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PHOTO-INDUCED DIMERIZATION OF 1-NAPHTHOXIDE ANION

ELECTRON TRANSFER MECHANISM

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Abstract—Irradiation of sodium 1-naphthoxide in MeOH gave selectively 1,4-dihydro-4',8-dihydroxy-1,1'-binaphthyl **2**. A similar reaction in PhH afforded the regioisomer **5**, along with **6**. Structural proof is presented for these hitherto unknown dimers. The reaction is completely quenched in the presence of naphthalene, a good electron scavenger. This new type of photodimerization was proved to be initiated by intermolecular electron-transfer from the excited 1-naphthoxide anion to the ground state one to give the oxidation–reduction dimers.

One of the characteristic chemical properties of phenols is the facile phenoxy-radical coupling forming C–C or C–O bond.[1] For instance, 1-naphthol is oxidized by $FeCl_3$ to all three possible *ortho* and *para* C–C coupled dimers. However, 1- and 2-naphthols have not undergone any photodimerization, although irradiation of phenol gives all five possible *ortho* and *para* C–C and C–O coupled dimers.[2] Methoxy-, cyano-, and methoxycarbonyl-substituted naphthalenes give cyclodimers formed by 1,4-1,4-coupling.[3]

We have pointed out that on UV irradiation the phenoxide anion ejected an electron in remarkably higher efficiency than the corresponding free phenol and sometimes gave products other than those derived from the neutral species.[4]

As an extension of this work, we now wish to report our finding that irradiation of 1-naphthoxide anion gives a new type of dimer having a 1,4-dihydrobenzene moiety differing from any of the above-mentioned coupling products, and to refer to the elucidation of the mechanism of this unprecedent reaction.[5]

RESULTS

Irradiation of sodium 1-naphthoxide **1a** in MeOH with a high pressure Hg lamp gave the photodimer **2** (conv. 40%; yield 81%), after acidification with AcOH. On being heated to its decomposition point (184°), **2** reverted to 1-naphthol **1b**. Hydrogenation of **2** (1 mole of H_2, PtO_2) gave a tetraline derivative **3**. Dehydrogenation[6] afforded a novel unsymmetrical binaphthol **4a**.

Irradiation of **1a** in benzene–MeOH (12:1) solution gave, after acidification with AcOH, a mixture of photodimers, **5** and **6**, in 16% yield. Separation of **5** and **6** in a ratio of 2:1 was attained by reversed phase liquid chromatography. Dehydrogenation followed by acetylation of **5** afforded an unsymmetrical binaphthol diacetate **7**.

