 ppm, *sec*- 116 ppm, and *t*- 82 ppm). The initial phosphorus nmr spectrum of II, however, was not resolved beyond a broadened triplet, suggesting two identical or nearly identical phosphorus atoms (within 10 cps) attached to the same carbon atom.

[11] One of these columns, a 30% silicone rubber on Chromosorb W, was capable of excellent resolution of mixtures of either *t*-, *sec*-, and *n*-butylphosphines or *t*-, iso-, and *n*-butylphosphines. The *sec*- and isobutylphosphines were not resolved on this column.

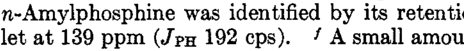
TABLE I

gem-DIPHOSPHINOALKANES

$RR'C(\overset{O}{\uparrow}PX_2)_2$								
R	R'	X	$RR'C(PH_2)_2$	% yield	Bp, °C (mm)	P^{31} nmr,[a] ppm	J_{PH},[a] cps	% yield of $RR'CHPH_2$
H	H	Cl	I	1–6	83–85	126[b,c]	199	*d*
C_4H_9	H	Cl	II	44–51	53–55 (9)	109	194	8–11[e]
C_4H_9	C_4H_9	Cl	III	2[f]	94–95 (9)	91	194	*g*
$C_{10}H_{21}$	H	Cl	IV	40	88–90 (0.1)	108	192	*h*
$C_{11}H_{23}$	H	Cl	V	28–52	103–105 (0.1)	107	193	6–13[i]
CH_3	CH_3	Cl	VI	2	*j*	74	192	*k*
C_9H_{19}	H	OEt	VII	18[l]	103–105 (4–5)	105	191	19[i,l]
H	H	O-*i*-Pr	I	*m*	...	126	198	*d*

[a] Under normal resolution all phoshorus nmr spectra were 1-2-1 "triplets" relative to 85% H_3PO_4. The accuracy of the chemical shift measurements is about ±1 ppm. Benzene was used as solvent in all cases except I where dibutyl ether was the solvent and VII where the spectrum was obtained on the neat sample. The J_{PH} values listed are the primary splittings of the "triplets" in the P^{31} spectra. Although there is additional structure on each member of the triplet from the influence of other spin couplings in the molecule, the primary splitting is believed very close to the directly bonded PH coupling. A detailed analysis will be taken up in a later communication. [b] Reference 6, lit. 121.8 ppm. [c] A gas phase infrared spectrum of a sample of I collected by gas chromatography showed an intense PH absorption at 4.32 μ along with medium absorptions at 3.38, 9.15, 9.28, 10.47, 10.99, and 13.42 μ. [d] Methylphosphine may have been formed but not observed. Phosphine was formed during the reductions and identified by infrared spectra of the effluent gases. [e] *n*-Amylphosphine was identified by its retention time, a mass peak at 104 *m/e* units, and its phosphorus nmr spectrum, a 1-2-1 triplet at 139 ppm (J_{PH} 192 cps). [f] A small amount of III was observed and isolated from one preparation of II. The identity of III was established by its mass spectrum (*m/e* 192) and phosphorus and proton nmr spectra. In the latter the PH portion of the spectrum consisted of two widely spaced multiplets centered at τ 6.95 (J_{PH} = 194 cps). Compound III resulted from the reduction of a small amount of 5,5-nonylidenediphosphonyl tetrachloride present in one of the samples of 1,1-pentylidenediphosphonyl tetrachloride. [g] A trace amount of material believed to be 5-nonylphosphine (a triplet at 116 ppm, J_{PH} = 190 cps) was observed in the gas chromatograph, mass spectrum (*m/e* 160), and phosphorus nmr spectrum of III. [h] The yield of undecylphosphine was not determined. [i] Dodecylphosphine and decylphosphine were isolated and identified by comparison of their retention times and phosphorus and proton nmr spectra with those of authentic samples. [j] Owing to the small amount of VI available, VI was distilled and trapped in a Dry Ice cooled trap under reduced pressure. The phosphorus (Table I) and proton nmr spectra were consistent with VI. The latter consisted of two widely spaced multiplets centered at τ 6.78 (J_{PH} = 192 cps) and a $PCCH_3$ triplet at τ 8.68 (J_{PCCH} = 12.1 cps). [k] A small amount of impurity in VI is believed to be isopropylphosphine based on its phosphorus nmr spectrum (a triplet at 106 ppm, J_{PH} = 195 cps) and the fact that monophosphines were isolated and positively identified from the preparations of II, V, and VII. [l] In addition to a larger ratio of mono- to diphosphine, 17% of unreacted starting material was recovered. [m] Diphosphinomethane was formed and oxidized to methylenediphosphonic acid in 6–12% yields without isolation of I. About 50% of the methylenediphosphonic acid obtained is attributed to unreacted starting material which was observed in the phosphorus nmr spectrum of a crude ether phase after refluxing with lithium aluminum hydride for 16 hr.

