STRUCTURE OF 3-METHYL-4-NITROISOXAZOLONE-5

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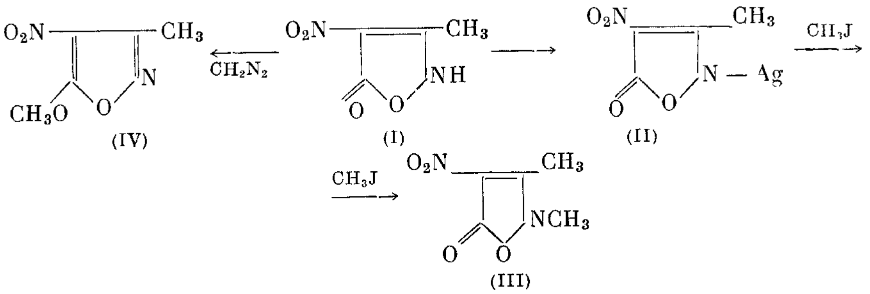
It was recently shown that the nitro group in 3,5-dimethyl-4-nitroisoxazole strongly activates the methyl group at C_5 in condensation reactions [1]. It could be expected that the nitro group also considerably facilitates the course of nucleophilic substitution reactions at C_5 in 3-methyl-4-nitroisoxazolone-5, if this compound could be obtained in the OH form (cf. [2]). However, all our attempts to synthesize chloroisoxazole from it by the action of thionyl chloride were of no avail; even in a solution of pyridine at 20° breakdown of the heterocyclic nucleus occurred. The impossibility of substituting chlorine for the hydroxyl group prompted the idea that nitroisoxazolone, to which the structure of a Δ^2-compound had previously been ascribed [3], is not converted in solutions into the enol form. It is well known that by methylation of tautomeric compounds, including isoxazolones-5 [4], it is possible to obtain derivatives of different tautomeric forms. To study the possible tautomerism of 3-methyl-4-nitroisoxazolone-5 (I) we synthesized two isomeric methyl derivatives of it according to the scheme



The structure of these compounds was established on the basis of studying their IR and UV absorption spectra, the findings of which are presented in the table and in Fig. 1.

Absorption Spectra of Compounds (I)-(IV)

Compound	IR-spectra		UV-spectra	
	characteristic frequencies cm^{-1}	λ_{max}, mμ	lg ε	solvent
I	1710 (c)	335 337 337	4,08 4,04 4,06	Methanol 0,1N HCl 0,1N NaOH
II	1648 (c)	—	—	—
III	1770 (c)	240 307	3,79 4,06	Methanol
IV	1624 (cp)	282	3,89	Methanol

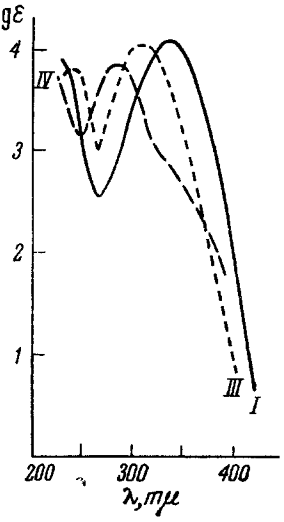


Fig. 1. UV spectra of substances (I), (III) and (IV).

The IR spectra of the solid substances, in the form of suspensions in vaseline oil, were taken on the apparati IKS-12 and IKS-14. The UV spectra were taken on the SF-4 spectrophotometer. The characteristic frequencies found in the IR spectra of (I), (II) and (III) correspond to the absorption of the C=O group in Δ^3 compounds of this class [4]. The reduced frequency of the C=O group in the Ag salt (II) is connected, apparently, with the presence in this substance of a N—Ag bond. The structure of these compounds is confirmed by the presence in their spectra of absorption bands corresponding to the valence variations of the nitro group, but not with the variations of the C=N bond of its aci-form [5]. Intermolecular hydrogen bonds (2640-2740 cm^{-1}) were also detected in nitroisoxazolone. The structure of compound (IV) as a derivative of the "aromatic" system of isoxazole follows from the occurrence in its IR spectrum of a frequency of 1624 cm^{-1}, characteristic of an isoxazole nucleus [6], and the absence of absorption bands in the region of 1700-1800 cm^{-1} (C=O group). The data of the UV spectra also present evidence in favor of the proposed structure of the compounds under consideration. Thus, the practically unchanged spectrum of 3-methyl-4-nitroisoxazolone-5 at any pH indicates the absence of tautomeric transformations in the solutions. Consequently, this compound in its solid form and in solutions exists in the NH form.The UV spectrum of its N-methyl derivative (III) agrees well with data in the literature on the spectra of similar compounds [4]. Thus, during the action of alkyl iodide on the Ag salt (II) there is formation of 2-alkyl- and not of 4-alkylisoxazolone, as Iovitschitsch mistakenly thought [3]. The UV spectrum of (IV), on the other hand, differs greatly from the spectra of isoxazolones-5 and is more like the spectrum of 3,5-dimethyl-4-nitroisoxazole [1]. At the present time we are studying the acid properties of (I). According to preliminary findings this compound is a strong acid (pK < 2).

EXPERIMENTAL

3-Methyl-4-nitroisoxazolone-5 (I), was obtained by the method described in [3]. After six crystallizations from acetone m.p. 129° (with ignition). Found· C 33.53, 33.46, H 2.87, 2.86% $C_4H_4N_2O_4$. Calculated: C 33.34, H 2.80%.

The Ag salt (II) was obtained by the action on (I) of silver nitrate and twice recrystallizing from water.

2,3-Dimethyl-4-nitroisoxazolone-5 (III). To a suspension of the Ag salt, obtained from 0.72 g 3-methyl-4-nitroisoxazolone in 10 ml methanol was added 0.6 ml methyl iodide and boiled with mixing for 3 hr. The precipitate of silver iodide was filtered off, the filtrate was evaporated, and the residue crystallized from methanol. Yield 0.1 g; m.p. 140-141°. Found: C 38.06; 37.93, H 3.90, 3.98% $C_5H_6N_2O_4$ Calculated: C 37.98, H 3.83%

3-Methyl-4-nitro-5-methoxyisoxazole (IV). To a suspension of 0.3 g 3-methyl-4-nitroisoxazolone-5 in ether was added, dropwise, with vigorous mixing, an ether solution of diazomethane in 10-fold excess. On completion of nitrogen evolution the residue of the original isoxazolone was filtered off, the filtrate was evaporated, and 80 ml of 3-methyl-4-nitro-5-methoxyisoxazole, m.p. 81-82° (from aqueous methanol), was obtained. Found C 38.38, 38.52, H 4.10, 4.07%. $C_5H_6N_2O_4$ Calculated: C 37.98, H 3.83%.

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SUMMARY

1. The IR and UV spectra of 3-methyl-4-nitroisoxazolone-5 and its derivatives were studied.

2. 3-Methyl-4-nitroisoxazolone-5, its Ag salt, and the N-methyl derivative appeared as Δ^3 compounds.

3. The action of diazomethane on nitroisoxazolone gave 3-methyl-4-nitro-5-methoxyisoxazole.

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