[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND HARVARD UNIVERSITY]

Preparation, Nuclear Resonance Spectra and Structure of Bis-(diethoxyphosphonyl)-methano Sodium[1]

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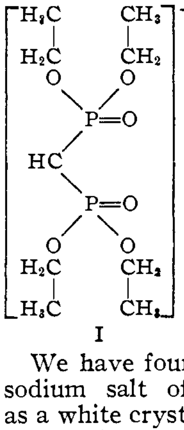
Bis-(diethoxyphosphonyl)-methane reacts readily with alkali metals with evolution of hydrogen. The sodium salt has been isolated and characterized chemically and by infrared spectrum, and both the starting compound and the sodium salt have been studied by proton nuclear resonance including proton–proton double resonance. The n.m.r. results strongly support the proposal that the sodium salt contains the anion $\{[(EtO)_2P(O)]_2CH\}^-$ and that this ion has a symmetrical planar structure. All data are in agreement with the assumption that some degree of resonance occurs in this anion which is formally similar to a β-ketoenol anion. Cryoscopic measurements in both CCl_4 and benzene show that the sodium salt is a hexamer of the simplest formula unit. Since the n.m.r. results can be completely interpreted using the simplest formula unit, it must be assumed that all six such units in the hexamer are either rigorously or to a high order of approximation equivalent symmetrically.

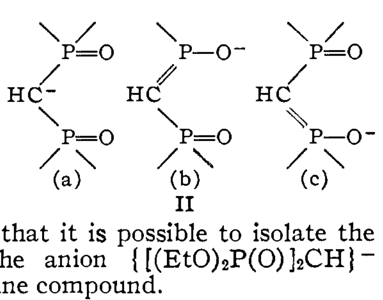
Introduction

Nearly a decade ago Kosolapoff[3] reported that bis-(diethoxyphosphonyl)-methane $[(EtO)_2P(O)]_2CH_2$, reacts with potassium in xylene and that on treating the solution so obtained with *n*-butyl bromide, $[(EtO)_2P(O)]_2CH—C_4H_9$ was produced in about 15% yield. Kosolapoff suggested that the intermediate potassium compound was very likely a salt of the anion $\{[(EtO)_2P(O)]_2CH\}^-$, and that the reaction of the diphosphonylmethane with potassium could be considered similar to the reaction of diethylmalonate with alkali metals. Kosolapoff's observations and postulate appeared interesting enough to warrant more detailed investigation and this paper is the first of several which will report our observations on systems of this type.

A chemically reasonable structure for the anion mentioned above would be I, and it might further be considered whether the anion would be stabilized by resonance of the sort depicted in II, which is quite analogous to the resonance occurring in β-keto enol anions. Also, it would appear reasonable that the alkali ion might be bound to the two phosphonyl oxygen atoms completing a 6-membered ring.



I



(a) (b) (c)

II

We have found that it is possible to isolate the sodium salt of the anion $\{[(EtO)_2P(O)]_2CH\}^-$ as a white crystalline compound.

In order to test the correctness of the structure discussed above nuclear resonance appeared to be the best available tool. However, in order to obtain a definitive analysis of the rather complex spectrum it was necessary to use the proton-proton double resonance technique.[4]

Experimental

All manipulations were performed in an atmosphere of prepurified nitrogen unless otherwise specified. Solvents were dried on a column of molecular sieves (Linde Co., type 4A) and alumina. Infrared spectra were recorded on a Perkin–Elmer Model 21 double beam spectrophotometer.

Bis-(diethoxyphosphonyl) methane, $[(C_2H_5O)_2PO]_2CH_2$, was prepared by the method of Schwarzenbach and Zurc[5] in 44% yield, b.p. 111–113° (0.15 mm.), $n^{25}D$ 1.4402. *Anal.* Calcd. for $[(C_2H_5O)_2PO]_2CH_2$: C, 37.50; H, 7.70; P, 21.49. Found: C, 37.22; H, 7.75; P, 21.76.

Preparation of Bis-(diethoxyphosphonyl)-methano Sodium $\{[(C_2H_5O)_2PO]_2CH\}Na$.—In a 200 cc. 3-neck flask equipped with condenser, addition funnel, inlet for nitrogen, magnetic stirrer and a pressure-equalizing gas collector, bis-(diethoxyphosphonyl)-methane (6.0 g., 20.8 mmoles) in 10 cc. THF was added slowly to a mixture of sodium sand (0.59 g., 25.6 mg. atoms) in 60 cc. THF. The mixture was stirred for one hour at room temperature and then refluxed for one-half hour. The volume of evolved gas was 265 cc. at 767 mm. and 22° (theor. for 1 equivalent of H_2 is 250 cc.). The resulting solution was filtered free of excess sodium and solvent was removed under vacuum to give a pale yellow oil. On addition of 40 cc. of petroleum ether (30–60°) and cooling to −78° the product separated as a white powder which was collected on a coarse glass filter, and dried at 47°/0.05 mm. for 17 hr.; yield, 3.8 g. (60%); m.p. 138–140° (uncorr.). *Anal.* Calcd. for $\{[(C_2H_5O)_2PO]_2CH\}Na$: C, 34.84; H, 6.82; P, 19.97. Found: C, 34.56; H, 7.03; P, 19.22.

