PHOTOLYSIS OF N-NITROSOMETHYLAMINOANTHRAQUINONES

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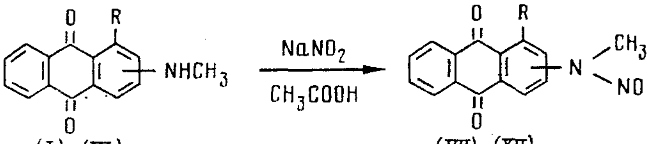
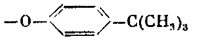
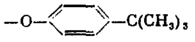
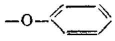
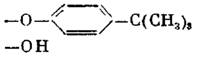
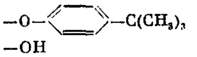
Irradiation of N-nitrosomethylaminoanthraquinones results in two photoreactions, namely denitrosation to give the methylanthraquinones, and rearrangement to 1,10-anthraquinones. Photolytic replacement of hydrogen by a nitroso group has been observed with 2-alkylamino-1,10-anthraquinones. An intermolecular homolytic mechanism is proposed for this reaction.

Photoirradiation of 1-aryloxy-9,10-anthraquinones is known to result in migration of the aryl group to the peri-oxygen atom to give 9-aryloxy-1,10-anthraquinones [1]. The greatest influence on the reversibility of this photoreaction, and on the stability of the photoinduced form, is exerted by the nature and position of the amino group in the anthraquinone nucleus [1, 2]. The photorearrangement of acylamino-1-aryloxyanthraquinones is reversible, results in considerable changes in the visible region of the spectrum, and is of practical value. It was thought desirable to modify the amino group by introducing, for example, a nitroso group as an analog of an acyl group. It is, however, known [3] that aromatic nitrosamines readily dissociate under the influence of light, so that in addition to photorearrangement, photodenitrosation might be expected to occur. The purpose of the present investigation was to prepare and examine the photochemical behavior of some N-nitrosoaminoanthraquinones.

Nitrosation of N-methylaminoanthraquinones (I)-(VI) by treatment with sodium nitrite in acetic acid afforded high yields of the novel nitrosamines (VII)-(XII). Compounds (X) (XII), which do not contain an aryloxy group, were synthesized for purposes of comparison.



(I)-(VI) (VII)-(XII)

Compound	Position of the $NHCH_3$ group	R	Compound	Position of the $NHCH_3$ group	R
(I)	2		(VII)	2	
(II) *	2		(VIII) *	2	
(III)	4		(IX)	4	
(IV)	2	$-OH$	(X)	2	$-OH$
(V)	2	$-OCH_3$	(XI)	2	$-OCH_3$
(VI)	4	H	(XII)	4	$-NCH_3NO$

*A chlorine substituent was present in the 3-position of the anthraquinone nucleus.

Solutions of these N-nitrosoaminoanthraquinones in nonpolar solvents (benzene or heptane) were subjected to photolysis at ~20°C. The colorless solutions rapidly turned reddish-violet (Table 1). The principal photolysis products were isolated and identified as the corresponding N-methylaminoanthraquinones (I)-(VI), i.e., the predominant process in the photolysis of these compounds was denitrosation.

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TABLE 1. Long Wavelength Absorption Maxima in the UV-Vis Spectra of N-Nitrosomethylaminoanthraquinones in Benzene

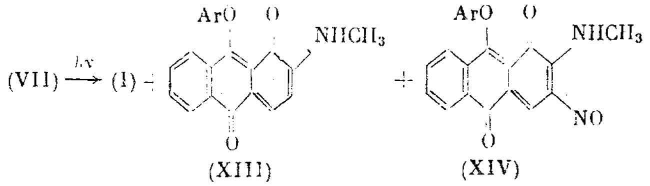
$$(\mathrm{VII})-(\mathrm{XII}) \xrightarrow[-\mathrm{NO}]{h\nu} (\mathrm{I})-(\mathrm{VI})$$

Compound	λ_{max}		
	before irradiation	after irradiation	
		77 K	298 K
(VII)	335	506	464, 580, 610
(VIII) *	335	507	426, 628
(IX)	335	–	512, 622
(X)	405	–	520
(XI)	335	–	438
(XII)	335	–	486

*A chlorine substituent was present in the 3-position of the anthraquinone nucleus.

In the case of compounds having an aryloxy group in the 1-position, (VII)-(IX), irradiation resulted in both denitrosation and rearrangement of the 1-aryloxymethylaminoanthraquinones (I)-(III) to the corresponding 1,10-anthraquinones, identified by comparison with known compounds [4, 5, 6].

