mosphere, was cooled in an ice bath and the 2-[(tetrahydropyranyl)oxy]propionitrile was added dropwise at such a rate as to maintain a gentle reflux. The solution was then refluxed for an additional 0.5 hr, chilled in an ice bath, and treated with a cold solution of 7 ml of H_2SO_4 and 84 ml of H_2O added in a steady stream. The mixture was swirled until the gummy deposit disappeared, and the desired product was obtained by decanting and washing the aqueous phase several times with ether. The combined ether layers were shaken with small quantities of dilute HCl until the washes were acidic. Considerable imine (1640 cm^{-1}) remained if this latter procedure was not carried out. The organic phase was dried ($MgSO_4$), concentrated, and distilled to give 2.8 g of forerun and 46.0 g (79.2%) of **1a**: bp 79–83° (0.09 mm); ir spectrum (CCl_4), 1720 cm^{-1}; nmr spectrum, 0.93 (CH_3 triplet), 1.15 and 1.24 (diastereomeric CH_3 doublets), 4.0 (overlapping quartets for adjacent CH), 2.44 (multiplet CH_2 adjacent to carbonyl), and 4.5 ppm (multiplet H on carbon bonded to two oxygens).

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.28; H, 10.49.

2-[(Tetrahydropyranyl)oxy]-3-nonadecanone (1b).—The reaction of the tetrahydropyranyl ether of lactonitrile with hexadecylmagnesium bromide was conducted as above. The crude reaction product was allowed to stand in acetone overnight and filtered to remove most of the dotriacontane, mp 69–71°, formed in the reaction. Attempts to distil the product were unsuccessful (decomposition) and it was purified by filtration through alumina. An analytical sample was prepared by refiltration, ir spectrum 1720 cm^{-1}.

Anal. Calcd for $C_{24}H_{46}O_3$: C, 75.34; H, 12.12. Found: C, 75.19; H, 12.08.

4-Hydroxy-4-methyl-3-pentylcrotonic Acid γ-Lactone (2a).—Triethyl phosphonoacetate (59.0 g, 0.263 mol) was converted into its sodio derivative with 11.6 g (0.27 mol) of 55.8% sodium hydride in 600 ml of anhydrous 1,2-dimethyoxyethane as previously described[2] (the sodium hydride had been washed with hexane to remove the mineral oil). The ketone, **1a**, (40.0 g, 0.175 mol) was added, and the mixture was kept at 70° in a nitrogen atmosphere for 20 hr, cooled, concentrated on a flash evaporator, diluted with H_2O, and extracted with ether. The crude ester was saponified with KOH in aqueous ethanol, and the acid which was obtained was dissolved in 2:1 dioxane–H_2O containing a little HCl. The mixture was warmed at 50–55° for 18 hr and then worked up to give a mixture of **1a** and the $\Delta^{\beta,\gamma}$ isomer. The ir spectrum had a very broad carbonyl absorption covering the area from 1750 to 1800 cm^{-1} and a rather weak 1640-cm^{-1} band. Gas chromatograms obtained with an SE 30 column (5% on base-washed Chromosorb P, 6 ft × 0.125 in.) revealed two major peaks. The earlier peak predominated (2:1), and treatment with base or alumina caused the latter peak to grow at the expense of the former. Distillation of the mixture through a packed column gave 13.4 g of liquid [bp 76–80° (0.10 mm)], 6.6 g of which was passed through 130 g of alumina with 1:1 ether–petroleum ether (exothermic) to give 4.8 g of pure **2a**: bp 85–87° (0.10 mm); ir spectrum (CCl_4), 1763, sh 1780, 1643 cm^{-1} s; nmr spectrum, 1.34 (CH_3 doublet), 4.85 (quartet for adjacent CH), 5.63 (singlet for vinyl H); uv spectrum (ethanol), strong end absorption.

Anal. Calcd for $C_{10}H_{16}O$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.62.

The yield of **2a** from the ketone was ~33%. Filtration yields were optimum when the material was allowed to traverse the column fairly rapidly.

