ACID—BASE PROPERTIES OF 1,2,5-OXADIAZOLES.

1. METHYLFURAZANS

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The basicities of 3-methyl-4-R-furazans (R = H, CH_3, C_2H_5, n-C_3H_7, NH_2, $NHAcOCH_3$, I, COOH, and NO_2) were investigated by PMR spectroscopy. It is shown that they are weak bases, the protonation of which is described by the H_A acidity function. Relationships between the chemical shifts of the protons of the methyl group and the σ_R° constants and the pK_{aBH^+} and the σ_M° constants of the substituents were found.

1,2,5-Oxadiazoles (furazans) are weak bases. Quantitative data are available only for benzofurazan, which is a Hammett base with a pK_{aBH^+} value of −8.4 ± 0.1 [1]. Judging from the shift of the ^{15}N signal in the NMR spectrum of a solution in trifluoroacetic acid, dimethylfurazan is protonated under these conditions [2].

To determine the basicities of noncondensed furazans we studied the PMR spectra of a number of 4-substituted 3-methylfurazans in sulfuric acid solutions with various concentrations. We observed that the signal of the methyl protons is shifted to weak field as the sulfuric acid concentration is increased, and the dependence of the chemical shift on the acidity function has sigmoid character. The pK_{aBH^+} values of the investigated compounds were calculated from the linear dependence of the logarithm of the ionization ratio on acidity function H_A [3, 4] by the method of least squares (see Table 1).

In contrast to benzofurazan, the protonation of the investigated compounds is described by an acidity function that is close to H_A.

As expected, V is protonated in two stages: The pK_{aBH^+} value of −2.2 was assigned to protonation of the amino group, and the pK_{aBH^+} value of −4.94 (which is close to the pK_{aBH^+} values of the remaining compounds) was assigned to ring protonation. The change in the chemical shift of the methyl protons in the PMR spectrum (for Vb) in the case of protonation in the ring is small, and the basicity of V was therefore determined by spectrophotometry. The two methods gave good convergence for the first constant.

No relationship between the pK_{aBH^+} values and the position of the signal of the methyl group in the PMR spectrum in the protonated or unprotonated state was observed for the investigated compounds. The chemical shift is correlated satisfactorily with respect to a two-parameter equation by the σ_I° and σ_R° substitutent constants:

$$\delta_{CH_3} = (2.45 \pm 0.04) + (0.13 \pm 0.10)\sigma_I^0 + (0.65 \pm 0.10)\sigma_R^0 \quad (1)$$

$$(n=9,\ r_{\text{fact}} = 0.960,\ S = 0.052,\ r_I = 0.484,\ r_R = 0.944)$$

It is apparent from Eq. (1) that the position of the signal of the methyl group is determined primarily by the contribution of the resonance effect of the substituent (Fig. 1). The one-parameter equation has the form

$$\delta_{CH_3} = (2.49 \pm 0.02) + (0.71 \pm 0.08)\sigma_R^0 \quad (2)$$

$$(n=9,\ r=0.954,\ S=0.051).$$

The pK_{aBH^+} values are correlated unsatisfactorily by the σ_I° and σ_R° constants (r_{fact} = 0.85). The pK_{aBH^+} values of most of the investigated substituted 3-methylfurazans are correlated by the σ_M° constants (Fig. 2):

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TABLE 1. Chemical Shifts in the PMR Spectra of 3-Methyl-4-R-furazans and Their Conjugate Acids, Parameters of the Regression Equations, and pK_{aBH^+} Values

Compound	R	PMR spectra, ppm			$\lg I = aH_A + b$		
		δ_{CH_3} (acetone)	δ_{CH_3}, δ_R (sulfuric acid) unprotonated form	protonated form	[a]	[b]	$-pK_{aBH^+}$*
I	H	2,47	CH_3, 2,46	2,90	0,68±0,04	3,36±0,17	4,94±0,21
			H, 8,57	9,05	1,23±0,04	6,28±0,18	5,11±0,22
II	CH_3	2,34	CH_3, 2,35	2,77	0,94±0,01	4,40±0,06	4,68±0,07
III	C_2H_5	2,36	CH_3, 2,41	2,80	1,08±0,04	5,26±0,17	4,87±0,21
			CH_2, 2,79	3,08	1,09±0,03	5,15±0,15	4,72±0,18
IV	n-C_3H_7	2,31	CH_3, 2,41	2,78	1,06±0,03	5,09±0,13	4,80±0,16
			α-CH_2, 2,79	3,09	1,10±0,05	5,41±0,22	4,92±0,27
Va	NH_2	2,32	CH_3, 2,24	2,60	1,03±0,04	2,29±0,08	2,22±0,12
					1,57±0,02	3,37±0,06	2,15±0,08 (245,5 nm)†
					1,17±0,03	2,69±0,08	2,30±0,11 (210 nm)†
Vb	NH_3^+	—	CH_3, 2,60	2,66	0,93±0,01	4,59±0,07	4,94±0,08 (245,5 nm)†
VI	NHAc	2,34		Decomposes in sulfuric acid			
VII	OCH_3	2,25	CCH_3, 2,31	2,70	0,82±0,04	4,04±0,20	4,93±0,24
			OCH_3, 4,11	4,49	0,75±0,05	3,61±0,25	4,81±0,30
VIII	I	2,42	CH_3, 2,40	2,75	0,75±0,03	3,80±0,17	5,07±0,20
IX	COOH	2,60	CH_3, 2,62	2,88	0,57±0,03	2,94±0,10	5,20±0,13
X	NO_2	2,72		The changes in the spectrum are slight			

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*In the case of slopes of the regression lines that differ significantly from unity the pK_{aBH^+} values were calculated at the half-neutralization point.

