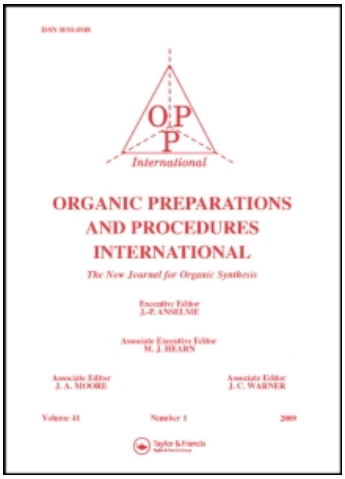

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1,3-DIALKYL-5,5-DIMETHYLHEXAHYDROPYRIMIDINES

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1,3-DIALKYL-5,5-DIMETHYLHEXAHYDROPYRIMIDINES

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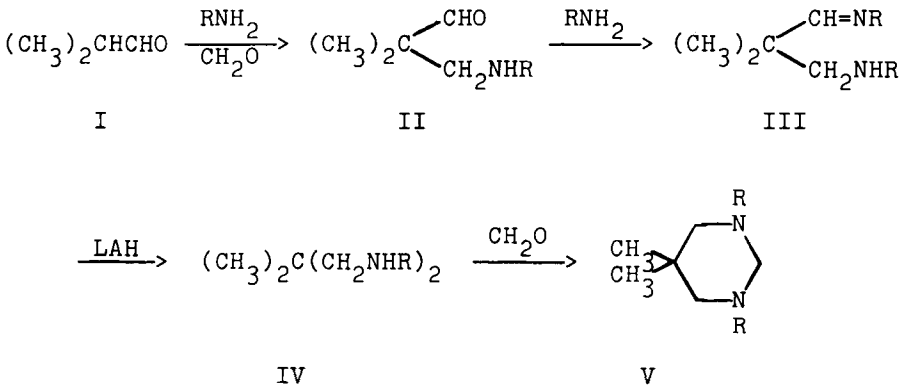

I II III IV V

One of the simplest methods[1] of preparing hexahydropyrimidines consists in the reaction of primary nitroparaffins 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 substantiated 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-propanediamine[2] and 1,3-dialkylhexahydropyrimidine.[3]

EXPERIMENTAL

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

R	bp.	Yield
CH_3	50.5-51°/15 mm.	30%
C_2H_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

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

R	bp.	Yield
CH_3	43-44.5°/15 mm.	47%
C_2H_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 = CH_3, bp. 49-50°/14 mm., yield 37.5%.

Anal. Calcd. for $C_7H_{18}N_2$: C, 64.6; H, 13.8; N, 21.5.
Found: C, 64.8; H, 13.8; N, 21.4.

R = $CH(CH_3)_2$, bp. 73.5-74°/5 mm., yield 82%.

Anal. Calcd. for $C_{11}H_{26}N_2$: C, 71.0; H, 14.0; N, 15.05.
Found: C, 71.2; H, 13.9; N, 15.3.

R = $C(CH_3)_3$, bp. 95-97°/19 mm., yield 68%.

Anal. Calcd. for $C_{13}H_{30}N_2$: C, 72.8; H, 14.1; N, 13.1.

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 = CH_3, bp. 56-57°/26 mm., yield 38%.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.5; H, 12.7; N, 19.7
Found: C, 67.7; H, 12.7; N, 20.0.

R = C_2H_5, bp. 72-73°/17 mm., yield 68%.

Anal. Calcd. for $C_{10}H_{22}N_2$: C, 70.7; H, 12.9; N, 16.45.
Found: C, 70.6; H, 13.1; N, 16.65.

R = $CH(CH_3)_2$, bp. 86-87°/5 mm., yield 74%.

Anal. Calcd. for $C_{12}H_{26}N_2$: C, 72.75; H, 13.1; N, 14.1.
Found: C, 72.7; H, 13.4; N, 14.3.

R = $C(CH_3)_3$, bp. 105-107°/19 mm., yield 84%.

Anal. Calcd. for $C_{14}H_{30}N_2$: 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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