lower molecular weight impurities was observed in the mass spectrum. Furthermore, in view of the mass spectral evidence, the phosphorus nmr spectrum of II (Table I) is consistent only with two PH_2 groups attached to the same carbon atom.[10b] Finally, unambiguous confirmation of the structure of II was achieved by oxidation to 1,1-pentylidenediphosphonic acid (VIII). The identity of VIII was established by elemental



$$\text{II} + \text{dilute HNO}_2 \xrightarrow[2.\ \Delta]{1.\ 0^\circ} C_4H_9CH[\overset{O}{\overset{\uparrow}{P}}(OH)_2]_2$$

VIII

analysis, the same phosphorus nmr spectrum, and mixture melting point with an authentic sample of 1,1-pentylidenediphosphonic acid.[12]

The major by-product[13] isolated from the preparation of II was shown to be *n*-amylphosphine by gas chromatographic retention time, mass spectral analysis (*m/e* 104), and a 1-2-1 triplet at 139 ppm (J_{PH} = 192 cps) in the phosphorus nmr spectrum.[14] *n*-Amylphosphine presumably arises from reductive cleavage of either the starting material or an intermediate to II. Compound II was shown to be stable to lithium aluminum hydride in refluxing diethyl ether for short periods of time, whereas the preparations of II were carried out at about 0–5°.

Two homologous 1,1-diphosphinoalkanes, IV and V, were prepared in moderate yields from the corresponding *gem*-diphosphonyl tetrachlorides using the conditions described above. The latter compounds are apparently reduced more easily with lithium aluminum hydride than are the analogous *gem*-diphosphonates. For example, the reduction of tetraethyl decylidenediphosphonate with excess lithium aluminum hydride was incomplete even after 32 hr in refluxing diethyl ether.[15] Work-up at this point gave 17% unreduced starting material, along with a larger ratio of monoprimary phosphine (19%) to *gem*-diphosphine (18%, VII) than was observed in the preparations of II, IV, and V. A possible explanation for incomplete reduction under these conditions is that part of the *gem*-diphosphonate is metalated by the hydride to give the carbanion or a complex of the carbanion which is not readily reduced. Subsequent hydrolysis regenerates the starting material. Although no direct evidence bearing on the reactivity of the carbanion (and/or complexed carbanion) with lithium aluminum hydride is available, this explanation

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(12) Early in this investigation O. T. Quimby supplied an authentic sample of 1,1-pentylidenediphosphonic acid obtained by the acid hydrolysis of tetraisopropyl 1,1-pentylidenediphosphonate. Later samples prepared in this study by essentially the same procedure and also by hydrolysis of the intermediate 1,1-pentylidenediphosphonyl tetrachloride were shown to be identical by proton and phosphorus nmr spectra, analytical data, and mixture melting point.

(13) A small amount of residual viscous liquid was observed from the initial distillation of II. A phosphorus nmr spectrum of this material showed only broad unresolved signals.

(14) In all cases with the exception of I the monoprimary phosphines were observed in the gas chromatographs and phosphorus nmr spectra of the crude products. The identities of decylphosphine and dodecylphosphine were established by comparison with authentic samples (Table I).

(15) Dibutyl dodecylphosphonate (0.15 *M* in diethyl ether) was reduced to dodecylphosphine in 77% yield after 2.5 hr at 0–5°. In more concentrated reductions, dodecylphosphine was obtained in 70–80% yields after addition of diethyl dodecylphosphonate (1 *M* in diethyl ether) at 0–5° followed by 5–6 hr at reflux.

appears reasonable for two reasons. These are the differences in apparent reactivity of the monophosphonate esters[15] *vs.* the *gem*-diphosphonates and the fact that *gem*-diphosphonates possessing an α-hydrogen atom are rapidly metalated with sodium hydride (see Experimental Section).

