MASS-SPECTROMETRIC STUDY OF BENZOPYRIDOFULVENES

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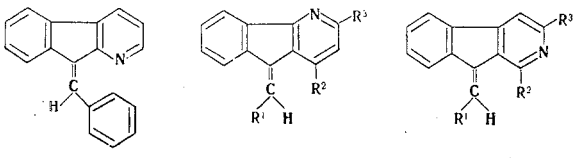
UDC 543.51:547.836

The dissociative ionization of benzopyridofulvenes that differ with respect to the position of the nitrogen atom in the azafluorene ring and the position and character of the substituents in the molecule was investigated. It is shown that the characteristic peculiarities of the fragmentation of these compounds can be explained by cyclization processes in the step involving the formation of $[M - R]^+$ ions, where $R = CH_3$ and C_6H_5 and are the substituents attached to the exocyclic carbon atom. Calculations of the π-bond energies of the molecular ion and the fragments by the Pariser–Parr–Pople method confirm the energic favorability of the formation of rings in the $[M - R]^+$ ions.

The possibility of the formation of cyclic structures in the fragment ions was noted in a study of the mass-spectral behavior of alkyl- and aryl-substituted fulvenes [1]. The probability of cyclization processes was also pointed out in an investigation of the fragmentation under electron impact of some dibenzofulvenes [2]. It follows from an analysis of the literature data on the mass spectra of fulvenes [1-3] that the principal fragmentation pathways of these compounds depend chiefly on the type of substituent attached to the exocyclic carbon atom. The dissociative ionization of fulvenes that contain heterocyclic fragments has not been previously examined. In the present research we investigated the fragmentation of benzopyridofulvenes – derivatives of 1-, 2-, and 4-azafluorenes – in order to establish the effect of the position of the nitrogen atom, as well as the character and position of the substituents in the azafluorene ring and attached to the exocyclic C_{10} atom, on the dissociative ionization of compounds of this series. The mass spectra of the following compounds were studied:



I II, IV, VI, VIII III, V, VII

II $R^1 = C_6H_5$, $R^2 = R^3 = H$; III $R^1 = C_6H_5$, $R^2 = H$; $R^3 = CH_3$; IV $R^1 = H$, $R^2 = R^3 = C_6H_5$; V $R^1 = H$, $R^2 = R^3 = C_6H_5$; VI, VII $R^1 = R^2 = R^3 = C_6H_5$; VIII $R^1 = CH_3$, $R^2 = R^3 = C_6H_5$

The mass spectra are completely identical for the Z and E isomers of I-III, and data only for the Z forms are therefore presented in Table 1. The identical character of the mass spectra of the geometrical isomers can be explained by the relatively low energy barrier in the conversion of the molecular ion of one isomer to the molecular ion of the other [4].

The mass spectra of benzopyridofulvenes I-VIII (Table 1) are characterized by high-intensity peaks of ions in the range of the m/z value of the molecular ion (M^+) and by intense peaks of the corresponding doubly charged fragments. The appearance of intense peaks of $[M - R']^+$ ions is also observed in the fragmentation of some of the compounds (VI-VIII) (Table 2). The stability of the molecular ions of I-VIII (see the W_M values in Table 2) is lower by a factor of 1.5-2 than the stability of the molecular ions formed in the fragmentation of azomethines of the azafluorene series [5]. It is apparent from a comparison of the W_M values of the isomeric (with respect to the position of the nitrogen atom) I-III, IV and V, VI, and VII that the stability of the molecular ions has its greatest value for 4-azafluorene derivatives. A similar dependence was previously observed in the fragmentation of other derivatives of 2- and 4-azafluorenes [6]. These data indicate that the electronic structures of the molecular ions depend on the position of the nitrogen atom in the azafluorene ring.

