# ORGANIC PHOTOCHEMICAL REACTIONS—III<sup>1</sup> CONVERSION OF 2-(N-SUBSTITUTED ANILINO)-1,4-NAPHTHOQUINONES INTO 5-BENZO[c]PHENOXAZONE DERIVATIVES

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Abstract—Irradiation of 2-(N-methylanilino)-1,4-naphthoquinone (Ia) in methanol using high pressure mercury arc lamp with Pyrex filter afforded 7-methyl-12a-hydroxy- and 7-methyl-12a-methoxy-5benzo[c]phenoxazones (IIa and IIIa). The reaction proceeded also in THF-H<sub>2</sub>O or THF-MeOH and yielded IIa. This reaction was extended to 2-(N-ethylanilino)-, 2-(N-hydroxyethylanilino)-, 2-(1',2',3',4'tetrahydroquinolyl)-, 2-(N-methyl-*m*- and *p*-anisidino)-1,4-naphthoquinones (Ic, Id, VII, XIa and XIb, which underwent similar conversion into the corresponding benzo[c]phenoxazone derivatives (IIc, IId, VIII, XIIa and XIIIa, and XIIb and XIIIb, respectively).

A possible mechanism for the formation of the products is presented.

1,4-NAPHTHOQUINONES are known to undergo dimerization<sup>2</sup> and addition to olefins under UV irradiation.

We now wish to report a photoinduced intramolecular cyclization of the quinone carbonyl and phenyl nucleus of 2-(N-methylanilino)-1,4-naphthoquinone<sup>4</sup> (Ia) and its analogs (Ic, Id, VII and XIa, b) in hydroxylic solvents.

The photolysis of Ia in methanol using high pressure mercury arc lamp through Pyrex glass gave two compounds: IIa,  $C_{17}H_{13}NO_3$  (29.7%) and IIIa,  $C_{18}H_{15}NO_3$ (4.9%) and the starting material was recovered in 38.5% yield. The same products (IIa; 33.7% and IIIa; 9.0%) were also obtained from the solution of Ia left in the sunlight. The product IIa is stable to reflux or irradiation in methanol. Its IR spectrum showed an OH band at 3060 cm<sup>-1</sup>, besides a CO band, although that of IIIa lacked an OH band. The UV absorption spectra of IIa and IIIa closely resemble each other (Fig. 1). The NMR spectrum of IIa in d<sup>6</sup>-DMSO showed aromatic (8H, 2.1-3.0  $\tau$ ), OH (1H, 2.27  $\tau$ , singlet, disappeared upon addition of D<sub>2</sub>O), olefinic (1H, 4.29  $\tau$ , singlet) and N-Me (3H, 6.57  $\tau$ ) proton signals, and that of IIIa in CDCl<sub>3</sub> showed aromatic (8H, 2.0-3.0  $\tau$ , olefinic (1H, 4.20  $\tau$ , singlet), N-Me (3H, 6.57  $\tau$ ) and O-Me (3H, 7.03  $\tau$ ) proton signals.

Treatment of IIa with methanolic hydrogen chloride or acetic acid gave IIIa, which was reconverted to IIa in good yield by the action of aqueous acetic acid. Treatment of IIa with acetic anhydride in pyridine gave a monoacetate (IV), which was converted to IIa on passage through a basic alumina column. The UV absorption spectrum of IV is similar to that of Ia (Fig. 1). From these spectral data and chemical evidences, the structures 7-methyl-12a-hydroxy-5-benzo[c]phenoxazone, 7-methyl-12a-methoxy-5-benzo[c]phenoxazone and 2-(N-methyl-2'-acetoxyanilino)-1,4-naphthoquinone were assigned to IIa, IIIa and IV respectively. The compound IIa was proved to be identical with an unequivocal specimen prepared from Nmethyl-o-aminophenol and 1,4-naphthoquinone by the method of Butenandt.<sup>4</sup>





TABLE 1. PHOTOLYSIS OF IA IN VARIOUS SOLVENTS

Solvent"	IIa, %	Recovery, %
THF		74-0
THF-H <sub>2</sub> O (15:1)	35.7	24.5
THF-MeOH (15:1)	18-1	<b>48</b> ·0
THF-H <sub>2</sub> O (15:0-05)	2.9	7 <del>6</del> ·5

\* 0.25% soln of Ia.

