Photolysis of $OFCCF_2OCF_2CFO$.[7]—A mixture of 390 g (1.85 mol) of perfluorooxydiacetyl fluoride, bp 38°, and 2197 g of FC-78[8] were photolyzed in a larger unit than that described above. Ultraviolet light was supplied by four 15-watt low-pressure mercury lamps (2537 Å). The reactor temperature was maintained at about 30° during the 10 days of the run. The yield of $OFC(CF_2OCF_2)_2CFO$, bp 82°, was 101 g (52% conversion).

Reaction of the diacyl fluoride with methanol at 0° in the presence of excess sodium fluoride produced the corresponding dimethyl ester, $CH_3O_2C(CF_2OCF_2)_2CO_2CH_3$, bp 123.5° (50 mm).

Anal. Calcd for $C_8F_8H_6O_6$: C, 27.5; F, 43.5; H, 1.7; mol wt, 350. Found: C, 27.5; F, 43.6; H, 1.8; mol wt, 339 (in acetone).

Acknowledgment.—The authors wish to express their gratitude to Dr. J. J. McBrady for infrared and ^{19}F nmr spectra, to M. S. Kulver for mass spectra, and to Mr. P. B. Olson for elemental analysis.

(7) The authors are indebted to Dr. W. B. Isaacson and Dr. S. T. Ting for carrying out this experiment in a wiped-film photoreactor. The description of this new photoreactor has been published in *Ind. Eng. Chem., Fundam.*, **9**, 171 (1970).

(8) A perfluorocarbon inert liquid, bp 50–52°, sold by the 3M Company, St. Paul, Minn.

The Synthesis of 2,5-Dialkoxy-1,4-diphosphoniacyclohexane Salts[1]

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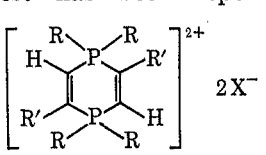
A new organophosphorus heterocycle, 1,4-diphosphoniacyclohexadiene-2,5 (**1**), of both theoretical and biological interest has been reported recently.[4-9]



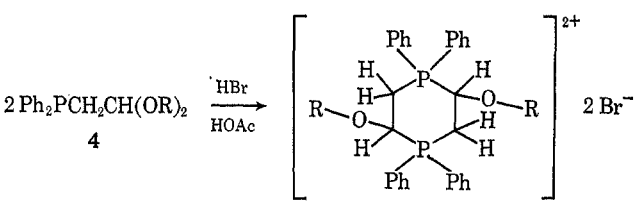
1

In an attempt at developing a new synthetic route to this system, we have found that a tetrahydrofuran solution of lithium diphenylphosphide (**2**) reacts with the dimethyl and diethyl acetals of chloroacetaldehyde (**3**) to give the corresponding acetal of diphenylphosphinoacetaldehyde (**4**) (eq 1).

$$\underset{\mathbf{2}}{Ph_2PLi} + \underset{\mathbf{3}}{ClCH_2CH(OR)_2} \xrightarrow{THF} \underset{\mathbf{4}}{Ph_2PCH_2CH(OR)_2} + LiCl \quad (1)$$

R = Me, Et

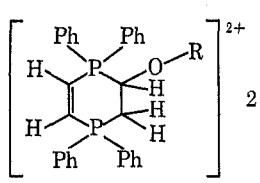
Upon reaction of **4** with hydrogen bromide in boiling glacial acetic acid, the new 2,5-dialkoxy-1,4-diphosphoniacyclohexane dibromide (**5**) could be isolated (eq 2).



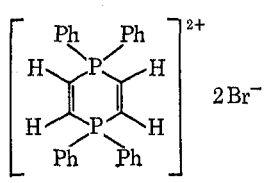
5 (2)

R = Me, Et

No mono- (**6**) or di- (**1a**) unsaturated heterocycles were isolated.



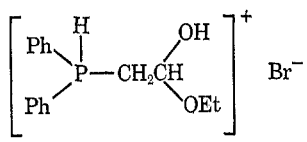
6



1a

It is surprising that under these conditions no **1a** is isolated since this could occur *via* the aldehyde, the acetylene, or even the dealcoholization of **5**. Dealcoholization of isolated **5** to **1a** was attempted employing boron trifluoride etherate with no success. At present the stability of **5** to Lewis acids is not clear. It may involve interaction of the unshared pair of electrons on the oxygen with the positive phosphorus.

