by the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The mass spectral data were provided by the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln, a National Science Foundation supported Regional Instrumentation Facility. The 60-MHz NMR spectrometer used in this work was purchased with a Research Instrumentation Grant (No. CDP-8006650) from the National Science Foundation. The assistance of J. Manion and F. Evans in obtaining NMR spectra and the encouragement and assistance of J. Stuckey and C. Goodwin are appreciated. We thank D. A. Evans for helpful discussions and Dr. K. L. Loening, Nomenclature Director, Chemical Abstracts Service, for nomenclature advice.

Registry No. 3a, 80317-38-0; **3b**, 80317-39-1; **4a**, 80317-40-4; **4b**, 80317-41-5; (*R**,*R**)-**4c**, 80317-42-6; (*R**,*S**)-**4c**, 80317-43-7; (*R**,*R**)-**4d**, 80317-44-8; (*R**,*S**)-**4d**, 80317-45-9; **6a**, 80317-46-0; **6b**, 80317-47-1; **6c**, 80317-48-2; **6d**, 80317-49-3; **7a**, 20047-50-1; **7a** 2,4-DNP derivative, 80317-50-6; **7b**, 56790-89-7; **7b** 2,4-DNP derivative, 80317-51-7; **7c**, 80317-52-8; **7c** 2,4-DNP derivative, 80317-53-9; **7d**, 80317-54-0; **7d** 2,4-DNP derivative, 80317-55-1; 2-methyl-3-phenyl-2-propen-1-ol, 1504-55-8; 2-methyl-3-phenyl-2-propenal, 101-39-3; (3-chloro-2-methyl-1-propenyl)benzene, 1507-88-6; 2-mercapto-1-methylimidazole, 60-56-0; 3-(4-chlorophenyl)-2-methyl-2-propenal, 24654-54-4; propanal, 123-38-6; 4-chlorobenzaldehyde, 104-88-1; 3-(4-chlorophenyl)-2-methyl-2-propen-1-ol, 80317-56-2; 1-chloro-4-(3-chloro-2-methyl-1-propenyl)benzene, 80317-57-3; methyl iodide, 74-88-4; tetrahydro-2-(iodomethyl)pyran, 43216-12-2.

Dibenzoxanthene Derivatives and Related Products from β-Naphthol and Aldehydes or Acetals

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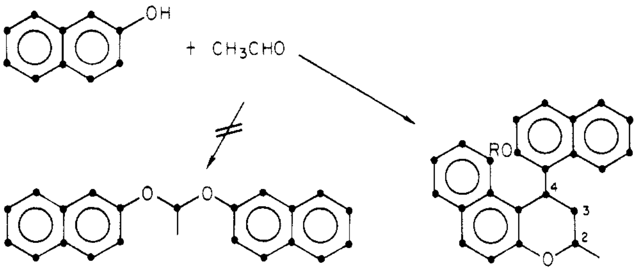
We have investigated several reactions of β-naphthol with aldehydes or aldehyde equivalents. Many of these reactions give novel structures. For example, reaction with paraldehyde does not yield the dinaphthyl acetal as previously reported but instead a compound which we show by spectroscopic methods to be 2-methyl-4-(2-hydroxy-1-naphthyl)benzo[*d*]chroman. Further, reaction with methyl dimethoxyacetate gives a furanone derivative and with malondialdehyde yields a dinaphthodioxabicyclo[3.3.1] derivative. The unusual reactions limit the utility of this reaction sequence for the preparation of xanthene derivatives.

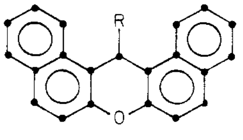
Results

Claisen[1] reported that β-naphthol and paraldehyde react to form a compound, mp 200–201 °C, to which he attributed the structure **1**, the dinaphthyl acetal of acetaldehyde. Under similar conditions, we isolated a material, mp 198–200 °C, which we show has instead structure **2a**, 2-methyl-4-(2-hydroxy-1-naphthyl)benzo[*d*]chroman.



