bonium ion which itself reacts with hydrazoic acid,[1] as was found to be the case in the reaction of pivalophenone[2]; rearrangement of the carbonium ion before reaction with hydrazoic acid[3]; or rearrangement of the original ketone in the reaction medium to an isomeric ketone.[4] A similar cleavage of tertiary carbonium ions is known to occur in the Beckmann rearrangement.[5,6]

When the Schmidt reaction was carried out in this Laboratory on α-methyl-α-ethylbutyrophenone, the products obtained were analogous to those obtained from pivalophenone.[2] Thus, products resulting from cleavage of a carbonium ion would include benzamide or benzonitrile, which could very likely be hydrolyzed in the reaction medium to benzoic acid and ammonia, as well as the ketimine hydrolysis products: methyl ethyl ketone, diethyl ketone, methylamine and ethylamine. Benzoic acid was isolated in 43% yield, and the above ketones and amines were also recovered.

Products related to either of the possible "normal" N-substituted amides were lacking unless the benzoic acid and the aniline, which was also found, arose from this source. However, there was no evidence for the corresponding tertiary alkyl amine, although α-methyl-α-ethylbutyric acid was most probably present in small quantity. Reaction of the benzoic acid with hydrazoic acid offers an alternative explanation for the formation of aniline.

If the carbonium ion had rearranged before further reaction, acetone and *n*-propylamine would be expected among the products.[3] However, there was no evidence that either of these was present.

Rearrangement of the original ketone by the mechanism recently proposed by Zook and Paviak[4] might lead to the formation of 3-ethyl-3-phenyl-2-pentanone or 4-methyl-4-phenyl-3-hexanone. However, the ketone which was recovered was identical with the starting material.

Experimental

Preparation of α-Methyl-α-ethylbutyrophenone.—Propiophenone (268 g.) in 250 ml. of dry benzene was refluxed five hours with sodamide (from 46 g. of sodium treated with 1000 ml. of liquid ammonia), ethyl bromide (220 g.) was added and stirring continued for 12 hours, following the general method of Haller and Bauer.[7] The product was washed with water, dried and fractionated to yield 240 g. of *sec*-butyl phenyl ketone, b.p. 105–110° at 10 mm. (lit. b.p. 107–109°[7]). The alkylation was repeated with sodamide and ethyl bromide to give 139 g. of a product boiling at 128.5–129° at 11 mm., $n^{24}\text{D}$ 1.5123.

Reaction with Hydrazoic Acid.—The ketone (0.1 mole) was dissolved in concentrated sulfuric acid at ice-bath temperature and sodium azide (0.27 mole) was added in small portions while stirring over three hours. The temperature was allowed to rise to 30–40° to maintain a moderate rate of gas evolution.

After complete addition, the acid solution was poured onto 150 g. of ice and the excess acid almost neutralized with sodium hydroxide. An insoluble oily layer was separated, and the water layer steam distilled. The steam distillate was combined with the oil, dried and the 7.5 g. of liquid was fractionated through a Todd column. Methyl ethyl ketone (1.6 g.) was collected at 77–80°; 2,4-dinitrophenylhydrazone m.p. 116–118°, mixed 117°. Diethyl ketone (0.6 g.) was collected at 98–101°; 2,4-dinitrophenylhydrazone m.p. 154–156°, mixed 154–155°. The stillpot residue was fractionated at 10 mm. 1.9 g. of an acid, probably α-methyl-α-ethylbutyric, was collected at 69–75° (α-methyl-α-ethylbutyric acid, b.p. 203–204° at 760 mm.[8]) but no derivative was formed. Unreacted α-methyl-α-ethylbutyrophenone (*ca.* 2.5 g.) was collected at 124–126°; oxime m.p. 119–121°, mixed 119–120°.

The aqueous acid layer was extracted with ether and the ether evaporated. Benzoic acid (4.6 g.) was obtained, m.p. 121–123°, mixed 122–123°; amide m.p. 130–131.5° (benzamide m.p. 130°).[9]

The aqueous layer was made basic and steam distilled into 12 *N* hydrochloric acid. The distillate was evaporated to dryness and yielded 11.5 g. of mixed amine hydrochlorides. The amines were separated by dissolving the hydrochlorides in the minimum volume of concentrated sodium hydroxide, and sweeping the liberated gases over magnesium sulfate and through a series of three traps by a slow air steam. The traps were immersed in (1) salt-ice, (2) carbon tetrachloride at its melting point, (3) Dry Ice–acetone. Concentrated hydrochloric acid was added to each trap and the hydrochloride solutions evaporated to dryness.

Trap 1 contained ethylamine, 1.6 g. as the hydrochloride, N-ethylbenzamide, m.p. 69–70° (lit. 71.5°).[9] Trap 2 contained methylamine, 0.7 g., as the hydrochloride, N-methyl-*p*-toluenesulfonamide, m.p. 72–74° (lit. 75°).[9] Trap 3 presumably contained ammonium chloride, 8.3 g.; it gave no Rimini amine test, and showed no melting or decomposition up to 300°. A non-volatile amine (2 g.) recovered from the surface of the caustic solution was aniline, b.p. 180–185°, N-phenylbenzenesulfonamide, m.p. 110–112° (lit. 112°[9]).

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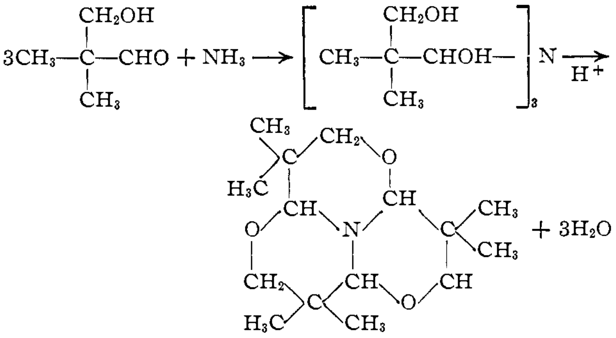
13-Aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo $[7,3,1,0^{5,13}]$tridecane

BY JOHN W. LYNN

RECEIVED JUNE 13, 1955

The reaction of 2,2-dimethyl-3-hydroxypropionaldehyde and ammonia followed by acid-catalyzed cyclodehydration gives rise to a novel heterocyclic condensed ring compound, 13-aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo$[7,3,1,0^{5,13}]$tridecane (I).



I

The structure described above has been assigned on the basis of molecular weight, equivalent weight, elemental analysis and infrared spectrum. The absence 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).

Acknowledgment.—The author is grateful to Mr. C. M. Lovell for infrared analyses and to Mr. Q. Quick for microanalyses.

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Higher Aliphatic Alkylheptamethylpyrophosphoramides

BY JOSEPH MATT AND H. J. HARWOOD[1]

RECEIVED JUNE 23, 1955

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 $C_9H_2OPONCl_2$: 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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