through Norit, gave 1.11 g (68%) of crude **9**, mp 176.5–178°. Further recrystallizations from acetonitrile and from water gave pure **9**: mp 186–187°; infrared spectrum (Nujol), N–H at 3200 and C=O at 1680 cm^{-1}; ultraviolet spectrum, λ_{max} 218 mμ (ϵ 25,800) and 294 (2150). *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.10; H, 6.85; N, 7.33. Found: C, 69.52; H, 6.88; N, 7.30.

1-Azatricyclo[7.2.1.0^{6,11}]dodecan-12-one (10). Method A. From 9.—A solution of 950 mg of **9** in 100 ml of 95% ethanol was stirred in the presence of 1.5 g of 5% ruthenium on carbon under 2000 psig of hydrogen at 160° for 43 hr in a stainless steel autoclave. The catalyst was removed by filtration. Evaporation of the solvent gave 800 mg of colorless oil. The oil was dissolved in 30–60° petroleum ether and filtered through a pad of Norit and the solvent was removed by evaporative distillation to give 760 mg (75.4%) of crude **10** as a coloress oil. Distillation *in vacuo* in a Hickman still gave pure **10**: bp 82° (0.05 mm); infrared spectrum (film), C=O at 1680 cm^{-1}. *Anal.* Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.40; H, 9.54; N, 7.97.

Method B. From 8.—A solution of 2.33 g of **8** in 200 ml of 95% ethanol containing 1 g of 5% rhodium on carbon was stirred under 1500 psig of hydrogen at 100° for 80 hr in a stainless steel reaction vessel. After cooling and filtering, the solvent was distilled *in vacuo* and the residual oil was dissolved in methylene chloride, washed with saturated brine, dried over sodium sulfate, filtered through a pad of Norit, and evaporated to 1.33 g of colorless gum. The gum was refluxed with 50 ml of concentrated hydrochloric acid for 42 hr, cooled, and filtered to remove 440 mg of **9** hydrochloride, mp 306–309°, which had separated as white needles on standing at room temperature overnight. The aqueous filtrate was evaporated *in vacuo* to a moist gum which was dissolved in 10 ml of water, neutralized to pH 4 with ammonium hydroxide, and evaporated to a white paste. The paste was boiled with methylene chloride and the solvent was separated by decantation; the product was dried and evaporated to give 460 mg of a white froth.

The crude amine was heated under nitrogen for 10 min at 250°, dissolved in methylene chloride, filtered through a pad of Norit, and washed with 5% sodium bicarbonate solution, water, and saturated brine. After drying with sodium sulfate, the solvent was evaporated and the residual yellow oil was dissolved in 30–60° petroleum ether, filtered through a pad of Norit, and evaporated to give 185 mg of colorless oil. Short-path distillation in a bulb-to-bulb distilling tube at 0.04 mm (bath temperature 120°) gave 166 mg (9.25%) of pure **10**, which was identical with the product obtained from **9** by method A.

Registry No.—**4,** 19886-89-6; **5,** 19886-87-4; **6,** 19886-90-9; **8,** 19886-88-5; **9,** 19886-91-0; **10,** 19922-51-1.

Effect of pH on ^{31}P–^{1}H Coupling Constants and ^{1}H Chemical Shifts in Methyl Phosphates[1]

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The effect of pH on the chemical shift of methyl groups bonded to phosphorus has been reported[3] for substituted phosphine oxides, phosphinic acids, and phosphinate esters. The p*K* values for these compounds were determined by measuring the chemical shift (δ) as a function of sulfuric acid concentration. However, there are no data available on the change in the coupling constant (J_{P-H}) as a function of pH. This report describes the effect of pH on both δ and J_{P-H} for monomethyl and dimethyl phosphates. Both δ and J_{P-H} are pH dependent for monomethyl phosphate (I) and pH independent for dimethyl phosphate (II). The change in δ and J_{P-H} for I occurs between pH 4 and 8 and is due to the ionization of the second proton of the phosphate group.

The spectrum obtained from either I or II consists of two peaks which are due to the splitting of the proton peak of the methyl group by ^{31}P. Below pH 5, the spectra of the two compounds are similar, but, as the pH is raised, the spectrum of II remains unchanged while that of I shifts to higher field and shows a decreased J_{P-H}. Figure 1 shows the dependence of δ and J_{P-H} on pD[4] for both I and II. Tsubori, *et al.*,[5] reported a J_{P-H} of 10.3 Hz for the disodium salt of I and 10.5 Hz for the barium salt of II. They did not report the pH at which their measurements were made and did not investigate the effect of pH on J_{P-H}. Their reported values are somewhat at variance with the values reported here.