Treatment of the Acid Residue to Obtain 2a.—The acidic material recovered from the above lactonization (13.3 g) was dissolved in 35 ml of benzene, and 4 ml of BF_3 etherate was added. The resulting solution was heated under reflux for 20 hr (~1 ml of H_2O was collected). The mixture was poured into H_2O and extracted with ether, and the latter was dried ($MgSO_4$) and concentrated: ir spectrum (film), 1760 and 1725 cm^{-1}. Short path distillation gave 6.6 g of light yellow liquid, bp 73–104° (0.10 mm), which was >80% pure by glpc. Further treatment of the undistilled residue (saponification, BF_3 treatment, distillation) provided another 0.5 g. Therefore, by glpc, a further 20% yield of **2a** from the acid portion of the above reaction is possible. Two distillations through a packed column provided material of 96–97% purity.

4-Hydroxy-4-methyl-3-hexadecylcrotonic Acid γ-Lactone (2b).—Crude ketone **1b** was converted directly into **2b** in an analogous manner. No effort was made to improve the yield by conversion of *trans*-hydroxy acid; the over-all yield from lactonitrile was 30%: ir spectrum (CCl_4), 1768 and 1643 cm^{-1}.

Anal. Calcd for $C_{21}H_{38}O_2$: C, 78.20; H, 11.88. Found: C, 78.35; H, 11.93.

***trans*-3-(1-Hydroxyethyl)-2-nonadecen-1-ol (3).**—Lactone **2b** (3.5 g, 10.9 mmol) was added to a suspension of 0.57 g (15 mmol) of lithium aluminum hydride in ether and the resulting mixture was heated under reflux for 2 hr. Excess hydride was destroyed with H_2O. The crude diol was chromatographed on a column containing 65 g of alumina. Diol **3** (2.6 g) was obtained. It could be sublimed to a wax: mp 40–44°; ir spectrum (CCl_4), 3610 w, 3340 cm^{-1} broad; nmr spectrum, 1.2 (CH_3 doublet partially obscured), 4.58 (quartet for adjacent CH), 4.1 (multiplet CH_2OH), and 5.34 (multiplet vinyl H).

Anal. Calcd for $C_{21}H_{42}O_2$: C, 77.23; H, 12.97. Found: C, 77.22; H, 12.97.

A less polar isomeric diol was also obtained (36 mg), mp 81–83.5° (ether–petroleum ether).

Anal. Calcd for $C_{21}H_{42}O_2$: C, 77.23; H, 12.97. Found: C, 77.08; H, 12.97.

3-Hexadecyl-2,5-dihydro-2-methylfuran (5).—The diol **3** (0.30 g, 9.2 mmol) was added to a slurry of 100 mg of hexane-washed sodium hydride in 25 ml of ether under nitrogen. The mixture was heated under reflux for 1 hr and cooled. Then 0.20 g of *p*-toluenesulfonyl chloride was added in portions with stirring. The mixture was heated under reflux for 2 hr. The product was worked up in the usual way. Excess sulfonyl chloride was removed by briefly treating the crude product with pyridine (5 min). Purification was achieved by filtration through alumina (Brockman, activity 1). A colorless oil was obtained (0.15 g, 54%): ir spectrum (film), 1080 cm^{-1} (2,5-dihydrofuran itself exhibits a band at 1075 cm^{-1}); nmr spectrum, 4.44 (CH_2–O multiplet), 4.60 (CH_3CH–O multiplet), and 5.26 (vinyl H multiplet).

Anal. Calcd for $C_{21}H_{40}O$: C, 81.75; H, 13.07. Found: C, 81.94; H, 13.27.

3-Hexadecyl-2-methyl-1-propyl-3-pyrroline (4b).—The diol **3** was converted into the dichloride by treatment with dry pyridine and thionyl chloride at 0°. The crude dihalide was heated under reflux in propylamine for 16 hr. After barium hydroxide had been added, the mixture was filtered, and the precipitate was washed with ether. The mother liquors were thoroughly stripped of propylamine, and the residue was dissolved in anhydrous ether. Dry HCl gas was then passed in, and the mixture was chilled. A total of 205 mg (29%) of the hydrochloride could be obtained as an amorphous solid: mp 115.5–117° (methanol–ether). The free base obtained by molecular distillation was a colorless mobile oil which absorbed CO_2 rather readily: nmr spectrum, 2.57 (triplet CH_2CH_2N) 3.24 (doublet ring CH_2–N), 4.28 (quartet CH_3CH–N), and 5.15 ppm (broadened triplet vinyl H).

