(*E*)-*N*,*N*-Dimethyl-3-hexenamide (23)[42] was prepared from (*E*)-3-hexenoic acid (97% Aldrich, 10.0 g) as described for amide **21** (53% yield): ^{1}H NMR δ 5.59 (td, *J* = 5, 17 Hz, 1 H), 5.52 (td, *J* = 5, 17 Hz, 1 H), 3.08 (d, *J* = 5 Hz, 2 H), 2.98 (br s, 6 H), 2.06 (tq, *J* = 5, 7 Hz, 2 H), 0.99 (t, *J* = 7 Hz, 3 H).

***N*,*N*-Dimethyl-2-hexenamide (Mixture of (*E*)-22 and *Z* Isomer 25).** (*Z*)-2-Hexenoic acid (1.0 g)[37,39] was treated with $SOCl_2$ (1.4 g) for 15 min at room temperature and then distilled during 10 min to give 2-hexenoyl chloride (0.85 g, 75%). The chloride was dissolved in dioxane (20 mL) and treated with dimethylamine gas for 30 min. After workup and distillation as detailed for **21** the amide mixture (0.61 g, 66%) was analyzed by gas chromatography and ^{1}H NMR, giving a product composition of 80% *Z*-amide **25** and 20% *E*-amide **22**. Anal. Found: C, 65.69; H, 10.80; N, 9.54. Calcd for $C_8H_{15}NO{\cdot}0.25H_2O$: C, 65.94; H, 10.72; N, 9.61. ^{1}H NMR δ 6.87 (td, *J* = 7, 15 Hz, 1 H, **22** CH_2CH=CH), 6.24 (br d, *J* = 15 Hz, 1 H, **22** CH=C*H*CO), 5.98 (br d, *J* = 12 Hz, 1 H, **25** CH=C*H*CO), 5.90 (td, *J* = 7, 12 Hz, 1 H, **25** CH_2CH=CH), 2.99 (br s, 6 H, **22** and **25** NCH_3), 2.31 (q, *J* = 7 Hz, 2 H, **25** CH_2CH_2CH=), 2.18 (q, *J* = 7 Hz, 2 H, **22** CH_2CH_2CH=), 1.49 (sextet, *J* = 7 Hz, 2 H, **22** $CH_3CH_2CH_2$), 1.44 (sextet, *J* = 7 Hz, 2 H, **25** $CH_3CH_2CH_2$), 0.93 (t, *J* = 7 Hz, 3 H, **22** CH_3CH_2), 0.92 (t, *J* = 7 Hz, 3 H, **25** CH_3CH_2).

***N*,*N*,*N*′,*N*′-Tetramethyl-2-((*Z*)-1-butenyl)-3-propylpentanediamide (24)**: by dimerization of **21** (mixture of diastereoisomers); ^{1}H NMR δ 5.49 (m, 2 H, CH_2CH=C*H*CH), 3.94 and 3.89 (dd, *J* = 5, 9 Hz, 1 H, CH=C*H*(COR)CH), 3.00 (m, 12 H), 2.63 (dd, *J* = 3, 16 Hz, 1 H, RCOC*H*HCH), 2.03 (sextet, *J* = 7 Hz, CH_3CH=CH), 0.95 (m, 6 H, CH_3CH_2). Irradiation at δ 2.03 simplified absorptions at δ 0.95 to br s and δ 5.49 to 5.53 (br d, *J* = 11 Hz, (*Z*) CH_2CH=CH) and 5.45 (major isomer) and 5.41 (minor isomer) (dd, *J* = 3.5, 11 Hz, 1 H, (*Z*) CH=C*H*CH)).

***N*,*N*,*N*′,*N*′-Tetramethyl-2-((*E*)-1-butenyl)-3-propylpentanediamide (24b)**: by dimerization of **23**; ^{1}H NMR δ 5.50 (m, 2 H, CH*CH*=*CH*CH_2), 3.49 (m, 1 H, CH*CH*(COR)CH=), 2.65 (dd, *J* = 4, 16 Hz, 1 H, COC*H*HCH), 2.31 (m, 2 H, COCH*HCH*), 2.07 (m, 2 H, =CHCH_2CH_3), 1.27 (m, 4 H, $CH_2CH_2CH_3$), 0.99 (m, 3 H, =CHCH_2CH_3), 0.90 (m, 3 H, CH_3). Irradiation at δ 3.49 simplified absorptions at δ 5.50 to 5.54 (br d, *J* = 16 Hz, 1 H, (*E*) CH*CH*=CH) and 5.45 (dt, *J* = 15, 5.5 Hz, 1 H, (*E*) CH=*CH*CH_2). Irradiation at δ 2.07 simplified absorptions at δ 5.50 to 5.54 (dd, *J* = 7, 16 Hz, 1 H, CH*CH*=CH) and 5.45 (br d, *J* = 15 Hz, 1 H, CH=*CH*CH_2).

