THE VIBRATIONAL, ELECTRONIC, AND MASS SPECTRA OF 2-AMINO-1-AZIRINES

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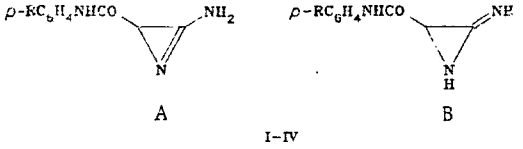
It is shown by IR, UV, and mass spectroscopy that the 2-amino-3-arylcarbamoyl-1-azirines, first represented as three-membered, cyclic amidines containing a primary amino group and able to undergo a prototropic rearrangement, exist exclusively in the aminoaziridine form.

The 2-amino-3-arylcarbamoyl-1-azirines I-IV that we synthesized previously [1] are the first representatives of three-membered, cyclic amidines containing a primary amino group, and can exist in two tautomeric forms resulting from the transfer of a proton from one nitrogen atom of the triad to the other; as an aminoazirine (A) or an iminoaziridine (B).



I-IV

I R=H; II R=CH_3; III R=CH_3O; IV R=Cl

In order to establish the structures of potentially tautomeric systems I-IV, we studied the vibrational, electronic, and mass spectra of azirines I-IV.

According to the IR spectroscopic data, a number of cyclic amidines, derivatives of 2-amino-Δ^1-pyrrolines and 2-amino-Δ^1-piperidines, exist in the amino form [2-4].

Similarly, it is convenient to use data from the vibrational spectroscopy of 2-amino-1-azirines I-IV for the unambiguous establishment of their structures. In the spectra of 2-amino-1-azirines I-IV, the characteristic frequencies of the amidine group stretches lie in the 3 and 6 μm region. The N—H stretching bands are of great analytical value as an indicator of the structure of 2-amino-1-azirines I-IV since one finds "mixed" vibrational transitions of C=O, NH, C—N, etc. bonds in the low-frequency region of the spectrum. The general features of the IR spectroscopy of 2-amino-1-azirines I-IV are treated in Tables 1 and 2 on the basis of an analysis of the vibrational spectrum of azirine I.

In the spectrum of 2-amino-1-azirine (I) (in mineral oil or KBr tablets), one finds a characteristic doublet of intense bands at 3130 and 3220 cm^{-1} in addition to the ν_{NH} band of the associated secondary amido group at 3050 and 3350 cm^{-1} in the 3 μm region. This doublet is assigned to the ν_s and ν_{as} stretches of the amino group. The shift of the NH stretching bands to lower frequencies is probably due to conjugation in amidine system I as well as to the intermolecular association that arises in the crystalline state.

In the spectrum of a chloroform solution of compound I, where intermolecular association is absent, all of these bands are shifted to larger wave numbers (3380, 3417, and 3510 cm^{-1}, respectively) that are characteristic of NH bond stretching bands.

It is known that the stretching and bending bands of the amino group can be successfully identified by means of isotopic replacement. For this reason, we studied the IR spectrum of deuterated azirines I-IV, prepared in various degrees of deuteration by the action of D_2O or CD_3OD on them at room temperature for a period of 2-30 min followed by evaporation of the solutions to dryness.

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TABLE 1. The IR Spectra of Compounds I-IV (ν and δ, cm^{-1})

Comp.	Medium	$\nu_{as\,NH_2}$	$\nu_{s\,NH_2}$	ν_{NH}	$\nu_{C=N}$	$\nu_{C=O}$	δ_{NH_2}	δ_{NH}	ν_{C-N}
I	Mineral oil	3220	3130	3050, 3350	1830	1650, 1660	1605	1550	1350
	KBr	3230	3140	3050, 3360	1830	1650, 1660	1610	1550	1355
	$CHCl_3$	3510	3417	3380	1815	1675—1685	1600	—	—
II	Mineral oil	3220	3130	3050, 3350	1830	1630, 1650	1605	1550	1350
	KBr	3220	3130	3060, 3350	1830	1630, 1650	1605	1555	1350
III	Mineral oil	3220	3130	3060, 3350	1830	1630, 1650	1605	1555	1350
	KBr	3220	3130	3060, 3350	1830	1630, 1650	1605	1555	1355
IV	Mineral oil	3220	3130	3050, 3340	1830	1630, 1650	—	1550	1350
	KBr	3220	3130	3050, 3350	1830	1630, 1650	—	1555	1350