Anal. Calcd for $C_{24}H_{48}ClN \cdot CH_3OH$: C, 71.86; H, 12.54; Cl, 8.48; N, 3.35. Found: C, 71.90; H, 12.54; Cl, 8.82; N, 3.68.

Registry No.—2-[(Tetrahydropyranyl)oxy]propionitrile, 17224-04-3; **1a**, 17223-97-1; **1b**, 17223-98-2; **2a**, 17223-99-3; **2b**, 17224-00-9; **3**, 17224-01-0; **4b**, 17224-05-4; **4b**·HCl, 17224-02-1; **5**, 17224-03-2.

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The Structure of an Alleged Triazetidine

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Datta and Chatterjee reported in 1922[1] that hydrolysis of the chlorination product of urethane gave a

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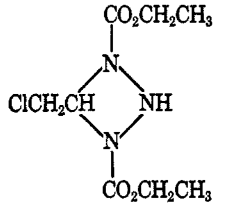
[1] R. L. Datta and B. C. Chatterjee, *J. Amer. Chem. Soc.*, **44**, 1538 (1922).

product, mp 143–144°, to which they assigned the structure 1,3-dicarbethoxy-4-(chloromethyl)-1,2,3-triazetidine (1).



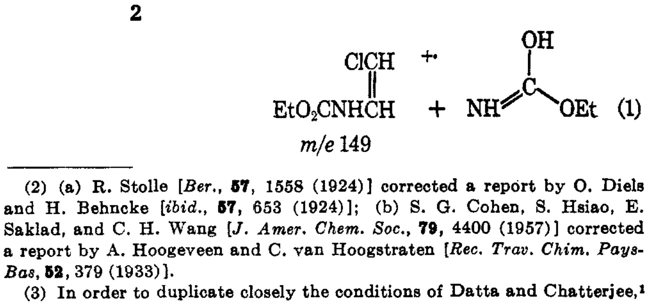
1

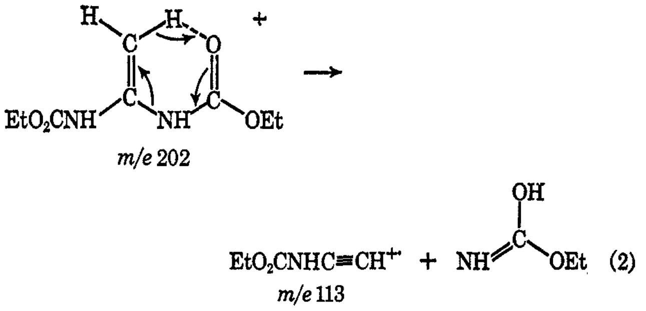
The same product could also be obtained from an aged solution of N-chlorourethane in ethanol. Inasmuch as this is the only report of a triazetidine derivative still extant in the literature,[2] we felt a reinvestigation of this material was in order.

Exhaustive chlorination of an aqueous solution of urethane produced a dense yellow liquid, the nmr spectrum of which suggested that it was a mixture of N-chloro- and N,N-dichlorourethane.[3-5] The mixture was stirred at room temperature for 6 days, during which time a small quantity of white crystals formed, mp 146–147° after recrystallization from water. The infrared spectrum showed N–H absorption at 2.9 and 6.65, C–H at 3.32, and C=O at 5.78 μ. The nmr spectrum showed a six-proton triplet at τ 8.73 (J = 7.2 cps), a two-proton doublet at τ 6.17 (J = 5.1 cps) a four-proton quartet at τ 5.84 (J = 7.2 cps) and a broad three-proton resonance between τ 4.3 and 5.2. The microanalysis of the compound suggested the formula $C_8H_{15}ClN_2O_4$.