Acknowledgment. R. B. acknowledges Deutsche Forschungsgemeinschaft (DFG). J.I.S. thanks Philip Morris, U.S.A., for sabbatical leave.

Registry No. **4**, 3724-55-8; **4** (acid), 625-38-7; **4** (acid chloride), 1470-91-3; **5**, 623-43-8; **6**, 4358-59-2; **6** (acid), 503-64-0; (*E*)-**7a**, 16657-04-8; (*Z*)-**7a**, 16657-03-7; (*R**,*R**)-**7b**, 97253-79-7; (*R**,*S**)-**7b**, 97253-78-6; **8**, 13894-61-6; **8** (acid), 1775-43-5; **8** (acid chloride), 97253-82-2; **9**, 13894-62-7; **9** (acid), 1577-18-0; **10**, 13894-63-8; **10** (acid), 13419-69-7; **11**, 13894-64-9; **11** (acid), 1577-28-2; **12a**, 89897-27-8; **12b**, 97253-80-0; **12c**, 21962-25-4; **13**, 41654-12-0; **14**, 56728-17-7; **15**, 17447-01-7; **16**, 17447-00-6; **17**, 97253-74-2; **18**, 97253-76-4; **19**, 14064-75-6; (*R**,*R**)-**20**, 97253-85-5; (*R**,*S**)-**20**, 97253-81-1; **21**, 72178-91-7; **22**, 97253-75-3; **23**, 72178-90-6; (*R**,*R**)-**24**, 97253-86-6; (*R**,*S**)-**24**, 97253-83-3; (*R**,*R**)-**24b**, 97277-61-7; (*R**,*S**)-**24b**, 97253-84-4; **25**, 97253-77-5; CH_2=C(Br)CH_2CH_3, 23074-36-4; $LiCH_2CO_2Bu$-*t*, 53503-61-0; Me_2NH, 124-40-3; C_6H_5COCl, 98-88-4; $CH_3(CH_2)_2CH$=CHCOCl, 18802-95-4.

(42) Jenkins, P. R.; Gut, R.; Wetter, H.; Eschenmoser, A. *Helv. Chim. Acta* **1979**, *62*, 1922.

Benzobicyclo[3.1.0]hexene Derivatives from Benzosemibullvalene. CO_2- and CO-Bridged Naphthalenes

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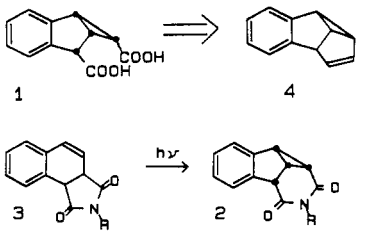
Transformation of benzosemibullvalene to various benzobicyclo[3.1.0]hexene derivatives is described. Reductive ozonolysis of benzosemibullvalene gave diol **9** which was oxidized with Fetizon's reagent to a mixture of lactones **10** and **11**. Lactone **11** was stereoselectively methylated via a protection–deprotection sequence. Hydrolysis and oxidation of methylated lactone **17** gave the target *cis-diendo*-diacid **18**. The diacid was cyclized to anhydride **19**. *trans*-Diacid **21**, generated on oxidation of acid alcohol **13**, was further oxidized to keto acid **23**. The ketone was reacted with 2 equiv of methyllithium and cyclized to yield lactone **25**. Anhydride **19** represents a novel "naphthalene + CO_2 + CO" system and lactone **25** is a "naphthalene + CO_2" system. Irradiation of anhydride **19** at 254 nm gives mainly lactone **25**. This result contrasts previous investigations of anhydride photolyses where decarboxylation predominates and suggests a different mechanism for decomposition. Irradiation of lactone **25** at 254 nm cleanly gives 1-methylnaphthalene. Preparations of several other benzobicyclo[3.1.0]hexene derivatives are detailed.

In the course of mechanistic studies of high-energy precursors to aromatic compounds,[1] centering on the bicyclo[3.1.0]hexene ring system, we required the *cis*-diacid **1**. The presence of four contiguous asymmetric centers in **1** presents a formidable synthetic challenge. To our knowledge, the only reported analogous ring system with similar substitution is imide **2**.[2] Unfortunately, **2** is only a very minor photoproduct of **3** in a complicated mixture, and is thus an unappealing starting point.



We felt that **1** might be synthesized from benzosemibullvalene (**4**), which has the required carbon framework endowed with the necessary stereochemistry. Interestingly, although **4** has been known for some years,[3] reports of its reactivity seem to only include photolysis,[3] thermolysis,[4]

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(2) Jones, D. W.; Kneen, G. *Chem. Commun.* **1971**, 1356; *J. Chem. Soc., Perkin Trans. 1* **1975**, 171.