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0009-3122/82/1803-0285$07.50

TABLE 1. Mass Spectra of Benzopyridofulvenes I-XI

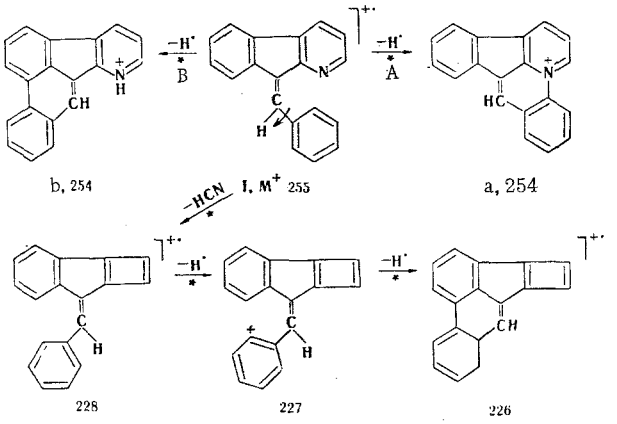
Compound	m/z values (relative intensities of the peaks in percent of the maximum peak)*
9-Benzylidene-1-azafluorene, cis and trans forms (I)	256 (4,9), 255 (30,8), 254 (100), 253 (8,3), 252 (6,8), 251 (3,5), 227 (2,9), 226 (5,4), 225 (2,2), 224 (2,0)
9-Benzylidene-4-azafluorene, cis and trans forms (II)	256 (18,1), 255 (96,0), 254 (100), 253 (22,1), 252 (8,3), 251 (7,0), 229 (1,3), 228 (7,1), 227 (6,4), 226 (15,8), 225 (4,7), 224 (4,0), 201 (2,5), 200 (3,0),
9-Benzylidene-3-methyl-2-azafluorene, cis and trans forms (III)	270 (20,6), 269 (100), 268 (87,1), 267 (13,0), 266 (6,3), 265 (2,5), 264 (2,7), 257 (2,7), 256 (3,6), 255 (3,2), 254 (12,8), 253 (8,7), 252 (4,3), 251 (4,1), 241 (3,4), 240 (5,4), 239 (10,9), 238 (2,0), 237 (2,2), 228 (5,4), 227 (5,4), 226 (11,3), 225 (3,1), 224 (2,9), 215 (2,9), 213 (2,5), 202 (2,5)
9-Methylene-1,3-diphenyl-4-azafluorene (IV)	332 (25,1), 331 (100), 330 (84,3), 329 (8,8), 328 (9,6), 327 (5,6), 326 (3,2), 302 (2,9), 300 (2,3), 254 (4,5), 253 (6,1), 252 (12,8), 251 (9,6), 250 (2,3), 229 (5,1), 228 (20,0), 227 (2,7), 226 (6,4), 225 (3,2), 224 (2,4)
9-Methylene-1,3-diphenyl-2-azafluorene (V)	332 (21,4), 331 (74,2), 330 (100), 329 (27,1), 328 (12,4), 327 (5,8), 326 (3,5), 325 (2,0), 302 (2,8), 301 (2,3), 300 (2,8), 254 (3,8), 253 (6,2), 252 (17,3), 251 (12,0), 250 (2,7), 229 (2,0), 228 (4,6), 227 (3,4), 226 (8,8), 225 (4,6), 224 (3,6), 84 (2,6)
9-Benzylidene-1,3-diphenyl-4-azaflourene (VI)	408 (31,5), 407 (100), 406 (31,1), 405 (4,6), 404 (4,5), 331 (8,2), 330 (29,0), 329 (19,1), 328 (13,3), 327 (9,0), 326 (4,3), 325 (3,2), 318 (2,5), 305 (2,8), 304 (9,6), 303 (2,5), 302 (4,3), 301 (3,0), 300 (4,3), 252 (5,4), 251 (3,6), 226 (2,1)
9-Benzylidene-1,3-diphenyl-2-azafluorene (VII)	408 (31,8), 407 (100), 406 (70,4), 405 (13,1), 404 (8,0), 334 (5,2), 333 (14,4), 332 (10,6), 331 (27,2), 330 (96,1), 329 (17,6), 328 (14,4), 327 (11,2), 326 (6,2), 325 (5,0), 320 (2,0), 319 (7,8), 318 (11,4), 317 (2,0), 304 (3,0), 303 (2,4), 302 (6,1), 301 (4,6), 300 (7,2), 299 (2,0), 276 (2,0), 253 (4,2), 252 (14,4), 251 (9,21), 250 (2,4), 227 (2,1), 226 (5,4), 225 (2,8), 224 (2,0)
9-Ethylidene-1,3-diphenyl-2-azafluorene (VIII)	346 (27,5), 345 (100), 344 (31,5), 343 (9,3), 342 (7,7), 341 (3,8), 340 (2,8), 331 (22,8), 330 (84,5), 329 (8,1), 328 (9,3), 327 (4,6), 326 (2,0), 319 (2,6), 318 (5,0), 317 (3,6), 316 (3,5), 315 (3,5), 314 (2,3), 302 (2,0), 268 (2,0), 267 (2,8), 266 (5,1), 265 (3,2), 264 (3,9), 253 (3,5), 252 (9,3), 251 (5,0), 242 (7,8), 241 (2,5), 240 (3,0), 239 (5,2), 226 (2,9), 83 (2,8)

* The peaks with intensities ≥2% are presented.

