PHOTOLYSIS OF 1,2-ANTHRAQUINONE DIAZIDE IN AROMATIC HYDROCARBONS

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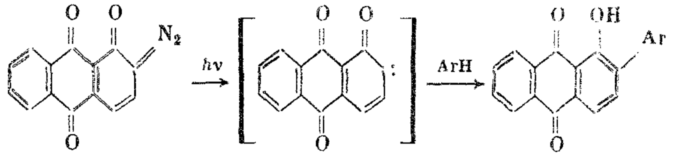
It has been determined that the main products of photolysis of 1,2-anthraquinone diazide in benzene, toluene, anisole, nitrobenzene, and pyridine are the corresponding 1-hydroxy-2-arylanthraquinones that form as a mixture of ortho, meta, *and* para *isomers with significant content of the* meta *isomer (40-55%).*

Keywords: *photolysis, 1,2-anthraquinone diazide, aromatic hydrocarbons, isomers.*

Quinone diazides are light-sensitive compounds and are used for photochemical information recording [1]. Regarding the pyrolysis of these compounds at ~20°C, it is known that 1,2- and 2,1-anthraquinone diazides (AQD) undergo ring contraction in aqueous or alcoholic solutions with formation of cyclopentadiene derivatives [2]. At the same time, 2-hydroxy-3-arylanthraquinones have been obtained from 2,3-AQD by photolysis in aromatic hydrocarbons [3]. Such a difference is explained by the unique dependence of the photochemical properties of *o*-quinone diazides on positional isomerism [2]. In our opinion, the direction of the photochemical reactions of *o*-AQD can depend on the type of solvent used to carry out the photolysis.

The purpose of the present paper is a study of the direction of photolysis of 1,2-AQD (**1**) in aromatic hydrocarbons.

Solutions of 1,2-AQD in benzene, toluene, anisole, nitrobenzene, and pyridine were subjected to photolysis at ~20°C. Irradiation was carried out with the total light of an SVD-120A mercury lamp for 1-2 h. The reaction products, 1-hydroxy-2-arylanthraquinones **3-7**, were obtained in high yields.



(1) (2a) (3—7)

Ar = C_6H_5(3), $C_6H_4CH_3$(4), $C_6H_4OCH_3$(5), C_5H_4N(6), $C_6H_4NO_2$(7).

Products **4-7** were mixtures of three possible isomers. From an analysis of the ^{1}H NMR spectra of the obtained mixtures, it was possible to determine their isomeric composition (Table 1). Previously, in investigations of photoinitiated reactions of *o*-quinone diazides, Griffiths and Lockwood [2] and Ried and Baumbach [3] postulated high electrophilic activity of the intermediately formed carbene and its predominant existence in an ionic-type resonance form. At the same time, the isomeric composition in photochemical reactions of quinone diazides with aromatic hydrocarbons was not established [4]. The high percentage of *meta* products that we observed experimentally indicates that the reaction of carbene **2a** with aromatic hydrocarbons has low selectivity. This fact may be related to the possible existence of **2a** as a biradical. Biradical properties were assumed previously for derivatives of 1,4-benzoquinone diazide [5].

Thus, depending on the photolysis conditions, two directions of the reaction of intermediately formed carbene **2a** are possible. In aqueous and alcoholic solutions at ~20°C and also in frozen matrices in low-temperature photolysis, the Wolff rearrangement occurs with formation of aromatic ketenes [6]. But in a medium of aromatic hydrocarbons, another, probably biradical (triplet) reaction mechanism occurs, which affords anthraquinone derivatives.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer using KBr tablets, electronic absorption spectra (EAS) were recorded on a Specord UV-VIS spectrophotometer using ethanol (concentration $1 \cdot 10^{-4}$ *M*), and PMR spectra were recorded on Bruker AC-200 and Bruker WP-200 SY instruments using $CDCl_3$. The peaks are presented in a δ scale. The molecular weights were determined mass-spectrometrically with a Finnigan HAT-8200 instrument.

