°C prior to the addition of a premixed solution of chlorotrimethylsilane (0.8 mL, 6.5 mmol) and triethylamine (1.4 mL, 9.75 mmol) in THF (5 mL). The reaction mixture was stirred at -78 °C for 60 min, allowed to warm slowly to 25 °C over 12 h, recooled to 0 °C, and quenched with saturated NH_4Cl solution (20 mL). Following dilution with ether (20 mL), the organic phase was washed with brine (2 × 10 mL) and the combined aqueous layers were extracted with ether. The ethereal solutions were dried and evaporated to leave a residue, which was chromatographed on silica gel (elution with hexanes) to give 46 mg (75%) of **13** as a clear colorless oil: IR (CCl_4, cm^{-1}) 1605, 1495, 1387, 1368, 1255, 1115, 1087, 1046, 1012, 946, 850; ^1H NMR (300 MHz, C_6D_6) δ 6.44 (m, 1 H), 6.41 (s, 1 H), 5.66 (m, 1 H), 5.62 (m, 1 H), 3.07 (dd, J = 20.6, 2.5 Hz, 1 H), 2.97 (dd, J = 20.6, 5.1 Hz, 1 H), 1.88 (dt, J = 16.9, 2.5 Hz, 1 H), 1.7 (ddd, J = 16.9, 5.4, 1.2 Hz, 1 H), 1.53 (s, 3 H), 1.21 (s, 3 H), 1.11 (s, 3 H), 0.26 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 161.0, 158.2, 147.4, 131.2, 124.6, 120.4, 118.1, 113.4, 41.7, 39.8, 35.6, 30.8, 29.41, 29.37, 24.7, -1.3 (3 C); MS m/z (M^+) calcd 286.1753; obsd 286.1722.

Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.01; H, 9.08.

Trimethyl(*trans*-4,5,5a,6,7,8,9,9a-octahydro-6,6,9a-trimethylnaphtho[1,2-*b*]furan-2-yl)silane (14). The hydrogenation of **13** (30 mg, 0.105 mmol) was affected as before except that an additional 30 mg of 5% Pd/C was added after 48 h and reduction was allowed to proceed for an additional day. Comparable workup furnished 21 mg (68%) of **14** as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1460, 1382, 1303, 1122; ^1H NMR (300 MHz, $CDCl_3$) δ 6.37 (s, 1 H), 2.52-2.32 (m, 2 H), 1.82 (dd, J = 13.2, 6.4 Hz, 1 H), 1.72 (dt, J = 13.7, 3.4 Hz, 1 H), 1.59-1.21 (series of m, 7 H), 1.19 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H), 0.21 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 164.3, 157.4, 120.3, 113.8, 52.4, 42.0, 36.9, 35.4, 33.5, 33.0, 22.6, 21.2, 19.6, 18.6, -1.5 (3 C); MS m/z (M^+) calcd 290.2066, obsd 290.2071.

Anal. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41. Found: C, 74.39; H, 10.51.

Desilylation of 14. To a solution of **14** (11 mg, 0.037 mmol) in THF (1 mL) was added 1 mL of 1 M tetra-*n*-butylammonium fluoride solution in THF, and the mixture was stirred at reflux for 8 h, cooled, and diluted with ether (5 mL) prior to washing with brine (2 × 5 mL). The organic phase was dried and concentrated to leave a residue that was chromatographed on silica gel (elution with hexanes). There was obtained 5 mg (66%) of racemic **1**.

Acknowledgment. We thank the National Institutes of Health (GM30827) for generous financial support of this research.

A Rapid, Convergent, and Regioselective Synthesis of Anthracenes

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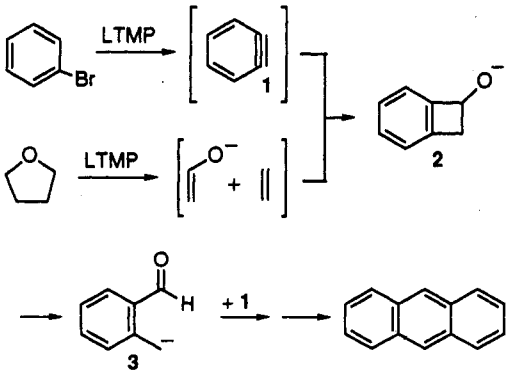
Anthracenes are obtained in moderate to good yield by the simultaneous treatment of benzocyclobutenols and halobenzenes with LTMP in tetrahydropyran. In the key step of this one-pot process, *o*-toluoyl anion intermediates from the known ring-opening of benzocyclobutenoxides add to halobenzene derived arynes. Methoxy-substituted benzocyclobutenols which are readily made regiospecifically by known methods also react regiospecifically with the single benzyne generated from either a 2- or 3-haloanisole. For example, the only trimethoxyanthracene isolated (48% yield) from the reaction of 6-methoxybenzocyclobutenol (**8**) with 5-chloro-1,3-dimethoxybenzene is the 1,3,8-isomer **20**. When 1,2-dihydrocyclobuta[*l*]phenanthren-1-ol (**14**) and/or halonaphthalenes are the reactants, benzannulated anthracenes are formed; e.g., tribenz[*a*,*c*,*h*]anthracene in 68% yield from **14** and bromonaphthalene. In another extension, pentaphene (**31**) was made in one pot from *o*-dichlorobenzene.