1

2a, R = H
2b, R = Ac



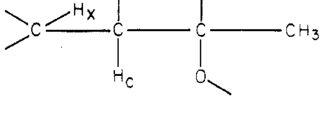
3a, R = CH_3
3b, R = $CH_2CH(OH)CH_3$

The mass spectrum and elemental analysis of **2a** are consistent with the structure shown. In the ^{13}C NMR spectrum, 19 of 20 possible aromatic resonances are observed, ruling out any structure with a plane of symmetry. Additional resonances indicated the presence of four aliphatic carbon atoms. On the basis of the off-resonance decoupled spectrum, these signals included one methyl (δ 22.3, q), one methylene (32.6, t), and two methine carbons, one bearing oxygen (25.3, d and 67.2, d).

Table I. ^1H NMR Data for Compound 2a (Me_2SO-d_6 Solvent)

chemical shifts (δ)		coupling constant (Hz)
CH_3	1.50	$J_{CH_3A} = 7.0$
H_A	3.68	$J_{AB} = 5.0$
H_B	2.84	$J_{AC} = 1.5$
H_C	1.88	$J_{BC} = 14.4$
H_X	6.37	$J_{BX} = 12.3$
OH	8.65	$J_{CX} = 2.1$

^1H NMR studies, facilitated by decoupling experiments, support the following connectivity:



Chemical shifts and coupling constants are shown in Table I.

Structure **3b** was also considered to be consistent with these data. For structure **3b**, the magnetic nonequivalence of the naphthyl rings would be attributed to the chiral center in the hydroxypropyl side chain. Further, we have observed the formation of the symmetrical compound **3a**

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[1] Claisen, L. *Justus Liebigs Ann. Chem.* 1887, *237*, 271.

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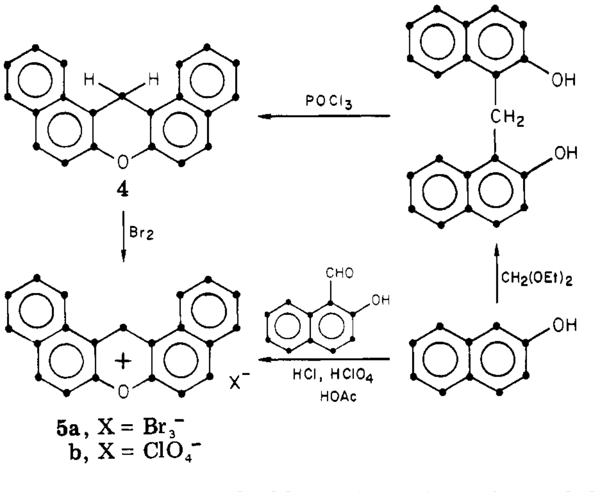
in the reaction of β-naphthol with acetaldehyde diethyl acetal. However, several lines of evidence favor structure **2a** over **3b**.

First, the magnetic environments of H_B and H_C in the aliphatic portion of the spectrum are quite dissimilar, and the large differences in coupling constants between these protons and H_A and H_X are more consistent with a rigid, cyclic structure than a freely mobile side chain such as that in **3b**. Second, the hydroxyl resonance appeared at δ 8.65, a chemical shift more consistent with a phenolic hydroxyl than with a secondary alcohol.

To distinguish firmly between these structures, we performed two experiments. Reaction of **2a** with acetic anhydride in pyridine gave an acetate, **2b**, which absorbed in the IR at 1765 cm^{-1}, more consistent with a phenolic than with an aliphatic acetate (expected[2] to absorb at ~1735 cm^{-1}). Further, proton H_A resonated at δ 3.73, essentially unperturbed from the parent compound (δ 3.68). If **3b** were the structure, a substantial downfield shift in this resonance would be expected.[3]

As final confirmation of structure **2a**, the ^{13}C NMR spectrum of the compound in the presence of base was compared with that of the parent. A peak at 150.9 ppm, assigned to one of the aromatic carbons bearing oxygen, shifted to 163.7 on addition of NaOD, as expected for the ionization of a phenolic hydroxyl.[4] The aliphatic carbon resonances were relatively unperturbed by this treatment (maximum shift, 1.4 ppm), as was the other aromatic carbon bearing the ether oxygen (152.4 vs. 151.9).

