SYNTHESIS, PHOTOLYSIS, AND REDOX PROPERTIES OF 2-DIALKYLAMINO-3-METHOXY-1,4-NAPHTHOQUINONES

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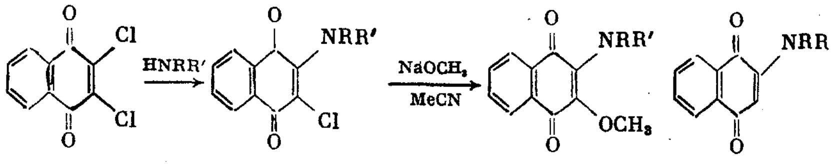
A synthesis is reported for 2-dialkylamino-3-methoxy-1,4-naphthoquinones. The photolysis of these compounds in the liquid phase was studied and their halfwave potentials ($E_{1/2}$) were determined. The introduction of a methoxy group at C^3 leads to a shift in the spectral absorption toward longer wavelengths, shift in $E_{1/2}$ toward positive values, and a slight change in the photolysis quantum yield. The physicochemical parameters were found to be dependent on the nature of the dialkylamino group.

There has been recent interest in silverless photographic film containing light-sensitive organic compounds such as naphthoquinones. Hydroquinones, which are formed upon the photochemical reduction of the corresponding quinones, are capable of reducing noble metal ions and this property is used in light-sensitive materials requiring physical development [1, 2]. The photographic sensitivity of such films depends not only on the quantum yield of the photolysis of the light-sensitive compound but also on its oxidation–reduction potential [2]. 2-Dialkylamino- [1, 3] and 2-alkoxy-1,4-naphthoquinones [3] have been proposed as light-sensitive components. Compounds containing two electron-donor groups hold interest in expanding the range of spectral sensitivity [4]. In the present work, we studied the pathways for the synthesis of 2-dialkylamino-3-methoxy-1,4-naphthoquinones (Ia)-(Ie), investigated their photolysis in the liquid phase, and measured their halfwave potential ($E_{1/2}$). The data obtained were compared with the physicochemical indices of 2-dialkylamino-1,4-naphthoquinones (IIa)-(IId).

In a study of the reaction of 2-chloro-3-methoxy-1,4-naphthoquinone with methylamine and aniline, Chu and Griffiths [4] discovered high nucleophilic mobility of the methoxy group in comparison with the chlorine atom and the corresponding 2-amino-3-methoxynaphthoquinones were obtained by the replacement of a methoxy group in 2,3-dimethoxy-1,4-naphthoquinones. The possibility of synthesizing 2-dialkylamino-3-methoxy-1,4-naphthoquinones (Ia)-(Ie) by this pathway was demonstrated in our laboratory in the case of the reaction of 2,3-dimethoxy-1,4-naphthoquinone and piperidine.

The introduction of an electron-donor group into 2,3-dichloro-1,4-naphthoquinones considerably deactivates the second chlorine atom toward nucleophilic substitution [4, 5]. However, the use of polar aprotic solvents, especially, acetonitrile, has permitted us, in contrast to the standard method using alcohols [4], to obtain (Ia)-(Ie) in good yield (Table 1) through replacement of the chlorine atom by a methoxy group in readily available 2-chloro-3-dialkylamino-1,4-naphthoquinones (IIIa)-(IIIe).



(IIIa—e) (Ia—e) (IIa—e)

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TABLE 1. 2-Dialkylamino-3-methoxy-1,4-naphthoquinones (Ia)-(Ie)

Compound	Reaction time, h	Yield, %	Mp., °C	Found/Calculated, % C	H	N	Chemical formula	IR spectrum, ν, cm^{-1}	Electronic absorption spectrum in ethanol, λ_{max}, nm (log ε)
(Ia)	1	65	92–94	67.68 67,53	5.35 5,63	6,14 6.06	$C_{13}H_{13}NO_3$	2955, 2830 (CH_3), 1675, 1650 (C=O), 1240 (OCH_3)	241 (4,20), 287 (4,27), 518 (3,64)
(Ib)	2,5	72	89–91	66,27 66,34	5.36 5,48	4.95 5,12	$C_{15}H_{15}NO_4$	2920, 2860 (CH_2), 1670, 1640 (C=O), 1250 (OCH_3)	240 (4,19), 285 (4,23), 500 (3,52)
(Ic)	3	70	82–84	71.15 70,85	6,39 6,27	5.16 5,16	$C_{16}H_{17}NO_3$	2940d, 2865 (CH_3, CH_2), 1675, 1645 (C=O), 1245 (OCH_3)	242 (4,22), 290 (4,26), 527 (3,64)
(Id)	1	66	158–160				$C_{15}H_{16}N_2O_3$ *	3450 (NH), 2960, 2855 (CH_2), 1675 (C=O), 1260 (OCH_3)	241 (3,94), 285 (4,01), 506 (3,32)
(Ie)	1	95	120–122	70,02 70,20	5.46 5,36	7.35 7,44	$C_{22}H_{20}N_2O_4$	2940, 2865 (CH_2), 1670–1640 br. (C=O), 1256 (OCH_3)	240 (4,29), 283 (4,27), 502 (3,53)