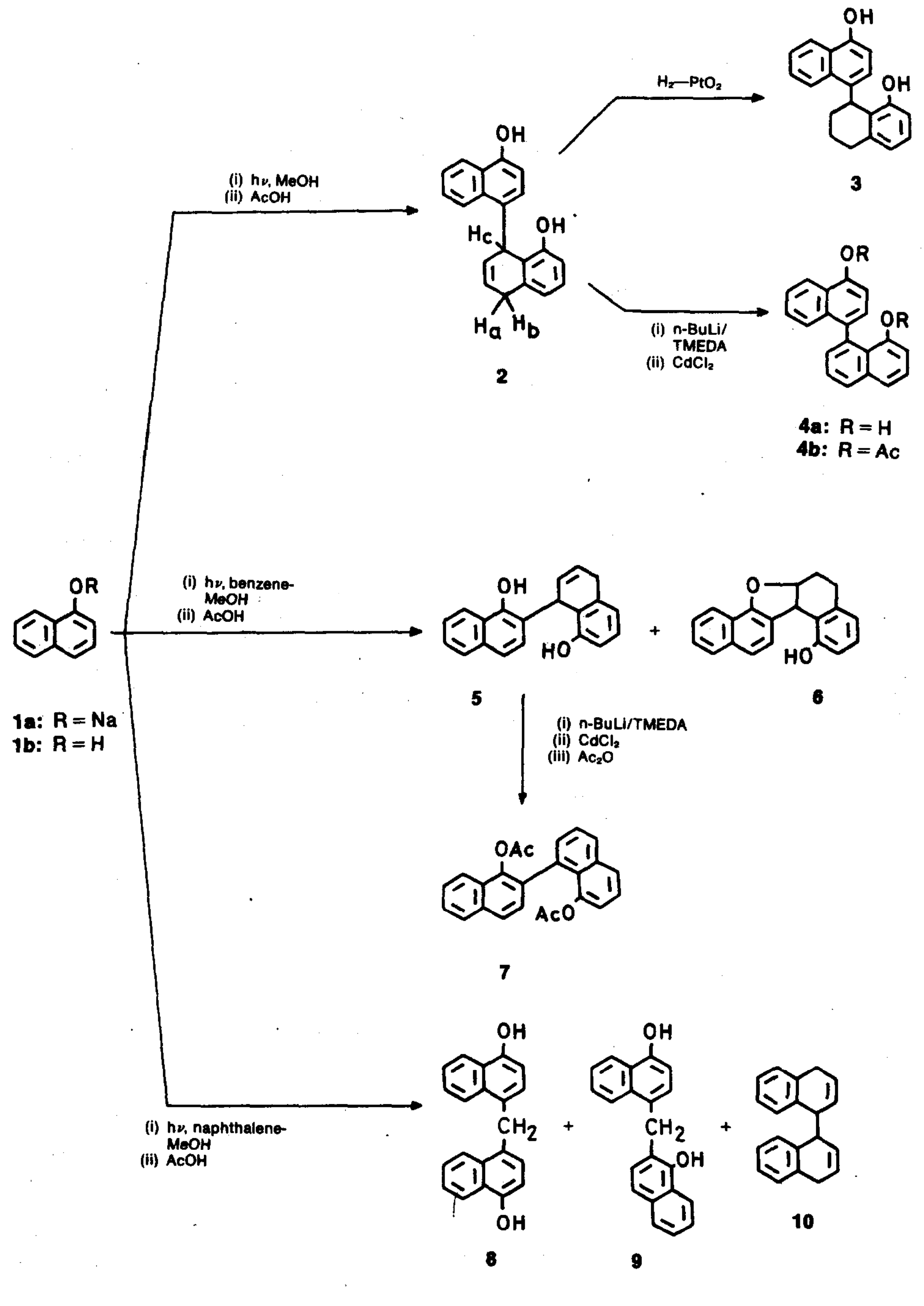
Irradiation of a mixture of **1a** and naphthalene (1:2) in MeOH solution gave the methylene-bridged dimers **8** (9%) and **9** (18%) in addition to tetrahydrobinaphthyl **10**. In this case none of the dimers of **1** such as **2**, **5**, and **6** was isolated.

The structures of new compounds, **2**, **5**, and **6**, were assigned in the following way: ^{13}C NMR spectrum of **2** (Table 1) showed 20 signals, two of which were due to sp^3-carbon. This fact strongly indicates that **2** is formed not by a cycloaddition reaction as discovered in the case of methoxynaphthalene,[3] but by formation of a single bond. The dihydronaphthol structure of **2** was suggested by the multiplicity of the sp^3-carbons and their chemical shifts (CH_2; δ 36.6 and CH; δ 30.2 ppm). Large homoallylic coupling constants in ^1H NMR (J_{ac} and J_{bc} about 4.5 Hz) are compatible with the 1,4-dihydrobenzene structure.[7] Additionally, chemical shifts of H_a and H_b (δ 3.45), and H_c (δ 5.55) are in agreement with the methylene and methine being surrounded by two and three double bonds, respectively.

