Spirodienone and Bis(spirodienone) Derivatives of Calix[4]naphthalenes

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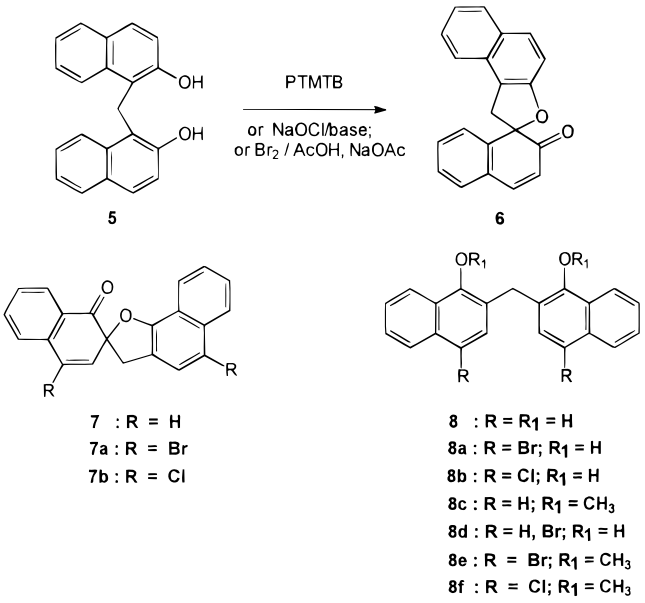
Calix[4]naphthalenes **11** and **12** in which hydroxyl groups are situated intraannularly can be oxidized with PTMATB and base to form the bis(spirodienone) **13**, from **11**, and bis(spirodienone) **20**−**21** and spirodienone **22**, from **12**. The prototype calix[4]naphthalenes **9** and **10** previously reported by us and which contain similar 1,5 dihydroxy functionalities extrannularly failed to afford the analogous spironaphthalenones. Model studies with the bis(1-hydroxy-2-naphthyl)methanes **8**−**8f** provided support for the putative mechanism proposed for the formation of spirodienone calix[4]arenes and spironaphthalenones. The synthesis of the novel *tert*-butylcalix[4]naphthalenes **12** is described.

Introduction

The serendipitous discovery by Biali *et al.* that *p-tert*-butylcalix[4]arenes **1** (Chart 1) can be easily oxidized with phenyltrimethylammonium tribromide (PTMATB)[1,2] and base into bis(spirodienones) **2**−**4** has provided a new synthetic route for derivatizing calix[4]arenes.[3] As a result, the carbonyl functionalities can be modified by a variety of different methods to effectively result in selective hydroxyl replacements of the parent calix[4]-arenes. Biali et al. have thus been able to replace the intraannular hydroxyls with hydrogens,[4] amino,[5] halogens,[6] and methyl[7] groups. Besides their synthetic utility, these spirodienones are interesting *per se* in that up to two stereogenic centers are generated from calix-[4]arenes, resulting in the isomerism observed and depicted in compounds **2**−**4**.

Abel[8] in 1892 reported that the mild alkaline oxidation of bis(2-hydroxy-1-naphthyl)methane (**5**) afforded a product that he deduced to be a peroxide. In 1937, Shearing and Smiles[9] concluded that the product was the spironaphthalenone **6**. More recently, Kasturi *et al.*[10] extensively studied the chemistry of these compounds. However, to our knowledge, there are no reports of the corresponding spironaphthalenone **7**, which can be derived from **8**.[11]

In this paper, the syntheses of spironaphthalenones



7a and **7b** are described from the corresponding 4,4′-dibromo and 4,4′-dichloro derivatives **8a**[12] and **8b** of bis(1-hydroxy-2-naphthyl)methane (**8**), respectively. The reactions of calix[4]naphthalenes[12] **9** and **10** with PTMATB are described, as are the syntheses and structural assignments of the products derived from the calix[4]-naphthalenes **11** and **12**. The synthesis of the novel *tert*-butylcalix[4]naphthalene **12** is also described, as are some of the properties of **11** and **12**.

Results and Discussion

Bis(1-hydroxy-2-naphthyl)methane (**8**) was synthesized from the previously described dimethoxy precursor **8c**.[12] However, when it was subjected to the same conditions

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(11) There is an erroneous reference to **7** and **8**, referred to as structures **2** and **3** in ref 2, which was subsequently corrected: *J. Org. Chem.* **1993**, *58*, 5024.
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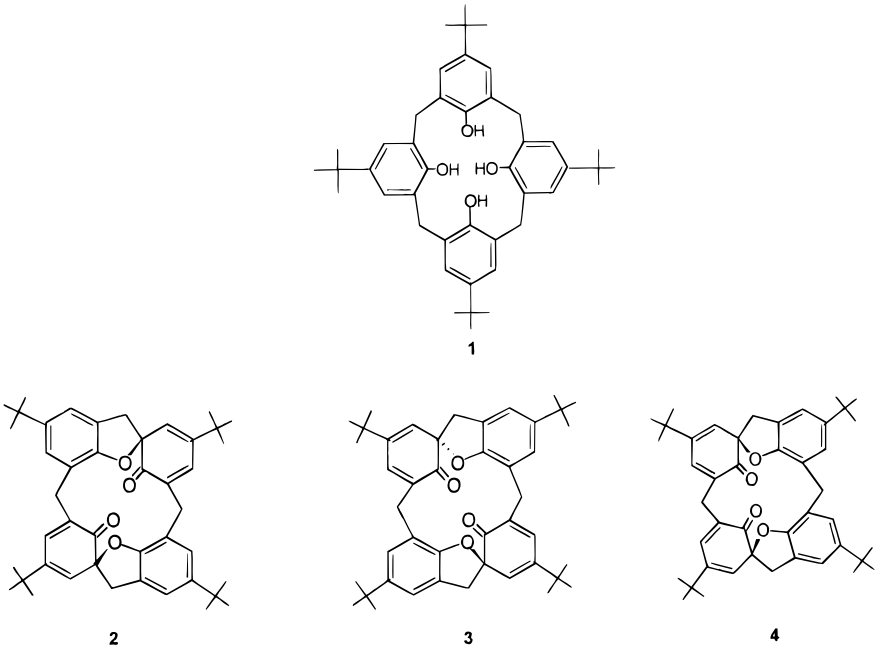
Chart 1



that Biali's group[2] have used to oxidize calix[4]arenes, using 1 molar equiv of PTMATB, even with refluxing for up to 48 h, no corresponding spironaphthalenone product could be detected, and the only product that could be characterized was the monobromo derivative **8d**. On the other hand, when the same conditions were employed with **5**, **8a**, or **8b**, the corresponding spirodienones **6**, **7a**, and **7b** were obtained easily. When **8** was reacted with 2 molar equiv of PTMATB, none of **7** was obtained; instead, a product containing two bromine atoms and which was identical to spirodienone **7a** was obtained in 20% yield. The reaction with 3 molar equiv of PTMATB gave the same product in a 40% yield. Spironaphthalenone **7** could not be obtained directly. These findings are consistent with the putative mechanism proposed by Biali et al. to account for their observed product formation. In this mechanism, the first step involves bromination at the *ortho* position, followed by a subsequent intramolecular nucleophilic substitution by the neighboring phenoxide anion. In fact, **7a** could be obtained directly from **8a** using 1 molar equiv of PTMATB, even in the absence of any added base.