Reaction of β-naphthol and diethoxymethane followed by dehydration with $POCl_3$ yielded the unsubstituted dibenzoxanthene 4, as described by Wolff.[5] Oxidation of 4 gave the dibenzoxanthylium salt **5a**, which was converted to the perchlorate **5b** with $HClO_4$ in acetic acid. The perbromide **5a** is apparently identical with a species previously prepared by Gomberg and Cone,[6] who assigned the structure as a brominated xanthylium salt. The proposed structure of **5b** was confirmed by synthesis from β-naphthol and 2-hydroxy-1-naphthaldehyde on treatment with $HClO_4$ and HCl in acetic acid.



4

5a, X = Br_3^-
b, X = ClO_4^-

We have investigated additional reactions of β-naphthol with other aldehydes or aldehyde equivalents. Many of these reactions give novel structures. For example, reaction of the naphthol with methyl dimethoxyacetate in the presence of acid yields the furanone derivative **6**. The structure of this material was confirmed by mass spectral data and elemental analysis. The IR spectrum shows bands at 3333 (br s, OH) and 1880 cm^{-1} (s, five-membered unsaturated lactone). In the NMR spectrum, resonances occur at δ 6.34 and 9.9 for the methine and OH protons, respectively.

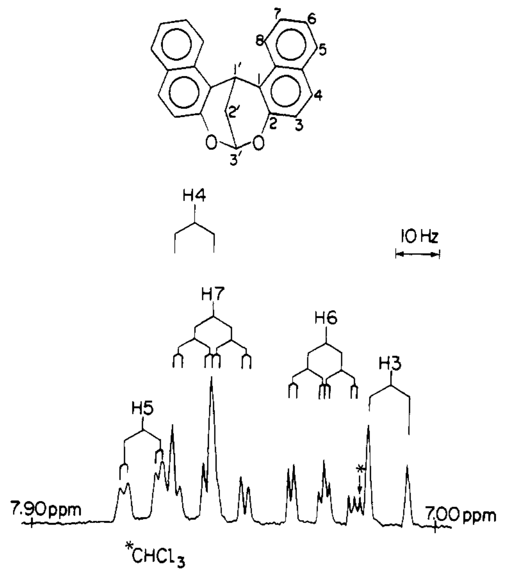
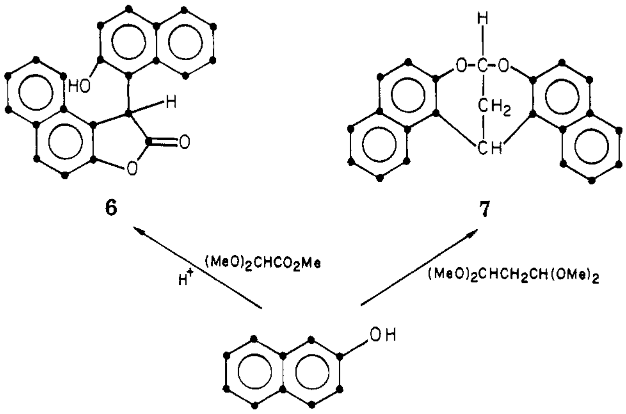


Figure 1. 100-MHz ^1H NMR spectrum of β-naphthol/malonaldehyde adduct. Analysis of splitting patterns showing assignments of aromatic protons H(3) through H(7).



6

7

More strikingly, reaction of β-naphthol and malonaldehyde tetramethyl acetal gave the dioxabicyclo[3.3.1]nonene derivative **7**. The structure of this material was deduced from the following spectral and analytical data. Combustion analysis was consistent with the elemental composition $C_{23}H_{16}O_2$. The molecular weight deduced from a strong parent ion (m/e 324) was likewise consistent with this formulation. The IR spectrum showed no carbonyl or hydroxyl.

The 100-MHz ^1H NMR spectrum showed chemical shifts and coupling patterns which uniquely define the bridge structure and the 1,2-disubstituted naphthalene ring. Figure 1 shows the analysis of the aromatic splitting patterns, and Table II gives the deduced chemical shifts and coupling constants.