The coupling position in **2** was elucidated by the ^1H-coupled ^{13}C NMR spectrum of the dehydrogenated product **4a**. Among the long range ^{13}C–^1H coupling constants in aromatic compounds,[8] $^3J_{CH}$ is 7–8 Hz, and $^2J_{CH}$ and $^4J_{CH}$ are at most 2 Hz. Consequently, the detailed analysis of the ^1H-coupled spectrum enables us to discern the number of H atoms on the next neighbouring carbon(s).[9] To our best knowledge this method has not been used to elucidate the structure of an unknown compound, although several reports have mentioned its possibility.[9]

In the fully ^1H-coupled spectrum of **1b** for comparison, the high-field portion of C_2 signals (Fig. 1a), easily assignable on the basis of the chemical shift,[10] appeared as a doublet of doublets ($^3J_{C_2-H_4} = 7.2$ Hz and $^2J_{C_2-H_3} = 2.7$ Hz). In the spectrum of binaphthol **4a**, two corresponding carbons (Fig. 1b) appeared as a broadened doublet ($^3J_{C_2-H_3} = 7.7$ Hz) and a broadened singlet. This fact shows that one of the naphthol moiety has a substituent at the *para*-position to the OH group. In the spectrum of **1b**, C_1 signal (Fig. 1c) appeared at the lowest field as a broadened doublet of doublets (8.2 and 4.0 Hz, $W_{h/2} = 14.7$ Hz) due to the coupling to H_3 and H_8. In the spectrum of **4a**, two signals of C_1 and $C_{1'}$ (Fig. 1d) appeared at the lowest field as a doublet of doublets (7.8 and 2.8 Hz) and a broad multiplet ($W_{h/2} = 17.0$ Hz). The former was simplified to a doublet of 8.7 Hz spacing (Fig. 1e) by an addition of $DCl + D_2O$ (in this case C_2 and C_4 were deuterated), indicating 2.8 Hz to be assignable to $^2J_{C_1-H_2}$. This fact shows that one of the naphthol moiety in **4a** has a substituent at the 8-position.

These observations are compatible with only 4,8'-dihydroxy-bi-1-naphthol **4a** among the possible structures for the binaphthol.



Scheme 1.

The long range J_{C-H} method for determination of the coupling position requires a large machine-time if the amount of the sample is limited. For this reason we have developed a more efficient method. As shown in Table 2, the acetate of **4a** showed a very high field shift (δ 1.12) for one of the two acetyl Me protons in its ^{1}H NMR spectrum. This shift is ascribed to the anisotropy of the *peri*-substituted naphthalene ring, which is strong support for the coupling site not to be at the 5- but 8-position with respect to the 1-OH group. For the sake of comparison, the chemical shifts of the acetyl Me protons for the acetates of three $FeCl_3$ induced coupling products of 1-naphthol,[11] were obtained.

Table 2 shows that the acetyl Me protons of 1-naphthol acetate resonate at δ 1.1 when substituted by an aromatic group at *peri*-position (e.g. **4b**), but at δ 1.9–2.1 when substituted at the *ortho*-position. Aromatic substitution at *para* position causes a small down-field shift. Although very small, a similar trend was found in ^{13}C-chemical shifts of the acetyl Me carbons. This Me proton

Table 1. ^{13}C NMR chemical shifts (ppm)

2		5		6*		3		4a		8		9	
155.2	C	154.6	C	156.5	C	155.7	C	154.7	C	152.6	C	152.8	C
151.9	C	149.3	C	137.6	C	152.1	C	153.6	C	134.0	C	150.0	C
137.5	C	136.9	C	134.5	C	139.9	C	136.6	C	127.8	CH	134.3	C
134.0	C	134.3	C	129.8	CH	134.1	C	136.6	C	126.8	CH	134.0	C
133.1	C	129.9	CH	128.5	CH	133.1	C	134.9	C	126.2	C	129.2	CH
130.3	CH	128.1	CH	128.1	CH	127.2	CH	132.7	C	125.5	C	128.3	CH
127.5	CH	127.8	CH	126.3	CH	127.0	C	129.8	CH	125.0	CH	127.9	C
126.6	CH	127.6	CH	125.5	CH	126.4	CH	128.6	CH	124.6	CH	127.5	CH
126.1	C	127.0	C	122.5	CH	126.4	CH	127.3	CH	123.4	CH	126.8	CH
125.9	C	127.0	C	120.8	CH	125.9	C	127.0	CH	108.3	CH	126.2	C
125.1	CH	126.2	CH	120.0	CH	124.5	CH	126.7	CH	35.1	CH_2	126.2	C
124.6	CH	125.6	CH	113.6	CH	124.2	CH	126.7	CH			126.0	CH
124.2	CH	125.3	CH	66.0	CH	123.5	CH	125.8	CH			125.6	CH
123.2	CH	123.0	CH	39.8	CH_2	120.9	CH	125.3	C			125.0	CH
123.2	CH	121.1	CH	30.5	CH	113.0	CH	125.1	CH			124.7	CH
120.1	CH	120.9	CH	28.4	CH_2	107.8	CH	124.2	C			123.4	CH
113.3	CH	117.5	C			34.3	CH	122.8	CH			122.4	CH
108.7	CH	113.2	CH			30.6	CH_2	120.7	CH			121.6	C
36.6	CH	34.5	CH			30.0	CH_2	111.0	CH			120.4	CH
30.2	CH_2	30.5	CH_2			18.9	CH_2	107.9	CH			108.3	CH
												32.9	CH_2