As part of a study on O-demethylation, we recently wanted several methoxyanthracenes. However, an examination of the literature indicated that the most desired compounds either were unknown or available only by multistep routes although related anthraquinones have received much attention as dye precursors and recently as anticancer agents. In the search for methodology for adaptation, the Fleming-Mah[1] synthesis of anthracene by treatment of bromobenzene with lithium 2,2,6,6-tetramethylpiperidide (LTMP) in refluxing THF was noted. In this process, an intermediate benzyne (**1**) reacts with acetaldehyde enolate (from metalation-fragmentation of THF by LTMP) to give benzocyclobutenoxide (**2**). This tautomerizes to the *o*-toluoyl anion **3** which adds to more **1** (two step anionic or [4 + 2] electrocyclic process) to produce anthracene after dehydration.



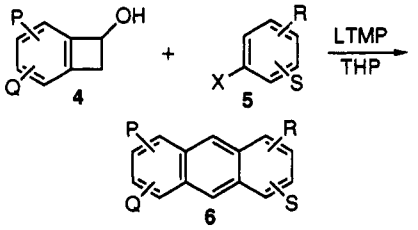
The success of the reaction depends on the fact that LTMP is an extremely poor trap for benzynes.[2] It is also important that **3** is generated in the absence of its conjugate acid and thus is not trapped in a self aldol condensation. Finally it is known that both *o*- and *m*-haloanisoles are converted to *o*-benzynes with bases and that the latter react with nucleophiles entirely at the 3-position.[3] Thus,

(1) Fleming, I.; Mah, T. *J. Chem. Soc. Perkin Trans 1* **1975**, 964.
(2) Dougherty, C. M.; Olofson, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 581, 582.
(3) Gilchrist, T. L. In *Arynes, The Chemistry of Functional Groups; Supplement C: The Chemistry of Triple Bonded Functional Groups*; Patai, S.; Rappoport, Z., Eds.; Wiley Interscience: New York, **1983**; Chapter 11.

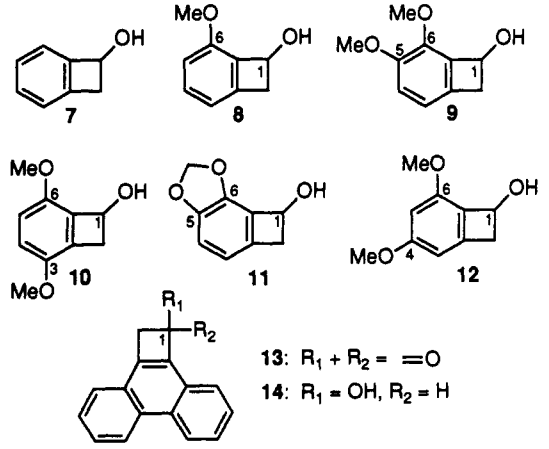
0022-3263/92/1957-7122$03.00/0

3-bromoanisole should be and indeed is converted exclusively to 1,8-dimethoxyanthracene under Fleming–Mah conditions as reported in a recent publication from this laboratory.[4]

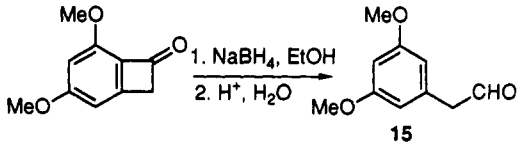
More interesting was the possibility of extending the Fleming–Mah scheme to the synthesis of unsymmetrical anthracenes. Here success would depend on the accessibility of substituted benzocyclobutenols and the discovery of a solvent which could facilitate reaction without undergoing a THF-type fragmentation. While benzocyclobutenol itself is easily made by diazotization of anthranilic acid in the presence of vinyl acetate,[5] this approach is not useful in the preparation of most substituted benzocyclobutenols. However, the latter are often available regiospecifically by methodology developed by Stevens and Bisacchi[6] and recently improved by Liebeskind.[7] In this process, a haloarene is dehydrohalogenated with $NaNH_2$ in the presence of ketene dimethyl- or diethylacetal, and the crude dimethoxybenzocyclobutene from a [2 + 2] cycloaddition is hydrolyzed quantitatively to the benzocyclobutenone with aqueous hydrochloric acid at room temperature.[6,7] High yield reduction to the alcohol with $NaBH_4$ completes the synthesis. The recent discovery by Choy and Yang[8] that benzocyclobutenoxides (unlike benzocyclobutenols) undergo ring-opening below room temperature further encouraged us to test the hypothetical scheme, **4** + **5** → **6**, with tetrahydropyran (THP) as the proposed reaction solvent.



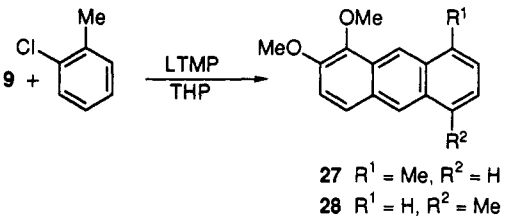
With this background, **7** was made[5] and the known benzocyclobutenones corresponding to alcohols **8**–**12** were prepared as described above.[6,7] The previously unknown 2*H*-cyclobuta[*l*]phenanthren-1-one (**13**) similarly was synthesized from 9-bromophenanthrene in 44% yield.