(3) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096. Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680.

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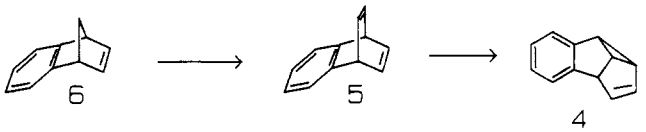
reduction,[3,4] and reaction with transition metals.[5] Similarly, despite numerous reports of substituted semibullvalenes, there appear to be only a handful of semibullvalene reactions that have been described.[4-6] Not surprisingly, the juxtaposition of conjugating functionality and significant ring strain lead to complications in the reactions of semibullvalenes with routine reagents. In contrast, a wide variety of dihydrosemibullvalenes[7] and keto derivatives[8] have recently drawn much interest as elegant precursors to natural products. Work in these areas is thus much better developed.

It was not clear at the onset of this work that the olefinic portion of benzosemibullvalene (4) could be functionalized without cyclopropyl involvement.[4-6,9] It was hoped, however, that the benzo substitution would moderate the reactivity somewhat, compared to semibullvalene. Although our mechanistic work is still in progress, we now wish to report the transformation of benzosemibullvalene to a methyl derivative of 1 and the characterization of several new compounds along the way. In these investigations, we have generated novel "naphthalene plus CO_2" and "naphthalene + CO + CO_2" systems, which will be described herein.

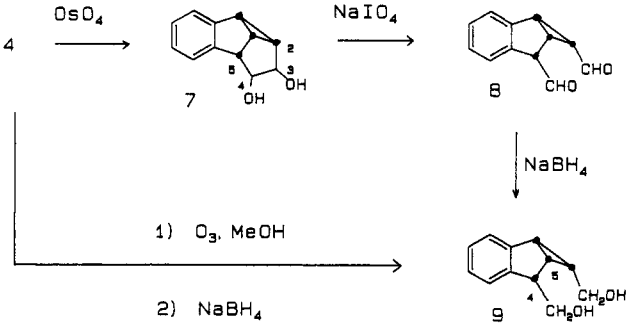
Results and Discussion

Benzosemibullvalene (4) has been synthesized by Zimmerman and co-workers[3] via the di-π-methane rearrangement of benzobarrelene (5), and this approach was followed. Benzobarrelene (5) has been generated directly



by Diels–Alder addition of benzyne to benzene[3] and by addition of tetrachlorobenzyne to benzene followed by reduction.[10] We found, however, that the recent procedure by Johnson et al.[11] was more convenient for the generation of larger quantities of 5. In this fashion, benzonorbornadiene (6) could be converted to ca. 20-g lots of 5 in reasonable periods of time. Although acetophenone has been used to effect the transformation of 5 to 4,[3] we found xanthone to be superior in large-scale photolyses. The greater extinction coefficient of xanthone at 300 nm effectively prevents direct irradiation of 5 at significantly lower concentrations than necessary with acetophenone. Large-scale product separation is thus facilitated.

In our initial approach to the diacid 1, we hoped to carefully bring 4 up to the desired oxidation state in stages. Benzosemibullvalene could be efficiently oxidized to the *cis*-diol 7 with catalytic OsO_4 and *N*-methylmorpholine



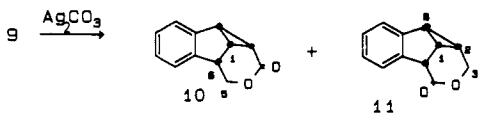
N-oxide. Proton NMR spectra indicate that the ring system is retained and that the diol has the expected cis-diexo stereochemistry.

In particular, $J_{3,4}$ = 2.9 Hz, which is consistent with cis substitution. The small cis coupling is similar to that observed in the exo-meta photoadduct of 1,3-dioxole and benzene.[12] Additionally, $J_{2,3} = J_{4,5} \approx 0$ Hz, in line with dihedral angles of ca. 90° indicated by molecular models.

The diol 7 could be oxidatively cleaved with periodate to give dialdehyde 8. The dialdehyde was extremely unstable, however, giving uncharacterizable material after several hours in solution. Two distinct aldehydic protons are observed at 9.76 and 8.42 ppm, and two carbonyl absorptions appear at 1725 and 1687 cm^{-1}. The structure was confirmed by $NaBH_4$ reduction to diol 9, which was independently synthesized as shown below. All attempts at oxidation of dialdehyde 8 to 1 gave only intractable material. Similarly, attempts to cleave diol 7 directly to 1 failed to give isolable products.

