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.

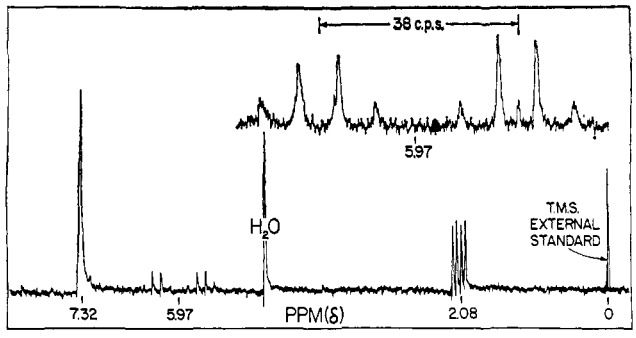


Figure 2. Proton nmr spectrum of *cis*-1-phenylpropenylphosphonic acid, as the dipotassium salt in D_2O. The integration of the peaks is consistent with that anticipated for a methyl group centered at δ 2.08, an olefinic proton at 5.97, and a phenyl group at 7.32. The methyl group appears as two intercalated 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.

(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]

George L. Kenyon[2] and F. H. Westheimer

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

(1) This work was supported by the National Science Foundation under Grant GP-2098.

(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).

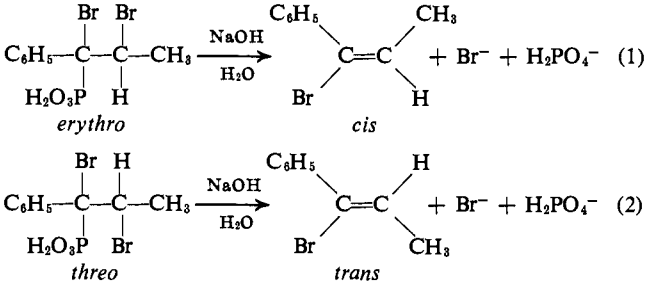
(4) E. Bergmann and A. Bondi, *Ber.*, **66**, 278, 286 (1933); P. Fay and H. P. Lankelma, *J. Am. Chem. Soc.*, **74**, 4933 (1952).

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

reinvestigated the reaction, and examined its mechanism. The fragmentation is of interest since it might proceed by the way of the unknown but postulated monomeric metaphosphate ion.[6-10]

Results and Discussion

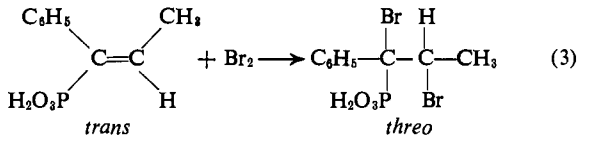
In connection with our investigations[6,8] of the chemistry of phosphate esters, we have studied the stereochemistry of this fragmentation reaction. Specifically, we have prepared both the *erythro*- and the *threo*-1,2-dibromo-1-phenylpropylphosphonic acids and shown that they decompose in aqueous base according to eq 1 and 2.



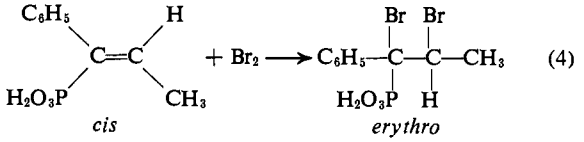
These reactions correspond to *trans*-elimination processes. In order to determine this stereochemistry it was necessary to know the configurations both of the diastereomeric dibromophosphonic acids and of the corresponding bromoolefins.

In an accompanying paper,[11] the preparation of salts of the two stereoisomeric 1-phenyl-1-propenylphosphonic acids has been outlined, and the configurations of these compounds have been established by comparison of their nmr spectra with those of phosphonic and phosphinic acids of known geometry.