Several features of these data are noteworthy. Because the structure for **7** is symmetrical, we expect and observe no more than six multiplets in the aromatic region. Double-resonance experiments permit unequivocal assignment of the vicinal and four-bond coupling constants

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(2) Nakanishi, K. "Infrared Absorption Spectroscopy"; Holden-Day Inc.: San Francisco, 1962; p 44.

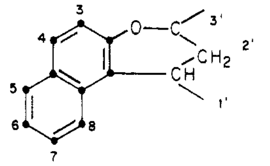
(3) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; p 256.

(4) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic: New York, 1972; p 197.

(5) Wolff, W. *Chem. Ber.* **1893**, *26*, 83.

(6) Gomberg, M.; Cone, L. H. *Justus Liebigs Ann. Chem.* **1910**, *376*, 183.

Table II. ^{1}H NMR Data for Compound 7

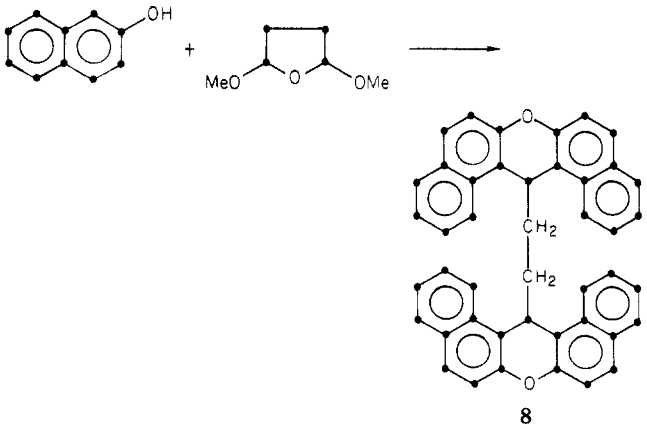


proton	chemical shift, δ	coupling constant (Hz ± 0.6)
1'	5.35	$J_{3,4} = 9.0$
2'	2.42	$J_{5,6} = 8.0$, $J_{5,7} = 1.5$
3'	6.25	
3	7.12	$J_{6,7} = 7.0$, $J_{6,8} = 1.0$
4	7.56	$J_{7,8} = 8.0$
5	7.67	
6	7.26	$J_{1',2'} = 2.9$, $J_{1',3'} = 1.3$
7	7.52	$J_{2',3'} = 2.0$
8	8.56	

for the aliphatic protons. The existence of a small ($J \le 0.2$ Hz) five-bond coupling between protons at 1' and 3 is indicated by irradiation of H(1'), which narrows each line of the H(3) doublet. Others[7] have shown evidence of similar long-range coupling in benzylic systems. The 1.3 Hz coupling between H(1') and H(3') supports the bicyclic structure and can be compared to the W coupling seen in norbornane derivatives.[8]

^{13}C chemical shifts for the aliphatic carbons of 7 are C(1'), 22.7 ppm; C(2'), 26.8; and C(3'), 91.5. Because the methine carbon, C(1'), appears unusually shielded, several model compounds were examined. The bridgehead carbon of bicyclo[3.3.1]nonane resonates at 27.9 ppm.[9] The effect of the two oxygen atoms on C(1') can be estimated from the chemical shifts of cyclohexane (27.1 ppm) and the γ carbon of pyran (25.1). The upfield shift of 2.0 ppm on substituting oxygen for carbon results in a calculated shift of 27.9 − 2(2.0) = 23.9, in reasonable agreement with observation. The influence of the naphthyl rings has been omitted in our calculations, since the bridgehead carbon (44.9 ppm)[10] in *trans*-decalin is insensitive to a fused aromatic ring (e.g., the equivalent carbon, C(9), in estra-1,3,5(10)-triene resonates at 45.1 ppm).[11]

