

Some Reactions of 1,3,5-Triaza-7-phosphaadamantane and its 7-Oxide

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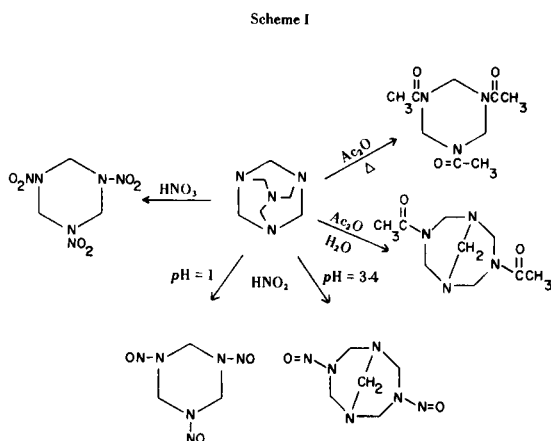
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The synthesis of 1,3,5,7-triazaphosphocine and 1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane derivatives *via* nitration, nitrosation and acetylation of 1,3,5-triaza-7-phosphaadamantane and its 7-oxide is reported. A comparison of the reactions of the triazaphosphaadamantane with the analogous reactions of hexamine is made.

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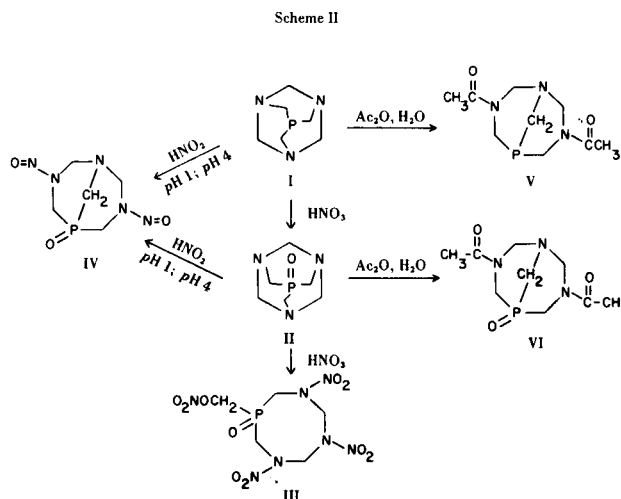
As part of a continuing program involving the synthesis of heterocyclic nitramines and related compounds, we became interested in the reactions of 1,3,5-triaza-7-phosphaadamantane (I) and its 7-oxide (II). These compounds, first reported by Daigle, *et al.*, (1), were of interest since the phosphaadamantane can be considered a monophosphorus analog of hexamethylenetetramine. A comparison between these analogs with respect to nitration, nitrosation and acetylation was undertaken and is reported here.

The chemical reactions of hexamine are well established. Its nitration with nitric acid (2), nitrosation (3,4) and acetylation (5,6) are depicted in Scheme I.

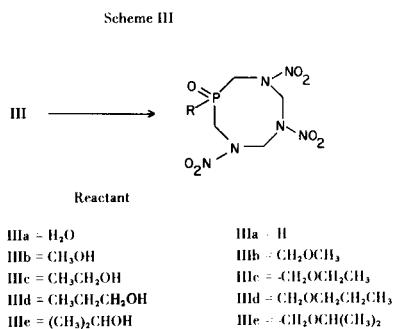


As a result of our study, the analogous reactions starting from the phosphaadamantane (I) and the 7-oxide (II) can be depicted as in Scheme II.

With respect to the nitration of these two materials, only one product was isolated. Instead of the hexahydro-1,3,5-trinitro-*s*-triazine formed by reaction of hexamine with nitric acid, we found that the product from I and II