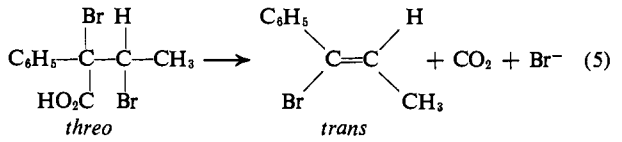
Pure *cis*-1-phenyl-1-propenylphosphonic acid was never isolated, although salts of this acid were prepared and identified. Nevertheless, it proved possible to prepare and to identify the two stereoisomeric dibromides. The *trans* acid reacts with bromine in chloroform in the dark to give a single dibromide in 56% yield; since its stereoisomeric dibromide is less soluble, it would have been isolated if present in appreciable concentration. The assumption of *trans* addition[12] of bromine leads to the prediction of the *threo* isomer, as shown in eq 3. The addition of bromine to



a mixture of the *cis*- and *trans*-olefinic acids gave a second compound, in addition to the *threo* dibromide. Since this second compound was less soluble in acetonitrile than the *threo* isomer, it was easily purified. It was identified by analysis, infrared spectrum, and the products of its alkaline fragmentation as *erythro*-1,2-dibromo-1-phenylpropylphosphonic acid, formed according to eq 4.



The configurations of the bromoolefins formed in the fragmentation reactions 1 and 2 rest on the work of Curtin and Crump,[13] who brominated the stable (presumably *trans*) isomer[14,14a] of 1-phenylcrotonic acid, and decarboxylated the resulting dibromo acid according to eq 5. The assignment of configuration to the resulting olefin is predicated on three lines of evidence. First, the *trans* olefin is that anticipated on the basis of the known stereochemistry of the corresponding reactions of cinnamic and dibromocinnamic acids.[15] Second, the olefin on treatment with *n*-butyllithium at −35° and then with water gave a 60% yield of *trans*-propenylbenzene plus 7% *cis*-propenylbenzene. Since other vinyllithium compounds are relatively stable[16] to isomerization at 0°, the bromoolefin has been assigned the *trans* configuration. Third, the phenyl peak in the nmr spectrum of *cis*-1-bromopropenylbenzene is not split, whereas that for the *trans* isomer is complex; this difference parallels that for the *cis*- and *trans*-stilbenes. This argument, however, is not compelling since the phenyl peaks of both *cis*- and *trans*-1-phenyl-1-propenylphosphonic acids are unsplit.



Although none of these lines of reasoning is entirely secure, the assignments in the literature have been used throughout this paper for purposes of identification. The decarboxylation process reported in the literature[13] was conducted with crude starting material. We have treated the pure (presumably *threo*) dibromocarboxylic acid with triethylamine in acetonitrile and have found that it gave a 71% yield of a single pure olefin, corresponding to the *trans*-1-bromo-1-propenylbenzene of Curtin and Crump.[17] The incomplete purity[17] of their sample of bromomethylstyrene might account for the relatively low yield in the *n*-butyllithium reaction.[13] These considerations lead

(6) W. W. Butcher and F. H. Westheimer, *J. Am. Chem. Soc.*, 77, 2420 (1955).
(7) P. W. C. Barnard, C. A. Bunton, D. R. Llewellyn, K. G. Oldham, B. L. Silver, and C. A. Vernon, *Chem. Ind.* (London), 760 (1955).
(8) F. H. Westheimer, Special Publication No. 8, The Chemical Society, London, 1957, p 181.
(9) A. R. Todd, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1389 (1959).
(10) W. P. Jencks, *Brookhaven Symp. Biol.*, **15**, 134 (1962).
(11) G. L. Kenyon and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3557 (1966).
(12) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 215–216.
(13) D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958); J. W. Crump, Ph.D. Thesis, University of Illinois, 1957.
(14) L. A. Carpino, *J. Am. Chem. Soc.*, **80**, 601 (1958).
(14a) NOTE ADDED IN PROOF. Mr. S. M. Coutts and Professor J. Z. Gougoutas have established the configuration of this acid (methyl *cis* to phenyl) by a single-crystal X-ray crystallographic study of its S-methylthiuronium salt.
(15) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, 75, 632, 2645 (1953); E. Grovenstein, Jr., and D. E. Lee, *ibid.*, **75**, 2639 (1953).
(16) D. Y. Curtin and E. E. Harris, *ibid.*, 73, 2716 (1951); 73, 4519 (1951); E. A. Brande and J. A. Coles, *J. Chem. Soc.*, 2078, 2085 (1951).
(17) The identification of our olefin with theirs was made by infrared spectroscopy. Although Curtin and Crump report a carbonyl band caused by an impurity, in their sample, the distinction between *cis* and *trans* isomers presented no problem. The carbonyl band (and the low carbon analysis) in the sample of Curtin and Crump presumably came from considerable α-bromopropiophenone as impurity. α-Bromostyrene is autoxidized to α-bromoacetophenone,[18] and the bromopropenylbenzenes undergo a similar reaction (see the Experimental Section).
(18) C. Dufraisse, *Compt. Rend.*, **172**, 162 (1921).

