MESOIONIC COMPOUNDS WITH A BRIDGE NITROGEN ATOM.

20.* THIAZOLOQUINOXALINIUM OXIDE SALTS

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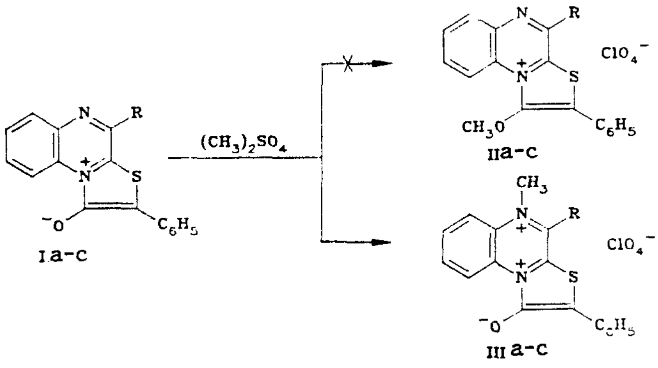
UDC 547.863.1'789.6.04:543.422.25:541.27

It was established that the protonation and alkylation of mesoionic thiazolo[3,2-a]quinoxalinium 1-oxides does not take places at the oxide oxygen atom but rather at the nitrogen atom in the 5-position. The π-electron structures of the compounds obtained were studied by the Pariser–Parr–Pople (PPP) method.

It is known that mesoionic condensed thiazolo azinium oxides react readily with alkylating agents [2, 3] to give the corresponding alkoxy-substituted thiazolo azinium salts. It is important that, in contrast to the starting mesoionic compounds the products of their alkylation are colorless substances. Depending on the structures of the heterocycles, the intensity of the coloration increases to different degrees. Thus the transition from 2-phenylthiazolo[3,2-*a*]pyridinium 3-oxide to the 3-methoxy-2-phenylthiazolo[3,2-*a*]pyridinium cation is accompanied by a hypsochromic shift of 105 nm [2]. In the case of mesoionic 5-R^1-7-R^2-2-phenylthiazolo[3,2-*a*]pyrimidinium 3-oxides the shift is even more significant (108-220 nm) [3]. In this connection, it seemed of interest to investigate the dependence of the reactivities and chromaticities of derivatives of mesoionic heterocycles on their chemical structures.

With this end in mind, we studied the reaction of dimethyl sulfate with 4-R-2-phenylthiazolo[3,2-*a*]quinoxalinium 1-oxides Ia-c [1].



I—III a R=H, b R=CH$_3$, c R=C$_6$H$_5$

In analogy with [2, 3] one might have assumed that 1-methoxythiazoloquinoxalinium salts II are formed. This reaction pathway is also in agreement with the results of quantum-chemical calculations of the distribution of the electron density on the atoms of the molecule of oxide Ia [4]. It is apparent from these results that the maximum (–0.754) electron density is localized precisely on the oxygen atom of the oxide group.

The methylation of oxides I is accomplished by heating with dimethyl sulfate. The compositions of the isolated compounds (Table 1) correspond to the proposed structure II. However, in contrast to the previously described compounds, solutions of the products obtained absorb more deeply than not only known methoxythiazolo azinium salts (330-390 nm [2, 3]) but even the starting oxides I (528-539 nm [1]) (Table 1). The bathochromic shifts of the absorption maxima for the substituted salts (a-c) are, respectively, 49, 60, and 64 nm.