A peculiarity of the dissociative ionization of I-VIII is the formation of intense peaks of $[M-H]^+$ ions (Table 1); their intensity depends on both the position of the nitrogen atom and the character and position of the substituents. The high probability of the appearance of an $[M-H]^+$ ion peak in the mass spectrum of I (Table 2) can be explained by cyclization of the phenyl group attached to the C_{10} atom with the azafluorene ring, which leads to the formation in the latter of a quaternized nitrogen atom (Scheme 1). In this case the phenyl group can form a ring both with the nitrogen atom (Scheme 1, pathway A) and with the α-carbon atom of the azafluorene fragment of the molecule (Scheme 1, pathway B). The absence of an $[M-C_6H_5]^+$ ion peak in the mass spectrum of I is an indirect confirmation of the participation of the phenyl group in the formation of a new ring. The considerably higher intensity of the peak of the double charged $[M-H]^{2+}$ ion as compared with the intensity of the peak of the M^{2+} ion [7] may serve as additional evidence for the formation of an aromatic condensed structure in the $[M-H]^+$ ion in the fragmentation of I due to cyclization. The energic favorability of the formation of a new ring in the $[M-H]^+$ ion is confirmed by calculation of the π-bond energy* of the I molecule (−3436.969 kJ/mole), the M^+ molecular ion (−2560.944 kJ/mole), and the $[M-H]^+$ ion (Scheme 1) in the *a* form (−3105.645 kJ/mole), as well as in the b form (−3091.470 kJ/mole). From the data presented above it is apparent that in the case of the formation of a cyclic structure in the $[M-H]^+$ ion its stability is considerably higher than in the case of the molecular ion. The data also show that of the two alternative cyclization pathways in the formation of an $[M-H]^+$ ion the formation of a ring between the exocyclic phenyl group and the nitrogen atom (Scheme 1, pathway A) leads to a somewhat more stable structure than in the case of cyclization with the phenylene ring of the azafluorene fragment (Scheme 1, pathway B).

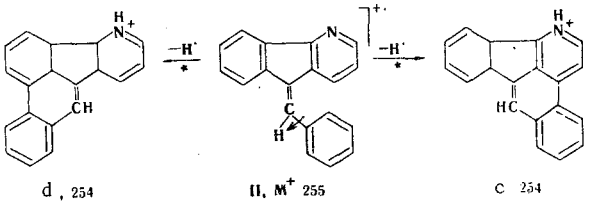
* The energic favorability in the π-electron approximation is estimated from the π-bond energies, which are defined as the differences between the π-electron energies of the molecule and the energies of the isolated atoms of which it is composed [8]. The π-bond energies of the molecules and the ions were calculated in the electron approximation by the Pariser–Parr–Pople method in the "variable β" approximation [9].

Scheme 1



As in the case of I, the fragmentation of benzopyridofulvenes II-V is determined by the appearance of a high-intensity $[M - H]^+$ ion peak and the absence of $[M - C_6H_5]^+$ ion peaks (or the appearance of the latter peaks with extremely low intensities) (Table 2). These data make it possible to assume that the phenyl group of the benzylidene grouping of the cited compounds participates in the cyclization processes in the formation of $[M - H]^+$ ions. The higher intensity of the peaks of the doubly charged $[M - H]^{2+}$ ions as compared with the M^{2+} ion peak in I-V (Table 2) also constitutes indirect evidence for the existence of a more condensed structure in the $[M - H]^+$ ions as compared with the molecular ions. The formation of a ring with the nitrogen atom is impossible in the dissociative ionization of II and III. The high intensity of the $[M - H]^+$ ion peaks in this case can be explained by cyclization of the phenyl group with the C_1 and C_8 atoms, which is accompanied by migration of a hydrogen atom to the nitrogen atom, as in the fragmentation of dipyridyls [10] (Scheme 2).