Attempts were made to cleave benzosemibullvalene (4) directly to 1 via oxidative ozonolysis. Treatment of 4 with ozone, followed by oxidation with H_2O_2, led, however, to complete destruction of the starting material, and no products could be isolated. Reductive workup of the ozonide showed that the ozonolysis occurred cleanly. Treatment of 4 with ozone in methanol, followed by $NaBH_4$ reduction, gave crystalline diol 9 in 90% yield. The ^1H NMR spectrum of 9 is complicated by a pronounced solvent dependence, suggesting the possible importance of intramolecular hydrogen bonding. Extensive proton decoupling confirms the proton assignments given, and subsequent chemical transformations (vide infra) support this structure. In particular, $J_{4,5}$ = 6.2 Hz, which is consistent with endo stereochemistry at C-4 as expected.

All attempts at simultaneous oxidation of both hydroxyl groups of 9 failed. Sequential oxidation was thus carried out. Treatment of diol 9 with silver carbonate on Celite[13] gave a mixture of lactones 10 and 11. Although all re-



action conditions gave nearly equal amounts of regioisomers, the lactones could be readily separated by flash chromatography.[14] Regiochemical assignments are based on extensive proton decoupling and on subsequent reac-

(4) Bender, C. O.; Bengston, D. L.; Dolman, D.; Herle, C. E. L.; O'Shea, S. F. *Can. J. Chem.* **1982**, *60*, 1942.
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(7) (a) Wender, P. A.; Howbert, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 688. (b) Wender, P. A.; Dreyer, G. B. *Tetrahedron* **1981**, *37*, 4445. (c) Wender, P. A.; Howbert, J. J. *Tetrahedron Lett.* **1982**, 3983. (d) Wender, P. A.; Dreyer, G. B. *J.Am. Chem. Soc.* **1982**, *104*, 5805. (e) Wender, P. A.; Dreyer, G. B. *Tetrahedron Lett.* **1983**, *24*, 4543. (f) Wender, P. A.; Howbert, J. J. *Tetrahedron Lett.* **1983**, *24*, 5325. (g) Hoye, T. R. *Tetrahedron Lett.* **1981**, *22*, 2523.
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(9) Ors, J. A.; Srinivasan, R. *J. Org. Chem.* **1977**, *42*, 1321.
(10) Hales, N. J.; Heaney, H.; Hollinshead, J. H. *Synthesis* **1975**, 707.
(11) Johnson, R. P.; Exarchou, A.; Jefford, C. W.; Hahn, R. C. *J. Org. Chem.* **1977**, *42*, 3758.
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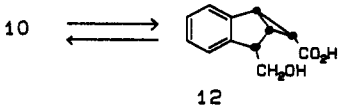
(14) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

tions (vide infra). The geminal protons were easily distinguished in both compounds by their large couplings of ca. 10–12 Hz.

Interestingly, one geminal proton in **11** is shifted upfield 1.4 ppm relative to the other, suggesting a geometry forcing the endo proton into the shielding face of the aromatic ring. In lactone **10**, H-6 is coupled only to the geminal pair at C-5 and to H-1. Similarly, in compound **11**, H-2 is coupled to the pair at C-3 and to both H-1 and H-9 as expected.

The structural assignments of **10** and **11** were confirmed by their reactions with base. Lactone **10** could be hydrolyzed to the corresponding hydroxy acid **12** with warm aqueous hydroxide followed by careful acidification. More vigorous protonation gave back lactone **10**. In contrast, basic hydrolysis followed by acidification of **11** gave a new compound which could not be recyclized. The crude ^1H NMR spectra suggested that epimerization to the exo carboxylic acid **13** had occurred. This was confirmed by



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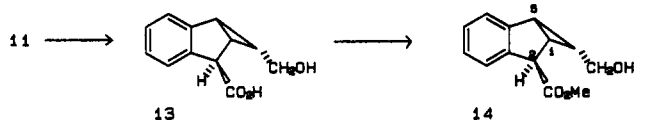
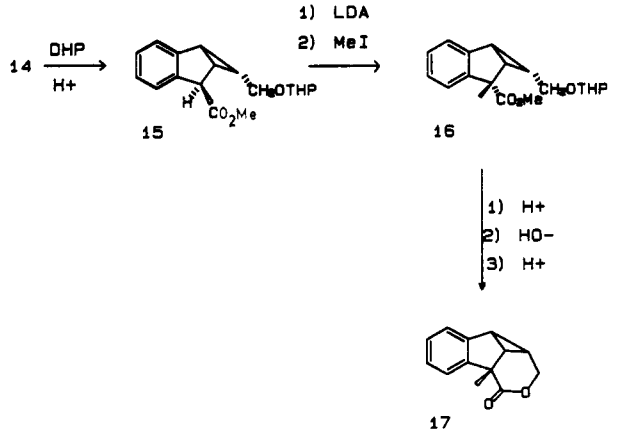