A similar explanation may be partly responsible for the low yields of I obtained when tetraisopropyl methylenediphosphonate was reduced under a variety of conditions (Table I, *m*, and Experimental Section). However, the preparation of I appears more complicated and is not fully understood. Phosphine evolution was observed in the reductions of both the methylenediphosphonate ester and the solid methylenediphosphonyl tetrachloride suggesting that reductive cleavage is also occurring in the preparation of I. The low yields of I from both the *gem*-diphosphonate and the *gem*-diphosphonyl tetrachloride seem to support this idea.[16] The preparation of I from the methylenediphosphonyl tetrachloride is further complicated by the fact that the latter is a solid, mp 101–102°, and relatively insoluble in diethyl ether. What effect these properties have on the yield of I is not clear. For example, reduction of the solid 2,2-propylidenediphosphonyl tetrachloride in one experiment gave only a low yield of 2,2-diphosphinopropane[16] (see Table I, *j* and *k* for proton and phosphorus nmr spectra of VI). In contrast, the reduction of the liquid, ether-soluble 1,1-alkylidenediphosphonyl tetrachlorides gave considerably better yields of the higher molecular weight and more easily handled 1,1-diphosphinoalkanes.

In general, the *gem*-diphosphinoalkanes appear to be quite thermally stable. The 1,1-diphosphinoalkanes IV, V, and VII were chromatographed on an Apiezon column at about 200°, collected, and rechromatographed without apparent decomposition. 1,1-Diphosphinopentane (II) was shown to be stable to lithium aluminum hydride for short periods of time in refluxing diethyl ether, to catalytic amounts of hydrochloric acid and sodium methoxide in refluxing methanol, and to catalytic amounts of azobisisobutyronitrile at 70–75°.

Experimental Section

General.—All reactions and manipulations were performed under an atmosphere of oxygen-free argon and in a well-ventilated hood. Gas chromatographic analyses of the *gem*-diphosphinoalkanes were carried out with columns composed of 20% Apiezon L on Chromosorb W and 30% silicone rubber on Chromosorb W and with helium as the carrier gas. Much lower column temperatures were required with the silicone column. Nuclear magnetic resonance spectra were obtained on Varian Associates spectrometers, the HR-60 at 24.3 MHz for phosphorus and an HA-100 at 100 MHz for proton spectra. The molecular weight determinations were made on an Atlas CH-4 mass spectrometer using a cold injection port.

Starting Materials.—Tetraisopropyl methylenediphosphonate,[17] tetraethyl methylenediphosphonate,[18] methylenediphosphonic acid,[17] and methylenediphosphonyl tetrachloride[17] were obtained by literature procedures. The alkylidenediphosphonate esters, diphosphonic acids, and diphosphonyl tetrachlorides, with the exceptions noted, were prepared according to the following preparations of the 1,1-pentylidene compounds.

Preparation of Tetraisopropyl 1,1-Pentylidenediphosphonate.—Tetraisopropyl methylenediphosphonate (609 g, 1.77 moles) was dropped slowly into a dispersion of 42.5 g of sodium hydride (1.77 moles) in 400 ml of toluene so that the temperature was kept below 50°. After hydrogen evolution was complete 303 g of *n*-butyl bromide (2.21 moles) was added, the mixture was heated slowly to reflux and kept at reflux 5 hr. Longer reflux periods (12–16 hr) were used with the nonyl, decyl, and undecyl bromides. The toluene was removed on a rotary evaporator, the product was dissolved in 1200 ml of chloroform and washed three times with 200 ml of water, and the chloroform was removed. The product was then distilled through a large bore head to give a fraction at 97–103° (0.02 mm), 462 g, 64%. At this point the product was about 70–80% pure by phosphorus nmr (an unresolved multiplet at −21.6 ppm). The impurities were starting material (a triplet at −17.8 ppm, $J_{PH} = 19$ cps) and the dialkylation product, tetraisopropyl 5,5-nonylidenediphosphonate (an unresolved multiplet at −24.5 ppm). At this point the desired product was distilled slowly through a spinning-band column and collected, 270 g (38% yield), bp 90–95° (0.012 mm). Distillations of this type were best carried out with a high-capacity pump at low pressures.