The possibility that the compound which we have designated **5b** is actually the hemiacetal phosphine hydrobromide (**7**) has been eliminated by ir spectrophotometry. The ir spectrum of **5b** contains no band between 2000 and 2500 cm^{-1}. It has been shown that phosphine hydrobromides exhibit a fairly intense peak in this region.[6] Furthermore, there was no change in the nmr spectrum of a $CDCl_3$ solution of **5b** upon treatment with D_2O. It is known that the proton of a phosphine hydrobromide undergoes rapid exchange with D_2O under these conditions.[6]



7

The structure of compound **5b** was unequivocally determined with the aid of its 100-MHz spectrum. The complex downfield nmr pattern centered at 7.90 ppm

(1) Taken in part from the dissertation of K. C. Hansen, Tulane University, 1967.

(2) NASA Fellow at Tulane University, 1964–1967.

(3) NASA Fellow, 1966–1967; NDEA Fellow, 1967–1969; NSF Fellow, 1969–1970.

(4) A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *J. Amer. Chem. Soc.*, **89**, 3087 (1967).

(5) A. M. Aguiar and K. C. Hansen, *ibid.*, **89**, 4235 (1967).

(6) A. M. Aguiar, J. R. S. Irelan, G. W. Prejean, J. P. John, and C. J. Morrow, *J. Org. Chem.*, **34**, 2681 (1969).

(7) A. M. Aguiar, J. R. Irelan, C. J. Morrow, J. P. John, and G. W. Prejean, *ibid.*, **34**, 2684 (1969).

(8) A. M. Aguiar, G. W. Prejean, J. R. S. Irelan, and C. J. Morrow, *ibid.*, **34**, 4024 (1969).

(9) R. Majeste and L. M. Trefonas, *J. Heterocycl. Chem.*, **6**, 269 (1969).

