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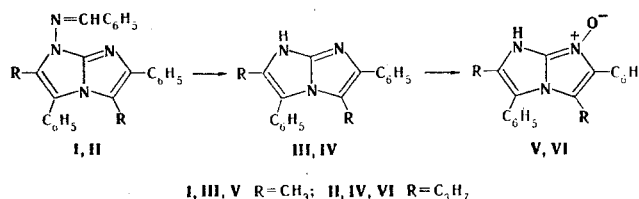
## SYNTHESIS AND INVESTIGATION OF IMIDAZO[1,2-a]IMIDAZOLE DERIVATIVES

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The reduction of 1-benzylideneamino-2,5-dialkyl-3,6-diphenylimidazo[1,2-a]imidazoles with zinc in acetic acid gave the corresponding 1H-imidazo[1,2-a]imidazoles, which are oxidized by air oxygen or by irradiation with UV light to give 1H-imidazo[1,2-a]imidazole 7-oxides. The latter were also obtained by the action of nitric acid on 1-amino-2,5-dialkyl-3,6-diphenylimidazo[1,2-a]imidazoles. The UV, IR, PMR, mass, and x-ray electron spectra of the synthesized compounds were studied.

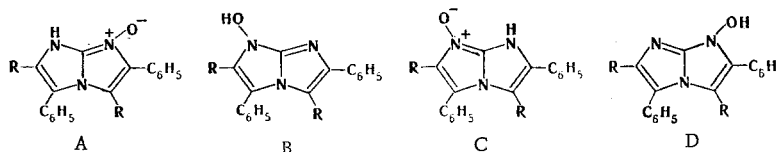
In a continuation of the synthesis and study of 1(7)H-imidazo[1,2-a]imidazole derivatives [1, 2] we obtained new derivatives of this series of compounds and investigated their structure. The reduction of 1-benzylideneaminoimidazo[1,2-a]imidazoles (I, II) with zinc in acetic acid gave 1(7)H-imidazo[1,2-a]imidazoles (III, IV), which during isolation from the reaction mixture undergo partial conversion to the corresponding N-oxides (V, VI). The latter are also formed when III and IV are heated in various organic solvents, viz., ethanol, benzene, chloroform, and dimethyl sulfoxide (DMSO), and when they are irradiated with UV light.



The compositions and structures of the synthesized III and VI were confirmed by the results of elementary analysis and data from the electronic, IR, x-ray electron, PMR, and mass spectra.

Like the electronic spectra of the known imidazo[1,2-a]imidazoles [3, 4], the electronic spectra of III and IV contain two absorption bands in the UV region, and an additional band with a maximum at 392 nm appears in the spectra of their N-oxides (V, VI). The IR spectra of dilute solutions of III and IV contain a diffuse absorption band at 2450-3500 cm<sup>-1</sup>, which is characteristic for associated N-H bonds.

N-Oxides V and VI can be described by structures A-D:

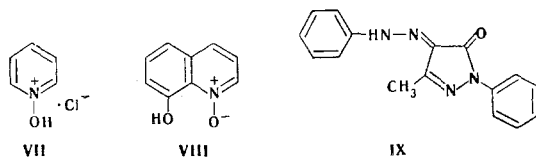


Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 384-387, March, 1982. Original article submitted May 14, 1981.

TABLE 1. Ions with Relative Intensities Greater Than 10% Observed in the Mass Spectrum of III

$m/z$	Composition	Proposed structure	$m/z$	Composition	Proposed structure
77	$C_6H_5$		130	$C_6H_5C_3H_3N$	
91	$C_6H_5N$		172	$M-C_9H_6$	
103	$C_6H_5CN$	PhCN	173	$M-C_9H_5$	
104	$C_6H_5CNH$	PhCN+H			
115	$C_6H_5C_3H_2$		286	$M-H$	
116	$C_6H_5C_3H_3$				

The IR spectra of dilute solutions of V and VI in  $CHCl_3$  and  $CCl_4$  in the region of stretching vibrations contain a  $\nu_{NH}$  band at  $3470\text{ cm}^{-1}$ , which is characteristic for free N-H bonds, and a  $\nu_{N^+-O^-}$  band at  $1135\text{ cm}^{-1}$ . N-Oxides V and VI consequently have structure A or C. In addition to the maxima that are characteristic for N1s, which are also present in the spectra of III and IV, the x-ray electron spectra of V and VI contain O1s maxima. A comparison of the energies of the O1s bond of V (O1s = 533.2 eV) and VI (O1s = 532.9 eV) with the energies of the O1s bonds of model compounds VII (O1s = 532.3 eV) and VIII (O1s = 532.1 and 533.4 eV) provides evidence for the N-oxide structure of V and VI (A or C), in agreement with the IR spectral data.