This photoinduced reaction of Ia also occurred in THF-MeOH (15:1) or THF-H<sub>2</sub>O (15:1) to yield IIa, but no IIIa could be detected in the photolysis mixture (as shown in Table 1). From these experiments, the following mechanism appears reasonable for the formation of IIa and IIIa from Ia. The reaction probably proceeds through the interaction of nonbonding oxygen orbital with the  $\pi$ -electron of the aromatic nucleus in excited state leading to transition state A, which affords intermediate B or C by addition of H<sub>2</sub>O or CH<sub>3</sub>OH, respectively. Elimination of H<sub>2</sub> or CH<sub>4</sub> from the intermediate B or C in aromatization process leads to IIa. The product IIIa would arise from methanolysis of IIa in the presence of an organic acid produced in the photolytic process.<sup>†</sup>

<sup>†</sup>After irradiation of Ia in MeOH or THF-H<sub>2</sub>O, the solvent was removed and the aqueous extract of the residue showed acidity (pH 4.5-5.3).

An analogous interaction between CO and isolated aromatic nucleus has been suggested in the photolytic cyclization of benzoin acetate and its derivatives into 2-phenylbenzofuran derivatives.<sup>5</sup>



We have further studied photoreactions of several analogous naphthoquinone derivatives (Ib,<sup>6</sup> Ic,<sup>7</sup> Id, VI, VII, Xa,  $b^8$  and XIa, b) under similar conditions and the products (except the last two cases) are listed in Table 2.

Starting material	Phenoxazone (%)	Cleavage product (%)	Recovery (%)
IÞ6			92.6
Ic <sup>7</sup>	IIc (26·5)	Ib <sup>6</sup> (3·8), Vb <sup>6</sup> (0·7)	1.5
Id	IId (2·8)	Ib <sup>6</sup> (15-9)	28.7
VI			86-0
VII	VIII (2·5)		79-8
Xa <sup>8</sup>		Va <sup>6</sup> (22·9)	
ХЬ		Va <sup>6</sup> (57·4), Vc <sup>13</sup> (0·3)	

The product obtained from 2-(N-ethylanilino)-1,4-naphthoquinone (Ic) was similarly assigned the structure of 7-ethyl-12a-hydroxy-5-benzo[c]phenoxazone (IIc) by its analytical and spectral data.

Irradiation of 2-(N-hydroxyethylanilino)-1,4-naphthoquinone (Id), which was

synthesized from N-hydroxyethylaniline<sup>9</sup> and 1,4-naphthoquinone in usual method, was carried out to study if intramolecular photoinduced addition of the alcohol group can occur. Id afforded Ib and 7-hydroxylethyl-12a-hydroxy-5-benzo[c]phenoxazone (IId) upon irradiation in dry THF. The structure of IId was assigned on the basis of the elemental analysis and spectral data. The formation of Ib and IId from Id can be explained as occurring from initial photocleavage of the N—C bond of Id into Ib and ethanol followed by photoreaction of Id and ethanol. No product apparently resulting from intramolecular addition of the alcohol group could be detected in the photolytic mixture.

Irradiation of 2-indolinyl-1,4-naphthoquinone (VI) resulted in recovery, but 2-(1',2',3',4'-tetrahydroquinolyl)-1,4-naphthoquinone (VII) gave an expected hydroxyl compound (VIII) although in low yield. The difference in the reactivity of VI and VII can be attributed to nonbonding interaction between the CO and phenylnucleus, because the latter is sterically more favorable than the former for such an interaction.

The structure of VIII was determined by the following evidences. VIII was converted to a methoxyl compound (IX) with methanolic hydrogen chloride for characterization. The UV absorption spectra of VIII and IX were similar to that of IIa, IIb or IIIa. The NMR spectrum of VIII in d°-DMSO showed aromatic (7H,  $1\cdot8-3\cdot3\tau$ ), OH (1H,  $2\cdot29\tau$ , singlet, disappeared upon addition of D<sub>2</sub>O), olefinic (1H,  $4\cdot37\tau$ , singlet), N-methylene (2H,  $6\cdot30\tau$ , multiplet), benzylic (2H,  $7\cdot17\tau$ , multiplet) and C-methylene (2H,  $7\cdot95\tau$ , multiplet) proton signals, and IX in CDCl<sub>3</sub> showed aromatic (7H,  $1\cdot8-3\cdot3\tau$ ), OMe (3H,  $7\cdot02\tau$ ) and methylene proton signals and lacked OH proton signal. From these facts, together with elemental analysis, the structures 7,8-trimethylene-12a-hydroxy- and -12a-methoxy-5-benzo[c]phenoxazones were assigned to VIII and IX, respectively.