Tetraethyl decylidenediphosphonate, bp 130–140° (0.004 mm), was prepared from tetraethyl methylenediphosphonate and nonyl bromide in 49% yield using the procedure described above. The phosphorus nmr spectrum of a neat sample was an unresolved multiplet at −23.4 ppm.

The tetraisopropyl esters of nonylidene- and undecylidenediphosphonates were prepared as described above; however, they decomposed upon attempted distillation. Consequently, they were partially purified by distilling off the tetraisopropyl methylenediphosphonate, leaving behind the desired product (a multiplet at −22.2 ppm) and some dialkylated product (a multiplet at −25.5 ppm). The latter product was eventually removed upon distillation of the *gem*-diphosphonyl tetrachloride as is described below. Tetraisopropyl 2,2-propylidenediphosphonate, bp 65–69° (0.005 mm), was prepared in 73% yield by two consecutive methylations of tetraisopropyl methylenediphosphonate using monoglyme as solvent. The phosphorus nmr spectrum of a neat sample consisted of a septuplet at −25.6 ppm ($J_{PCCH_3} = 15.5$ cps). The proton nmr spectrum showed a multiplet at τ 5.25 (CHO), and a doublet at τ 8.75 ($CHCH_3$) superimposed on the $PCCH_3$ triplet at τ 8.76.

1,1-Pentylidenediphosphonic acid was prepared by refluxing 340 g of the ester (0.85 mole) for 16 hr with 670 g of concentrated hydrochloric acid. The aqueous hydrochloric acid was distilled away and the partially hydrolyzed product heated to 170–175° (but not above 180°) until propene evolution was complete. Above 180° the product slowly turned black. Three recrystallizations of the product from 5:1 benzene–acetic acid mixtures gave a 45% yield of 1,1-pentylidenediphosphonic acid, mp 150–152°. The phosphorus nmr spectrum consisted of a multiplet at −23.5 ppm in butyl alcohol. The 1,1-undecylidene- and the 1,1-dodecylidenediphosphonic acids were prepared in the same manner; however, they were refluxed with the concentrated hydrochloric acid for 50–60 hr. Attempts to purify the C_{11}- and C_{12}-diphosphonic acids resulted in considerable loss; consequently, the acids upon drying were converted directly to the respective *gem*-diphosphonyl tetrachloride (see below).

1,1-Pentylidenediphosphonyl tetrachloride was prepared by adding a slight excess of phosphorus pentachloride (106 g, 0.51 mole) to 28 g of the corresponding diphosphonic acid (0.12 mole) at 20–25° in 40 ml of phosphorus oxychloride. After 1 hr at 20–25° the excess phosphorus pentachloride was destroyed with sulfur dioxide. Distillation gave 26.8 g of 1,1-pentylidenediphosphonyl tetrachloride, bp 115–120° (0.028 mm). The phosphorus nmr spectrum in phosphorus oxychloride consisted of a quartet at −34.6 ppm ($J_{PCH} = J_{PCCH_2} = 21$ cps). The proton nmr spectrum showed a triplet of triplets for the methinyl proton at τ 6.05 ($J_{PCH} = 21$ cps, $J_{CHCH_2} = 5$ cps), multiplets centered at 7.92, 8.41, and 8.77 for the α, β-, and γ-methylene protons, respectively, and a methyl triplet at 9.15. Care was required to avoid any rise in temperature during these preparations because the 1,1-pentylidenediphosphonyl tetrachloride reacts with phosphorus pentachloride to give 1-chloro-1,1-pentylidenediphosphonyl tetrachloride (a triplet at −32.9 ppm, $J_{PCCH_2} = 20$ cps). The proton nmr spectrum of the latter consisted of a broad multiplet at τ 7.16–7.84, a pentuplet at 8.29, and a sextet at 8.73 (α-, β-, and γ-methylene protons) and a methyl triplet at 9.14. This impurity, once formed, was nearly impossible to remove from the desired product by distillation. Owing to overlap of the phosphorus signals, small amounts of this impurity are difficult to see in phosphorus nmr spectra;

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(16) Low molecular weight phosphines are sometimes difficult to isolate in good yield because of their extreme affinity for oxygen.

(17) J. A. Walmsley and S. Y. Tyree, *Inorg. Chem.*, **2**, 312 (1963).

