

π-AMPHOTERIC HETEROCYCLES

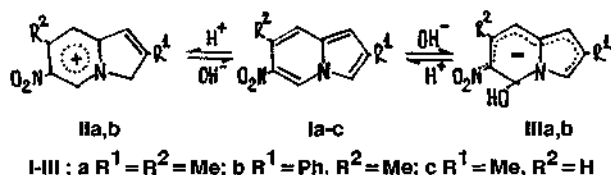
Eugeny V. Babaev

Chemical Department, State University Moscow, 119899, Russia

Received : 24/08/1992 - Accepted : 08/09/1992

The formation of the Wheland or Meisenheimer σ -complexes - the wellknown phenomena in chemistry of aromatics and heteroaromatics [1, 2] - is a key step in the both classical S_E2Ar and S_N2Ar substitution. The ability of arenes and hetarenes to form predominantly the cationic or the anionic type of σ -complexes is, in general, determined by the π -excessive or π -deficient character of aromatic nucleus (cf. known C-protonation of azulenes, indoles, donor-substituted benzenes or *vice versa* addition of nucleophiles to nitroazines and polynitroarenes). To our knowledge the simple aromatics, capable of undergoing easy transformation in the both directions - into the anionic, as well as the cationic σ -complexes - are still unknown. The simplest possible aromatics of this type would be expected to contain two condensed rings together with a high asymmetry of the π -electron density.

With the indolizines **1a,b**, we found the first example of the bicyclic arenes, which easily form cationic and anionic σ -complexes on carbon atoms with a simple variation in the pH of the solvent system.



Thus, indolizines **1a,b** [3] are reversibly transformed in the strong acids (CF_3COOH , HCl , H_2SO_4) into the cations **IIa,b** and in the alkaline solution ($NaOH/aq$ $EtOH$, $MeOH/MeONa$) into the anions **IIIa,b**. The corresponding spectral changes in acidic and alkaline media for indolizine **1a** are illustrated in the Table; the picture observed for **1b** is quite analogous. The typical red color (λ_{max} 440-450 nm, $EtOH$) of the indolizines **1a,b** disappeared during basification or acidification due to the formation of pyridinium-like cations **II** or pyrrole-like anions **III**. In PMR spectra of the cations **II** (in CF_3COOH) the strong downfield shift of the pyridinium proton H-5 and the appearance of CH_2 -signal in the region, expected for 3H-indolizinium cations (i.e., at 5.3 - 6.3 ppm, according to [4]), confirms that protonation takes place at C-3. In anions **III** (CD_3ONa/CD_3OD , 20°C) all the proton signals (including H-5) undergo the upfield shift.

TABLE

Structure	λ_{max} (lgε) /media/	1H chemical shifts (δ ppm, TMS) ^{*)}					
		H-1	2-Me	H-3	H-5	7-Me	H-8
Neutral 1a	440 (2.97) /EtOH/	6.25	2.35	7.25	8.95	2.65	7.05
Cation IIa	310 (3.73) /1N HCl, 50% EtOH/	1H(s)	3H(s)	1H(s)	1H(s)	3H(s)	1H(s)
Anion IIIa	327 (4.05) /2N KOH, EtOH/	1H(s)	3H(s)	1H(s)	1H(s)	3H(s)	1H(s)

^{*)} **1a** in CCl_4 ; **IIa** in CF_3COOH ; **IIIa** in CD_3ONa/CD_3OD

Our CNDO/2-calculations [3a] of the molecules **1c** and 2-methyl indolizine show that a 6-NO₂-group does not change neither the topology of HOMO, nor the highest π -charge on C-3 but strongly decreases both the π - and the ($\pi + \sigma$)-charges on C-5; the LUMO of **1c** is very similar to that of nitroethylene. The resulted electron density in indolizines **1** turns out to be highly polarized: the *peri*-positions C-3 and C-5 in the molecule **1c** have the highest charges of the opposite signs. Since the known addition of dienophiles to indolizines occurs just across the C-3 and C-5 positions (usually treated as the rare [8 + 2] cycloaddition type [5]), one would expect a rather unusual mechanism of Diels-Alder reaction for nitroindolizines **1**, their derivatives and analogs.

The unique " π -amphoteric" chemical behavior of indolizines **1a,b** is analogous to the chemistry of *peri*-condensed tricyclic perimidine [6], while the reactivity of simplest possible carbocyclic analog - the known 5-nitroazulene [7] (π -isoelectronic to the indolizines **1**) - have been still not studied.

REFERENCES AND NOTES

1. Recent works: Organic Reaction Mechanisms - 1988, A.C. Kripe, W.E. Watts, eds., Interscience, Chichester, 1990, pp. 305, 323.
2. For numerous examples see: Comprehensive Heterocyclic Chemistry, A.R. Katritzky, C.W. Rees eds., Pergamon Press, Oxford, 1984, Vol. 1-8.
3. For the synthesis of **1a,b** see a) E.V. Babaev, *Diss. Moscow University*, 1987; b) S.I. Bobrovskii, E.V. Babaev, Yu.O. Vasiljev, Yu.G. Bundel, *Moscow Univ. Chem. Bull.* **42**, 93 (1987) (Engl. transl.).
4. W.L.F. Armarego, *J. Chem. Soc. (B)*, 191 (1966).
5. a) F.J. Swinborne, J.H. Hunt, G. Klinkert, *Adv. Heteroc. Chem.*, **23**, 443 (1987); b) W. Fitch, *Ref. [2]*, Vol. 4, p. 443.
6. A.F. Pozharskii, V.V. Dal'nikovskaya, *Russ. Chem. Rev.*, **50**(9), 816 (1981) (Engl. transl.).
7. T. Severin, I. Ipach, *Synthesis*, **12**, 981 (1979).