The Stereochemistry of Unsaturated Phosphonic Acids[1]

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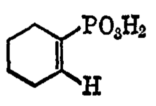
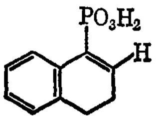
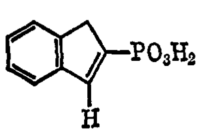
Abstract: The stereochemistry of unsaturated phosphonic acids of formula $R_1CH{=}CR_2PO_3H_2$ can be established by nmr spectroscopy. P–H coupling constants were measured for three unsaturated cyclic phosphonic acids where phosphorus and hydrogen are locked in the *cis* position and compared with that for a cyclic phosphinic acid where phosphorus and hydrogen are locked in the *trans* position. A consideration of these and other nmr spectra has led to the tentative conclusion that for unsaturated phosphonic acids with a hydrogen atom *cis* to phosphorus the coupling constant is about 10–20 cps, whereas for a hydrogen atom *trans* to phosphorus, the coupling constant is about 30–50 cps.

In alkaline solution β-halophosphonic acids undergo fragmentation to yield olefin, halide ion, and phosphate.[3,4] In an accompanying paper,[5] the stereochemistry of this type of process has been reported for the fragmentation of the stereoisomeric 1,2-dibromo-1-phenylpropylphosphonic acids. In order to find the configuration of the *threo* and *erythro* isomers, we needed to know the stereochemistry of the corresponding *cis*- and *trans*-unsaturated phosphonic acids. Three compounds were therefore synthesized where the phosphonic acid group was locked by a ring system in the *cis* configuration, *i.e.*

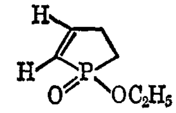
$$RCHX{-}CH_2PO_3H_2 \xrightarrow[H_2O]{NaOH} RCH{=}CH_2 + X^- + H_2PO_4^-$$





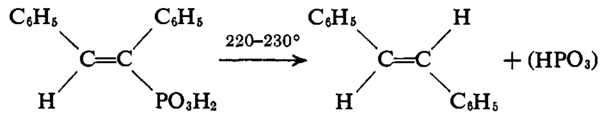


The nmr spectra of these compounds were compared with that of a compound where a phosphinic acid group and a hydrogen atom are locked by a ring system in the *trans* configuration. Such a compound had been prepared, and its spectrum was measured by Weitkamp and Korte.[6] An unambiguous assignment of the proton signals could be made by a comparison of the nmr spectrum of this compound with those of its methyl-substituted analogs.



In addition, both the *cis* and *trans* isomers of 1-phenyl-1-propenylphosphonic acid have now been prepared, as well as a number of other olefinic phosphonic acids where only one isomer of each pair has been obtained. Where possible, both the proton and the ^{31}P nmr spectra of these compounds have been measured. The results suggest that, for unsaturated phosphonic acids, the stereochemistry can be assigned with high probability on the basis of the nmr phosphorus–hydrogen coupling constant; the absolute magnitude of the constant for *trans* P–H is considerably greater than that for *cis*, in analogy with the corresponding constants for pairs of *cis* and *trans* hydrogen atoms.[7]

Many of the unsaturated phosphonic acids were prepared by the pyrolysis of the corresponding α-halophosphonic acid. The low yields sometimes obtained may be attributed in part to the subsequent pyrolytic cleavage of the unsaturated phosphonic acid to produce olefin. A specific example of such a cleavage is shown in the equation for the pyrolysis of stilbenephosphonic acid given below, where HPO_3 is the hypothetical monomeric metaphosphoric acid, which presumably polymerizes.



Experimental Section

Materials. 1-Chloro-1-phenylethylphosphonic acid was prepared by the method of Conant and Coyne,[3] mp 172.5–173.5° (lit.[3] mp 174–175°). The major infrared peaks in KBr were at 2.8 to 5.4 (broad), 6.68, 6.92, 8.15, 8.31, 8.57, 9.81, 10.63, 10.88, 12.82, 13.59, and 14.51 μ. α-Styrenephosphonic acid,[3] mp 113–115° (lit.[3] mp 112–113°), gave major infrared peaks in KBr at 2.7 to 5.4 (broad), 6.68, 6.90, 7.88, 8.29, 9.25, 9.36, 10.11, 10.37, 12.84, 14.05, and 14.64 μ. 1,2-Dibromo-1-phenylethylphosphonic acid[3] melted at 186–188° (lit.[3] mp 186–188°) and showed major infrared peaks in KBr at 2.7 to 5.3 (broad), 6.67, 6.89, 7.96, 8.38, 9.90, 10.19, 10.82, 13.48, and 14.45 μ.