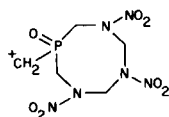


was octahydro-1,3,5-trinitro-1,3,5,7-triazaphosphocine-7-(2*H*)methanol nitrate 7-oxide (III). This tends to indicate that I, in the presence of nitric acid, undergoes oxidation to II followed by cleavage of a C-N bond to form the methanol nitrate ester derivative. The fact that the C-N rather than the P-C bond is cleaved is not surprising, since the strength of the P-C bond is greater than that of the C-N bond as reported by Huggins (7). Although the ir spectra indicated the presence of -P=O, -NNO₂ and -ONO₂ groups and elemental analysis was in agreement with the indicated structure of III, we were unable to conclusively establish the structure due to 1) the complicated nmr spectrum, 2) the instability of the molecule under the conditions of mass spectrometry and 3) the instability of the -ONO₂ group in the presence of trace amounts of moisture. Indirect proof of the structure was accomplished through the examination of a number of derivatives formed by reaction of III with water and aliphatic alcohols. These

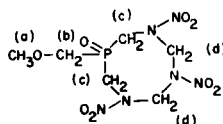


derivatives are shown in Scheme III.

As in the case of III described above, the ir patterns and elemental compositions for IIIa-IIIe were in agreement with the proposed structures. Nmr, although again giving complicated spectra, did indicate P-CH₂ bonding. For these derivatives, however, the correct molecular weights were obtained by mass spectrometry. Examination of the fragmentation patterns for IIIb-IIIe and mass analysis indicated the loss of alkoxy group producing the ion.



Further confirmation was obtained on IIIb utilizing C¹³ nmr. For the structure there are four different kinds of carbon atoms. (a = 1, b = 1, c = 2, and d = 2). Since ³¹P should split carbons b and c into doublets, the spectrum would be expected to exhibit 6 lines. Indeed 6 lines were observed although at this time we have not assigned the lines to specific carbon atoms.



Referring once again to Scheme II, nitrosation of I and II at the pH levels shown produce a common product IV, 3,7-dinitroso-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane 5-oxide, rather than the two products obtained under identical conditions from hexamine (Scheme I). With regard to the phosphadamantanes, increased acidity is apparently not a factor, whereas, with hexamine, increasing acidity results in the formation of the six-membered ring as opposed to the bridged product formed under conditions approaching neutrality. Nitrosation of I again easily oxidizes the trivalent phosphorus to the pentavalent state.

Acetylation of I and II produced separate products (V) 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane and (VI) 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane 5-oxide respectively, without oxidation of the trivalent phosphorus in I to the pentavalent state initially

present in II.

Analytical data, including elemental analysis, ir, nmr, and molecular weight *via* mass spectrometry, on the products of nitrosation and acetylation were in agreement with the structures depicted.

EXPERIMENTAL

Melting points were taken in capillary tubes in a Thomas Hoover apparatus and are uncorrected. Ir spectra were determined in potassium bromide pellets with a Perkin-Elmer Model 457 spectrometer. Nmr spectra were determined in DMSO-d₆ on a Varian T-60 spectrometer using tetramethylsilane as internal reference. Molecular weights were determined by mass spectrometry using the DuPont GC/MS 21-492. Microanalysis were run by Schwartzkopf Microanalytical Laboratory.

Starting Compounds.

Compounds I and II (1) were supplied by Dr. D. Daigle of the Southern Regional Research Center, New Orleans, Louisiana. Prior to use both were recrystallized from ethanol. The analytical data are shown below.

Compound I.

Anal. Calcd. for C₆H₁₂N₃P: C, 45.85; H, 7.70; N, 26.74; P, 19.71. Found: C, 45.87; H, 7.79; N, 26.50; P, 19.69.

Compound II.

Anal. Calcd. for C₆H₁₂N₃OP: C, 41.62; H, 6.99; N, 24.27; P, 17.87. Found: C, 41.61; H, 7.15; N, 24.36; P, 17.79.

Octahydro-1,3,5-trinitro-1,3,5,7-triazaphosphocine-7-(2H)methanol Nitrate (Ester) 7-Oxide (III).

1,3,5-Triaza-7-phosphadamantane (I) (1 g., 0.0064 mole) or the 7-oxide (II) (1.1 g., 0.0064 mole) was added to 100% nitric acid (22.5 g., 0.358 mole) over a period of 30 minutes while stirring and maintaining the temperature at 0°. After stirring for an additional 1½ hours at 0° the solution was added to 100 g. of ice. The product was then filtered, washed with ice-water and dried under vacuum. A crude yield of 1.56 g. (68%), m.p. 146° dec., was obtained; ir (potassium bromide): 1660 and 1275 (-ONO₂), 1540 and 1305 (-NNO₂), 1190 and 1180 (P=O, doublet) cm⁻¹.