*Other carbons were not found.

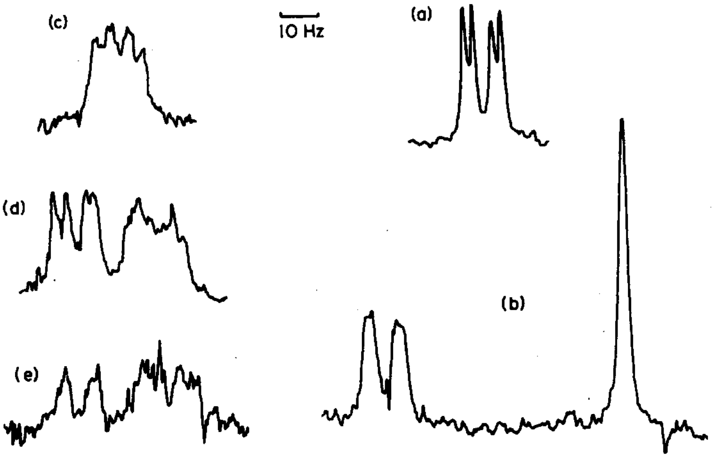


Fig. 1. ^1H-coupled ^{13}C NMR spectra: (a) the high field portion of C_2 signal of **1b** in acetone-d_6; (b) those of C_2 and $C_{2'}$ of **4a** in acetone-d_6; (c) C_1 signals of **1b** in acetone-d_6; (d) C_1 and $C_{1'}$ signals of **4a** in acetone-d_6, and (e) in acetone-d_6 + DCl + D_2O.

shift method elucidated the coupling position of **7**, which was derived from **5** having a 1,4-dihydrobenzene moiety (^{13}C and ^1H NMR).

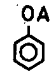
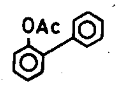
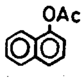
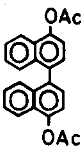
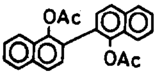
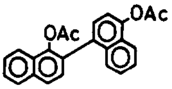
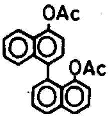
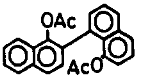
The structure of **6** was determined by ^1H and ^{13}C NMR spectra; the latter (Table 1) showed nine sp^2-CH and four sp^3-carbons, one of which was assigned to be linked to oxygen (δ 66.0).

DISCUSSION

In the presence of naphthalene, the product **10** is well established[12] because of the dimerization of naphthalene anion radical formed by one electron transfer to naphthalene. The other products **8** and **9** are thought to be owing to the reaction of **1a** with formaldehyde, which is derived from MeOH by hydrogen abstraction with the naphthoxy radical. The reaction scheme was confirmed by a nonphotochemical reaction[13] of formaldehyde and **1a** to give **8** and **9** (in the ratio of 7:6).

Since the reported ability of electron capture of naphthalene is higher than that of benzene,[14] based on the assumption of the order of naphthalene > 1-naphthoxide > benzene, the reaction scheme can be best rationalized as intermolecular electron-transfer to give the oxidation-reduction dimer(s) in the following way.

