sence of characteristic absorptions for primary or secondary amine function and the fact that the compound dissolved in strong hydrochloric acid and reprecipitated on basification led to the conclusion that the compound was a tertiary amine. The relatively high melting point, 186–187°, is indicative of a highly symmetrical condensed ring system.

Experimental

2,2-Dimethyl-3-hydroxypropionaldehyde.—The procedure originally described by Wessely[1] was slightly modified by treating formaldehyde and isobutyraldehyde in methanol solution using sodium hydroxide as catalyst. The product was not isolated, but used directly in the methanolic solution in the succeeding step to avoid dimer formation.[2]

13-Aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo-[7,3,1,0^{5,13}]tridecane (I).—An aliquot (0.2 mole) of the 2,2-dimethyl-3-hydroxypropionaldehyde solution was treated with 3.0 g. (0.05 mole) of 29% ammonium hydroxide and allowed to stand at ambient temperature for 4 hours. The solution was acidified to *p*H 4 with sulfuric acid and refluxed for 2 hours. A white crystalline precipitate which formed on evaporation of the methanol was removed by filtration and recrystallized from hot water to give 1.6 g. of 13-aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo[7,3,1,0^{5,13}]tridecane, m.p. 186–187°; infrared maxima: 7.27, 7.32 (*gem*-dimethyl system), 8.4, 8.8, 9.2, 9.5 μ (ether bands, particularly acetal bands).

Anal. Calcd. for $C_{15}H_{27}NO_3$: C, 66.91; H, 10.05; N, 5.20; mol. wt., 269; neut. equiv., 269. Found: C, 66.77; H, 10.00; N, 5.28; mol. wt., 275 ± 5 (Menzies–Wright method); neut. equiv., 270 (perchloric acid titration).

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Higher Aliphatic Alkylheptamethylpyrophosphoramides

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During an investigation of the higher aliphatic homologs of octamethylpyrophosphoramide, $(Me_2N)_2P(O)OP(O)(NMe_2)_2$, compounds were prepared wherein one of the methyl groups has been replaced by a higher aliphatic radical (octyl, dodecyl). The syntheses followed Schrader's method for Pestox III[2] wherein heating of a mixture of N,N,N′,N′-tetramethylphosphorodiamidic chloride, $(Me_2NO)_2POCl$, and ethyl N,N,N′,N′-tetramethylphosphorodiamidate, $(Me_2N)_2P(O)OEt$, with the concomitant loss of ethyl chloride resulted in the desired pyrophosphoramide. An N-octyl or N-dodecyl-N,-N′,N′-trimethylphosphorodiamidic chloride was used in place of the tetramethyl analog in these experiments.

Several new intermediates were prepared and characterized.

Support for the findings of Tolkmith[3] was afforded by the formation of high-boiling fractions, probably triphosphoramides, arising from partial decomposition of the pyrophosphoramides. The by-product of the octyl analog had nitrogen and phosphorus contents corresponding to a triphosphoramide containing 1.75 octyl groups.

Tests of the systemic toxicity of the substituted pyrophosphoramides described herein have been reported elsewhere.[4] The octyl and dodecyl homologs are less effective than the octamethyl derivative.

Experimental[5]

Preparation of the octyl compounds is given in detail; the dodecyl derivatives were prepared by similar procedures.

N-Octyl-N-methylphosphoramidic Dichloride (a).—N-Methyloctylamine hydrochloride (35 g., 0.2 mole) was heated under reflux with phosphoryl trichloride (92 g., 0.6 mole) for 36 hours, after which time excess of the latter was removed *in vacuo* and the product was obtained as a clear liquid, b.p. 118–120° at 1.0–1.5 mm., in 95% yield (48.5 g.).

Anal. Calcd. for $C_9H_{20}OPONCl_2$: Cl, 27.3. Found: Cl, 26.0.

N-Dodecyl-N-methylphosphoramidic dichloride: colorless liquid, b.p. 145–150° at 0.25 mm., obtained in 67–80% yields.

Anal. Calcd. for $C_{13}H_{28}PONCl_2$: Cl, 22.5. Found: Cl, 22.0.

N-Octyl-N,N′,N′-trimethylphosphorodiamidic Chloride (b).—Treatment of (a) (48.5 g., 0.18 mole) with two equivalents of dimethylamine (16.8 g., 0.37 mole) in benzene at 15° gave 36 g. (72%) of N-octyl-N,N′,N′-trimethylphosphorodiamidic chloride, $C_8H_{17}N(Me)P(NMe_2)(O)Cl$, b.p. 119° at 0.08 mm.

Anal. Calcd. for $C_{11}H_{26}PON_2Cl$: Cl, 13.25. Found: Cl, 13.6.

N-Dodecyl-N,N′,N′-trimethylphosphorodiamidic Chloride: colorless liquid, b.p. 148–50° at 0.07 mm., obtained in 69–81% yields.

Anal. Calcd. for $C_{15}H_{34}PON_2Cl$: Cl, 10.9. Found: Cl, 10.6.

Ethyl N,N,N′,N′-tetramethyl Phosphorodiamidate (c).—Ethyl phosphorodichloridate (116 g., 0.71 mole) was treated with four equivalents of dimethylamine (128 g., 2.85 moles) in benzene at 0°. After removal of solvent *in vacuo*, and dimethylamine hydrochloride by washing with water, the desired ester was obtained as a colorless liquid in 86% yield, 110 g., $n^{25}D$ 1.4355, b.p. 98–99° at 15 mm.

Anal. Calcd. for $C_6H_{17}PO_2N_2$: N, 15.6. Found: N, 15.4.

N-Octyl-N,N′,N′,N″,N″,N‴,N‴-heptamethylpyrophosphoramide.—A mixture of the acid chloride (b) (36 g., 0.13 mole) and the ester (c) (42 g., 0.23 mole) was refluxed for 44 hours in 100 ml. of xylene. After removal of solvent, a colorless, water-soluble liquid was obtained, $n^{24}D$ 1.4605, b.p. 120–180° at 0.005–0.75 mm., 31 g., 0.08 mole, 61% yield.

Anal. Calcd. for $C_{15}H_{38}P_2O_3N_4$: N, 14.6; P, 16.1. Found: N, 14.7; P, 15.6.

An unstable yellow oil, less soluble in water than the above product, also was obtained. *Anal.* Found: N, 12.7; P, 16.4.

N-Dodecyl-N,N′,N′,N″,N″,N‴,N‴-heptamethylpyrophosphoramide: colorless, water-soluble, surface-active liquid, b.p. 150–165° at 0.05 mm., obtained in 38–58% yields.

Anal. Calcd. for $C_{19}H_{46}N_4P_2O_3$: N, 12.7; P, 14.1. Found: N, 13.0; P, 15.3.

A higher-boiling (200° at 0.05 mm.) yellow, unstable, oily by-product, insoluble in water, was obtained. *Anal.* Found: N, 8.9; P, 12.1.

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