2-Bromo-1-styrenephosphonic acid, generated by the pyrolysis at 200° of 1,2-dibromo-1-phenylethylphosphonic acid,[3] formed colorless needles (from carbon tetrachloride), which melted over a wide range. All attempts to separate the material into *cis* and *trans* isomers failed. When an aqueous solution of the monosodium salt of the acid was treated with a solution of S-benzylthiuronium chloride, a mono-S-benzylthiuronium salt precipitated from the solution. This salt was filtered and recrystallized from aqueous ethanol. The free acid was regenerated by passing the solution of the recrystallized salt through a column of Dowex-50 (H^+) ion-exchange resin. After removal of water from the acidic solu-

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(2) National Institutes of Health Trainee, 1963–1964; National Institutes of Health Predoctoral Fellow, 1964–1965, 1 F1 GM-23, 765-01.

(3) J. B. Conant and A. A. Cook, *J. Am. Chem. Soc.*, **42**, 830 (1920); J. B. Conant and S. M. Pollack, *ibid.*, **43**, 1665 (1921); J. B. Conant and E. L. Jackson, *ibid.*, **46**, 1003 (1924); J. B. Conant and B. B. Coyne, *ibid.*, **44**, 2530 (1922).

(4) J. A. Maynard and J. M. Swan, *Proc. Chem. Soc.*, 61 (1963); *Australian J. Chem.*, **16**, 596 (1963).

(5) G. L. Kenyon and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3561 (1966).

(6) H. Weitkamp and F. Korte, *Z. Anal. Chem.*, **204**, 245 (1964).

(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 238 ff.

tion *in vacuo*, the compound was recrystallized from carbon tetrachloride to give needles, mp 143–145° (lit.[3] mp 133–135°). (The compound presumably is the isomer with phenyl *cis* to bromine; see Table I.) The principal infrared peaks in KBr are at 2.7 to 5.4 (broad), 6.22, 6.29, 6.69, 6.91, 8.56, 8.77, 9.94, 10.15, 10.79, 10.98, 11.94, 13.03, 14.16, and 14.37 μ. *Anal.* Calcd for $C_8H_8BrO_3P$: C, 36.53; H, 3.07; Br, 30.38; P, 11.78. Found: C, 36.62; H, 3.31; Br, 30.41; P, 11.90.

1,2-Dichloro-1-phenylethylphosphonic acid, prepared according to Conant and Coyne[3] and recrystallized from chloroform, melted at 195.5–197° (lit.[3] mp 175–178°). Principal infrared peaks in KBr are at 2.7 to 5.4 (broad), 6.67, 6.89, 7.69, 8.36, 9.80, 10.14, 10.43, 10.80, 11.27, 13.49, and 14.42 μ. *Anal.* Calcd for $C_8H_9Cl_2O_3P$: C, 37.67; H, 3.56; Cl, 27.80; P, 12.14. Found: C, 37.61; H, 3.49; Cl, 27.63; P, 12.02.

2-Chloro-1-styrenephosphonic Acid. Pyrolysis of 16.6 g of 1,2-dichloro-1-phenylethylphosphonic acid *in vacuo* at 200°, followed by recrystallization of the product from carbon tetrachloride, gave a low yield (0.3 g, 2%) of needles of 2-chloro-1-styrenephosphonic acid, mp 145–146.5°. The infrared spectrum in KBr (major peaks at 2.7 to 5.2 (broad), 6.20, 6.31, 6.67, 6.91, 7.59, 8.34, 8.46, 9.16, 9.85, 9.95, 10.13, 12.15, 13.00, 13.15, and 14.35 μ) is similar to that of the corresponding bromo compound. The low yield may result from the pyrolysis of the product after it is formed to generate β-chlorostyrene. *Anal.* Calcd for $C_8H_8ClO_3P$: C, 43.97; H, 3.67; Cl, 16.22; P, 14.17. Found: C, 43.48; H, 3.68; Cl, 16.49; P, 14.46.

1-Chloro-1-phenylpropylphosphonic acid was prepared in essentially the same way as 1-chloro-1-phenylethylphosphonic acid,[3] except that propiophenone was substituted for acetophenone. In the last step, acetic acid and acetyl chloride were removed *in vacuo;* addition of chloroform and cooling gave a 20% yield of crude acid. Recrystallization from chloroform yielded prisms, mp 182.5–184.5°, with a loss of HCl on melting. The principal infrared bands in KBr are at 2.7 to 5.4 (broad), 6.68, 6.90, 7.23, 8.19, 8.38, 8.66, 9.76, 10.25, 10.75, 10.87, 11.44, 11.79 ,11.96, 13.48, and 14.46 μ. *Anal.* Calcd for $C_9H_{12}ClO_3P$: C, 46.07; H, 5.16; Cl, 15.11; P, 13.20. Found: C, 45.91; H, 4.99; Cl, 14.99; P, 13.12.