The intensities of the ν_{NH} band of the amido group at 3350 cm^{-1} and the bands characteristic of the NH_2 group at 3130 and 3220 cm^{-1} were found to decrease in the spectra of compound I on deuteration. This was accompanied by the simultaneous appearance of new bands at 3140, 3190, 2380, and 2410 cm^{-1} belonging to the monodeuterated amino group. The intensities of these bands grew with the extent of the deuteration process to a maximum and then diminished with the simultaneous appearance of strong bands at 2320 and 2520 cm^{-1} belonging to the stretching vibration of the ND bonds of the fully deuterated amino group. The presence of four NH stretching bands (3140, 3190, 2380, and 2410 cm^{-1}) in the spectra of azirine I allows one to conclude that it exists in rotationally isomeric forms, apparently as a consequence of the hindered rotation of the amino group about the exocyclic C—N bond [2, 3, 5] (Table 2). In the 6 μm region there is an intense band from the NH bond deformation of an amido group at 1550 cm^{-1} in the spectrum of aminoazirine I. The intensity of this band is decreased sharply by deuteration. There is also a band at 1605 cm^{-1} which can be assigned to the deformation of an amino group, in as much as it disappears on deuteration while in the spectrum of a solution of I it is shifted to a lower frequency (1600 cm^{-1}), behavior characteristic of the deformation mode of an amino group [6].

The bands at 1650 and 1660 cm^{-1} correspond to C=O stretches in as much as the intensities do not change on deuteration and dissolution of the sample leads to a shift of the bands to higher frequencies up to 1675-1685 cm^{-1}. This is apparently due to the disappearance of the intermolecular associations present in the crystalline state.

The band of the endocyclic C=N stretching modes, which can be seen at 1830 cm^{-1}, does not change its position on going from the solid sample to a solution. However, its intensity strongly depends on the sample's state of aggregation. This band is most intense in the absorption of a solid sample of I, apparently because of the intermolecular association. At the same time, it is comparatively weak for a solution and shifted to a lower frequency (~5 cm^{-1}).

Thus, the results of the study of the vibrational spectra of azirines I-IV show that they exist in the aminoazirine form, A, and indicate the presence of strong intermolecular associations in the solid state. The aminoazirinic structure of 1-azirines I-IV is further supported by a comparative analysis of their UV spectra with the absorption spectra of analogs with fixed structure: 2-phenyl-3-alkyl(aryl)azirines (V-VII) (Table 3).

In the electronic spectra of 2-amino-1-azirines I-III, one finds an intense absorption band in the 245-255 nm region that agrees in position with those for 2-phenyl-1-azirines V-VII, but 1.5 times less intense. At the same time, simple imines have a weak absorption band in the 235 nm region [7]. The decrease in the intensity of the absorption in the spectra of I-III is, apparently, an indication of less effective conjugation in the 2-aminoazirines compared to 2-phenylazirines V-VII, despite the similarity of the effects of an amino group and a π-electron substituent on conjugation [8]. We turn our attention to the fact that the position of the band at 245-255 nm in azirines I-III and V-VII is virtually unchanged by the changing polarity of the solvent; i.e., there is either no solvatochromic effect or it is fully compensated.