CAUTION:

The reaction is extremely exothermic and if the addition of I or II is too rapid brilliant flash fires occur on the surface of the nitric acid.

Anal. Calcd. for C₅H₁₀N₇O₁₀P: C, 16.72; H, 2.81; N, 27.30; P, 8.63. Found: C, 16.93; H, 3.10; N, 26.95; P, 8.65.

Derivatives of Octahydro-1,3,5-trinitro-1,3,5,7-triazaphosphocine-7-(2H)methanol Nitrate (Ester) 7-Oxide (IIIa-IIIe).

These derivatives were prepared by refluxing 1 g. of III in 130 ml. of solvent; (IIIa, water; IIIb, methanol; IIIc, ethanol; IIId, 1-propanol; IIIe, 2-propanol). On refluxing a solution was obtained. In approximately 10 minutes crystallization occurred. The mixtures were then cooled and the solids filtered and dried. No further purification was required, yield, m.p.: IIIa, 87%, 182°; IIIb, 60%, 194°; IIIc, 84%, 169°; IIId, 76%, 153°; IIIe, 71%, 177°.

Octahydro-1,3,5-trinitro-1,3,5,7-triazaphosphocine 7-Oxide (IIIa).

This compound had ir (potassium bromide): 1550 and 1315 (-NNO₂); 1155 (P=O) cm⁻¹; nmr (DMSO-d₆): δ 4.24 (d, J = 5 Hz, PCH₂), δ 4.4-6.8 (m. not interpretable).

Anal. Calcd. for C₄H₉N₆O₇P: C, 16.91; H, 3.19; N, 29.58; P, 10.90; MW, 284. Found: C, 17.21; H, 3.28; N, 29.16; P, 11.14; MW, 284.

Octahydro-7-(methoxymethyl)-1,3,5-trinitro-1,3,5,7-triazaphosphocine 7-Oxide (IIIb).

This compound had ir (potassium bromide): 2830 (-OCH₃), 1535 and 1290 (-NNO₂), 1185 (P=O) cm⁻¹; nmr (DMSO-d₆): δ 3.35 (s, -OCH₃), δ 4.58 (d, J = 5 Hz, PCH₂), δ 4.4-6.8 (m. not interpretable); nmr C¹³ (DMSO-d₆): 6 lines at 82.53, 62.38, 57.20, 50.85, 48.60, and 46.00 ppm. (no assignments made); mass spectrum: m/e 328 (molecular weight), 297 (loss of OCH₃).

Anal. Calcd. for C₆H₁₃N₆O₆P: C, 21.96; H, 3.99; N, 25.61; P, 9.43; MW, 328. Found: C, 22.09; H, 4.05; N, 25.74; P, 9.46; MW, 328.

Octahydro-7-(ethoxymethyl)-1,3,5-trinitro-1,3,5,7-triazaphosphocine 7-Oxide (IIIc).

This compound had ir (potassium bromide): 1535 and 1300 (-NNO₂), 1185 (P=O) cm⁻¹; nmr (DMSO-d₆): δ 1.05-1.30 (t, CH₃), δ 3.45-3.83 (q, OCH₂), δ 4.60 (d, J = 5 Hz, PCH₂), δ 4.2-6.6 (not interpretable).

Anal. Calcd. for C₇H₁₅N₆O₈P: C, 24.56; H, 4.42; N, 24.56; P, 9.05; MW, 342. Found: C, 24.82; H, 4.33; N, 24.15; P, 9.28; MW, 342.

Octahydro-7-(propoxymethyl)-1,3,5-trinitro-1,3,5,7-triazaphosphocine 7-Oxide (IIId).

This compound had ir (potassium bromide): 1562, 1535 and 1300 (NNO₂), 1182 (P=O) cm⁻¹; nmr (DMSO-d₆): δ 0.75-1.03 (t, CH₃), δ 1.30-1.83 (m, C-CH₂-C), δ 3.44-3.68 (t, OCH₂), δ 4.60 (d, J = 5 Hz, PCH₂), δ 4.48-6.60 (m. not interpretable).

