REACTION OF 5-CHLOROANTHRA[1,9-cd]-6-ISOXAZOLONE WITH OXYGEN-CONTAINING NUCLEOPHILES

G. I. Zolotareva and L. M. Gornostaev

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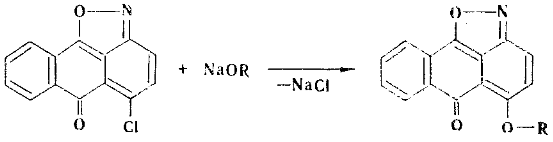
Facile nucleophilic substitution of the chloride ion to give 5-alkoxy- or 5-aryloxy-anthra[1,9-cd]-6-isoxazolones occurs in the reaction of 5-chloroanthra[1,9-cd]-6-isoxazolone with alcohols and phenols. The possibility of conversion of the synthesized isoxazolones to 1-amino-4-alkoxyanthraquinones is demonstrated.

It is known that anthra[1,9-cd]-6-isoxazolones (I) can serve as intermediates for the synthesis of 5,6-phthalylphenothiazines [1, 2], 5,6-phthalylphenoxazines [3], and 4-halo-1-aminoanthraquinones [4]. It has been shown [5, 6] that a halogen atom in the 5 position of I is readily replaced under the influence of nitrogen-containing nucleophiles.

The aim of the present research was to study the reaction of 5-chloroanthra[1,9-cd]-6-isoxazolone (Ia) with alcohols and phenols. We found that isoxazole Ia reacts readily with sodium alkoxides and phenoxides to give 5-alkoxy- and 5-aryloxyanthra[1,9-cd]-6-isoxazolones (IIa-j) (Table 1).

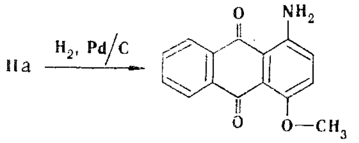
Dioxane was used as a cosolvent in the investigated reaction in order to increase the solubility of starting Ia. It is characteristic that this reaction proceeds under mild conditions (at room temperature), whereas the reaction of α-haloanthraquinones with the same nucleophiles is carried out under more severe conditions [7].



Ia IIa-j

The synthesized IIa-j are yellow crystalline substances that are moderately soluble in organic solvents. An intense absorption band at 445-470 nm, which is characteristic for isoxazoles with a similar structure [1], is observed in their UV spectra. The IR spectra contain intense bands of stretching vibrations of C=N and C=O bonds at 1640 and 1670 cm^{-1}.

The ease of formation of products IIa-j predetermines the possibility of their use for the synthesis of various 1-amino-4-alkoxy- and 1-amino-4-aryloxyanthraquinones, which are pink disperse dyes. We demonstrated this in the case of the reduction of isoxazole IIa to 1-amino-4-methoxyanthraquinone (IIIa):



IIIa

The structure of amine IIIa was confirmed by PMR spectroscopy and also by comparison of its UV spectrum with the data in [8].

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 alcohol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in CD_3Cl were recorded with a Tesla

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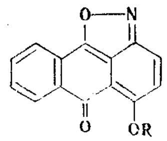
TABLE 1. Synthesis and Characteristics of Products with the Structure



Compound	R	mp, °C	λ_{max}, nm (lg ε)	N found, %	Empirical formula	N calc., %	Yield, %
IIa	CH_3	227—228	244 (4,99); 249 (5,1); 445 (4,16); 467 (4,16)	6,0	$C_{15}H_9NO_3$	5,6	70,8
IIb	C_2H_5	204—206	244 (5,00); 249 (5,10); 445 (4,12); 466 (4,12)	5,5	$C_{16}H_{11}NO_3$	5,3	62,5
IIc	C_3H_7	171—172	244 (4,99); 249 (5,10); 445 (4,14); 466 (4,13)	4,7	$C_{17}H_{13}NO_3$	5,0	77,1
IId	*iso*-C_3H_7	143—145	244 (4,99); 249 (5,06); 446 (4,12); 465 (4,12)	4,6	$C_{17}H_{13}NO_3$	5,0	53,0
IIe	C_4H_9	146—148	243 (4,99); 249 (5,08); 446 (4,17); 464 (4,17)	4,2	$C_{18}H_{15}NO_3$	4,8	50,0
IIf	*iso*-C_4H_9	154—155	244 (4,98); 249 (5,07); 446 (4,13); 465 (4,13)	4,5	$C_{18}H_{15}NO_3$	4,8	56,3
IIg	C_6H_5	185—186	243 (5,03); 248 (5,07); 443 (4,16); 455 (4,19)	4,2	$C_{20}H_{11}NO_3$	4,5	56,0
IIh	*p*-$CH_3C_6H_4$	186—187	243 (5,03); 249 (5,08); 444 (4,14); 456 (4,14)	3,9	$C_{21}H_{13}NO_3$	4,3	85,0
IIi	*p*-ClC_6H_4	222—223	243 (5,06); 248 (5,19); 442 (4,14); 459 (4,14)	3,9	$C_{20}H_{10}ClNO_3$	4,0	68,0
IIj	*p*-$C(CH_3)_3C_6H_4$	221—222	243 (5,06); 248 (5,11); 442 (4,17); 459 (4,16)	3,7	$C_{24}H_{19}NO_3$	3,8	58,0

BS-467 spectrometer (60 MHz); the chemical shifts were measured relative to the residual signal of the solvent (δ 7.25 for CCl_3H) [9]. The course of the reaction was monitored by thin-layer chromatography (TLC) in toluene–acetone on Silufol UV-254 plates. The melting points were determined with a PTP-1 apparatus; the melting point of IIa was determined with a Boetius microheating stage.