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*See [1] for Communication 19.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 842-845, June, 1990. Original article submitted July 21, 1988; revision submitted January 13, 1989.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C	λ_{max}, nm (log ε)	Solvent	Chemical shift, δ, ppm				Yield, %
					R	N—CH₃	Ar—H	9-H	
IIIa	$C_{17}H_{13}ClN_2O_5S$	266...267	588 (4,44)	DMSO-D_6	9,74	4,32	7,60 (3H); 8,05 (2H); 8,25...8,50 (3H)	10,04	69
IIIb	$C_{18}H_{15}ClN_2O_5S$	246...247	588 (4,44)	CF_3COOD	8,29	4,47	7,5...7,8 (3H); 8,0...8,4 (5H)	10,24	52
IIIc	$C_{23}H_{15}ClN_2O_5S$	245...246	603 (4,35)	DMSO-D_6	—*	4,01	7,50 (2H); 7,88 (5H); 8,06 (2H); 8,38 (4H)	10,13	23
IV	$C_{16}H_{11}ClN_2O_5S$	241...242	586 (4,55)	—	—	—	—	—	95
V	$C_{27}H_{24}ClN_3O_5S$	231...232	578 (4,44) 667 (4,25)	CF_3COOD	—*	4,23; 3,10 (6H)	6,85 (d, 1H, J=9 Hz); 7,50 (4H); 7,90 (5H); 8,30 (5H)	10,11	52

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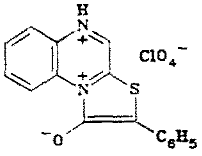
*The signal coincides with the multiplet of aromatic protons.

The oxide I molecule contains yet another nucleophilic center, viz., the nitrogen atom in the 5 position, at which [despite the considerably smaller negative charge (–0.187)] alkylation is possible. On the basis of this we assumed the formation of salts with structure III. According to the results of quantum-chemical calculations (the calculated absorption maxima λ_{max} are 558, 550, and 598 nm for Ia, IIa, and IIIa, respectively) the absorption maxima of III, in contrast to methoxy-substituted salts of the II type, should actually be shifted bathochromically as compared with starting oxides I.

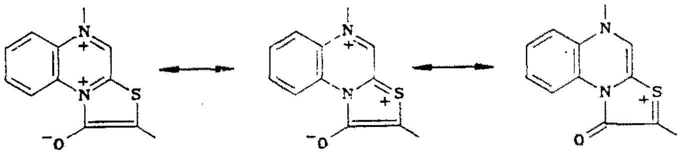
Structures IIIa-c of the isolated compounds are also confirmed by data from the PMR spectra (Table 1). In them, as in the case of oxides I [1], the signal of the proton in the 9 position is shifted to weak field from the multiplet of aromatic protons under the influence of the neighboring oxide oxygen atom. The signal of the methyl group has a chemical shift of 4.0-4.5 ppm. This constitutes evidence that the group is bonded precisely to the nitrogen atom rather than to the oxygen atom, for otherwise one would observe a signal with a chemical shift at 3.5-3.6 ppm, as in the case of 3-methoxy-2-phenylthiazolo[3,2-*a*]pyrimidinium salts [3]. Moreover, let us direct the reader's attention to the fact that for 4-phenyl-substituted salt IIIc the signal of the $N{-}CH_3$ group is shifted to the strong-field region (0.3 ppm) as compared with perchlorate IIIa. This shift of the signal is explained by the effect of the ring currents of the phenyl ring as in the previously noted [5] effect of substituents in ordinary quaternary salts of nitrogen heterocycles.

One might have assumed that the unusual reactivities of thiazoloquinoxalinium oxides are due in part to the certain amount of steric hindrance of the oxygen atom that is introduced by the neighboring atoms of the benzene rings, and isomeric products might therefore be obtained when reagents with a smaller volume are used. However, salts with the same structure are formed not only in the case of alkylation, but also in the case of protonation of oxide Ia. Thus, for example, the absorption maxima of perchlorate IV obtained by the action of perchloric acid and of N-methyl salt IIIa virtually coincide.



