peaks in the 31, 45, 59, 73, etc., series and can be used in low-resolution mass spectrometry to differentiate from the 43, 57, 71, etc., series of hydrocarbon peaks.

Infrared spectra. The fundamental frequencies for related epoxides in the frequency range 2.5-8.0 μ were the same for all compounds. Henbest et al. (*4*) report specific C—H stretching bands in the range of 3050-2990 cm^{-1} for the epoxide function. We should have been able to determine these bands with the instrument used but were unable to detect them.

The 1,2-epoxides substantiate data published by Shreve et al. (9) for the characteristic absorption pattern at 11.0 and 12.0 μ for the oxirane derivative of terminally unsaturated compounds. This pattern is eliminated as the epoxide moves closer to the center of the molecule. A single diagnostic peak is shown for all the 2,3-epoxides at 11.7 μ, for all the 3,4-epoxides at 11.3 μ, and for all the 4,5-epoxides between 11 and 11.2 μ.

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Synthesis of a Triazaphosphahomoadamantane[1]

Donald J. Daigle and Armand B. Pepperman, Jr.
Southern Regional Research Center,[2] New Orleans, La. 70179

The compound, 1,3,5-triaza-7-phosphatricyclo[3.3.2.1^{3,7}]-undecane, a triazaphosphahomoadamantane, was prepared in 68% yield from the reaction of ethylenediamine, ammonia, and tris(hydroxymethyl)phosphine in excess formaldehyde. The oxide was prepared by conventional means.

The chemistry of tetrakis(hydroxymethyl)phosphonium chloride (Thpc) has been the subject of much interest in recent years because it is used commercially in the production of flame retardant cellulosic textiles (*1*). Textile workers have neutralized Thpc and referred to the solution as "THPOH," realizing that it is a mixture of products, principally tris(hydroxymethyl)phosphine (THP) and formaldehyde (*2*). "THPOH" reacts rapidly with ammonia and diamines to form water-insoluble precipitates; this reaction is the basis for a well-known flame retardant finish (*4*).

Other workers found that copper salts inhibit the reaction of "THPOH" with aqueous ammonium hydroxide at room temperature by formation of a complex (*5*). Excess formaldehyde also prevents this reaction between THPOH and ammonium hydroxide and allows another product to be formed (*3*). This product is 1,3,5-triaza-7-phosphaadamantane (PAA).

To prepare the next member of this series, a phosphahomoadamantane, both ammonia and ethylenediamine must be used. However, copper salts did not inhibit the reaction between "THPOH" and the diamines to form a water-insoluble precipitate. We wish now to report that formaldehyde can inhibit this reaction between "THPOH" and ethylenediamine. To prepare PAA and to prevent formation of the water-insoluble precipitate, a 4:1 excess of formaldehyde to THP ("THPOH") was needed, and a larger excess (10:1) increased the yield of PAA from 40 to 70% (*4*). However, not even an 8:1 excess of formaldehyde to THP ("THPOH") inhibited the reaction of THP with ethylenediamine to form a water-insoluble precipitate. A 16:1 excess of formaldehyde to THP (THPOH) did prevent premature precipitation, and workup yielded a white crystalline compound.

This solid was 1,3,5-triaza-7-phosphatricyclo-[3.3.2.1^{3,7}]-undecane (I) by elemental analysis. The infrared spectrum of I showed bands between 6.8 and 9.2 μ, similar to those exhibited by PAA. The NMR spectrum was complex and exhibited a series of peaks between δ 4.8 and δ 3.0. Dreiding models showed that the addition of a methylene group between two nitrogens in the PAA structure to form the phosphahomoadamantane produced nonequivalence among the protons. This nonequivalence would be expected to give rise to a complex NMR spectrum.

The oxide, prepared as an additional proof of structure, also gave an excellent elemental analysis. The ir spectrum showed the strong band at 8.55 μ characteristic of the P=O stretch. The NMR spectrum is complex and exhibited a multiplet of peaks from δ 4.43 to δ 3.0.

Attempts to prepare a methyl iodide derivative resulted in either orange decomposition products or solids which showed by NMR spectroscopy that methyl group incorporation had not been achieved. This failure to produce a methyl iodide derivative may be due to the instability of the phosphahomoadamantane. Both compounds are soluble in polar solvents, but heating them in solution produced decomposition as evidenced by elemental analyses of the recrystallized materials.