us to the conclusion that, although the stereochemical assignments in eq 1–5 are not certain, they are reasonable. In any event, the essentially quantitative nature and stereochemical specificity of the Conant–Swan reaction is assurance that the fragmentation is concerted; even if the *trans* nature of the fragmentation is unproved, it is quite probable.

The detailed mechanism of the fragmentation is less well established. It can be written as a displacement reaction

$$C_6H_5\text{—}\underset{\displaystyle PO_3^{2-}}{\underset{|}{C}}Br\text{—}CHBr\text{—}CH_3 + H_2O \longrightarrow C_6H_5\text{—}CBr{=}CHCH_3 + Br^- + H_2PO_4^- \quad (6)$$

with attack of water at the phosphorus atom, or as a fragmentation to monomeric metaphosphate ion

$$C_6H_5\text{—}\underset{\displaystyle PO_3^{2-}}{\underset{|}{C}}Br\text{—}CHBr\text{—}CH_3 \longrightarrow C_6H_5\text{—}CBr{=}CHCH_3 + Br^- + [PO_3^-] \quad (7)$$

followed by rapid hydration of the highly electrophilic (and presumably solvated) monomeric metaphosphate

$$[PO_3^-] + H_2O \xrightarrow{\text{fast}} H_2PO_4^- \quad (8)$$

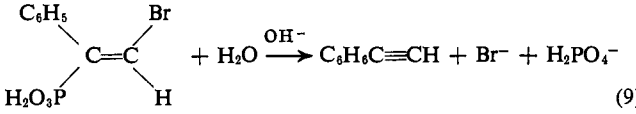
Maynard and Swan[5] favor the former mechanism (eq 6), and the argument has been advanced that monomeric metaphosphate ion is never formed (or, at any rate, never free) in solution. However, a number of chemical reactions are usefully correlated on the basis of the hypothesis that monomeric metaphosphate is a chemical intermediate[6–10] in them. The following evidence suggests that, to the extent that monomeric metaphosphate is ever formed,[19–21] it participates here.[22] (a) Maynard and Swan[5] have shown that β-chlorodecylphosphonic acid reacts with base in *t*-butyl alcohol to yield *t*-butyl phosphate. Since *t*-butyl alcohol is not an active nucleophile, a displacement reaction seems improbable. (b) Maynard and Swan preferred the displacement (eq 6) to the fragmentation (eq 7) in part because cyclohexylamine failed to promote the over-all reaction in acetone solution; they concluded that an alcohol (or water) is required in the essential step of the process. Putting aside the fact that cyclohexylamine is a much stronger mucleophile than an alcohol or water, the particular experiment of Maynard and Swan does not lead to reaction probably because the cyclohexylamine is largely bound as its Schiff base. Semiquantitative experiments (ours and those of others[3,5]) have shown that only the anions, and preferably the dianions, of β-halophosphonates undergo the Conant–Swan reaction. If, therefore, the cyclohexylamine is consumed by formation of a Schiff base, it cannot neutralize the phosphonic acid, and therefore cannot promote the fragmentation.