Table 2. Acetyl-methyl shifts (ppm) of acetates in ^{1}H NMR

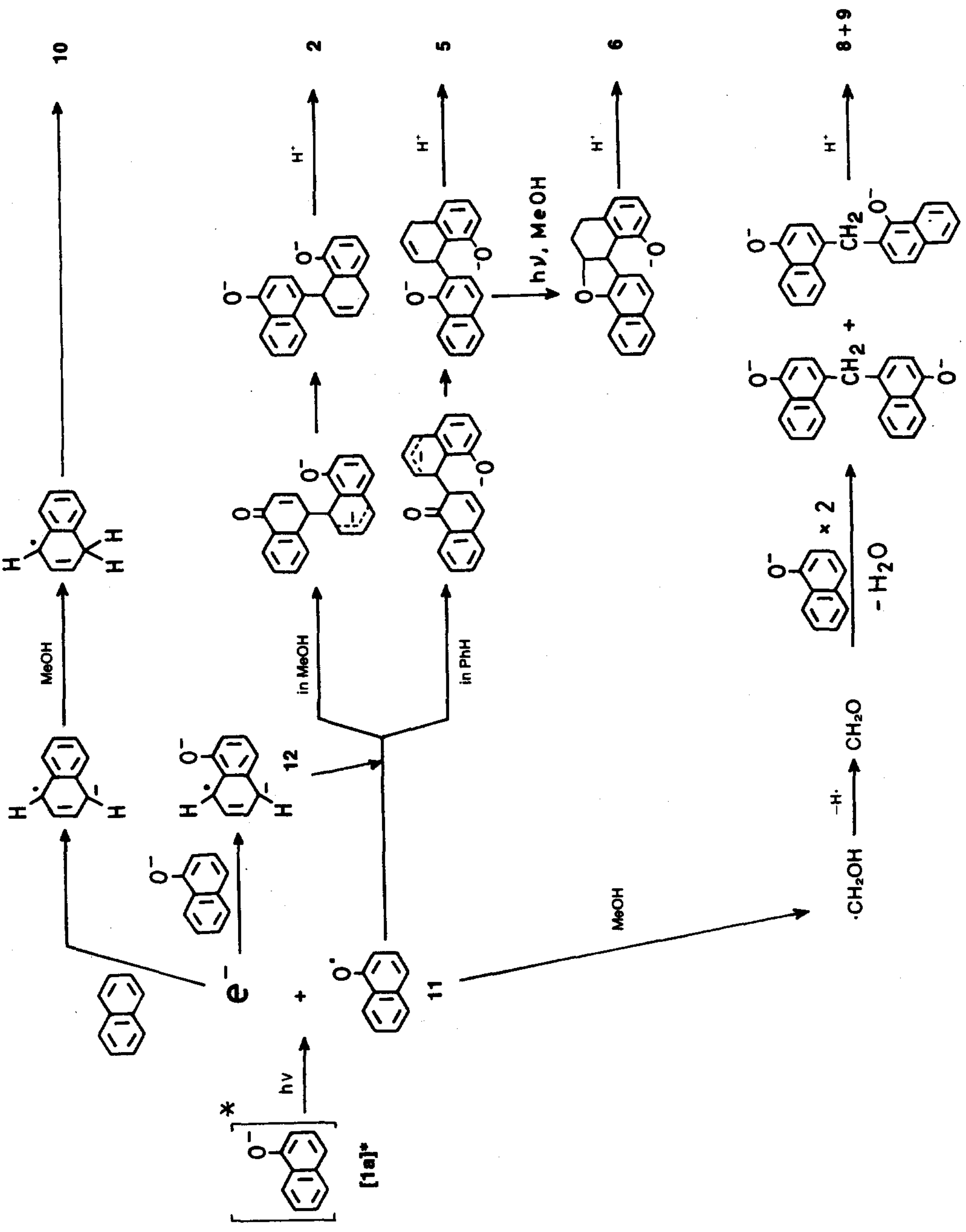
	none	p	o	peri
	2.28			
			2.05	
	2.37			
		2.53		
			2.12	
		2.47	1.88	
 4b		2.51		1.12
 7			1.81	1.02

(i) Irradiation induces the electron ejection from the excited **1a** to give 1-naphthoxide radical **11**. (ii) The electron is captured by a ground-state **1a** to give an anion radical **12** of **1a**.[16] (iii) The final products **2**, **5**, **6** are produced by the coupling of 1-naphthoxy radical **11** with the anion radical **12**. (iv) In the presence of a good electron scavenger (naphthalene),[14] 1-naphthoxy radical **11** solely induces another radical reaction.