Scheme 2

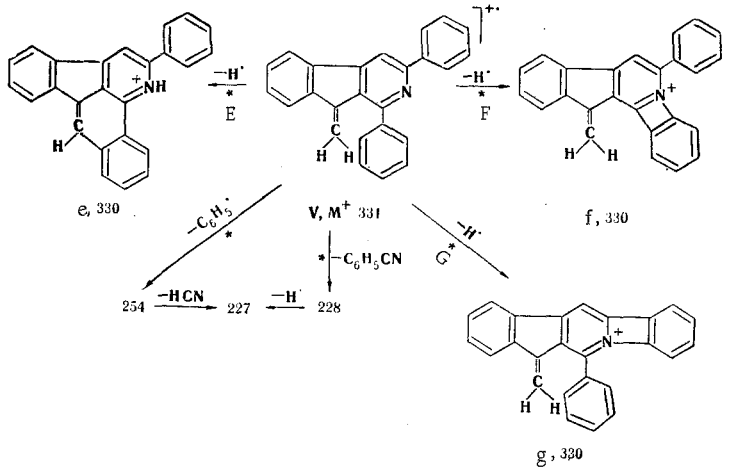


It follows from a comparison of the π-bond energies for II (−3435.889 kJ/mole), its molecular ion M^+ (−2562.535 kJ/mole), and for two possible structures of the $[M - H]^+$ ion in the c form (−3144.318 kJ/mole) and in the d form (−3143.669 kJ/mole) that in the case of the formation of a condensed structure in the $[M - H]^+$ ion this fragment is more stable than the molecular ion. The virtually equal π-bond energies for the c and d structures of the $[M - H]^+$ ion of II evidently constitute evidence that cyclization in this case can be realized with both the pyridine ring and the phenylene ring. The probability of the formation of such rings was previously noted [2] in an investigation of the mass spectra of derivatives of 9-benzylidenefluorenes, viz., benzazo analogs of I-III. It should be emphasized that in the fragmentation of benzopyridofulvenes I-III cyclization is realized in the step involving the formation of the $[M - H]^+$ ion, whereas dibenzofulvenes form similar rings only in the $[M - 2H]^+$ ion. This conclusion is confirmed by the significantly greater intensity of the peak of the doubly charged $[M - 2H]^{2+}$ ion as compared with the peaks of M^{2+} and $[M - H]^{2+}$ ions in the mass spectrum of 9-benzylidenefluorene [2].

In the case of the dissociative ionization of benzopyridofulvenes IV and V, which do not contain a phenyl substituent attached to the exocyclic carbon atom, the high intensity of the $[M - H]^+$ ion peak can be explained by cyclization in the latter of the phenyl group in the C_1 position with the exocyclic C_{10} atom (Scheme 3, pathway E). This process is also accompanied by the formation of a quaternized nitrogen atom. A comparison of the intensities of the peaks of the double charged $[M - H]^{2+}$ and M^{2+} ions in the mass spectra of IV and V (Table 2) indirectly confirms the formation of an additional system of conjugated π bonds in the $[M - H]^+$ ion. It should be noted that in the isomeric (with respect to the position of the nitrogen atom) IV and V the formation of an $[M - H]^+$ ion takes place with a different probability. This result can be explained if it is assumed that the

* In the schemes the numbers that characterize the ions are the mass-to-charge ratios (m/z).

Scheme 3



formation of a ring between the o-phenyl substituent and the nitrogen atom (Scheme 3, pathways F and G) may be realized in addition to cyclization via pathway E (Scheme 3). It has been established [11] that a similar process is energically favorable in the fragmentation of 2(6)-phenylpyridines. Our calculations of the π-bond energies of the V molecule (−4456.363 kJ/mole), its molecular ion M^+ (−3580.836 kJ/mole), and the $[M-H]^+$ ion in the e form (Scheme 3, −4187.918 kJ/mole), in the f form (−4131.575 kJ/mole), and in the g form (−4126.745 kJ/mole) show that both cyclization with the participation of the exocyclic carbon atom and ring formation between the o-phenyl group and the nitrogen atom of the azafluorene fragment are responsible for the greater stability of the $[M-H]^+$ as compared with the M^+ ion. However, in the fragmentation of IV cyclization pathway g indicated in Scheme 3 cannot be realized because of the presence of only one phenyl group in the ortho position relative to the nitrogen atom. The latter fact evidently also explains the lower intensity of the $[M-H]^+$ ion peak in the mass spectrum of IV.