13 **14**

treatment with acidic methanol and full characterization of the resultant ester alcohol **14**. A small vicinal coupling constant $J_{1,2}$ of 1.3 Hz indicates the endo stereochemistry of H-2, with a dihedral angle of ca. 90°. Moreover, a large long-range coupling of 2.1 Hz is observed between H-2 and H-5. Although the reason for this long-range coupling is not readily apparent from models, similar couplings, on the order of 2-3 Hz, are generally observed for analogous protons in trans relationships in bicyclo[3.1.0]hexenes.[15]

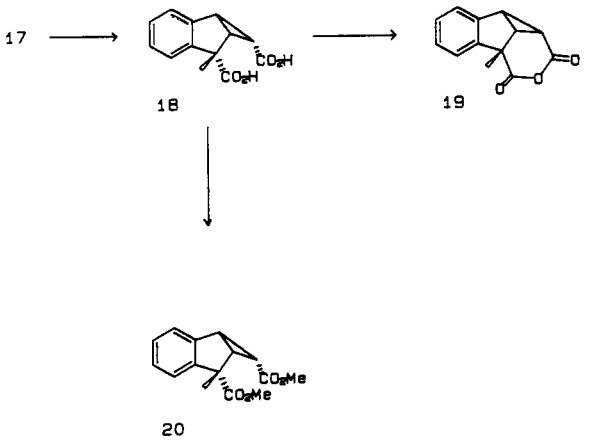
The facile epimerization to acid alcohol **13** posed a serious threat to further chemistry planned for diacid **1**. Moreover, proton loss followed by retro-Michael cleavage[16] was a possible source of instability in **1** and its derivatives. To circumvent these possibilities, the epimerizable center was blocked by stereoselective methylation. Advantage was taken of the rigid bicyclic structure to direct the resulting carboxyl group into the desired endo position. Ester **14** was subjected to the sequence shown below to give methylated lactone **17**, via the protected esters **15** and **16**.



15 **16** **17**

The spectra of lactone **17** are consistent with expectations for a methyl derivative of **11**. The proton at C-6 is absent, and H-1 has simplified to a doublet of doublets.

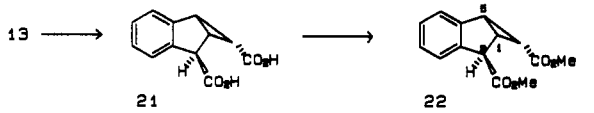
Once methylated, the lactone was converted to the desired diacid without complication. Basic hydrolysis of **17**, followed by basic permanganate oxidation, gave diacid **18**.



18 **19** **20**

The solid diacid **18** is only sparingly soluble in most NMR solvents. For easier characterization, the diacid was readily cyclized into the corresponding anhydride **19**. The diacid could also be converted to the diester **20**. The three derivatives **18–20** exhibit similar characteristic ABX spin systems for the three cyclopropyl protons. The observed coupling constants are all on the order of 6–8 Hz as expected for the all-cis geometry.[17] The spectra are also similar to those reported for imide **2** in both chemical shifts and coupling constants.[2]

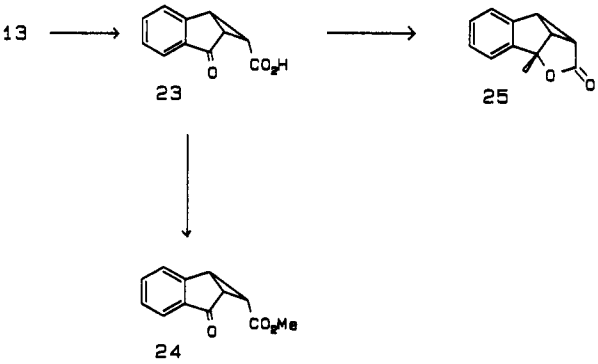
For comparison, oxidation of the acid alcohol **13** to *trans*-diacid **21** was carried out. Conversion with Jones



21 **22**

reagent was straightforward. The diacid **21** was in turn converted to diester **22** for easier characterization. Compound **22** shows the expected near-zero coupling between H-1 and H-2 and again exhibits long-range coupling between H-2 and H-5 as in **14**. Similar attempts at oxidation of acid alcohol **12** to the *cis*-diacid **1** unfortunately gave no isolable products. The reason for this difference in behavior is not known.

When excess alkaline $KMnO_4$ was used to oxidize **13** a new product, keto acid **23** was formed. In addition to the



23 **24** **25**

acid carbonyl in the IR, **23** exhibits a conjugated carbonyl

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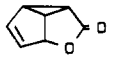
(17) Jackman, L. M.; Sternhell, S. "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chmeistry, 2nd ed."; Pergamon Press: New York, 1969.

stretch at 1698 cm^{-1}. For easier purification and characterization, methyl ester **24** was generated. The ^1H NMR of **24** shows the ABX pattern characteristic for the cyclopropyl protons in these compounds and appropriate other spectral characteristics.