Photoreactions of 2-dimethylamino-<sup>8</sup> and 2-benzylmethylamino-1,4-naphthoquinones (Xa and Xb) resulted in dealkylation. The mechanism of these N—C bond cleavage on photolysis seems not clear.<sup>10</sup>

2-(N-methyl-m-anisidino)- and 2-(N-methyl-p-anisidino)-1,4-naphthoquinones (XIa and b) were synthesized from the corresponding N-methylanisidine<sup>11,12</sup> and 1,4-naphthoguinone in usual method. The quinone XIa, when irradiated in methanol under similar conditions as in Ia, afforded expected hydroxyl compound XIIa 37.9 %), methoxyl compound XIIIa (6.8 %) and recovery (0.4 %), whereas XIb afforded only 3.4% of expected hydroxyl compound XIIb and recovery (76.7%). Prolonged irradiation of XIb in methanol gave 17.4% of XIIb and 1.2% of XIIb. The structures of these compounds were confirmed by the following spectra data and elemental analyses. The UV absorption spectra of XIIa, b and XIIIa, b were similar to that of IIa or IIIa. In the NMR spectrum of XIIIa in CDCl<sub>3</sub>, H<sub>a</sub> proton appeared as a doubling doublets at 2.95  $\tau$  ( $J_{ab} = 8.0$  c/s, or the coupling;  $J_{ac} = 1.0$  c/s, para coupling); H<sub>b</sub> proton, as doubling doublets at 3.46  $\tau$  ( $J_{ab} = 8.0$  c/s, ortho coupling;  $J_{bc} = 2.5$  c/s, meta coupling) and H<sub>e</sub> proton as almost singlet at 3.39  $\tau$  due to the small coupling constant of meta  $(J_{bc})$  and para  $(J_{ac})$  coupling. Accordingly, the structures 7-methyl-9methoxy-12a-hydroxy-, 7-methyl-10-methoxy-12a-hydroxy-5-benzo[c]phenoxazones and their 12a-methoxy compounds were assigned to XIIa, b and XIIIa, b, respectively.

The observed substituent effect in the reaction of XIa and XIb may be explained by a mechanism involving attack of  $n-\pi^*$  excited carbonyl oxygen having cation character to the *para* or *meta* position of each OMe group. The *para* position of the OMe group in XIa is more susceptable to the attack than the *meta* position of the same group in XIb. Similar substituent effect was also observed in photolytic cyclization of 3,3'-dimethoxybenzoin acetate<sup>5</sup> to benzofuran derivatives.

# EXPERIMENTAL

All m.ps are uncorrected. The light source for the photolysis was a high pressure Hg arc lamp with Pyrex filter. During irradiation a steady stream of argon was bubbled through the soln. Adequate cooling with water was provided to maintain the soln at room temp. PMR spectra were measured with a Varian Associate Model A-60 instrument, using TMS as an internal standard.

# Irradiation of 2-(N-methylanilino)-1,4-naphthoquinone<sup>4</sup> (Ia) in methanol

(a) A soln of 200 mg (0.76 mmole) of Ia in 80 ml MeOH was irradiated for 2.5 hr. The solvent was evaporated and the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with  $CH_2Cl_2$  gave IIIa (11 mg, 4.9%, m.p. 198–200° after crystallization from isopropylether-MeOH). Repeated recrystallization from MeOH gave yellow prisms, m.p. 200–203°, UV (EtOH): 257 and 386 mµ (log  $\varepsilon$  4.36 and 4.28); IR (Nujol): 1637 cm<sup>-1</sup>. (Found: C, 73.79; H, 5.30; N, 4.86. C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> requires: C, 73.70; H, 5.15; N, 4.78%). The residue from the fraction eluted with  $CH_2Cl_2$ -MeOH (10:1) gave IIa [63 mg, 29.7%, m.p. 205° (dec) after crystallization from  $CH_2Cl_2$ ]. Repeated recrystallization from CHCl<sub>3</sub>-MeOH gave yellow prisms, m.p. 205° (dec) (lit., <sup>4</sup> m.p. 198°), UV (EtOH): 256 and 385 mµ (log  $\varepsilon$  4.36 and 4.29); IR (Nujol): 3060 cm<sup>-1</sup> and 1615 cm<sup>-1</sup>. (Found: C, 72.52; H, 4.79; N, 4.92. Calc. for  $C_{1.7}H_{1.3}NO_3$ ; C, 73.11; H, 4.69; N, 5.02%). This material was identical with the sample prepared by the method of Butenandt.<sup>4</sup>

