

## Synthesis of 3,7-Dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane and Derivatives

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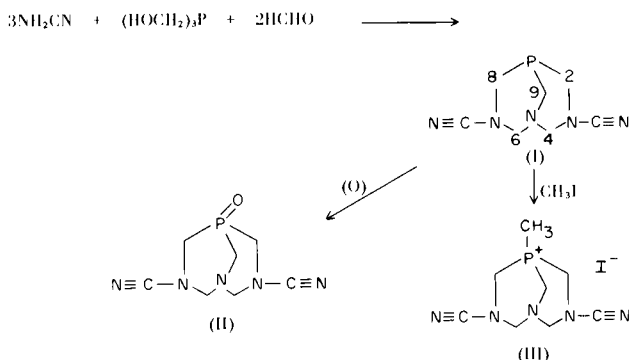
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The reaction of tetrakis(hydroxymethyl)phosphonium chloride (THPC) with secondary amines gives well defined monomeric products (3,4). With primary amines, such as cetylamine (5,7,8), the products are polymeric (2,6,8,9,10). Tris(hydroxymethyl)phosphine (THP) and THP-formaldehyde solutions react with these amines in much the same manner (4,5). Normand and co-workers (7) have produced polymers and flame retardant finishes for cotton based on the reaction of THPC with cyanamide in the presence of phosphoric acid or sodium phosphate salts.

While working with solutions containing formaldehyde, THP, cyanamide, and phosphoric acid, the authors obtained a white crystalline compound as a precipitate.

This solid was shown to be 3,7-dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane (I) by elemental analysis, ir, and nmr spectra. The ir spectrum of I clearly showed the very strong C≡N stretch at 4.45 microns. The nmr spectrum of I was simple. The doublet ( $J = 11$  Hz) centered at  $\delta$  3.5 was assigned to the methylene protons at C-9. The doublet ( $J = 8$  Hz) centered at  $\delta$  4.02 was assigned to the methylene protons at C-2 and C-8. The AB quartet ( $J = 13$  Hz) with one doublet centered at  $\delta$  4.66 and the other at  $\delta$  4.41, was assigned to the methylene protons at C-4 and C-6. The ratio of these bands was 2:4:4, respectively. The product was obtained in a 6% yield based on formaldehyde.

This compound can also be prepared from THPC-cyanamide solution ( $pH = 4$ ) containing dibasic sodium phosphate. The oxide (II), prepared as an additional proof of structure, gave excellent elemental analysis and molecular weight. The ir spectrum showed the strong peak at 8.5 microns characteristic of the P=O stretch. However, the nmr spectrum of II showed a complex of peaks from  $\delta$  5.8 to  $\delta$  3.65. This is due to the very similar chemical shift of the methylene protons caused by the deshielding effect of the phosphoryl group. The methyl iodide (III) derivative of I also gave a good elemental analysis. The nmr spectrum of III showed the methylene protons as a complex of peaks ( $\delta$  5.0 to 4.23) due to the increased electronegativity of the P and the methyl protons as a doublet ( $J = 16$  Hz) centered at  $\delta$  1.93. The ratio of 10:3 protons, respectively, confirmed the structure of (III).



The compounds were more soluble in polar solvents than in nonpolar solvents and were extremely hard to recrystallize. Slow heating of the compounds resulted in a steady decomposition until they were finally black at temperatures above  $300^\circ$ . Rapid heating caused an explosive decomposition. These temperatures are reported as the melting points and were reproducible.

Efforts to increase the yield by infinite dilution techniques and various changes in the concentration of the reagents were unsuccessful.