5-Alkoxyanthra[1,9-cd]-6-isoxazolones (IIa-f). The alkoxide obtained by dissolving 0.46 g (20 mmole) of sodium in 15-20 ml of the absolute alcohol was added to a suspension of 0.64 g (2.5 mmole) of isoxazolone I in 20 ml of dioxane, and the mixture was maintained at normal temperature for 15-20 min. It was then diluted with water (acidified with 5-10 ml of acetic acid) to 500 ml, and the precipitate was removed by filtration and air dried. All of the substances were recrystallized from benzene.

5-Aryloxyanthra[1,9-cd]-6-isoxazolones (IIg-j). A solution of the phenoxide obtained by heating 20 ml of dioxane, 10 mmole of the phenol, and 0.56 g (10 mmole) of KOH was added to a suspension of 2.5 mmole of isoxazolone I in 20 ml of dioxane. During the addition the mixture became homogeneous, after which a precipitate formed. The precipitate was removed by filtration, dried, and recrystallized from benzene.

1-Amino-4-methoxyanthraquinone (IIIa). A 1.26-g (5 mmole) sample of IIa was hydrogenated at atmospheric pressure at 40-50°C in solution in 100 ml of methanol over 1 g of 0.2% Pd on carbon for 3 h. After hydrogenation was complete, 50 ml of methanol was added to the reaction mixture, and the mixture was heated to the boiling point and filtered. The solution was evaporated to 20 ml to give 0.71 g (56%) of a product with mp 168-169°C. PMR spectrum: 3.95 ppm (s, 3H, $O-CH_3$). UV spectrum, λ_{max} (log ε): 502 nm (3.85). Found: N 5.51%. $C_{15}H_{11}NO_3$. Calculated: N 5.53%.

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MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.
6.* CYCLIZATION OF 1-DIAZO-3-AROYLAMINOPROPAN-2-ONES AND 2-PHENYL-5,6-DIHYDRO-4H-1,3-OXAZIN-5-ONES

A. T. Lebedev, P. A. Sharbatyan,
A. M. Sipyagin, V. G. Kartsev,
and V. S. Petrosyan

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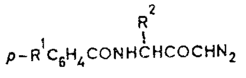
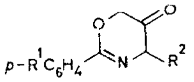
An analysis of the electron-impact mass spectra of 1-diazo-3-aroylaminopropan-2-ones made it possible to conclude that some $[M - N_2]^+$ ions have the 1,3-oxazin-5-one structure, some exist in the form of a cyclic intermediate that is produced in the first step of the cyclization process, and some decompose without rearrangements, i.e., they exist in a linear form. The Wolff rearrangement does not occur. Alkyl substituents in the 4 position of the resulting heterocycle hinder cyclization. Under chemical-ionization conditions the $[MH - N_2]^+$ ions exist in similar forms. The analysis of the mass spectra in this case is complicated by ion-molecular reactions.

Continuing our investigation of the cyclization of diazo ketones in the gas phase we studied the electron-impact (EI) and chemical-ionization (CI) mass spectra of a series of 1-diazo-3-aroylaminopropan-2-ones (I) and 2-aryl-5,6-dihydro-4H-1,3-oxazin-5-ones (II). Compounds II were obtained from the corresponding diazo ketones I by the action of concentrated sulfuric acid, and their structure was established by a number of spectral methods [2].



$p\text{-}R^1C_6H_4CONH\overset{R^2}{C}HCOCHN_2$

I a-i



II a-i

I, II a $R^1=R^2=H$; b $R^1=CH_3$, $R^2=H$; c $R^1=OCH_3$, $R^2=H$; d $R^1=Cl$, $R^2=H$; e $R^1=Br$, $R^2=H$; f $R^1=NO_2$, $R^2=H$; g $R^1=H$, $R^2=CH_3$; h $R^1=H$, $R^2=C_2H_5$; i $R^1=H$, $R^2=Bz$

The mass-spectrometric fragmentation of oxazinones II under the influence of electron impact was discussed in detail in [3].

In the present research we again subjected heterocycles II to mass-spectrometric analysis under conditions identical to those under which diazo ketones I were analyzed. In addition, all of the mass spectra were calculated by hand, which made it possible to introduce certain corrections in the fragmentation scheme and in the table of intensities of the peaks of the characteristic fragment ions that are presented in [3].

Molecular-ion peaks (M^+) were not recorded in the electron-impact spectra of diazo ketones I, and the $[M - N_2]^+$ ions, which may have different structures, considering the possibility of cyclization at the heteroatoms and the Wolff rearrangement [4-6], had the maximum m/z values:

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*See [1] for communication 5.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1332-1338, October, 1983. Original article submitted January 6, 1983.

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