Lactone **25** is a likely product in mechanistic studies planned for **18**, and an independent sample was desirable. We found that **25** could be conveniently synthesized from **23** by MeLi addition followed by cyclization with methyl chloroformate. The rigid bicyclic framework again directs reaction to the exo face. The infrared spectrum of **25** shows the expected lactone carbonyl at 1757 cm^{-1}. The methyl absorption in the ^1H NMR is shifted downfield relative to the methylated derivatives **17–20**, consistent with the α-oxygen substituent.

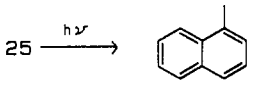
Lactone **25** represents an interesting "methylnaphthalene plus CO_2" system. Other workers have recently reported two independent syntheses of the corresponding parent compound **26**.[18,19] Unfortunately, solu-



26

tion thermolysis of **26** is reported to give no benzene,[18,19] but only polymer. Döpp et al.[19] have suggested, on the basis of thiophenol trapping, that thermolysis of **26** gives cyclopropane cleavage rather than CO_2 loss. These results may be more consistent with a radical chain process, however.

Pyrolysis of lactone **25** in solution (benzene or acetone, 200 °C sealed tube) gave no 1-methylnaphthalene and only intractable material. Gas-phase pyrolysis through a quartz wool packed tube at 300 °C, however, generated 1-methylnaphthalene (**27**) as a major product along with a complicated mixture of other compounds as yet unidentified. Irradiation of **25** at 254 nm, in contrast, cleanly gave only 1-methylnaphthalene (**27**). No methylnaphthvalene **28** was observed. These results are consistent with pho-



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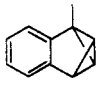
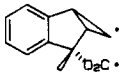
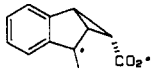


28

tochemical cleavage to biradicals **29** or **30**. Although both



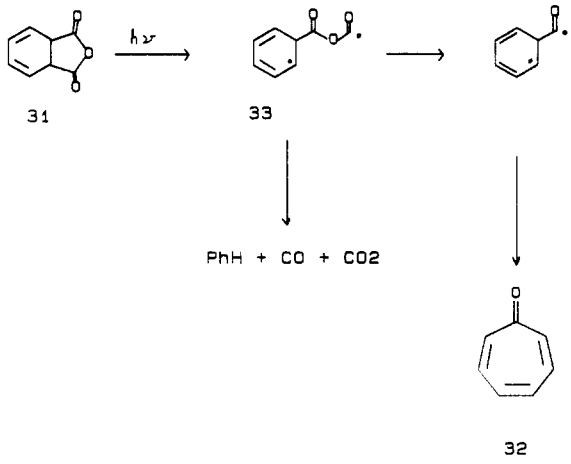
29



30

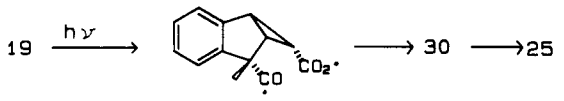
processes have been observed in ester photochemistry,[20] cleavage at the benzylic position is more likely than generation of a cyclopropyl radical.[21]

Interestingly, irradiation of anhydride **19** at 254 nm gives mainly lactone **25** with only a trace of naphthalene **27**. Formation of **25** is somewhat puzzling since photolyses of anhydrides most generally lead to CO_2 rather than CO loss. For example, Fuchs and Scharf[22] found that photolysis of anhydride **31** gave mainly benzene and a small amount of tropone (**32**). These products were interpreted to arise



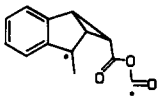
32

from common biradical **33**, produced on α-cleavage. Our results, however, may be better rationalized by C-O cleavage to biradical **34**.



34

Cleavage to the alternative biradical **35** seems unlikely since CO_2 loss would be expected to predominate.[20,22]



35

On the other hand, a reason for predominant cleavage of the indicated C–O bond is not readily apparent on electronic grounds or on the basis of models. We have, as yet, not ascertained whether **19** gives 1-methylnaphthalene as a primary photoproduct or whether this product arises exclusively from lactone **25** which is formed. Further investigation of these novel compounds is in progress.

