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# REACTION OF 5-CHLOROANTHRA[1,9-cd]-6-ISOXAZOLONE WITH PYRIDINE BASES

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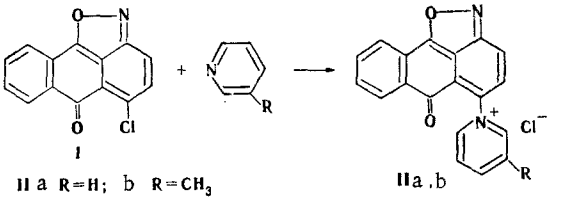
In the reaction of 5-chloroanthra[1,9-cd]-6-isoxazolone with pyridine bases the chlorine atom is substituted to give the corresponding pyridinium salts. The pyridine ring of the synthesized anthra[1,9-cd]isoxazol-6-one-5-pyridinium chloride was cleaved by the Zincke method. The reduction of the cleavage product, viz., N-(anthra[1',9'-cd]isoxazol-6-on-5-yl)-5-amino-2,4-pentadienal, under various conditions was investigated.

In [1, 2] it was shown that 5-haloanthra[1,9-cd]-6-isoxazolones are readily aminated by alkyl- and arylamines. It seemed of interest to study the behavior of isoxazolone I with respect to pyridine bases. We found that pyridine and β-picoline are quaternized by isoxazole I under mild conditions; pyridinium chlorides IIa,b were isolated in high yields.




I

IIa R=H; b R=CH$_3$ IIa,b

This confirms the higher lability of the chlorine atom in I as compared with 1-chloroanthraquinone, which reacts with pyridine only under severe conditions [3].

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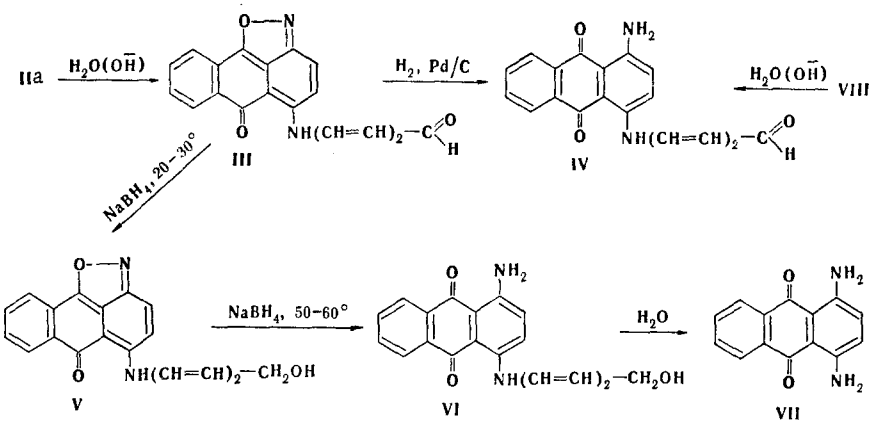
Considering the accessibility of IIa, we investigated the synthetic possibilities of its use. We found that salt IIa under the influence of a dilute solution of alkali readily undergoes opening of the pyridine ring via the Zincke method [4] to give N-(anthra[1',9'-cd] isoxazol-6-on-5-yl)-5-amino-2,4-pentadien-1-al (III).

The IR spectrum of III contains a band at 1670 $cm^{-1}$, which virtually corresponds to the C=O vibrations in α, β, γ, δ-unsaturated aldehydes ($\nu_{C=O}$ 1675 $cm^{-1}$) [5]. A doublet of a pro-




ton of an aldehyde group (9.49 ppm, J = 8 Hz) and a doublet of a proton of a secondary amino group (11.54 ppm) are observed in its PMR spectrum. The UV spectrum of this compound in the visible region is similar to the spectrum of 5-phenylaminoanthra[1,9-cd]-6-isoxazolone but is bathochromically shifted 30 nm.

In order to obtain additional data that confirm the structure of isoxazolone III we investigated its reduction under various conditions. In the case of catalytic hydrogenation we observed reductive cleavage of the isoxazole ring to give N-(1-amino-4-anthraquinonyl)-5-amino-2,4-pentadien-1-al (IV). The absorption of the C=O group of a conjugated aldehyde at 1670 $cm^{-1}$ is observed in the IR spectrum of IV, and a band of N–H stretching vibrations is found at 3260 and 3360 $cm^{-1}$. In the PMR spectrum the signal of an aldehyde proton is observed in the form of a doublet (9.38 ppm, J = 8.0 Hz). The position of the doublet signal of a secondary amino group at weak field (12.63 ppm, J = 11.5 Hz) corresponds to the analogous signals of secondary 1,4-diaminoanthraquinones [6]. The structure of IV is also confirmed by alternative synthesis. In the reaction of 1-aminoanthraquinone-4-pyridinium chloride (VIII) with a dilute solution of alkali we obtained a product that is completely identical to IV with respect to its spectral characteristics (the UV and IR spectra were compared).