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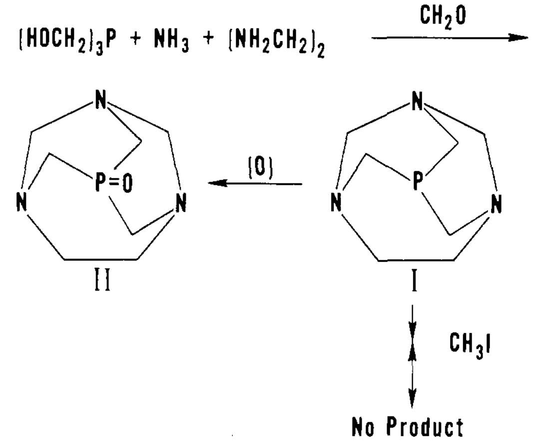
[1] Address correspondence to Wilson A. Reeves, Cotton Textile Chemistry Laboratory, Southern Regional Research Center, ARS, USDA, P.O. Box 19687, New Orleans, La. 70179.

[2] One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture.

Elemental analyses (C, H, N, P) in agreement with theoretical values were obtained and submitted for review. It appears from the evidence that I and II are not stable to heat and certain reactions.



Work is continuing on the reactions of the phosphahomoadamantane, and an X-ray structure analysis of I is currently being performed by L. Trefonas of the University of New Orleans.

Experimental

1,3,5-Triaza-7-phosphatricyclo[3.3.2.1^{3,7}]-undecane (I). A solution of Thpc (36.6 grams, 51.1%, 0.098 mol) neutralized (pH = 7) by NaOH (6.4 grams, 50%, 0.08 mole) was added to a cold (0–10°C) solution of formalin (120 ml, 40% by volume, 1.6 moles), ammonium hydroxide (6 grams, 29%, 0.1 mole), and ethylenediamine (6 grams, 0.1 mole). After 15 min the solution was allowed to warm to room temperature and stand overnight (17 hr). Evaporation of 95% of the water at room temperature, dissolution into chloroform, drying with sodium sulfate, and evaporation of the chloroform at room temperature led to 11.55 grams of I (67.5% yield). Dissolution of I (2.0 grams) in methanol (10 ml), the addition of 10 times excess dimethyl sulfoxide, and room temperature evaporation of the alcohol produced the analytical sample (decomposition > 248°C).

The infrared spectrum (potassium bromide) (Perkin-Elmer Model 137B Infracord) exhibited bands 3.4 (m), 3.45 (m), 6.93 (m), 7.1 (m), 7.25 (w), 7.49 (m), 7.72 (s), 8.02 (m), 8.2 (w), 8.5 (m), 9.02 (m), 9.35 (m), 9.5 (m), 9.85 (w), 10.05 (s), 10.12 (s), 10.28 (m), 10.52 (w), 10.75 (w), 10.95 (s), 11.75 (m), 12.37 (w), 12.7 (m), 13.06 (w), 13.48 (w), and 14.5 μ (m). The NMR spectrum (Varian A-60A spectrometer) of a deuterium oxide solution of I at 60 MHz exhibited the bands relative to an internal standard of sodium-3-trimethylsilyl-1-propane sulfonate: a series of peaks from δ 4.8 to δ 3.0.

1,3,5-Triaza-7-phosphatricyclo[3.3.2.1^{3,7}]-undecane 7-oxide (II). Compound I (0.425 gram, 0.0025 mole) was dissolved in 10 ml methanol, and 25 ml benzene was added. *Tert*-butyl hydroperoxide (0.32 gram, 70%, 0.0025 mole) in 2 ml methanol and 8 ml benzene was added slowly dropwise. The mixture was allowed to stir for 1 hr at room temperature. Evaporation to half volume at room temperature, addition of benzene to full volume, evaporation to half volume, and filtration yielded 0.5 gram of II. Two moles of water was associated with the product isolated as shown by elemental analyses and an infrared spectrum. Drying for 6 hr at 70°C at 30 mm pressure removed the water to produce the analytical sample (decomposition > 260°C). The infrared spectrum (potassium bromide) exhibited bands at 3.4 (m), 6.92 (m), 7.1 (m), 7.3 (m), 7.47 (m), 7.75 (s), 7.97 (m), 8.12 (w), 8.2 (m), 8.55 (s), 9.1 (m), 9.29 (m), 9.66 (m), 10.1 (s), 10.72 (m), 10.95 (s), 11.57 (m), 12.35 (w), 12.78 (m), 13.1 (w), and 14.5 μ (w). The nmr spectrum of a deuterium oxide solution of II showed a complex of peaks from δ 4.43 to δ 3.0.

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