In any event, *threo*-1,2-dibromo-1-phenylpropylphosphonic acid readily undergoes carbon–phosphorus bond cleavage when treated in acetonitrile solution with cyclohexylamine, triethylamine, or 2,6-lutidine. The phosphorus appears in various incompletely characterized polyphosphates and phosphoramidates.

(19) P. Traylor and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 553 (1965).
(20) H. K. Hall, *J. Org. Chem.*, **21**, 248 (1956).
(21) J. D. Chanley and E. Feageson, *J. Am. Chem. Soc.*, **85**, 1181 (1963).
(22) A. J. Kirby and W. P. Jencks, *ibid.*, **87**, 3209 (1965).

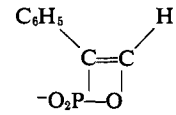
The sparse data so far assembled do not distinguish between fragmentation to $[PO_3^-]$ or nucleophilic attack by the amine (or by acetonitrile, to form an active phosphorylating agent such as $CH_3\text{—}C{\equiv}N^+\text{—}PO_3^{2-}$). But the general characteristics of the reaction are similar to those of other processes for which monomeric metaphosphate has been postulated.

A third mechanistic possibility, originally suggested for consideration by Conant,[3] is that the reaction takes place by way of a four-membered phostonate. (Five-membered phostonates are known, and readily hydrolyzed;[23] four-membered phostonates, if formed, might cleave to olefin, in analogy with the corresponding cleavage of a postulated four-membered intermediate in the Wittig reaction.[24]) This pathway is consistent with the stereochemistry that has now been established for the reaction. A four-membered phostonate, if it occurred, would be formed by displacement of a bromine atom *trans* to the phosphonate group and so lead to the results shown in eq 1 and 2. But the mechanism is nevertheless relatively improbable, since unsaturated β-bromophosphonic acids can fragment to form acetylenes.[3,4] Particular examples concern the fragmentation of β-bromo-α-styrenephosphonic acid and of β-chloro-α-styrenephosphonic acid to yield phenylacetylene, halide ion, and phosphate, *e.g.*



(9)

Since halogen attached to a double bond does not easily undergo a displacement reaction, the unsaturated phostonate



is not likely to be an intermediate in the over-all process. It should, however, be noted that the reaction of eq 9 with an unsaturated β-halophosphonate is much slower[25] than those of eq 1 and 2, which involve saturated β-bromophosphonates. Here, and in several other aspects of this problem, mechanistic answers await kinetic measurements. Such experiments are planned.

Experimental Section

Materials. ***threo*-1,2-Dibromo-1-phenylpropylphosphonic Acid.** *trans*-1-Phenyl-1-propenylphosphonic acid[11] (6.37 g, mp 158.5–160°) and 5.13 g of bromine in 100 ml of chloroform were allowed to stand overnight in the dark at 4°. As the reaction proceeded, needles of starting material dissolved and crystals of product were deposited. After recrystallization from chloroform, 6.44 g (56%) of dibromide, mp 181–182.5°, was obtained; its principal infrared bands in KBr are at 2.8 to 5.3 (broad), 6.69, 6.96, 8.34, 9.80 (broad), 10.32, 11.46, 12.06, 13.40, and 14.31 μ. *Anal.* Calcd for $C_9H_{11}Br_2O_3P$: C, 30.20; H, 3.10; Br, 44.65; P, 8.65. Found: C, 30.21; H, 3.07; Br, 44.85; P, 8.78. At its melting point this compound loses bromine to regenerate *trans*-1-phenyl-1-propenylphos-

(23) A. Eberhard and F. H. Westheimer, *ibid.*, **87**, 253 (1965).
(24) S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).
(25) Conant and his co-workers[3] reported that the process shown in eq 9 takes place rapidly at room temperature. Repetition of their work shows that the fragmentation occurs only at elevated temperatures; in the experiments of Conant and Coyne, the reaction presumably accompanied the steam distillation used for work-up.

phonic acid, which was identified by its melting point and infrared spectrum.