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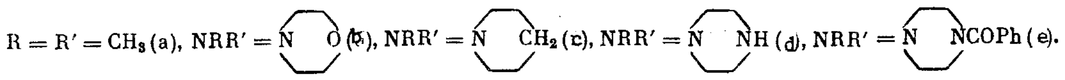
*Found: M 272.1150. Calculated: M 272.1161.



1,4-Naphthoquinones (Ia)-(Ie) with two electron-donor (+M) groups (NRR' and OMe) in the quinone ring are characterized by a bathochromic shift of the long-wavelength maximum in the electronic absorption spectrum by 40-60 nm in comparison with 2-dialkylamino-1,4-naphthoquinones (IIa)-(IIe) (Tables 2 and 3).

1,4-Naphthoquinones (Ia)-(Ie) undergo photolysis in hexane, toluene, and acetonitrile with the retention of all the isosbestic points until the completion of the photolysis and formation of a colorless form, which, as in the photolysis of 2-dialkylaminonaphthoquinones [6, 7], in all likelihood, is a naphthoxazole derivative. The photolysis of 2-dimethylamino-(Ia) and 2-piperidino-3-methoxy-1,4-naphthoquinones (Id) in 2-propanol features a hypsochromic shift in the long-wavelength absorption band and breakdown in isosbesticity. This behavior is probably related to the low stability of the photolysis product. The dielectric properties of the medium have the major effect on the quantum yield. The greatest quantum yield for (Ia)-(Ie) is found in hexane and decreases with increasing solvent polarity (Table 2), indicating an intramolecular course for the photolysis reaction [7]. Comparison of the results of the photolyses of 2-dialkylamino-3-methoxy-1,4-naphthoquinones with those for 2-dialkylamino-1,4-naphthoquinones (IIa)-(IId) shows only a slight effect of the methoxy group on the quantum yield (Tables 2 and 3).

The photographic sensitivity of the films is related to the polarographic halfwave potential ($E_{\frac{1}{2}}$) of (Ia)-(Ie) and (IIa)-(IIc). The data in Table 4 show that the compounds containing two electron-donor groups are irreversibly reduced using two electrons (the wave slope $\beta \geq 0.04$). Substituents displaying +I and +M effects shift $E_{\frac{1}{2}}$ for the reduction of 1,4-naphthoquinones toward more negative values. Substituents displaying –I and –M effects

TABLE 2. Quantum Yields in the Photodecomposition of 2-Dialkylamino-3-methoxy-1,4-naphthoquinones

Solvent	(Ia)			(Ib)			(I c)			(I d)			(I e)		
	φ*	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$
Hexane	0,44	500	0,33	0,24	500	0,32	0,25	507	0,35				0,11	494	0,43
Toluene	0,145	510	0,33	0,061	510	0,32	0,056	520	0,36	0,015	510	0,32	0,073	500	0,32
2-Propanol	0,050	518	0,45	0,027	507	0,35	0,034	520	0,34	0,012	516	0,35	0,020	490	0,39
Acetonitrile	0,007	510	0,43	0,003	505	0,40	0,002	520	0,40	0,002	520	0,29	0,004	496	0,38

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*φ is the quantum yield and ε is the extinction in the visible region at the absorption maximum.

TABLE 3. Quantum Yields for the Photodecomposition of 2-Dialkylamino-1,4-naphthoquinones

Solvent	(IIa)			(II b)			(II c)			(II d)		
	φ	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$	φ	λ_{max}	$\varepsilon\cdot10^4$
Toluene	0,096	464	0,35	0,065	453	0,30	0,089	465	0,32	0,017	472	0,33
2-Propanol	0,038	467	0,41	0,023	460	0,41	0,040	473	0,41	0,013	486	0,40

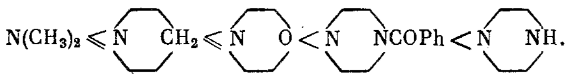
TABLE 4. Polarographic Parameters of 2-Dialkylamino-3-X-1,4-naphthoquinones in 75% Ethanol ($\Delta E_{1/2} = E_{1/2} - E_{1/2}(H)$)

