AZIRIDINYL KETONES AND THEIR CYCLIC ANILS.

6.* PROTON-ACCEPTOR CAPACITIES OF AZIRIDINYL KETONES

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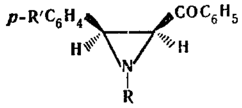
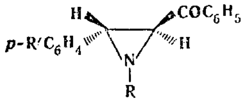
The proton-acceptor capacities of a number of cis- and trans-aziridinyl ketones were estimated by IR spectrometry from the shifts of the ν_{OH} bands of phenol, p-bromophenol, and trichloroacetic acid. It is shown that the cis isomers interact with all of the proton donors, whereas the trans isomers interact only in CCl_3COOH. The latter is due to the fact that a strong intramolecular hydrogen bond exists in the trans-NH-aziridinyl ketones, whereas considerable steric hindrance to complexing develops in the trans-N-alkylaziridinyl ketones. It was established that the formation of complexes takes place at the carbonyl group of the aziridinyl ketones.

The chemical behavior of aziridinyl ketones is determined by the presence of two basicity centers, viz., the nitrogen atom of the three-membered ring and the oxygen atom of the carbonyl group. An a *priori* solution of the problem of their relative basicities is difficult. The fact that the three-membered ring of aziridinyl ketones is opened in the presence of strong acids [2] is not convincing evidence for the increased basicity of the nitrogen atom, since under such conditions protonation of the aziridine ring may be a secondary process vis-à-vis primary protonation of the keto group.

Information regarding the relative basicities of both centers of aziridinyl ketones can evidently be obtained by investigating H complexing with organic acids, and the present research was devoted to this. The interaction was monitored from the IR spectra. Phenol, p-bromophenol, and CCl_3COOH were used as the acids, while cis- (I-IV) and trans-aziridinyl ketones (V-X) and model compounds XI-XIV were used as the subjects of the investigation.

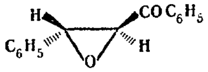


I-IV cis



V-X trans

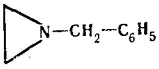
I R=*i*-Pr, R'=H; II R=*i*-Pr, R'=NO_2; III R=$PhCH_2$, R'=H; IV R=$PhCH_2$, R'=NO_2; V R=R'=H; VI R=H, R'=Br; VII R=H, R'=NO_2; VIII R=Me, R'=NO_2; IX R=$PhCH_2$, R'=NO_2; X R=Cl, R'=NO_2



XI

$C_6H_5CH_2N(CH_3)_2$

XII



XIII

$CH_3COC_6H_5$

XIV

cis-Aziridinyl Ketones

These compounds exist in solutions in the form of mixtures of the s-cis and gauche forms [3], to which two bands of carbonyl absorption in the IR spectra correspond (see Table 1); the low-frequency band is related to the s-cis conformer. The decrease in $\nu_{C=O}$ in the s-cis form as compared with the gauche form is explained by the presence in the former of σ–π conjugation of the three-membered ring with the CO group.

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*See [1] for Communication 5.

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TABLE 1. $\nu_{C=O}$ (CCl_4) and $\Delta\nu_{OH}$ Values in the Aziridinyl Ketone–Proton Donor–CCl_4 System*

Compound	$\nu C=O$, cm^{-1}	$\Delta\nu_{OH}$, cm^{-1}		
		C_6H_5OH	p-BrC_6H_4OH	CCl_3OOH
I	1670, 1698	203	224	570
II	1669, 1693	188	208	537
III	1675, 1697	207	234	599
IV	1677, 1693	190	—	—
V	1676	No interaction observed		564
VI	1676	" "		551
VII	1678	" "		558
VIII	1677	" "		548
IX	1676	" "		540
X	1691	78	109	206
XI	1685, 1702	133	141	328
XII	—	661	958	1316
XIII	—	600	—	—
XIV	1670	197	—	537

*The $\Delta\nu_{OH}$ values of the free hydroxy groups are 3610, 3605, and 3508 cm^{-1}, respectively, for phenol, p-bromophenol, and trichloroacetic acid.

