# 2-METHYL-4-(o-NITROBENZYLIDENE)OXAZOL-5-ONES

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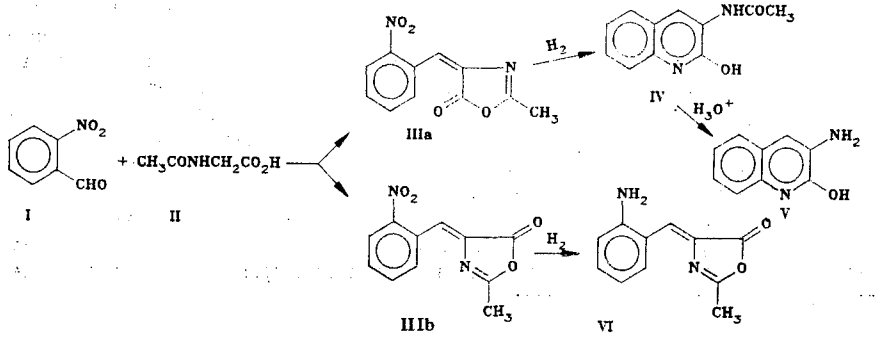
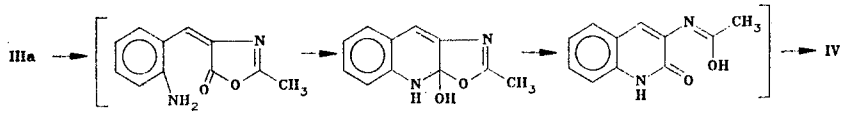
The cis and trans isomers of 2-methyl-4-(o-nitrobenzylidene)oxazol-5-one have been obtained. On reduction, the cis isomer formed 3-acetamidoquinolin-2-ol, and the trans isomer formed 4-(o-aminobenzylidene)-2-methyloxazol-5-one. Details of the IR, UV, PMR, and mass spectra of the compounds obtained are given.

The preparation of 2-methyl-4-(o-nitrobenzylidene)oxazol-5-one (III) by the condensation of o-nitrobenzaldehyde (I) with aceturic acid (II) is described in the literature [1]. The presence of an exocyclic double bond is responsible for the existence of cis and trans isomers of the oxazolone (III). Lur'e et al. [1] isolated only the low-melting isomer of the oxazolone (IIIa) and did not establish its configuration.



We have performed the reaction described and have isolated the two isomeric oxazolones (IIIa) and (IIIb) from the reaction mixture by column chromatography and fractional crystallization.

When the oxazolone (IIIa) was reduced over Raney nickel, 3-acetamido-quinolin-2-ol (IV) was formed, the hydrolysis of the latter in an acid medium giving 3-aminoquinolin-2-ol (V); the reduction of the isomeric oxazolone (IIIb) yielded 4-(o-aminobenzylidene)-2-methyloxazol-5-one (VI). The formation of the quinoline derivative (IV) can be represented by the following scheme:



The spatial propinquity of the amino group formed on the reduction of the nitro group in the cis isomer (IIIa) to the carbonyl group promotes the formation of the dihydroquinoline ring. 3-Acetamidoquinolin-2-ol (IV) is formed as a result of the cleavage of the C—O bond followed by the aromatization of the quinoline. In the trans isomer (IIIb) the possibility of an intramolecular approach of the amino and carbonyl groups is excluded.

The dissimilar electron density distributions in the isomers (IIIa) and (IIIb) is reflected in the UV spectra and in the PMR spectra. The UV spectra of these compounds each contain two absorption bands. The first band with a maximum in the 207 and 204 nm regions for compounds (IIIa), and (IIIb), respectively, is due to the $\pi$, $\pi^*$ transitions of the benzene rings. The second band, with maxima in the 268 nm region for the isomer (IIIa) and the 250

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nm region for the isomer (IIIb) characterizes an electronic transition of an aromatic system conjugated with a nitro group. In the PMR spectra of the stereoisomers (IIIa) and (IIIb) in deuteroacetone a multiplet is observed in the 6.40-7.50 ppm region corresponding to the signals of the protons of benzene rings and of a methine proton. The protons of the methyl group of the azlactone ring of the isomer (IIIa) give a singlet peak at 2.40 ppm, and those of (IIIb) at 2.16 ppm.