Standard $NaBH_4$ reduction[9] smoothly converted these benzocyclobutenones to the known alcohols **8**[9] and **10**[10] and the previously unknown alcohols **9**, **11**, and **14** in 90–99% yield. However, attempts to reduce 4,6-dimethoxybenzocyclobutenone gave only (3,5-dimethoxyphenyl)acetaldehyde[11] (**15**), presumably from ring opening of an intermediate **12** during workup. This proximal bond scission is unusual but has been noted in the basic hydrolysis of a few benzocyclobutenones.[12–14] The present reaction is not in accord with the literature rationale[12] for this cleavage.



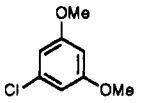
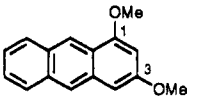
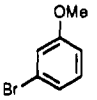
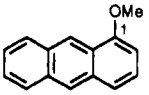
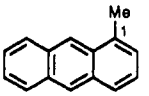
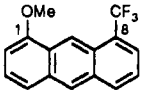
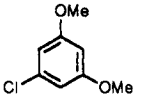
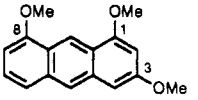
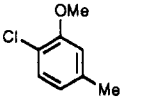
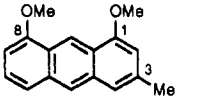
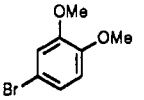
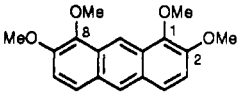
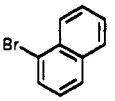
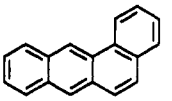
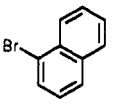
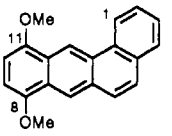
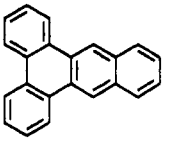
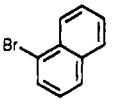
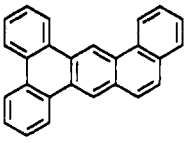
Reaction of benzocyclobutenols and commercially available aryl halides with LTMP under aryne-forming conditions afforded the anthracenes **16**–**25** in moderate to good yield (Table I). Best results were obtained when a mixture of the benzocyclobutenol and haloarene in THP was added to a freshly refluxing solution of LTMP. Reactions were complete in 20–30 min and, after standard acid extraction workup, the anthracenes were purified by flash chromatography followed by recrystallization. Isolation of the methylanthracenes **18** and **21** demonstrates that alkyl groups tolerate the reaction conditions. However, the process failed with 5,6-(methylenedioxy)benzocyclobutenol (**11**) possibly due to a decomposition initiated by deprotonation of the somewhat acidic acetal protons. This also would explain the failure of 4-bromo(methylenedioxy)benzene as a benzyne precursor. As expected, the substituted benzocyclobutenols **8** and **9** reacted regiospecifically to give the anthracenes **19**–**22**, where methoxy and trifluoromethyl groups completely controlled the direction of annulation to the intermediate benzynes.[3,15] In contrast, a reaction of 2-chlorotoluene with **9** and LTMP gave the predicted[3] mixture (1.3:1, 42% yield) of isomers **27** and **28**. The experiments involving the dihydrocyclobutaphenanthrenol **14** and/or bromonaphthalene to give the benzannulated anthracenes **23**–**26** illustrate the value of the present process in the synthesis of polybenzenoid aromatics.



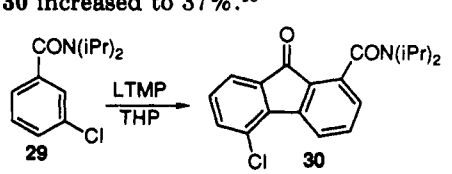
In an attempt to prepare an anthracene substituted with a carbonyl available for later manipulation, *N*,*N*-diisopropyl 3-chlorobenzamide (**29**[16]) and **7** were treated with LTMP in refluxing THP. However the main product (19% yield) was the fluorenone **30** confirming the unique stability of *o*-lithio anions of benzamides.[17] Here the