erythro-**1,2-Dibromo-1-phenylpropylphosphonic Acid.** 1-Chloro-1-phenylpropylphosphonic acid[11] (23.0 g, mp 173–177°) was pyrolyzed *in vacuo* at 200°. The resulting mixture of *cis*- and *trans*-1-phenyl-1-propenylphosphonic acids[11] was dissolved in the minimum amount of chloroform with 15.6 g of bromine, and allowed to stand overnight at room temperature. The chloroform was removed *in vacuo*. Several recrystallizations from acetonitrile yielded 3.56 g (10%) of needles, mp 185.5–187.5°, with principal infrared bands in KBr at 2.7 to 5.3 (broad), 6.69, 6.93, 8.16, 8.40, 8.51, 9.77, 10.38, 10.77, 13.32, and 14.44 μ. A mixture with *threo*-1,2-dibromo-1-phenylpropylphosphonic acid melted at 173–180°. *Anal.* Calcd for $C_9H_{11}Br_2O_3P$: C, 30.20; H, 3.10; Br, 44.65; P, 8.65. Found: C, 30.15; H, 3.13; Br; 44.57; P, 8.73. Like the *threo* diastereomer, this compound releases free bromine (brown gas) at its melting point.

threo-**1,2-Dibromo-1-phenylbutyric acid** was prepared according to Curtin and Crump;[13] after several recrystallizations from chloroform–petroleum ether (bp 38–56°), a low yield of needles, mp 130–132° (lit.[13] mp 131–133°), was obtained, with principal infrared bands in KBr at 3.0 to 4.8 (broad), 5.82, 6.68, 6.93, 7.08, 7.26, 7.82, 8.17, 8.45, 9.19, 10.78, 10.93, 11.98, 13.09, 13.49, 14.33, and 14.67 μ. *Anal.*[26] Calcd for $C_{10}H_{10}Br_2O_2$: C, 37.30; H, 3.13; Br, 49.63. Found: C, 37.23; H, 3.19; Br, 49.71.

Dibenzyl cyclohexylphosphoramidate was prepared by the procedure of Atherton, Openshaw, and Todd,[27] and after recrystallization from cyclohexane melted at 80–81° (lit.[27] mp 79–80°). *Anal.* Calcd for $C_{20}H_{26}NO_3P$: C, 66.84; H, 7.29; N, 3.90; P, 8.62. Found: C, 67.02; H, 7.43; N, 3.92; P, 8.64. **Benzyl hydrogen cyclohexylphosphoramidate** was prepared from dibenzylcyclohexylphosphoramidate by the method of Clark, Kirby, and Todd.[28] Benzyl hydrogen cyclohexylphosphoramidate (0.40 g) was dissolved in methanol and hydrogenated at atmospheric pressure in the presence of 0.05 g of 10% palladium-on-charcoal catalyst. After filtering the mixture, cyclohexylamine was added to the methanol solution, and the cyclohexylammonium salt of the product was precipitated. After five reprecipitations from methanol–ether, a low yield of product with principal infrared bands in KBr at 3.39, 3.49, 3.6 to 4.6 (multiple bands), 6.20, 6.39, 6.88, 7.08, 8.53, 8.74, 8.99, 9.08, 9.16, 10.08, and 14.06 μ was obtained. *Anal.* Calcd for $C_{18}H_{43}N_3O_7P_2$: C, 45.57; H, 9.12; N, 8.84; P, 13.03. Found: C, 45.02; H, 9.37; N, 8.87; P, 13.12. This product is presumably the cyclohexylammonium salt of a pyrophosphoramidate. The trisodium salt of trimetaphosphoric acid was prepared by the method described by Latimer and Hildebrand.[29] This salt (3.00 g) was dissolved in water and passed through a column of Dowex-50 in the hydrogen form. Trimeric metaphosphoric acid is known to survive these conditions.[30] Redistilled cyclohexylamine (2.91 g) was added, and the water removed *in vacuo*. The product, **tricyclohexylammonium trimetaphosphate,** was recrystallized four times from 50% ethanol–50% acetonitrile (by volume) as long needles. It gave a single spot with R_f 0.48 on ascending chromatography using an isopropyl alcohol–isobutyl alcohol–ammonia–water solvent (120:67:2.2:111 by volume) and Whatman No. 1 paper; the spot was visualized with molybdate spray. The principal infrared bands of the cyclohexylammonium salt in KBr are at 3.39, 3.50, 3.6 to 4.1 (multiple bands), 6.09, 6.18, 6.53, 6.79, 6.86, 7.14, 8.03, 8.12, 9.20, 10.03, and 13.07 μ. The ^{31}P nmr spectrum (H_2O) showed a singlet at +21.9 ppm from 85% phosphoric acid. The ^{31}P nmr signal for trisodium trimetaphosphate has been reported at +21.4 ppm.[31] *Anal.* Calcd for $C_{18}H_{42}N_3O_9P_3$: C, 40.22; H, 7.88; N, 7.82; P, 17.29. Found: C, 40.19; H, 8.04; N, 7.94; P, 16.90.