(b) A soln of 300 mg (1.14 mmole) of Ia in 80 ml MeOH was exposed for 100 hr to sunlight. The reaction mixture was treated in the same way as described above. 107 mg (33.7%) if IIa and 30 mg (9.0%) of IIIa were obtained.

(c) The photoreaction of Ia (0.76 mmole) was carried out in THF, THF-H<sub>2</sub>O, and THF-MeOH and the results are shown in Table 1.

#### 7-methyl-12a-methoxy-5-benzo[c]phenoxazone (IIIa)

(a) A soln of 200 mg of IIa in 20 ml MeOH and 1 drop of conc HCl was refluxed for 5 min. After evaporation of MeOH, the residue was recrystallized from MeOH to give 140 mg of yellow prisms, m.p. 194-196°. Repeated recrystallization from MeOH gave yellow prisms, m.p. 200-203°. This was identified with IIIa derived from Ia by comparison of their IR spectra. The mother liquor was chromatographed on neutral alumina (activity IV) and the residue from the fraction eluted with CH<sub>2</sub>Cl<sub>2</sub> gave 32 mg yellow prisms, m.p. 195-196°. Repeated recrystallization from MeOH gave yellow prisms, m.p. 200-203°. This was identified with IIIa derived from Ia by comparison of their IR spectra.

(b) A soln of 100 mg of IIa in 10 ml MeOH and 0-1 ml glacial AcOH was refluxed for 30 min. After evaporation of MeOH, the residue was washed with  $CH_2Cl_2$ . The starting material (75 mg, 75.0%) was recovered. The mother liquor was chromatographed on neutral alumina (activity IV) and the residue from the fraction eluted with  $CH_2Cl_2$  gave IIIa (2 mg, 1.9%, after recrystallization from MeOH). This was identified with IIIa derived from Ia by comparison of their IR spectra.

# Hydrolysis of 7-methyl-12a-methoxy-5-benzo[c]phenoxazone (IIIa)

A soln of 70 mg of IIIa in 80% aq AcOH was heated on a water bath for 15 min. After evaporation of the solvent, the residue was recrystallized from  $CHCl_3$  to give yellow prisms, m.p. 205° (dec), yield, 24 mg. This was identified with IIa derived from Ia by comparison of their IR spectra.

# Treatment of 7-methyl-12a-hydroxy-5-benzo[c]phenoxazone (IIa) with acetic anhydride-pyridine

A soln of 300 mg of IIa in 10 ml pyridine and 5 ml acetic anhydride was heated at 70° for 30 min. After evaporation of the solvent, the residue was diluted with water, and extracted with ether. The extract was washed successively with dil HCl, dil NaOH and water then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was chromatographed on neutral alumina (activity IV). The fraction eluted with benzene and benzene-CH<sub>2</sub>Cl<sub>2</sub> (10 1) gave IV as orange red scales (145 mg, m.p. 98–99° after recrystallization from MeOH), UV (EtOH): 275 and 453 mµ (log  $\varepsilon$  4:40 and 3:64); IR (Nujol): 1768 cm<sup>-1</sup>, 1682 cm<sup>-1</sup> and 1635 cm<sup>-1</sup>. (Found: C, 69.96; H, 4.90; N, 4.36.  $C_{19}H_{15}NO_4$  requires: C, 71.02; H, 4.71; N, 4.36%). The residue from the fraction eluted with  $CH_2Cl_2$ -MeOH (10:1) gave starting material IIa (58 mg).

### Irradiation of 2-anilino-1,4-naphthoquinone<sup>6</sup> (Ib)

A soln of 500 mg of Ib in 600 ml MeOH was irradiated for 15 hr. After evaporation, the starting material (463 mg) was recovered.