***trans*-1-Phenyl-1-propenylphosphonic acid** was prepared in low yield by pyrolysis of 5.0 g of 1-chloro-1-phenylpropylphosphonic acid at 200° *in vacuo*, until evolution of hydrogen chloride ceased. The viscous oil obtained by the process was dissolved in 100 ml of water, and *trans*-propenylbenzene removed by extraction with ether. The aqueous solution of crude acid was refluxed for 12 hr to convert any *cis* acid to *trans.* The resulting solution was brought to pH 11 with saturated barium hydroxide solution, and barium phosphate was removed by centrifugation. The supernatant was made 60% by volume in ethanol, and the insoluble barium salt of the product was removed by centrifugation. The crystals were dissolved in a little water and the solution was acidified with concentrated HCl. The water was removed *in vacuo*, and the acid was then crystallized several times from chloroform, giving only 0.64 g (15%) of pure product. The acid was crystallized from chloroform in either of two forms: needles, mp 159–160°, or plates, mp 158–160°. Although each gave a different infrared spectrum in KBr matrix, the infrared spectra in chloroform were identical, and either form could be converted to the other by seeding on crystallization. Major infrared peaks, in chloroform, were found at 2.7 to 5.0 (broad), 6.12, 6.68, 6.93, 8.69, 9.89, 10.73, and 11.24 μ. *Anal.* Calcd for $C_9H_{11}O_3P$: C, 54.55; H, 5.60; P, 15.63. Found: C, 54.23; H, 5.46; P, 15.61.

S-Methylthiuronium Hydrogen 1-Phenyl-1-propenylphosphonate, *trans* Isomer. *trans*-1-Phenyl-1-propenylphosphonic acid (1.00 g) was dissolved in water, and the solution was brought to pH 4 with barium hydroxide solution. An aqueous solution of 0.705 g of di-S-methylthiuronium sulfate (Aldrich Chemical Co.) was added. After removing barium sulfate and water, the residue was recrystallized from a mixture of ethanol and acetonitrile to yield 1.15 g (79%) of salt, mp 177–179° dec; principal infrared bands in KBr were at 2.7 to 4.9 (broad), 5.99, 6.69, 6.93, 8.95, 9.14, 9.42, 10.04, 10.81, 10.92, 11.73, 12.56, 13.08, 13.54, 14.27, and 14.40 μ. *Anal.* Calcd for $C_{11}H_{17}N_2O_3PS$: C, 45.83; H, 5.94; N, 9.72; P, 10.74; S, 11.12. Found: C, 45.80; H, 6.11; N, 9.90; P, 10.78; S, 11.00.

S-Methylthiuronium Hydrogen 1-Phenyl-1-propenylphosphonate, *cis* Isomer. 1-Chloro-1-phenylpropylphosphonic acid (30 g) was pyrolyzed *in vacuo* until all bubbling ceased. The nmr spectrum suggested that the resulting viscous oil consisted of a 50–50 mixture of the *cis* and *trans* isomers of 1-phenyl-1-propenylphosphonic acid. The mixture was neutralized with 4 *N* sodium hydroxide, and the water was removed *in vacuo.* The salt was further dried by addition and vacuum removal of benzene. The dry salt was ground in a mortar and washed with two 150-ml portions of anhydrous ether (washings discarded). A 150-ml portion of boiling anhydrous ethanol was then stirred into the dry salt, and filtered through a sintered glass funnel. The alcoholic filtrate was added to 3 l of anhydrous ether, and the crude disodium *cis*-1-phenyl-1-propenylphosphonate (6.6 g, 21%) that separated was filtered and dried.

The crude salt was dissolved in water and the solution was passed through an ion-exchange column of Dowex-50 (H^+) and quickly brought to pH 4 with barium hydroxide solution. An aqueous solution of 3.45 g of di-S-methylthiuronium sulfate was added. After removal of the barium sulfate and water, the product was recrystallized from 50% acetonitrile–50% ethanol to give 1.81 g of long needles, mp 184.5–186.5° dec. The mixture melting point with the corresponding salt of the *trans* isomer was 161–176°. The ^1H and ^{31}P nmr spectra were determined with the very soluble dipotassium salt, prepared from the mono-S-methylthiuronium salt by ion exchange. The principal infrared bands in KBr are at 2.7 to 4.7 (broad), 5.98, 6.70, 6.93, 8.66, 9.13, 9.42, 10.82, 11.34, 12.71, 13.20, 13.57, and 14.30 μ. *Anal.* Calcd for $C_{11}H_{17}N_2O_3PS$: C, 45.83; H, 5.94; P, 10.74; S, 11.12. Found: C, 45.57; H, 5.97; P, 10.85; S, 11.12.