The PMR spectra of III-VI contain signals of the corresponding aliphatic and aromatic protons and the NH protons; signals of the ortho protons of one of the phenyl rings, which are shifted  $\sim 0.6$  ppm to weak field as compared with the corresponding signals in the spectra of III and IV, are observed in the spectra of V and VI. This character of the shift indicates that V and VI have structure A. The shift of the ortho protons of one of the phenyl rings may be due to the magnetic anisotropy of the  $N^+-O^-$  bond with respect to the phenyl substituent in the ortho position relative to it. Similar shifts of the protons are observed, for example, in the spectra of compounds of the IX type, for which the shift of the ortho protons of the phenyl substituent is 0.5 ppm. The latter is due to the magnetic anisotropy of the C=O bond.

The formation of 1H-imidazo[1,2-a]imidazole 7-oxides (V, VI) as a result of the oxidation of III and IV constitutes evidence that the latter have the 1H-form.

The mass spectra of III-V contain intense molecular-ion peaks. The principal fragmentation pathway due to electron impact is associated with destruction of the imidazo[1,2-a]imidazole ring of III-V, which is accompanied by detachment of  $[PhCN]^+$  or  $[PhC_3H_2]^+$ . The charge is localized on both the residual portion of the molecule and on the fragment that is split out. The masses, compositions, and proposed structures of the ions formed from III under the influence of electron impact are presented in Table 1. The formation of similar ions is observed in the mass spectra of IV and V.

In conclusion, let us note that N-oxide VI rather than 1H-imidazo[1,2-a]imidazole (IV), as reported in [1], is formed by the action of nitric acid on 1-amino-3,6-diphenyl-2,5-diphenyl-2,5-dipropylimidazo[1,2-a]imidazole (X).

## EXPERIMENTAL

The electronic absorption spectra of  $1 \cdot 10^{-4}$  M solutions of the compounds in ethanol were recorded with a Specord UV-vis spectrophotometer. The IR spectra of  $5 \cdot 10^{-3}$  M solutions of the compounds in  $\text{CHCl}_3$  were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in  $d_6$ -DMSO were measured with a Varian X-100-12 spectrometer (100 MHz) with tetramethylsilane as the internal standard. The mass spectra were measured with an MS-702 spectrometer with a system for internal introduction of the samples. The x-ray electron spectra were recorded with an ES-100 x-ray electron spectrometer; the Cls line (bond energy 285 eV) from diffusion oil vapors was taken as the reference. The individuality of the compounds was monitored on Silufol UV-254 plates; the  $R_f$  values for chloroform as the eluent are presented.

2,5-Dimethyl-3,6-diphenyl-1H-imidazo[1,2-a]imidazole (III) and Its 7-Oxide (V). A 4-g sample of zinc dust was added with stirring at  $75^\circ\text{C}$  in four portions every 10 min to a solution of 4.07 g (10.4 mmole) of I in 40 ml of acetic acid, after which the reaction mixture was stirred at  $70$ – $75^\circ\text{C}$  for 30 min. It was then filtered, and the filtrate was poured into water (100 ml). The aqueous mixture was extracted with chloroform, and the extract was dried with anhydrous sodium sulfate and evaporated in vacuo. The residue was recrystallized twice from the minimum amount of benzene–heptane (1 : 1) to give 1.5 g (50.3%) of III with mp  $237$ – $238^\circ\text{C}$ . Found: C 79.4; H 6.1; N 14.5%.  $\text{C}_{19}\text{H}_{17}\text{N}_3$ . Calculated: C 79.5; H 5.9; N 14.6%. Electronic spectrum,  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 206 (4.19) and 274 nm (4.06). Mass spectrum,  $m/z$  (I, % > 10%): 77 (16.2), 91 (19.0), 103 (21.1), 104 (13.4), 115 (34.4), 116 (16.3), 130 (13.5), 172 (14.3), 173 (21.1), 286 (33.5), 287 (100). X-ray electron spectrum: N1s –398.5 and 400.6 eV with a relative intensity ratio of  $\sim 1.2$ . PMR spectrum,  $\delta$ : 1.89 (s,  $\text{CH}_3$ ), 2.18 (s,  $\text{CH}_3$ ), and 7.22–7.90 ppm (m,  $\text{C}_6\text{H}_5$ ).