In the case of **8**, however, bromination occurs preferentially at the unsubstituted *para* position, and subsequent intramolecular nucleophilic substitution by the neighboring phenoxide anion cannot occur. Only after both *para* positions are brominated to give **8a** does a third bromination occur at the *ortho* position, which results in the formation of spirodienone **7a**. This mechanism is consistent with the fact that **8b** also reacts with 1 equiv of PTMATB to give **7b**.

When the previously reported[12] calix[4]naphthalenes **9** or **10** were each subjected to these same oxidative conditions, even with prolonged heating, or under a variety of different modified conditions, none of the corresponding spirodienones (Scheme 1) could be detected. Only polar intractable products were formed that could not be further characterized. Even when subjected to PTMATB alone, without added base, **10** gave an intractable mixture of polar products that could not be characterized. Under identical conditions, *tert*-butylcalix[4]arene **1** cleanly afforded a single product previously identified by Grynszpan *et al.*[13] as being a bromo dispiro compound.

It is possible that since both **9** and **10** possess 1,5-dihydroxy systems that are not located in the intraannular positions, as are found in the calix[4]arenes, they are unable to form the corresponding spirodienones, and instead they more easily undergo oxidative degradation.

Compound **11** can also be classified as a calix[4]-naphthalene (Chart 2). It was first described by Andreetti *et al.* in 1993[14] and, later, by us in 1996.[15] Whereas **9** and **10** more closely resemble calix[4]resorcinarenes, **11** more closely resembles the calix[4]arenes, since its hydroxyl groups are located on the lower rim, in the intraannular sites. It is, however, conformationally more mobile than the *tert*-butylcalix[4]arenes since the methylene bridge protons appear as a sharp singlet in its ambient-temperature ^{1}H NMR spectrum.[15]

A single crystal of **11** that was suitable for X-ray crystallographic analysis was obtained from toluene. The numbering scheme for the X-ray analysis is shown in Figure 1, as is also the fact that the molecule exists in a "pinched-cone" conformation in which one pair of distal (1,3) naphthalene rings are closer to each other than the other distal pair. Figure 2 is a stereoview that indicates that the unit cell contains a pair of calix[4]naphthalene molecules that are packed in such a way that a naphthalene unit of one molecule is situated within the hydrophobic cavity of the second molecule. This type of occurrence has not been noted in the calix[4]arenes. Three toluene molecules surround this "supramolecular dimer".

When **11** was treated with 2 equiv of PTMATB and base, a single product was obtained whose yellow color

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Scheme 1

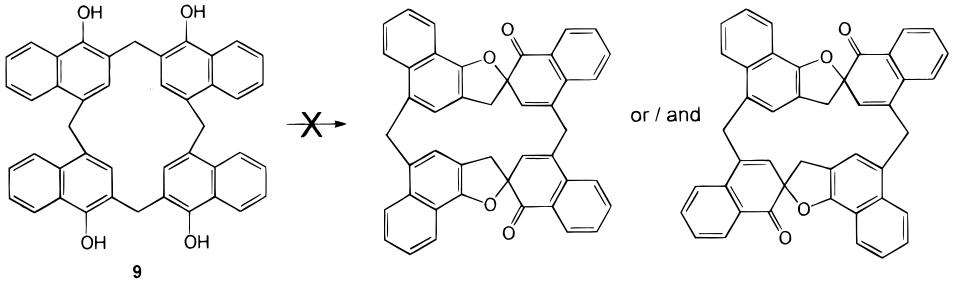
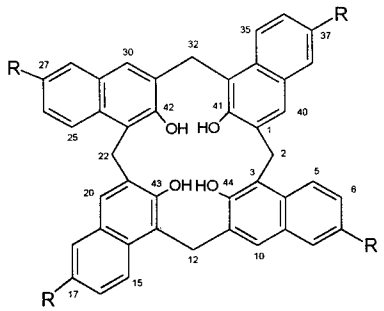
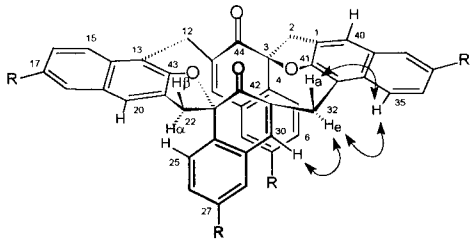


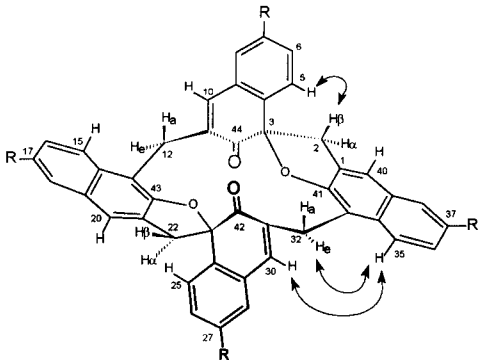
Chart 2



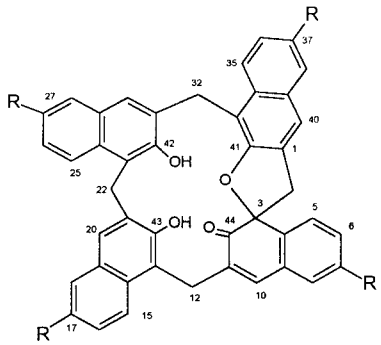
11: R = H
12: R = C(CH$_3$)$_3$



13: R = H *(Including selected NOED correlations.)*
21: R = C(CH$_3$)$_3$ *(Including selected NOED correlations.)*



14: R = H
20: R = C(CH$_3$)$_3$ *(Including selected NOED correlations.)*



22: R = C(CH$_3$)$_3$

was indicative of the presence of a dienone functional group. Infrared spectroscopy showed that the product contained a carbonyl group (1678 cm^{-1}) and no hydroxyl groups. Its ^{13}C NMR spectrum indicated that in addition to the carbonyl signal at 195.4 ppm there were 18 signals in the 112−154 ppm region, corresponding to aromatic carbons. A signal at 83.1 ppm was attributed to C-3 (C-23), the quaternary carbon that is attached to the tetrahydrofuran oxygen. The two signals at 29.2 and 41.7 ppm correspond to C-2 (C-22) and C-12 (C-32), respectively. In its ^{1}H NMR spectrum, the two low-field singlets were clearly evident at 7.01 and 7.57 ppm (integrated for two protons each) and correspond to the two cyclohexadienone protons (H-10 and H-30) and the two aromatic protons (H-20 and H-40), respectively. There were also four doublets between 3.4 and 4.53 ppm that correspond to the methylene protons.