(4) Fitzgerald, J. J.; Drysdale, N. E.; Olofson, R. A. *Synth. Commun.* **1992**, *22*, 1807.
(5) Bubb, W. A.; Sternhell, S. *Aust. J. Chem.* **1976**, *29*, 1807.
(6) Stevens, R. V.; Bisacchi, G. S. *J. Org. Chem.* **1982**, *47*, 2393.
(7) Liebeskind, L. S.; Lescosky, L. J.; McSwain, C. M. *J. Org. Chem.* **1989**, *54*, 1435.
(8) Choy, W.; Yang, H. *J. Org. Chem.* **1988**, *53*, 5796.
(9) Kametani, T.; Takeshita, M.; Nemoto, H. *Chem. Pharm. Bull.* **1978**, *26*, 556.
(10) Wallace, W. T.; Azadi-Ardakani, M. *Tetrahedron* **1988**, *44*, 5939.
(11) Plieninger, H.; Kiefer, B. *Chem. Ber.* **1957**, *90*, 617.
(12) Iskander, G. M.; Stansfield, F. *J. Chem. Soc.* **1965**, 1390. Amupitan, J. O.; Stansfield, F. *J. Chem. Soc. Perkin Trans 1* **1974**, 1949.
(13) Cava, M. P.; Muth, K. *J. Am. Chem. Soc.* **1960**, *82*, 652.
(14) For a report of proximal bond fusion in the deprotonation of certain tricarbonyl(cyclobutabenzene)chromium(0) complexes see: Brands, M.; Wey, H. G.; Butenschon, H. *J. Chem. Soc. Chem. Commun.* **1991**, 1541.
(15) Although **22** is more easily available by another method,[4] its synthesis is included here because the product symmetry demonstrated by its NMR spectra further confirms the regiochemistry of these transformations.
(16) Johnson, H. L.; Skinner, W. A.; Skidmore, D.; Maibach, H. I. *J. Med. Chem.* **1968**, *10*, 1265.

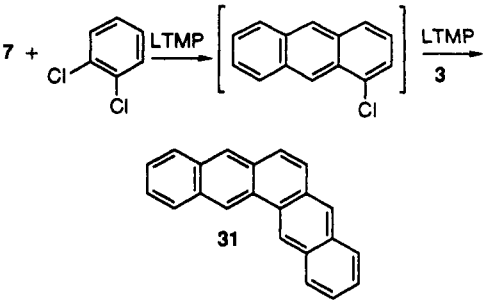
Table I. Synthesis of Anthracenes

benzocyclobutenol	benzyne precursor	product structure	product no.	product yield (%)
7			16	45
7			17	62
7			18	50
8			19	35
8			20	48
8			21	44
9			22	57
7			23	62
10			24	40
14			25	56
14			26	68

o-lithio anion must add to a benzyne to give another intermediate *o*-lithio benzamide, which, on elimination of LDA affords **30**. When just **29** was added to LTMP, the yield of **30** increased to 37%.[18]



In another extension, pentaphene[19] (**31**) was prepared in 20% yield by a one-pot double addition of **7** to *o*-dichlorobenzene. Here, the intermediate should be 1-chloroanthracene which dehydrochlorinates to the anthracyne and adds another molecule of **3**.



While this study of the scope and limitations of the new process, **4** + **5** → **6**, cannot be complete, it should prove predictively useful. Other uses of benzocyclobutenoxides

(17) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34.
(18) The isolation of an oxazolinyl chlorofluorenone by the similar treatment of a 2-(3-chlorophenyl)oxazoline with BuLi has been reported: Pansegrau, P. D.; Rieker, W. F.; Meyers, A. I. *J. Am. Chem. Soc.* **1988**, *110*, 7178.
(19) Camenzind, R.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1914.

as reactants will be described in future reports from this laboratory.

Experimental Section

General.[20] Melting points are uncorrected. Reactions were performed under anhydrous N_2. All aryl halide reactants were of the highest commercially available purity. The known ketones corresponding to the alcohols 8–12 were made as previously described by the process outlined for the synthesis of 13. Similarly, the $NaBH_4$ reduction used to obtain the alcohols 9, 11, and 14 was followed in the preparation of the known alcohols 8[9] and 10.[10] The LTMP was prepared in situ by dripping MeLi (1.4 M in ether) into HTMP in THP at room temperature slowly enough to permit methane evolution at a convenient rate. The THP was distilled from benzophenone sodium ketyl and stored over 4-Å molecular sieves.

5,6-Dimethoxybenzocyclobutenol (9). 5,6-Dimethoxybenzocyclobutenone[7] (0.392 g, 2.20 mmol) in EtOH (5 mL) was dripped into a suspension of $NaBH_4$ (0.423 g, 11.2 mmol) in EtOH (30 mL) at 0 °C. After 30 min, the mixture was cautiously transferred to a separatory funnel containing ice, 10% HCl (50 mL), and ether (50 mL), separated, extracted with ether (3 × 50 mL), dried ($MgSO_4$), concentrated, and chromatographed (20% EtOAc/hexane) to afford the alcohol 9 as white crystals: mp 78–80 °C, 0.391 g (99% yield); ^1H NMR ($CDCl_3$) δ 6.81 (d, J = 7.3 Hz, 1 H), 6.62 (d, J = 7.3 Hz, 1 H), 5.27 (dd, 1 H, J = 4.6, 1.9 Hz), 4.05 (s, 3 H), 3.79 (s, 3 H), 3.52 (dd, 1 H, J = 14.3, 4.6 Hz), 2.90 (dd, 1 H, J = 14.3, 1.9 Hz), 2.6 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 147.6, 144.5, 134.9, 130.8, 115.4, 114.2, 69.8, 57.7, 56.2, 41.2.