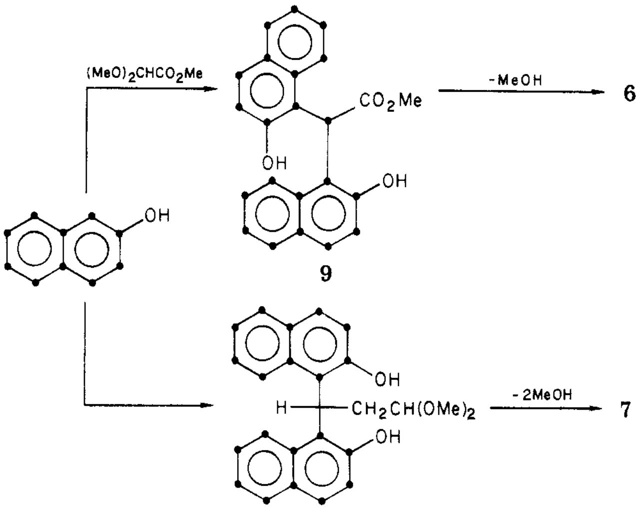
The reaction of β-naphthol with 2,5-dimethoxytetrahydrofuran gave the expected product, 1,2-bis(13-dibenzo[*a,j*]xanthyl)ethane, 8. The field-desorption mass spectrum of 8 shows a parent ion at *m/e* 590. The electron-impact mass spectrum shows only a very small parent ion (1.1%) together with the dibenzoxanthylium cation (*m/e* 281, 100%) and little further fragmentation. NMR data are also consistent with the structure. ^{13}C NMR shows two aliphatic resonances for the methine (30.7 ppm) and methylene (29.1) carbons, respectively, and 10 aromatic resonances, consistent with the overall mirror symmetry. The ^{1}H NMR spectrum shows a triplet for the methine hydrogens as expected. Surprisingly, the methylenes also appeared as a three-line pattern. Spectral simulation demonstrated that this multiplicity is the result of virtual coupling[12] in the $XA_2A'_2X'$ spin system, with parameters as follows: $J_{A'X'} = J_{AX} = 4$ Hz, $12 \le J_{AA'} \le 15$ Hz, $J_{AX'} = J_{A'X} = 0$.



8

Discussion

The reactions reported here gave a variety of products which are not the expected xanthene derivatives. Some of them, for example, furanone 6 and the dioxabicyclononene 7, can be explained in terms of observed intermediates in similar reactions. Thus, if initial reaction with a protected aldehyde leads to condensation at the α position of the naphthalene ring, as observed for formaldehyde and acetaldehyde diethyl acetal, the expected products from methyl dimethoxyacetate and malonaldehyde tetramethyl acetal would be 9 and 10. Loss of methanol from these intermediates might reasonably be expected to yield 6 and 7.



10

The formation of chroman 2a is slightly more problematical. Apparently, self-condensation of acetaldehyde to yield aldol under the reaction conditions is more rapid than condensation with 2-naphthol. Reaction of the naphthol with aldol yields 11, which then dehydrates to 2a. Interestingly, use of the aldehyde-protected acetal prevents the condensation, with formation of the expected 13-methylxanthene.

Experimental Section

The melting points were determined with a Mel-Temp apparatus and are uncorrected. The NMR spectra were obtained with a Varian EM390 spectrometer and a Varian HA-100 system converted to pulsed FT and interfaced with a Varian 620i data system; the ^{13}C spectra were run on a JEOL FX-60Q spectrometer.

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(7) Newsoroff, G. P.; Steinhell, S. *Tetrahedron Lett.* **1964**, 3499.

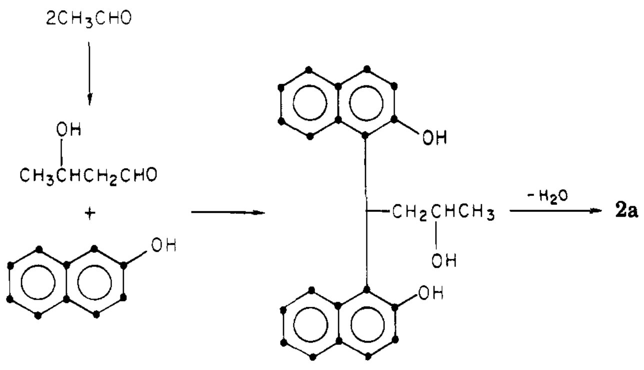
(8) Jackman, L. M.; Steinhell, S. "Applications of Nuclear Magnetic Resonance in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 334.

(9) Heumann, A.; Kolshorn, H. *Tetrahedron* **1975**, *31*, 1571.

(10) Reference 4, p 66.