The position of the $\nu_{C=O}$ bands remains virtually unchanged when small amounts of phenol are added, but a new broad band (3403-3422 cm^{-1}), which attests to the formation of H complexes of phenol with the aziridinyl ketone, appears in the region of the stretching vibrations of associated OH groups. The shift of this band ($\Delta\nu_{OH}$) as compared with the absorption of the free OH group of phenol (3610 cm^{-1}) is regarded as a measure of the relative basicity of the compound [4]. It was shown by the Ostromyslenko–Zhob method that this H complex has a 1:1 composition. Consequently, only one of the basicity centers of the aziridinyl ketone is protonated under the influence of phenol. A decrease in the intensity of the $\nu_{C=O}$ band of the s-cis form is observed in the presence of excess phenol (in individual cases up to the point at which it vanishes). Hence one might have concluded that H complexing takes place at the C=O group. However, one should bear in mind that the populations of the conformers of cis-aziridinyl ketones in solutions depend on the polarity of the medium (for example, according to the data in [5], exclusively the gauche form is present in acetonitrile). Thus the possibility that there is another reason for the decrease in the intensity of the $\nu_{C=O}$ band of the s-cis form of I-IV in addition to complexing is not excluded.

The $\Delta\nu_{OH}$ values (Table 1), which are typical for complexes with ketones (for example, compare them with the value for XIV and the data in [6]) and are considerably lower than for complexes with amines (XII, as well as triethylamine – $\Delta\nu_{OH}$ 550 cm^{-1} [7]) or aziridines (XIII), constitute evidence in favor of the relatively increased basicity of the C=O group in aziridinyl ketones. This is also confirmed by the association constants (K_{as}) for the association of the cis-aziridinyl ketones with phenol (13.3 ± 0.6, 7.6 ± 0.2, and 8.5 ± 0.6 liters-mole^{-1} for I-III, respectively), which proved to be of the same order of magnitude as in the case of ketones (for example, 9.9 ± 0.3 for XIV [8]). The K_{as} values for triethylamine and aziridine are 49.5 [7] and 110.1 [9], respectively.

An increase in the acidity of the proton donor is accompanied by a regular increase in the $\Delta\nu_{OH}$ values (Table 1). The minimum values obtained for II and IV, which contain an NO_2 group, serve as evidence in favor of conjugation of the aryl group with the aroyl group through the aziridine ring, which is more likely in the case of a mutual s-cis orientation of this ring and the associated C=O group.

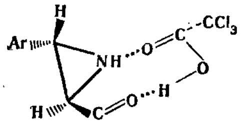
trans-Aziridinyl Ketones

We did not observe interaction of NH- and N-alkylaziridinyl ketones with a set of proton donors with a rather wide range of acidities (PhOH, p-BrC_6H_4OH, C_6Cl_5OH, $MeCO_2H$, and $BrCH_2CO_2H$).

This is natural for NH derivatives V-VII, since they are characterized by a strong intramolecular hydrogen bond that is not cleaved by strong bases such as triethylamine and pyridine [10]. At the same time, the absence of an interaction for N-alkylaziridinyl ketones was unexpected and is evidently explained by the peculiarities of the geometry of these compounds, viz., a primarily cisoid orientation of the aroyl group and the substituent attached to the nitrogen atom [11]. On the basis of this, it may be assumed that the absence of an interaction of trans-N-alkylaziridinyl ketones is due to steric factors.

The behavior of N-chloroderivative X, which, with respect to the inversion state, is of the same type as other trans-aziridinyl ketones [12], constitutes evidence in favor of this. However, the significant decrease in the conformational energy on passing from an alkyl group to a halogen atom [13] creates possibilities for the association of ketone X with various proton donors, including phenol. The marked decrease in the $\Delta\nu_{OH}$ values for X is evidently associated with both an increase in the steric hindrance to solvation and a decrease in the electron-donor character of the N-chloroaziridine ring.

The addition of a trans-aziridinyl ketone to a solution of trichloroacetic acid is accompanied by effects that constitute evidence for the presence of an interaction in this system. One should first of all note the decrease in the intensity of the band of the free OH group of the acid and the simultaneous increase in the intensity of the bands of associated OH groups. In addition, a new band at 3261-3262 cm^{-1}, the intensity of which increases as the percentage of the complex in solution increases, is observed in the IR spectra of H complexes of the trans-aziridinyl ketone and trichloroacetic acid obtained by differential spectroscopy (with compensation of the absorption of the ketone). In our opinion, this band is due to stretching vibrations of an NH group that participates in the formation of a new H bond:



The absence of interaction of trans-alkylaziridinyl ketones with relatively weak acids and the formation of H complexes with trichloroacetic acid are probably explained by the fact that the steric effects in these compounds are extremely pronounced, and an energy gain is achieved only when they interact with strong acids.

