REACTION OF VINYL ETHERS OF THE PYRIDINE SERIES WITH BROMINE AND IODINE

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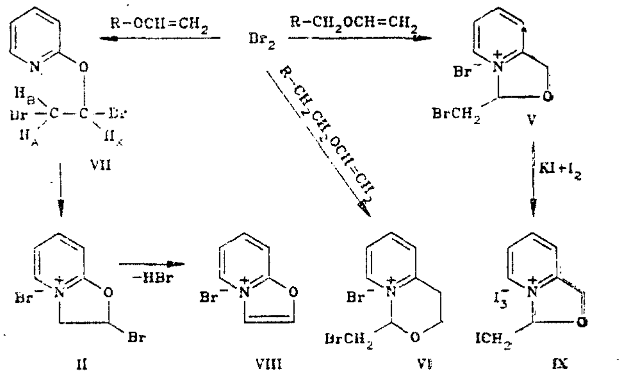
The reaction of 2-vinyloxypyridine and 2-vinyloxymethyl(ethyl)pyridines with halogens gives intramolecular, quaternized compounds, the halides of dihydrooxazolo[3,2-a]-, dihydrooxazolo[3,4-a]-, and dihydrooxazino[3,4-a]pyridine.

It was shown previously [1] that 2-vinyloxypyridine (I) reacts with bromine in CCl_4 to form the bromide of 2-bromodihydrooxazolo[3,2-a]pyridine (II). In the present work, the halogenation of 2-vinyloxymethylpyridine (III) and 2-(2-vinyloxyethyl)pyridine (IV) is studied for the first time.

Ethers III and IV react with bromine in CCl_4 at 0°C via a halogencyclization reaction [2] to form new, intramolecular, quaternized compounds — the bromides of 3-bromomethyl-1,3-dihydrooxazolo[3,4-a]pyridine (V), and 4-bromomethyl-1,2-dihydro-4H-oxazino[3,4-a]pyridine (VI).



R=2-pyridyl

Unlike bromides V and VI, bromide II does not precipitate from the reaction solution. This gave rise to the idea that the reaction takes place through a step in which a bromine atom is added along the double bond. In order to demonstrate this, we used PMR to study the reaction solution formed by mixing equimolar amounts of ether I and bromine in CCl_4 at 20°C. The PMR spectra (Table 1) taken after 1 and 4 h are identical and show that 2-(1,2-dibromoethoxy)pyridine (VII) is present in the solution, whereas ether I and bromide II are not found. On distilling off the CCl_4 in vacuum, bromide II begins to be formed, with the highest yield being observed after a day.

At 125°C, bromide II readily splits out hydrogen bromide to form the high-melting bromide of oxazolo[3,2-a]pyridine (VIII).

Ether III reacts with iodine in a diethyl ether medium, regardless of the ratio of the starting compounds, to form a product containing 2 moles of iodine per mole of ether III. We assume that the reaction goes to form the iodide of 3-iodomethyl-1,3-dihydrooxazolo[3,4-a]pyridine (IV). It is also obtained by the reaction of bromide V with potassium iodide and iodine in ethanol. Unlike ether III, ethers I and IV do not react with iodine in diethyl ether, CCl_4, or ethanol at up to 50°C.

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TABLE 1. PMR Spectra of Compounds II, V-VIII in CD_3OD

Compound	Chemical shifts, δ, ppm (J, Hz);
II	5,64 (2H, m, 3-CH_2), 7,57 (1H, q 2-H), 7,75 (2H, m, 6 and 8-H), 8,64 (1H, m, 7-H), 8,87 (1H, d, $J=6{,}0$, 5-H)
V	4,33 (2H, m CH_2Br), 5,75 (2H, t, $J=3{,}0$, 1-CH_2), 6,87 (1H, m 3-H), 8,23 (2H, m, 6 and 8-H), 8,72 (1H, m 7-H), 9,22 (1H, d.d. $J=6{,}0$, 5-H)
VI	3,53 (2H, m 1-CH_2), 4,27 (2H, m CH_2Br), 4,50 (2H, m 2-CH_2), 6,52 (1H, m 4-H), 8,10 (2H, m 7-and 9-H), 8,53 (1H, 8-H), 9,01 (1H, d, $J=6{,}0$, 6-H)
VII*	4,01 (1H, m H_A), 4,07 (1H, m, H_B), 6,83 (1H, m 5-H), 7,01 (1H, m 3-H), 7,33 (1-H, q, $J_{AX}=4{,}0$, $J_{BX}=8{,}5$, H_X), 7,63 (1H, m 4-H), 8,22 (1H, d.d., $J=5{,}5$, 6-H)
VIII	7,95 (1H, m, 6-H), 8,0—8,8 (4H, m 2-, 3-, 7 and 8-H), 9,15 (1H, d, $J=6{,}0$, 5-H)

*CCl_4 solvent.

In the IR spectra of salts II and V-IX, there are bands in the 1630-1650 cm^{-1} region that are characteristic of the pyridinium cation [3]. In their PMR spectra, the signals from the pyridine ring protons are shifted to considerably weaker fields than the corresponding signals in the ethers [4, 5]. Thus, in the spectrum of bromide V, the signals of the protons in the 1-CH_2 group form a distorted triplet. The signals of the diastereotypic protons undergo further splitting.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument with KBr discs. The PMR spectra were taken on a BS-487 B (80 MHz) instrument with TMS as an internal standard.