Experimental Section

General. All reactions were run under a positive pressure of nitrogen and magnetically stirred with a Teflon-coated stir bar unless otherwise noted. Glassware used for anhydrous reactions was flame-dried and cooled under nitrogen. Ethereal diazomethane was generated from Diazald (Aldrich) according to label procedures. Benzene, dimethyl sulfoxide (Me_2SO), acetonitrile, *tert*-butyl alcohol, methanol, dichloromethane and hexanes were dried by distillation from calcium hydride. Tetrahydrofuran (THF) was freshly distilled before use from sodium benzophenone ketyl. Anhydrous diethyl ether was used as received (Mallinckrodt). Thin layer chromatography (TLC) was performed on precoated plastic plates (silica gel 60 F_{254}, 0.2 mm thick, EM Reagents). Preparative TLC was performed on Analtech (silica gel GF, 2 mm thick) precoated plates. Flash chromatography was performed as specified by Still[14] (silica gel 60, 230–400 mesh, EM Reagents). Melting points were determined with a Thomas–Hoover Unimelt open capillary melting point apparatus. All

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melting and boiling points are uncorrected. Infrared spectra (IR) were recorded on a Beckman Acculab 7 or a Beckman IR 4250 spectrophotometer. Proton NMR spectra were recorded on a Jeolco MH-100 (100 MHz), a Bruker WP-200 (200 MHz), or a Bruker WH-270 (270 MHz) instrument as indicated. ^{13}C NMR spectra were recorded at 15.04 MHz on a Jeolco FX-60 spectrometer. Chemical shifts are reported in δ units, parts per million downfield from tetramethylsilane. Mass spectra were obtained on an AEI-902 instrument at an ionizing current of 98 mA and an ionizing voltage of 70 eV. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Benzosemibullvalene (4). Benzobarrelene[11] (7.70 g, 50.0 mmol), xanthone (2.56 g, 13.1 mmol), and acetonitrile (500 mL) were placed in a quartz reaction vessel of 5 cm diameter, and the resulting solution was purged for 30 min with a slow stream of dry nitrogen. The reaction vessel was fitted with a condenser and irradiated at 300 nm for 11 h in a Rayonet photoreactor. The solvent was removed at reduced pressure; the resulting material was placed on a 3 × 30 cm silica gel column and eluted with 800 mL of hexane. Removal of the solvent at reduced pressure yielded benzosemibullvalene (6.96 g, 45.1 mmol, 92%) as a colorless oil. Spectral properties were identical with those previously reported.[3] No benzocyclooctatetraene[3] was observed by ^1H NMR.

6,7-Benzotricyclo[3.3.0.0^{2,8}]oct-6-ene-3-*exo*,4-*exo*-diol (7). Benzosemibullvalene (0.62 g, 4.0 mmol), *N*-methylmorpholine *N*-oxide (1.03 g, 8.8 mmol), 10 mL of water, 20 mL of acetone, 2 mL of *tert*-butyl alcohol, and a catalytic amount of osmium tetroxide were stirred at room temperature for 5 days. Sodium hydrosulfite (0.10 g, 0.57 mmol), 2 g of Florisil, and 10 mL of water were added, and the mixture was stirred for 10 min. The solids were filtered, and the pH of the filtrate was adjusted to 7 with 1 N sulfuric acid. Acetone was removed at reduced pressure, and the pH of the remaining solution was adjusted to 2. The solution was saturated with salt and extracted with ether (5 × 40 mL). Drying ($MgSO_4$) and removal of the solvent at reduced pressure left **7** as a white solid which was recrystallized from ether/hexane (0.65 g, 3.44 mmol, 88%): mp 112 °C; IR (KBr, cm^{-1}) 3500–3400 (br), 1070 (s), 1030 (s); ^1H NMR ($CDCl_3$, 270 MHz) δ 7.3–6.9 (4 H, m), 3.96 (1 H, d, J = 2.9 Hz), 3.68 (1 H, d, J = 2.9 Hz), 3.64 (1 H, d, J = 5.8 Hz), 2.99 (1 H, dt, J = 5.8, 7.3, 7.3 Hz), 2.80 (1 H, br, exchangable), 2.60 (1 H, br, exchangable), 2.55 (1 H, t, J = 7.3 Hz), 1.82 (1 H, t, J = 7.3 Hz); ^{13}C NMR (Me_2CO-d_6, 15.04 MHz) δ 143.2, 142.4, 126.7, 125.3, 123.7, 123.6, 86.1, 71.8, 54.7, 36.8, 33.4, 33.2; mass spectrum, m/e calcd (M^+) 188.0834, obsd 188.0834.