The fact that replacement of the hydrogen atom by an alkyl group does not have a substantial effect on the $\Delta\nu_{OH}$ values is an argument in favor of the proposed specificity of the interaction. There is a direct analogy with chalcone oxides, for which it has been established [6] that the primary reaction center in the case of H complexing with phenol is the oxygen atom of the carbonyl group. In addition, it is apparent in the case of XI (Table 1) that the oxirane ring substantially reduces the basicity of the carbonyl group as compared with the aziridine ring, i.e., the latter has greater donor character.

In conclusion, it should be noted that the primary participation of the carbonyl group in the formation of H bonds is, in our opinion, due, on the one hand, to its greater steric accessibility and, on the other, to its increased basicity owing to conjugation with the three-membered ring.

EXPERIMENTAL

The synthesis and purification of the investigated compounds were described in [1]. The IR spectra were measured with a UR-20 spectrometer in NaCl and LiF cuvettes at layer thicknesses ranging from 0.006 to 5 cm at 700-3650 cm^{-1}.

The $\Delta\nu_{OH}$ and K_{as} values and the compositions of the complexes were determined by the methods in [6, 8]. All of the measurements were repeated no less than six times, and the results were treated statistically. The error in the determination of the $\Delta\nu_{OH}$ values was ±2-3 cm^{-1} for phenol and p-bromophenol and ±5-6 cm^{-1} for trichloroacetic acid. In the measurement of the $\Delta\nu_{OH}$ values for the complexes with trichloroacetic acid we took into acccount the fact that a number of bands of associates, regarding the nature of which there is no unified point of view [14], are observed in the IR spectra of even dilute solutions of trichloroacetic acid. When excess aziridinyl ketone was added, these bands were shifted to the low-frequency region. The shift of only the highest-frequency A band was taken into account in the analysis of the $\Delta\nu_{OH}$ values.

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DIRECTION OF DEPROTONATION OF 4-(3-INDOLYL)PYRIDINIUM SALTS IN ALKALINE MEDIA

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A proton is split out from the NH group of indole to give the anhydro bases in all cases when 4-(3-indolyl)pyridinium salts with alkyl, benzyl, phenacyl, and quinolylmethyl residues attached to the pyridinium nitrogen atom are treated with alkali.

The CH acidity of the N-methyl group in pyridinium methiodide is ∿15 orders of magnitude greater than that of the methyl group in toluene [1]; this is associated with the effect of

TABLE 1. Characteristics of the Quaternary Salts of Pyridylindoles and Their Anhydro Bases

Compound	mp, °C (from alcohol)	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	Hal	N		C	H	Hal	N	
Ia	249—250	51,2	4,5	36,1	8,2	$C_{15}H_{15}IN_2$	51,4	4,3	36,3	8,0	95
Ib	185—186	52,8	4,9	35,0	7,5	$C_{16}H_{17}IN_2$	52,7	4,7	34,9	7,6	93
Ic	120—121	56,4	5,5	31,1	7,0	$C_{19}H_{23}IN_2$	56,2	5,7	31,3	6,9	95
Id	165—166	75,1	5,1	11,3	8,6	$C_{20}H_{17}ClN_2$	74,9	5,3	11,1	8,7	91
Ie	195—196	64,0	4,5	20,5	6,9	$C_{21}H_{17}BrN_2O$	64,1	4,3	20,4	7,1	95
IIa	100—102	81,2	6,2	—	12,8	$C_{15}H_{14}N_2$	81,1	6,3	—	12,6	91
IIb	119—120	81,1	6,9	—	12,1	$C_{16}H_{16}N_2$	81,4	6,8	—	11,9	90
IId	251—252	84,7	5,8	—	9,7	$C_{20}H_{16}N_2$	84,5	5,6	—	9,9	93
IIe	244—245	81,2	4,9	—	8,7	$C_{21}H_{16}N_2O$	80,8	5,1	—	9,0	90
IV	347—348	66,1	4,6	19,0	10,5	$C_{23}H_{18}BrN_3$	66,3	4,3	19,2	10,1	97

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