the solvent was distilled off under reduced pressure and the residue was distilled in vacuum.

The IR spectra were recorded by I. Ya. Evtushenko on a UR-10 double-beam spectrophotometer in the 670–2400 cm^{-1} region with NaCl and LiF prisms in the form of the pure liquids.

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Chernyshevskii Saratov
State University

INVESTIGATIONS IN THE FIELD OF 1-AZA BICYCLIC COMPOUNDS

VIII. The Catalytic Reduction of 5-(β-Cyanoethyl)-1,2-dihydropyrrolizines*

A. A. Ponomarev and V. M. Levin

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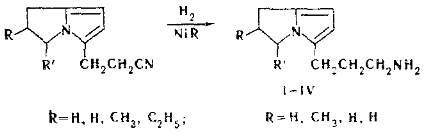
1,2-Dihydropyrrolizin-5-ylpropylamines have been obtained by the reduction of 5-(β-cyanoethyl)-1,2-dihydropyrrolizines on Raney nickel. Some properties of the amines obtained and of their acetyl derivatives have been studied and their IR spectra have been recorded.

One of the well-studied methods of obtaining primary amines is the reduction of nitriles on Raney nickel catalysts [2–4].

We have performed the reduction of 5-(β-cyanoethyl)-1,2-dihydropyrrolizines on Raney nickel in methanol saturated with ammonia at 80–90° C with a hydrogen pressure of 100–120 atm. The yields of amines amounted to 80–85%.



In this way we have obtained: 1,2-dihydropyrrolizin-5-ylpropylamine (I), (3-methyl-1,2-dihydropyrrolizin-5-yl)propylamine (II), (2-methyl-1,2-dihydropyrrolizin-5-yl)propylamine (III), and (2-ethyl-1,2-dihydropyrrolizin-5-yl)propylamine (IV).

The acetyl derivatives of compounds I–IV were obtained: N-(1,2-dihydropyrrolizin-5-ylpropyl)acet-

1,2-Dihydropyrrolizin-5-ylpropylamines and Their Acetyl Derivatives

Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %			Calculated, %			Yield, %
				found	calculated		C	H	N	C	H	N	
I	124—125 (3)	1.0218	1.5385	50.32	50.41	$C_{10}H_{16}N_2$	73.41 73.36	10.19 10.29	16.85 16.89	73.13	9.81	17.05	80
II	110—111 (1)	1.0030	1.5308	54.97	55.03	$C_{11}H_{18}N_2$	74.10 74.20	10.19 9.73	15.38 15.46	74.16	10.12	15.71	81
III	120—121 (2)	0.9946	1.5273	55.13	55.03	$C_{11}H_{18}N_2$	74.16 74.15	10.34 10.33	15.61 15.80	74.16	10.12	15.71	83
IV	132—133 (2)	0.9847	1.5225	59.61	59.64	$C_{12}H_{20}N_2$	75.16 74.92	10.62 10.73	14.30 14.48	74.95	10.48	14.56	85
V	196—197 (3)	1.0883	1.5410	59.59	59.83	$C_{12}H_{18}N_2O$	69.38 69.38	8.74 8.38	13.46 13.52	69.87	8.79	13.58	50
VI	178—179 (3)	1.0569	1.5330	64.67	64.45	$C_{13}H_{20}N_2O$	70.59 70.62	9.15 9.32	12.63 12.75	70.88	9.15	12.72	58
VII	194—195 (3)	1.0572	1.5305	64.62	64.45	$C_{13}H_{20}N_2O$	70.61 71.26	9.53 9.65	12.53 12.81	70.88	9.15	12.72	59
VIII	194—195 (2)	1.0450	1.5267	68.89	69.07	$C_{14}H_{22}N_2O$	71.75 72.04	9.70 9.60	11.86 12.06	71.75	9.46	11.95	53

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*For part VII, see [1].

amide (V), N-(3-methyl-1,2-dihydropyrrolizin-5-ylpropyl)acetamide (VI), N-(2-methyl-1,2-dihydropyrrolizin-5-ylpropyl)acetamide (VII), and N-(2-ethyl-1,2-dihydropyrrolizin-5-ylpropyl)acetamide (VIII). Information on compounds I–VIII, obtained for the first time, is given in the table.