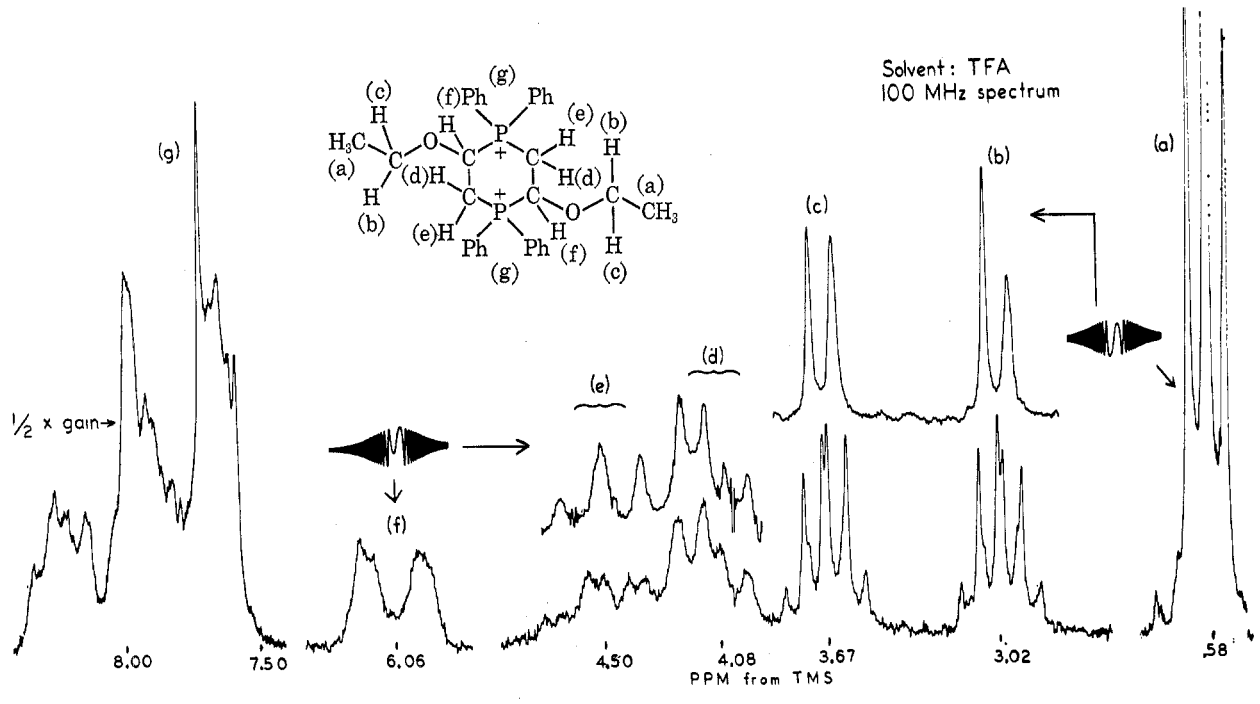


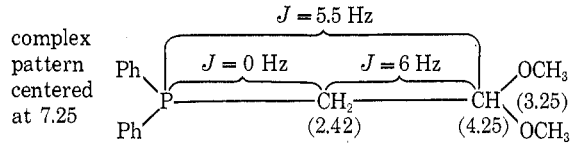
Figure 1.

representing 20 protons is ascribed to the hydrogen atoms of the four phenyl rings. The (6 H) triplet at $\delta = 0.58$ and the almost identical (4 H) multiplets at $\delta = 3.02$ and 3.67 are assigned to the methyl and nonequivalent methylene protons, respectively, of the ethoxy groups at C-2 and C-5. The nonequivalence of the methylene protons and the unusually high-field chemical shift of the methyl protons is attributed to the anisotropic effects of the phenyl groups located on the phosphorus atoms. The slightly broadened doublet (16 Hz) of doublets (9 Hz) at $\delta = 4.08$ (labeled D in the nmr spectrum) and a doubled (5 Hz) triplet (16 Hz) at $\delta = 4.50$ (labeled E) representing two protons each are assigned to the two nonequivalent methylene hydrogen atoms at C-3 and C-6. The 16-Hz splitting in the two resonances is due to the mutual geminal coupling between the two protons. The other large couplings of 9 and 16 Hz observed in the D and E resonances, respectively, are due to the spin interactions of the two protons with the phosphorus nuclei in the molecule. The small splittings of approximately 1.0 and 5.0 Hz present in the D and E absorptions are caused by the coupling of these two protons with the vicinal methine protons at C-2 and C-5, which resonate at $\delta = 6.06$ and are labeled F in the spectrum. This was confirmed when the broad doublet (20 Hz) of doublets (5 Hz) at $\delta = 6.06$ was irradiated in the frequency sweep mode of the 100-MHz spectrometer and the decoupled resonances of D and E at $\delta = 4.08$ and 4.50, respectively, were examined (see Figure 1). The magnitude of these spin couplings designated an equatorial orientation for F. The large coupling of 20 Hz observed in the resonance at $\delta = 6.06$ is due to the spin interaction of H-2 and H-5 with those of the phosphorus nuclei. By analogy, the proton labeled E is assigned an equatorial configuration from the magnitude of the PH coupling (16 Hz) seen in the resonance at $\delta = 4.50$. This assignment is in harmony with the observation that equatorial protons usually resonate downfield from their geminal axial neighbors.

Experimental Section

Diphenylphosphinoacetaldehyde Dimethyl Acetal (4a).—Lithium diphenylphosphide (made from 0.1 mol of diphenylphosphinous chloride and excess lithium) in tetrahydrofuran (THF) was added slowly to a stirred THF solution of 12.5 g (0.1 mol) of chloroacetaldehyde dimethyl acetal. An immediate, mildly exothermic reaction ensued with the decolorization of the lithium diphenylphosphide. The reaction mixture was stirred for 0.5 hr at room temperature. The THF was stripped off at reduced pressure and the residue was vacuum distilled yielding 20.3 g (74%) of a colorless liquid, bp 138–139° (0.2 mm).

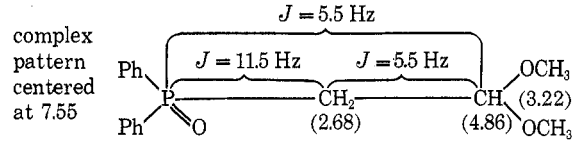
Nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



The above phosphine was characterized as the oxide by treatment of an acetone solution with 3% hydrogen peroxide. Evaporation of the acetone yielded an oil which crystallized upon drying, mp 111° (from cyclohexane). The ir spectrum showed strong phosphoryl absorption at 1180 cm^{-1}.

