4-OXO-3-OXA-6,7-DIAZABICYCLO[3.3.0]OCT-6-ENE AND ITS ISOMERIZATION

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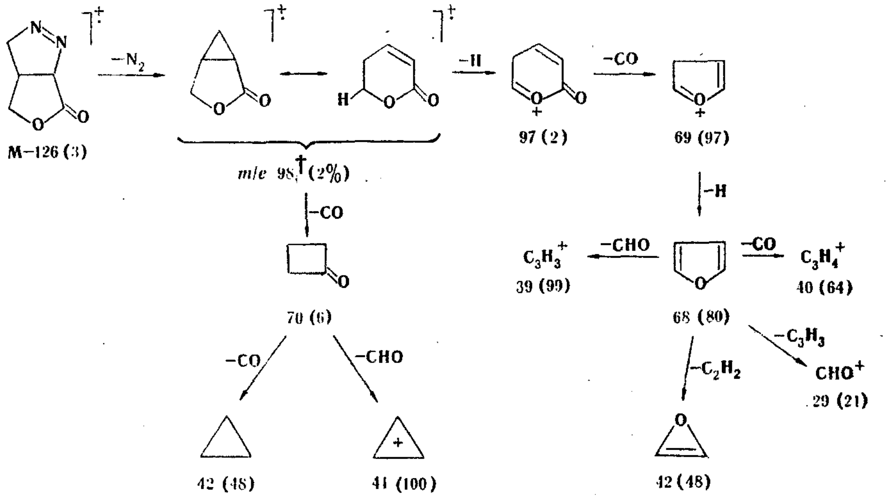
A product of addition of diazomethane to the double bond of crotonolactone — Δ^1-pyrazolinolactone — was obtained, and its isomerization to Δ^2-pyrazolinolactone in dry chloroform in the presence of triethylamine was studied. The structures of the compounds were confirmed by elementary analysis and the IR, UV, and PMR spectra.

The double bond of crotonolactone is strongly polarized, as a consequence of which it readily adds nucleophilic agents (amines, alcohols, and thiols) [1]. It is known that 1,3-dipolar cycloaddition of diazoalkanes proceeds rapidly in such systems [2]. Independently of Pelletier and co-workers [3], we also obtained 4-oxo-3-oxa-6,7-diazabicyclo[3.3.0]oct-6-ene (I) by reaction of diazomethane with crotonolactone. The reaction in ether solution at room temperature proceeds unambiguously (we did not observe nitrogen evolution or the formation of products of decomposition of diazomethane). The direction of addition is evidently determined by the electronic effect of the lactone carbonyl group conjugated with the double bond. The IR spectrum of I does not contain absorption bands above 3100 cm^{-1} (NH group), but a band due to the stretching vibrations of an N=N bond is observed at 1560 cm^{-1}; this is in agreement with the literature data [4]. The strongest band in the IR spectrum is that of the carbonyl group, which absorbs at 1780 cm^{-1}; this is characteristic for butyrolactone [5]. The UV spectrum also displays the typical (for Δ^1-pyrazolines) absorption maximum at 320 nm, which is explained by an n,π^* transition in the azo group [6].

A mass spectral study confirmed the proposed structure of I.



Signals that confirm the proposed structure of I were observed in the PMR spectrum. The signal of the 5-H proton, which is under the anisotropic influence of two double bonds, is found at weak field (5.50 ppm). However, the signal of the proton attached to 1-C is split to the greatest extent and appears at stronger field (2.24 ppm). The methylene group of the lactone ring at 2-C gives two doublets (4.86 ppm). The protons of the methylene group of the pyrazoline ring at 8-C are nonequivalent because of their immediate proximity to the azo group and for this reason give two signals at 3.90 and 4.54 ppm [7].

[†] The m/e values (intensities in percent of the maximum ion) are presented for all ion peaks.

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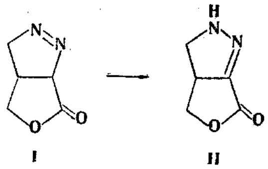
The PMR data indicate that the addition of diazomethane to crotonolactone proceeds stereospecifically, and cis ring fusion [8] is observed for I.

It is known that Δ^2-pyrazolines are thermodynamically more stable [9]. For this reason, Δ^1-pyrazolines are readily isomerized to the Δ^2 isomers in the presence of acids and bases [6]. Correspondingly, our compound I undergoes rapid isomerization to 4-oxo-3-oxa-6,7-diazabicyclo[3.3.0]oct-5-ene (II) in acidic and basic media. From a preparative point of view it is best to carry out the isomerization in benzene or chloroform under the influence of triethylamine. Hydrolysis of the lactone ring takes place simultaneously with isomerization in aqueous solutions.



The IR spectrum of II contains a very strong absorption band at 1655 cm^{-1} (stretching vibrations of the C=N bond of the pyrazoline ring) [4]. The substantial decrease in the frequency of the absorption of the carbonyl group (1730 cm^{-1}) is probably due to conjugation with the C=N bond. The broad and intense absorption band at 3350 cm^{-1} is due to the stretching vibrations of the N—H group, which participates in the formation of an intermolecular hydrogen bond. The absorption maximum at 276 nm in the UV spectrum is characteristic for an azomethine group conjugated with an ester group [10]. This absorption band can be explained by interaction of the π electrons of the two double bonds. We were unable to record the PMR spectrum of II, since it is only very slightly soluble in all ordinary solvents.