The NMR spectra are consistent only with a symmetrical structure having alternating cyclohexadienone and aromatic rings and possessing either C_2 (**13**) or C_i (**14**) symmetry.[1,2] X-ray crystallography (Figure 3) provided unequivocal evidence that the correct solid-state structure for this product was the C_2-symmetrical structure **13**. Figure 3 shows the numbering scheme that was

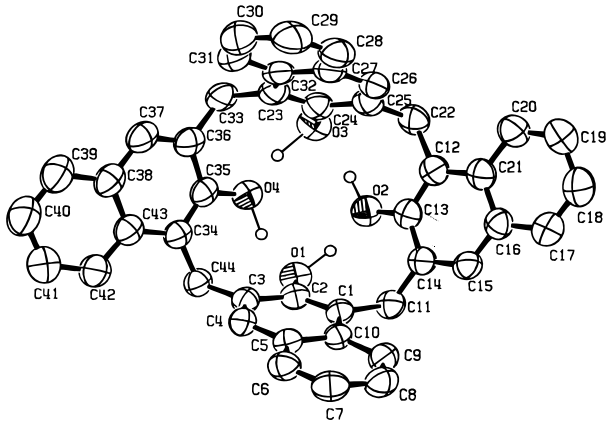


Figure 1. Crystal structure and numbering scheme used in X-ray analysis of **11**.

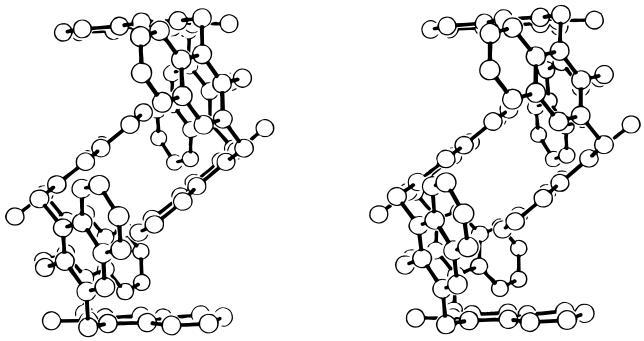


Figure 2. Stereoview of unit cell containing a pair of associated molecules of **11**.

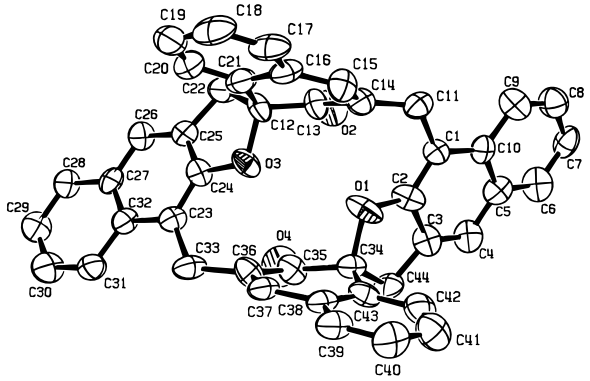
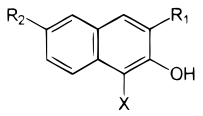


Figure 3. Crystal structure and numbering scheme used in X-ray analysis of **13.**

used in the X-ray analysis of **13**, which is depicted here as the (3*S*,23*S*) enantiomer and is the naphthalene analogue of Biali *et al.*'s compound **4A**.[2] NOED experiments confirmed that this conformation also exists in solution. Thus, irradiation of the aromatic doublets centered at 7.91 ppm (H-15, H-35) simultaneously enhances the two methylene doublets at 3.73 (H_e-12, H_e-32) and 4.50 (H_a-12, H_a-32). This cross-coupling through-space could not occur unless in solution the molecule adopts the same conformation as was depicted in structure **13**. On the basis of the *J* values and NOED experiments, the pair of doublets centered at 3.42/4.01 ppm are coupled to each other and the pair of doublets at 3.73/4.50 ppm are coupled to each other. Inspection of molecular models reveals that the "equatorial" protons H_e-12 (H_e-32) are in closer proximity to the cyclohexadienone protons H-10 (H-30) than are the "axial" ones (H_a-12, H_a-32).[16] The doublet at 3.73 ppm was therefore assigned to H_e-12 and H_e-32 since NOED enhancement occurs for cyclohexadienone protons H-10 (H-30) at 7.01 ppm when this doublet was irradiated.

The *tert*-butyl-substituted calix[4]naphthalene **12** could be synthesized in 30% yield from the corresponding 6-*tert*-butyl-3-(hydroxymethyl)-2-naphthol (**15**) using Andreetti



15: X = H ; $R_1 = CH_2OH$; $R_2 = C(CH_3)_3$
16: X = H ; $R_1 = CO_2CH_3$; R_2 = H
17: X = Br; $R1 = CO_2CH_3$; R_2 = H
18: X = H ; $R1 = CO_2CH_3$; $R_2 = C(CH_3)_3$
19 : X = H ; $R_1 = CH_2OH$; R_2 = H

and co-workers' $TiCl_4$ conditions.[14] The precursor compound **15** was synthesized according to the Friedel–Crafts methodology for *tert*-butylation of naphthols previously reported.[17] In this synthetic approach, methyl 3-hydroxy-2-naphthoate (**16**) was initially brominated to block the 4-position to give **17**. When **17** was treated with $AlCl_3$/*tert*-butyl chloride, only the debrominated product **18** was obtained in 50% yields. Blocking the 4-position with a bromine atom was therefore deemed to be unnecessary, and indeed, **16** itself afforded **18** directly in 73% yield. The position of *tert*-butyl substitution was determined by NOED determinations.[17] Lithium aluminum hydride reduction of **18** gave **15** in 90% yield. Self-condensation of **15** using $TiCl_4$ gave **12** in 27–31% yields. These yields compare very favorably with the cyclotetramerizationof 3-(hydroxymethyl)-2-naphthol, **19**, which affords **11** in only 13–15% yields. As with **11**, the *tert*-butyl compound **12** is also conformationally flexible at ambient temperature since the methylene protons appear as a sharp singlet in its ambient-temperature ^{1}H NMR spectrum. At lower temperatures, it clearly freezes in a *cone* or *crown* conformation,[18] since the methylene bridge splits into a cleanly resolved AB quartet.

The *tert*-butyl compound **12** was oxidized to spirodienone derivatives using similar reaction conditions as were used for **11**. With **12**, however, two products were obtained in 20% yield for the least polar one (**20**) and in 30% yield for the other (**21**). Both products were yellow, and IR spectroscopy confirmed that the two products contained carbonyl groups (**20**, 1681 cm^{-1}; **21**, 1681 cm^{-1}) and no hydroxyl groups. Their ^{13}C NMR spectra revealed carbonyl signals at 194.4 and 195.5 ppm for **20** and **21**, respectively, and signals at 85.1 and 82.9 ppm, respectively, which were assigned to the spiro carbons C-3, C-23. Both spectra had 18 signals in the 111–154 ppm region corresponding to the aromatic carbons and six aliphatic signals in the region 20.0–34.0 ppm. The ^{1}H NMR spectra of **20** and **21** displayed similar patterns for

(16) In this paper, "axial" protons, indicated by the subscript "a", refer to bridging methylene group protons that are directed above, or below, the annulus; "equatorial" protons, indicated by the subscript "e", refer to bridging methylene group protons that are pointing away from and are out of the plane of the annulus; the methylene protons on the tetrahydrofuran rings are designated "α" or "*β*" to designate those that are located, respectively, below, or above the plane of the annulus, as depicted in formulas **13**, **14**, **20**, and **21**.

(17) Georghiou, P. E.; Ashram, M. *J. Org. Chem.* **1995**, *60*, 2909.