(18) J. A. Cade, *J. Chem. Soc.*, 2266 (1959).

consequently, samples were analyzed by hydrolysis to the respective diphosphonic acids. The phosphorus nmr spectrum of 1-chloro-1,1-pentylidenediphosphonic acid is a singlet at −15.9 ppm.

1,1-Dodecylidenediphosphonyl tetrachloride, bp 185–205° (0.02 mm), and 1,1-undecylidenediphosphonyl tetrachloride, bp 190–192° (0.07 mm), were prepared in the same manner with the exception that benzene was used as the solvent. Yields of 78 and 33–41%, respectively, were obtained.

2,2-Propylidenediphosphonyl tetrachloride was prepared by slowly adding 221 g of tetraisopropyl 2,2-propylidenediphosphonate (0.6 mole) to 670 g of phosphorus pentachloride (2.97 moles), followed by heating at 115° for 2 hr. The excess phosphorus pentachloride was decomposed with sulfur dioxide. After two distillations under reduced pressure 85 g (51% yield) of solid 2,2-propylidenediphosphonyl tetrachloride (melting above 100°) was collected. The proton (a 1-2-1 triplet at τ 8.05, J_{PCCH} = 24 cps) and the phosphorus (a septuplet at −45.1 ppm) nmr spectra in phosphorus oxychloride were consistent with 2,2-propylidenediphosphonyl tetrachloride.

Preparation of Diphosphinomethane. A. From Methylenediphosphonyl Tetrachloride.—Finely powdered methylenediphosphonyl tetrachloride (75 g, 0.3 mole) was added in small portions to 25 g of lithium aluminum hydride (0.66 mole) in 300 ml of dibutyl ether at 0–5° in a 1-l. flask equipped with a solid addition funnel, stirrer, Dry Ice condenser, thermometer, argon source, two traps, and a dilute nitric acid (10%) scrubber. The argon flow through the scrubber was continued at all times to prevent the dilute nitric acid from sucking back into the traps. The reduction appeared to be very rapid as the temperature rose markedly and the gas evolution also increased on addition of methylenediphosphonyl tetrachloride to the lithium aluminum hydride. Part of this gas was phosphine, identified by its infrared spectrum. Upon completion of the addition the ice bath was removed for 1 hr, then replaced, and 420 ml of 1:1 hydrochloric acid added slowly so that the temperature did not exceed 5°. Upon warming to room temperature the acid layer was removed *via* a stopcock in the bottom of the flask. The remaining dibutyl ether layer was washed with 25 ml of 1:1 hydrochloric acid, three times with 25 ml of water, and then with 25 ml of saturated sodium chloride solution. The organic layer was then transferred to a distillation apparatus. Distillation up to a head temperature of 120° gave a layer of water and 6 ml of diphosphinomethane and dibutyl ether. The organic layer was shown to be 39% diphosphinomethane and 61% dibutyl ether by gas chromatographic analysis and its proton and phosphorus nmr spectra. After drying over sodium carbonate, distillation gave 1 ml of diphosphinomethane, bp 83–85°. By gas chromatographic analysis the product was estimated to be about 90% pure; however, the sample ignited and was lost upon exposure to a trace of air.

B. From Tetraisopropyl Methylenediphosphonate.—The same equipment was used as in A with the exception that the solid addition funnel was replaced with a standard addition funnel. Tetraisopropyl methylenediphosphonate (34 g, 0.1 mole) was dropped slowly into 9.5 g of lithium aluminum hydride (0.25 mole) in 200 ml of either diethyl ether or dibutyl ether at 0–5°. Reaction was evident by a rise in temperature and gas evolution during the addition. A gas phase infrared spectrum showed phosphine in the effluent gases. Subsequently, the mixture was either hydrolyzed with 250 ml of 1:1 hydrochloric acid at 0–5° or refluxed up to 16 hr, then hydrolyzed at 0–5°. Attempts to isolate I as a residue from the preparations using diethyl ether and as a forerun from dibutyl ether gave only traces of highly impure I identified by its retention time and its phosphorus nmr spectrum. Treatment of the diethyl ether phases obtained from two reductions at 0–5° for 30 min and at reflux for 16 hr with nitric acid (see below) gave 12 and 6% crude yields of methylenediphosphonic acid, respectively. A phosphorus nmr spectrum of the diethyl ether phase obtained after refluxing 16 hr showed a 1:1 ratio of unreduced starting material and I. Undoubtedly the starting material was hydrolyzed to methylenediphosphonic acid since the oxidation was carried out in the following manner. To the diethyl ether solution at 0°, 40 g of 1:1 nitric acid–water was added dropwise and cautiously. Weaker nitric acid should be used as considerable smoke was observed. After stirring 1 hr at 0°, the temperature was raised slowly while the diethyl ether was removed by distillation. Following this the remaining liquid was heated on a steam bath for 1 hr then removed on a rotary evaporator to give the crude methylenediphosphonic acid. After digestion with acetic acid, then acetone, the methylenediphosphonic acid melted at 199–200° (lit.[17] mp 202–203°).

