PHOTOCHEMICAL REACTION OF 9,10-ANTHRAQUINONE WITH ACETONITRILE

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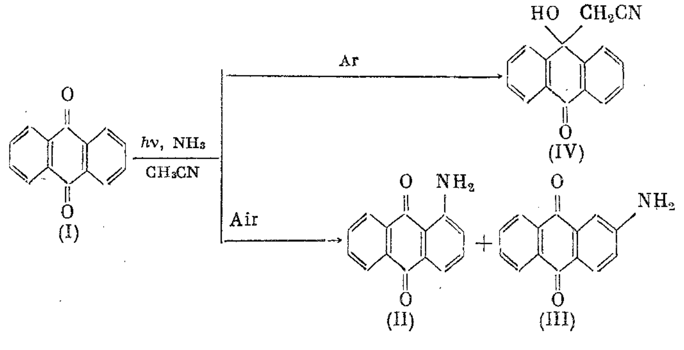
The photochemical reaction of 9,10-anthraquinone (I) with ammonia in acetonitrile solution, which leads to the formation of the 1- and 2-aminoanthraquinones ((II) and (III) respectively), was described previously [1]. In view of the recent communications on the photochemical addition reactions of weak CH donors [2, 3] and dienes [4] to the carbonyl group of anthraquinone it was impossible to exclude the possibility that acetonitrile would react in a similar manner during the photoamination of (I), especially as ammonia, based on the data given in [2], is a catalyst of the indicated addition reaction.

In the present paper we established that the irradiation (λ ≥ 300 nm) of (I) in acetonitrile solution, containing ammonia, gives, along with the direct amination products, also the adduct of quinone (I) with the solvent, which, on the basis of the analytical and spectral data, was assigned the structure of 9-hydroxy-9-cyanomethyl-10-anthrone (IV). The reaction of anthraquinone with acetonitrile was previously unknown, despite its extensive use as a solvent in photochemical reactions. A study of the conditions that affect the photoaddition of acetonitrile disclosed that the photoreaction of (I) with acetonitrile practically does not go in the absence of ammonia. In the presence of ammonia under aerobic (or anaerobic) conditions the photolysis of (I) is the same using either aqueous or gaseous ammonia (Table 1). In an argon atmosphere the yield of anthrone (IV) exceeds that of the amination products. The amount of anthrone (IV) increases with increase in the photolysis time and reaches 54% after 8 h of irradiation, in which connection the yield of amines (II) and (III) is 7%.

The formation of (IV) could not be established in the presence of atmospheric oxygen. The possible reasons for this are: 1) that the photoaddition of acetonitrile to (I) proceeds with the involvement of radical intermediate particles that are unstable to aerobic conditions (cf. [2]), and 2) the low stability of the anthrone itself under aerobic photolysis conditions.* The presence of small amounts (1-5%) of anthrone (IV) during the photolysis of (I), with a simultaneous bubbling of air and ammonia gas through the reaction mixture (see Table 1), can also be related to the local creation of anaerobic conditions during reaction.



As a result, depending on the conditions, when (I) is irradiated in acetonitrile, containing ammonia, the reaction can proceed either as direct replacement of the hydrogen atom by the amino group [1] or as reaction with the solvent at the carbonyl group. The presence of atmospheric oxygen favors direct amination, while in an inert atmosphere the principal process is the photoaddition of acetonitrile to give the anthrone.

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* It was shown by special experiment that when a mixture of anthrone (VI), anthraquinone (I), and aqueous ammonia is irradiated (4 h) in the presence of atmospheric oxygen the anthrone is ~ 20-30% converted to anthraquinone and its subsequent partial amination.

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TABLE 1. Photolysis of 9,10-Anthraquinone (I) in Acetonitrile at 25-30°C

Photolysis conditions		Irradiation time h	Yield of reaction products*, %			Conversion of (I), %	$C_{(III)}$†, %
			anthrone (IV)	2-aminoanthraquinone (III)	1-aminoanthraquinone (II)		
Argon	NH_3 gas	1	9	3	2	40	21,7
	NH_3 aq.	1	12	1	1	50	9,6
	"	4	36	8	3	67	16,5
	"	8	54	6	1	89	8,5
Air	NH_3 gas	1	2	8	4	14	80,7
	"	4	1	16	6	30	96,2
	"	8	5	24	10	46	77,8
	NH_3 aq.	8	–	24	14	57	100

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* Calculation of the yield of (III) and (IV) was based on the quantitative analysis data for chromatographically pure mixtures of (III) and (IV).