(18) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989.

the methylene region, consisting of four doublets in a ratio of 1:1:1:1. The spectrum of compound **21** indicated two *tert*-butyl signals, at 1.22 and 1.42 ppm, and four doublets at 3.41 (J = 16.5 Hz), 3.68 (J = 16.2 Hz), 3.98 (J = 16.5 Hz), and 4.49 ppm (J = 16.2 Hz). COSY confirmed that the doublets at 3.41 and 3.98 ppm were coupled and that the doublets at 3.68 and 4.49 ppm are coupled. The spectrum of compound **20** displays two *tert*-butyl signals at 1.21 and 1.47 ppm and four doublets at 3.71 (J = 17.1, Hz), 3.73 (J = 15.6 Hz), 4.04 (J = 15.6 Hz), and 4.38 ppm (J = 16.8 Hz). These spectra are consistent only with structures **20** and **21**, which possess C_i and C_2 symmetry, respectively.

The geminal coupling constant values for the methylene protons in both bis(spirodienones) **13** and **21** are almost equal (16.5 Hz), which suggested that the conformation of bis(spirodienone) **21** could be similar to that of bis(spirodienone) **13**. NOED determinations on **21** confirmed this by revealing that irradiation of the aromatic doublet centered at 7.87 ppm simultaneously enhanced the coupled doublets at 3.68 and 4.49 ppm. These aromatic and methylene doublets therefore correspond to H-15/H-35 and H-12/H-32, respectively. Indeed, inspection of molecular models and molecular modeling calculations reveals that, among several possible conformations, the conformation of bis(spirodienone) **21** in which the two carbonyl groups are syn to each other is the only conformation in which the aromatic protons H-15 (H-35) are in close proximity to the methylene protons H-12 (H-32) with the $C_{15}-H_{15}$ and $C_{35}-H_{35}$ bonds approximately bisecting the $H_{12a}-C_{12}-H_{12e}$ and $H_{32a}-C_{32}-H_{32e}$ bond angles, respectively. The other methylene protons H-2 (H-22), which are part of the tetrahydrofuran rings, are bisected by the aromatic protons H-20 (H-40) that appear as a singlet in the aromatic region. The remainder of the NOED data are in accordance with this conclusion. Thus, irradiation of the aromatic singlet signal at 7.09 ppm resulted in enhancement of one methylene doublet of H-12 (H-32) at 3.68 ppm, clearly indicating that these protons are in close proximity to one another. Therefore, we assigned the doublet at 3.68 ppm to the equatorial protons H-12 (H-32) and the singlet at 7.09 ppm to the cyclohexadienone protons H-10 (H-30).

The ^{1}H NMR spectrum of compound **20** revealed two *tert*-butyl signals at 1.21 and 1.47 ppm and four doublets centered at 3.71 (J = 17.1 Hz), 3.73 (J = 15.6 Hz), 3.75 (J = 15.6 Hz), and 4.38 ppm (J = 16.8 Hz). COSY revealed that the doublets centered at 3.71 and 4.38 ppm are coupled to each other, whereas the doublets centered at 3.73 and 4.04 ppm are coupled to each other. The doublets at 3.71 and 4.38 ppm (J = 16.9 Hz) were assigned to the methylene protons, which are part of the five-membered rings, by comparison with the correspondingly larger coupling constant value, noted in the bis(spirodienone) derived from calix[4]arenes.[1,2] The conformation of compound **20** was assigned with the aid of NOED determinations, which revealed that irradiation of the aromatic doublet (H-15, H-35) centered at 8.03 ppm simultaneously enhanced the methylene doublet at 3.73 ppm (H_e-12, H_e-32) and the aromatic singlet at 6.83 ppm (H-10, H-30) and *vice versa*. Also, irradiation of the aromatic doublet at 7.26 ppm (H-5, H-25) enhanced only the methylene doublet at 3.71 ppm (H_b-2, H_a-22). Inspection of molecular models suggests that among several conformational possibilities the one in which each pair of carbonyl and ether oxygens are pointing in different directions (C_i symmetry) is the only conformation that is consistent with the NOED observations made above. Indeed, this NOED prediction was confirmed by single-crystal X-ray crystallography. The structure thus obtained is shown in Figure 4, which includes the numbering scheme used in the X-ray analysis.

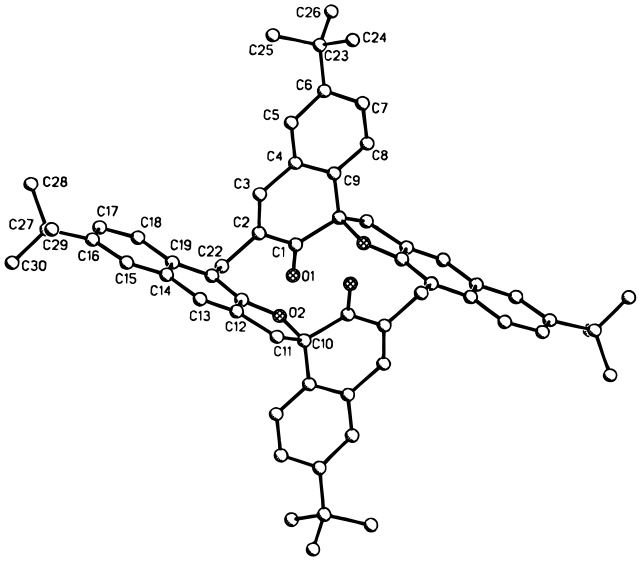


Figure 4. Crystal structure and numbering scheme used in X-ray analysis of **20**.

When calix[4]naphthalene **12** was oxidized under milder conditions (aqueous saturated $NaHCO_3$ at 0 °C, 4 h) a new major product, mono(spirodienone) **22** (36%), was obtained in addition to bis(spirodienones) **20** and **21** (18% and 26% yields, respectively). Its spectroscopic properties are consistent with structure **22**. Its ^{1}H NMR spectrum displays four *tert*-butyl signals (1.33, 1.39, 1.42, and 1.43 ppm), and eight doublets for the methylene protons (3.54, 4.00, 4.06, 4.12, 4.36, 4.37, 4.54, and 4.61 ppm), and its ^{13}C NMR spectrum shows signals at 85.1 and 194.3 ppm corresponding to the spiro and carbonyl carbons, respectively. Its IR spectrum confirmed the presence of a carbonyl group (1,677 cm^{-1}) and also of hydroxyl group(s) (3,368 cm^{-1}).

In conclusion, it has been shown that calix[4]naphthalenes in which hydroxyl groups are situated intraaanularly can be oxidized under conditions similar to those described by Biali *et al.* to form the bis(spirodienone) **13** from **11** and bis(spirodienones) **20**−**22** from **12**. The prototype calix[4]naphthalenes **9** and **10** previously reported by us and which contain similar 1,5 dihydroxy functionalities failed to afford the analogous spirodienones. Model studies with the bis(1-hydroxy-2-naphthyl)methanes **8**−**8f** provided support for the putative mechanism proposed for the formation of spirodienone derivatives of calix[4]arenes and calix[4]naphthalenes.

Experimental Section

For general experimental conditions and instrumentation employed, see ref 2.

