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## 3,3,6,6,9,9-Hexamethyldodecahydro-1,4,7,9b-tetraazaphenalene (I)

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The reaction of 2,2-dimethyl-3-hydroxypropanal and ammonia gives rise to the formation of a novel heterocycle, 3,3,6,6,9,9-hexamethyldodecahydro-1,4,7,9b-tetraazaphenalene (I). The structure shown for I has been assigned on the basis of molecular weight, elemental analysis, infrared spectrum, n.m.r. spectra, and the relationship to the following investigations.

From an investigation initiated by Wurtz (2) and furthered by Delepine (3), it was shown that crotonaldehyde reacts with ammonia to yield two isomeric tricrotonylidene tetramines (2,5,8-trimethyldodecahydro-1,4,7,9b-tetraazaphenalenes). Delepine (3b) accounted for the two isomeric structures by the relative spatial positions of the three methyl groups.

Lynn (4) reported the formation of 13-aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo [7,3,1,0<sup>5,13</sup>] tridecane (3,3,6,6,9,9-hexamethylhexahydro-2H,5H,8H-1,4,7-trioxa-9b-azaphenalene) from the reaction of 2,2-dimethyl-3-hydroxypropanal and ammonia followed by acid-catalyzed cyclodehydration.

By using a maximum temperature of 130° in the procedure for the formation of I, the authors have obtained small amounts of II. Compound II, however, is not a probable intermediate in the formation of I, as II when heated with ammonia, ammonium chloride, and calcium chloride at 160° does not yield I. The formation of I appears to be an isolated reaction as 2,2-dimethyl-3-hydroxybutanal fails to yield the corresponding tetraazaphenalene.

The infrared spectrum (5) of I shows the following significant maxima: 1372, 1350 (*gem*-dimethyl), 1172, 1133, 1081, 1042 (assigned to the N-C-N system), 3280 cm<sup>-1</sup> (N-H stretch, extremely weak). It is interesting to note the similarity between the infrared spectra of I and II. Lynn (4) reported the following maxima for II: 1376, 1366 (*gem*-dimethyl), 1190, 1136, 1087, 1053 cm<sup>-1</sup> (assigned to the O-C-N system). This

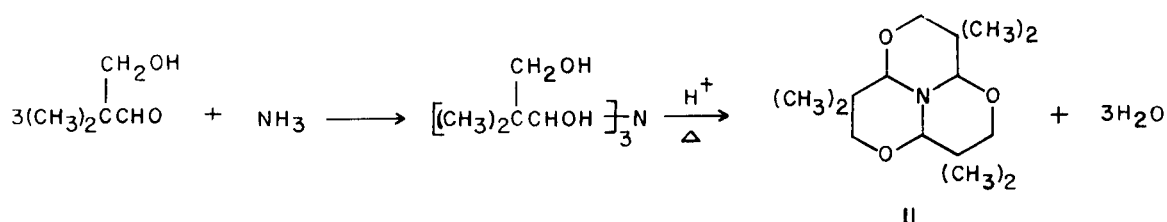
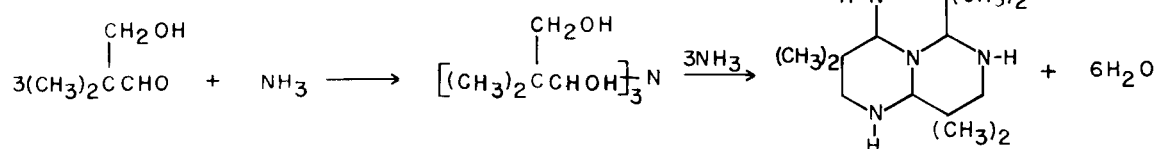
similarity is not unusual as Bergmann *et al.* (6) have stressed the similarity of the infrared spectra of five membered heterocycles which contain the X-C-Y system, where X and Y may be O, N, or S.

The n.m.r. spectra (7) of I, taken at 60 and 100 Mc., are in complete agreement with the structure shown. The compound shows two methyl peaks (0.79 and 0.92 p.p.m.) of equal intensity which can be shown (by comparing the 60 and 100 Mc.) to be peaks due to a chemical shift rather than a spin interaction which indicates two sets of non-equivalent methyl groups. With the total proton count taken as 30, the proton count is 18 for the two methyl peaks. A broad low intensity peak at about 1.1 p.p.m. was shown to be from exchangeable protons because this resonance disappears upon shaking the solution with deuterium oxide. Moreover, the quintet centered at about 2.4 p.p.m. has a chemical shift suitable for the secondary and tertiary protons indicated in I and shows a relative proton count of nine. These latter peaks show an obvious AB spin interaction pattern with another single resonance superimposed upon it. The AB system is an indication that the methylene protons are non-equivalent: this is to be expected after noting the non-equivalence of the *gem*-dimethyl groups (8). The peaks of the AB system show considerable sharpening after the secondary-amino protons were exchanged with deuterium indicating that these protons are probably slightly coupled with the amino protons.

### EXPERIMENTAL

2,2-Dimethyl-3-hydroxypropanal, b.p. 80-82° (4 mm.) (reported b.p. 78-85° (4 mm.)) was obtained in a 96% yield by the method of Hagemeyer (10).

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A pressure reaction apparatus (Parr Series 4500, medium pressure, stirrer type, 1000 ml. capacity) was charged with 81.5 g. (0.81 mole) of 2,2-dimethyl-3-hydroxypropanal, 16.1 g. of calcium chloride, and 4.0 g. of ammonium chloride. Anhydrous ammonia was introduced, with stirring, until a pressure of 85 p.s.i.g. was obtained. The contents of the bomb were heated to 160° (pressure at 790 p.s.i.g.) and this temperature was maintained for 6.5 hr. Air was bubbled through the mixture to expel dissolved ammonia and the mixture was then extracted with three 150 ml. portions of ether. The solid which was obtained by evaporation of the ether was recrystallized from 70% ethanol yielding 15.0 g. (21%) of the tetraazaphenalene, m.p. 160-161° (colorless needles).

*Anal.* Calcd. for  $C_{15}H_{10}N_4$ : C, 67.62; H, 11.35; N, 21.0; Mol. wt., 266. Found: C, 67.74; H, 11.35; N, 20.9 (micro Kjeldahl); mol. wt., 264 (modified Rast).

## REFERENCES

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(2) V. Wurtz, *Comp. rend.*, **88**, 940 (1897).

(3) (a) M. Delepine, *ibid.*, **144**, 1125 (1907); (b) M. Delepine, *ibid.*, **216**, 649 (1943); (c) M. Delepine, *ibid.*, **216**, 788 (1943).

(4) J. W. Lynn, *J. Am. Chem. Soc.*, **77**, 6067 (1955).

(5) The infrared spectrum was obtained as a 5-10% solution in carbon tetrachloride using a Perkin-Elmer Infracord, Model 137B.

(6) E. D. Bergmann, E. Zimkin and S. Pinchas, *Rec. trav. chim.*, **71**, 168 (1952).

(7) The authors are indebted to Mr. G. A. Pier of Varian Associates for the n.m.r. spectra and their interpretations. The n.m.r. resonances reported here are relative to an external sample of tetramethylsilane.

(8) The non-equivalence of the methyl groups and the methylene hydrogens is clearly shown by construction of the molecule with molecular models.

(9) The melting point is uncorrected.

(10) H. J. Hagemeyer, Jr., British Patent 834,100, Oct. 26, 1957; *Chem. Abstr.*, **52**, 3852b (1958).

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