The IR spectra of the amines I–IV show absorption bands associated with the stretching vibrations of a primary NH_2 at 3265 cm^{-1} ($\nu_{NH_2}^{sym}$) and 3365 cm^{-1} ($\nu_{NH_2}^{as}$). The IR spectra of compounds V–VIII are characterized by a strong absorption band at 1655 cm^{-1} (C=O). Compounds I–VIII have strong absorption bands in the 1270–1300 cm^{-1} region probably relating to the C—N stretching vibrations of the 1,2-dihydropyrrolizine ring.

EXPERIMENTAL

1,2-Dihydropyrrolizin-5-ylpropylamine (I). A mixture of 21 g (0.131 mole) of 5-(2-cyanoethyl)-1,2-dihydropyrrolizine, 49 ml of methanol saturated with ammonia, and 5 g of Raney nickel was charged into a 250-ml rotating autoclave. The reaction was carried out at 80–90° C with a hydrogen pressure in the autoclave of 100–120 atm. The calculated amount of hydrogen was absorbed in 1 hr. Then the catalyst was filtered off, the methanol was driven off on the water bath under reduced pressure, and the residue was distilled in vacuum. Compounds II–IV were obtained similarly; they consisted of colorless liquids turning yellow on standing. Compounds V–VIII were obtained by a published method [5].

The IR spectra were taken on a UR-10 double-beam spectrophotometer in the 700–4000 cm^{-1} region. The substances were recorded in the form of the pure liquids as a capillary-thin layer between plates of NaCl.

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Chernyshevskii Saratov
State University

INDOLES

V. The Question of the Role of Enamines in the Fischer Reaction*

I. I. Grandberg and N. M. Przheval'skii

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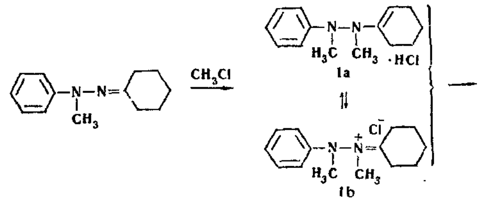
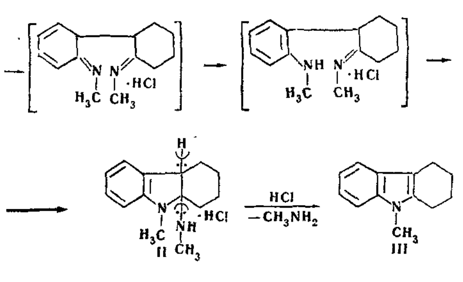
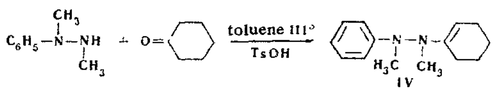
It has been found that the enamine obtained from N,N'-dimethylphenylhydrazine and cyclohexanone under the conditions of the Fischer reaction rearranges into N-methyl-1,2,3,4-tetrahydrocarbazole with the liberation of methylamine.

Previously, in a study of the preparation of tryptamines from arylhydrazines and γ-halogenocarbonyl compounds [2, 3] and of the rearrangement of arylhydrazones into indoles under the action of alkylating agents [4] we put forward a hypothesis concerning the probable mechanisms of the process:





In order to confirm this hypothesis, we have carried out the synthesis of the enamine IV from N,N'-dimethylphenylhydrazine and cyclohexanone:



The protonation of IV must form a quaternary salt of the type of Ia or Ib with subsequent rearrangement into N-methyl-1,2,3,4-tetrahydrocarbazole (III). In

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*For part IV, see [1].