Phenoxy radicals are a widely accepted species in the chemistry of phenols, and the coupling reaction of phenoxy radicals has been extensively studied because of their synthetic and biosynthetic importance. On the other hand, the fate of the electron ejected from the excited phenols is hardly elucidated except in only a few cases,[16] although one electron is stoichiometrically necessary for a phenoxy-radical formation and the hydrated electron has been reported to be detected in some cases on spectroscopic grounds.[17] Consequently, this reaction occupies an unique position in the photochemical reaction of a phenol from the standpoint that the ejected electron participates in the main reaction path.

The regiospecificity of the coupling reaction between naphthoxy radical and anion radical is significant. A phenoxy radical gave preferentially *ortho* coupling products.[18] In contrast, $FeCl_3$ promoted coupling of 1-naphthol in water gave the *para-para* dimer as the major product.[11] Our reaction in MeOH gave the *para*-coupled product in regard to the naphthoxy radical. The reaction in benzene gave the *ortho* coupled product, but the ratio of benzene-MeOH seems to be critical, since the ratio of 6:1 produced only the *para*-coupled product **2**. No satisfactory explanation can be offered with regard to the position where the observed solvent effect operates in the reaction steps.[19]

The naphthoxide anion would receive an electron apart


[1a]*
hν
e⁻
+
11
12
10
2
5
6
8+9
MeOH
in MeOH
in PhH
H⁺
hν, MeOH
·CH₂OH
-H·
CH₂O
× 2
- H₂O

Scheme 2.

from the pre-residing anionic charge and this makes the coupling position in regard to the anion radical regiospecifically at the 8-position. A comparable phenomenon has been observed in the Birch reduction of 1-naphthol to give exclusively 5,8-dihydro-1-naphthol.[20]

The formation of **6** occurs presumably via electron transfer from the naphthoxide moiety in **5** to the allylic double bond, followed by protonation and subsequent intramolecular radical coupling.[21]

This reaction also constitutes an example of the facility of electron ejection in the phenoxide anion compared to its neutral state since the reaction does not occur in the neutral solution. Although this photochemical coupling reaction of the 1-naphthoxide anion occurred in much higher efficiency than photocoupling of phenol itself, we are unable to induce any photoinduced coupling reaction of phenoxide or 2-naphthoxide anion.

EXPERIMENTAL

All the m.ps were uncorrected. IR spectra were determined using a Shimadzu IR-27 spectrophotometer. ^1H NMR spectra were obtained with a Varian EM-360 spectrometer, using TMS as an internal standard. ^{13}C NMR spectra were obtained with a Varian CFT-20 spectrometer with 16 K memory, using TMS as an internal standard. ^1H-Coupled ^{13}C-spectra were obtained using gated mode over 1202 Hz (digital resolution 0.3 Hz).

Irradiation of 1-*naphthoxide anion* **1a** *in* MeOH. A MeOH soln of **1a** was prepared by dissolving **1b** (1.20 g; 8.33 mmole) in a soln of equimolar NaOMe in MeOH (150 ml). The soln was irradiated with a 100-W high pressure Hg lamp (quartz filter) under N_2 for 70 hr. The soln was neutralized with AcOH and the solvent was removed by evaporation. Chromatographic separation (SiO_2), with AcOEt–hexane (1:3) as eluent, from starting **1b** (723 mg) gave 304 mg of **2** (conversion 40%; yield 81% based on used **1b**); m.p. 184° (dec); IR (Nujol): 3440 and 3330 cm^{-1}; ^1H NMR (acetone-d_6): δ 3.45 (m, 2H, CH_2), 5.55 (dt, 1H, J = 4.5 Hz, CH), 5.76 (m, 1H, $CH_2C\underline{H}=$), 6.13 (m, 1H, $CHC\underline{H}=$), 6.48 (m, 4H), 7.02 (m, 1H), 7.45 (m, 2H), 7.55 (s, 1H, OH), 8.30 (m, 2H) and 8.41 (s, 1H, OH). found: C, 83.26; H, 5.53. Calc. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

