NMR SPECTRA OF ARYLAZIRIDINES

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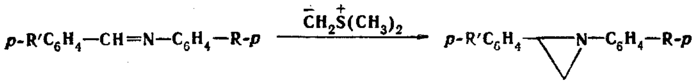
The ^{13}C and ^{1}H NMR spectra of 1-arylaziridines, 2-phenyl-1-arylaziridines, and 2-aryl-1-phenylaziridines were studied. The additive contributions of aziridinyl, 1-phenyl-2-aziridinyl, and 2-phenyl-1-aziridinyl substituents to the shielding of the aromatic protons were calculated. It is shown that with respect to its donor capacity the aziridine ring occupies an intermediate position between amines and amides. The temperature dependences of the PMR spectra of 1-aryl-substituted aziridines were investigated, and the barriers to inversion of the latter were calculated. The dependence of $\Delta G^{\neq}$ on the σ^{-} constants was correlated.

A large amount of research has been devoted to the study of the physical and chemical properties of the aziridine ring. However, very little data on the ^{13}C NMR spectroscopy of 1-arylaziridines are available: Only the spectrum of 1-phenylaziridine has been described [1]. We therefore studied the ^{13}C NMR spectra of 1-aryl- and 1,2-diarylaziridines. The synthesis of 1-arylaziridines I-V was described in [2], and the 1,2-diarylaziridines were obtained by the method in [3]:



The physicochemical characteristics of VI-XIV are presented in Table 1, and the parameters of the ^{13}C NMR spectra are presented in Tables 2 and 3. The resonance of the carbon atoms of the aziridine ring was assigned to the 2 and 3 positions by the off-resonance method. The assignment of the carbon atoms of the aromatic substituents was made by a means of the additive contributions for monosubstituted benzenes [4].

It follows from the data in Tables 1-4 that the substituents in the aryl rings have only a slight effect on the chemical shifts of the carbon atoms of the aziridine ring. We determined the additive contributions of 1-aziridinyl, 2-phenyl-1-aziridinyl, and 1-phenyl-2-aziridinyl groups to the shielding of the carbon atoms of the aryl groups in 1-aryl- and 2-aryl-1-phenyl- and 2-phenyl-1-arylaziridines by calculation of the differences in the

TABLE 1. Physicochemical Characteristics of 2-Phenyl-1-arylaziridines (VI-X) and 2-Aryl-1-phenylaziridines (XI-XIX)

Compound	R	R′	bp, °C (mm)	n_D^{25}	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
VI	F	H	86—89 (0,07)	1,5833	78,5	5,6	6,8	$C_{14}H_{12}FN$	78,8	5,6	6,5	56
VII	Cl	H	93—95 (0,08)	1,6042	72,3	5,3	6,0	$C_{14}H_{12}ClN$	73,2	5,3	6,1	58
VIII	Br	H	125—130 (0,01)	—	60,2	4,5	4,5	$C_{14}H_{12}BrN$	61,3	4,4	5,0	55
IX	CH_3	H	112—113 (0,05)	1,6297	85,9	6,8	6,6	$C_{15}H_{15}N$	86,5	6,7	6,7	58
X	OCH_3	H	118—120 (0,05)	1,6401	77,8	6,8	5,7	$C_{15}H_{15}ON$	78,9	7,1	6,2	62
XI	H	H	71—73 (0,01)	1,6078	85,6	6,5	7,7	$C_{14}H_{13}N$	86,1	6,7	7,2	60
XII	H	OCH_3	82—84 (0,1)	1,5960	77,8	6,8	5,7	$C_{15}H_{15}ON$	78,9	7,1	6,2	56
XIII	H	Br	125—127 (0,2)	—	60,2	4,5	4,6	$C_{14}H_{12}BrN$	61,3	4,4	5,0	55
XIX	H	F	98—99 (0,1)	1,5903	78,8	5,5	6,7	$C_{14}H_{12}FN$	78,8	5,6	6,5	52

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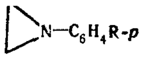
TABLE 2. ^{13}C Chemical Shifts (δ, ppm) of 1-Arylaziridines (I-V)



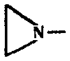
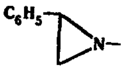
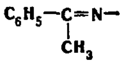
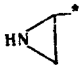
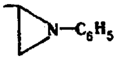
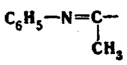
Compound	R		C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_R
I	CH_3	27,0	152,3	120,3	129,0	126,8	20,2
II	H	27,0	154,9	120,5	128,4	121,8	—
III	F	27,1	150,9	121,4	114,8	157,8	—
IV	Cl	27,3	153,5	121,8	128,5	126,8	—
V	Br	27,1	153,7	122,2	131,2	114,0	—