Two products are formed in the reduction of isoxazole III with $NaBH_4$. At ordinary temperatures reduction leads to N-(anthra[1',9'-cd]isoxazol-6-on-5-yl)-5-amino-2,4-pentadien-1-ol (V), whereas at high temperatures it leads to VI; the latter readily forms 1,4-diaminoanthraquinone (VII) in an acidic medium and in water. The PMR spectra of V and VI do not contain signals in the region of aldehyde protons, but a broad signal at 4.77 and 4.70 ppm (O–H) appears in the case of V and VI, respectively. Signals of a methylene group bonded to a hydroxy group are found at 4.07 ppm for V and at 4.02 ppm for VI; this is in agreement with the position of the signal of the methylene group in allyl alcohol (4.13 ppm) [7]. Doublet signals of protons of a secondary amino group of V and VI are found at 11.6 (J = 11.5 Hz) and 12.7 ppm (J = 11.0 Hz), respectively.

The ratios of the integral intensities of all of the signals in the spectra of III-VI correspond to the proposed structures.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-75 spectrometer. The UV spectra of solutions of IIa, b in water and of the remaining compounds in dimethylacetamide were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in $(CD_3)_2SO$ were recorded with a Tesla BS-467 spectrometer (60 MHz). The chemical shifts were reckoned from the signal of the solvent (δ 2.5-$cd_2$-H) [sic] [8]. The course of the reaction and the purity of the substances were monitored by thin-layer chromatography (TLC) in a toluene–acetone system on Silufol UV-254 plates. The melting points were determined with a Boetius microheating stage.

Anthra[1,9-cd]-6-isoxazolone-5-(N-pyridinium) Chloride (IIa). A 5.1-g (0.02 mole) sample of anthra[1,9-cd]-6-isoxazolone was heated to the boiling point with stirring in 50 ml of pyridine, and the mixture was refluxed for 5 min. The reaction product began to crystallize from the hot solution. It was separated by filtration and washed successively with toluene and ether to give 6.1 g (91.3%) of product. UV spectrum, $\lambda_{max}$ (log ε): 293 (4.16) and 468 (3.89). IR spectrum: 1620, 1650, and 1660 $cm^{-1}$ (C=N, C=O). Found: Cl 10.1; N 8.3%. $C_{19}H_{11}ClN_2O_2$. Calculated: Cl 10.6; N 8.4%.

Anthra[1,9-cd]-6-isoxazolone-5-(N-β-picolinium) Chloride((IIb). This compound was obtained in 89.6% yield by the method indicated above. UV spectrum, $\lambda_{max}$ (log ε): 292 (4.16) and 465 (3.84). IR spectrum: 1620, 1650, and 1660 $cm^{-1}$ (C=N, C=O). Found: Cl 10.5; N 7.8%. $C_{20}H_{13}ClN_2O_2$. Calculated: Cl 10.2; N 8.0%.

N-(Anthra[1',9'-cd]isoxazol-6-on-5-yl)-5-amino-2,4-pentadien-1-al (III). A 6.68-g (0.02 mole) sample of salt IIa was dissolved in 300 ml of water, 50 ml of 5% aqueous KOH solution was added, and the mixture was maintained at ordinary temperatures with stirring for 2 h. Ice (50 g) was then added to the resulting suspension, and the mixture was acidified acetic acid. Product III was removed by filtration and washed with water to give 6.22 g (98%) of a product with mp 195°C (from acetonitrile). UV spectrum, $\lambda_{max}$ (log ε): 360 (4.42) and 560 (4.35). Found: N 8.8%. $C_{19}H_{12}N_2O_3$. Calculated: N 8.9%.

N-1-Amino-4-anthraquinonyl)-5-amino-2,4-pentadien-1-al (IV). A 0.79-g (2.5 mole) sample of III was hydrogenated with stirring at atmospheric pressure in solution in a mixture of 50 ml of ethanol and 50 ml of dioxane over 0.5 g of 0.2% Pd on carbon at 60-70°C for 5 h. The hot solution was then filtered and concentrated *in vacuo* to a volume of 40 ml, and 50 ml of water was added to the concentrate. The mixture was cooled and filtered to give 0.76 g (95.6%) of IV with mp 246-248°C (from aqueous dioxane). UV spectrum, $\lambda_{max}$ (log ε): 358 (4.35), 425 (4.45), 620 (4.18), and 655 nm (4.16). Found: N 8.6%. $C_{19}H_{14}N_2O_3$. Calculated: N 8.8%.

Alternative Synthesis of IV. A 1.68-g (5 mmole) sample of salt VIII, which was synthesized by the method in [9], was dissolved in 300 ml of water, 100 ml of 20% aqueous NaOH solution was added to the resulting solution at room temperature, and the mixture was stirred at ordinary temperatures for 4 h. The solid material was then removed by filtration, washed with water, and crystallized from aqueous dioxane to give 1.2 g (75%) of a compound that was identical to IV with respect to data from the IR and UV spectra.