Molecular Weight.—The molecular weight of $\{[(C_2H_5O)_2PO]_2CH\}Na$ was determined cryoscopically in carbon tetrachloride and in benzene, using in the former case a thermistor circuit and in the latter a Beckman thermometer to measure the freezing point depressions; results obtained were: in CCl_4, 1830 ± 90; in C_6H_6, 1820 ± 90; calculated for a monomer, 310.2.

N.m.r. Spectra.—N.m.r. spectra at 40 and 60 Mc. were obtained with a Varian Associates V-4300 high resolution n.m.r. spectrometer. The proton–proton double resonance was accomplished with audiofrequency field modulation and lock-in detection using circuits similar to those described by Elleman and Manatt.[6]

Results

Chemical Characterization.—The sodium salt of bis-(diethoxyphosphonyl)-methane can be isolated as a white crystalline power. It appears to be indefinitely stable toward oxygen but it is very hygroscopic and must therefore be protected from the atmosphere. It is thermally quite stable, melting without decomposition at 138–140° to a colorless liquid. It failed to sublime at temperatures up to the melting point at pressures as low

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[2] Alfred P. Sloan Foundation Fellow.

[3] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).

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[6] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

TABLE I

INFRARED SPECTRA OF BIS-(DIETHOXYPHOSPHONYL)-METHANE AND ITS SODIUM SALT[a]

Bis-(diethoxyphosphonyl)-methane	Bis-(diethoxyphosphonyl)-methano sodium
2970 (20)[b]	2970 (25)
2920 (sh)	2930 (40)
2900 (40)	2890 (45)
1480 (55)	1480 (70)
1445 (45)	1445 (60)
1390 (30)	1390 (45)
1370 (30)	1365 (70)
1245 (sh)	1290 (70)
1265 (5)	1205 (5) (broad)
1175 (20)	1170 (sh)
1170 (sh)	1160 (sh)
1095 (25)	1100 (25)
1045 (5) (broad)	1050 (5) (broad)
965 (5) (broad)	945 (5) (broad)
825[c] (5)	845 (60)
805[c] (sh)	785[d] (15)
	740[d] (20)
720[c] (80)	725 (55)

[a] The spectra were taken in a 0.1 mm. sodium chloride cell; solutions were 10% w./w. in CCl_4 except as noted. [b] Figures in parentheses are per cent. transmission. [c] These bands observed in CS_2, 10% w./w. [d] These bands observed in tetrahydrofuran, concentration unknown.

as 0.05 mm. However, it is readily soluble in various organic media, *viz.*, carbon tetrachloride, benzene, ether, tetrahydrofuran, acetone, cyclohexane and petroleum ether. It reacts slowly with CCl_4 and quite rapidly with CS_2 giving orange to red solutions. The CCl_4 solutions, however, are sufficiently stable for use in studying the infrared and n.m.r. spectra.

In both carbon tetrachloride and benzene, at the freezing points of these liquids, cryoscopic measurements show that the molecular units are hexamers of the simplest formula unit, $\{[(EtO)_2PO]_2CH\}Na$. At the present time it is impossible to do more than speculate about the structure of the hexamer. The only restriction which can be imposed on possible models is that they must permit all or nearly all of the formula units to be chemically equivalent or very nearly so since the n.m.r. observations can be completely interpreted using only the simplest formula unit.

The infrared spectra of both bis-(diethoxyphosphonyl)methane and its sodium salt (summarized in Table I) are in agreement with the structures assumed for these compounds. The PO stretching frequency in the former occurs as a rather broad band at ~1265 cm.$^{-1}$ and in the sodium salt at ~ 1200 cm.$^{-1}$. This decrease in frequency is consistent with the structure inasmuch as the resonance shown in II, with IIb and IIc being enhanced by the presence of a sodium ion coördinated to the oxygen atoms would tend to reduce the PO bond order.

In agreement with Kosolapoff's observations and supposition, we have found that the sodium salt reacts readily with alkyl halides giving products which are alkylated at the bridging carbon atom. These and other chemical studies will be reported fully later.

