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The Photochemical Synthesis of 5-Aryl-7,12-benz[*a*]anthracenediones from 1,4-Naphthoquinones and 1,1-Diarylethylenes

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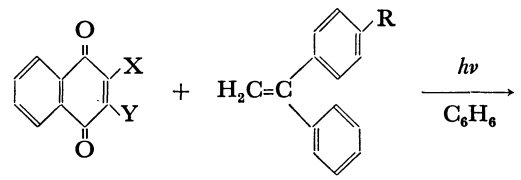
Synopsis. By the photolysis of the benzene solution of a variety of 2,3-disubstituted (halogeno, methoxy, and acetoxy) 1,4-naphthoquinones, **1**, and 1,1-diarylethylenes, **2**, 5-aryl-7,12-benz[*a*]anthracenediones, **3**, are obtained in fairly good yields (22—68%).

In a previous study[1] the photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone, **1a**, with 1,1-diphenylethylene has been found to give 5-phenyl-7,12-benz[*a*]anthracenedione, **3a**. As an extension of that work, we wish now to report a more facile and general route for the preparation of 5-aryl-7,12-benz[*a*]-anthracenediones, **3**.

In the photochemical reaction of 2-alkoxy-3-bromo-1,4-naphthoquinones, *e.g.*, **1a**, with 1,1-diphenylethylene, **2a**, the methoxyl group and the bromine atom were both found to be missing during the course of the photolysis to give 5-phenyl-7,12-benz[*a*]anthracenedione, **3a**. Although 2-alkoxy-3-bromo-1,4-naphthoquinones are good substrates for the preparation of **3a**, several steps are required to prepare them as starting materials.[2]

In this work the reactivities of other 2,3-disubstituted 1,4-naphthoquinones, such as 2,3-dichloro-1,4-naphthoquinone, **1b**, 2,3-dibromo-1,4-naphthoquinone, **1c**, and 2-acetoxy-3-bromo-1,4-naphthoquinone, **1d**, in the photolysis were investigated. Since 5-phenyl-7,12-benz[*a*]anthracenedione, **3a**, was obtained in a satisfactory yield in every case examined here (see Table 1), not only alkoxyl group but also halogen atoms were concluded to be good leaving groups in the photochemical reaction. Because of the accessibility of quinones, such as 2,3-dichloro-1,4-naphthoquinone **1b**, our photochemical reaction could provide a more facile synthetic route to 5-phenyl-7,12-benz[*a*]anthracenedione, **3a**. The use of other substituted 1,1-diphenylethylenes, **2b**—**e**, in the reaction opens the route to give 5-aryl-7,12-benz[*a*]anthracenediones. Every combination of a quinone, **1**, and a 1,1-diarylethylene, **2**, resulted in a similar, smooth photochemical reaction to yield 5-aryl-7,12-benz[*a*]anthracenediones, **3** (Table 1).[3] The photochemical reaction of monosubstituted 1,1-diarylethylenes, **2b**—**e**, with the quinone, **1**, produced two possible isomers, **3I** and **3II**; they were isolated separately in some cases. The differentiation of the two isomers, **3I** and **3II**, depends on their NMR spectra; that is, the presence or the absence of the spin-spin coupling of the aromatic proton at C-1 (δ: 9.40—9.97 ppm, characterized by its lower chemical shifts) is the indicator. The C-1 aromatic proton of the isomer, **3II**, invariably shows a doublet signal (J=8—12 Hz) due to the spin-spin coupling with the C-2 aromatic proton, while the C-1 aromatic proton of the isomer, 3I, appears as a singlet or a slightly split doublet signal (J=2 Hz) (Table 2). Thus, the isomer ratio, **3I**/**3II**, was estimated from the integration of the NMR signals of the mixture (Table 1).

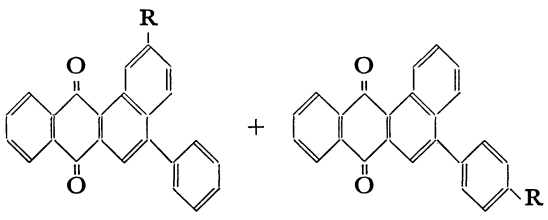


1

a: X=OCH_3, Y=Br
b: X=Y=Cl
c: X=Y=Br
d: X=O·CO·CH_3, Y=Br

2

a: R=H
b: R=CH_3
c: R=OCH_3
d: R=Cl
e: R=Br



3I

a: R=H
b: R=CH_3
c: R=OCH_3
d: R=Cl
e: R=Br

3II

a: R=H(≡**3Ia**)
b: R=CH_3
c: R=OCH_3
d: R=Cl
e: R=Br

TABLE 1. THE YIELD OF 5-ARYL-7,12-BENZ[*a*]-ANTHRACENEDIONE, **3**, AND THE ISOMER RATIO (**3I**/**3II**)[a,b]

Quinone	Olefin				
	2a	**2b**	**2c**	**2d**	**2e**
1a	65%(**3a**)	50%(**3b**) (44/56)	68%(**3c**) (54/46)	61%(**3d**) (36/64)	62%(**3e**) (42/58)
1b	49%(**3a**)	28%(**3b**) (52/48)	28%(**3c**) (68/32)	34%(**3d**) (35/65)	30%(**3e**) (34/66)
1c	46%(**3a**)	29%(**3b**) (50/50)	34%(**3c**) (85/15)	22%(**3d**) (31/69)	42%(**3e**) (37/63)
1d	46%(**3a**)				

a) The yield was calculated on the basis of the quinone consumed. b) The isomer ratio was estimated from the integration of the NMR signal due to the aromatic proton at C-1.