α-**Bromopropiophenone** was prepared by the procedure of Aldous, Riebsomer, and Castle.[32] The principal infrared bands in CCl_4 are at 3.23, 3.33, 3.40, 5.91, 6.90, 7.44, 8.12, 8.59, 10.52, 14.17, and 14.62 μ, and the ^1H nmr spectrum (neat) showed δ 7.55 (2 H, multiplet), 6.95 (3 H, multiplet), 4.92 (1 H, quartet, J = 7 cps), and 1.47 (3 H, doublet, J = 7 cps). **N-Isopropylidenecyclohexylamine** was prepared by refluxing a mixture of 10 ml of cyclohexylamine and 100 ml of acetone for 10 min. After removing the excess acetone *in vacuo*, the product was distilled at 67–69° (13 mm) (lit.[33] 70–72° (16 mm)). Its principal infrared bands in CCl_4 fell at 3.40, 3.50, 6.00, 6.90, 7.30, 7.38, and 8.18 μ, and its ^1H nmr spectrum (CCl_4) showed δ 3.09 (1 H, broad peak), 1.80 (3 H, singlet), 1.68 (3 H, singlet), and 1.33 (10 H, broad multiplet).

When a solution of acetone (62.3 mole %) and cyclohexylamine (37.7 mole %) was allowed to stand at room temperature, the infrared spectrum slowly changed to that of a mixture containing 47 mole % acetone, 44 mole % N-isopropylidenecyclohexylamine, and 9 mole % cyclohexylamine.

trans-**1-Bromo-1-propenylbenzene,** prepared by the fragmentation of *threo*-1,2-dibromo-1-phenylpropylphosphonic acid (*vide infra*), was introduced into the MS-9 high-resolution mass spectrometer. *Anal.* Calcd for C_9H_9Br: 195.9888. Found: 195.9899. In addition to the parent peak at 196, a peak at 198 had almost as great an intensity, as expected[34] for a monobromo compound. The base peak was at 117 (parent less Br), with a metastable as expected at 69.9. Other strong peaks appeared at 115, 116, and at 91 (benzyl cation).

The corresponding mass spectrum of *cis*-1-bromo-1-propenylbenzene (obtained by the fragmentation of *erythro*-1,2-dibromo-1-phenylpropylphosphonic acid) gave identical peaks; the parent peak had a mass of 195.9895.

When *cis*- or *trans*-1-bromo-1-propenylbenzene was exposed to the air for several hours in an open container, the infrared spectrum of the olefin in CCl_4 showed a gradual increase in a carbonyl band at 5.91 μ. Vacuum removal of the unreacted olefin left a high-boiling oil which was identified as α-bromopropiophenone by comparison of its infrared and nmr spectra with those of an authentic sample.