***trans*-β-Styrenephosphonic acid** was prepared according to Bergmann and Bondi,[8] and Kosolopoff and Huber.[9] After recrystallization from ethyl acetate, the compound melted at 157.5–159.5° (lit.[8,9] mp 146° and 154.5–156°). The principal infrared bands in KBr are at 2.7 to 5.2 (broad), 6.21, 6.34, 6.71, 6.90, 8.08, 8.90, 10.02, 10.48, 13.44, and 14.51 μ. The S-methylthiuronium salt of *trans*-β-styrenephosphonic acid was prepared in 77% yield by the same method as that of *trans*-1-phenyl-1-propenylphosphonic acid and recrystallized from two parts ethanol and one part acetonitrile, mp 188.5–190.5° dec; principal infrared bands in KBr were found at 2.7 to 4.9 (broad), 5.97, 6.14, 6.34, 6.40, 6.70, 6.91, 7.03, 7.92, 8.58, 8.64, 9.11, 9.38, 10.04, 10.16, 11.07, 12.47, 13.39, 13.64, 14.30, and 14.52 μ. *Anal.* Calcd for $C_{10}H_{15}N_2O_3PS$: C, 43.79; H, 5.51; P, 11.29; S, 11.69. Found: C, 43.69; H, 5.60; P, 11.41; S, 11.74.

***cis*-Stilbenephosphonic Acid.** A mixture of deoxybenzoin (Eastman, 5.5 g), phosphorus trichloride (3.0 ml), and glacial acetic acid (10 ml) was stirred overnight. Hydrogen chloride gas was bubbled through the mixture for 0.5 hr, and the solution was allowed to stand for an additional 2 hr. The mixture was heated on a rotatory evaporator, finally at 200°, until bubbling ceased. A solution of 4 *N* sodium hydroxide was added until the pH was 11, and *trans*-stilbene was removed from the mixture by filtration. Acidification precipitated crude stilbenephosphonic acid, which was recrystallized from glacial acetic acid to yield 3.05 g (41%) of needles, mp 191–202°. Further recrystallization from a large quantity of water gave fluffy needles, mp 208.5–210°, with principal infrared bands in KBr at 2.8 to 5.2 (broad), 6.17, 6.69, 6.92, 8.26, 8.46, 8.83, 9.24, 9.68, 9.93, 10.03, 10.16, 10.64, 10.78, 10.89, 11.03, 12.93, 13.13, 13.20, 13.87, 14.31, and 14.45 μ. The ultraviolet spectrum showed λ_{max} (H_2O) 259 mμ (ε 15,000). *Anal.* Calcd for $C_{14}H_{13}O_3P$: C, 64.62; H, 5.04; P, 11.90. Found: C, 64.36; H, 5.07; P, 12.04.

S-Methylthiuronium Hydrogen Stilbenephosphonate. *cis*-Stilbenephosphonic acid (1.0 g) in 50 ml of water was brought to pH 4 with 10% sodium hydroxide solution, and a solution of 5.0 g of S-methylthiuronium iodide was added. Large, flat plates of the product formed; recrystallization from water gave 0.91 g (67% yield) of plates, mp 217–219° dec. The principal infrared bands in KBr are at 2.7 to 4.6 (broad), 6.00, 6.69, 6.94, 8.70, 9.46, 10.26, 11.08, 13.20, 14.33, and 14.44 μ. *Anal.* Calcd for $C_{16}H_{19}N_2O_3PS$: C, 54.85; H, 5.47; P, 8.84; S, 9.15. Found: C, 54.50; H, 5.46; P, 8.94; S, 9.36.

Attempts[10] to prepare the stereoisomeric stilbenephosphonic acid have led to equivocal results, and further investigation is required to establish the identity of a putative *trans* isomer.