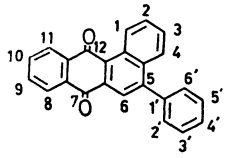
Experimental

General Procedure. The benzene solution (20 ml) of a quinone (1 mmol) and a 1,1-diarylethylene (2 mmol) was

Table 2. Some physical and spectral properties of 5-aryl-7,12-benz[*a*]anthracenedione

	Mp	IR[a]	UV, λ_{max}[b,d] (ε)	NMR[c]	Mass (*m/e*)
3Ia	167.0—167.5 °C	1668 cm^{-1}	417nm (4.35×10^3)	7.4—8.4 ppm (13H, m)	334(M^+)
(**3IIa**)		(C=O)	368 (3.05×10^3)	9.78 (1H, C-1 CH, d, J=8.0 Hz)	
			334 (4.03×10^3)		
			291 (3.91×10^4)		
			249 (2.68×10^4)		
3Ib[d]	186 —189 °C	1666 cm^{-1}	424 (4.45×10^3)	2.60 (3H, CH_3, s)	348(M^+)
		(C=O)	371 (3.22×10^3)	7.1—8.3 (12H, m)	
			337(sh) (4.39×10^3)	9.52 (1H, C-1 CH, s)	
3IIb[d]			293 (3.63×10^4)	2.45 (3H, CH_3, s)	
			250 (2.98×10^4)	7.1—8.3 (12H, m)	
			245(sh) (2.77×10^4)	9.70 (1H, C-1 CH, d, J=10.0 Hz)	
3Ic[d]	177 —179 °C	1663 cm^{-1}	430 (5.32×10^3)	4.04 (3H, OCH_3, s)	364(M^+)
		(C=O)	293 (3.61×10^4)	7.0—8.5 (12H, m)	
			248 (3.20×10^4)	9.40 (1H, C-1 CH, d, J=2.0 Hz)	
3IIc[d]				3.93 (3H, OCH_3, s)	
				7.0—8.5 (12H, m)	
				9.84 (1H, C-1 CH, d, J=9.0 Hz)	
3Id[d]	197 —200 °C	1651 cm^{-1}	416 (2.30×10^3)	7.2—8.3 (12H, m)	370(M^+(Cl^{37}), 38%)
		(C=O)	366 (1.62×10^3)	9.74 (1H, C-1 CH, s)	368(M^+(Cl^{35}), 100%)
3IId[d]			290 (2.00×10^4)	7.2—8.3 (12H, m)	
			250 (1.56×10^4)	9.71 (1H, C-1 CH, d, J=12.0 Hz)	
3Ie	219.0—219.5 °C	1658 cm^{-1}	416 (4.84×10^3)	7.4—8.5 (12H, m)	414(M^+(^{81}Br), 100%)
		(C=O)	367 (3.42×10^3)	9.97 (1H, C-1 CH, d, J=2.0 Hz)	412(M^+(^{79}Br), 97%)
3IIe	231.5—233.0 °C	1663 cm^{-1}	290 (4.16×10^4)	7.4—8.5 (12H, m)	
		(C=O)	249 (3.35×10^4)	9.71 (1H, C-1 CH, d, J=8.0 Hz)	

a) The IR spectrum was measured as the state of the KBr disk. b) The UV spectrum was measured as the solution of chloroform. c) The NMR spectrum was measured as the solution of deuterated chloroform, and the chemical shifts were calibrated from TMS as the internal standard. d) The data were measured as a mixture of two isomers.



irradiated by means of a high-pressure Hg arc lamp (300 W) through a 5-cm-thick water layer at room temperature. After the complete consumption of the quinone —in general, it takes about 10 h of irradiation, the solvent was distilled off under a reduced pressure. The subsequent purification of the reaction mixture by using chromatography on silica gel gave 5-aryl-7,12-benz[*a*]anthracenediones as a mixture of two isomers; this mixture was further purified by recrystallization from benzene–hexane. The yields, the isomer ratios, and the physical properties of the products are summarized in Tables 1 and 2. The general procedures for the elucidation of the structure, **3**, were given in the previous communication.[1]

Starting Materials. 2-Bromo-3-methoxy-1,4-naphthoquinone,[2] 2,3-dibromo-1,4-naphthoquinone,[4] 2-acetoxy-3-bromo-1,4-naphthoquinone,[5] 1-(*p*-methylphenyl)-1-phenylethylene,[6] 1-(*p*-methoxyphenyl)-1-phenylethylene,[6] 1-(*p*-chlorophenyl)-1-phenylethylene,[7] and 1-(*p*-bromophenyl)-1-phenylethylene[8] were all synthesized according to the usual method; the physical and spectral data were all compatible with those described in the literature.

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