Compound	X	$E_{1/2}$, mV	β	$\Delta E_{1/2}$,	Compound	X	$E_{1/2}$, mV	β	$\Delta E_{1/2}$
(Ia)	OCH_3	−252	0,088	−132	(IIa)	H	−313	0,034	−193
(Ib)	OCH_3	−231	0,046	−111	(IIb)	H	−250	0,043	−130
(Ic)	OCH_3	−243	0,066	−123	(IIc)	H	−268	0,044	−148
(Id)	OCH_3	−201	0,069	−80	1,4-naphthoquinone*		−120	0,032	0
(Ie)	OCH_3	−229	0,038	−109					

*$E_{1/2}$ = −124 mV [8].

have the opposite effect. OCH_3 groups display both a +M effect and slight −I effect. The $E_{1/2}$ values of all the compounds studied are strongly shifted toward negative potentials in comparison with unsubstituted 1,4-naphthoquinones due to the action of the +M effect of the amino group. According to Vladimirtsev and Stromberg [8], the introduction of a methoxy group at C^2 in naphthoquinone leads to a cathodic shift of $E_{1/2}$ by −125 mV. If the effects of the substituents were additive, the $E_{1/2}$ values of (Ia)-(Ic) would be even more negative than for compounds (IIa)-(IIc). However, the $E_{1/2}$ values of these compounds are shifted toward positive potentials. There is apparently steric hindrance to the action of the +M effect of both substituents. This may result in increased significance of the −I effect of the OCH_3 group, leading to a shift in $E_{1/2}$ toward positive potentials.

The $E_{1/2}$ values for both 2-dialkylamino-1,4-naphthoquinones (II) without a substituent at C^3 and 2-dialkylamino-3-methoxy-1,4-naphthoquinones (I) increase in the following series depending on the nature of the dialkylamino group:



The photolysis quantum yields of dialkylaminonaphthoquinones (I) and (II) increase in the same series with one exception.

Furthermore, the introduction of a methoxy group at C^3 of 2-dialkylamino-1,4-naphthoquinones leads to a shift in the spectral sensitivity toward longer wavelengths, a shift in the halfwave potential toward positive values, and slight shift in the photolysis quantum yield. These results may be used in evaluating the effect of various factors on the photographic properties of films containing dialkylaminonaphthoquinones as the light-sensitive component.

EXPERIMENTAL

The IR spectra were taken on UR-20 spectrometer in KBr pellets, while the electronic absorption spectra were taken on a Specord UV-VIS spectrophotometer in ethanol. The molecular mass and elemental composition of (Id) were determined using the mass of the molecular ion on a Finnigan MAT 8200 mass spectrometer. The thin-layer chromatography was carried out on Silufol plates using chloroform as the eluent.

2-Chloro-3-dialkylamino-1,4-naphthoquinones (IIIa)-(IIIe) were obtained by the reaction of 2,3-dichloronaphthoquinone with the corresponding amines in ethanol according to reported procedures: (IIIa) was obtained according to a standard procedure [9], morpholino and piperdino derivatives (IIIb) and (IIIc) were obtained according to Acharya [10], while piperazino derivatives (IIId) and (IIIe) were obtained according to our procedure [11].

Quartz cells with different pathlengths were used to study the photolysis of the naphthoquinones in the liquid phase. The solutions were irradiated with monochromatic light at 436 nm from a DRSh-250 mercury lamp in the air. In order to separate out the monochromatic light beam, ZhS-12 and SS-15 light filters were used. The light intensity was determined by a standard procedure using a ferric oxalate actinometer [12]. The relative error was 10%. The purification of the samples of hexane and 2-propanol were carried out according to standard methods [13], while the purification of acetonitrile was carried out according to O'Donnell [14]. Analytical grade toluene was used.

The polarograms were taken on a PU-1 polarograph using a three-electrode scheme. A mercury dropping electrode served as the cathode (m = 2.71 mg/sec, t = 3-5 sec), while a platinum wire served as the anode. A saturated silver chloride electrode separated from the solution studied by an agar-agar salt bridge served as the reference electrode. We used $5 \cdot 10^{-4}$ M solutions of the naphthoquinones in 75% ethanol containing 0.1 M acetic acid and 0.1 M sodium acetate as the inert electrolyte with buffer pH 6.7 (measured on an ÉV-74 universal pH-meter equipped with a glass electrode). Rectified grade ethanol was initially distilled. The acetic acid sample was purified by freezing. High-purity sodium acetate was used. Oxygen was removed from the polarographic solution by flushing with argon for 30 min. The solution resistance was about 7000 Ω.

A curve for each component was plotted for log (i/(I – i)) vs. E, where E is the potential of the mercury dropping electrode, i is the current through the cell at potential E, and I is the limiting current of the polarographic wave. The values of $E_{1/2}$ and the wave slope β were determined from the curves obtained.

