INVESTIGATION OF THE IR, PMR, UV, AND MASS SPECTRA OF BETAINES OF THE AZOLE SERIES

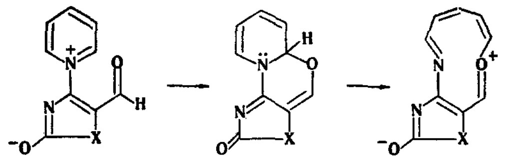
R. O. Kochkanyan, A. N. Zaritovskii,
N. A. Klyuev, B. M. Zolotarev,
and S. N. Baranov

UDC 547.781.5'867'897:543.422.25.4.6'51

It was established by a complex spectral method that 5-formyl-4-(1-pyridinia)thiazole 2-oxide and 1-phenyl-5-formyl-(1-pyridinia)imidazole 2-oxide have betaine structures.

We have previously reported [1, 2] the synthesis of stable betaines of the azole series (I) that contain a heteroaromatic cation.

Considering the literature data [3, 4] on the high reactivities of betaines and their tendency to undergo spontaneous intramolecular cyclizations, one might have proposed a number of isomeric cyclic structures of the b and c type for the synthesized compounds.



In this connection, we studied their IR, PMR, UV, and mass spectra. Thus a shift of the frequencies of the vibrations of the carbonyl groups to the low-frequency region (1640 and 1690 cm^{-1}) as compared with their salts is observed in the IR spectra of the betaines; this can be explained by a decrease in the double bond character of the carbonyl groups due to delocalization of the negative charge as in the case of phenacylphosphonium ylids. When the compounds are protonated, both the vibrations of the carbonyl group in the 2 position and of the formyl group are shifted to the high-frequency region and take on values of 1680 and 1730 cm^{-1}. This fact makes it possible to assign structure a rather than b and c to the betaines, since in the case of protonation of structure c one would have observed a shift to the high-frequency region only of the vibrations of the carbonyl group in the 2 position of the azole ring. This is also in agreement with the PMR spectra of 5-formyl-4-(1-pyridinia)thiazole 2-oxide (I, X=S), in which the presence of three multiplets at weak field with δ_1 8.30, δ_2 8.84, and δ_3 9.58 ppm and an integral intensity ratio of 2:1:2, which characterize the β, γ, and α protons of the pyridinium ring, as in the case of pyridinium salts, are observed. In addition, a singlet in the weak-field portion of the spectrum at δ 9.21 ppm, which we assigned to the resonance of the proton of an aldehyde group, is observed in the spectrum. In the case of 1-phenyl-5-formyl(1-pyridinia)imidazole 2-oxide (I, X=N—Ph) an additional multiplet at δ 7.35 ppm, which corresponds to the resonance of the protons of the phenyl ring, appears in the PMR spectrum. The position of the protons of the aldehyde group was determined unambiguously by synthesis of betaines with a completely deuterated pyridinium cation and by a study of their PMR spectra.

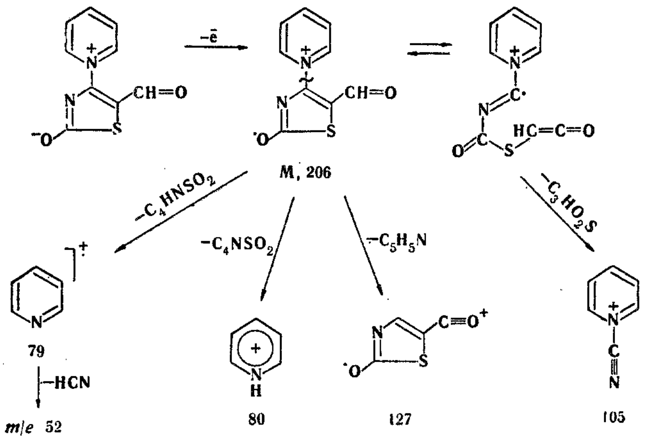
Little study has been devoted to the mass spectra of compounds with betaine structures [5-7]. It is known that the interannular bond between the hetaryl rings is usually cleaved under the influence of electron impact. Both fragments that make up the starting compound are recorded in the mass spectrum.

Institute of Physical Organic Chemistry and Coal Chemistry, Donetsk 340048. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 255-257, February, 1978. Original article submitted March 14, 1977.