2-Bromodihydrooxazolo[3,2-a]pyridinium Bromide (II). A solution of 1.60 g (10 mmoles) of bromine in 50 m of CCl_4 is added dropwise at 0°C to a solution of 1.21 g (10 mmoles) of ether I in 50 ml of CCl_4 over a period of 30 minutes. After a day, the CCl_4 is distilled off under vacuum and the residue treated with acetone. Yield 2.39 g (85%), T_{mp} 105°C (ethanol). IR spectrum: 1500, 1570, 1640 cm^{-1} (C=C, C=N). Found, %: C 29.1; H 2.8; Br 57.2. $C_7H_7Br_2NO$. Calculated, %: C 29.9; H 2.5; Br 56.9.

Oxazolo[3,2-a]pyridinium Bromide (VIII). Heat 1.4 g (5 mmoles) of bromide II at 125°C for 15 minutes. After cooling, treat it with acetone and dry. Yield 0.96 g (96%) VIII. T_{mp} 283°C (ethanol). IR spectrum: 1497, 1560, 1645 cm^{-1} (C=C, C=N). Found, %: C 41.7; H 2.8; Br 40.6. C_7H_6BrNO. Calculated, %: C 42.0; H 3.0; Br 40.0.

3-Bromomethyl-1,3-dihydrooxazolo[3,4-a]pyridinium Bromide (V). A solution of 1.6 g (10 mmoles) of bromine in 40 ml of CCl_4 is added dropwise to a solution of 1.35 g (10 mmoles) of ether III in 40 ml of CCl_4 at 0°C with stirring over a period of 30 minutes. The reaction mixture is allowed to stand for a day, during which a deposit separates from the solution. Wash with acetone and dry. Yield 1.1 g (37%). T_{mp} 180°C (ethanol). IR spectrum: 1500, 1590, 1638 cm^{-1} (C=C, C=N). Found, %: C 32.7; H 3.3; Br 54.6. $C_8H_9Br_2NO$. Calculated, %: C 32.5; H 3.1; Br 54.2.

4-Bromomethyl-1,2-dihydro-4H-1,3-oxazolo[3,4-a]pyridinium Bromide (VI). Obtained in an analogous fashion from ether IV and bromine. Yield 32%. T_{mp} 189°C (ethanol). IR spectrum: 1510, 1585, 1630 cm^{-1} (C=C, C=N). Found, %: C 31.1; H 3.6; Br 52.0. $C_9H_{11}Br_2NO$. Calculated, %: C 31.1; H 3.6; Br 51.6.

3-Iodomethyl-1,3-dihydrooxazolo[3,4-a]pyridinium Triiodide (IX). A. A solution of 5.08 g (20 mmoles) of iodine in 50 ml of ether is added to a solution of 1.35 g (10 mmoles) of compound III in 10 ml of ether and the mixture allowed to stand for a day. The deposit which separates out is dissolved in 10 ml of acetone and reprecipitated with ether. Yield 4.95 g (77%). T_{mp} 84°C (acetone–ether). IR spectrum: 1510, 1590, 1630 cm^{-1} (C=C, C=N). Found, %: C 15.3; H 1.3; I 78.6. $C_8H_9I_2NO\cdot I_2$. Calculated, %: C 14.9; H 1.4; I 79.0.

B. A mixture of 0.29 g (1 mmole) of bromide V and 0.33 g (2 mmoles) of KI in 20 ml of ethanol is boiled under reflux for one hour. After cooling and filtering, a solution of 0.25 g (1 mmole) of iodine in 10 ml of ethanol is added to the filtrate. After 3 h, the deposit settling out is filtered off, dissolved in acetone, and reprecipitated with ether. Yield 0.43 g (67%).

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STRUCTURE OF THE ALKALINE SALTS OF 2-PHENYL- AND 2-p-METHOXYPHENYLIMINO-4-THIAZOLIDINONES

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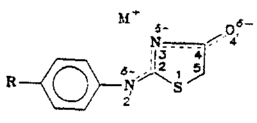
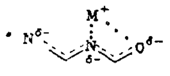
The structure of the undissociated molecule of the alkali salt of 2-arylimino-4-thiazolidinone conforms with the more stable tautomer of the NH acid: the iminotautomer. In the free anion formed by the dissociation of the salt the negative charge is concentrated mainly at the ring nitrogen atom; however, a negligible resonance delocalization of the charge to the exocyclic oxygen and nitrogen atoms takes place. Such a charge distribution of the anion is also retained in the crystalline state, thanks to the fact that the lattice structure allows the coordination of the cation with the heteroatoms of the mesomeric fragment of the anion.

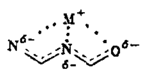
The alkaline salts of 2-phenylimino-4-thiazolidinone (Ia-d) and 2-p-methoxyphenylimino-4-thiazolidinone (II) are of interest as objects for the study of dual reactivity [1, 2]; nevertheless, their structure has not been studied so far. The objective of the present work was to obtain a qualitative picture of the distribution of the negative charge in mesomeric anions of the salts I and II, based on their spectrometric characteristics. Starting from the fact that O-alkylation takes place not only in the case of the above-mentioned salts, but also in the case of other 4-azolidinones [3], it is particularly important to establish whether exclusive N-alkylation is related to the exclusive localization of the negative charge of the anion at the nitrogen atoms.



Ia-dII



IV



V

I a–d R=H, a M=Li, b M=Na, c M=K, d M=Cs; II R=p-OCH_3, M=Na

Comparison of the UV spectra of the solutions of the salts Ia-d in acetonitrile shows a noticeable difference between the distribution of electrons in the anion and in the corresponding undissociated molecule. At concentrations of $3 \cdot 10^{-5}$ M the spectra of the potassium salt (Ic) and the cesium salt (Id) are very similar and represent two overlapping bands with

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