(11) Blunt, J. W.; Stothers, J. B. *Org. Magn. Reson.* **1977**, *9*, 439.

(12) (a) Musher, J. I.; Corey, E. J. *Tetrahedron Lett.* **1962**, 791. (b) Silverstein, R. M.; Bassler, G. C. "Spectrometric Identification of Organic Compounds", 2nd ed.; Wiley: New York, 1967; p 130.



11

The electron-impact mass spectra were obtained with an AEI MS-30 spectrometer.

2-Methyl-4-(2-hydroxy-1-naphthyl)benzo[*d*]chroman (2a). A mixture of β-naphthol (14.4 g, 0.1 mol), 6 mL of acetaldehyde (0.13 mol), 4 mL of ethanol, and 10 mL of hydrochloric acid was heated for 18 h. The mixture was cooled, and the product was collected, washed with alcohol, and dried to give 16 g (97%) of product, **2a**, mp 198–200 °C. Crystallization from toluene gave 14 g of **2a**: mp 200 °C; IR (KBr) ca. 3300 cm^{-1} (OH); ^{1}H NMR, see Table I; ^{13}C NMR (Me_2SO-d_6) δ 22.3 (CH_3), 25.3 (CH), 32.6 (CH_2), 67.2 (CHO), 18 lines between 116.8 and 132.1 (aromatic C), 152.0 (=CO), 150.9 (=COH, shifts to 164.6 on addition of NaOD); mass spectrum, *m/e* 340, 296, 281, 252.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.6; H, 5.9. Found: C, 84.6; H. 5.9.

Acetate of 2a. Compound **2a** (44 mg) was dissolved in 2 mL of pyridine. Acetic anhydride (0.5 mL) was added, and the solution was heated under reflux for 5 min. The solution was cooled, and 5 mL of water was added. The white solid was filtered, recrystallized from ethanol/water, and air-dried: IR 1765, 1235, 1195 cm^{-1} (acetate); NMR ($CDCl_3$) δ 6.15 (dd, J_{CX} = ca. 2 Hz, J_{BX} = 12 Hz, H_X), 3.73 (m, H_A), 2.89 (ddd, J_{BC} = 14 Hz, J_{AB} = 6 Hz, J_{BX} = 12 Hz, H_B), 2.28 (s, CH_3CO), 2.02 (ddd, J_{BC} = 14 Hz, J_{AC} = ca. 2 Hz, J_{CX} = ca. 2 Hz), 1.65 (d, J_{CH_3A} = 7 Hz, CH_3C).

Preparation of 14-Methyl-14*H*-dibenzo[*a,j*]xanthene (3a). A solution of 7.2 g of 2-naphthol (0.05 mol), 2 mL of acetaldehyde diethyl acetal, 20 mL of ethanol, and 7 mL of concentrated hydrochloric acid was allowed to stand at room temperature for 3 days. The white crystals that separated were removed by filtration and dried (2.3 g, 16%): mp 173 °C; ^{1}H NMR ($CDCl_3$) δ 1.62 (d, 3 H, *J* = 6 Hz, CH_3), 5.48 (q, 1 H, *J* = 6 Hz, CH), 7.2–8.3 (m, 14 H, ArH); ^{13}C NMR δ 23.7 (CH_3), 25.4 (CH), nine lines between 138.7 and 117.2 (ArC), 148.0 (CO); mass spectrum, *m/e* 296, 281, 252.

3-(2-Hydroxynaphth-1-yl)naphtho[2,1-*b*]furanone (6). A mixture of 7.2 g (0.05 mol) of β-naphthol and 3.1 mL of methyl dimethoxyacetate in 10 mL of methanol containing 8 mL of concentrated hydrochloric acid was heated under reflux for 20 h. The mixture was cooled, and the white crystals of **6** were collected: yield 7.1 g (87%); mp 225 °C; IR 3333 (hydroxyl), 1880 cm^{-1} (lactone); NMR ($CHCl_3$) δ 6.34 (benzylic H), 9.9 (hydroxyl).

Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.8; H, 4.3. Found: C, 80.7; H, 4.5.

