evolved is trapped with Nessler's reagent. After the end of the period, the solvent is removed and the remaining product washed with ether and acetone. The ether is removed from the ether extract and the reaction product is recrystallized from a mixture of ethanol and benzene to give 5-nitroaminotetrazole. T_{mp} 139°C (with explosion). According to [1], T_{mp} is about 140°C. The UV spectrum of the compound isolated is identical with the UV spectrum of 5-nitroaminotetrazole [2]. After the washing with ether and acetone, the diammonium salt of 5-nitroaminotetrazole is left. T_{mp} 219-220°C. According to [1], T_{mp} is 220-221°C. Found: N 68.0%. Calculated for $CH_8N_8O_2$, N 68.3%.

Decomposition of Nitroguanylazide in Alcoholic Solutions. A solution of 0.5-1.0 g of (4-8 mmoles) nitroguanylazide in alcohol is heated in a flask under reflux at a given temperature (see Table 2) for 2 h. The solvent is then removed and the crystalline product remaining washed in 15 ml of 25% ammonia. After the removal of the water, the product is washed with acetone, dried and weighed. The product is the diammonium salt of 5-nitroaminotetrazole with T_{mp} 219-220°C. Found: N 68.3%. Calculated from $CH_8N_8O_2$: N 68.3%. The amount of nitroguanylazide having decomposed was calculated from the yield of the diammonium salt of 5-nitroaminotetrazole.

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NEW 2,2,6,6-TETRASUBSTITUTED 4-PIPERIDONES

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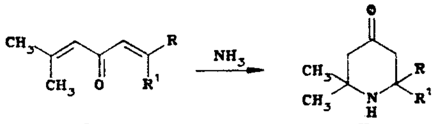
Heterocyclization of tetrasubstituted divinyl ketones formed during the condensation of mesityl oxide with aromatic ketones by the action of ammonia leads to new 2,2-disubstituted 6,6-dimentyl-4-piperidones.

A large number of papers [1] have been devoted to the synthesis of 2,2,6,6-tetramethyl-4-piperidone (triacetoneamine) and its different derivatives, but despite the increasing interest in the chemistry of sterically hindered piperidines, practically no information is available on the change in the nature of the substitution at the carbon atoms bound to nitrogen. There are data only on the preparation of 6,6-dimethyl-4-piperidone-2-spirocycloalkanes in the reaction of diacetoneamine with cyclopentanone and cyclohexanone [2].

We showed that the previously unreported 2,2,6,6-tetrasubstituted 4-piperidones (IIa-c) containing, in their structures, aromatic and heterocyclic radicals as well as methyl groups can be obtained by heterocyclization of divinyl ketones (Ia-c) by the action of ammonia: the divinyl ketones in their turn are formed by mixed condensation of mesityl oxide with aromatic ketones in the presence of N-ethylanilinomagnesium bromide [3].



I a-c II a-c

I, II a $R=CH_3$, $R^1=C_6H_5$; b $R=CH_3$, $R^1=$2-thienyl; c $R=R^1=C_6H_5$

The composition and the structure of piperidones IIa-c were confirmed by data of elemental analysis, and IR and PMR spectroscopy. In the IR spectra of these compounds in mineral

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oil, the stretching vibrations of the N–H bond appear in the form of two absorption bands at 3590 and 3330-3340 cm^{-1}, while the stretching vibrations of the C=O group, as in unsubstituted cyclohexanone, appear in the form of an intense band at 1710-1715 cm^{-1}.