Nuclear Resonance Spectra.—The proton resonance spectrum of bis-(diethoxyphosphonyl)-methano sodium consists of three groups of bands. A high field, 1–2–1 triplet centered at τ = 9.52 with a splitting of 7.4 c.p.s. is readily assigned from its intensity to the unique proton. For the proposed structure of the simplest formula unit, the two phosphorus nuclei are "nmr equivalent"[7] in their coupling with the bridge proton. The coupling of the phosphorus nuclei to the bridge proton is identical, and thus the multiplet structure observed on the bridge proton resonance is independent of the magnitude of the phosphorus–phosphorus coupling. The simple 1–2–1 triplet pattern can therefore be assigned to the coupling of two equivalent P^{31} nuclei in the bridge proton with $J_{P\text{-}CH}$ = 7.4 c.p.s. A second 1–2–1 triplet centered at τ = 8.78 with a splitting of 7.1 c.p.s. is also readily assigned, from its intensity, to the four methyl groups. The fine structure is attributable to coupling of the two methylene protons in each ethyl group with the methyl group. Finally, there is a symmetrical complex multiplet consisting of at least nine components centered at τ = 6.13 which must then be attributed to the methylene groups. This multiplet is shown in Fig. 1a. If the structure on the methyl resonance is properly assigned to coupling with the methylene groups, then the methylene proton resonance must involve at least four peaks spaced at 7.1 c.p.s. The additional structure on this multiplet could arise from non-equivalence of the two protons on a given methylene group, non-equivalence of two different sets of methylene groups, coupling with the P^{31} nuclei, or a combintaion of these effects.

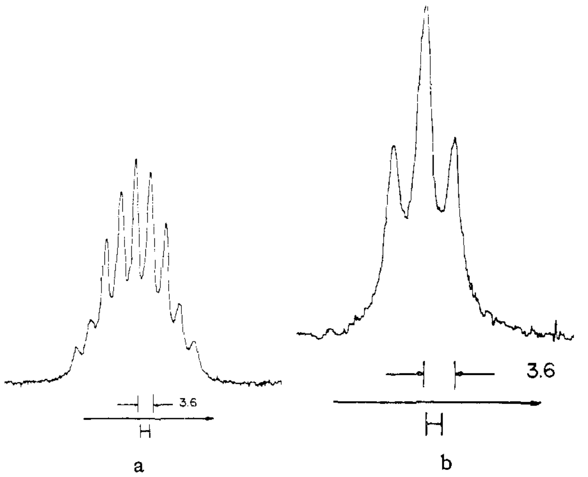

Fig. 1.—Methylene proton resonance of bis-(diethoxyphosphonyl)-methano sodium at 60 Mc.p.s.: (a) normal spectrum, (b) with methyl protons decoupled.

Decoupling the methyl protons from the methylene groups results in a simple 1–2–1 triplet, with a spacing between lines of 3.6 c.p.s. as shown in Fig. 1b. Numerous examples of the non-equivalence of protons on a methylene group close to an asymmetric center have been reported.[8–12] With

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(7) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 116.

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(9) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

(10) P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan and J. D. Roberts, *Proc. Natl. Acad. Sci. (U. S.)*, **47**, 29 (1961).

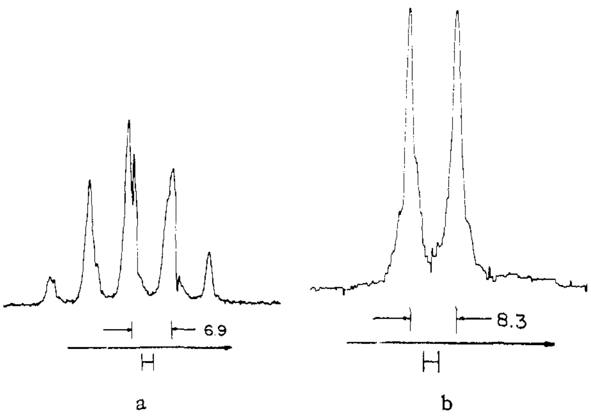

Fig. 2.—Methylene proton resonance of bis-(diethoxyphosphonyl)-methane at 60 Mc.p.s.: (a) normal spectrum; (b) with methyl protons decoupled.

this type of non-equivalence, the methylene group resonance should reduce to a four-line AB multiplet. It is difficult to reconcile the observed triplet with an AB spectrum, or an AB spectrum further split by coupling with the adjacent P^{31} nucleus.