The fragmentation of VI-VIII is characterized by an appreciable decrease in the relative intensity of the $[M-H]^+$ ion peak as compared with I-V. The simultaneous presence of bulky substituents attached to the exocyclic C_{10} atom and in the α,α' positions relative to the nitrogen atom is responsible for steric hindrance to the formation of a new ring in the $[M-H]^+$ ion. The low intensity of the peaks of doubly charged $[M-H]^{2+}$ ions also indicates the absence of cyclization processes in the $[M-H]^+$ ions in the case of VI-VIII (Table 2).

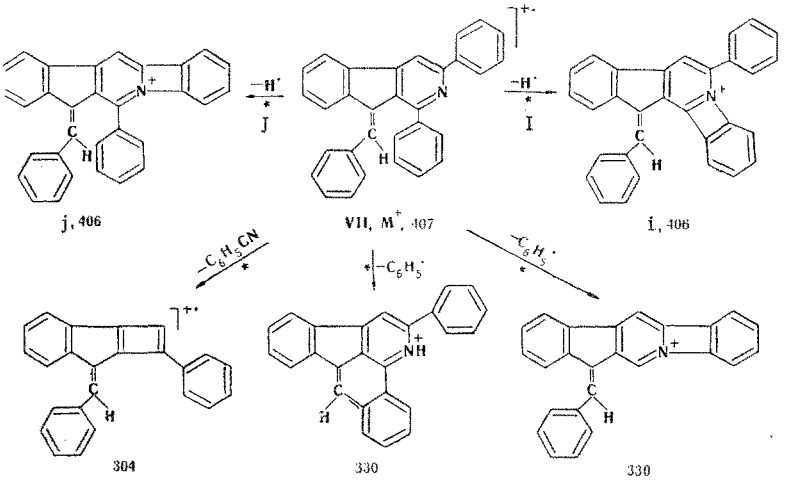
TABLE 2. Stabilities (W_M) of the Molecular Ions and Relative Intensities of the Peaks of the Characteristic Fragments (in percent of the total current, Σ_{50}) in the Mass Spectra of Benzopyridofulvenes

Compound	W_M	$[M-H]^+$	M^{2+}	$[M-H]^{2+}$	$[M-R^*]^+$	$[M-R^*]^{2+}$	$[M-HCN]^+$	$[M-C_6H_5CN]^+$
I (cis and trans forms)	14,1	45,4	2,3	5,1	—	—	1,3	—
II (cis and trans forms)	24,2	25,0	1,8	4,1	0,10	—	1,8	—
III (cis and trans forms)	21,0	18,1	1,1	1,2	—	—	0,3	—
IV	20,3	17,1	1,1	1,8	0,9	—	0,1	4,1
V	12,1	16,4	1,3	1,7	0,6	—	0,1	0,7
VI	24,3	7,6	—	0,2	7,1	0,8	—	2,3
VII	14,2	10,0	0,3	0,8	13,7	1,0	—	0,4
VIII	15,3	4,8	1,1	0,3	13,1	3,2	—	1,2

* For a substituent (not hydrogen) attached to the exocyclic C_{10} atom.

In the fragmentation of the isomeric (with respect to the position of the nitrogen atom) VI and VII considerably higher intensity of the $[M - H]^+$ ion peak is observed for 2-azafluorene derivative VII. This result is evidently associated with the possibility of cyclization in the $[M - H]^+$ ion in the case of VII of one of the phenyl groups in the α,α' positions of the pyridine fragment with the nitrogen atom of the azafluorene ring (Scheme 4, pathways I and J). In the case of the fragmentation of VI the probability of this process, which is due to the presence of one phenyl substituent in the ortho position relative to the nitrogen atom, is considerably lower. In contrast to benzopyridofulvenes I-V, high-intensity $[M - R']^+$ ion peaks, where R' is the substituent attached to the exocyclic carbon are recorded in the mass spectra of VI-VIII (Table 2). Steric hindrance to the formation of a new ring in the $[M - R']^+$ ion is evidently removed in the elimination of a bulky substituent (a phenyl or methyl group) by the molecular ions of VI and VII, and in this case one can assume the formation of a ring between the phenyl group attached to the C_1 atom with the exocyclic C_{10} atom (Scheme 4). This assumption is confirmed by the formation of relatively high-intensity $[M - R']^+$ ion peaks in the mass spectra of VI-VIII. The more facile formation of the $[M - R']^+$ ion in the fragmentation of VII can be explained, as in the case of other 2-azafluorene derivatives, by the increased stability of the $[M - R']^+$ ion due to the additional possibilities of cyclization of the two α,α'-phenyl groups of the azafluorene ring with the nitrogen atom.