1-Hydroxy-1-cyclohexylphosphonic acid was prepared from cyclohexanone (Eastman), phosphorus trichloride, and glacial acetic acid by the method of Fay and Lankelma.[11] Recrystallization of the hydroxy acid from ethanol gave needles, mp 187.5–188.5° (lit.[11] mp 191–192°). The principal infrared bands in KBr are at 2.7 to 5.2 (broad), 3.12, 3.39, 3.48, 6.92, 7.15, 7.83, 7.92, 8.30, 8.48, 8.62, 8.70,

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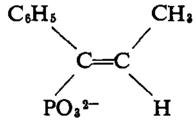
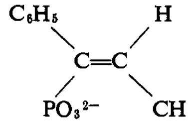
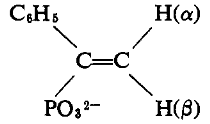
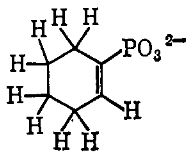
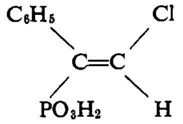
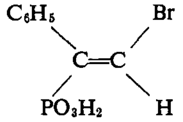
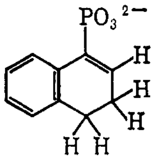
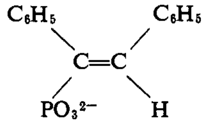
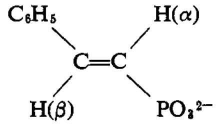
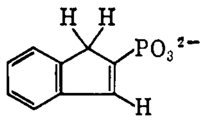
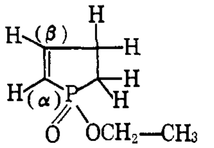
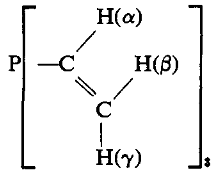
[8] E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930).

[9] G. M. Kosolopoff and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 2540 (1946).

[10] G. L. Kenyon, Thesis, Harvard University, 1965.

[11] P. Fay and H. P. Lankelma, *J. Am. Chem. Soc.*, **74**, 4933 (1952).

Table I. Nmr Spectra for Some α,β-Unsaturated Phosphorus Compounds[a]

		^{1}H nmr			^{31}P nmr		
Compound	Structure	J_{PH}, cps	Vinyl proton signal	δ, ppm	J_{PH}, cps	^{31}P signal	Chemical shift,[b] ppm
trans-1-Phenyl-1-propenylphosphonic acid		20	Two quartets	6.50	21	Doublet	−14.8
cis-1-Phenyl-1-propenylphosphonic acid		38	Two quartets	5.97	39	Doublet	−8.9
α-Styrenephosphonic acid		α, 45 β, 22	Two Doublets	α, 5.58 β, 5.93	α, 45 β, 22	Even quartet[c]	−14.4
1-Cyclohexenephosphonic acid		19	Doublet	6.52	19	Doublet	−14.0
β-Chloro-α-styrenephosphonic acid					13	Doublet	−12.3
β-Bromo-α-styrenephosphonic acid		15	Doublet	7.32	14	Doublet	−11.5
3,4-Dihydro-1-naphthalenephosphonic acid		17	Two triplets	6.83	18	Doublet	−11.0
cis-Stilbenephosphonic acid					20	Doublet	−11.0
β-Styrenephosphonic acid					α, 16 β, 16	Triplet, ratio about 1:2:1	−4.7
2-Indenephosphonic acid					9	Doublet	−8.5
1-Ethoxy-2,3-dihydrophosphole 1-oxide[d]		α, 23.1 β, 48.8		α, 6.20 β, 7.10			
Trivinylphosphine[e]		α, 11.74 β, 30.21 γ, 13.62					

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[a] In general, the ^{1}H nmr spectra for the phosphonic acids were taken as disodium or as dipotassium salts in D_2O while the ^{31}P nmr spectra were taken in H_2O; the spectra for β-chloro- and β-bromo-α-styrenephosphonic acids were taken using the free acids dissolved in acetonitrile. [b] Ppm, relative to 85% H_3PO_4. [c] Equal spacing, equal height. [d] See ref 6. [e] See S. L. Mannatt, G. L. Juvinall, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 2664 (1963); W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963).

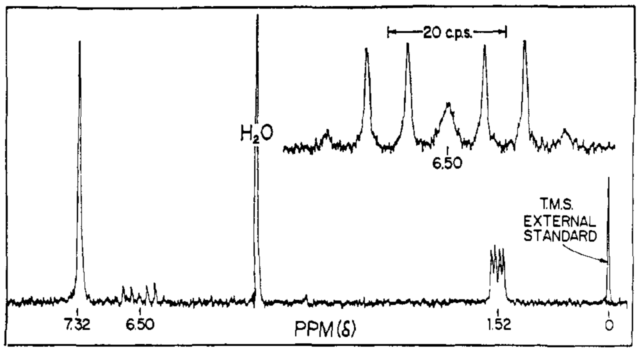

Figure 1. Proton nmr spectrum of *trans*-1-phenylpropenylphosphonic acid, as the disodium salt in D_2O. The integration of the peaks is consistent with that anticipated for a methyl group centered at δ 1.52, an olefinic proton at 6.50, and a phenyl group at 7.32. The methyl group appears as two intercalated doublets, with splitting by the olefinic proton and by ^{31}P. The signal for the olefinic proton is shown in the insert at increased sensitivity and greater dispersion. It consists of two overlapping quartets with splitting by the hydrogen atoms of the methyl group (J = 6.5 cps), and by ^{31}P *cis* to the olefinic proton with J = 20 cps.