The possibility that the molecule contains two sets of non-equivalent methylene groups may be considered next. This could occur, for example, if the two $-OCH_2CH_3$ groups bonded to a given phosphorus atom had axial and equatorial orientations with respect to a non-planar six membered ring. If the methylene group resonance were split by 3.6 c.p.s. by coupling with an adjacent P^{31}, the relative shift between two non-equivalent methylene groups were also 3.6 c.p.s. at 60 Mc., and $J_{P-P} = 0$, then a 1–2–1 triplet pattern could arise. The double resonance spectrum obtained at 40.0 Mc., however, is a 1–2–1 triplet with 3.6 c.p.s. spacing, identical to the 60.0 Mc.p.s. spectrum. Thus, a relative chemical shift between non-equivalent methylene groups is not responsible for the triplet pattern in the double resonance spectrum.

A satisfactory explanation of the fine structure of the methylene resonance is as follows. It is important to note that the two P^{31} nuclei are not equivalent in their coupling to the protons of a given methylene group. Thus the structure that is observed on the methylene protons depends on the magnitude of the coupling between the two phosphorus nuclei. For a sufficiently large value of J_{P-P}, the multiplet structure on the methylene proton resonance arising from the P^{31} nuclei reduces to a simple triplet.[13] A lower limit on J_{P-P} can be estimated by consideration of an AXX'A' system. If it is assumed that $J_{AX} = J_{A'X'} = 7.2$ c.p.s., $J_{AX'} = J_{A'X} = J_{AA'} = 0.0$ c.p.s., and if it is further assumed that features spaced at less than 1 c.p.s. cannot be resolved in the double resonance spectrum, then a simple 1–2–1 triplet with lines spaced at 3.6 c.p.s. results for J_{P-P} larger than about 25 c.p.s. Thus a consistent explanation of the single and double resonance spectra of the methylene groups at 60.0 and 40.0 Mc. requires that $J_{CH_2-P} = 7.2$ c.p.s., and J_{PP} be larger than about 25 c.p.s. The values of J_{CH_2-P} observed in a variety of compounds with the interacting nuclei in the configuration P–O–C–H are of the order of 10 c.p.s.[14] Furthermore, J_{P-P} has been found to be 17 c.p.s. in both of the polyanions $[O_3POP(O)_2OPO_3]^{4-}$ and $[O_2HPOPO_3]^{3-}$, where the bridges are isoelectronic with the CH bridge in bis-(diethoxyphosphonyl)-methano sodium.[15]

The assignment of the structure of the methylene proton resonance to coupling with a pair of strongly coupled P^{31} nuclei and a methyl group rather than to some non-equivalence of the methylene protons is consistent with the proposed planar structure for this ion.

The proton resonance of bis-(diethoxyphosphonyl)-methane at 60 Mc. also consists of three multiplets. At highest field is a 1–2–1 triplet centered at $\tau = 8.67$ with a splitting of 6.9 c.p.s. This multiplet is assigned to the methyl protons split by the methylene protons. A second 1–2–1 triplet centered at $\tau = 7.71$ with a splitting of 20.3 cps can be assigned to the bridging methylene group; from the structure of this multiplet it follows that the two P^{31} nuclei are again "n.m.r. equivalent." The coupling of the P^{31} nuclei to the bridge protons is apparently very sensitive to the bonding of the P^{31} and H^1 nuclei to the bridging carbon. Finally, there is a symmetrical multiplet consisting of at least five components centered at $\tau = 5.95$. This is assigned from its intensity to the methylene protons of the ethoxy groups. This multiplet is reduced to a simple 8.3 c.p.s. doublet by decoupling the methyl groups at 60.0 Mc. The double resonance spectrum at 40.0 Mc. consists of a doublet with 8.3 c.p.s. splitting, identical to the 60.0 Mc. result. This splitting can be assigned simply to the coupling of the ethyl-CH_2-groups with the adjacent P^{31} nuclei with $J_{P-CH_2} = 8.3$ c.p.s. Since no additional structure is observed on this resonance, J_{P-P} must be less than about 1 c.p.s. It seems surprising that J_{P-P} must be greater than 25 c.p.s. in bis-(diethoxyphosphonyl)-methano sodium, and less than 1 c.p.s. in bis-(diethoxyphosphonyl)-methane. However the nature of the bridging groups is considerably different in these two molecules.

The phosphorus resonance in bis-(diethoxyphosphonyl)-methane has recently been measured.[16] A triplet of poorly resolved multiplets was observed with an intensity distribution in the main triplet of 1–2–1. The assignment of the P^{31} spectrum required J for P to bridging CH_2 as 21.0 c.p.s., and J for P to OCH_2 as 7.5 c.p.s.[16]

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(16) K. Moedritzer and R. R. Irani, *J. Inorg. Nuclear Chem.*, **22**, 297 (1961), and private communication from M. M. Crutchfield, Monsanto Chemical Co.