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TABLE 1. Distribution of Isomers in Products **4-7***

Compound	Ortho, %	Meta, %	Para, %
4	10	55	35
5	40	55	5
6	40	40	20
7	40	40	20

*The ratio of the isomers was determined by measurement of the integrated intensities of the peaks of each isomer in the PMR spectra of the mixtures. The accuracy of the determination was ±5%.

TABLE 2. 1-Hydroxy-2-arylanthraquinones

Compound	Yield, %	*M* found	*M* calculated	Formula	IR spectrum, cm^{-1} C=C	IR spectrum, cm^{-1} C=O	EAS in ethanol λ_{max} (log ε), nm
3	67	300.0738	300.0786	$C_{20}H_{12}O_3$	1580	1630, 1665	257(4.69), 335(3.61), 430(3.87)
4	76	314.0928	314.0943	$C_{21}H_{14}O_3$	1590	1630, 1670	256(4.60), 333(3.56), 427(3.91)
5	70	330.0885	330.0892	$C_{21}H_{14}O_4$	1590	1640, 1670	256(4.62), 333(3.41), 430(3.94)
6	65	301.0736	301.0739	$C_{19}H_{11}NO_3$	1590	1645, 1670	254(4.57), 277 sh (4.15), 333(3.48), 424(3.85)
7	72	345.0611	345.0637	$C_{20}H_{11}NO_5$	1590	1635, 1670	254(4.62), 277 sh (4.32), 333(3.75), 424(3.92)

Chromatography was carried out on columns with SiO_2 ($L \sim$ 100-250 μm), and thin-layer chromatography (TLC) was carried out on silica gel ($L \sim$ 0-140 μm) and on Silufol UV-254 plates.

Photolysis of 1,2-AQD (1) in Benzene, Toluene, Anisole, Pyridine, and Nitrobenzene. With light from mercury lamp SVD-120A, 0.12 g (0.5 mmole) of compound **1** in 150 ml of the dry solvent was irradiated for 1-2 h until disappearance of the starting compound (the course of the reaction was monitored by TLC). The solvent was driven off to dryness, and nitrobenzene was driven off by steam distillation. The residue was chromatographed on SiO_2, and the eluent was $CHCl_3$. A yellow fraction was recovered. Thin-layer chromatography (benzene as the eluent) enabled recovery of *ortho* isomers in the case of compound **6** and *meta* isomers in the case of compound **7**. The yields and spectral characteristics of compounds **3-7** are given in Table 2. The peaks in the PMR spectra were assigned in accordance with the known patterns of chemical shifts and spin—spin coupling constants of aromatic protons in the series of disubstituted benzenes [7, 8].

Compound (3). Mp 110-111°C (from EtOH). PMR spectrum (δ, ppm, *J*, Hz): 13.32 s (OH); 8.30 m ($H^{5,8}$); 7.89 d (J = 8, H^4); 7.80 m ($H^{6,7}$); 7.73 d (J = 8, H^3); 7.67 m ($H^{2',6'}$); 7.45 m ($H^{3',4',5'}$).

Compound (4). PMR spectrum (δ, ppm, *J*, Hz): 13.28 s (0.35 H, OH_p); 13.02 s (0.55 H, OH_m); 12.58 s (0.10 H, OH_o); 8.31 m (2.0 H, $H^{5,3}$); 7.89 d (1.0 H, J = 8, H^4); 7.81 m (2.0 H, $H^{6,7}$); 7.72 d (1.0 H, J = 8, H^3); 7.65 m (0.10 H, $H_o{}^6$); 7.60 m (0.70 H, $H_p{}^{2',6'}$); 7.56 m (0.55 H, $H_m{}^{2'}$); 7.53 m (0.55 H, $H_m{}^{5'}$); 7.44 m (0.20 H, $H_o{}^{3',4'}$); 7.30 m (1.10 H, $H_m{}^{4',6'}$); 7.26 m (0.70 H, $H_p{}^{3',5'}$); 7.20 m (0.10 H, $H_o{}^{5'}$); 2.42 s (1.65 H, $CH_3{}^m$); 2.41 s (1.05 H, $CH_3{}^p$); 2.22 s (0.30 H, $CH_3{}^o$).