5,6-(Methylenedioxy)benzocyclobutenol (11). Similar reaction of 5,6-(methylenedioxy)benzocyclobutenone[7] (0.510 g, 3.15 mmol) in EtOH (20 mL) with $NaBH_4$ (1.19 g, 31.5 mmol) in EtOH (10 mL) at 0 °C followed by workup and chromatography as above gave white crystals of 11; mp 100–101 °C, 0.501 g (97% yield); ^1H NMR ($CDCl_3$) δ 6.79 (d, J = 7.8 Hz, 1 H), 6.58 (d, J = 7.8 Hz, 1 H), 5.92 (dd, 2 H, J = 4.6, 1.2 Hz), 5.31 (dd, 1 H, J = 4.6, 1.8 Hz), 3.51 (dd, 1 H, J = 14.0, 4.6 Hz), 2.96 (dd, 1 H, J = 14.0, 1.8 Hz), 2.65 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 147.9, 140.2, 136.1, 126.6, 116.1, 110.3, 101.1, 68.3, 41.5.

2*H*-Cyclobuta[*l*]phenanthren-1-one (13). A mixture of 9-bromophenanthrene (3.30 g, 12.9 mmol), $NaNH_2$ (1.00 g, 25.9 mmol), and ketene diethyl acetal (3.00 g, 25.9 mmol) in THF (6 mL) was refluxed for 7 h. Hydrolysis (10% HCl at room temperature for 12 h) and chromatography afforded the ketone 13 as a yellow solid: mp 165–167 °C dec, 1.20 g (44% yield); ^1H NMR ($CDCl_3$) δ 8.6–8.4 (m, 2 H), 8.1–7.9 (m, 1 H), 7.8–7.5 (m, 5 H), 3.99 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 184.8, 155.0, 141.8, 134.0, 131.2, 130.1, 128.1, 127.4, 127.2, 127.0, 126.5, 124.7, 124.2, 124.0, 123.4, 50.2.

1,2-Dihydrocyclobuta[*l*]phenanthren-1-ol (14). A solution of 13 (0.349 g, 1.60 mmol) in THF (3 mL) was added slowly to $NaBH_4$ (0.295 g, 7.80 mmol) in EtOH (10 mL) at 0 °C. After 2 h, standard workup–chromatography gave 14 as a white solid: mp 129–130 °C from hexane, 0.317 g (90% yield); ^1H NMR ($CDCl_3$) δ 8.8–8.7 (m, 2 H), 8.0–7.95 (m, 1 H), 7.85–7.75 (m, 1 H), 7.7–7.6 (m, 4 H), 5.62 (dd, 1 H, J = 3.9, 1.3 Hz), 3.87 (dd, 1 H, J = 13.8, 3.9 Hz), 3.22 (dd, 1 H, J = 13.8, 1.3 Hz), 2.2 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 360 MHz) δ 141.6, 138.4, 131.7, 130.8, 128.6, 127.6, 127.0, 126.9, 126.8, 126.7, 126.0, 123.8, 123.5, 122.9, 70.4, 41.4.

Attempted Reduction of 4,6-Dimethoxybenzocyclobutenone: (3,5-Dimethoxyphenyl)acetaldehyde (15). When 4,6-dimethoxybenzocyclobutenone[7] (0.694 g, 3.90 mmol) in EtOH (10 mL) was dripped into a suspension of $NaBH_4$ (0.745 g, 19.7 mmol) in EtOH (30 mL) at 0 °C, standard workup–chromatography (20% EtOAc/hexane) after 30 min afforded 15[11] as a yellow oil: 0.323 g (46% yield); ^1H NMR ($CDCl_3$) δ 9.72 (t, J = 2.5 Hz, 1 H), 6.4–6.35 (m, 3 H), 3.77 (s, 6 H), 3.58 (d, J = 2.5 Hz, 2 H).

General Procedure for the Synthesis of Anthracenes: 1,3-Dimethoxyanthracene (16). A mixture of 7 (1.00 g, 8.3 mmol) and 5-chloro-1,3-dimethoxybenzene (1.40 g, 8.3 mmol) in THP (5 mL) was added over 5 min to refluxing LTMP (17.4 mmol) in 20 mL of THP. After 30 min, the cooled solution was poured into cold 10% HCl (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The dried ($MgSO_4$), concentrated organic extract was chromatographed (20% EtOAc/hexane) and recrystallized from MeOH to afford a yellow solid: mp 84–86 °C, 0.889 g (45% yield); ^1H NMR ($CDCl_3$) δ 8.74 (s, 1 H), 8.22 (s, 1 H), 8.00 (dd, 2 H, J = 8.1, 6.5 Hz), 7.5–7.35 (m, 2 H), 6.83 (d, J = 2.0 Hz, 1 H), 6.46 (d, J = 2.0 Hz, 1 H), 4.04 (s, 3 H), 3.95 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.8, 156.7, 133.2, 132.7, 130.0, 129.0, 127.4, 125.9, 124.3, 123.8, 122.3, 121.3, 97.5, 96.3, 55.6, 55.3.

1-Methoxyanthracene (17). Reaction of 7 (0.30 g, 2.5 mmol) and 3-bromoanisole (0.47 g, 2.5 mmol) in THP (5 mL) with LTMP (10 mmol) in THP (15 mL) gave 17 as yellow crystals: mp 70–72 °C from hexane (lit.[21] 70 °C), 0.31 g (62% yield); ^1H NMR δ 8.82 (s, 1 H), 8.33 (s, 1 h), 8.1–7.6 (m, 7 H), 4.01 (s, 3 H).