Anal. Calcd. for C₈H₁₇N₆O₈P: C, 26.98; H, 4.81; N, 23.60; P, 8.70; MW, 356. Found: C, 27.05; H, 5.02; N, 23.32; P, 8.78; MW, 356.

Octahydro-7(iso-propoxymethyl)-1,3,5-trinitro-1,3,5,7-triazaphosphocine 7-Oxide (IIIe).

This compound had ir (potassium bromide): 1565, 1540 and 1300 (NNO₂), 1180 (P=O) cm⁻¹; nmr (DMSO-d₆): δ 1.12-1.23 (d, CH₃), δ 3.63-4.10 (m, CH), δ 4.53 (d, J = 5 Hz, PCH₂).

Anal. Calcd. for C₈H₁₇N₆O₈P: C, 26.98; H, 4.81; N, 23.60; P, 8.70; MW, 356. Found: C, 27.29; H, 4.72; N, 23.31; P, 8.84; MW, 356.

3,7-Dinitroso-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane 5-Oxide (IV).

At pH 4.5.

A solution of sodium nitrite (4.4 g., 0.06 mole) in 10 ml. of ice-water was added rapidly to a solution of I (1.57 g., 0.01 mole) in dilute acetic acid (3.6 g. in 90 ml. of water). The addition was carried out at 0-5° while stirring rapidly. Stirring was continued and the temperature was maintained for an additional hour. The precipitate which separated was then filtered off, washed with ice-water and dried in vacuum, crude yield, m.p.: 70%, 197°.

At pH 1.

Compound IV was also obtained under more acidic conditions.

A solution of I (1.5 g., 0.0095 mole) in 6 ml. of 36% hydrochloric acid (2.16 g., 0.06 mole) and 80 g. of ice was prepared. A solution of sodium nitrite (2.07 g., 0.03 mole) in 10 ml. of water was then added rapidly. After 15 minutes of 0° the product was filtered off and dried, crude yield, m.p.: 89%, 201°.

The identical product was obtained when II (7-oxide) was substituted for I at both pH 1 and pH 4.5. The crude yields and melting points at these pH's were 75%, 200° and 87%, 201°, respectively. After recrystallization from nitromethane the following data was obtained: ir (potassium bromide): 1430 (-N=N=O), 1190 (P=O) cm⁻¹; nmr (DMSO-d₆): δ 4.20 (d, J = 5 Hz, PCH₂), complex spectrum from δ 3.40-6.05 was not interpretable.

Anal. Calcd. for C₅H₁₀N₅O₃P: C, 27.39; H, 4.59; N, 31.95; P, 14.13; MW, 219. Found: C, 27.59; H, 4.50; N, 32.30; P, 14.27; MW, 219.

3,7-Diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (V).

Acetic anhydride (3.1 g., 0.03 mole) was added to a solution of I (1.57 g., 0.01 mole) in 20 ml. of water over 15 minutes at 0-5° while stirring. After aging for 20 minutes the solution was evaporated under vacuum. The crude material was recrystallized from acetone, yield, m.p.: 39%, 183°; ir (potassium bromide): 1615 (>C=O, t-amide), cm⁻¹, no P=O bonding; nmr (deuteriochloroform): δ 2.15 (s, CH₃), δ 3.05-6.05 (m. not interpretable).

Anal. Calcd. for C₉H₁₆N₃O₂P: C, 47.16; H, 7.04; N, 18.33; P, 13.51; MW, 229. Found: C, 47.35; H, 6.97; N, 18.13; P, 13.52; MW, 229.

3,7-Diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane 5-Oxide (VI).

The acetylation of II was carried out in an identical manner as described for the preparation of V, yield, m.p.: 41%, 236°; ir (potassium bromide): 1615 (>C=O, t-amide), 1190 (P=O) cm⁻¹; nmr (deuteriochloroform): δ 2.15 (s, CH₃), δ 3.77-5.9 (m. not interpretable).

Anal. Calcd. for C₉H₁₆N₃O₃P: C, 44.05; H, 6.57; N, 17.12; P, 12.64; MW, 245. Found: C, 44.10; H, 6.65; N, 17.43; P, 12.89; MW, 245.

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