†Determined spectrophotometrically; the analytical wavelength is indicated in parentheses.

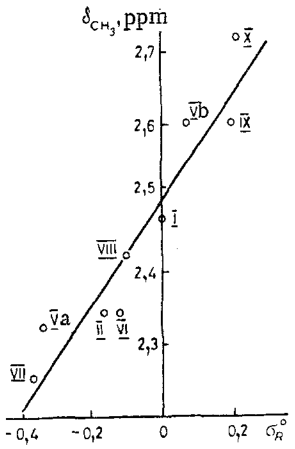

Fig. 1

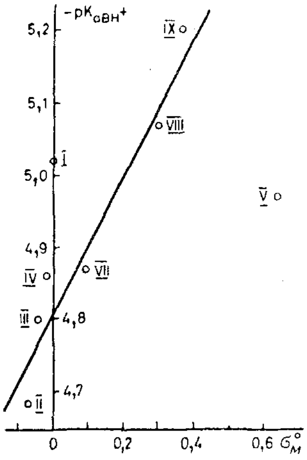

Fig. 2

Fig. 1. Dependence of the chemical shifts of the protons of the methyl group (d_6-acetone) on the σ_R^0 substituent constants.

Fig. 2. Dependence of pK_{aBH^+} on the σ_M^0 substituent constants.

$$pK_{aBH^+} = -(4.81 \pm 0.03) - (0.98 \pm 0.13)\sigma_M^0 \quad (3)$$

$$(n = 6, \; r = 0.963, \; S = 0.037).$$

and this constitutes evidence for the primary influence of the inductive effects of the substituents on the basicities of the compounds.

EXPERIMENTAL

The 25-90% (through 5% intervals) sulfuric acid solutions were prepared by dilution of 96% pure-grade sulfuric acid with distilled water and were titrated with an accuracy of ±0.1%. Solutions with intermediate concentrations were prepared by a gravimetric method.

The PMR spectra of 90-110 mg/ml solutions of the compounds in deuteroacetone (with hexamethyldisiloxane as the internal standard) and in sulfuric acid (with tetramethylammonium bromide as the internal standard) were measured with a Perkin–Elmer R-12 spectrometer (60 MHz) at 40°C.

The UV spectra of V were measured with a Perkin–Elmer 402 spectrophotometer (the layer thickness was 1 cm, and the concentration was 10^{-4} mole/liter). The optical densities at the analytical wavelengths were recorded by means of a V2-23 digital voltmeter.

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SYNTHESIS AND STEREOCHEMISTRY OF 2,2,3-TRIMETHYL-5-ARYL-4-AROYLOXAZOLIDINES

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cis-2,2,3-Trimethyl-5-aryl-4-aroyloxazolidines were obtained by heating complex boron trifluoride salts of trans-1-methyl-2-aryl-3-aroylaziridines with acetone. The reaction of complex boron trifluoride salts of cis-1-methyl-2-aryl-3-aroylaziridines leads to substituted benzaldehydes and ω-N-methylaminoacetophenones.

In [1] it was demonstrated that the simplest 1H-aziridines react readily with aldehydes with expansion of the three-membered ring and the formation of oxazolidines. However, it was later [2-4] found that the products of the reaction of 1H-aziridines with carbonyl compounds are α-alkyl-N-methylolethyleneimines and β-aminoethylethyleneimine derivatives. Nevertheless, it was established in [5, 6] that 5-azoniadispiro[4.0.5.1]dodecane perchlorates react with ketones and aldehydes upon heating to give substituted oxazolidines.

In the present paper we present data on the reaction of complex salts of N-alkyl-3-aroylaziridines with acetone.

We have shown that complexes of trans-1-methyl-2-aryl-3-aroylaziridines with boron trifluoride react upon heating with excess acetone to give cis-2,2,3-trimethyl-5-aryl-4-aroyloxazolidines (VIII-XIV, Table 1) in 50-80% yields. In contrast to [7], according to the results of thin-layer chromatography (TLC) and PMR spectroscopy of the reaction mixtures, the formation of trans analogs of VIII-XIV was not observed. The relative reactivities of complexes I-VII change as a function of the electron-donor properties of the substituents in the 4 position of the aryl group in the order $CH_3 > H > Br \approx Cl$. This makes it possible to propose that the benzyl center undergoes attack by the nucleophile.

The hydrolysis of VIII in an acidic medium led to the formation of acetone, which was identified from its 2,4-dinitrophenylhydrazone, and 1-phenyl-2-N-methylamino-3-hydroxy-3-(p-bromophenyl)-1-propanone (XV). By means of retroaldol cleavage of the latter we obtained p-bromobenzaldehyde (XVI) and ω-N-methylaminoacetophenone (XVII), which confirms opening of the C–N bond of aziridine by acetone on the β-carbon atom side with respect to the carbonyl group.

In addition to absorption bands of aromatic rings (3080, 3040, 1600, and 1500 cm^{-1}), the IR spectra of VIII-XIV contain bands of stretching and deformation vibrations of C–H (2987, 2800, 1450, and 1380 cm^{-1}) and C–O (1095 cm^{-1}) bonds. The intense band of stretching vibra-

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