The I → II conversion also evidently occurs spontaneously, since both of these compounds, since they are weak bases, themselves catalyze the isomerization. Thus, in a comparison of the UV spectra of freshly prepared I and a sample that had been stored for a month, it is observed that the spectrum of the latter displays, in addition to a maximum at 320 nm, intense absorption at 276 nm. Similarly, intense bands appear in the IR spectrum at 3300 and 1650 cm^{-1}. However, pure I is stable when it is stored in a refrigerator or at room temperature in the dark.

EXPERIMENTAL

The UV spectra of aqueous solutions of the compounds were recorded with a Specord spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of deuteroacetone solutions of the compounds were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded by P. A. Sharbatyan with a Varian Mat CH-8 spectrometer.

4-Oxo-3-oxa-6,7-diazabicyclo[3.3.0]oct-6-ene (I). A twofold excess of an ether solution of diazomethane was added with stirring to 0.84 g (0.01 mole) of crotonolactone in the course of 30 min, after which the mixture was stirred for another 2 h. The resulting precipitate was removed by filtration to give 1.1 g (87%) of I. Recrystallization from benzene gave a product with mp 109-110°C. Found, %: C 47.5; H 4.8; N 22.1. M (by mass spectrometry) 126. $C_5H_6N_2O_2$. Calculated, %: C 47.6; H 4.8; N 22.2. M 126. IR spectrum: 1765 vs (C=O) and 1560 cm^{-1} m (N=N). UV spectrum, λ_{max} (ε): 320 nm (315). PMR spectrum: 5.50 (1H, two t, 5-H), 4.86 (2H, dd, 2-H), 4.54 (1H, t, 8-H), 3.90 (1H, q, 8-H), and 2.24 ppm (1H, m, 1-H).

4-Oxo-3-oxa-6,7-diazabicyclo[3.3.0]oct-5-ene (II). A solution of 1.26 g (0.01 mole) of I was stirred for 3 days in 200 ml of anhydrous chloroform with 2 ml of triethylamine at room temperature. The precipitated II was removed by filtration (the yield was quantitative) and had mp 183-184°C. Found, %: C 47.4; H 4.7; N 22.1. $C_5H_6N_2O_2$. Calculated, %: C 47.6; H 4.8; N 22.2. IR spectrum: 1730 s (C=O) and 1655 vs (C=N), and 3350 cm^{-1} vs (NH). UV spectrum, λ_{max} (ε): 276 nm (1675).

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SYNTHESIS AND LUMINESCENCE PROPERTIES OF 4-(2-METHYL-5-OXAZOLYL)NAPHTHALIC ANHYDRIDE AND THE PRODUCTS OF ITS CONDENSATION WITH AROMATIC AMINES

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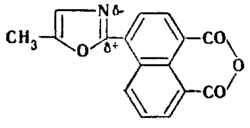
4-(2-Methyl-5-oxazolyl)naphthalic anhydride was synthesized by heating ω-aminomethyl 5-acenaphthyl ketone hydrochloride with acetic anhydride and subsequent oxidation of the resulting 2-methyl-5-(5-acenaphthyl)oxazole. 4-(2-Methyl-5-oxazolyl)-naphthalic acid phenylimide and 4(3)-(2-methyl-5-oxazolyl)-7-oxo-7H-benzimidazo-[1,2-b]benzo[de]isoquinoline were obtained by condensation of 4-(2-methyl-5-oxazolyl)naphthalic anhydride with aniline and o-phenylenediamine. The coincidence of the directions of polarization of the C=N bond of the oxazole ring and the electronic shifts in the π system of the anhydride and phenylimide molecules leads to an increase in the quantum luminescence yield.

We have explained the intense luminescence of 4-(5-methyl-2-oxazolyl)naphthalic anhydride (Ia), in contrast to 5-methyl-2-(1-naphthyl)oxazole, which is practically devoid of luminescence properties, by donor—acceptor interaction, although weak, of the methyl and carbonyl groups [1].



Ia

Polarization of the C=N bond of the oxazole ring, which has the opposite direction and is reinforced when the molecule passes into the excited state, can to a certain extent counteract this interaction. To evaluate its effect we synthesized and investigated isomeric Ib, in which the direction of polarization of the C=N bond coincides with the direction of the shift of π electrons from the methyl group to the carbonyl group.

The synthesis was accomplished by heating ω-aminomethyl 5-acenaphthyl ketone hydrochloride with acetic anhydride and subsequent oxidation of the resulting 2-methyl-5-(5-acenaphthyl)-oxazole. 4-(2-Methyl-5-oxazolyl)naphthalic acid phenylimide (IIb) was synthesized by condensation of anhydride Ib with aniline. (See scheme on following page.)

The PMR spectrum of Ib in trifluoroacetic acid contains a singlet of a methyl group of the oxazole ring [2] with a chemical shift of 3.26 ppm (relative to tetramethylsilane). This

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