# Irradiation of 2-(N-ethylanilino)-1,4-naphthoquinone<sup>7</sup> (Ic)

A soln of 200 mg (0.72 mmole) of Ic in 75 ml THF and 5 ml water was irradiated for 2.5 hr. The solvent was evaporated to dryness, and the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with benzene was chromatographed on preparative thin-layer plates to give Ib<sup>6</sup> (7 mg, 3.8%), recovery (3 mg, 1.5%) and Vb<sup>6</sup> (1 mg, 0.7%). These compounds were identified with authentic sample by comparison of their IR spectra. The residue from the fraction eluted with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) gave IIc [59 mg, 26.5%, m.p. 200° (dec) after crystallization from CH<sub>2</sub>Cl<sub>2</sub>]. Repeated recrystallization from CHCl<sub>3</sub> gave yellow prisms, m.p. 200° (dec), UV (EtOH): 257 and 386 mµ (log  $\varepsilon$  4.35 and 4.29); IR (Nujol): 3200 cm<sup>-1</sup> and 1615 cm<sup>-1</sup>. (Found: C, 73.26; H, 5.10; N, 4.79. C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>N requires: C, 73.70; H, 5.15; N, 4.78%).

### 2-Indolinyl-1,4-naphthoquinone (VI)

A mixture of 1.58 g of 1,4-naphthoquinone, 2.30 g of indoline and 100 ml of EtOH was allowed to stand for overnight at room temp.

After evaporation of EtOH, the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with benzene-pet ether (1:1) was recrystallized from MeOH to give violet needles, 1.23 g, m.p. 137-142.5°, UV (EtOH): 283 and 528 mµ (log  $\varepsilon$  4.37 and 3.84); IR (Nujol): 1615 cm<sup>-1</sup> and 1676 cm<sup>-1</sup>. (Found: C, 78.30; H, 4.55; N, 4.86. C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub> requires: C, 78.53; H, 4.76; N, 5.09%).

### Irradiation of 2-indolinyl-1,4-naphthoquinone (VI)

(a) A soln of 200 mg of VI in 80 ml MeOH was irradiated for 4.5 hr. After evaporation of MeOH, the starting material (172 mg) was recovered.

(b) A soln of 200 mg of VI in 75 ml THF and 5 ml water was irradiated for 2.5 hr. After evaporation of MeOH, the starting material (157 mg) was recovered.

#### 2-(1',2',3',4'-Tetrahydroquinolyl)-1,4-naphthoquinone (VII)

A mixture of 6.33 g of 1,4-naphthoquinone, 2.66 g of 1,2,3,4-tetrahydroquinoline and 200 ml MeOH, the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with benzene-pet. ether (1:1) was recrystallized from MeOH to give violet plates, 990 mg (17-0%), m.p. 144-150°, UV (EtOH): 281 and 508 mµ (log  $\varepsilon$  4.25 and 3.72); IR (Nujol): 1675 cm<sup>-1</sup> and 1628 cm<sup>-1</sup>. (Found: C, 78.92; H, 5.50; N, 5.12. C<sub>19</sub>H<sub>15</sub>NO<sub>2</sub> requires: C, 78.87; H, 5.23; N, 4.84%).

#### Irradiation of 2-(1',2',3',4'-tetrahydroquinolyl)-1,4-naphthoquinone (VII)

A soln of 450 mg of VII in 188 ml THF and 12 ml water was irradiated for 2 hr. The solvent was evaporated to dryness, and the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with benzene gave the starting VII (359 mg, 79-8%) after recrystallization from MeOH. The residue from the fraction eluted with  $CH_2Cl_2$ -MeOH (10:1) gave VIII as orange yellow prisms, [12 mg, 2-5%, m.p. 246° (dec) after recrystallization from  $CHCl_3$ -MeOH], UV (EtOH): 258 and 391 mµ (log  $\varepsilon$  4·33 and 4·29); IR (Nujol): 3000 cm<sup>-1</sup> and 1605 cm<sup>-1</sup>. (Found : C, 74-56; H, 5·00; N, 4·53.  $C_{19}H_{13}NO_3$  requires : C, 74·74; H, 4·95; N, 4·59%).