Compound (5). PMR spectrum (δ, ppm, *J*, Hz): 13.32 s (0.40 H, OH_o); 13.05 s (0.55 H, OH_m); 12.58 s (0.05 H, OH_p); 8.28 m (2.0 H, $H^{5,8}$); 7.86 d (1.0 H, J = 8, H^4); 7.78 m (2.0 H, $H^{6,7}$); 7.67 d (1.0 H, J = 8, H^3); 7.60 m (0.40 H, $H_o{}^6$); 7.43 m (0.10 H, $H_p{}^{2',6'}$); 7.39 m (0.55 H, $H_m{}^{2'}$); 7.35 m (0.55 H, $H_m{}^{5'}$); 7.31 m (0.40 H, $H_o{}^{4'}$); 7.22 m (1.10 H, $H_m{}^{4',6'}$); 7.07 m (0.40 H, $H_o{}^{3'}$); 7.01 m (0.40 H, $H_o{}^5$); 6.96 m (0.10 H, $H_p{}^{3',5'}$); 3.85 s (1.20 H, $OCH_3{}^o$); 3.80 s (1.65 H, $OCH_3{}^m$); 3.64 s (0.15 H, $OCH_3{}^p$).

Compound (6). *Ortho* isomer. Recovered: 0.04 g (39%). Mp 230-232°C (ethanol). PMR spectrum (δ, ppm, *J*, Hz): 13.31 s (OH); 8.73 m ($H^{6'}$); 8.35 d (J = 8, H^4); 8.31 m ($H^{5,8}$); 8.15 m ($H^{3'}$); 7.93 d (J = 8, H^3); 7.80 m ($H^{6,7,4'}$); 7.28 m ($H^{5'}$).

Mixture of *para* and *meta* Isomers. PMR spectrum (δ, ppm, *J*, Hz): 13.35 s (0.33 H, OH_p); 13.31 s (0.67 H, OH_m); 8.87 m (0.67 H, $H_m^{2'}$); 8.71 m (0.67 H, $H_p^{2',6'}$); 8.03 m (0.67 H, $H_m^{4'}$); 7.92 d (1.0 H, $J = 8$, H^4); 7.82 m (2.0 H $H^{6,7}$); 7.74 d (1.0 H, $J = 8$, H^3); 7.59 d (0.67 H, $J = 4.5$, $H_p^{3',5'}$); 7.40 m (0.67 H, $H_m^{5'}$).

Compound (7). *Meta* isomer. Recovered: 0.05 g (40%). Mp 246-248°C (chloroform). PMR spectrum (δ, ppm, *J*, Hz): 13.39 s (OH); 8.55 m ($H^{2'}$); 8.32 m ($H^{5,8}$); 8.02 m ($H^{4'}$); 7.95 d ($J = 8$, H^4); 7.85 ($H^{6,7}$); 7.79 m ($H^{6'}$); 7.68 d ($J = 8$, H^3); 7.65 m ($H^{5'}$).

Mixture of *ortho* and *para* isomers. PMR spectrum (δ, ppm, *J*, Hz): 13.02 s (1.0 H, OH_o, OH_p); 8.30 m (2.0 H, $H^{5,8}$); 8.10 d (0.67 H, $J = 8$, $H_p^{3',5'}$); 7.95 d (1.0 H, $J = 8$, H^4); 7.94 m (0.67 H, $H_o^{3'}$); 7.82 m (2.0 H, $H^{6,7}$); 7.76 m (0.67 H, $H_o^{6'}$); 7.71 d (1.0 H, $J = 8$, H^3); 7.54-7.63 m (1.34 H, $H_o^{4',5'}$); 7.44 d (0.67 H, $J = 8$, $H_p^{2',6'}$).

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