1,1-Diphosphinoalkanes. A. From 1,1-Alkylidenediphosphonyl Tetrachlorides.—1,1-Pentylidenediphosphonyl tetrachloride (59.5 g, 0.195 mole) was added dropwise to 17.1 g of lithium aluminum hydride (0.45 mole) in 400 ml of diethyl ether at 0–2°. After stirring 30 min the mixture was hydrolyzed with 500 ml of 1:1 hydrochloric acid and warmed to room temperature. The ether phase was washed with 50 ml of water and 30 ml of saturated sodium chloride, and distilled to give the yields of products shown in Table I.

1,1-Diphosphinoundecane and 1,1-diphosphinododecane were prepared using the same procedure as for the preparation of II.

B. From Tetraethyl Decylidenediphosphonate.—Tetraethyl decylidenediphosphonate (110 g, 0.25 mole) was added to 25 g of lithium aluminum hydride (0.6 mole) in 1 l. of diethyl ether at 0°. After stirring 24 hr at room temperature the reaction was incomplete; the mixture was refluxed 32 hr, then hydrolyzed at 0° with 600 ml of 1:1 hydrochloric acid. The ether phase was separated, washed, dried, and distilled to give the products shown in Table I.

2,2-Diphosphinopropane.—2,2-Propylidenediphosphonyl tetrachloride (66 g, 0.24 mole) was added in small portions *via* a solid addition funnel to 18 g of lithium aluminum hydride in 200 ml of diethyl ether at 0–5°. The reaction was quite exothermic. After 30 min at 0°, 325 ml of 1:1 hydrochloric acid was added slowly. Following separation and washing, the diethyl ether was removed by slow distillation through an 18-in. column to give a small amount of residual liquid. This liquid (about 0.5 g) was trapped in a Dry Ice cooled trap when a vacuum was applied to the system. Benzene (3 ml) was used as solvent to dissolve the product and obtain the nmr spectra in Table I.

Reactions of 1,1-Diphosphinopentane (II). A. Oxidation of II.—1,1-Diphosphinopentane (1.36 g, 0.01 mole) was mixed cautiously with a mixture of 7.2 g of concentrated nitric acid and 31 g of water at 0°. After stirring overnight the solution was slowly heated to reflux and most of the water was removed. A phosphorus nmr spectrum of the remaining liquid showed an unresolved multiplet at −21.2 ppm. Benzene (50 ml) was added and the product azeotroped dry, resulting in the formation of nitro- and dinitrobenzenes. These impurities were removed by dissolving the product in water and extracting three times with chloroform. After removing the water, the 1,1-pentylidenediphosphonic acid was recrystallized several times from hot ethyl acetate to give, after drying, 0.7 g (30% yield) of 1,1-pentylidenediphosphonic acid, mp and mmp 150–152°.[12] The phosphorus nmr spectrum consisted of an unresolved multiplet at −22 ppm in D_2O.

Anal. Calcd for $C_5H_{14}O_6P_2$: C, 25.9; H, 6.04; P, 26.7. Found: C, 25.9; H, 6.2; P, 26.8.

B. Attempted Reduction of II.—A 10:1 mixture of 1,1-diphosphinopentane and *n*-amylphosphine (1 g) was added to 0.12 g of lithium aluminum hydride in 5 ml of diethyl ether and refluxed 30 min. After hydrolysis at 0°, gas chromatographic analysis of the ether phase gave a ratio greater than 9:1 of II to *n*-amylphosphine.

C. Stability of II.—1,1-Diphosphinopentane (1-g amounts) was heated at 70–75° for 2.5 hr with catalytic amounts of azobisisobutyronitrile, of methanolic hydrochloric acid, and methanolic sodium methoxide, without observing any change in the gas chromatographs.

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