"Sodium metaphosphate glass" (an old sample from the firm of Dr. Bender and Dr. Hobein, Munich) in aqueous solution showed peaks in its ^{31}P nmr spectrum at +6.2 and +20.6 ppm relative to 85% phosphoric acid. An aqueous solution of 0.42 g of the sodium metaphosphate glass was passed through a column of Dowex-50 in the hydrogen form, and an excess of cyclohexylamine was added, with cooling, to the eluate. The product of this reaction (obtained in quantitative yield) showed infrared bands at 2.7 to 5.1 (broad), 3.39, 3.49, 6.10, 6.48, 6.88, 7.17, 8.03, 9.10 (broad), and 11.34 μ.

Acetonitrile, used as solvent, was Eastman's Spectro Grade. Other compounds were of reagent grade.

Methods. Infrared spectra were measured with a Perkin-Elmer Infracord spectrometer. Mass spectra were taken with an Associated Electrical Industries, Ltd., MS-9 by Mr. Martin Semmelhack and Mr. Paul Ortiz de Montellano. Proton nmr spectra were obtained with a Varian Model A-60 analytical nmr spectrometer, as explained previously.[11] Phosphorus nmr spectra were taken with a Varian high-resolution nmr spectrometer, Model V 4300B, operating at 15.1 Mc and about 8000 gauss.[11] Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are corrected.

Studies of Fragmentation Reactions. *threo*-1,2-Dibromo-1-phenylphosphonic acid (0.30 g) was dissolved in 25 ml of 1.0 *N* sodium hydroxide solution at room temperature. The solution become turbid instantaneously. The mixture was extracted three times with 10-ml portions of ether. After drying the solution over anhydrous sodium sulfate, the ether was removed *in vacuo* giving 0.16 g (97%) of *trans*-**1-bromo-1-propenylbenzene,** with principal infrared bands in CCl_4 at 3.25, 3.28, 3.43, 3.49, 6.10, 6.69, 6.92, 11.56, and 14.45 μ; its ^1H nmr spectrum (CCl_4) showed δ 7.18 (5 H, multiplet), 6.03 (1 H, quartet, J = 7 cps), 1.80 (3 H, doublet, J = 7 cps). This was the material that was examined mass spectrometrically.

A solution of the *threo* acid in water rapidly became turbid. When the *threo* acid (1 g) was boiled in water (50 ml) for a few minutes, it generated *trans*-1-bromo-1-propenylbenzene in 75% yield. When the *threo* acid was dissolved in 1.0 *N* hydrobromic acid, no turbidity appeared at room temperature for 20 min. The solution was heated to near boiling for 10 min; the product ob-

(26) No analysis of this compound is reported in ref 13.

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(34) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 17.

tained by ether extraction was a mixture of *trans*-1-bromo-1-propenylbenzene and α-bromopropiophenone.

The *threo* acid (0.72 g) was dissolved in 10 ml of acetonitrile, treated with 0.84 ml of freshly distilled triethylamine, and allowed to stand at room temperature for 25 min. The solvent and excess amine were removed *in vacuo* at room temperature and the product was dried overnight over P_2O_5. It was taken up in carbon tetrachloride; after removing the solvent, the material weighed 0.28 g (70%), and was identified as *trans*-1-bromo-1-propenylbenzene by infrared and nmr spectroscopy.

The *threo* acid (0.72 g) was dissolved in 10 ml of acetonitrile and 0.72 ml of freshly distilled cyclohexylamine was added. A precipitate formed immediately. It was removed by centrifugation, washed with acetonitrile, and dried *in vacuo*. Its infrared spectrum corresponded to that for the cyclohexylammonium salt, $C_{18}H_{43}N_3O_7P_2$, obtained by the hydrogenation of benzyl hydrogen cyclohexylphosphoramidate. The material in water was passed through a Dowex-50 ion-exchange resin in the sodium form. The compound retained part of its characteristic cyclohexyl absorption in the infrared, *i.e.*, it was at least in part a phosphoramidate. When a solution of the *threo* acid and cyclohexylamine in acetonitrile was heated at 110° for 5 hr, the resulting product was insoluble in acetonitrile; after washing with acetonitrile and absolute ethanol, it consisted of 0.28 g (77%) of tricyclohexylammonium trimetaphosphate, as identified by infrared spectroscopy.