Spironaphthalenone (7a). General Procedure. To a solution of **8a** (175 mg, 0.39 mmol) in CH_2Cl_2 (10 mL) was added a solution of phenyltrimethylammonium tribromide (PTMATB) (145 mg, 0.39 mmol) in 2 mL of CH_2Cl_2 at room temperature. An aqueous 28% solution of NaOH (6.5 mL) was

added dropwise at room temperature. The reaction was left stirring at room temperature for 1 h. The reaction mixture was diluted with 20 mL of CH_2Cl_2. The organic layer was separated and washed with 20 mL of brine followed by 20 mL of water. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent removed on a rotary evaporator. The crude product was purified by PLC on silica gel using CH_2Cl_2:petroleum ether 1:1 to give **7a** as yellow crystals (62 mg, 36%): mp 185−188 °C dec; IR ($CHCl_3$, cm^{-1}) 1693, 1589, 1451, 1388, 1358, 1297, 1271, 1190, 1090, 758; ^1H NMR ($CDCl_3$) δ 3.45 (d, J = 15.6 Hz, 1H), 3.80 (d, J = 15.6 Hz, 1H), 6.88 (s, 1H), 7.47−7.58 (m, 3H), 7.60 (s, 1H), 7.72−7.80 (m, 2H), 7.96 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 40.8, 87.6, 113.8, 118.4, 121.4, 122.1, 122.4, 126.1, 126.4, 127.3, 127.5, 128.0, 128.3, 128.6, 123.0, 132.0, 134.4, 135.3, 135.5, 194.4; MS m/z 458 ($M^{+81}Br^{81}Br$, 7), 456 ($M^{+81}Br^{79}Br$, 14), 454 ($M^{+79}Br^{79}Br$, 8), 442 (12), 441 (49), 440 (25), 439 (100), 438 (13), 437 (52), 377 (17), 375 (17), 296 (11), 222 (5), 188 (9), 187 (12), 148 (12), 139 (13), 134 (36); HRMS M^+ 453.9182, calcd for $C_{21}H_{12}Br_2O_2$ 453.9204.

Spironaphthalenone 7b. Compound **8b** was oxidized as above to give **7b** as yellow crystals (39%): mp 175−177 °C dec; IR ($CHCl_3$, cm^{-1}) 1693, 1593, 1511, 1452, 1391, 1362, 1271, 1191, 1091, 759; ^1H NMR ($CDCl_3$) δ = 3.43 (d, J = 15.5 Hz, 1H), 3.79 (d, J = 15.6 Hz, 1H), 6.61 (s, 1H), 7.40 (s, 1H), 7.47−7.59 (m, 3H), 7.72−7.82 (m, 2H), 7.95 (d, J = 8.1, 1H), 8.09 (d, J = 8.7 Hz, 1H), 8.20 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 41.1, 86.8, 117.9, 121.1, 122.1, 122.6, 124.0, 124.8, 125.9, 126.4, 127.1, 128.1, 128.2, 130.0, 130.1, 130.8, 131.5, 134.7, 135.4, 153.1, 194.3; MS m/z 368 (M^+ + 2, 9), 367 (M^+ + 1,4), 366 (M^+, 16), 353 (13), 352 (16), 351 (68), 350 (24), 349 (100), 331 (16), 239 (22), 237 (9), 202 (10), 166 (9), 134 (11); HRMS M^+ 366.0274, calcd for $C_{21}H_{12}Cl_2O_2$ 366.0214.

Oxidation of Bis(1-hydroxy-2-naphthyl)methane (8). (a) Using 1 equiv of PTMATB at reflux temperature for 48 h produced **8d** as a light brown solid: mp 161−163 °C; ^1H NMR (acetone-d_6) δ = 4.37 (s, 2H), 7.41−7.51 (m, 4H), 7.53−7.63 (m, 2H), 7.74 (s, 1H), 7.80−7.83 (m, 1H), 8.05−8.08 (m, 1H), 8.27−8.35 (m, 2H); ^{13}C NMR (acetone-d_6) δ = 30.95, 113.1, 121.6, 122.2, 122.3, 122.5, 123.3, 123.8, 126.0, 126.2, 126.4, 126.5, 126.9, 127.4, 127.7, 128.0, 128.7, 129.5, 132.3, 132.9, 134.8; MS m/z 380 (1), 378 (2), 300 (2), 281 (4), 225 (5), 224 (21), 223 (7), 222 (22), 145 (30), 144 (100); HRMS M^+ 378.0277, calcd for $C_{21}H_{15}79BrO_2$ 378.0255.

(**b**) Using 3 equiv of PTMATB at room temperature for 1.5 h produced after purification by PLC on silica gel using $CHCl_3$: petroleum ether 50:50 yellow crystals whose mp and spectroscopic properties were identical to those of **7a**.

Bis(1-hydroxy-2-naphthyl)methane (8). To a solution of bis(1-methoxy-2-naphthyl)methane[12] (0.50 g, 1.5 mmol) in 25 mL of anhydrous CH_2Cl_2 maintained at −78 °C and under N_2 was added BBr_3 (0.58 mL, 6.2 mmol) dropwise with stirring. The reaction was stirred at −78 °C for 5 h, at −20 °C for 1 h, at 0 °C for 1 h, and finally at room temperature for 2 h. Aqueous saturated $NaHCO_3$ was added dropwise until the mixture became basic. A precipitate formed that was filtered and washed several times with aqueous saturated $NaHCO_3$ and then with water. Oven drying (at <100 °C, overnight) gave **8** as a light brown solid, 0.37 g (82%): mp 168−170 °C; ^1H NMR ($CDCl_3$) δ = 4.28 (s, 2H), 6.73 (s, 2H, 2OH), 7.45 (m, 4H), 7.76 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 31.4, 120.4, 120.6, 121.2, 125.6, 125.7, 127.9, 128.3, 147.7; MS m/z (%) 301 (M^+ + 1, 1), 300 (M^+, 8), 296 (4), 282 (27), 281 (60), 157 (9), 156 (34), 145 (12), 144 (100), 141 (11), 128 (29), 127 (10), 126 (11), 116 (12), 115 (29).

Bis(4-bromo-1-hydroxy-2-naphthyl)methane (8a). Bis-(4-bromo-1-methoxy-2-naphthyl)methane (**8e**)[12] (0.75 g, 1.6 mmol) was demethylated with BBr_3 (0.58 mL, 6.2 mmol) exactly as described above for **8** to give **8a** as a brown solid, 0.54 g (77%): mp 205−208 °C dec; ^1H NMR (acetone-d_6) δ = 4.40 (s, 2H), 7.47−7.65 (m, 4H), 7.79 (s, 2H), 8.07−8.10 (m, 2H), 8.34−8.37 (m, 2H), 9.05 (s, 2H); ^{13}C NMR (acetone-d_6) δ = 30.8, 79.3, 113.5, 123.3, 123.6, 127.2, 127.6, 128.2, 132.5, 132.9; MS m/z 440 (M^+-O, 1.4), 439 (M^+-OH, 4), 362 (1), 361 (6), 359 (6), 281 (5), 236 (17), 234 (16), 224 (32), 222 (36), 144 (23), 128 (11), 127 (23), 126 (12), 115 (100); HRMS M^+ 455.9382 and 457.9346, calcd for $C_{21}H_{14}{}^{79}Br_2O_2$ 455.9361 and $C_{21}H_{14}{}^{79}Br^{81}BrO_2$ 457.9340.