The photolysis of (VII) is more complex. The reaction mixture contained three principal components, two of which decomposed rapidly on isolation. The mixture was separable by rapid chromatography on silica gel in vacuo. The products isolated were: (I), 2-methylamino-9-(p-tert-butylphenoxy)-1,10-anthraquinone (XII), and a compound (XIV) with λ_{max} 580 nm. Compounds (I) and (XIII) were chromatographically and spectrally identical with a sample obtained as described in [4]. From its IR, UV, and PMR spectral data, and its molecular weight (by mass spectrometry), (XIV) was assigned the structure 2-methylamino-3-nitroso-9-(p-tert-butylphenoxy)-1,10-anthraquinone.



(XIII) (XIV)

Ar = 4-$(CH_3)_3CC_6H_4$.

The ana-quinonoid structure (XIV) is supported by the UV-Vis absorption (580 nm), the shift of the C=O absorption to lower frequencies (1650 cm^{-1}), and the shift in the signals for protons H^5, H^8, and the NH group in the PMR spectrum (see [4]). The presence in the spectrum of a single signal for H^4 at low field (8.90 ppm) indicates the presence of a substituent in the 3-position. In the case of (VIII), in which the 3-position is blocked by a substituent, photolysis products containing a nitroso group were not found.

The structures established for these products indicate that photolysis of the nitrosoamine (VII) involves two competing reactions, namely denitrosation to give (I), and rearrangement with the formation of 2-(N-nitrosomethylamino)-9-(p-tert-butylphenoxy)-1,10-anthraquinone (VIIa). Further irradiation probably leads to homolysis of the N–NO bond followed by attack of NO on the 3-position to give (XIV). It is assumed that replacement of hydrogen by the nitroso group is a dark reaction involving the ground state of the ana-quinone. The formation of the nitroso compound (XIV) may thus be represented as a sequence of two photochemical steps (see scheme on following page).

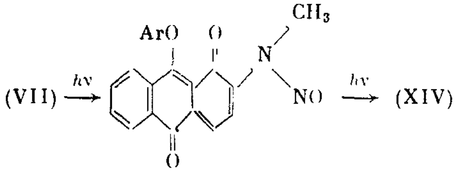
Photodenitrosation of (VIIa) to give the ana-quinone (XIII) is also possible. The latter ana-quinone is a product of the photorearrangement of (I). The formation of (XIII) on photolysis of the nitroso compound (XIV) has been established by chromatography.

According to this photolytic scheme, and ana-quinone (VIIa) is a precursor of the product (XIV), but it has not been possible to establish its formation when photolysis is carried

TABLE 2. N-Nitrosomethylamino-9,10-anthraquinones

Compound	Yield, %	Found/Calculated, %			M	Empirical formula
		C	H	N		
(VII)	85	72.32/72.46	5.44/5,31	6.42/6,76	414	$C_{25}H_{22}N_2O_4$
(VIII) *	78	64.65/64.20	3,12/3.31	6.85/7.13	392	$C_{21}H_{13}ClN_2O_4$
(IX)	83	72,20/72,46	5,05/5,31	6.91/6.76	414	$C_{25}H_{22}N_2O_4$
(X)	80	62,36/63,83	3,39/3,55	9.79/9,93	282	$C_{15}H_{10}N_2O_4$
(XI)	83	64,34/64,86	4,00/4,05	9.31/9,46	296	$C_{16}H_{12}N_2O_4$
(XII)	90	68.09/67,67	3,76/3,76	10,50/10,53	266	$C_{15}H_{10}N_2O_3$

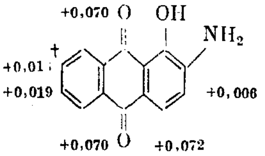
*Found/Calculated, %: C 9.39/9.04.

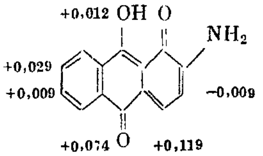


(VIIa)

out in solvents at ~20°C. The formation of (VIIa) was established spectroscopically by irradiating the nitrosamine (VII) in solid matrices, namely polymer layers (PVA or polystyrene) at 298 K, or in ethanol glass at 77 K (Table 1). The UV-Vis absorption spectrum of photoinduced (VIIa) is similar to those of 9-aryloxy-1,10-anthraquinones [1]. The spectral changes do not affect any of the isobestic points. Irradiation with visible light (λ_{exc} > 500 nm) results in conversion of (VIIa) into the starting (VII). The forward and reverse reactions may be repeated many times, behavior characteristic of 1-aryloxyanthraquinones [1]. No photodenitrosation products were found when photolysis was carried out at 77 K.