1-Methylanthracene (18). Treatment of 7 (1.50 g, 12.5 mmol) and 2-chlorotoluene (3.16 g, 25.0 mmol) in THP (10 mL) with LTMP (38.8 mmol) in THP (30 mL) gave 18 as yellow crystals: mp 86–88 °C from MeOH (lit.[22] 83–84 °C), 1.20 g (50% yield); ^1H NMR ($CDCl_3$) δ 8.58 (s, 1 H), 8.45 (s, 1 H), 8.1–8.0 (m, 2 H), 7.90 (d, J = 8.0 Hz, 1 H), 7.5–7.3 (m, 4 H), 2.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 134.3, 132.0, 131.6, 131.5, 131.4, 129.0, 128.0, 126.9, 126.8, 125.7, 125.4, 125.3, 125.2, 122.8, 19.7.

1-Methoxy-8-(trifluoromethyl)anthracene (19). This was made from 8 (0.165 g, 1.10 mmol), 2-chloro-1-(trifluoromethyl)-benzene (0.199 g, 1.10 mmol), THP (2 mL), and LTMP (2.30 mmol, 3 mL THP): yellow crystals of mp 142–144 °C from MeOH, 0.106 g (35% yield); ^1H NMR ($CDCl_3$) δ 9.21 (s, 1 H), 8.43 (s, 1 H), 8.15 (d, J = 7.3 Hz, 1 H), 7.85 (d, J = 7.3 Hz, 1 H), 7.60 (d, J = 7.3 Hz, 1 H), 7.5–7.4 (m, 2 H), 6.78 (d, J = 7.3 Hz, 1 H), 4.08 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.7, 133.0, 132.7, 132.0, 126.9, 126.5, 125.9, 125.8, 124.6 (q, J = 2.7 Hz), 124.0 (q, J_{CF} = 269 Hz), 123.4, 120.1, 118.3, 102.6, 96.2, 55.6.

1,3,8-Trimethoxyanthracene (20). Reaction of 8 (0.500 g, 3.30 mmol) and 5-chloro-1,3-dimethoxybenzene (0.575 g, 3.30 mmol) in THP (2 mL) with LTMP (6.70 mmol, 10 mL THP) gave 20 as yellow crystals: mp 158–159 °C from EtOH, 0.425 g (48% yield); ^1H NMR ($CDCl_3$) δ 9.13 (s, 1 H), 8.15 (s, 1 H), 7.50 (d, J = 8.6 Hz, 1 H), 7.35 (t, J = 8.6 Hz, 1 H), 6.79 (d, J = 1.9 Hz, 1 H), 6.70 (d, J = 8.6 Hz, 1 H), 6.44 (d, J = 1.9 Hz, 1 H), 4.06 (s, 3 H), 4.04 (s, 3 H), 3.94 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.1, 157.2, 156.2, 133.7, 133.5, 125.9, 123.4, 123.1, 121.6, 119.8, 115.9, 101.0, 97.3, 96.2, 55.6, 55.5, 55.3.

3-Methyl-1,8-dimethoxyanthracene (21). Treatment of 8 (0.541 g, 3.60 mmol) and 4-chloro-3-methoxytoluene (0.563 g, 3.60 mmol) in THP (5 mL) with LTMP (7.3 mmol, 5 mL THP) gave 21 as yellow crystals: mp 150–151 °C from MeOH, 0.399 g (44% yield); ^1H NMR ($CDCl_3$) δ 9.18 (s, 1 H), 8.20 (s, 1 H), 7.52 (d, J = 7.4 Hz, 1 H), 7.4–7.3 (m, 2 H), 6.70 (d, J = 7.4 Hz, 1 H), 6.57 (s, 1 H), 4.06 (s, 6 H, OMe's), 2.51 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.0, 155.7, 135.4, 133.1, 125.5, 124.1, 123.9, 123.2, 120.1, 118.5, 115.5, 104.3, 101.2, 55.4 (2 OMe's), 22.5.

1,2,7,8-Tetramethoxyanthracene (22). This was made from 9 (0.121 g, 0.67 mmol), 4-bromoveratrole (0.145 g, 0.67 mmol), THP (2 mL), and LTMP (1.5 mmol, 5 mL THP): yellow crystals of mp 120–122 °C from EtOH, 0.114 g (57% yield); ^1H NMR ($CDCl_3$) δ 8.88 (s, 1 H), 8.34 (s, 1 H), 7.74 (d, J = 9.3 Hz, 2 H), 7.31 (d, J = 9.3 Hz, 2 H), 4.08 (s, 6 H), 4.02 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 147.0, 142.2, 128.1, 127.9, 126.4, 124.8, 116.6, 112.8, 61.1, 57.4.

Benz[*a*]anthracene (23). Reaction of 7 (0.769 g, 6.40 mmol) and 1-bromonaphthalene (1.33 g, 6.40 mmol) in THP (15 mL) with LTMP (13.0 mmol, 10 mL THP) gave 23 as yellow needles: mp 157–159 °C from EtOH (lit.[23] 157 °C), 0.905 g (62% yield); ^1H NMR ($CDCl_3$) δ 9.20 (s, 1 H), 8.86 (d, J = 7.9 Hz, 1 H), 8.39 (s, 1 H), 8.2–8.0 (m, 2 H), 7.9–7.6 (m, 7 H).