The mother liquor from the isolation of III was evaporated, and the residue was recrystallized twice from the minimum amount of benzene to give 0.3 g (9.5%) of V with mp  $187.5$ – $188.5^\circ\text{C}$ . Found: C 75.3, H 6.8, N 14.0%.  $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$ . Calculated: C 75.2, H 5.6, N 13.9%. Electronic spectrum,  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 200 (4.26), 265 (4.27), and 392 nm (4.04). Mass spectrum,  $m/z$  (I, % > 10%): 77 (29.2), 78 (22.6), 85 (13.8), 89 (20.5), 103 (31.4), 104 (23.2), 115 (31.5), 116 (23.2), 130 (24.8), 142 (22.4), 157 (14.5), 158 (24.8), 260 (100), 261 (22.0), 303 (40.1). X-ray electron spectrum: broad N1s peak at 399.6 eV, which can be broken down into three peaks at 398.9, 399.7, and 400.6 eV, and O1s peak at 533.2 eV. PMR spectrum: 1.85 (s,  $\text{CH}_3$ ), 2.58 (s,  $\text{CH}_3$ ), 7.22–7.90 (m, 8H from  $\text{C}_6\text{H}_5$ ), 8.22 (m, 2H from  $\text{C}_6\text{H}_5$ ), and 12.5 ppm (s, NH).

3,6-Diphenyl-2,5-dipropyl-1H-imidazo[1,2-a]imidazole (IV) and Its 7-Oxide (VI). This compound was obtained as described above by the reduction of 4.01 g (9 mmole) of II, obtained by the method in [1], with 4 g of zinc in 40 ml of acetic acid. Workup gave 48.5% of IV with mp  $163.5$ – $164.5^\circ\text{C}$  (heptane). Found: C 80.7; H 7.4; N 12.0%.  $\text{C}_{23}\text{H}_{25}\text{N}_3$ . Calculated: C 80.5; H 7.3; N 12.2%. Electronic spectrum,  $\lambda$  (log  $\epsilon$ ): 207 (4.19) and 274 nm (4.08). Mass spectrum,  $m/z$  (I, % > 10%): 77 (32.3), 89 (22.2), 91 (19.4), 103 (26.8), 104 (25.7), 115 (71.9), 116 (22.6), 117 (12.3), 128 (29.2), 129 (17.4), 130 (21.0), 131 (13.2), 141 (15.0), 142 (13.5), 143 (11.5), 155 (10.2), 284 (29.7), 285 (17.5), 286 (11.9), 300 (17.5), 314 (100), 315 (92.2), 316 (18.5), 342 (10.5), 343 (83.2). X-ray electron spectrum: N1s peak at 399.8 and 400.9 eV with an intensity ratio of 1 : 2. PMR spectrum: 0.40 (t), 1.00 (m,  $\text{CH}_3$ ,  $\text{CH}_2$ ), 2.5 (m,  $\Sigma \text{CH}_2$ ), 0.86 (m, tr), 1.69 (m,  $\text{CH}_3$ ,  $\text{CH}_2$ ), 7.61 (m,  $\text{C}_6\text{H}_5$ ), and 14.26 ppm (broad s, NH). The yield of VI, with mp  $146.0$ – $147.0^\circ\text{C}$  (benzene), was 9%. The product was identical to the compound obtained from X by the action of nitric acid by the method in [1]. Found: C 80.1; H 6.9; N 11.8%.  $\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}$ . Calculated: C 76.9, H 7.0; N 11.7%. Electronic spectrum,  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 203 (4.34), 265 (4.24), and 392 nm (4.09). X-ray electron spectrum: broad N1s peak at 399.6 eV, which can be broken down into three peaks at 398.7, 399.6, and 400.5 eV, and O1s peak at 532.9 eV. PMR spectrum: 0.90 (t), 1.69 (m,  $\text{CH}_3$ ,  $\text{CH}_2$ ), 2.76 (m,  $\Sigma \text{CH}_2$ ), 7.22–7.70 (m, 8H from  $\text{C}_6\text{H}_5$ ), 8.22 (m, 2H from  $\text{C}_6\text{H}_5$ ), and 12.49 ppm (s, NH).