These data suggested that the compound obtained by Datta and Chatterjee was in fact $ClCH_2CH(NHCO_2CH_2CH_3)_2$ (2). This compound has also been obtained by decomposition of a solution of N-chlorourethane in ether;[6] the reported melting point was 148°.

The mass spectrum (see Experimental Section) shows no parent ion at *m/e* 238 as expected for 2; instead, the highest mass peak observed is at *m/e* 202, resulting from loss of HCl from the unseen parent. The highest mass peaks containing chlorine are found at *m/e* 149 and 151, corresponding to loss of the elements of urethane from the parent. Loss of the elements of urethane presumably occurs by a McLafferty rearrangement mechanism[7] (eq 1). An analogous process may also occur from the ion at *m/e* 202 (eq 2); alternatively, the ion at *m/e* 113 may arise from loss of HCl from the ion at *m/e* 149. Other prominent peaks in the spectrum, particularly those at *m/e* 103 (ClCH=CHN=C=O$^+$), 77 (ClCH$_2$CH=NH$^+$), and 43 (HNCO$^+$) also support the structure 2.





The formation of 2 in this reaction mixture is presumably a result of (a) hydrolysis of urethane to ethanol, (b) oxidation of ethanol to acetaldehyde, (c) chlorination of acetaldehyde, and (d) condensation of chloroacetaldehyde with urethane to give the product.[8]

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137B; nmr spectra were obtained on a Varian A-60, calibrated against a tetramethylsilane internal standard (τ 10.00). The mass spectrum was obtained from Morgan-Schaffer Corporation, Montreal, using a Hitachi Perkin-Elmer RMU-6D, with the indirect inlet at 250° and a 70-V ionizing voltage. The microanalysis was obtained from Galbraith Laboratories, Knoxville, Tenn.

Chlorination and Hydrolysis of Urethane.—A stream of chlorine gas was slowly passed into a magnetically stirred solution of 20.0 g of urethane (mp 47–48.5°, 0.28 mol) in 100 ml of distilled water. A dense yellow oil slowly separated from solution. Only after no further change seemed to be occurring (about 5 hr) was introduction of chlorine discontinued; 24.5 g of chlorine (0.345 mol) was taken up. An nmr spectrum of the yellow lower layer diluted with CCl$_4$ showed two overlapping triplets at τ 8.57 and 8.65, two overlapping quartets at 5.65 and 5.79, and a broad resonance at *ca.* 3.1. This suggested that the oil was a mixture of N-chloro- and N,N-dichlorourethanes; the peak heights showed a 3:2 ratio, respectively.

The two phase mixture was stirred magnetically at room temperature. After 5 days some white crystals had appeared; these were collected and used for further work. The same material continued to precipitate over a period of several weeks; a total of 0.863 g was obtained (3.9%, based on 3 mol of urethane per mole of product). Recrystallization of the crude product from water yielded white needles, mp 146–147° (lit. mp for 2, 148°,[6] 148.5–149°[9]). The infrared spectrum (CHCl$_3$) showed bands at 2.9 (m), 3.32 (w), 5.78 (s), 6.65 (s), 7.25 (w), 7.52 (m), 8.00 (s), 9.5 (m), and 12.4 (m) μ; mass spectrum, *m/e* (% abundance) 202 (0.31), 173 (0.26), 156 (0.95), 152 (0.17), 151 (2.76), 150 (0.44), 149 (7.79), 143 (0.94), 130 (0.64), 114 (2.0), 113 (10.9), 112 (1.38), 110 (0.90), 106 (0.85), 105 (2.2), 104 (2.8), 103 (5.9), 92 (3.5), 90 (10.3), 86 (4.3), 85 (29.4), 84 (2.2), 79 (5.2), 78 (3.4), 77 (16.5), 76 (7.9), 75 (2.4), 74 (2.1), 71 (1.8), 70 (1.6), 69 (1.4), 68 (2.7), 64 (3.8), 63 (1.8), 62 (8.2), 61 (2.3), 57 (11.3), 56 (7.2), 55 (3.6), 51 (2.1), 50 (3.4), 49 (6.5), 48 (8.2), 47 (1.6), 46 (15.9), 45 (44.4), 44 (38.8), 43 (53.1), 42 (28.3), 41 (6.4), 40 (10.7), 39 (4.7), 38 (2.6), 32 (1.8), 31 (93.5), 30 (17.8), 29 (100.0), 28

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(2) (a) R. Stolle [*Ber.*, **57**, 1558 (1924)] corrected a report by O. Diels and H. Behncke [*ibid.*, **57**, 653 (1924)]; (b) S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang [*J. Amer. Chem. Soc.*, **79**, 4400 (1957)] corrected a report by A. Hoogeveen and C. van Hoogstraten [*Rec. Trav. Chim. Pays-Bas*, **52**, 379 (1933)].