As far as we are aware, there have been no literature reports of the photoreplacement of hydrogen by the nitroso group in the anthraquinone nucleus. That we have found such replacement to take place may be due to the increased reactivity of the photoinduced 1,10-anthraquinone molecule as compared with the 9,10-anthraquinone molecule. The high reactivity observed experimentally of 9-aryloxy-1,10-anthraquinones towards nucleophiles has been rationalized by calculations [5]. The facile reaction with electrophiles, and the mode of this reaction can also probably be rationalized in terms of the distribution of the whole charge on the carbon atoms of 1-hydroxy-2-amino-9,10-anthraquinone, and the hypothetical 2-amino-9-hydroxy-1,10-anthraquinone:





A study of the calculated values shows that the only possible site of attack of an electrophile is at the 3-position of the ana-quinone molecule, at which, unlike in the 9,10-anthraquinones, there is excess electron density. The calculations were carried out for the ground state of the molecules.

Attention is drawn to the fact that of the compounds studied (VII)-(XII), only photolysis of (VII) results in replacement of hydrogen by the nitroso group. In the case of compounds (X)-(XII), this is due to the impossibility of generating the reactive 1,10-anthra-

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†Number obscured in Russian original — Editor

quinone system during photolysis. With (VIII) and (IX), photorearrangement to give 1,10-anthraquinones does occur, but no compounds containing a nitroso group were found in the photolysis products. The absence of photosubstitution for the nitrosamine (VIII) has been rationalized in the foregoing. In the case of 4-methylamino-1-aryloxyanthraquinones (IX), conversion into 1,10-anthraquinones on irradiation occurs only to a small extent [6].

Both intramolecular (acid-catalyzed Fischer—Hepp rearrangement [7]) and intermolecular mechanisms (photorearrangement of N-nitroso-di-(p-tolyl)amine [8]) have been put forward for the conversion of N-nitroso- into C-nitroso compounds. The most likely mechanism for the photosubstitution under discussion is an intermolecular one. This conclusion is based on the results of photolysis of a mixture of equimolar amounts of the nitrosamine (VII) and 1-(p-tert-butylphenoxy)-2-ethylaminoanthraquinone. According to PMR, the photolysate contained the ana-quinone (XIV) and 9-(p-tert-butylphenoxy)-2-ethylamino-3-nitroso-1,10-anthraquinone in a ratio of 2:1.

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EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer in KBr disks, and UV-Vis spectra on a Specord UV-VIS spectrophotometer, in ethanol (concentration 10^{-4} mole/liter). PMR spectra were obtained in $CDCl_3$ on Bruker AC-200 and Bruker WP-200-SY instruments, the signals being given on the δ scale. Molecular weights were determined by mass spectrometry on a Finnigan MAT-8200.

Nitrosomethylaminoanthraquinones (VII)-(XII). To 1 mmole of the appropriate N-methylaminoanthraquinone (I)-(VI) suspended in 30 ml of acetic acid was added 2 mmoles of sodium nitrite, gradually, with vigorous stirring. After 30 min, the mixture was diluted with water, and the solid which separated was filtered off, washed with water, and dried. Purification was effected on a column of silica gel (L 100/250), with chloroform as eluent. The yields and properties of the products are shown in Table 2. Compound (VII) melted over the range 168-175°C with decomposition. UV absorption spectrum (λ_{max}, nm (log ε), in heptane): 260 (4.61), 280 sh (4.34), 335 (3.81). PMR spectrum (δ, ppm, J, Hz): 1.22 s $[C(CH_3)_3]$, 3.35 s ($N{-}CH_3$), 6.68 d (2-m-H, J = 9), 7.20 d (2-o-H, J = 9), 7.75 m (H^6, H^7), 7.97 d (H^3, J = 8.5), 8.15 m, 8.29 m (H^5, H^8), 8.40 d (H^4, J = 8.5).