Hydrogenation of **2**. The naphthol dimer **2** (148 mg, 0.514 mmole) in 10 ml abs. MeOH was hydrogenated over PtO_2 (6 mg) until uptake of one mole of H_2. The catalyst was removed by filtration and the soln was concentrated to give 78 mg (52%) of **3**; m.p. 230° (dec); IR (Nujol): 3350 and 3480 cm^{-1} (OH); ^1H NMR (acetone-d_6) δ 1.50 (m, 2H), 1.90 (m, 2H), 2.68 (m, 2H), 3.25 (bs, 1H, OH), 5.00 (m, 1H, CH), 6.2–7.7 (m, 7H), 8.14 (m, 2H) and 8.55 (bs, 1H, OH). Found: C, 82.58; H, 6.15. Calc. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

Dehydrogenation of **2**. A soln of n-BuLi (19.7 mmole) in hexane was introduced by a syringe into a soln of **2** (908 mg; 3.15 mmole) and tetramethylethylenediamine (TMEDA, 9 ml) in dry cyclohexane (18 ml). The color of the resulting soln changed from deep red to intense purple. After 1 hr under reflux, the mixture was allowed to cool and anhyd. $CdCl_2$ (1.716 g; 9.36 mmole) was added. After acidification with HCl aq, the crude product was extracted with ether and purified with preparative TLC (SiO_2) using EtOAc–hexane (4:1) as eluent to give 430 mg (48%) of **4a**: m.p. 185° (dec); IR (Nujol); 3330 cm^{-1} (OH); ^1H NMR (acetone-d_6) δ 2.00 (s, 1H, OH), 4.20 (s, 1H, OH), 6.75 (m, 1H), 7.0–7.7 (m, 9H). 7.83 (m, 1H) and 8.45 (m, 1H). Found: C, 83.60; H, 4.96. Calc. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%.

Acetylation of **4a**. To an ice-cold soln of **4a** (268 mg; 0.937 mmole) in pyridine (1 ml) Ac_2O (0.4 ml) was added. After 20 hr at room temp., the soln was poured onto crushed ice. The ppt was filtered off and washed with 2% HCl aq followed by water to give 284 mg (82%) of **4b**; m.p. 161–162°; ^1H NMR ($CDCl_3$): δ 1.12 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 6.8–7.6 (m, 9H), and 7.6–8.0 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 169.6 (CO), 169.3 (CO), 146.7 (C), 146.0 (C), 139.7 (C), 135.6 (C), 134.6 (C), 134.0 (C), 130.7 (CH), 128.7 (CH), 127.0 (CH), 126.9 (CH), 126.5 (CH) 117.5 (CH), 20.7 (CH_3) and 19.5 (CH_3). Found: C, 77.55; H, 5.20. Calc. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

Irradiation of **1a** *in benzene*–MeOH *solution*. (a) A soln of **1a** (8.69 mmole) in benzene (48 ml) and MeOH (4 ml) was irradiated with 100-W high pressure Hg lamp (quartz filter) under N_2 for 190 hr. The soln was neutralized with AcOH and the solvents were removed by vacuum evaporation. Chromatographic separation (SiO_2) with Et_2O–hexane (1:9) gave the starting **1b** (31 mg) and 183 mg (16%) of a mixture of dimers (**5** and **6**) in a ratio of 2:1. Separation of **5** and **6** was attained by reversed-phase liquid chromatography (μ Bondapack C_{18} column, MeOH–H_2O (3:2) as eluent).

