REACTION OF 5-(N-PYRIDINIA)ANTHRA[1,9-cd]ISOXAZOL-6-ONE CHLORIDE WITH AMINES

L. M. Gornostaev, G. I. Zolotareva,
and E. N. Platonova

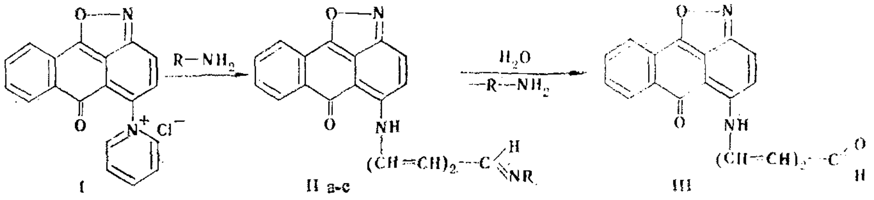
UDC 547.712.36'786.37'333.2'38.07:543.422

In the reaction of 5-(N-pyridinia)anthra[1,9-cd]isoxazol-6-one chloride with primary aliphatic amines in methanol the pyridine ring is cleaved to give N-(anthra[1',9'-cd]isoxazol-6'-on-5'-yl)-5-amino-2,4-pentadienalimines.

In [1] it was shown that 5-(N-pyridinia)anthra[1,9-cd]isoxazol-6-one chloride (I) under the influence of a dilute alkaline solution readily undergoes opening of the pyridine ring via the Zincke cleavage to give N-(anthra[1',9'-cd]-isoxazol-6'-on-5'-yl)-5-amino-2,4-pentadienal (III).

It seemed of interest to us to study the behavior of salt I with respect to amines. If successful, this reaction could be used in the synthesis of modified sorbents for affine chromatography [2].

We found that I is very sensitive to various amines. Upon reaction with salt I, amines with high nucleophilicities formed difficult-to-separate mixtures of products; this is probably associated with the high activity with respect to the action of these amines not only of the pyridine ring but also the 3 and 5 positions [3] in such compounds. The reaction of I with primary aromatic amines aldo proceeded similarly. The reaction proceeded more unambiguously only when primary aliphatic amines with bulky substituents attached to the nitrogen atom were used.



II a R=C$_6$H$_{11}$; b R=t-C$_4$H$_9$; c R=CH$_2$—C$_6$H$_5$

The resulting N-(anthra[1',9'-cd]isoxazol-6'-on-5'-yl)-5-amino-2,4-pentadienalalkylimines (IIa-c) are hydrolyzed to aldehyde III when they are stored in air or when they are obtained from I in aqueous solution, and their synthesis was therefore carried out in anhydrous methanol.

The structure of imines IIa-c was confirmed by data from UV, IR, and PMR spectroscopy. The electronic spectra of IIa-c are similar to the spectrum of aldehyde III [1], and the almost complete coincidence of the λ_{max} bands in the visible portion of the spectra (555 nm) constitutes evidence for the identical character of the chromophore systems.

Intense bands at 1610, 1640, and 1670^{-1}, which are associated with the absorption of the C=N and C=O groups, are observed in the IR spectra of IIa-c.

The positions of the signals of the protons of the secondary amino group and the alkyl and cycloalkyl groups in the PMR spectra of products IIa,b are also in agreement with the literature data [1, 4]. The ratios of the integral intensities of the signals of the alkyl or cycloalkyl groups to the integral intensities of the proton of the secondary amino group in IIa,b are in agreement with the proposed structure.

Krasoyarsk State Pedagogical Institute, Krasnoyarsk 660049. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 467-468, April, 1983. Original article submitted July 28, 1982.

0009-3122/83/1904-0377$07.50

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-75 spectrometer. The UV spectra of solutions in dioxane were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Tesla BS-467 spectrometer (60 MHz). The chemical shifts were measured relative to the remanent signal of the solvent (δ 7.25 for $H—CCl_3$) [5]. The course of the reaction was 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.

N-(Anthra[1',9'-cd]isoxazol-6'-on-5'-yl)-5-amino-2,4-pentadienal-1-cyclohexylimine (IIa). A 0.84-g (2.5 mmole) sample of salt I was dissolved in 25 ml of absolute methanol, a solution of 0.5 g (5 mmole) of cyclohexylamine in 5 ml of absolute methanol was added to the resulting solution, and the mixture was stirred at ambient temperature for 30 min. The resulting precipitate was removed by filtration and washed with 15-30 ml of methanol to give 0.80 g (80.6%) of a product with mp 126-127°C. PMR spectrum: 1.00-2.05 (m, 11H, cyclohexyl), 5.85-8.50 (m, 11H, unsaturated and aromatic protons), and 11.58 ppm (d, 1H, N—H) (J = 12.0 Hz). UV spectrum, λ_{max} (log ε): 555 nm (4.35). Found: N 10.2%. $C_{25}H_{23}N_3O_3$. Calculated: N 10.6%.

N-(Anthra[1',9'-cd]isoxazol-6'-on-5'-yl)-5-amino-2,4-pentadienal-1-tert-butylimine (IIb). This compound was obtained by a procedure similar to that used to prepare IIa, but the starting salt was dissolved in 10 ml of methanol, and 1 g of tert-butylamine was used. Workup gave 0.70 g (75%) of a product with mp 126-127°C. PMR spectrum: 1.25 (s, 9H, tert-butyl), 5.85-8.50 (m, 11H, unsaturated and aromatic protons), and 11.75 ppm (s, 1H, N—H). UV spectrum, λ (log ε): 555 nm (4.28). Found: N 10.9%. $C_{23}H_{21}N_3O_2$. Calculated: N 11.3%.

N-(Anthra[1,9-cd]isoxazol-6'-on-5'-yl)-5-amino-2,4-pentadienal-1-benzylimine (IIc). This compound was obtained by a procedure similar to that used to prepare IIa. Workup gave 0.75 g (74%) of a product with mp 127-129°C. UV spectrum, λ_{max} (log ε): 555 nm (4.17). Found: N 10.0%. $C_{26}H_{19}N_3O_2$. Calculated: N 10.4%.

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