(3) In order to duplicate closely the conditions of Datta and Chatterjee,[1] it was not desirable to isolate and hydrolyze separately N-chlorourethane[4] and N,N-dichlorourethane.[5]

(4) K. Schrage, *Tetrahedron*, **23**, 3033, 3039 (1967).

(5) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

(6) W. Traube and H. Gockel, *Ber.*, **56**, 384 (1923).

(7) See, for example, F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 123–128.

(8) A similar scheme was proposed by Datta and Chatterjee to account for the formation of 1.[1] A referee has also suggested addition of N-chlorourethane to the enol of acetaldehyde to give $ClCH_2CH(OH)NHCO_2CH_2CH_3$, which would then readily produce **2**. However, we would expect the enol to react much more readily with excess chlorine, to give chloroacetaldehyde, than with N-chlorourethane, which normally requires free-radical initiators and ultraviolet irrdiation to add to C=C bonds.[4]

(9) G. E. Hall and F. M. Ubertini, *J. Org. Chem.*, **15**, 715 (1950).

(73.8), 27 (61.5), 26 (20.9), 25 (3.4). The nmr spectrum was obtained in $CDCl_3$ solution and is described in the text.

Anal. Calcd for $C_8H_{15}ClN_2O_4$: C, 40.25; H, 6.29; N, 11.72; Cl, 14.90%. Found: C, 40.07; H, 6.29; N, 11.62; Cl, 15.05%.

Registry No.—2, 5336-13-0.

Studies Concerning the Neutralization of Tetrakis(hydroxymethyl)phosphonium Chloride and the Reaction of Tris(hydroxymethyl)phosphine with Formaldehyde

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The unusual behavior of tetrakis(hydroxymethyl)phosphonium chloride (tetrakis) toward base has been a subject of interest since its original synthesis.[1] Most tetraalkylphosphonium salts require temperatures above 100° in order to react with metal hydroxides, giving phosphine oxide plus hydrocarbon.[2] However, tetrakis reacts facilely with base; in fact it is a monoprotic acid, having an apparent[7] pK_a of 5.5 and a true[3] pK_d of 7.06. Many authors have written the neutralization reaction as

$$R_4P^+OH^- \longrightarrow R_3P{=}O + RH$$

$$\underset{\text{tetrakis}}{(HOCH_2)_4PCl} + NaOH \longrightarrow NaCl + HCHO + H_2O + \underset{\text{THP}}{(HOCH_2)_3P}$$

since there is ample chemical evidence for the formation of tris(hydroxymethyl)phosphine (THP) and formaldehyde.[3-7,19b]

Various other species have been suggested as being in equilibrium with tetrakis and THP. In his study of the hydroxide-induced oxidation of the THPC to tris(hydroxymethyl)phosphine oxide (THPO), Grayson[7] proposed an equilibrium between THP and structure **1** or, less favorably, **2** or **3**.

$^-OCH_2\overset{+}{P}(CH_2OH)_3$

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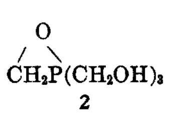

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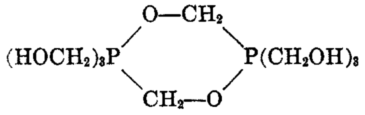