TABLE 2. Absorption Frequencies of the C=N and C=O Bonds and the Amino Group in Deuterated Azirines I-IV

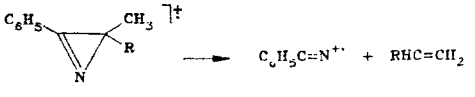
Comp.	ν, cm⁻¹					
	NHD		ND_2	C=N	C=O	ND
	NH	ND				
I	3190 3140	2410 2380	2510 2320	1825	1640 1630	2480
II	3200 3180	2410 2370	2520 2320	1825	1650 1630	2470
III	3220 3180	2410 2380	2520 2320	1825	1640 1625	2480
IV	3210 3165	2405 2370	2510 2320	1830	1640 1625	2460

TABLE 3. Position of the Maxima of the Absorption Bands of 1-Azirines I-III and V-VII ($c = 10^{-5}$ mole/liter)

Comp.	λ_{max}, nm (ε)		
	in ethanol	in THF	in hexane
I	247 (18 380)	247 (18 300)	insoluble
II	251 (19 800)	252 (19 680)	insoluble
III	255 (14 600)	255 (14 450)	insoluble
V	245 (31 000)	247 (30 900)	242 (21 600)
VI	246 (15 000)	252 (14 800)	240 (12 800)
VII*	247 (21 000)	246 (20 800)	243 (19 800)

*2,3-Diphenyl-1-azirine.

The mass spectra of 2-amino-1-azirines I-IV were studied in comparison with data on the fragmentation under electron impact of the 2-phenyl-1-azirine series, V and VI. The mass spectra of compounds V and VI are characterized by an intense molecular ion (55 and 34% of the maximum ion, respectively). A feature of the fragmentation of the molecular ion is the extremely low intensity of the ion formed by splitting off a substituent from the carbon atom: For compound V, the intensity of the $[M - CH_3]^+$ ion is no more than 2%, while for compound VI this ion is generally absent. These mass spectra of V and VI differ from the mass spectra of other substituted azirines in which one sees the splitting off of substituents from the azirine ring [9-12]. The fundamental fragmentation process of the molecular ion of compounds V and VI is the cleavage of the azirine ring with the ejection of a molecule of C_2H_4 and C_3H_6, respectively, and the formation of the odd-electron ion $C_6H_5CN^{+\cdot}$ that is the maximum one in the spectrum. The remaining ions with lower mass numbers are the products of the fragmentation of the $C_6H_5CN^{+\cdot}$ ion (see the Experimental section).



V-VI

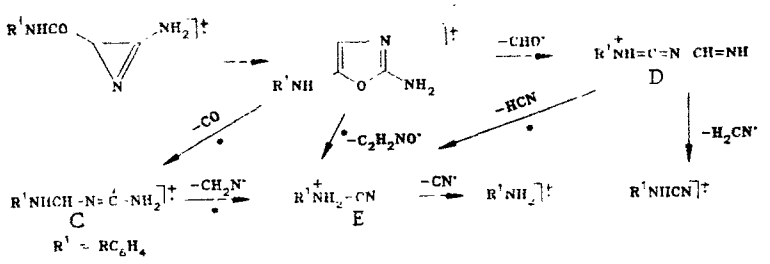
V, VI R=H, CH_3

In the mass spectra of compounds I-IV, one sees an intense molecular ion (31-94%) (Table 4). The initial fragmentation processes of the molecular ion are the ejection of CO molecules and the parallel splitting out of a CHO· radical (Table 4). It is possible that the ejection of neutral particles precedes the rearrangement of the azirine ring into an oxazole ring in a manner similar to the fragmentation of benzoylazirine [13] and esters of azirinecarboxylic acids [14, 15] under electron impact. A subsequent step in the fragmentation is the ejection of a CH_2N· radical. The proposed rearrangement of the azirine ring to an oxazole ring is confirmed by the fact that along with the two-step fragmentation process,