Bis(4-chloro-1-methoxy-2-naphthyl)methane (8f). Compound **8f** was prepared in the same manner as previously[12] described for **8e** to produce a colorless solid in 34% yield: mp 122.5−124 °C; ^1H NMR ($CDCl_3$) δ = 3.95 (s, 6H), 4.35 (s, 2H), 7.31 (s, 2H), 7.57−7.60 (m, 4H), 8.13−8.17 (m, 2H), 8.19−8.22 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 28.8, 62.3, 122.5, 124.9, 126.8, 127.4, 128.1, 128.9, 129.1, 130.9, 152.8; MS m/z 399 ($M^{+37}Cl^{35}$-Cl, 65), 396 (M^+, 100), 361 (20), 351 (22), 349 (33), 345 (13); HRMS M^+ 396.0689, calcd for $C_{23}H_{18}Cl_2O_2$ 396.0684.

Bis(4-chloro-1-hydroxy-2-naphthyl)methane (8b). To a solution of bis(4-chloro-1-methoxy-2-naphthyl)methane (**8f**) (244 mg, 0.62 mmol) in 55 mL of anhydrous benzene was added BBr_3 (0.58 mL, 6.20 mmol) dropwise, with stirring under N_2 at room temperature. The reaction was left stirring at room temperature for 24 h. The reaction was quenched by adding 5 mL of H_2O, followed by 20 mL of aqueous saturated $NaHCO_3$. The mixture was extracted with portions of $CHCl_3$ (100 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and filtered and the solvent evaporated on rotary evaporator to give **8b** as a colorless solid (150 mg, 66%): mp 207−209 °C dec; ^1H NMR (acetone-d_6) δ = 2.80 (b, 2H), 4.39 (s, 2H), 7.59 (s, 2H), 7.57−7.65 (m, 4H), 8.11−8.15 (m, 2H), 8.34−8.37 (m, 2H); ^{13}C NMR (acetone-d_6) δ = 30.7, 122.9, 123.2, 124.8, 127.1, 127.9, 129.3; MS m/z 372 (M^+ + 3, 1), 369 (M^+, 2), 368 (8), 351 (4), 331 (2), 268 (3), 250 (3), 239 (6), 180 (32), 179 (11), 178 (100), 162 (4), 144 (10), 127 (9), 115 (17); HRMS M^+ 368.0369, calcd for $C_{21}H_{14}Cl_2O_2$ 368.0370.

Calix[4]naphthalene (11). To a solution of 3-(hydroxymethyl)-2-naphthol (**19**) (0.87 g, 5.1 mmol) in dioxane (70 mL) was added $TiCl_4$ (0.61 mL, 5.5 mmol) dropwise at 60 °C under N_2. The mixture was refluxed for 36 h. Workup of the reaction mixture was effected by first evaporating the dioxane under vacuum. The crude product was dissolved in 30 mL of $CHCl_3$, and the resulting mixture was subjected to flash chromatography on silica gel using CH_2Cl_2−petroleum ether (1:1) to give **11** as a light brown solid (0.104 g, 13%): mp >300 °C dec (lit.[14] mp 384−386 °C); IR (Nujol, cm^{-1}) 3406 (br, OH), 1256, 1182, 1091, 1048, 844, 747; ^1H NMR ($CDCl_3$) δ = 4.58 (s, 8H), 7.23 (dd, J = 7.8, 0.9 Hz, 4H), 7.51 (m, 4H), 7.61 (d, J = 7.8 Hz, 4H), 7.86 (s, 4H), 8.38 (d, J = 8.7 Hz, 4H), 10.96 (s, 4H); ^{13}C NMR (DMSO-d_6) δ = 25.6, 119.4, 122.8, 123.0, 125.9, 128.1, 128.4, 128.6, 129.3, 131.4, 149.7; MS m/z 626 (M^+ + 2, 12), 625 (M^+ + 1, 47), 624 (M^+, 100), 607 (9), 606 (15), 588 (7), 467 (10), 450 (8), 449 (11), 325 (8), 324 (8), 311 (21), 297 (7), 296 (8), 295 (23), 294 (11), 281 (15), 169 (38), 157 (58), 141 (19).

X-ray data for calix[4]naphthalene (11): $C_{44}H_{32}O_4$, triclinic, space group P-1 (#2), a = 12.688(2) Å, b = 14.108(4) Å, c = 11.955(2) Å, α = 98.15(2)°, β = 105.56(2)°, γ = 100.80(2)°, Z = 2, D_{calc} = 1.278 g/cm^3. Intensity data were measured at 296 K on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα (λ = 1.541 78 Å) to $2\theta_{max}$ (deg) 120.2°; a final R = 0.064 for 4487 reflections with $I > 2.00\sigma(I)$; R_w = 0.063, gof = 4.78.[19]

***tert*-Butylcalix[4]naphthalene (12).** To a solution of **15** (0.41 g, 1.8 mmol) in dioxane (60 mL) was added $TiCl_4$ (0.21 mL, 1.8 mmol) dropwise at 60 °C under N_2. The mixture was refluxed for 24−30 h. Workup of the reaction was effected by evaporating the solvent under vacuum and then dissolving the crude product in 50 mL of $CHCl_3$. Insoluble material was removed by filtration. The solution was concentrated to about 10 mL and subjected to flash chromatography on silica gel using CH_2Cl_2−petroleum ether (1:1) to give **12** as a light brown solid (102 mg, 31%): mp 246−249 °C dec; IR (Nujol, cm^{-1}) 3284 (br, OH), 1305, 1232, 1162, 1097, 899; ^1H NMR ($CDCl_3$) δ = 1.32 (s, 36H), 4.52 (s, 8H), 7.51 (d, J = 1.8 Hz, 4H), 7.58 (dd, J = 9.0, 1.8 Hz, 4H), 7.76 (s, 4H), 8.28 (d, J = 9.0 Hz, 4H), 10.62 (s, 4H); ^{13}C NMR ($CDCl_3$) δ = 26.0, 31.2, 34.4, 119.3,

(19) Atomic coordinates for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

122.6, 123.7, 125.0, 128.2, 129.2, 129.7, 129.9, 145.8, 147.6; +FAB-MS *m/z* 848 (M^+, 17), 847 (6), 829 (11), 813 (5), 811 (11), 630 (4), 619 (5), 618 (5), 617 (8), 545 (3), 437 (16), 425 (7), 423 (11), 407 (18), 406 (9), 393 (13), 391 (12), 389 (7), 377 (11), 367 (10), 351 (11), 289 (12), 265 (12), 253 (10), 252 (11).