# Treatment of 7,8-trimethylene-12a-hydroxy-5-benzo[c]phenoxazone (VIII) with methanolic hydrogen chloride A soln of 238 mg of VIII in 30 ml MeOH and 1 drop of conc HCl was refluxed for 5 min. After evaporation of MeOH, the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with $CH_2Cl_2$ gave IX as yellow plates, (78 mg, m.p. 156–159° after recrystallization from MeOH), UV (EtOH): 258 and 392 mµ (log $\varepsilon$ 4·33 and 4·29); IR (Nujol): 1640 cm<sup>-1</sup> and 1612 cm<sup>-1</sup>. (Found: C, 74·92; H, 5·50; N, 4·24. $C_{20}H_{17}NO_3$ requires: C, 75·22; H, 5·37; N, 4·39%).

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### Irradiation of 2-dimethylamino-1,4-naphthoquinone<sup>8</sup> (Xa)

A soln of 200 mg (1.05 mmole) of Xa in 80 ml MeOH was irradiated for 4 hr. After evaporation, MeOH was added to the residue to give Va as orange red needles (37 mg, 20.7%), m.p. 243°. This was identified with an authentic sample<sup>6</sup> prepared from 1,4-naphthoquinone and methylamine. The filtrate was chromatographed with preparative thin-layer plates, and gave starting Xa (30 mg, 15.0%) and Va (4 mg, 2.2%) after crystallization from MeOH.

#### Irradiation of 2-(N-benzylmethylamino)-1,4-naphthoquinone (Xb)

A soln of 200 mg (0.72 mmole) of Xb in 80 ml MeOH was irradiated for 1.5 hr. After evaporation,  $CH_2Cl_2$  was added to the residue to give Va<sup>6</sup> as orange red needles (43 mg, 31.4%). The residue from the filtrate was chromatographed on preparative thin-layer plates to give Va (35.5 mg, 26.0%), starting material (2 mg, 1.0%) and Vc<sup>13</sup> (0.5 mg, 0.3%). Va and Vc were identified with sample derived from 1,4-naphthoquinone and methylamine or benzylamine, by comparison of their IR spectra.

### 2-(N-Hydroxyethylanilino)-1,4-naphthoquinone (Id)

A mixture of 9-23 g of 1,4-naphthoquinone, 4 g of N-hydroxyethylaniline<sup>9</sup> and 500 ml MeOH was allowed to stand for 12 days. The product obtained by the similar procedure as in VII (CH<sub>2</sub>Cl<sub>2</sub> elution) was recrystallized from MeOH to orange yellow needles, 900 mg, m.p. 155–157°, UV (EtOH): 238, 276, 359 and 468 mµ (log  $\varepsilon$  4·15, 4·06, 3·96 and 3·29); IR (Nujol): 3000 cm<sup>-1</sup> and 1613 cm<sup>-1</sup>. (Found: C, 73·72; H, 5·27; N, 5·01. C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> requires: C, 73·70; H, 5·15; N, 4·78%).

### Irradiation of 2-(N-hydroxyethylanilino)-1,4-naphthoquinone (Id)

A soln of 200 mg (0.68 mmole) of Id in 80 ml dry THF was irradiated for 2.5 hr. After evaporation of THF, the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with  $CH_2Cl_2$  gave Ib<sup>6</sup> (10 mg, 5.9%) after recrystallization from MeOH. The residue from the mother liquor was chromatographed on preparative thin-layer plates and gave starting Id (37 mg, 28.5%) and Ib (27 mg, 15.9%). The fraction eluted with  $CH_2Cl_2$ -MeOH (7:3) gave IId as yellow prisms [6 mg, 2.8%, m.p. 219° (dec) after recrystallization from MeOH], UV (EtOH): 257 and 385 mµ (log  $\varepsilon$  4.34 and 4.27); IR (Nujol): 3230 cm<sup>-1</sup> and 1615 cm<sup>-1</sup>. (Found: C, 69.70; H, 4.94; N, 4.46.  $C_{18}H_{15}NO_4$  requires: C, 69.89; H, 4.89; N, 4.53%).

#### 2-(N-Methyl-m-anisidino)-1,4-naphthoquinone (XIa)

A mixture of 4.88 g 1,4-naphthoquinone, 2.10 g of N-methyl-m-anisidine,<sup>11</sup> and 200 ml MeOH was allowed to stand for 4 days at room temp. The product obtained by the similar manner as in VII was recrystallized from MeOH to give XIa as red needles, m.p.  $102-103^{\circ}$ , yield, 496 mg, UV (EtOH): 279 and 462 mµ (log  $\varepsilon$  4.37 and 3.69); IR (Nujol): 1632 cm<sup>-1</sup> and 1676 cm<sup>-1</sup>. (Found: C, 73.94; H, 5.45; N, 4.71. C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> requires: C, 73.70; H, 5.15; N, 4.78%).