TABLE 4. Characteristic Ions in the Mass Spectra of 2-Amino-1-azirines I-IV

Comp.	R	m/z (relative intensity, %)								
		$M^{+\cdot}$	M−H	C	D	E	D−CH_2N	$RC_6H_4NH_2$	RC_6H_4	remainder
I	H	175 (48)	174 (39)	147 (54)	146 (6)	119 (100)	118 (45)	93 (67)	77 (54)	92 (15), 91 (37), 66 (25), 65 (16), 56 (28), 51 (18)
II	CH_3	189 (31)	188 (6)	161 (5)	160 (5)	133 (18)	—	107 (73)	91 (22)	106 (100) − $CH_3C_6H_4NH^+$, 79 (15), 77 (20)
III	CH_3O	205 (37)	204 (5)	177 (48)	176 (5)	149 (100)	148 (19)	123 (54)	107 (5)	133 (24), 108 (80) − $CH_3OC_6H_4$, 92 (13), 80 (22), 77 (15); 55 (28)
IV	Cl	209 (94)	208 (7)	181 (5)	180 (8)	153 (22)	152 (100)	127 (29)	111 (16)	125 (20), 90 (15), 75 (17), 55 (13)

$M^{+\cdot} \rightarrow (M - CO)^{+\cdot} \rightarrow (M - CO - CH_2N)^{+\cdot}$, the ejection of $COCH_2N^{\cdot}$ also takes place in one step. This is difficult to explain starting from a structure with an azirine ring (the one-step ejection of $COCH_2N^{\cdot}$ is confirmed by the presence of the corresponding metastable peak). The formation of an oxazole ring is in accord with the existence of compounds I-IV in the aminoazirine form, A. Further fragmentation takes place with the splitting out of the CN group.



Asterisks mark the fragmentation paths confirmed by metastable transitions; the composition of ions C-E was determined at high-resolution for compound I.

Thus, from a study of the vibrational, electronic, and mass spectra of 2-amino-1- azirines I-IV it has been shown unambiguously that these azirines, capable of undergoing a photogropic rearrangement, exist exclusively in the aminoazirine form.

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 instrument in petroleum oil, in KBr disks, and in $CHCl_3$ solution ($c = 10^{-4}$ mole/liter). The electronic spectra were taken on a Hitachi-557 spectrophotometer in ethanol, THF, and hexane solution ($c = 10^{-5}$ mole/liter). The mass spectra were recorded on an MS-50 (AEI) instrument at an ionization energy of 70 eV. Admission of the samples was effected by direct introduction (I-IV) and through a glass inlet system (V and VI). The temperature of the ionization chamber was 150°C. The measurement of the precise masses of the ions was done at a resolution of ~60,000.

Mass spectra of azirine I (high resolution): $C_8H_9N_3$, experimental 147.0803, calculated 147.0810; $C_7H_7N_2$, experimental 119.0582, calculated 110.0555.

Mass spectrum of azirine V, m/z (relative intensity, %)*: 131 (55) $-M^{+\cdot}$, 130 (73), 104 (100) $-C_6H_4CN^{+\cdot}$, 103 (87), 77 (41), 76 (27), 51 (20).

Mass spectrum of azirine VI: 145 (34) $-M^{+\cdot}$, 144 (7), 104 (100) $-C_6H_5N^{+\cdot}$, 103 (22), 77 (19), 76 (9), 51 (13), 50 (7), 42 (16), 41 (19). High resolution: C_7H_6N, experimental 104.0475, calculated 104.0500.

LITERATURE CITED

1. A. V. Eremeev, I. P. Piskunova, and R. S. Él'kinson, Khim. Geterotsikl. Soedin., No. 9, 1202 (1985).
2. H. U. Sieveking and W. J. Lüttke, Lieb. Ann. Chem., No. 2, 189 (1977).
3. A. G. Moritz, Spectrochim. Acta, 20, 1555 (1964).
4. V. Granik, Usp. Khim., 52, 669 (1983).
5. A. N. Hambly and V. B. O'Grady, Chem. Ind., No. 1, 86 (1963).
6. Ya. F. Freimanis in: The Chemistry of Eneaminoketones, Eneaminoimines, and Eneaminothiones [in Russian], Zinatne, Riga (1974), p. 128.
7. P. Gilgen, H. Heimgartner, and H. Schmid, Heterocycles, 6, 187 (1977).
8. O. V. Sverdlova, Electronic Spectra in Organic Chemistry [in Russian], Khimiya, Leningrad (1973), p. 142.
9. C. S. Cbaver and C. G. Krespan, J. Am. Chem. Soc., 87, 3716 (1965).
10. R. Hawey and K. W. Ratts, J. Org. Chem., 31, 3907 (1966).
11. Yu. V. Zeifman, V. V. Tyuleneva, A. P. Pleshkova, R. G. Kostyanovskii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2732 (1975).
12. C. G. Krupan, J. Org. Chem., 34, 1248 (1969).
13. H. Nakata, H. Sakurai, H. Yoshizumi, and A. Tatemalsu, Mass Spectrom., 1, 199 (1968).