9.36, 9.75, 10.30, 10.63, 11.00, 11.14, 11.84, 12.30, and 14.31 μ. **1-Cyclohexenephosphonic acid** was prepared according to Fay and Lankelma,[11] mp 129–131° (lit.[11] mp 130.5–132°), and showed principal infrared bands in KBr at 2.7 to 5.2 (broad), 3.40, 3.49, 6.19, 6.89, 6.96, 8.42, 9.14, 9.94, 10.52, 10.90, and 13.56 μ. **2-Indenephosphonic acid** was prepared by the method of Bergmann and Bondi[8] from indene (Matheson Coleman and Bell) and phosphorus pentachloride (Mallinckrodt) suspended in dry benzene. Recrystallization of the acid from water gave plates, mp 184–185.5° (lit.[8] mp 184°), with principal infrared bands in KBr at 2.7 to 5.2 (broad), 6.44, 6.85, 7.18, 7.51, 8.24, 8.31, 9.08, 9.16, 9.40, 9.77, 10.59, 10.77, 11.39, 13.03, and 13.88 μ.

3,4-Dihydro-1-naphthalenephosphonic acid was prepared from 6.1 g of α-tetralone (Aldrich), 4.5 g of phosphorus trichloride, and 12.0 ml of glacial acetic acid. The mixture was allowed to stand overnight at room temperature, and hydrogen chloride was bubbled for 0.5 hr into the solution; it was then allowed to stand at room temperature for 2 hr. The mixture was pyrolyzed on a rotatory evaporator to remove volatile starting materials and products. At about 200°, all bubbling ceased, and on cooling the crude product solidified. After two recrystallizations from glacial acetic acid, 6.9 g (78%) of product, mp 210–218°, was obtained; several recrystallizations from water raised the melting point to 227–229.5°. The ultraviolet spectrum showed λ_{max} (H_2O) 262 mμ (ε 5800); for comparison, the corresponding absorptions in ethanol for 1,2-dihydronaphthalene[12] and for 1,2-dihydronaphthalene-3-carboxylic acid[13] are at 262 mμ (ε 10,230) and 260.5 (ε 9780), respectively. The principal infrared bands in KBr are at 2.7 to 5.2 (broad), 6.19, 6.69, 6.88, 6.99, 8.11, 8.22, 8.32, 8.49, 9.30, 9.49, 9.93, 10.35, 10.73, 10.82, 10.94, 11.70, 11.83, 12.68, 13.00, 13.13, and 13.58 μ. *Anal.* Calcd for $C_{10}H_{11}O_3P$: C, 57.15; H, 5.28; P, 14.74. Found: C, 56.90; H, 5.22; P, 14.85. Other chemicals were of reagent grade.

The Pyrolysis of Olefinic Phosphonic Acids. *cis*-Stilbenephosphonic acid (0.20 g) was heated for 15 min at 220–230° in a sublimation apparatus at atmospheric pressure. *trans*-Stilbene, mp 122–124°, was collected on the coldfinger, yielding 0.034 g (25%). It was identified by comparison of its infrared spectrum with that of an authentic sample. 1-Chloro-1-phenylpropylphosphonic acid (5.0 g) was heated at 200° until all bubbling ceased (20 min). The product was added to 100 ml of water, and extracted with ether until the solution became clear. After drying the ether over anhydrous sodium sulfate and removing it *in vacuo*, a small amount of oil was isolated; its infrared spectrum was identical with those previously published[14,15] for *trans*-propenylbenzene. Bromination of the olefin in carbon tetrachloride solution gave 1,2-dibromopropylbenzene, mp 66–67° (lit.[16] mp 66–66.5°). β-Styrenephosphonic acid (0.203 g), pyrolyzed at 200° for 5 min, yielded 7 mg of styrene (identified by its infrared spectrum). Indenephosphonic acid gave about a 1% yield of indene (identified by its infrared spectrum). On the other hand, α-styrenephosphonic acid did not yield even a trace of styrene on pyrolysis at 205–210° for 20 min.