Dibenzo[*a,j*]xanthylium Perbromide (5a). To a solution of 3.0 g (0.01 mol) of **4** in 50 mL of warm dichloromethane was added slowly 3 mL of bromine in 10 mL of dichloromethane. The mixture was heated under reflux for 5 min, and the yellow crystals of **5a** were collected by filtration: yield 5.1 g (98%); mp 220 °C (lit.[4] mp 280 °C); UV λ_{max} 508 nm (ε 24000).

Anal. Calcd for $C_{21}H_{13}Br_3O$: C, 48.4; H, 2.5; Br, 46.0. Found: C, 48.6; H, 2.4; Br, 45.6.

Dibenzo[*a,j*]xanthylium Perchlorate (5b). A suspension of 7.2 g (0.05 mol) of β-naphthol and 8.6 g (0.05 mol) of 2-hydroxy-1-naphthaldehyde in 50 mL of acetic acid and 5 mL of 70% perchloric acid was treated with gaseous HCl for 2 h. The mixture was allowed to stand for 2 days, and the salt was collected by filtration: yield 7.4 g; mp 330 °C; UV λ_{max} 508 nm (ε 23000).

Anal. Calcd for $C_{21}H_{13}ClO_5$: C, 66.2; H, 3.4; Cl, 9.3. Found: C, 66.3; H, 3.6; Cl, 9.1.

Bis(1,2-naphtho)-2,8-dioxabicyclo[3.3.1]nona-3,6-diene (7). A solution of 7.2 g (0.05 mol) of 2-naphthol, 4 mL (0.025 mol) of malonaldehyde tetramethyl acetal, and 10 mL of trifluoroacetic acid was allowed to stand for 48 h. The reaction mixture solidified. After addition of 20 mL of acetic acid, the product was collected by filtration and washed with acetic acid and methanol: yield 6.4 g (79%). One recrystallization from acetic anhydride gave 5.5 g of **7** as white crystals, mp 238 °C; ^{1}H NMR, see Table II; ^{13}C NMR δ 22.7 (C(1′)), 26.8 (C(2′)), 91.5 (C(3′)), eight lines between 118.5 and 131.3 (aromatic C), 150.2 (=CO); mass spectrum, *m/e* 324.

Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.2; H, 5.0. Found: C, 85.2; H, 5.1.

1,2-Bis(14-dibenzo[*a,j*]xanthyl)ethane (8). A solution of 14.4 g (0.1 mol) of 2-naphthol and 6.6 g (0.05 mol) of 2,5-dimethoxytetrahydrofuran in 150 mL of methylene chloride containing 2 g of *p*-toluenesulfonic acid was heated under reflux for 5 h. The reaction mixture was extracted with 200 mL of 10% sodium hydroxide followed by 200 mL of water. Addition of methanol (100 mL) to the methylene chloride solution gave 6.1 g of **8** (42%): mp 300 °C after recrystallization from pyridine; mass spectrum, *m/e* 590 (1.1), 308 (0.03), 281 (100), 252 (1.6); ^{1}H NMR ($CDCl_3$) δ 1.83 (m, see text, 4 H), 5.19 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 149.6, 130.9, 130.7, 128.6, 128.0, 126.3, 123.7, 121.9, 116.9, 115.1, 30.7, 29.1.

Anal. Calcd for $C_{44}H_{30}O_2$: C, 89.5; H, 5.0. Found: C, 89.4; H, 4.7.

Acknowledgment. We thank Dr. Richard P. Szajewski for helpful discussions, particularly regarding the structure of **2a**, and Mr. L. Kelts and Mr. S. Gross for obtaining several spectra.

Registry No. **2a**, 22248-11-9; **2b**, 80410-29-3; **3a**, 6639-05-0; **4**, 224-48-6; **5a**, 80422-14-6; **5b**, 80422-15-7; **6**, 80410-30-6; **7**, 80410-31-7; **8**, 80410-32-8; β-naphthol, 135-19-3; acetaldehyde, 75-07-0; acetaldehyde diethyl acetal, 105-57-7; methyl dimethoxyacetate, 89-91-8; 2-hydroxy-1-naphthaldehyde, 708-06-5; malonaldehyde tetramethyl acetal, 102-52-3; 2,5-dimethoxytetrahydrofuran, 696-59-3.