The *threo* acid (0.44 g) was dissolved with warming in 3.0 ml of acetonitrile in a ^{31}P nmr tube. The single peak was at −15.1 ppm relative to 85% phosphoric acid as an external standard. When freshly distilled triethylamine (0.36 ml) was added, crystals of triethylammonium bromide formed in 30 sec. After about 3 hr, they settled, and the spectrum was again determined. The downfield ^{31}P nmr peak had disappeared, and two new peaks, one at +10.8 and one at +23.8 ppm relative to 85% phosphoric acid, had appeared. The compound was converted to its cyclohexylammonium salt, which had an infrared spectrum quite similar to that of the cyclohexylammonium salt of polymetaphosphoric acid. If the triethylamine solution of the *threo* acid was heated at 110° for 5 hr prior to work-up, addition of excess cyclohexylamine precipitated an 80% yield of tricyclohexylammonium trimetaphosphate.

threo-1,2-Dibromo-1-phenylpropenylphosphonic acid (0.72 g) was dissolved in 10 ml of acetonitrile. Freshly distilled 2,6-lutidine (Matheson Coleman and Bell, 0.69 ml) was added, and the solution was sealed under nitrogen and allowed to stand for 18 hr at room temperature. The carbon tetrachloride soluble reaction product consisted of 0.17 g (43%) of *trans*-1-bromo-1-propenylbenzene, identified by its infrared spectrum. Additional experiments of this type are reported elsewhere.[35]

erythro-1,2-Dibromo-1-phenylpropylphosphonic acid (0.30 g) was dissolved in 25 ml of 1.0 *N* sodium hydroxide solution at room temperature. The solution became turbid instantly. The product was isolated in the same fashion as for that from the *threo* isomer, giving 0.14 g (85%) of ***cis*-1-bromo-1-propenylbenzene.** Its infrared spectrum had principal bands in CCl_4 at 3.25, 3.26, 3.43, 3.49, 6.09, 6.70, 6.95, 11.75, 14.34, 14.78 μ. Its ^1H nmr spectrum (CCl_4) shows δ 7.17 (5 H, singlet), 6.11 (1 H, quartet, J = 7 cps), 1.52 (3 H, doublet, J = 7 cps).

2-Bromo-1-styrenephosphonic acid[11] (56 mg) was dissolved in 2 ml of 1.0 *N* sodium hydroxide solution. The compound dissolved readily to give a clear solution. This was heated at 105° in a sealed tube. After about 1 hr, some turbidity appeared. After 3 hr, the contents of the tube was extracted with ether; after drying the solution and evaporating the ether, 4 mg (18%) of phenylacetylene was obtained, and identified by comparison of its infrared spectrum with that of an authentic sample. 2-Chloro-1-styrenephosphonic acid[11] (210 mg) in 5 ml of 1.0 *N* sodium hydroxide solution was similarly heated for 15 hr at 105°, and yielded 47 mg (48%) of phenylacetylene.

threo-1,2-Dibromo-1-phenylbutyric acid (0.39 g, mp 130–132°) was dissolved in 5 ml of acetonitrile, and 0.25 g of freshly distilled triethylamine was added. After 1 hr at room temperature, evolution of carbon dioxide had ceased. Acetonitrile and excess triethylamine were removed *in vacuo*, and the residue extracted with three 10-ml portions of carbon tetrachloride. When the carbon tetrachloride was removed *in vacuo*, 0.17 g (71%) of *trans*-1-bromo-1-propenylbenzene was obtained. Its infrared spectrum was identical with that for the olefin obtained from *threo*-1,2-dibromo-1-phenylpropylphosphonic acid, and with that of the product reported by Crump,[18] except that it was free of the carbonyl-absorbing impurity.

(35) G. L. Kenyon, Thesis, Harvard University, 1965.