Photolysis of (VII)-(XII). A solution of 0.5 mmole of (VII)-(XII) in 300 ml of dry benzene was irradiated with the total spectrum of an SVD-120A mercury vapor lamp for 1-1.5 h at a distance of 20 cm from the sample. The photolysate was evaporated under reduced pressure at 30°C to a volume of 50 ml, then chromatographed on a column of silica gel (L 100/250 μm) under reduced pressure, with a 10:1 mixture of benzene and acetone as eluent.

a) From 0.20 g of (VII) there were obtained 0.06 g (33%) of (I), 0.07 g (35%) of (XIV), and 0.05 g (27%) of (XIII). Compounds (I) and (XIII) were identified by comparison with material reported in [4]. Compound (XIV) decomposed above 60°C. IR spectrum (ν, cm^{-1}): 1590 (C=C), 1650 (C=O); 2830, 2970 (C—H), 3440 (N—H); UV spectrum (λ_{max}, nm (log ε), in heptane): 258 (4.36), 333 sh (3.92), 358 sh (3.86), 580 (3.81). Mass spectrum: 414 (M^+), $C_{25}H_{22}N_2O_4$. PMR spectrum (δ, ppm, J, Hz): 1.27 s $[C(CH_3)_3]$; 3.09 d (NCH_3, J = 8.5), 6.82 d (2-m-H, J = 9), 7.30 d (2-o-H, J = 9), 7.66 m (H^6, H^7), 8.37 m (H^5), 8.69 m (H^8), 8.90 s (H^4), 10.25 br. s (NH).

b) From 0.20 g of (VIII) there were obtained 0.07 g (39%) of (II) and 0.08 g (44%) of 2-methylamino-3-chloro-9-phenoxy-1,10-anthraquinone. IR spectrum (ν, cm^{-1}): 1590 (C=C), 1630 (C=O), 2870, 2970 (C—H), 3390 (N—H).

c) 0.20 g of (IX) gave 0.16 g (88%) of (III).

d) 0.15 g of (X) gave 0.12 g (90%) of (IV).

e) 0.15 g of (XI) gave 0.11 g (81%) of (V).

f) 0.15 g of (XII) gave 0.07 g (53%) of (VI) and 0.04 g (33%) of 1-aminoanthraquinone.

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SYNTHESIS AND REACTIONS OF S,S-DIALKYL TRIMETHYLSILYL DITHIOPHOSPHITES

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S,S-Dialkyl-O-trimethylsilyl dithiophosphites (III)-(VI) have been obtained by reacting dialkyl dithiochlorophosphites with bis(trimethylsilyl)acetamide. Compounds (III)-(VI) react with aldehydes in the presence of catalytic amounts of tertiary amines to give S,S-dialkyl-1-trimethylsilyloxyalkyl-dithiophosphonates (VII)-(IX) and (XII). Hydrolysis of (III) and (V) affords dialkyl dithiophosphites (XVI) and (XVII), which readily add to azomethines and chloral.

Silyloxy derivatives of P(III) thioacids with the SPOSi bond system have not been reported. The usual method of synthesis of silyl phosphites is by silylation of hydrophosphoryl compounds [1]. This method was, however, found to be inapplicable to the synthesis of silyl phosphites with alkylthio groups attached to phosphorus, since the requisite hydrophosphoryl compounds bearing alkylthio groups at phosphorus are extremely labile [2]. The best method was found to be by replacing the chlorine in P(III) acid chlorides by the trimethylsilyloxy group with bis(trimethylsilyl)acetamide [3]. We have found that the reaction of dialkyl dithiochlorophosphites with acetamide occurs in two steps. The first step occurs on mixing the reactants, under mild conditions, with the elimination of a molecule of trimethylchlorosilane, and phosphorylation of the ambident triad NCO system of the acetamide. This reaction could in theory give three isomers, namely the N-silylated-O-phosphoryl (a), the O-silylated-N-phosphoryl (b), or the N-silylated-N-phosphoryl compound (c) (see scheme at top of following page).

The ^{31}P NMR spectra of the reaction mixture at this stage showed clearly that compounds of two types were present, both containing three-coordinate phosphorus. When, for example, diisopropyl dithiochlorophosphite was used in this reaction, the spectrum showed two signals with δP 118 and 108 ppm in a ratio of 3:2. With diethyl dithiochlorophosphite, two products were formed with δP 128 and 117 ppm in a ratio of 4:1. Comparison of the chemical shifts of these signals with literature values [4] enables structure (a) to be excluded, since the S_2PO environment usually gives rise to a shift in the range 160-180 ppm. The IR spectra of the reaction mixtures show two bands at 1620 and 1660 cm^{-1}, clearly due to the C=N and C=O groups of isomers (b) and (c), respectively. This assignment is based on the fact that the carbonyl group absorbs at a longer wavelength than an azomethine group in approximately the same environment [5]. This assignment is supported by the absorptions of C=N and C=O groups

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