Scheme 4



The elimination of an RCN particle by the molecular ions that is characteristic for azafluorene derivatives [5] is retained in the dissociative ionization of benzopyridofulvenes I-VIII (Table 2). The magnitude of the $[M - RCN]^+$ ion peak in the mass spectra of the isomeric (with respect to the position of the nitrogen atom) I and II, IV and V, and VI and VII is inversely dependent on the probability of the occurrence of cyclization processes in the fragmentation of these compounds: the higher the probability of cyclization with the formation of a quaternized nitrogen atom in the azafluorene ring (I, V, and VII), the lower the intensity of the $[M - RCN]^+$ ion peak.

EXPERIMENTAL

The mass spectra of I-VIII were measured with an MKh-1303 spectrometer equipped with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and an admission temperature of 50°C. The compounds were synthesized by the method in [12]. The purity and individuality of the compounds were monitored by means of data from TLC and IR, UV, and PMR spectroscopy.

LITERATURE CITED

1. Y. Kitahara, I. Murata, and K. Shikanata, Bull. Chem. Soc. Jpn., 39, 629 (1966).
2. C. Lifshitz, E. D. Bergman, M. Rabinovitz, and I. Arganat, J. Chem. Soc., B, 723 (1968).
3. M. Neuenschwander, R. Vögeli, H. P. Fahrni, H. Lehman, and J. P. Ruder, Helv. Chim. Acta, 60, 1073 (1977).
4. H. O. Kalinovski and H. Kessler, Topics in Stereochemistry, 7, 299 (1973).
5. V. K. Shevtsov, P. I. Zakharov, V. P. Zvolinskii, V. G. Pleshakov, T. S. Seitembetov, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 3, 397 (1979).
6. P. I. Zakharov, V. P. Zvolinskii, V. K. Shevtsov, V. G. Pleshakov, T. S. Seitembetov, A. V. Varlamov, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 1, 89 (1979).
7. F. W. McLafferty and M. M. Bursey, Chem. Commun., No. 11, 535 (1967).

8. A. L. Chung and M. J. S. Dewar, J. Chem. Phys., 42, 756 (1965).
9. K. Nishimoto and L. S. Forster, Theor. Chim. Acta, 3, 407 (1965); 4, 155 (1966).
10. R. A. Khmel'nitskii, N. A. Klyuev, and P. B. Terent'ev, Zh. Org. Khim., 7, 395 (1971).
11. P. B. Terent'ev, R. A. Khmel'nitskii, I. S. Khromov, A. N. Kost, I. P. Gloriozov, and M. Islam, Zh. Org. Khim., 6, 606 (1970).
12. N. S. Prostakov, S. S. Moiz, A. T. Soldatenkov, V. P. Zvolinskii, and G. I. Cherenkova, Khim. Geterotsikl. Soedin., No. 10, 1398 (1971).

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

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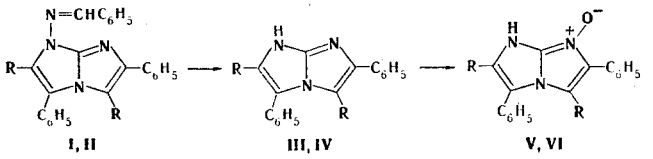
UDC 547.785.5.07

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.



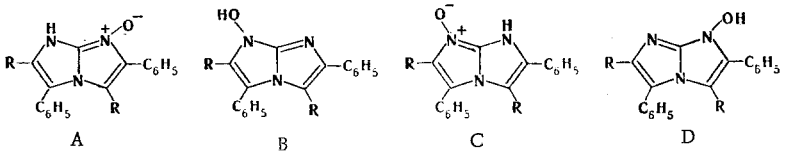
I, II III, IV V, VI

I, III, V R = CH_3; II, IV, VI R = C_3H_7

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^{-1}, which is characteristic for associated N–H bonds.

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



A B C 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.

 0009-3122/82/1803-0290$07.50