Bis(spirodienone) 13 Derived from 11. General Procedure. To a solution of calix[4]naphthalene **11** (40 mg, 0.064 mol) in CH_2Cl_2 (7 mL) was added PTMATB (48 mg, 0.128 mmol) in one portion, followed by aqueous 28% NaOH (0.255 g) at room temperature under N_2. The reaction was refluxed for 2 h, then the reaction mixture was cooled to room temperature and diluted with 15 mL of $CHCl_3$ and 10 mL of water. The organic layer was separated and washed with 10 mL of brine followed by 10 mL water. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude product was purified by PLC on silica gel using $CHCl_3$ to give **13** as yellow crystals (13 mg, 30%): mp 248−250 °C dec; IR ($CHCl_3$, cm^{-1}) 3070, 3025, 2926, 1678, 1636, 1435, 1384, 1261, 1149, 1097, 976, 750.3; ^{1}H NMR ($CDCl_3$) δ = 3.42 (d, *J* = 16.5 Hz, 2H), 3.73 (d, *J* = 16.5 Hz, 2H), 4.01 (d, *J* = 16.5 Hz, 2H), 4.50 (d, *J* = 16.2 Hz, 2H), 6.80−6.83 (m, 2H), 7.01 (s, 2H), 7.03−7.07 (m, 4H), 7.19 (dd, *J* = 2.4, 6.5 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.57 (s, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.40, 2H); ^{13}C NMR ($CDCl_3$) δ = 29.2, 41.7, 83.1, 112.0, 121.8, 122.4, 123.2, 125.8, 126.9, 128.0, 128.3, 128.6, 128.7, 129.7, 130.0, 130.8, 133.2, 134.3, 140.0, 141.4, 154.3, 195.4; MS *m/z* 620 (M^+, 51), 619 (100), 602 (25), 601 (35), 592 (10), 587 (11), 574 (17), 377 (8), 376 (10), 335 (12), 311 (19), 310 (25), 309 (13), 297 (11), 296 (14), 295 (29), 294 (20), 293 (15), 282 (17), 281 (39), 280 (11), 279 (10).

X-ray data for bis(spirodienone) 13: $C_{44}H_{28}O_4$, monoclinic, space group $P2_1/n$ (#14), a = 13.744(3) Å, b = 11.839(5) Å, c = 18.438(4) Å, β = 94.12(2)°, Z = 4, D_{calc} = 1.378 g/cm^3. Intensity data were measured at 296 K on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα (λ = 0.710 69 Å) to $2\theta_{max}$ (deg) 50.1°; a final R = 0.101 for 2061 reflections with $I > 2.00\sigma(I)$; R_w = 0.088, gof = 3.38.[19]

Oxidation of *tert*-Butylcalix[4]naphthalene (12). Compound **12** was oxidized as above, but the crude product was purified by PLC on silica gel using CH_2Cl_2:petroleum ether 50:50 to give two yellow products, **20** and **21**. Compound **20** was the less polar of the two.

Bis(spirodienone) 20. Bis(spirodienone) **20** was isolated as dark yellow crystals (19.0 mg, 20%): mp > 300 °C dec; IR ($CHCl_3$, cm^{-1}) 2962, 2869, 1681, 1603, 1451, 1410, 1363, 1096, 991; ^{1}H NMR ($CDCl_3$) δ = 1.21 (s, 18H), 1.47 (s, 18H), 3.71 (d, *J* = 17.1 Hz, 2H), 3.73 (d, *J* = 15.6 Hz, 2H), 4.04 (d, *J* = 15.6 Hz, 2H), 4.38 (d, *J* = 16.8 Hz, 2H), 6.83 (d, *J* = 1.8 Hz, 2H), 7.00 (d, *J* = 1.8 Hz, 2H), 7.16 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.62 (dd, *J* = 9.0, 1.8 Hz, 2H), 7.69 (s, 2H), 7.79 (d, *J* = 1.8 Hz, 2H), 8.03 (d, *J* = 9.0, 2H); ^{13}C NMR ($CDCl_3$) δ = 21.9, 31.0, 31.4, 34.6, 34.9, 85.1, 114.9, 121.7, 123.0, 123.8, 124.8, 126.0, 126.7, 127.0, 129.7, 130.0, 131.0, 131.7, 135.5, 135.7, 141.7, 145.4, 152.7, 153.6, 194.4; FAB MS *m/z* 867 ($M^+ + Na^+$, 45), 844 (M^+, 57), 843 (30), 842 (11), 841 (13), 811 (31), 799 (12), 783 (10), 771 (16), 631 (11), 617 (16), 615 (14), 603 (12), 589 (10), 587 (10), 575 (10), 573 (11), 423 (21), 407 (34), 377 (35), 265 (41), 213 (100).

X-ray data for bis(spirodienone) 20. $C_{60}H_{60}O_4 \cdot 2CH_3CN \cdot 2CHCl_3$, triclinic, space group P-1 (#2), a = 12.455(4) Å, b = 13.527(3) Å, c = 9.6046(19) Å, α = 100.216(19)°, β = 102.082(2)°, γ = 85.77(3)°, Z = 1, D_{calc} = 1.244 g/cm^3. Intensity data were measured at 296 K on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα (λ = 1.541 78 Å) to $2\theta_{max}$ (deg) 60.08°; refinement on F^2, R_1 = 0.0983 for 3036 reflections with $I > 2.00\sigma(I)$; R_{2w} = 0.3418, gof = 1.328 for all reflections.[19]

Bis(spirodienone) 21. Bis(spirodienone) **21** was isolated as light yellow crystals (29 mg, 30%): mp softens 265−270 °C, melting 270−272 °C; IR ($CHCl_3$, cm^{-1}) 2952, 2904, 2869, 1681, 1504, 1447, 1426, 1363, 1269, 1099, 979; ^{1}H NMR ($CDCl_3$) δ = 1.22 (s, 18h), 1,42 (s, 18H), 3.41 (d, *J* = 16.5 Hz, 2H), 3.68 (d, *J* = 16.2 Hz, 2H), 3.98 (d, *J* = 16.5 Hz, 2H), 4.49 (d, *J* = 16.2 Hz, 2H), 6.98 (d, *J* = 1.8 Hz, 2H), 7.09 (s, 2H), 7.10 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H,), 7.53 (s, 2H), 7.57 (d, *J* = 1.8 Hz, 2H), 7.69 (d, *J* = 1.8 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 30.3, 31.1, 31.4, 31.5, 34.5, 41.9, 82.9, 111.2, 121.5, 122.1, 123.5, 124.3, 124.8, 125.7, 127.1, 129.6, 129.9, 130.8, 131.2, 134.3, 138.7, 140.3, 145.5, 151.6, 154.1, 195.5; FAB MS *m/z* 882 ($M^+ + K^+$, 18), 868 (100), 867 ($M^+ + Na^+$, 15).

3-(Hydroxymethyl)-2-naphthol (19). A solution of **16** (1.88 g, 9.31 mmol) in anhydrous THF (30 mL) was added at room temperature to a suspension of LAH (0.71 g, 19 mmol) in dry THF (50 mL) over 30 min and the mixture stirred at room temperature for 3 h. The reaction was quenched by pouring the suspension into cold, wet diethyl ether, then the mixture was treated with aqueous 10% HCl at 0 °C. The ether layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and evaporated to give a pale yellow solid, 1.52 g (94%), which was crystallized for analysis from ethanol−water: mp 186−188 °C (lit.[14] mp 185 °C); ^{1}H NMR (acetone-d_6) δ = 4.50 (t, *J* = 5.7 Hz, 1H), 4.88 (d, *J* = 5.7 Hz, 2H), 7.18 (s, 1H), 7.25 (m, 1H), 7.33 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H, H-4), 8.79 (s, 1H, OH); ^{13}C NMR (acetone-d_6) δ = 61.7 (C-9), 109.7, 123.9, 126.5, 126.7, 126.9, 128.4, 129.5, 131.7, 135.1, 154.6 (C-2); MS *m/z* 174 (M^+, 28), 156 (39), 129 (12), 128 (100), 127 (15), 115 (13), 64 (13), 63 (9), 51 (9).

