CONCLUSIONS

Employing dyanmic NMR, it was shown that the Z,E-isomerization of α-β-arylaminoacrylic esters in nitrobenzene and o-dichlorobenzene is accomplished by the thermal mechanism of rotation around the C=C bond.

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PARAMAGNETIC DERIVATIVES OF 1,6-NAPHTHYRIDINE

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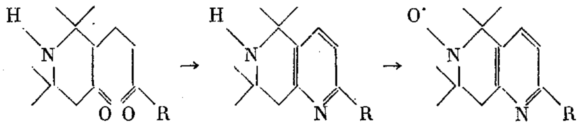
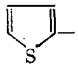
The synthesis of 2,2,6,6-tetramethylpiperidine derivatives substituted in the 3 position, and of the corresponding nitroxyl radicals, is hindered by the steric shielding of the reaction center. For this reason, despite the great interest in such compounds, the methods for their synthesis are restricted. Only several examples exist on the preparation of the 2-substituted triacetoneamine derivatives and the corresponding stable radicals [1-3]. The 1,5-diketones of the 2,2,6,6-tetramethylpiperidine series, described by us previously [3], offer wide possibilities for obtaining paramagnetic compounds of variable structure. The present paper is devoted to obtaining some paramagnetic 1,6-naphthyridines.

1,6-Naphthyridines (IIa-d) were obtained in 80-90% yield by refluxing the hydrochlorides of 1,5-diketones (Ia-d) with $HONH_2 \cdot HCl$. The synthesis is successful only if the hydrochlorides of the diketones are used at pH 1-2. The oxidation of compounds (IIa-d) with excess H_2O_2 in the presence of sodium tungstate for 3 days at room temperature gives the paramagnetic 1,6-naphthyridines (IIIa-d) as the end reaction products.



(I) (II) (III)

$R = C_6H_5$ (a), —(b), $C_6H_5CH=CH$ (c), p-$CH_3OC_6H_4$ (d)

The structure of the obtained compounds was confirmed by the IR, EPR, and mass spectral data. The spectra of compounds (IIa-c) have four bands of aromatic absorption (benzene and pyridine rings) in the 1600-1500 cm^{-1} region. In the spectrum of (IId) these bands are shifted toward higher frequencies, which is characteristic for 1,4-disubstituted benzene derivatives. Absorption at 1400 cm^{-1} (thiophene ring) is observed in the spectrum of (IId). The exocyclic double bond of (IIc) appears in the spectrum as a weak band at 1630 cm^{-1}.

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TABLE 1. Peaks of Characteristic Ions in Mass Spectra of (IIIa-d)*

(IIIa)		(III b)		(III c)		(III d)	
m/e	I	*m/e*	*I*	*m/e*	*I*	*m/e*	*I*
282 ($C_{18}H_{22}N_2O$)	4,4	288	4,3	308	8,4	312	8,0
281 ($C_{18}H_{21}N_2O$)	29,7	287	29,7	307	61,5	311	38,8
						310	2,8
267 ($C_{17}H_{19}N_2O$)	2,0	273	5,1	294	7,0	297	4,6
266 ($C_{17}H_{18}N_2O$)	1,5	272	2,3	293	3,5	296	4,0
				292	2,1		
252 ($C_{17}H_{21}N$)	4,9	258	10,1	278	13,3	282	9,7
251 ($C_{18}H_{21}N$)	42,4	257	61,6	277	75,5	281	28,5
251 ($C_{16}H_{15}N_2O$)	1,5						
250 ($C_{18}H_{20}N$)	33,2	256	41,3	276	40,5	280	27,4
237 ($C_{16}H_{17}N_2$)	18,0	243	24,6	263	18,2	267	30,8
236 ($C_{16}H_{16}N_2$)	100	242	100	262	100	266	100
235 ($C_{17}H_{17}N$)	5,4	241	5,1	261	6,3	265	5,1
		240	9,4	260	7,7	264	5,7
222 ($C_{16}H_{16}N$)	2,9	228	5,1	248	4,2	252	2,3
221 ($C_{16}H_{15}N$)	4,4	227	7,8	247	4,9	251	4,6
220 ($C_{16}H_{14}N$)	14,6	226	18,1	246	14,0	250	6,3
219 ($C_{16}H_{13}N$)	1,9					249	8,6
		216	18,1	236	5,6		
209 ($C_{15}H_{15}N$)	9,7	215	34,0	235	10,5	239	3,4
208 ($C_{15}H_{14}N$)	21,5	214	6,5	234	19,6	238	9,7
207 ($C_{15}H_{13}N$)	3,9	213	13,0	233	4,9	237	16
206 ($C_{15}H_{12}N$)	9,3			232	8,4	236	4,5
194 ($C_{14}H_{12}N$)	8,3	200	12,3	220	7,0	224	1,7
193 ($C_{14}H_{11}N$)	6,8	199	9,4	219	2,3	223	5,1

*The I values are given in % of I_{max}.

The absorption of the NH group (3340 cm^{-1}) appears only at a high concentration of the specimen. The spectra of all of the compounds have a band at 830 cm^{-1} (pyridine ring). In this region the spectra of (IIa) and (IIc) have strong absorption at 700 and 750 cm^{-1} (monosubstituted benzene ring). Oxidation has little effect on the IR spectra of compounds (IIa-d). The absorption of the N–O group (1300-1200 cm^{-1}) cannot be isolated, since it is masked by the absorption of the other groups in this region.