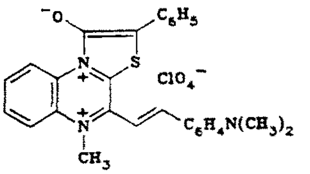
IV

The structures of cations III can be represented by the following boundary structures:

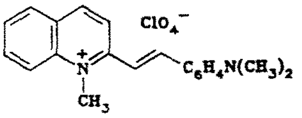


In contrast to starting oxides I, in the case of cations III on passing to the first excited state one observed primarily not transfer of electron density from one fragment of the molecule to another [1], but rather alternation of charges (Fig. 1). Consequently, with respect to their electron structures these compounds approximate typical polymethine dyes.

It is interesting to note that the methyl group in the 4 position of thiazoloquinoxalinium salt IIIb, as in the case of quaternary quinaldinium salts, is quite active in cyanine condensations. Thus, styryl V is formed with p-dimethylaminobenzaldehyde.



V



VI

Two bands are observed in the absorption spectrum of dye V; this is characteristic for cyanines with two chromophores. It is important that the maximum of the long-wave band has a greater bathochromic shift (143 nm) as compared with styryl VI based on a quinaldinium perchlorate [6, p. 198]. This spectral effect, as in biscyanine dyes [7, p. 666], is evidently due to interaction of the electron transitions, which in this case are localized, respectively, on the atoms of the polymethine chain and the terminal mesoionic heteroring. Consequently, the synthesized salts of mesoionic thiazoloquinoxalinium oxides can be used to obtain new deeply colored dyes with a short polymethine chain.

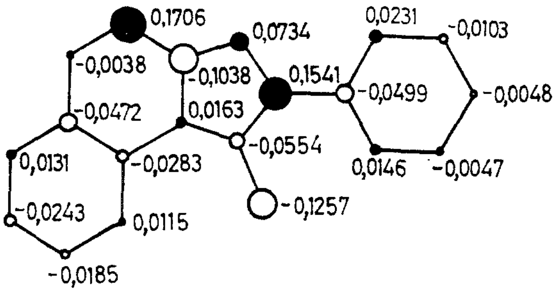


Fig. 1. Distribution of the electron density on the atoms of model cation III.

EXPERIMENTAL

The PMR spectra were obtained with a WP-100SY spectrometer (100 MHz) with tetramethylsilane (TMS) as the internal standard. The electronic spectra of solutions in acetonitrile were obtained with an SF-8 spectrophotometer. The quantum-chemical calculations were made within the Pariser–Parr–Pople (PPP) approximation. The parameters for the calculation were the same as in [2].

The characteristics of the synthesized compounds are presented in Table 1. The results of elementary analysis for N and Cl were in agreement with the calculated values.

5-Methyl-4-R-2-phenylthiazolo[3,2-*a*]quinoxalinium 1-Oxide Perchlorates IIIa-c. A mixture of 2 mmoles of the corresponding oxide Ia-c and 2 ml of dimethyl sulfate was heated for 3 h at 115°C, after which the product was precipitated with ether and dissolved in alcohol. A solution of 0.26 g (2.1 mmoles) of sodium perchlorate in 10 ml of alcohol was then added, and the precipitate was removed by filtration and crystallized from acetonitrile.

2-Phenylthiazolo[3,2-*a*]quinoxalinium 1-Oxide Perchlorate (IV). A 0.2-ml (3 mmoles) sample of 70% perchloric acid was added dropwise to a solution of 0.27 g (1 mmole) of oxide Ia in 10 ml of acetonitrile, and the precipitated product was removed by filtration, washed with acetonitrile and ether, and crystallized from acetonitrile. The yield was 0.35 g.

5-Methyl-1-oxo-4-(4-dimethylaminostyryl)-2-phenyl-1,5-dihydrothiazolo[3,2-*a*]quinoxalin-3-yl Perchlorate (V). A mixture of 0.2 g (0.5 mmole) of perchlorate IIIb, 0.08 g (0.5 mmole) of p-dimethylaminobenzaldehyde, and 2 ml of acetic anhydride was heated to the boiling point, after which it was cooled, and the precipitated dye was removed by filtration, washed with alcohol and ether, and crystallized from acetic anhydride. The yield was 0.14 g.

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