Anal. Calcd for $C_{16}H_{19}O_3P$: C, 66.20; H, 6.55; P, 10.68. Found: C, 66.36; H, 6.63; P, 10.53.

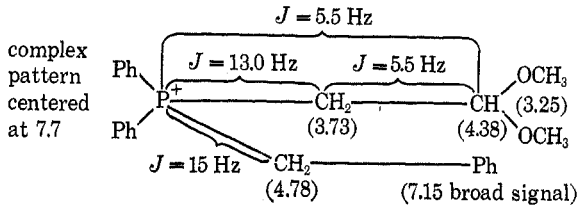
The nmr spectrum of this compound, obtained in $CDCl_3$ solution at 60 MHz, was in good accord with this structure.



The phosphine was further characterized as the benzyl bromide salt by reaction at room temperature with 1 equiv of benzyl bromide in dry benzene. A white solid precipitated, mp 163–164° (from ethyl acetate–methanol).

Anal. Calcd for $C_{23}H_{26}BrO_2P$: C, 62.06; H, 5.84. Calcd for $C_{23}H_{26}BrO_2P \cdot H_2O$: C, 59.65; H, 6.04. Found: C, 60.00, 59.97; H, 6.06, 5.92.

Nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



2,5-Dimethoxy-1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane Dibromide (5a).—Diphenylphosphinoacetaldehyde dimethyl acetal (12.0 g, 0.047 mol) was dissolved in 200 ml of glacial acetic acid and this solution was brought to reflux. Hydrogen bromide was then passed slowly through the refluxing solution for 1 hr. The acetic acid was stripped off under reduced pressure and the residue was triturated with acetone yielding 9.1 g (50%) of a white solid, mp 208–210° dec (from acetonitrile–methanol).

Anal. Calcd for $C_{30}H_{32}Br_2O_2P_4$: C, 55.77; H, 4.95; Br, 24.70. Calcd for $C_{30}H_{32}Br_2O_2P_4 \cdot H_2O$: C, 54.26; H, 5.12; Br, 24.06. Found: C, 53.66; H, 4.94; Br, 24.50.

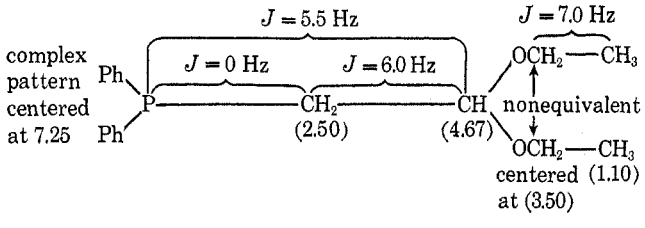
The dibromide was converted into a dipicrate by the metathetical reaction with sodium picrate in methanol yielding a yellow solid, mp 160° (from acetonitrile). Sodium fusion of a sample of the picrate gave a negative analysis for bromine.

Anal. Calcd for $C_{42}H_{36}N_6O_{16}P_2$: C, 53.53; H, 3.82; N, 8.91. Found: C, 52.56, 53.3; H, 3.39, 3.89; N, 8.72, 8.88.

Diphenylphosphinoacetaldehyde Diethyl Acetal (4b).—A tetrahydrofuran solution of 0.1 mol of lithium diphenylphosphide was added slowly with stirring over a period of 30 min to a solution of 15.3 g (0.1 mol) of chloroacetaldehyde diethyl acetal (Aldrich) in 100 ml of tetrahydrofuran. The reaction was not very exothermic and rather slow. The reaction mixture was stirred for 30 min at room temperature. The tetrahydrofuran was stripped off and the residue was vacuum distilled, yielding 20.8 g (69%) of **4b**, bp 163–165° (1.5 mm).

The infrared spectrum of a chloroform solution of **4b** showed no phosphoryl absorption between 8.0 and 9.0 μ.