Methods. Infrared spectra were measured on a Perkin-Elmer Infracord spectrometer. Ultraviolet spectra were measured either with a Cary 11 or Cary 14 recording spectrometer. Proton nmr spectra were determined with a Varian Model A-60 analytical nmr spectrometer, using tetramethylsilane as an external standard. The complete spectra may be seen elsewhere.[10] For accurate coupling constant measurements the instrument was calibrated by an audiooscillator monitored by a frequency counter. Phosphorus nmr spectra were taken on a Varian high-resolution nmr spectrometer, Model V 4300B, operating at 15.1 Mc and about 8000 gauss. Chemical shifts and coupling constants were measured by the audiooscillator monitored by a frequency counter. A solution of the compound to be measured was placed in the outer of two concentric tubes, with 85% phosphoric acid in the inner tube. Usually about 1 g of material dissolved in 3 ml of solvent gave a satisfactory spectrum. Microanalyses were carried out by the Galbraith Laboratories Inc., Knoxville, Tenn. Melting points are corrected.

Results and Discussion

The ^1H and ^{31}P nmr spectra for various unsaturated phosphorus compounds are shown in Table I.

The nmr spectra in the olefinic region are in general quite simple. For most of the compounds, only one olefinic hydrogen atom is strongly coupled to phosphorus, so that the coupling constant can be easily determined. In a few examples, however, coupling with two or more hydrogen atoms is involved. The phosphorus nmr signal from β-indenephosphonic acid is only a doublet, while the methylene group in the proton nmr spectrum is only a singlet; apparently the vinyl hydrogen splits the phosphorus signal, but the hydrogen atoms of the methylene group do not (or, at least, the splitting is minimal); presumably their spatial orientation is unfavorable for coupling. Similarly, the vinyl hydrogen atom in cyclohexenephosphonic acid couples with the phosphorus atom to yield a doublet; the hydrogen atoms of the adjacent methylene group do not cause large splittings. Our resolutions generally were such that only splitting greater than 1 cps could be observed.

The proton nmr coupling constants were not determined for stilbenephosphonic acid, for β-styrenephosphonic acid, for chlorostyrenephosphonic acid, or for indenephosphonic acid. In each of these cases, at least part of the signals for the vinyl proton fell within the envelope of the signals from the phenyl protons; the needed data were obtained from phosphorus nmr. In all those examples where both phosphorus and hydrogen nmr spectra were determined, the results agree reasonably well. For example, the ^{31}P–^1H coupling for *trans*-1-phenyl-1-propenylphosphonic acid from the ^1H nmr spectrum was found as 20 cps, whereas that from the ^{31}P spectrum is 21 cps.

Three unequivocal examples of *cis* coupling of phosphorus and hydrogen atoms in phosphonic acids are shown in Table I. These are cyclohexenephosphonic acid (J = 19 cps), dihydronaphthalenephosphonic acid (J = 17 cps), and indenephosphonic acid (J = 9 cps). Only a few phosphinic acids and esters (and no phosphonic acids) are known where the phosphorus atom and an olefinic hydrogen atom are held in an unambiguously *trans* configuration; an example is 1-ethoxy-

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[12] E. Boyland and J. B. Solomon, *Biochem. J.*, **59**, 518 (1955).

[13] A. W. Schrecker, G. Y. Greenberg, and J. L. Hartwell, *J. Am. Chem. Soc.*, **74**, 5669 (1952).

[14] J. W. Crump, Ph.D. Thesis, University of Illinois, 1957.

[15] R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

[16] R. C. Huston and D. D. Sager, *ibid.*, **48**, 1955 (1926).

2,3-dihydrophosphole 1-oxide. Here two signals have been reported[6] with chemical shifts (δ) of 6.20 and 7.10 ppm, and with P–H coupling constants of 23 and 49 cps, respectively. The spectra of a number of α,β-unsaturated cyclic phosphinic acids had previously been determined, including some substituted in the α or β positions with methyl groups. Comparisons among these had enabled Weitkamp and Korte[6] to assign the larger coupling constant to the interaction of the phosphorus with the β proton, *i.e.*, to the proton *trans* to the phosphorus across the double bond. These data suggest the tentative generalization that the coupling constant for *cis* phosphorus and hydrogen in unsaturated phosphonic acids is about 10–20 cps, whereas that for *trans* phosphorus and hydrogen is much larger.