Methyl 7-*tert*-Butyl-3-hydroxy-2-naphthoate (18). To a solution of methyl 3-hydroxy-2-naphthoate (**16**) (307 mg, 1.52 mmol) in 1,1,2,2-tetrachloroethane (5 mL) at 0 °C under Ar was added *tert*-butyl chloride (0.66 mL, 6.1 mmol) followed by adding $AlCl_3$ (410 mg, 3.04 mmol) in portions over 15 min. The reaction solution was stirred at room temperature for 24 h. Workup was effected by adding cold water at 0 °C and then extracting with 50 mL of $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent removed by vacuum distillation. The crude product was purified by PLC on silica gel using ethyl acetate−petroleum ether (10:90) to give **18** as a light yellow solid (0.28 g, 73%): mp 102−103 °C; ^{1}H NMR ($CDCl_3$) δ = 1.39 (s, 9H, H-12), 4.02 (s, 3H, H-10), 7.27 (s, H-4), 7.62 (m, 2H, H-7, H-8), 7.71 (s, 1H, H-5), 8.46 (s, 1H, H-8), 8.46 (s, 1H, H-1), 10.93 (s, 1H, OH); ^{13}C NMR (C_6D_6) δ = 31.5 (C-12), 35.0 (C-11), 52.2 (C-10), 112.3, 114.9, 124.6, 127.0, 127.3, 128.9, 133.0, 137.3, 146.8, 157.5 (C-2), 170.9 (C-9); MS *m/z* 259 ($M^+ + 1$, 12), 258 (M^+, 67), 243 (49), 227 (23), 226 (100), 212 (15), 211 (93), 183 (16), 155 (11), 139 (11), 115 (13); HRMS M^+ 258.1246 calcd for $C_{16}H_{18}O_3$ 258.1256.

6-*tert*-Butyl-3-(hydroxymethyl)-2-naphthol (15). A solution of **18** (1.1 g, 3.9 mmol) in anhydrous THF (15 mL) was added at room temperature to a suspension of LAH (0.29 g, 7.8 mmol) in anhydrous THF (20 mL) over 40 min and the reaction mixture stirred at room temperature for 2 h. The reaction was quenched by pouring the suspension into cold, wet diethyl ether followed by addition of aqueous 10% HCl at 0 °C. After the separation of the organic layer, the aqueous layer was extracted with 30 mL of diethyl ether. The combined ether layers were dried over anhydrous $MgSO_4$, filtered, and evaporated to give **15** as a light yellow solid (0.81 g, 90%): mp 174−176 °C; ^{1}H NMR (acetone-d_6) δ = 1.38 (s, 9H), 4.87 (d, *J* = 5.4 Hz, 2H), 7.13 (s, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.73 (s, 1H), 7.79 (s, 1H), 8.68 (s, 1H); ^{13}C NMR (acetone-d_6) δ = 30.4, 62.2, 109.8, 109.9, 123.9, 125.8, 127.0, 127.5, 129.8, 131.8, 131.4, 133.7, 146.8, 154.7; MS *m/z* 231 ($M^+ + 1$, 8), 230 (48), 213 (20), 212 (100), 198 (10), 197 (59), 184 (41), 169 (32), 152 (10), 141 (10); HRMS M^+ 230.1317, calcd for $C_{15}H_{18}O_2$ 230.1307.

Partial Oxidation of Calix[4]naphthalene (12). To a solution of calix[4]naphthalene (**12**) (55 mg, 0.45 mmol) in CH_2Cl_2 (5 mL) was added PTMATB (24 mg, 0.45 mmol) at 0 °C followed by the addition of 5 mL of aqueous saturated $NaHCO_3$ at 0 °C. The reaction was left to stir at 0 °C for 4 h. The reaction mixture was worked up by diluting the reaction mixture with 10 mL of chloroform and 10 mL of water. The organic layer was separated and washed first twice with 20 mL of brine and then with 10 mL of water. The crude product was purified by PLC on silica gel using benzene/hexane 50:50 to give according to their increasing polarity the following three

products: **Bis(spirodienone) 20**: 10 mg (18%) whose melting point and spectroscopic properties are identical to those of **20** isolated above. **Spirodienone 22**: orange solid (36%); mp 278−280 °C; IR ($CHCl_3$, cm^{-1}) 3368 (br, OH), 2870, 1677 (CO), 1607, 1506, 1450, 1364, 1231, 1097, 998, 923, 818; ^1H NMR ($CDCl_3$) δ = 1.33 (s, 9H), 1.39 (s, 9H), 1.42 (s, 9H), 1.43 (s, 9H), 3.54 (d, J = 17.7 Hz, 1H), 4.00 (d, J = 15.9 Hz, 1H), 4.06 (d, J = 15.9 Hz, 1H), 4.12 (d, J = 18.0 Hz, 1H), 4.36 (d, J = 15.6 Hz, 1H), 4.37 (d, J = 14.7 Hz, 1H), 4.54 (d, J = 14.7 Hz, 1H), 4.61 (d, J = 14.7 Hz, 1H), 7.31 (s, 1H), 7.44 (s, 1H), 7.49 (br s, 1H), 7.52 (m, 1H), 7.55−7.58 (m, 3H), 7.62 (br s, 1H), 7.64−7.68 (m, 3H), 7.73 (s, 1H), 7.75 (br s, 1H), 8.10 (d, J = 9 Hz, 1H), 8.28 (br, OH), 8.32 (d, J = 9.3 Hz, 1H), 8.37 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 24.91, 25.5, 28.6, 31.1, 31.3, 34.4, 34.5, 34.75, 39.4, 85.1, 114.4, 119.7, 121.6, 121.8, 122.3, 122.4, 122.8, 123.4, 123.9, 124.3, 124.9, 125.0, 126.6, 126.7, 127.5, 127.8, 128.2, 128.3, 129.5, 129.9, 130.2, 130.8, 135.1, 136.7, 143.6, 144.9, 145.2, 145.7, 146.1, 148.9, 150.1, 152.4, 153.3, 194.3; +FAB MS m/z 846 (M^+, 10), 830 (12), 829 (21), 828 (16), 813 (14), 812 (23), 811 (34), 614 (11), 423 (13), 407 (24), 406 (14), 405 (12). **Bis(spirodienone) 21**: 14 mg (26%) whose melting point and spectroscopic properties are identical to those of **21**, described above.

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Supporting Information Available: High-resolution ^1H and ^{13}C NMR spectra and mass spectra of compounds **7a**,**b**, **8**, **8a**,**b**,**d**,**e**, **11**−**13**, **15**, **18**, **20**−**22** and X-ray crystallographic data for **11, 13,** and **20** (148 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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