N-(Anthra[1',9'-cd]isoxazol-6-on-5-yl)-5-amino-2,4-pentadien-1-ol (V). A suspension of 0.3 g (8 mmole) of $NaBH_4$ in 100 ml of isopropyl alcohol was added to a suspension of 1.58 g (5 mmole) of III in 100 ml of dioxane, and the mixture was stirred at room temperature for 2 h. It was then diluted with 800 ml of water and acidified with 5 ml of acetic acid. The precipitated V was removed by filtration to give 1.2 g (75.5%) of a product with mp 142-145°C. UV spectrum, $\lambda_{max}$ (log ε): 560 nm (4.15). Found: N 8.5%. $C_{19}H_{14}N_2O_3$. Calculated: N 8.8%.

N-(1-Amino-4-anthraquinonyl)-5-amino-2,4-pentadien-1-ol (VI). A suspension of 0.38 g (0.01 mole) of $NaBH_4$ in 50 ml of tetrahydrofuran (THF) was added to a suspension of 1.58 g (5 mmole) of III in 150 ml of absolute THF, and the mixture was heated with stirring at 50-60°C for 1-1.5 h. The hot mixture was filtered, and the filtrate was concentrated to a volume of 30 ml and cooled. The resulting precipitate was removed by filtration and crystallized from absolute THF to give 1.05 g (65.6%) of a product with mp 198-200°C. UV spectrum, $\lambda_{max}$ (log ε): 400 (3.86) and 625 nm (4.13). Found: N 8.5%. $C_{19}H_{16}N_2O_3$. Calculated: N 8.8%.

A 0.9-g (75.6%) sample of 1,4-diaminoanthraquinone, which was identified by comparison with a genuine sample, was isolated by salting out when 500 ml of 5% acetic acid was added to the reaction mixture from the preceding experiment at the end of the reaction, and the resulting mixture was stirred for 1 h.

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# PREPARATION OF β-(2,2-DIMETHYLTETRAHYDRO-4-PYRANYL)-β-OXOPROPIONIC ACID ANILIDE

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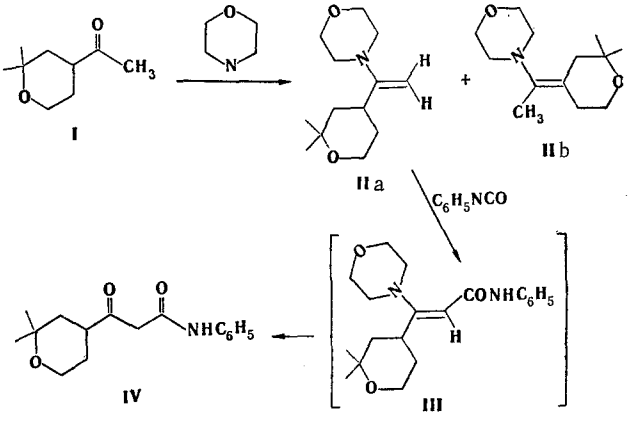
A method for the synthesis of β-(2,2-dimethyltetrahydro-4-pyranyl)-β-oxopropionic acid anilide by the successive conversion of methyl 2,2-dimethyltetrahydro-4-pyranyl ketone to an enamine and reaction of the latter with phenyl isocyanate with subsequent hydrolysis in an acidic medium is proposed.

In a continuation of our research on the synthesis of β-dicarbonyl compounds, viz., derivatives of saturated six-membered heterocycles [1, 2], we undertook the synthesis of β-(2,2-dimethyltetrahydro-4-pyranyl)-β-oxopropionic acid anilide starting from methyl 2,2-dimethyltetrahydro-4-pyranyl ketone (II) [3], which was converted to a morpholino enamine by the method proposed in [4] with titanium tetrachloride as the catalyst. Despite our expectations, instead of two alternative enamines IIa,b we obtained only enamine IIa. The desired β-keto anilide IV was obtained by reaction of the latter with phenyl isocyanate and subsequent hydrolysis. The indicated transformations are presented in the following scheme:




## EXPERIMENTAL

Analysis by gas–liquid chromatography was carried out with a Khrom-4 chromatograph with glass packed columns with XE-60 silicone on Chromaton N-AW silanized with hexamethyldisiloxane as the liquid phase. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard.

1-Morpholino-1-(2,2-dimethyltetrahydro-4-pyranylidene)ethane (IIa). A solution of 7.6 g (0.04 mole) of $TiCl_4$ in 30 ml of pentane was added gradually to a cooled (to 0°C) mixture of 12 g (0.077 mole) of ketone I and 21 g (0.24 mole) of morpholine in 50 ml of absolute ether in a nitrogen atmosphere, after which the reaction mixture was warmed up to room temperature and refluxed for 6 h. The resulting precipitate was removed by filtration and washed with absolute ether, the filtrate was distilled to remove the solvent, and the residue was vacuum

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