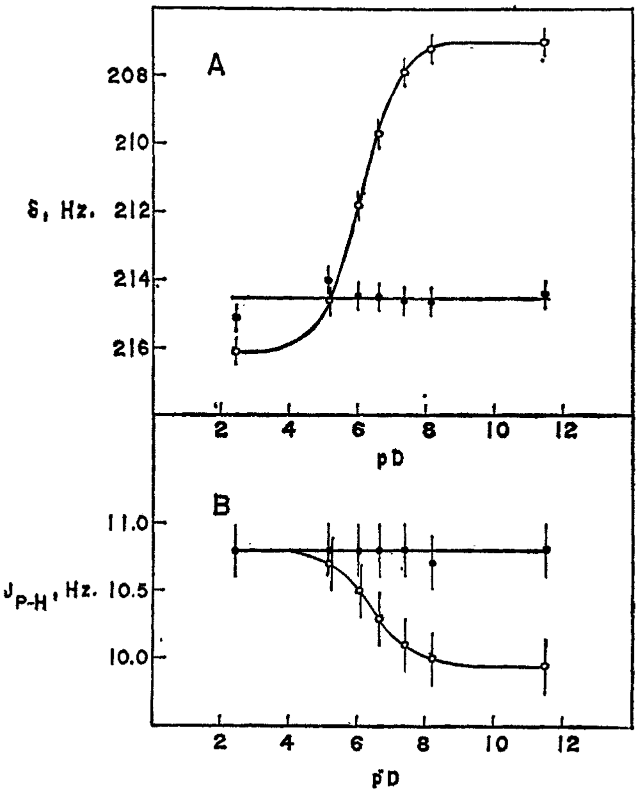

Figure 1.—Dependence of chemical shift and coupling constant on pD. Curve A gives chemical shifts and curve B gives coupling constants for monomethyl phosphate (—○—) and dimethyl phosphate (—●—). Each point represents an average of several determinations at each pH.

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[3] P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967).

[4] pD was calculated from the equation pD = pH + 0.41. See A. K. Covington, M. Paabo, R. A. Robinson, and R. G. Bates, *Anal. Chem.*, **40**, 700 (1968).

[5] M. Tsubori, F. Kuriyagawa, K. Matsuo, and Y. Kyogoku, *Bull. Chem. Soc. Jap.*, **40**, 1813 (1967).

The pK of II is 1.29,[6] and at pH 2 and above it is present only as a monoanion. One would not expect any change in structure with pH, and indeed the nmr spectrum of II remains constant with changing pH. I, on the other hand, is a dibasic acid with a pK_1 of 1.54[6] and a pK_2 of 6.4.[7] From pH 2 to 4 it exists as a monoanion, and, as the pH is increased, the second proton is removed, giving rise to a phosphate group with two negative charges. The shift of δ to higher field owing to this increased negative charge is similar to that described by Haake, *et al.*,[3] and is in agreement with the relationship between δ and distribution of electron charge established by Mavel and Martin[8] for a series of compounds bearing the CH_3OP moiety but containing different substituent groups of different electronegativity, magnetic anisotropy, and δ. In the present case, I represents a single compound whose average electronic distribution can be altered in a continuous manner without greatly altering its molecular structure and introducing a multiplicity of complicating effects. As the pH of a solution of I is increased, the change in the value of δ or J_{P-H} is a direct measure of the proportion of total I converted into its dianionic form and can be used to estimate the pK value. Figures 1A and 1B can be considered as titration curves and the average of the inflection points is 6.35, the pK_2 value for I. This value agrees well with the reported pK_2 for I of 6.4.

The above results show that not only δ but also J_{P-H} of I is pH dependent. Electronegative substituents have a profound effect on the value of the coupling constant[9] and, in a series of substituted CH_3OP compounds,[8] J_{P-H} decreases as the average electron-donating character of the substituent group increases. In the present case, J_{P-H} decreases as the negative charge on the phosphate group increases. In addition, a plot of δ *vs.* J_{P-H} for I shows a linear relationship between these two parameters similar to that described by Mavel and Martin.[8] This linearity is interpreted as being due to the fact that δ and J_{P-H} in these compounds are both dominated by inductive effects.

Experimental Section

Practical grade dimethyl phosphate (II) and reagent grade monomethyl phosphate (I) were obtained from K and K Laboratories, Plainview, N. Y., and the practical grade II was purified as described by Harlay.[10] The samples were dissolved in D_2O to give 1 *M* solutions, and the pH was adjusted by the addition of 37% DCl in D_2O or 50% NaOD in D_2O. pH measurements were carried out on a Radiometer pH meter TTT1a with a scale expander, making possible pH measurements accurate to ±0.01 pH unit. Nmr spectra were obtained on a Varian DA-60-El spectrometer using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as an internal standard.

Registry No.—I, 812-00-0; II, 813-78-5.

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[6] W. D. Kumler and J. J. Eiler, *J. Amer. Chem. Soc.*, **65**, 2356 (1943).

[7] The value 6.4 is an average of 6.31 reported by Kumler and Eiler[6] and 6.58 reported by C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 3575 (1958).

[8] G. Mavel and G. Martin, *J. Chim. Phys.*, **59**, 762 (1962).

[9] G. Mavel, *ibid.*, **59**, 683 (1962).

[10] M. V. Harlay, *J. Pharm. Chim.*, **20**, 161 (1934).