### EXPERIMENTAL

#### 3,7-Dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane (I).

Tris(hydroxymethyl)phosphine (12.4 g., 0.1 mole) and formalin (8.0 g., 0.1 mole) were dissolved in 16 g. of water and the resulting solution cooled to  $5-10^\circ$ . Phosphoric acid (8.0 g., 0.08 mole) was added slowly to this solution taking care to prevent the temperature from rising above  $25^\circ$ . Cyanamide (50% solution; 16.8 g., 0.2 mole) was then added and this final solution allowed to stand at room temperature for 24 hours. The viscous solution was filtered and yielded 0.6 g. (6% yield) of crude I [m.p.  $246-247^\circ$  (acetonitrile-benzene)]. The infrared spectrum (potassium bromide) (Perkin-Elmer Model 137B Infracord) exhibited peaks at 3.35 (W), 3.4 (W), 4.05 (W), 4.45 (S), 6.0 (W), 6.12 (W), 6.15 (W), 6.9 (M), 6.92 (W), 7.01 (S), 7.2 (S), 7.40 (M), 7.5 (S), 7.6 (S), 7.82 (M), 7.93 (M), 8.13 (S), 8.30 (S), 8.53 (M), 8.90 (S), 9.35 (S), 9.95 (S), 11.05 (S), 11.20 (S), 12.4 (S), 12.8 (M), 13.12 (W), 14.00 (W), and 14.50 (M) with a shoulder at 14.35 microns (M). The nmr spectrum (Varian A-60A spectrometer) of a deuterated dimethyl sulfoxide solution of I at 60 MHz exhibited the following bands relative to an internal standard (tetramethylsilane): a doublet centered at  $\delta$  3.5 with a coupling constant of 11 Hz, a doublet centered at  $\delta$  4.02 with a coupling constant of 8 Hz and an AB quartet centered at 4.53 with a coupling constant of 13 Hz

in the ratio of 2:4:4, respectively.

*Anal.* Calcd. for  $C_7H_{10}N_5P$ : C, 43.08; H, 5.13; N, 35.90; P, 15.90. Found: C, 42.82; H, 4.94; N, 35.75; P, 16.04.

1-Oxo-3,7-dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane (II).

Compound I (0.3 g., 0.0015 mole) and *t*-butyl hydroperoxide, (70% solution, 0.38 g., 0.003 mole) were stirred in 300 ml. of butanol for 4 hours at room temperature. The solution was filtered to yield 0.29 g. of crude II (90% yield) [m.p. 285-286° (acetonitrile-water)]. The infrared spectrum (potassium bromide) showed peaks at 3.52 (M), 4.09 (W), 4.47 (S), 6.10 (W), 6.83 (W), 6.92 (M), 7.05 (M), 7.20 (M), 7.43 (W), 7.54 (S), 7.70 (S), 7.9 (M), 8.23 (S), 8.50 (S), 8.95 (M), 9.28 (S), 9.5 (S), 10.01 (S), 10.06 (S), 11.00 (S), 11.45 (M), 12.30 (W), 12.60 (S), and 14.5 microns (W). The nmr spectrum of deuterated dimethyl sulfoxide solution of II showed a complex of peaks from  $\delta$  5.18 to  $\delta$  3.65.

*Anal.* Calcd. for  $C_7H_{10}N_5OP$ : C, 39.81; H, 4.74; N, 33.18; P, 14.69; mol. wt., 211. Found: C, 40.2; H, 4.65; N, 32.67; P, 14.93; mol. wt., 210 (boiling point elevation, water).

1-Methyl-3,7-dicyano-3,5,7-triaza-1-phosphoniabicyclo[3.3.1]nonane iodide (III).

Compound I (0.3 g., 0.0015 mole) and methyl iodide (0.6 g., 0.004 mole) were refluxed in 30 ml. acetone for 3 hours. The solution was filtered to yield 0.5 g. of crude III (96% yield) [m.p. 276-277° (acetonitrile-dimethyl sulfoxide)]. The infrared spectrum (potassium bromide) exhibited peaks at 3.32 (W), 3.39 (M), 4.49 (S), 6.10 (W), 6.92 (W), 6.95 (M), 7.12 (S), 7.40 (W), 7.55 (S), 7.77 (S), 7.88 (M), 8.00 (W), 8.33 (M), 8.38 (M), 8.58 (W), 8.83 (W), 9.18 (M), 9.42 (S), 9.95 (S), 10.55 (S), 10.65 (S), 11.1 (M), 11.55 (W), 12.30 (S), 12.60 (M), 12.92 (W), 13.50 (W), and 14.34 microns (M). The nmr spectrum of a deuterated dimethyl sulfoxide solution of III showed a complex of peaks from  $\delta$  5.0 to  $\delta$  4.23 and a doublet centered at  $\delta$  1.93 with a coupling at 16 Hz in the

ratio of 10:3, respectively.

*Anal.* Calcd. for  $C_8H_{13}N_5PI$ : C, 28.49; H, 3.86; N, 20.78; P, 9.20; I, 37.67. Found: C, 28.45; H, 3.91; N, 20.55; P, 9.32; I, 37.49.

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