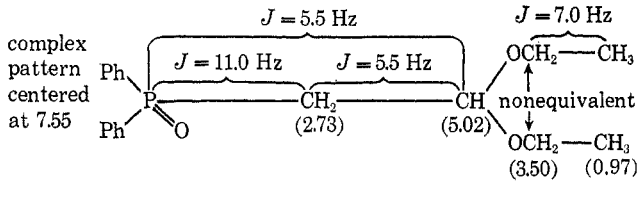
The nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



The above phosphine was characterized as the oxide by reaction of an acetone solution with 3% hydrogen peroxide in acetone. An exothermic reaction was noted, and evaporation of the solvent yielded a white crystalline solid, mp 101° (from hexane–cyclohexane).

Anal. Calcd for $C_{18}H_{23}O_3P$: C, 67.92; H, 7.23; P, 9.74. Found: C, 67.83; H, 7.01; P, 9.59.

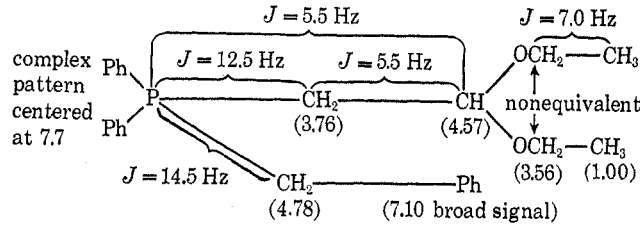
The nmr spectrum of this compound, obtained in $CDCl_3$ solution at 60 MHz, was in good accord with this structure.



The phosphine was further characterized as the benzylphosphonium bromide by reaction with excess benzyl bromide in benzene at reflux for 1 hr. The solid precipitate was recrystallized from ethyl acetate–methanol, mp 199–201°.

Anal. Calcd for $C_{25}H_{30}BrO_2P$: C, 63.42; H, 6.34; Br, 16.91; P, 6.55. Found: C, 63.56; H, 6.48; Br, 17.12; P, 6.53.

The nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



2,5-Diethoxy-1,1,4,4-tetraphenyldiphosphonia-1,4-cyclohexane Dibromide (5b).—Diphenylphosphinoacetaldehyde diethyl acetal (20 g, 0.066 mol) was dissolved in 150 ml of glacial acetic acid and hydrogen bromide was passed slowly through the solution at reflux for 2 hr and the solution allowed to stand at room temperature for 12 hr. The acetic acid was stripped off at reduced pressure and the residue was triturated with acetone yielding 13.5 g (61%) of **5b**, mp 208–210° (from acetonitrile–methanol).

Anal. Calcd for $C_{32}H_{36}Br_2O_2P_2 \cdot H_2O$: C, 55.49; H, 5.49; Br, 23.12. Found: C, 55.61; H, 5.68; Br, 23.16.

The infrared spectrum of a potassium bromide disk of **5b** showed absorptions at 6.98, 9.00, and 10.04 μ which are typical of aryl phosphonium salts. Strong absorption was also observed at 9.40 μ assigned to a carbon-to-oxygen single bond stretching frequency.

Picrate of 5b.—A sample of **5b** in methanol was mixed with an aqueous solution of sodium picrate and the immediate precipitation of a yellow solid resulted, mp 182–183° dec (from acetonitrile).

Anal. Calcd for $C_{44}H_{40}N_6O_{16}P_2$: C, 54.43; H, 4.12; N, 8.65; Br, 0.00. Found: C, 53.91; H, 3.73; N, 8.01; Br, 0.00.

Fluoroborate Salt of 5b.—A warm aqueous solution of **5b** and an aqueous solution of sodium fluoroborate were mixed and a white solid immediately precipitated, mp 260–262° (from ethyl acetate–methanol). The nmr spectrum of a trifluoroacetic acid solution of the fluoroborate salt was identical with that of the bromide.

Registry No.—**4a**, 24744-62-5; **4a** (oxide), 24744-63-6; **4a** (benzyl bromide salt), 24744-64-7; **4b**, 24744-65-8; **4b** (oxide), 24744-66-9; **4b** (benzyl bromide salt), 24744-67-0; **5a**, 24744-68-1; **5a** (dipicrate), 24744-69-2; **5b**, 24744-70-5; **5b** (picrate), 24799-52-8; **5b** (fluoroborate), 24806-55-1.

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^{19}F Nuclear Magnetic Resonance Spectra of Some Trifluoroacetanilides

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We have become interested in the transmission of electronic activation effects through the amide link from groups attached to the nitrogen atom to a reactive site on a carbon atom attached to the carbonyl

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