0009-3122/78/1402-0208$07.50

Baker and Ollis [8] have shown that the molecular ion in the mass spectra of compounds of this type can be transformed and can exist in the form of an ion radical in the open form. As a rule, the intensity of the molecular-ion peak in the spectra of compounds of this type is insignificant (5-10% of the maximum ion peak in the spectrum); however, in a number of cases the intensity reaches 70%. A rather intense molecular-ion peak (52.6% of the maximum peak) and the corresponding fragment ions that are formed by detachment of a formyl group (the $[M—CHO]^+$ ion peak) are recorded during examination of the mass spectrum of 5-formyl-4-(1-pyridinia)thiazole 2-oxide; this is extremely characteristic for most aromatic aldehydes. Cleavage of the interannular C—N bond in the molecular ion procede extremely specifically. The ion peak corresponding to the pyridine structure is the maximum peak in the spectrum, while the other fragment ion ($[M—C_5H_5N]^+$) is of low intensity. This fact to a certain degree attests to the possibility of the existence of the molecular ion in the open form. The latter is confirmed by the presence in the mass spectrum of an ion peak with m/e 105.

Proceeding from the mass-spectrometric data, the fragmentation of the molecular ion of the thiazole betaine can be represented by the following scheme:



Mass spectrum, m/e (the ion peaks with intensities ≥ 3% of the maximum intensity are presented):

39 (28.5), 40 (3.7), 41 (10.7), 42 (6.2), 43 (19.0), 44 (13.6), 45 (5.9), 50 (20.0), 51 (48.1), 52 (59.2), 53 (17.9), 55 (10.5), 57 (19.4), 60 (7.6), 63 (7.6), 64 (11.6), 65 (15.7), 70 (35.9), 71 (13.0), 73 (21.5), 77 (36.8), 78 (26.3), 79 (100.0), 80 (59.4), 91 (18.7), 92 (9.3), 93 (24.8), 99 (5.5), 105 (40.0), 108 (13.1), 115 (3.0), 119 (16.6), 121 (60.4), 122 (6.5), 127 (5.3), 133 (4.9), 149 (10.0), 150 (6.4), 165 (9.5), 177 (23.7), 197 (63.0), 198 (38.7), 205 (9.4), 206 (52.6), 207 (6.5), 208 (6.6).

According to the mass-spectrometric data, the molecular weight of 1-phenyl-5-formyl-4-(1-pyridinia)imidazole 2-oxide is 265; i.e., it corresponds to the true molecular weight of the imidazole betaine.

The character of the fragmentation of the molecular ion of this compound differs little from that of the compound examined above. In addition to the ion peaks at 79, 78, 52, and 51 characteristic for pyridine, an ion peak with m/e 77, which indicates the presence of a phenyl substituent, is observed in the spectrum. The detachment of a formyl radical from the molecular ion takes place with greater intensity than in the case of the thiazole betaine. The intensity of the $[M—C_5H_5]^+$ ion peak with the structure of an imidazole fragment is low; this is explained by its low stability.

Mass spectrum, m/e (≥ 3%):

41 (6.3), 42 (5.1), 43 (8.2), 44 (20.1), 50 (70.3), 51 (79.6), 52 (89.1), 53 (15.3), 63 (6.7), 64 (8.7), 77 (23.5), 78 (18.4), 79 (100.0), 80 (8.6), 91 (14.2), 104 (6.6), 105 (10.7), 119 (28.5), 186 (4.8), 236 (16.3), 265 (8.3), 266 (3.2).

Bands of weak intensity at 400 (I, X=S) and 450 nm (I, X=N—Ph), which are due to an intramolecular donor—acceptor interaction, are observed in the electronic spectra of the be-

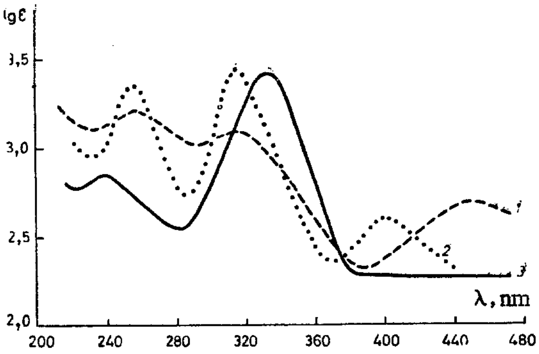


Fig. 1. UV spectra: 1) I (X=S) in methanol; 2) I (X=N—PH) in methanol; 3) 4-chloro-5-formylimidazol-2-one in methanol.

taines in the short-wave region, in addition to the absorption maxima (Fig. 1). This fact is confirmed by the absence of analogous bands in the spectra of chloroformylazolinones, in which this interaction is excluded.

Thus the data obtained in this research unambiguously confirm the betaine structure of I.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The mass spectra were recorded with a Varian MAT-311 mass spectrometer at an ionizing-electron energy of 70 eV. The samples were introduced directly into the ion source of the mass spectrometer at 100-150°C. The PMR spectra were recorded with a Varian XL-100 spectrometer with an operating frequency of 100 MHz at 30°C; the solvent was deuterodimethyl sulfoxide, and the internal standard was hexamethyldisiloxane. The UV spectra of methanol solutions of the compounds were recorded with an SF-4 spectrophotometer.

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