In the PMR spectrum of piperidone IIc, the aliphatic protons appear in the form of three peaks, which correspond to the methyl α- and α'-methylene protons, which is the result of rapid conversion between the conformers. The presence of a chiral center in piperidones IIa, b results in a specific character in their PMR spectra, in contrast to the achiral piperidone IIc, since the protons of the two methylene groups, as well 6-CH_3, become diastereotopic. This should lead to the appearance of three singlets of the methyl groups and two quartets of the AB system of the methylene groups in the PMR spectra of the chiral piperidones IIa, b. However, in fact, only the protons of themethylene group neighboring with the chiral carbon (position 3) have different chemical shifts and appear in the spectra of compounds IIa, b in the form of quartets (J = 14 Hz) with centers at 2.81 and 2.75 ppm, respectively. The signal of the methylene group (position 5) at a distance from the chiral center has the form of a singlet. In assigning the signals of the methyl groups, the data in [4] are taken into account, according to which the strong-field singlets at 0.65 and 0.86 ppm in piperidones IIa, b should be assigned to axial groups at $C_{(6)}$, located in the screening region of the phenyl or 2-thienyl substituents, also occupying the axial position. The protons of the methyl group at $C_{(2)}$ are descreened (1.47 and 1.56 ppm for compounds IIa, b, respectively), since they lie about the edge of the aromatic substituent. The singlets at 1.60, 1.65, and 1.96 ppm in the spectra of compounds IIa-c disappear after deuteration, which confirms their assignment to the NH group protons.

With regard to the properties of the tetramethyl-substituted piperidines, it can be assumed that compounds IIa-c will find wide application in organic synthesis, in particular in the preparation of stable nitroxyl radicals.

EXPERIMENTAL

The IR spectra were run in mineral oil on a UR-20 spectrophotometer. The PMR spectra were recorded in $CDCl_3$ on a Varian EM-390 spectrometer (90 MHz) using TMS as internal standard The course of the reaction and the purity of the compounds obtained were monitored by TLC on Silufol UV-254 plates in chloroform, with development in iodine vapors.

2,6,6-Trimethyl-2-phenyl-4-piperidone (IIa). A 10-g portion (0.05 mole) of dienone Ia, 50 ml of ethanol, and 17 g (1 mole) of liquid ammonia are placed in a 300 ml steel autoclave. The reaction mixture is heated with periodic shaking on a boiling water bath for 8 h, and then distilled in vacuo and chromatographed on silica gel column using chloroform as eluent. First unreacted dienone Ia emerges from the column (TLC control), and then piperidone IIa. Yield 32%, mp 44°C (from pentane). IR spectrum: 3330, 3590 (ν_{NH}), 1715 cm^{-1} (ν_{CO}). PMR spectrum: 0.65 and 1.25 (s, 6-CH_3); 1.47 (s, 2-CH_3); 1.60 (s, NH); 2.23 (s, 5-H); 2.81 (q, 3-H); 7.30 ppm (m, C_4H_5). Found: C 77.7, H 8.7%. $C_{14}H_{19}NO$. Calculated: C 77.4, H 8.8%.

2,6,6-Trimethyl-2-(2-thienyl)-4-piperidone (IIb), yield 28% mp 68°C. IR spectrum: 3340, 3590 (ν_{NH}), 1710 cm^{-1} (ν_{CO}). PMR spectrum: 0.86 and 1.21 (s, 6-CH_3), 1.56 (s, 2-CH_3), 1.65 (s, NH), 2.24 (s, 5-H), 2.75 (q, 3-H), 6.95 ppm (m, C_4H_3S). Found: C 64.6, H 7.9%. $C_{12}H_{17}NOS$. Calculated: C 64.5, H 7.7%, and 6,6-dimethyl 2,2-diphenyl-4-piperidone (IIc) yield 18%, mp 98°C. IR spectrum: 3335 and 3590 (ν_{NH}), 1715 cm^{-1} (ν_{CO}). PMR spectrum: 0.94 (s, 6-CH_3), 1.96 (s, NH), 2.27 (s, 5-H), 3.03 (s, 3-H), 7.20 ppm (m, C_4H_5). Found: C 81.14, H 7.5%. $C_{13}H_{21}NO$. Calculated: C 81.7, H 7.6% are obtained similarly.

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