#### Irradiation of 2-(N-methyl-m-anisidino)-1,4-naphthoquinone (XIa)

A soln of 223 mg (0.76 mmole) of XIa in 80 ml MeOH was irradiated for 2.5 hr. After evaporation of MeOH, the residue was chromatographed on neutral alumina (activity IV). The residue from the fractions eluted with benzene was chromatographed on thin-layer plates, and gave the starting XIa (1 mg, 0.4%) and XIIIa as yellow needles (19 mg, 7.7%, m.p. 192–194° after recrystallization from MeOH), UV (EtOH): 223, 255 and 390 mµ (log  $\varepsilon$  4.52, 4.25 and 4.25); IR (Nujol): 1634 cm<sup>-1</sup> and 1598 cm<sup>-1</sup>. (Found: C, 70.57; H, 5.30; N, 4.25. C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub> requires: C, 70.57; H, 5.30; N, 4.33%). The residue from the fraction eluted with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) gave XIIa (89 mg, 37.9%, m.p. 212–216°, dec). Repeated recrystallization from CHCl<sub>3</sub>-MeOH gave yellow needles, m.p. 218° (dec), UV (EtOH): 223, 253 and 390 mµ (log  $\varepsilon$  4.32, 4.25 and 4.89); IR (Nujol): 3210 cm<sup>-1</sup> and 1616 cm<sup>-1</sup>. (Found: C, 69.32; H, 5.00; N, 4.60. C<sub>18</sub>H<sub>13</sub>NO<sub>4</sub> requires: C, 69.89; H, 4.89; N, 4.53%).

### 2-(N-Methyl-p-anisidiono)-1,4-naphthoquinone (XIb)

A mixture of 7 g of 1,4-naphthoquinone, 3 g of N-methyl-*p*-anisidine<sup>12</sup> and 250 ml MeOH was allowed to stand overnight at room temp. The product obtained by the similar manner as in VII was recrystallized from MeOH to XIb as red needles, m.p. 153–155°, yield, 2.45 g (38.3%), UV (EtOH): 278 and 476 mµ (log e 4.39 and 3.67); IR (Nujol): 1628 cm<sup>-1</sup> and 1680 cm<sup>-1</sup>. (Found: C, 73.76; H, 5.20; N, 4.77. C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub> requires: C, 73.70; H, 5.15; N, 4.78%).

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# Irradiation of 2-(N-methyl-p-anisidino)-1,4-naphthoquinone (XIb)

(a) A soln of 223 mg (0.76 mmole) of XIb in 80 ml MeOH was irradiated for 2.5 hr. After evaporation of MeOH, the residue was chromatographed on neutral alumina (activity IV). The residue from the fraction eluted with benzene gave starting material (170 mg, 76.7%) after washing with ether. The residue from the fraction eluted with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) gave XIIb [8 mg, 3.4%, m.p. 193-195° (dec) after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>], UV (EtOH): 256 and 398 mµ (log  $\epsilon$  4.36 and 4.26); IR (Nujol): 3000 cm<sup>-1</sup>, 1627 cm<sup>-1</sup> and 1614 cm<sup>-1</sup>. (Found: C, 69.01; H, 4.91; N, 4.05. C<sub>18</sub>H<sub>15</sub>NO<sub>4</sub> requires: C, 69.89; H, 4.89; N, 4.53%).

(b) A soln of 1.0 g (3.4 mmole) of XIb in 600 ml MeOH was irradiated for 11 hr. The reaction mixture was treated in the same way as described above. The starting material (540 mg, 54.0%) and XIIb (183 mg, 17.4%) were obtained. The residue from the fraction eluted with  $CH_2Cl_2$  gave XIIIb as yellow prisms (13 mg, 1.2%, m.p. 176.5–178.5° after recrystallization from  $CH_2Cl_2$ -ether), UV (EtOH): 257 and 400 mµ (log  $\varepsilon$  4.36 and 4.27); IR (Nujol): 1632 cm<sup>-1</sup> and 1609 cm<sup>-1</sup>. (Found: C, 70.39; H, 5.43; N, 4.20.  $C_{19}H_{17}NO_4$  requires: C, 70.57; H, 5.30; N, 4.33%).

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