Oxidation of III and IV. A) A 0.05-mole sample of III or IV was refluxed in 300 ml of benzene until it dissolved completely, after which the solution was worked up to give 83.9% V or 87.5% VI. The oxidation of III and IV to V and VI was also observed when they were recrystallized from ethanol or chloroform.

B) A drop of a 1% solution of III ( $R_f$  0) in benzene–heptane (1 : 1) was applied to the start of a Silufol UV-254 plate, and the plate was dried in air and irradiated with UV light from a chromatoscope. A yellow spot, the intensity of which increased and reached a maximum after  $\sim 3$  sec, appeared at the start during the irradiation period. A drop of a similar solution of V was applied to the plate next to this spot, and the plate was dried. The  $R_f$  values of V and the compound obtained after irradiation of III were equal [0.145 (chloroform)].

Compound VI ( $R_f$  0.217) was obtained as described above by irradiation of IV ( $R_f$  0) with UV light on a Silufol UV-254 plate.

In conclusion, the authors thank I. A. Krasavin for providing us with samples of oxides VII and VIII and T. M. Ivanov and R. V. Linko for recording the x-ray electron spectra.

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#### UNUSUAL CLEAVAGE OF PHENACYL-SUBSTITUTED BENZIMIDAZOLIUM SALTS. SYNTHESIS OF 1,4-DIARYLIMIDAZOLES

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The action of ammonium acetate in acetic acid on 1-alkyl(aralkyl)-3-phenacylbenzimidazolium bromides leads, in addition to the formation of a new imidazole ring, to cleavage of the benzimidazole fragment of the molecule at the 1,2 bond to give 1-alkyl(aralkyl)aminoaryl-4-arylimidazoles. 1,2-Dimethyl-3-(p-nitrophenacyl)benzimidazolium bromide is converted under similar conditions to the corresponding 2-methylimidazole. 4,4'-Dimethyl-2,2'-bis(p-nitrophenyl)-1,1'-dipyrrolo[1,2-a]benzimidazole was isolated as a side product of this reaction.

Up until recently the action of ammonium acetate in acetic acid on phenacyl-substituted salts of nitrogen heterocycles with unsubstituted  $\mu$ -carbon atoms had been studied only in the case of pyridine, quinoline, and isoquinoline. According to the data in [1], phenacylpyridinium bromide does not react with ammonium acetate when the compounds are heated in solution in acetic acid, whereas the corresponding quinolinium and isoquinolinium salts are converted under the indicated conditions to three-ring systems, viz., 4,5-dihydroimidazo[1,2-a]quinoline and 5,10-dihydroimidazo[1,2-b]isoquinoline [2-5].

In the opinion of Kröhnke and Zecher [1], the decreased reactivity of phenacylpyridinium bromide is due chiefly to the insufficient magnitude of the positive charge on the  $\mu$ -carbon atom of its cation. In this connection, it seemed expedient to investigate the action of ammonium acetate in acetic acid on phenacyl-substituted benzimidazolium salts, the cations of which have higher electrophilicity as compared with salts of azines [6].

The starting 1-alkyl(aralkyl)-3-phenacylbenzimidazolium bromides (Ia-k) were obtained by a known method [7-9]. As a rule, the quaternization of 1-alkyl(aralkyl)benzimidazoles by  $\omega$ -bromoacetophenones takes place at 20°C, and prolonged refluxing of an alcohol solution of the components is necessary only for 1-methyl-5-nitrobenzimidazole.

The action of ammonium acetate on a solution of 1-methyl-3-phenacylbenzimidazolium bromide (Ia) in acetic acid initially gives rise to the development of a brown coloration, which is probably due to the formation of the anhydro base described in [8], after which it leads to a colorless low-melting compound that is resistant to the action of acids and alkalis. In analogy with [2], we did not exclude the possibility of the formation in this case of the known 9-methyl-2-phenyl-2,3-dihydroimidazo[1,2-a]benzimidazole (II) [10]. However, a comparison of the melting points of the hydrochlorides of the compound obtained and II showed that they are not identical, although they do have the same elementary composition.

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