8,11-Dimethoxybenz[*a*]anthracene (24). Reaction of 10 (0.440 g, 2.44 mmol) and 1-bromonaphthalene (0.505 g, 2.44 mmol) in THP (5 mL) with LTMP (5.0 mmol, 10 mL THP) gave 24 as a yellow-orange needles; mp 133–135 °C from hexane, 0.279 g (40% yield); ^1H NMR ($CDCl_3$) δ 9.64 (s, 1 H), 8.99 (d, J = 8.0 Hz, 1 H), 8.79 (s, 1 H), 7.9–7.8 (m, 2 H), 7.7–7.6 (m, 3 H), 6.44 (apparent

(20) For apparatus used in physical and spectral measurements and procedures used in solvent–reagent purification see: Dang, V. A.; Olofson, R. A.; Wolf, P. R.; Piteau, M. D.; Senet, J.-P. G. *J. Org. Chem.* **1990**, *55*, 1847.

(21) Dienel, H. *Chem. Ber.* **1905**, *38*, 2862.
(22) Mosby, W. L. *J. Org. Chem.* **1953**, *18*, 964.
(23) Hayworth, R. D.; Mavin, C. R. *J. Chem. Soc.* **1933**, 1012.

s, 2 H), 4.04 (s, 3 H), 4.01 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 150.0, 149.7, 132.4, 131.2, 130.6, 128.9, 128.8, 127.9, 127.3, 127.1, 126.9, 125.6, 125.5, 123.4, 121.5, 115.9, 101.9 (C_9 and C_{10}), 55.4 (2 OMe's).

Dibenz[*a*,*c*]anthracene (25). Treatment of **15** (0.141 g, 0.64 mmol) and chlorobenzene (0.072 g, 0.64 mmol) in THP (1 mL) with LTMP (2.6 mmol, 6 mL THP) gave **25** as yellow crystals; mp 202–205 °C from EtOH (lit.[23] 205 °C), 0.101 g (55% yield); ^{1}H NMR ($CDCl_3$) δ 9.11 (s, 2 H), 8.8–8.7 (m, 2 H), 8.65–8.55 (m, 2 H), 8.15–8.1 (m, 2 H), 7.7–7.6 (m, 6 H).

Tribenz[*a*,*c*,*h*]anthracene (26). This was made from **15** (0.100 g, 0.45 mmol), 1-bromonaphthalene (0.093 g, 0.45 mmol), THP (1 mL), and LTMP (0.95 mmol, 6 mL THP): yellow crystals of mp 227–228 °C from AcOH (lit.[24] 225–228 °C), 0.100 g (68% yield); ^{1}H NMR ($CDCl_3$) δ 9.90 (s, 1 H), 9.03 (s, 1 H), 8.94 (t, *J* = 8.7 Hz, 2 H), 8.8–8.7 (m, 1 H), 8.7–8.6 (m, 2 H), 8.6–8.0 (m, 9 H).

1,2-Dimethoxy-5-methylanthracene (27) and 1,2-Dimethoxy-8-methylanthracene (28). Reaction of **9** (0.749 g, 4.16 mmol) and 2-chlorotoluene (0.527 g, 4.16 mmol) in THP (5 mL) with LTMP (8.7 mmol, 8 mL THP) gave a mixture (0.439 g of a yellow oil, 42% yield) of **27** and **28** which were inseparable by flash chromatography or HPLC: ^{1}H NMR ($CDCl_3$) δ (isomer ratio 1.3:1) 8.80 (s, 0.44 H), 8.70 (s, 0.56 H), 8.54 (s, 0.56 H), 8.41 (s, 0.44 H), 8.0–7.75 (m, 2 H), 7.4–7.2 (m, 3 H), 4.18 (s, 1.3 H), 4.16 (s, 1.7 H), 4.05 (s, 3 H), 2.88 (s, 1.3 H), 2.82 (s, 1.7 H). An effort to designate **27** and **28** as the major isomer by NOE was inconclusive.

Reaction of 7 and 29 in the Presence of LTMP: *N*,*N*-Diisopropyl-5-chlorofluorenone-1-carboxamide (30). A mixture of **7** (1.00 g, 8.3 mmol) and **29**[16] (2.00 g, 8.3 mmol) in THP (8 mL) was added over 5 min to a refluxing solution of LTMP (17.0 mmol, 20 mL THP). After 30 min, workup, chromatography, and recrystallization from hexane afforded the pure fluorenone **30** as yellow plates; mp 260–261 °C, 0.269 g (19% yield).

