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} ($\nu^{sym}_{NH_2}$) and 3365 cm^{-1} ($\nu^{as}_{NH_2}$). 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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INDOLES

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

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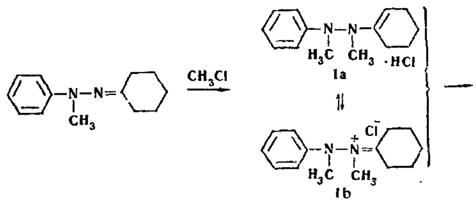
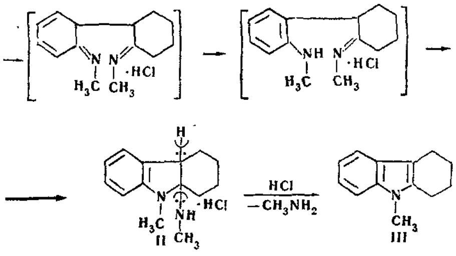
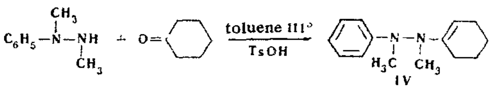
It has been found that the enamine obtained from N,N'-dimethylphenylhydrazine and cyclohexanone under the conditions of the Fischer reaction rearranges into N-methyl-1,2,3,4-tetrahydrocarbazole with the liberation of methylamine.

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].

actual fact, when the enamine **IV** was heated in benzene in a current of dry HCl a rearrangement took place as a result of which we obtained **III** and methylamine hydrochloride.

The enamine **IV** is extremely unstable and has somewhat unusual physicochemical characteristics, probably due to the elongated chain of conjugation of the aromatic sextet with the π-electrons of the double bond, with the participation of the free pairs of both nitrogen atoms. The maximum in the UV region of absorption is shifted strongly in the long-wave direction and is extremely strong (λ_{max} 277 nm; log ε 3.93). In the IR spectrum* of compound **IV** (Fig. 1), both in CCl_4 solution (c 0.02 M; d 0.25 mm) and in a liquid film there is a strong band at 1712 cm^{-1}.

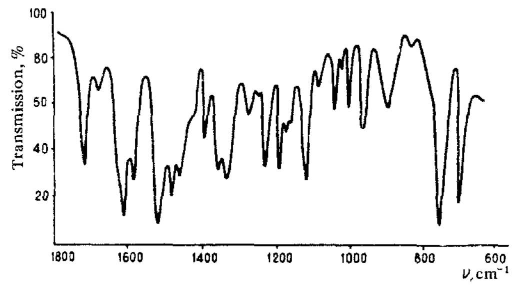

Fig. 1. IR spectrum of N,N'-dimethylphenylhydrazinocyclohex-1-ene (liquid film).

In the PMR spectrum (Fig. 2) (INM-3H-60) taken in CCl_4 with tetramethylsilane as internal standard there are: a multiplet of the phenyl protons with the center at 7.55 ppm, a strongly distorted triplet (center at 6.1 ppm) of a proton on a double bond, single signals of methyl groups on the nitrogen atoms (α, 3.48 ppm; β, 3.10 ppm) and highly diffuse peaks of the methylene protons of the cyclohexene nucleus in the 2.0–1.4 ppm region.

EXPERIMENTAL

N,N'-Dimethylphenylhydrazine was obtained by Harries' method [5]. Bp 88–90° C (6 mm); n_D^{20} 1.5612.

N,N'-Dimethylphenylhydrazinocyclohex-1-ene (IV). A flask with a Dean and Stark trap and a reflux condenser was charged with 3.2 g (0.02 mole) of N,N'-dimethylphenylhydrazine and 1.94 g (0.02 mole) of cyclohexanone. Dry toluene in an amount equal to the volume of the trap and 0.05 g of p-toluenesulfonic acid were added and the mixture was boiled with the removal of water by distillation for 17 hr. Then vacuum distillation yielded 3.4 g (80%) of a light yellow oil. Bp 152–154° C (8 mm); n_D^{20} 1.5640. Found, %: C 77.25, 77.38; H 8.55, 8.92. Calculated for $C_{14}H_{20}N_2$, %: C 77.73; H 9.25. It was chromatographed on "fast" type paper of the Volodarskii mill impregnated with dimethylformamide using benzene as the solvent system. R_f 0.73. The spot was revealed with Ehrlich's reagent.

N-Methyl-1,2,3,4-tetrahydrocarbazole (III). A two-necked flask fitted with a reflux condenser was charged with a solution of 2.1 g (0.011 mole) of the enamine **IV** in 20 ml of dry benzene and this was heated to the boil. Then a gentle current of dry hydrogen chloride was passed through the reaction mixture for 10 min. The benzene solution was separated from the methylamine hydrochloride that had deposited (after recrystallization from ethanol, mp 225° C) and was evaporated in vacuum. The residue was treated with petroleum ether, which gave 1 g (55%) of colorless crystals with mp 51° C (from petroleum ether). A mixture with authentic N-methyl-1,2,3,4-tetrahydrocarbazole gave no depression of the melting point. The substance was chromatographed on "fast" type paper of the Volodarskii mill in the butanol–acetic acid–water (4 : 1 : 5) system. R_f 0.89 (dirty blue spot), which agrees with the R_f value of an authentic sample of **III**. The spots were revealed with Ehrlich's reagent.

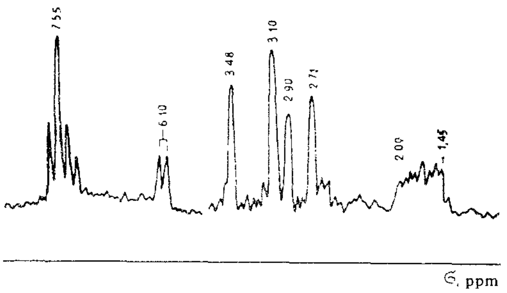

Fig. 2. NMR spectrum of N,N'-dimethylphenylhydrazinocyclohex-1-ene.

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*The IR spectra were recorded on a Jasco IR-S double-beam infrared spectrometer with an NaCl prism.