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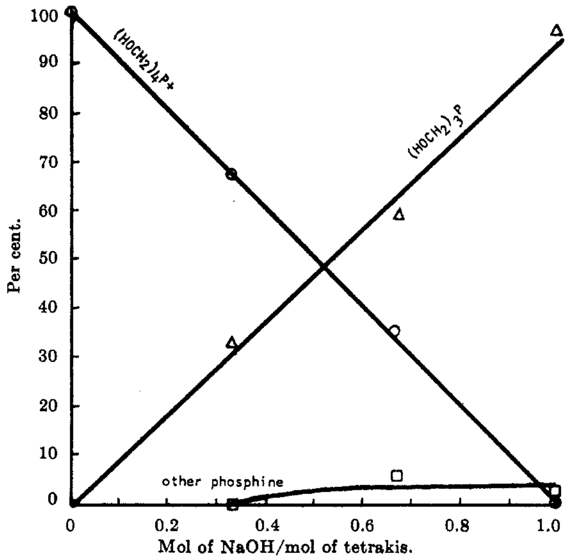

Figure 1.—Neutralization of tetrakis by NaOH in methanol.

French workers,[8] and more recently Filspescu, *et al.*,[9] proposed an equilibrium between THP and tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH).

$$(HOCH_2)_4PCl \xrightarrow[\text{or MOH}]{PbCO_3} (HOCH_2)_4POH$$

$$(HOCH_2)_3POH \rightleftharpoons (HOCH_2)_3P + H_2O + HCHO$$

The synthesis of THPOH by the reaction of phosphine with formaldehyde in the presence of transition metal halide catalysts[10a,b] or pressure[10c] has recently been reported.

We were therefore encouraged to study the neutralization of tetrakis by ^{31}P nuclear magnetic resonance spectroscopy. The chemical shifts of tetrakis (−27 ppm), THP (+25 ppm), and THPO (−48 ppm) are widely different. Phosphonium salts absorb over a fairly narrow range[11] around −30 ppm, so that zwitterion **1** and THPOH, should it be ionic, would be recognized either by a less than quantitative reduction in the −27-ppm peak or by a new peak very near. It is not possible to predict with certainty where pentacovalent structures **2** and **3** and a pentacovalent THPOH might absorb owing to the lack of suitable models.[12]

The course of the neutralization of tetrakis by sodium hydroxide in water and in methyl alcohol using ^{31}P nuclear magnetic resonance spectroscopy was followed. The results are shown in Figures 1 and 2 and may be summarized as follows: (1) in methyl alcohol the concentration of tetrakis diminishes in direct proportion to the amount of base added. During the early portion of the neutralization THP is the only species produced. After a third of a mole of base has been added, a new peak appears at +29.1 ppm, amounting to about

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[1] A. Hoffman, *J. Amer. Chem. Soc.*, **43**, 1684 (1921); **52**, 2995 (1930).

[2] A. Cahours and A. W. Hofmann, *Ann.*, **104**, 1 (1957).

[3] L. M. Fodor, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1963.

[4] H. Hellman and O. Schumacker, *Angew. Chem.*, **72**, 211 (1960).

[5] K. A. Petrov, V. A. Parshina, and M. B. Luzanova, *J. Gen. Chem. USSR*, **32**, 553 (1962).

[6] W. J. Vullo, *Ind. Eng. Chem. Prod. Res. Develop.*, **5**, 344 (1966).

[7] M. Grayson, *J. Amer. Chem. Soc.*, **85**, 79 (1963).

[8] French Patent 1,011,978 (1952).

[9] N. Filipescu, L. M. Kindley, H. E. Podall, and F. A. Serafin, *Can. J. Chem.*, **41**, 821 (1963).

[10] (a) M. Reuter and L. Orthner, German Patent 1,041,957 (1958); (b) M. Reuter, German Patent 1,064,061 (1960); (c) Kh. R. Raver, A. B. Brecker, and L. Z. Soborovski, *J. Gen. Chem. USSR*, **32**, 588 (1961).

[11] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer in "Topics in Phosphorus Chemistry," Vol. V, "P^{31} Nuclear Magnetic Resonance," M. Grayson and C. Griffith, Ed., Interscience Publishers Inc., New York, N. Y., 1967, Chapter 4.

[12] A positive (to phosphoric acid reference) chemical shift might be expected by analogy with phosphoranes and oxyphosphoranes, ref 11, pp 434–442.