Fluorenone **30** also was prepared by adding **29** (0.500 g, 2.10 mmol) in THP (5 mL) to a refluxing solution of LTMP (2.3 mmol, 5 mL THP): 0.133 g (37% yield) of mp 260–261 °C after workup and purification; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, *J* = 7.7 Hz, 1 H), 7.6–7.5 (m, 2 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 7.12 (d, *J* = 7.7 Hz, 1 H), 3.7–3.5 (m, 2 H), 1.73 (d, *J* = 6.8 Hz, 3 H), 1.58 (d, *J* = 6.8 Hz, 3 H), 1.10 (d, *J* = 3.2 Hz, 3 H), 1.08 (d, *J* = 3.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 191.3, 167.4, 152.1, 143.5, 140.2, 137.2, 136.3, 135.4, 130.4, 129.8, 129.1, 126.6, 123.8, 122.6, 51.2, 46.0, 20.9, 20.8, 20.4, 19.9.

Pentaphene (31). Reaction of **7** (2.00 g, 16.6 mmol) and *o*-dichlorobenzene (1.16 g, 7.9 mmol) in THP (8 mL) with LTMP (32.5 mmol, 30 mL THP) gave **31** as greenish crystals: mp 256–258 °C from AcOH (lit.[19] 257 °C), 0.439 g (20% yield); ^{1}H NMR ($CDCl_3$) δ 9.27 (s, 2 H), 8.28 (s, 2 H), 8.2–8.15 (m, 2 H), 8.1–8.0 (m, 2 H), 7.66 (s, 2 H), 7.6–7.55 (m, 4 H). The analogous reaction of 1,3,5-trichlorobenzene failed.

Registry No. **7**, 35447-99-5; **8**, 66947-61-3; **9**, 144493-71-0; **10**, 87046-36-4; **11**, 144493-72-1; **13**, 87180-87-8; **14**, 144493-73-2; **15**, 63165-30-0; **16**, 144493-74-3; **17**, 54458-84-3; **18**, 610-48-0; **19**, 144493-75-4; **20**, 144493-76-5; **21**, 144493-77-6; **22**, 142778-09-4; **23**, 56-55-3; **24**, 144493-78-7; **25**, 215-58-7; **26**, 215-26-9; **27**, 144493-79-8; **28**, 144493-80-1; **29**, 35306-66-2; **30**, 144493-81-2; **31**, 222-93-5; LTMP, 38227-87-1; 5,6-dimethoxybenzocyclobutenone, 81447-58-7; 5,6-(methylenedioxy)benzocyclobutenone, 118112-19-9; 9-bromophenanthrene, 573-17-1; ketene diethyl acetal, 2678-54-8; 4,6-dimethoxybenzocyclobutenone, 118112-18-8; 5-chloro-1,3-dimethoxybenzene, 7051-16-3; 3-bromoanisole, 2398-37-0; 2-chlorotoluene, 95-49-8; 2-chloro-1-(trifluoromethyl)benzene, 88-16-4; 4-chloro-3-methoxytoluene, 73909-16-7; 4-bromoveratrole, 2859-78-1; 1-bromonaphthalene, 90-11-9; chlorobenzene, 108-90-7; *o*-dichlorobenzene, 95-50-1.

Supplementary Material Available: Additional spectral (e.g., IR, MS, and HRMS) data, copies of ^{1}H and ^{13}C NMR spectra of new compounds, and details on other experiments noted in discussion (26 pages). This material is contained in many 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.

(24) Buu-Hoi, N. P.; Saint-Ruf, G. *J. Chem. Soc.* **1960**, 2845.

Diastereoselective Ring-Opening Aldol-Type Reaction of 2,2-Dialkoxycyclopropanecarboxylic Esters with Carbonyl Compounds. 1. Synthesis of Cis 3,4-Substituted γ-Lactones[1]

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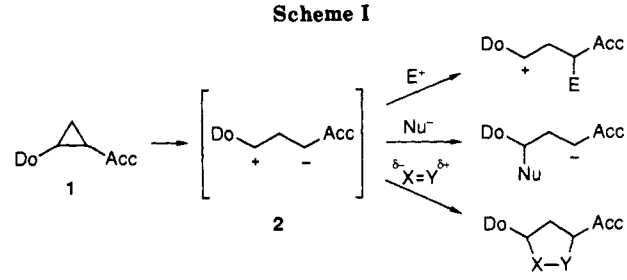
The Lewis acid-promoted reactions of 2,2-dialkoxycyclopropanecarboxylic esters **4a–c** with aldehydes and unsymmetrical ketones to give γ-lactones were investigated. $TiBr_4$ is an excellent catalyst and gives cis 3,4-substituted γ-lactones in good yields with high diastereoselectivity. $SnBr_4$ promotes the reaction of **4a–c** with aldehydes with high cis-selectivity, but does not promote the reaction of **4a** with unsymmetrical ketones. $ZrCl_4$ is moderately trans-selective in the reaction of **4a** with aldehydes, while being moderately cis-selective in the reaction of **4a** with unsymmetrical ketones. Cis γ-lactones can be converted into their trans-isomers by treatment with NaOEt in EtOH.

Introduction

Cyclopropanes activated by an electron-withdrawing or -donating group are susceptible to ring-opening reactions, and many types of activated cyclopropanes are used in organic synthesis as valuable building blocks.[2] Their utility was well demonstrated by their participation as three-carbon units into [3 + 2]-type reactions for syntheses of 5-membered carbo-[3] and heterocycles.[4] Among such activated cyclopropanes, vicinally donor–acceptor-substituted cyclopropane **1** is an equivalent of ring-opened

Scheme I



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