Synthesis of 2-Dialkyl- and 2-Cycloalkylamino-3-methoxy-1,4-naphthoquinones (Ia)-(Ie). A sample of 16 ml 1 M MeONa was added to a suspension or solution of 10 mmoles (IIIa)-(IIIe) in 80 ml acetonitrile and stirred at ~20°C until the starting compound disappeared. The reaction mixture was poured into water, acidified with dilute hydrochloric acid to pH 6-7, extracted with petroleum ether,and concentrated in vacuum. Product (Id) was recrystallized from ethanol, while the other products were recrystallized from petroleum ether. The retention times, yields, and physical indices of (Ia)-(Ie) are given in Table 1.

2-Methoxy-3-piperidino-1,4-naphthoquinones (Ic). A sample of 0.38 g 2,3-dimethoxy-1,4-naphthoquinone was added with stirring in portions to a solution of 2.6 ml piperidine in 30 ml ethanol over 5 min. After 4 h, the solvent was evaporated in vacuum and the residue was recrystallized from petroleum ether to give 0.28 g (60%) (Ic).

A sample of 8 ml 1 M MeONa was added to a mixture of 1.38 g (5 mmoles) (IIIc) in 40 ml methanol and stirred for 12 h at 50°C. The solvent was evaporated in vacuum and the residue was subjected to chromatography on a silica gel column using benzene as the eluent. The product yield was 0.51 g (40%).

A sample of 1.5 ml 1 M MeONa was added to a solution of 1 mmole (IIIc) in 10 ml DMSO and maintained at 20°C for 30 min. The reaction mixture was poured into water and acidified with dilute hydrochloric acid to pH 6-7. The precipitate formed was filtered off, washed with water, and dried to give 0.11 g (41%) (Ic). An additional 0.09 g (30%) was extracted by chloroform from the filtrate. The total yield of (Ic) was 71%.

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AZO COUPLING OF 5(6)-HYDROXYBENZIMIDAZOLE AND ITS DERIVATIVES

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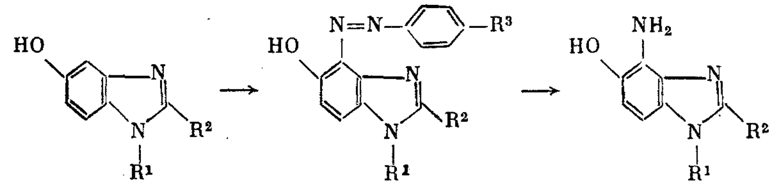
The azo coupling of 5(6)-hydroxybenzimidazole and its derivatives is directed toward C^4.

In a continuation of a study of the reactivity of 5(6)-hydroxybenzimidazole (I) and its derivatives [1-3], we investigated one of the classical examples of electrophilic substitution in aromatic compounds, namely, azo coupling, in which the aryldiazonium cation $\mathrm{Ar}-\overset{+}{N}\equiv N \leftrightarrow \mathrm{Ar}-N-\overset{+}{N}$. serves as the electrophile. The azo coupling of (I), 2-methyl-5(6)-hydroxybenzimdazole (II), and 1-ethyl-2-methyl-5(6)-hydroxybenzimidazole (III) was studied using diazonium salts of different reactivity prepared from aniline, p-nitroaniline, and p-sulfoaniline. The azo coupling was carried out in alkaline media using conditions similar to those described for 3-hydroxypyridine and its derivatives [4].



(I)—(III) (IV)—(VI) (VII)—(IX)

$R^1 = R^2 = H$ (I), (IV), (VII); $R^1 = H$, $R^2 = CH_3$ (II), (V), (VIII); $R^1 = C_2H_5$, $R^2 = CH_3$ (III), (VI), (IX); $R^3 = H$ (a), NO_2 (b), SO_3H (c).

The azo coupling of (I) with the phenyldiazonium cation proceeds quantitatively, while (III) gives traces of several colored side products although the yield of the major product (VIa) is rather high. Under these conditions, (II) reacts with a lower yield of major product (Va).

The azo coupling with the p-nitrophenyldiazonium cation confirms an increase in reactivity in electrophilic reactions in the 5(6)-hydroxybenzimidazole series in the following order: (II) < (I) < (III) [2]. The reaction proceeds virtually without side products, especially in the case of (III).

The azo coupling of (I)-(III) with the p-sulfophenyldiazonium cation proceeds with higher yields than with the p-nitrophenyldiazonium cation and with greater selectivity than with the phenyldiazonium cation although it gives a lower yield of the final product than with the phenyldiazonium cation.

The azo coupling was directed toward C^4 of the benzimidazole system. The 4,6-bisazo product could not be obtained (Table 1).

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