*Ions with intensity >5% are shown.

14. T. Nishiwaki, Tetrahedron Lett., No. 25, 2049 (1969).
15. T. Nishiwaki, T. Kitamura, and A. Nakano, Tetrahedron, 26, 451 (1970).

meta-SUBSTITUTED ARYLHYDRAZIDES IN THE KOST REACTION

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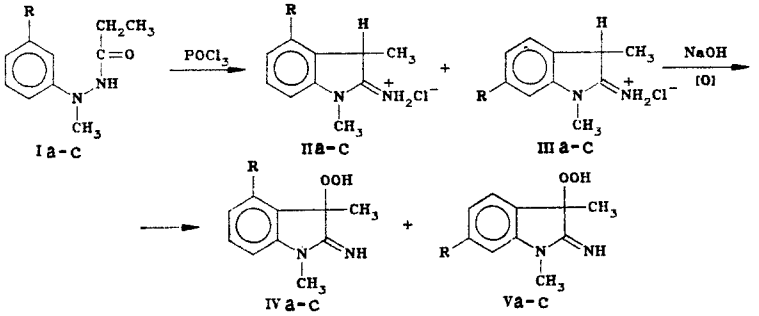
Kost cyclization of meta-substituted arylhydrazides results primarily in the formation of mixtures of 4- and 6-substituted 2-aminoindoles.

The Fischer cyclization of meta-substituted arylhydrazides invariably affords mixtures of 4- and 6-substituted indoles [1]. It would be expected that the use of meta-substituted arylhydrazides in the Kost reaction would give similar results, since the latter reaction proceeds by a mechanism very similar to that involved in the Fischer synthesis [2]. This report is concerned with a study of this problem. The principal compounds chosen as models were the meta-substituted hydrazides (Ia-c).

Rearrangement of the hydrazides (Ia-c) gave the chromatographically homogeneous hydrochlorides (II) and (III).



I—V a R=CH_3, b R=OCH_3, c R=Cl

Despite changes in the carriers used and the use of different systems, TLC failed to reveal the presence of isomeric compounds. In the PMR spectrum of (II) (Table 2), the Ar—CH_3 and OCH_3 signals appear as narrow singlets, and the aromatic proton signals were not susceptible to reliable interpretation. On the basis that there is no reason for such high stereoselectivity in this reaction, leading to the formation of only one isomer, we assumed that the physicochemical parameters and PMR spectral characteristics of the isomeric hydrochlorides (II) and (III) were similar. It was therefore necessary to modify these compounds in such a way as to change their physicochemical properties to a sufficient extent. For this purpose, we took advantage of such properties of the 2-aminoindoles as their oxidizability. It is well known that in the presence of atmospheric oxygen 2-aminoindoles as the free bases undergo ready autoxidation to give, depending on the substituents on the nitrogen, hydroxy or hydroperoxy-derivatives [3, 4].

In fact, following appropriate treatment and the isolation of bases both from mixtures of the pure hydrochlorides (II) and (III), and directly from the reaction mixture, compounds were obtained which according to TLC were mixtures of two isomers (IVa-c) and (Va-c). The free bases from the 2-aminoindoles (II) and (III), like other 1,3-disubstituted iminoindolines [3], form relatively stable peroxy-derivatives (IV) and (V). This was confirmed by elemental analyses and mass spectrometry. It is noteworthy that the molecular ion peaks for

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