For **5**; m.p. 187° (dec); ^1H NMR (acetone-d_6): δ 2.26 (m, 2H), 3.12 (bs, 1H, OH), 3.58 (m, 2H, CH_2), 5.32 (m, 1H, CH), 6.08 (m, 2H, CH=CH), 6.5–7.8 (m, 8H), 8.32 (m, 1H) and 8.70 (bs, 1H, OH). Found: C, 83.08; H, 5.81. Calc. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

For **6**; m.p. 194° (dec); ^1H NMR (acetone-d_6): δ 2.26 (m, 2H), 3.0–3.5 (m, 3H), 6.06 (m, 1H), 6.4–7.1 (m, 3H), 7.1–7.5 (m, 4H), 7.73 (m, 1H), 8.16 (m, 1H) and 8.65 (m, 1H, OH). found: C, 83.15; H, 5.76. Calc. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

(b) A solution of **1a** (7.0 mmole) in benzene (120 ml) and MeOH (20 ml) was irradiated for 70 hr. Neutralization with AcOH followed by chromatographic separation gave 170 mg of starting **1b** and 164 mg (16%) of **2**.

Dehydrogenation of **5** *followed by acetylation*. A soln of n-BuLi (8 mmole) in hexane was introduced by a syringe into a soln of **5** (155 mg; 0.54 mmole) in dry cyclohexane (12 ml) and TMEDA (6 ml). After 1 hr reflux, the mixture was allowed to cool and anhyd. $CdCl_2$ (733 mg; 4 mmole) was added. Ac_2O (1.0 ml) was added to the soln. After 10 hr, the soln was acidified with HCl aq and extracted with Et_2O. Chromatographic purification of the crude product gave 45 mg (23%) of **7**; m.p. 139–144°; ^1H NMR ($CDCl_3$): δ 1.02 (s, 3H, CH_3), 1.81 (s, 3H, CH_3) and 7.0–8.1 (m, 12H); ^{13}C NMR ($CDCl_3$); δ 169.3 (CO), 168.9 (CO), 148.0 (C), 146.6 (C), 135.6 (C), 134.9 (C), 133.8 (C), 132.7 (C), 132.1 (C), 130.7 (CH), 128.7 (CH), 128.5 (CH), 127.9 (CH), 127.0 (CH), 127.0 (CH), 126.4 (CH), 125.5 (CH), 125.5 (CH), 125.3 (CH), 121.6 (CH), 120.3 (CH), 20.1 (CH_3) and 19.7 (CH_3). Found: C, 77.65; H, 5.12. Calc. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90%.

Irradiation of **1a** *and naphthalene in* MeOH. A soln of **1a** (11.6 mmole) and naphthalene (2.96 g, 23.2 mmole) in MeOH (150 ml) was irradiated with a 100-W high pressure Hg Lamp (quartz filter) under N_2 for 160 hr. After neutralization of the soln with AcOH, the solvent was removed by vacuum evaporation. The residue was chromatographed (SiO_2) with ether–hexane (1:9) as eluent to give 117 mg (9%) of **8**, 237 mg (18%) of **9**, and 127 mg of **10**, in addition to recovered naphthalene (1.492 g) and **1b** (371 mg).

For **8**:[21] ^1H NMR (acetone-d_6): δ 4.68 (s, 2H, CH_2), 6.5–8.6 (m, 12H) and 8.95 (bs, 2H, 2xOH).

For **9**:[21] ^1H NMR (acetone-d_6): δ 4.56 (s, 2H, CH_2), 6.7–7.6 (m, 8H), 7.78 (m, 1H), 8.02 (m, 1H), 8.32 (m, 2H) and 8.92 (bs, 2H, 2xOH).

For **10**:[11] ^1H NMR ($CDCl_3$): δ 2.7–3.4 (m, 4H), 3.7–4.1 (m, 2H), 5.94 (m, 4H, CH=CH) and 6.3–7.4 (m, 8H).

Thermal reaction of **1a** *with formaldehyde*. To a soln of **1b** (1 g) and KOH (1.2 g) in water (5 ml), aqueous HCHO (0.5 ml) was added and allowed to stand for 7 days at room temp. The mixture was acidified with HCl aq, extracted with CH_2Cl_2, and separated with preparative tlc to give 28 mg of **8** and 24 mg of **9**, identical with those obtained photochemically with respect to ^1H and ^{13}C NMR and R_f values in tlc.

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