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1,3-DIALKYL-5,5-DIMETHYLHEXAHYDROPYRIMIDINES

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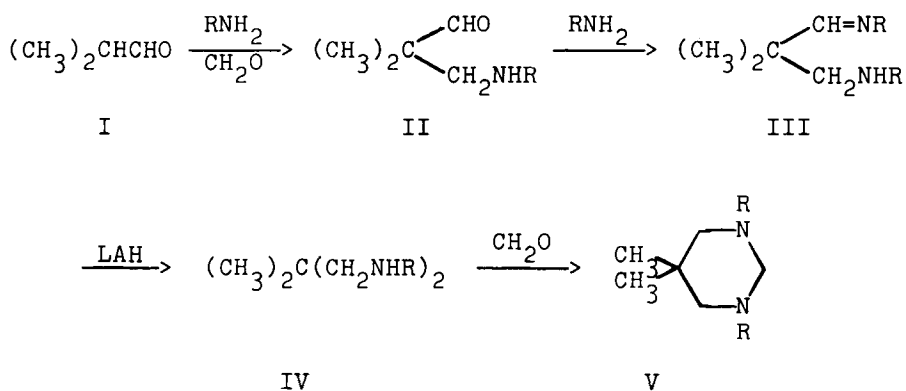
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1,3-DIALKYL-5,5-DIMETHYLHEXAHYDROPYRIMIDINES

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One of the simplest methods¹ of preparing hexahydro-
 pyrimidines consists in the reaction of primary nitro-
 paraffins with formaldehyde and primary amines in the molar
 ratio 1:3:2. The nitro group influences considerably the
 chemical properties of such compounds. In order to examine
 the analogous compounds without the nitro group, we obtained
 a number of hexahydropyrimidine derivatives of general formula
 V starting from isobutyraldehyde (I).

Infrared absorption spectra of compounds II-V substan-
 tiated their structures. Compounds II exhibited a strong
 band 1730-1725 cm⁻¹ and a weak one at 2700-2690 cm⁻¹, both
 typical for aldehydes. They also showed a band 3330-3315 cm⁻¹

of a secondary amino group. The Schiff's bases (III) were characterized by the presence of a strong absorption at 1670-1665 cm^{-1} , typical for C=N which disappeared after reduction to IV. Both groups of compounds III and IV had a strong absorption band near 3325-3300 cm^{-1} and 3300-3290 cm^{-1} respectively, typical for NH vibration. They disappeared in the spectra of V.

The sequence of reactions described above constitutes a novel and convenient method of preparation of derivatives of N,N'-dialkyl-1,3-propanediamine² and 1,3-dialkylhexahydro-pyrimidine.³

EXPERIMENTAL

α,α -Dimethyl- β -alkylaminopropionaldehydes (II) were prepared according to Mannich.⁴ The bp. and yields are given below.

<u>R</u>	<u>bp.</u>	<u>Yield</u>
CH ₃	50.5-51°/15 mm.	30%
C ₂ H ₅	56-57.5°/14-15 mm.	52%
CH(CH ₃) ₂	58.5-59°/9 mm.	59%
C(CH ₃) ₃	80.5-83°/20-21 mm.	19% ⁵

Preparation of Schiff's bases III. The aldehydes (II, 1 mole) were mixed with an alkylamine (5 moles) in the form of the pure base or as a 33% solution in ethanol, gently refluxed on water bath for 3 hrs (in the case of methylamine no warming was required), left overnight at room temperature, and dried over potassium carbonate. If the pure base was used, the reaction solution was first diluted with anhydrous ether and

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then dried. The solvent was evaporated and the oily product distilled under reduced pressure. The bp. and yield of products (III) are given below.

<u>R</u>	<u>bp.</u>	<u>Yield</u>
CH ₃	43-44.5°/15 mm.	47%
C ₂ H ₅	70.5-71°/23 mm.	59%
CH(CH ₃) ₂	70.5-71°/11 mm.	88%
C(CH ₃) ₃	88.5-91°/25-26 mm.	62%

N,N'-Dialkyl-2,2-dimethylpropane-1,3-diamines (IV). To a solution of lithium aluminum hydride (1.56 mole) in 300 ml. of anhydrous ether was added the Schiff's base (III, 1 mole) dissolved in 100 ml. of ether at such a rate so as to maintain a gentle reflux. Then the solution was refluxed for 1-1.5 hr and poured carefully into ice water. Aqueous 50% potassium hydroxide (100 ml.) was added to produce a homogeneous aqueous phase. The ethereal layer was separated and the aqueous layer extracted with ether. The ethereal extracts were dried over potassium carbonate and distilled.

R = CH₃, bp. 49-50°/14 mm., yield 37.5%.

Anal. Calcd. for C₇H₁₈N₂: C, 64.6; H, 13.8; N, 21.5.

Found: C, 64.8; H, 13.8; N, 21.4.

R = CH(CH₃)₂, bp. 73.5-74°/5 mm., yield 82%.

Anal. Calcd. for C₁₁H₂₆N₂: C, 71.0; H, 14.0; N, 15.05.

Found: C, 71.2; H, 13.9; N, 15.3.

R = C(CH₃)₃, bp. 95-97°/19 mm., yield 68%.

Anal. Calcd. for C₁₃H₃₀N₂: C, 72.8; H, 14.1; N, 13.1.

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Found: C, 72.8; H, 14.2; N, 13.2.

1,3-Dialkyl-5,5-dimethylhexahydropyrimidines (V). A mixture of 1 mole of N,N'-dialkyl-2,2-dimethylpropane-1,3-diamine(IV) and 82.5 ml. of aqu. 40% formaldehyde (1.1 mole) was allowed to stand 8-16 hours at room temperature. The product was extracted with ether, the extract dried over magnesium sulfate and distilled.

R = CH₃, bp. 56-57°/26 mm., yield 38%.

Anal. Calcd. for C₈H₁₈N₂: C, 67.5; H, 12.7; N, 19.7

Found: C, 67.7; H, 12.7; N, 20.0.

R = C₂H₅, bp. 72-73°/17 mm., yield 68%.

Anal. Calcd. for C₁₀H₂₂N₂: C, 70.7; H, 12.9; N, 16.45.

Found: C, 70.6; H, 13.1; N, 16.65.

R = CH(CH₃)₂, bp. 86-87°/5 mm., yield 74%.

Anal. Calcd. for C₁₂H₂₆N₂: C, 72.75; H, 13.1; N, 14.1.

Found: C, 72.7; H, 13.4; N, 14.3.

R = C(CH₃)₃, bp. 105-107°/19 mm., yield 84%.

Anal. Calcd. for C₁₄H₃₀N₂: C, 74.4; H, 13.25; N, 12.4.

Found: C, 74.5; H, 13.65; N, 12.6.

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5. The yield was lowered by a side reaction which gave the Schiff's base from (II) and the unreacted amine.

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