TABLE 3. ^{13}C Chemical Shifts (δ, ppm) of 1,2-Diarylaziridines (VI-XIV)

Compound	Aziridine ring		1-Aryl				2-Aryl				C_R or $C_{R'}$
	C_1	C_2	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_1	$C_{2,6}$	$C_{3,5}$	C_4	
VI	42,1	37,5	150,8	121,8	115,7	158,7	139,4	127,2	128,8	127,7	—
VII	42,0	37,4	153,2	122,0	129,2	129.3	139,1	126,5	128,7	127,6	—
VIII	41,9	37,3	153,5	122,5	132,1	115,2	139.0	126.5	128.7	127.7	—
IX	41,9	37,4	152,0	120,5	129,6	130,7	139,5	126,4	128,5	126.9	20,6
X	41,9	37,4	147,9	121,6	113,9	156,6	139,7	125,9	128,6	127,1	55,2
XI	41,8	38,0	155,1	121,0	129,5	122,8	140,1	127,2	128,9	127.7	—
XII	41,1	31,7	155,3	121,0	120,5	122,5	132,0	127,8	114,5	159,6	55,5
XIII	41,3	38,1	154,7	121,0	129,8	123.2	139,1	128.4	132,0	121,6	—
XIV	41,2	37,8	155,0	121,0	129,6	123,0	135,8	128,2	116,2	162,7	—

TABLE 4. Additive Contributions (ppm) of Some Substituents to the Shielding of the Aromatic Carbon Atoms (average values)

Group	Δ_1	$\Delta_{2,6}$	$\Delta_{3,5}$	Δ_4
	26,6±0,2	−8,0±0,2	−0,6±0,3	−7,9±0,6
	26,7±0,2	−7,8±0,2	+0,2±0,3	−5,6±0,8
 $C_6H_5{-}\underset{CH_3}{\underset{\vert}{C}}{=}N{-}$	23,8	−8,6	+0,3	−4,2
 *	12,2	−2,9	−0,3	−1,8
	11,7±0,2	−1,6±0,2	+0,4±0,3	−0,8±0,5
 $C_6H_5{-}N{=}\underset{CH_3}{\underset{\vert}{C}}{-}$	11,4	−0,8	+1,0	+2,4

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*Calculated from the data in [5].

chemical shifts of the corresponding carbon atoms in these groups and monosubstituted benzenes [4] (Table 4). In order to compare these contributions, the increments for a model compound — acetophenone anil — are also presented in Table 4. A comparison of the calculated increments (Δ_4) with the contributions of other amines [4, 5] to the shielding of aromatic

TABLE 5. Parameters of the PMR Spectra of 1-Arylaziridines I-V

Content	Chemical shifts, δ, ppm		ΔV*, Hz	t, °C (±1°)	$\Delta\sigma_{c}^{\neq}$, kcal/mole (±0,1)
	$(CH_2)_2N$	remaining protons			
I	1,92	6,67 (H_2; H_6) 6,98 (H_3; H_5) 2,18 (CH_3)	21,3	−26	12,5
II	2,00	7,1−6,6	20,7	−38	11,9
III	2,00	6,70 (H_2; H_6) 6,95 (H_3; H_5)	21,6	−29	12,2
IV	2,03	6,76 (H_2; H_6) 7,05 (H_3; H_5)	21,9	−42	11,6
V	2,06	6,70 (H_2; H_6) 7,18 (H_3; H_5)	20,6	−44	11,5
XV†		7,1−6,6	20,7	−37	11,0

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*At −70°C.

†2,2-Dideutero-1-phenylaziridine was obtained by the method in [2].

carbon atoms makes it possible to assert that with respect to its donor capacity the 1-aziridine ring occupies an intermediate position between amines, on the one hand, and amides and imines, on the other.

Replacement of any hydrogen atom of the aziridine ring by a phenyl ring gives rise to a considerable increase in the algebraic value of the Δ_4, $\Delta_{2,6}$, and $\Delta_{3,5}$ increments (Table 4). Consequently, the electronic effect of a substituent in the aziridine ring is rather easily transmitted to the 1- or 2-phenyl rings.

A comparison of the ^{13}C chemical shifts for 1-aryl- and 2-phenyl-1-arylaziridines makes it possible to ascertain the α and β effects of the phenyl ring on the resonance of the carbon atoms of the heteroring: The α effect amounts to +14.8 ppm, and the β effect comes to +11.0 ppm. The values found with allowance for the trans effect of the 1-phenyl ring are extremely close to the values presented in [6] for nitrogen-unsubstituted aziridines. This may constitute evidence that the 1-aryl substituent only slightly changes the electronic structure of the aziridine ring, i.e., the conjugation between the unshared electron pair of the nitrogen atom and the 1-aryl ring is small.