† $C_{(III)}$ is the average amount of (III) in %, which was found from the UV spectra of chromatographically pure mixtures of (III) and (IV).

EXPERIMENTAL

The IR spectra were recorded on a Carl Zeiss UR-20 spectrophotometer, the electronic absorption spectra were recorded on a Beckman DU-8 spectrophotometer (in ethanol), and the PMR spectrum was recorded on a Varian A-56/56A instrument (60 MHz) in $CDCl_3$. The chromatographic separation of the products was done on silica gel columns, using a 1 : 1 benzene–$CHCl_3$ mixture as the eluent.

General Photolysis Method. A solution of 0.150 g of (I) in 150 ml of acetonitrile was blown for 15-20 min with argon (or air), ammonia gas was passed through (or 20 ml of 25% aqueous ammonia solution was added), and the mixture was irradiated in Pyrex vessels with the light from a DRSh-500 mercury lamp at 25-30°C, maintaining the bubbling of argon (air) and ammonia gas. At the end of photolysis the solvent was distilled off under reduced pressure, the oily residue was rubbed in petroleum ether (or washed with water), and the precipitate was filtered, dried, and chromatographed, eluting in sequence the unreacted quinone, 1-aminoanthraquinone, and a mixture of 2-aminoanthraquinone and the anthrone, which was quantitatively analyzed via the UV spectra. The mixture can be separated chromatographically, but due to the close R_f values it is difficult to obtain quantitative data. The amount of amine (III) in % (C_{III}) in the mixtures was determined at a wavelength of 453 nm under programmed spectrophotometer operating conditions. Here the amount of anthrone (IV) was estimated via the difference $(100 - C_{III})$%, on the assumption that other components are absent in the mixture. To check the obtained results the amounts of (III) and (IV) were calculated from the optical density at wavelengths of 275 nm (ε (IV) 30129, ε (III) 25199) and 453.3 nm (ε (IV) 0, ε (III) 3945). Both variations gave results that agreed within the limits of measurement error, which was 1.5% of the absolute value.

The analytical sample of 9-hydroxy-9-cyanomethyl-10-anthrone (IV) was obtained by successive recrystallization of a chromatographically pure mixture of 2-aminoanthraquinone and the anthrone from benzene and CCl_4 as white needles with mp 169-173°C (decompn.); IR spectrum ($CHCl_3$, ν, cm^{-1}): 1060 (CO), 1680 (C=O), 2260 ($C\equiv N$), 3585 (OH). Ultraviolet spectrum: λ_{max} 235 sh, 275 nm, log ε 3.96, 4.21. PMR spectrum (δ, ppm): 2.80 s (2H, CH_2), 3.06 s (1H, OH), 7.20-8.25 m (8H arom.). Found: C 77.37; H 4.43; N 5.74%. $C_{16}H_{11}NO_2$. Calculated: C 77.11; H 4.42; N 5.62%.

CONCLUSIONS

When 9,10-anthraquinone is irradiated in acetonitrile solution, containing ammonia, in an argon atmosphere, the photoaddition of the solvent to the carbonyl group of the quinone occurs to give 9-hydroxy-9-cyanomethyl-10-anthrone.

LITERATURE CITED

1. V. A. Loskutov, S. M. Lukonina, and E. P. Fokin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 9 (4), 135 (1978).
2. G. G. Wubbels, W. J. Monaco, D. E. Johnson, and R. S. Meredith, J. Am. Chem. Soc., 98, 1036 (1976).
3. V. A. Loskutov, A. V. Konstantinova, and E. P. Fokin, Izv. Akad. Nauk SSSR, Ser. Khim., 1142 (1981).