The mass spectral data for naphthyridines (IIIa-d), given in Table 1, show that the character of the decomposition of (IIIa-d) under electron impact is practically the same. In view of this we will discuss below only the fragmentation of (IIIa), for which the high-resolution mass spectrum was obtained. An intense peak of M^+ with m/e 281 is observed in the spectrum of (IIIa). The decomposition of this ion is realized via the successive elimination of the CH_3 and OCH_2 groups to give the ion with m/e 236, whose peak has the highest intensity in the mass spectrum. The M^+ ion also decomposes with the elimination of the NO group to give the ion with m/e 251 and composition $C_{18}H_{21}N$. The possible paths for the fragmentation of (IIIa) are shown in the following scheme:

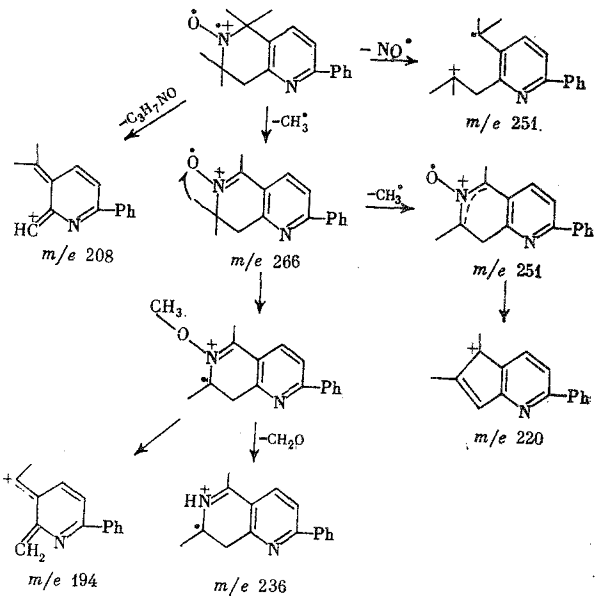

TABLE 2. Characterization of Compounds (II) and (III)

Compound	Yield, %	MP, °C	Empirical formula	N $\frac{\text{Found}}{\text{Calculated}}$, %
(IIa)	77	91	$C_{18}H_{22}N_2$	$\frac{10,48}{10,51}$
(IIb)	90	114	$C_{16}H_{20}N_2S$	$\frac{10,17}{10,28}$
(IIc)	95	150	$C_{20}H_{24}N_2$	$\frac{9,08}{9,57}$
(IId)	97	106	$C_{19}H_{24}N_2O$	$\frac{9,47}{9,45}$
(IIIa)	76	113	$C_{18}H_{21}N_2O$	$\frac{9,49}{9,43}$
(IIIb)	93	123	$C_{16}H_{19}N_2OS$	$\frac{9,59}{9,68}$
(IIIc)	95	146	$C_{20}H_{23}N_2O$	$\frac{8,83}{8,82}$
(IIId)	87	130	$C_{19}H_{23}N_2O_2$	$\frac{8,60}{8,55}$

The mass spectrum of (IIIa) also has the peak of the ion $(M + H)^+$ with m/e 282. This ion decomposes by the elimination of CH_3 and NOH groups. It should be mentioned that the form of the mass spectrum changes radically when the (IIIa) sample is heated for a long time in the admittance system of the apparatus. Here the peak of the $(M + H - CH_3)$ ion with m/e 267 becomes predominant, which decomposes with the elimination of NOH groups, as well as of CH_3 and OH groups.

The EPR spectra of benzene solutions of compounds (IIIa–d) represent a triplet of lines of equal intensity, which is characteristic for radicals of this type, with a splitting of 15.6 Oe between the components. The yield, properties, and elemental analysis data for the obtained compounds are given in Table 2.

EXPERIMENTAL

The EPR spectra were measured on an EPR-B instrument, the IR spectra were taken on a Specord HIR spectrometer, and the mass spectra were recorded on RMU-6D and MS-902 instruments, using the DS-30 system (British) to process the data.

Preparation of (II) Compounds. To 0.01 mole of the diketone (I) was added 10% HCl solution to pH 1 and the mixture was evaporated in a rotor evaporator to dryness. The dry residue was dissolved in 20 ml of alcohol, 0.02 mole of $NH_2OH \cdot HCl$ was added, and the mixture was refluxed for 4 h. Then the alcohol was distilled off, and the residue was dissolved in water and made alkaline with K_2CO_3. The (II) precipitate was filtered, washed with water, and recrystallized from heptane.

Preparation of (III) Compounds. To a solution of 0.005 mole of (II) in 10 ml of methanol were added 2 ml of 30% H_2O_2, 0.1 g of Trilon B, and 0.1 g of Na_2WO_4, and the mixture was kept in the dark for several days. The end of reaction was determined chromatographically. The oxidation of compounds (IIa), (IIc), and (IId) is complete in 3 days, while that of (IIb) takes 12-13 days. The reaction products that crystallize from the reaction mixture were recrystallized from heptane.

CONCLUSIONS

Some stable nitroxyl radicals of the 2,2,6,6-tetramethylpiperidine series, namely 2-aryl(heteryl)-5-oxyl-5,5,7,7-tetramethyl-5,6,7,8-tetrahydro-1,6-naphthyridines, were obtained.

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