## EXPERIMENTAL

UV spectra were taken on Spectromom-204 and Specord UV-vis spectrophotometers in ethanol. Mass spectra were obtained on a Varian MAT-112 spectrometer with an ionizing energy of 70 eV. IR spectra were recorded on an IKS-29 spectrophotometer in chloroform. PMR spectra were taken on a Tesla BS-487C spectrometer with a working frequency of 80 MHz in deuteroacetone with tetramethylsilane as internal standard. The purity of the compounds was checked with the aid of TLC on Silufol plates.

cis- and trans-2-Methyl-4-(o-nitrobenzylidene)oxazol-5-ones (IIIa and b, respectively). A mixture of 5 g (33 mmole) of o-nitrobenzaldehyde, 3.8 g (33 mmole) of aceturic acid, and 2.7 g (33 mmole) of anhydrous sodium acetate in 40 ml of acetic anhydride was heated on the boiling water bath for 2 h. Then the reaction mixture was evaporated in vacuum and the residue was chromatographed on silica gel (with chloroform as the eluant). The chloroform solution was eveaporated and the residue was purified by fractional crystallization from ether. This gave 3.5 g (45%) of the cis isomer (IIIa) (mp 114-115°C [1]) and 1.4 g (18%) of the trans isomer (IIIb) [mp 216°C (acetone)]. UV spectra, $\lambda_{max}$, nm (log $\varepsilon$): (IIIa) 207 (4.20), 268 (4.05); (IIIb) 205 (4.10), 250 (4.05). PMR spectra, ppm: (IIIa) 2.40 (s, $CH_3$), 6.40-7.50 (m, 5 H); (IIIb) 2.16 (s, $CH_3$), 6.40-7.35 (m, 5 H). Mass spectrum, m/z (%): 232 (17) $M^+$, 189 (43) $[M-CH_3CO]^+$, 175 (20) $[M-CH_3NCO]^+$, 162 (97) $[M-CH_3CO, -HCN]^+$, 148 (31) $[M-CH_3CO, -NCO]^+$. IR spectrum $cm^{-1}$: (IIIa) 3090-3000 (CH arom.), 1800 (C=O), 1650 (C=N), 1510 and 1330 (N-O); (IIIb) 3090-3000 (CH arom.), 1740 (C=O), 1650 (C=N), 1520 and 1350 (N-O). Found: (IIIa): C 57.0; H 3.6; N 11.9%; (IIIb): C 57.1; H 3.5; N 12.1%. $C_{11}H_8N_2O_4$. Calculated: C 56.9; H 3.4; N 12.1%.

3-Acetamidoquinolin-2-ol (IV). A solution of 1.9 g (8.2 mmole) of the oxazolane (IIIa) in 100 ml of ethanol was reduced with hydrogen over Raney nickel. After the absorption of hydrogen had ceased (550 ml), the reaction mixture was filtered, the filtrate was evaporated to a volume of 15 ml, and the precipitate was separated off to give 1 g (62%) of compound (IV), mp 280°C. IR spectrum, $cm^{-1}$: 3600 (OH), 3400 (NH), 3090-3000 (CH arom.), 1680 (C=O). Mass spectrum, m/z (%): 202 (100) $M^+$, 159 (71) $[M-CH_3CO]^+$, 132 (60) $[M-CH_3CO, -HCN]^+$, 104 (48) $[M-CH_3CO, -HCN, -CO]^+$. Found: C 65.2; H 4.8; N 13.7%. $C_{11}H_{10}N_2O_2$. Calculated: C 65.3; H 4.9; N 13.8%.

3-Aminoquinolin-2-ol (V). A solution of 0.2 g (0.99 mmole) of compound (IV) in 10 ml of 1 N hydrochloric acid solution was boiled for 35 min. Then the reaction mixture was evaporated in vacuum, the residue was dissolved in the minimum amount of water, and the solution was neutralized with 1 N sodium carbonate solution and extracted with ether. The ethereal extract was dried over anhydrous magnesium sulfate, filtered, and evaporated, to give 0.15 g (94%) of compound (V), mp 200-202°C. IR spectrum, $cm^{-1}$: 3530 (OH), 3400 (NH), 3090-3000 (CH arom.). Found: C 67.6; H 15.1; N 17.1%. $C_9H_8N_2O$. Calculated: C 67.5; H 5.0; N 17.5%.

4-(o-Aminobenzylidene)-2-methyloxazol-5-one (VI). A solution of 1 g (4.3 mmole) of the oxazolone (IIIb) in 100 ml of ethanol was reduced with hydrogen over Raney nickel. After the absorption of hydrogen had ceased (290 ml), the catalyst was separated off, the solution was evaporated in vacuum, and the residue was purified by column chromatography on silica gel. Elution performed successively with chloroform (50 ml), chloroform–methanol [(1:1), 20 ml], and methanol (30 ml) yielded 0.25 g (28%) of compound (VI), mp 222-223°C. IR spectrum, $cm^{-1}$: 3380 (NH), 3090-3010 (CH arom.), 1690 (C=O), 1620 (C=N). Mass spectrum, m/z, %: 202 (67), $M^+$, 159 (100) $[M-CH_3CO]^+$, 146 (64) $[M-CH_3CONH_2]^+$, 132 (58) $[M-CH_3CO, -HCN]^+$, 117 (96) $[M-CH_3CO, -NCO]^+$. Found: C 65.5; H 4.8; N 13.8%. $C_{11}H_{10}N_2O_2$. Calculated: C 65.3; H 4.9; N 13.8%.

## LITERATURE CITED

1. S. N. Lur'e, E. S. Chumak, and T. A. Ravdel', Zh. Obshch. Khim., 23, 1392 (1953).