4. H. Inou, A. Ezaki, D. Nakajima, H. Tomono, and M. Hida, J. Chem. Soc. Perkin Trans. 1, 1771 (1982).

HYDROLYSIS OF β-ETHYLTHIOCROTONALDEHYDE DIETHYL ACETAL

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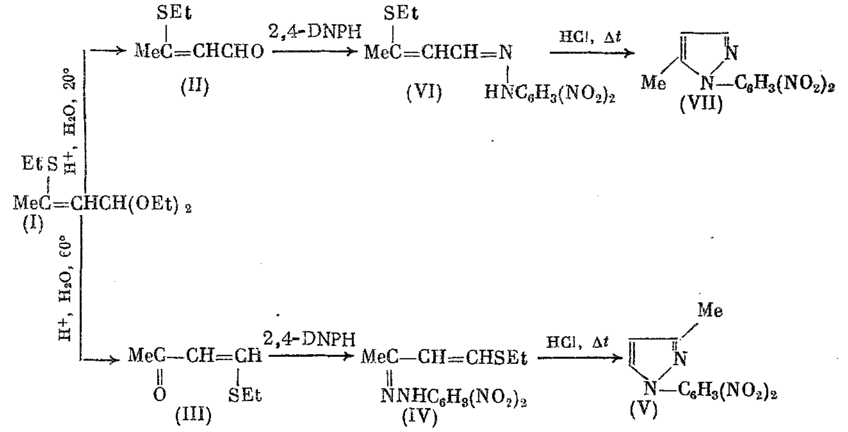
We found that the hydrolysis of β-ethylthiocrotonaldehyde diethyl acetal (I) at 60°C does not lead to the expected β-ethylthiocrotonaldehyde (II) [1], but instead to its isomer, namely methyl β-ethylthiovinyl ketone (III) (60% yield), which is formed as a mixture of the cis and trans isomers in a 1 : 9 ratio. The structure of (III) was proved by the PMR and IR spectroscopy methods [2], and also by preparing the corresponding 2,4-dinitrophenylhydrazone (IV) (2,4-DNPH).



When hydrazone (IV) is heated (80°C) for a long time in an acid medium it is converted to 1-(2,4-dinitrophenyl)-3-methylpyrrazole (V), whose structure is confirmed by the PMR spectrum (Table 1). Under milder conditions (20°C) the hydrolysis of acetal (I) leads to the expected β-ethylthiocrotonaldehyde (II) (70% yield). Its 2,4-dinitrophenylhydrazone (VI) differs from the isomeric hydrazone (IV) in its melting point and PMR spectrum. When (VI) is heated in an acid medium it cyclizes to 1-(2,4-dinitrophenyl)-5-methylpyrrazole (VII), which isomeric with pyrrazole (V).

In contrast to the 2,4-dinitrophenylhydrazone of β-ethylthioacrolein [3], hydrazone (VI) when heated with excess 2,4-dinitrophenylhydrazine does not form the rearrangement product. When aldehyde (II) is heated in an aqueous acid medium (60°C, 1.5 h) it is quantitatively converted to ketone (III), and consequently the yield of ketone (III) from acetal (I) can be explained by the intermediate formation of aldehyde (II).

EXPERIMENTAL

The PMR spectra were obtained on a Tesla BS-487B spectrometer (80 MHz). The IR spectra were recorded on a UR-20 instrument.

1-Ethylthio-1-buten-3-one (III). A mixture of 41.4 g of (I), 32 ml of water, 0.1 ml of conc. HCl, and 40 ml of EtOH was stirred at 60°C for 4 h. The organic layer was separated, the aqueous layer was extracted with ether, and the ether extracts were combined with the oil layer and dried over $MgSO_4$. The ether was removed and the residue was vacuum-distilled to give 15.5 g (60%) of (III), bp 70°C (1 mm), n_D^{20} 1.5340, d_4^{20} 1.0270. Found: C 55.39; H 7.50; S 24.40%. $C_6H_{10}OS$. Calculated: C 55.37; H 7.67; S 24.63%. Infrared spectrum (microlayer, ν, cm^{-1}): 1555 (C=C), 1660 (C=O) (cf. [2]).

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