In addition, this conjugation is sufficient for a significant lowering of the barrier to inversion of the nitrogen atom in 1-arylaziridines as compared with 1-alkylaziridines. The barriers to inversion of the nitrogen atom ($\Delta G^{\neq}_{c}$) calculated by the method in [7] from the coalescence temperature of the resonance signals of the cis and trans protons of the aziridine ring are presented in Table 5. The $\Delta G^{\neq}_{c}$ values found for 1-phenylaziridine and its 2,2-dideutero analog in solution in deuteroacetone differ somewhat from the values in CS_2 solution [8] (12.8 kcal/mole).

The electronic effects have an appreciable effect on the $\Delta G^{\neq}_{c}$ values. A correlation between the latter and the σ^- constants of the substituents in the phenyl ring was found ($r = 0.95$, $s_0 = \pm 0.12$ kcal/mole). The ρ coefficient is −2.4 ± 0.06.

In principle, when the temperature is raised (and inversion is accelerated), one might expect an increase in the degree of overlapping of the unshared electron pair of the nitrogen atom with the π system of the 1-aryl ring. The latter in turn should lead to a corresponding change in the chemical shifts of the nuclei of the aryl ring. Since this may be manifested most markedly in the ^{19}F NMR spectra, we studied the temperature dependence of the ^{19}F chemical shift changes very slightly (9.11 ppm at −60°C and 9.18 ppm at +30°C relative to C_6H_5F, 10% solution in deuteroacetone). This result shows that conjugation between the nitrogen atom and the aryl ring evidently changes little as the temperature rises (i.e., as the inversion process is accelerated).

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra of 10% solutions of the compounds in deuteracetone were recorded with a Perkin—Elmer R 12A spectrometer with tetramethylsilane as the internal standard. The ^{13}C NMR spectra of 30% solutions of the compounds in $CDCl_3$ were obtained with a Bruker WH-90 spectrometer (22.63 MHz). The accuracy in the measurements of the ^{13}C chemical shifts was ±0.1 ppm.

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REACTIONS OF 2,2-DIMETHYL-3-PHENYLAZIRINE WITH HYDRAZINE AND ITS DERIVATIVES

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The corresponding α-amino ketone hydrazones were obtained by reaction of 2,2-dimethyl-3-phenylazirine with hydrazine, N,N-dimethylhydrazine, methylhydrazine, and semicarbazide. It was established that unsymmetrical azines are formed in the reaction of 2-amino-2-methyl-1-phenyl-1-propanone hydrazone with aliphatic and cyclic ketones. The corresponding tetrahydro-1,2,4-triazines were obtained in the case of the analogous reaction with aliphatic and aromatic aldehydes.

2,3-Diaryl-2H-azirine-2-carboxamide reacts with hydrazine hydrate and phenylhydrazine to give 1,2,4-triazin-6-one derivatives [1, 2]. In addition to the latter, an addition product — trans-3-hydrazinoaziridine-2-carboxamide — is formed in <10% yield. The principal product of the reaction of 3-aryl-2H-azirine-2-carboxylate with hydrazine was rubazonic acid [2]. Singh and Ulmann [3] have shown that hydrazine reacts with phenyl 2-phenyl-2H-azirin-3-yl ketone to give 4-amino-3,5-diphenylpyrazole.

In the light of the above, we decided to investigate the possibility of the preparation of hydrazinoaziridines from 2,2-dimethyl-3-phenylazirine (I).

Compounds with the formula $C_{10}H_{13}N_2RR'$ (where R and R' are substituents of the hydrazine fragment) were obtained by reaction of azirine I with hydrazine, N,N-dimethylhydrazine, methylhydrazine, and semicarbazide. The band of a C=N bond is observed in the IR spectra of these compounds (Table 1).

A singlet, which can be assigned only to the resonance of the carbon atom of the C=N bond, is noted in their ^{13}C NMR spectra at 155-170 ppm (Table 2). Consequently, the indicated compounds can have only a noncyclic structure. The presence in the PMR spectrum of the product of azirine I with hydrazine of two broad singlets of the NH_2 groups, of which one (δ 1.3 ppm) is attached to an sp^3 carbon atom and the other (δ 4.8 ppm) is attached to a C=N bond, provides evidence in favor of this conclusion. The equivalence of the CH_3 groups in both the ^1H NMR spectra (Table 3) and the ^{13}C NMR spectra also confirms the noncyclic structures of the products.

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