Both isomers of 1-phenyl-1-propenylphosphonic acid have been prepared; their proton nmr spectra are shown in Figures 1 and 2. The coupling constants for the olefinic proton with phosphorus are 20 and 38 cps. (The proton nmr spectra of these compounds show an additional coupling constant, with $J = 2$ cps, between the phosphorus atom and the methyl group; because of the lower resolution of the ^{31}P nmr measurements, this coupling constant was not observed in these spectra.) On the basis of analogy with known compounds, the isomer with a coupling constant of 20 cps is assigned the *cis* P–H configuration, and the isomer with a coupling constant of 38 cps, the *trans* configuration. Similarly, α-styrenephosphonic acid has two vinyl hydrogen atoms, one *cis* and one *trans* to the phosphonic acid group. The spectra are consistent with that of an ABX compound[17] where $J_{AX} = 45$ cps (*trans*) and $J_{BX} = 22$ cps (*cis*). J_{AB}, as for α-methylacrylonitrile,[18] is apparently quite small. In the other cases reported in Table I, the coupling constants fall in the range 10–20 cps, and allow the assignment of *cis* configuration to the olefinic hydrogen and the phosphorus atoms of the phosphonic acid.

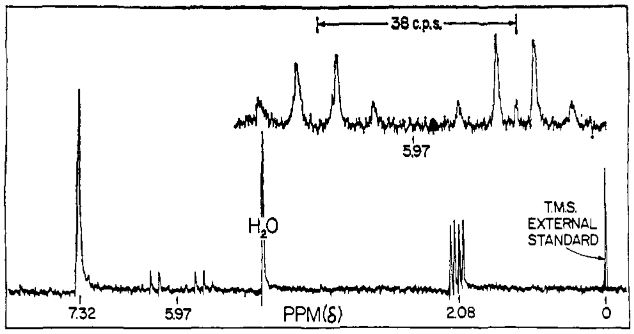

Figure 2. Proton nmr spectrum of *cis*-1-phenylpropenylphosphonic acid, as the dipotassium salt in D_2O. The integration of the peaks is consistent with that anticipated for a methyl group centered at δ 2.08, an olefinic proton at 5.97, and a phenyl group at 7.32. The methyl group appears as two intercalated doublets, with splitting by the olefinic proton and by ^{31}P. The signal for the olefinic proton is shown in the insert at increased sensitivity and greater dispersion. It consists of two well-separated quartets, with splitting by the hydrogen atoms of the methyl group ($J = 6.5$ cps), and by the ^{31}P *trans* to the olefinic proton with $J = 38$ cps.

An additional example—although of a quite different chemical type—concerns trivinylphosphine, where Anderson and Freeman[19] have assigned 30.2 cps to the *trans* and 13.6 cps to the *cis* coupling constants for the two hydrogen atoms β to phosphorus.

Although the number of examples given here is small, the results allow the tentative assignment of configurations to unsaturated phosphonic acids.

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[17] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin Inc., New York, N. Y., 1962, p 21.

[18] "Varian NMR Spectra Catalog," Vol. I, The National Press, Palo Alto, Calif., 1962, Spectrum No. 97.

[19] See Table I, footnote *e*.

The Stereochemical Course of the Fragmentation of β-Halophosphonates[1]

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Contribution from the James Bryant Conant Laboratory of Harvard University, Cambridge, Massachusetts. *Received March 21, 1966*

Abstract: In aqueous base, each of the two stereoisomeric 1,2-dibromo-1-phenylpropylphosphonic acids decomposes stereospecifically to yield inorganic phosphate and bromide ions, and a single isomer of 1-bromo-1-propenylbenzene. Evidence is presented to show that the *erythro* dibromide yields the *cis*-bromopropenylbenzene, and the *threo* dibromide yields the *trans*-bromopropenylbenzene. The fragmentation proceeds by a *trans* elimination of halide ion and a phosphorus moiety which behaves like the hypothetical monomeric metaphosphate ion.

In the 1920's, Conant and his co-workers[3] discovered the fragmentation in alkaline solution of β-halophosphonic and β-halophosphinic acids, and a few additional examples[4] were added in the following decades. More recently Maynard and Swan[5] have

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[2] National Institutes of Health Trainee, 1963–1964; National Institutes of Health Predoctoral Fellow, 1964–1965, 1 F1 GM-23,765-01.

[3] J. B. Conant and A. A. Cook, *J. Am. Chem. Soc.*, **42**, 830 (1920); J. B. Conant and S. M. Pollack, *ibid.*, **43**, 1665 (1921); J. B. Conant and E. L. Jackson, *ibid.*, **46**, 1003 (1924); J. B. Conant and B. B. Coyne, *ibid.*, **44**, 2530 (1922).

[4] E. Bergmann and A. Bondi, *Ber.*, **66**, 278, 286 (1933); P. Fay and H. P. Lankelma, *J. Am. Chem. Soc.*, **74**, 4933 (1952).

[5] J. A. Maynard and J. M. Swan, *Proc. Chem. Soc.*, 61 (1963); *Australian J. Chem.*, **16**, 596 (1963).