3,4-Benzobicyclo[3.1.0]hex-3-ene-2-*endo*,6-*endo*-dicarbaldehyde (8). Diol **7** (100 mg, 0.52 mmol) and sodium periodate (0.36 g, 1.5 mmol) were stirred for 2 h at −10 °C in 30 mL of 1:1 aqueous acetone. The cooling bath was removed, and the solution was allowed to warm to room temperature. The acetone was removed at reduced pressure, and the remaining solution was extracted with ether (4 × 30 mL). Drying ($MgSO_4$) and removal of the solvent at reduced pressure afforded **8** (75 mg, 0.40 mmol, crude yield 75%) as an unstable brown oil: IR ($CHCl_3$, cm^{-1}) 2920 (s), 2823 (m), 1725 (s), 1687 (s), 1264 (s); NMR ($CDCl_3$, 100 MHz), 9.76 (1 H, s), 8.42 (1 H, d, J = 6 Hz), 7.3–7.0 (4 H, m), 4.42 (1 H, d, J = 7 Hz), 3.24 (1 H, dd, J = 6, 8 Hz), 2.60 (1 H, ddd, J = 7, 8, 3 Hz), 2.14 (1 H, ddd, J = 6, 7, 8 Hz).

4-*endo*,6-*endo*-Bis(hydroxymethyl)-2,3-benzobicyclo[3.1.0]hex-2-ene (9). Benzosemibullvalene **4** (1.54 g, 10 mmol) in 90 mL of methanol was ozonized at −78 °C until the solution turned a deep blue. Excess ozone was removed from the solution by purging with a slow stream of nitrogen. An excess of sodium borohydride (2 g, 50 mmol) was added, and the solution was stirred at −78 °C for 30 min. Removal of the cooling bath resulted in rapid warming along with considerable hydrogen evolution. When the solution reached room temperature, the cooling bath was replaced, and the excess sodium borohydride was quenched with acetone. Water (50 mL) was added, and the methanol was removed at reduced pressure. The resulting solution was saturated with salt and extracted with ether (5 × 80 mL). Drying ($MgSO_4$) and solvent removal at reduced pressure left an oil which was placed on a 5 × 15 cm flash chromatography column and eluted with ethyl acetate. Fractions of 100 mL were collected. Removal of the solvent from fractions 7 through 18 afforded **9** (1.68 g, 9.0 mmol, 90%) as an oil which crystallized upon standing at −20 °C: mp 59 °C; IR (neat, cm^{-1}) 3600–3000 (br), 1475 (s), 1025 (s); ^1H NMR (Me_2CO-d_6, D_2O, 200 MHz) δ 7.20–7.00 (4 H, m), 4.0–3.7 (3 H, m), 3.10 (AB portion of ABX, J_{AX} = 8.1 Hz, J_{BX} = 7.1 Hz, J_{AB} = 11.3 Hz, ν_A = 622.4 Hz, ν_B = 613.4 Hz), 2.61 (1 H, dd, J = 8.2, 6.2 Hz), 1.92 (1 H, dt, J = 6.2, 6.2, 8.2 Hz), 1.38 (1 H, broadened quintet, J = 8.2, 8.2, 8.1, 7.1 Hz); ^{13}C NMR (Me_2CO-d_6, 15.04 MHz) δ 144.1, 141.5, 126.2, 125.5, 124.3, 123.1, 62.9, 58.1, 48.2, 26.5, 25.3, 21.7; mass spectrum, m/e (M^+) calcd 190.0994, obsd 190.0997.

Reduction of 8 to 9. Dialdehyde **8** (100 mg, 0.54 mmol) was dissolved in 10 mL of ethanol and cooled to 0 °C. Sodium borohydride (50 mg, 1.3 mmol) was added, and the resulting solution was stirred at 0 °C for 1 h. The solution was then diluted with water (40 mL), quenched with acetone (1 mL), saturated with salt, and extracted with ether. The ether solution was dried (Na_2SO_4), and the ether was removed at reduced pressure to afford an oil consisting primarily of **9**. The oil was submitted to TLC (ethyl acetate) to yield **9** (75 mg, 0.40 mmol, 74%).

Lactones 10 and 11. A solution of diol **9** (1.33 g, 7.07 mmol) in 200 mL of toluene was heated to reflux, and silver carbonate on Celite[13] (8.0 g) was added. After a 3-h reflux, the black solution was cooled to room temperature and filtered. Removal of the solvent at reduced pressure left a brown oil which crystallized on standing. The solid was placed on a flash chromatography column (180 × 50 mm) and eluted with 1.5 L of 20% ethyl acetate in hexane (v/v) followed by 1 L of 70% ethyl acetate in hexane (v/v). Fractions of 40 mL were collected. Fractions 22 through 30 contained **11** (0.59 g, 3.16 mmol, 44%) and fractions 54 through 61 contained **10** (0.56 g, 2.99 mmol, 41%).

4-Oxa-7,8-benzotricyclo[4.3.0.0^{2,9}]non-7-en-5-one (11): mp (ether/hexanes) 114 °C; IR (KBr, cm^{-1}) 1735, 1215, 1198; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.4–7.0 (4 H, m), 4.66 (1 H, dd, J = 8.8, 13.0 Hz), 4.25 (1 H, d, J = 6.7 Hz), 3.25 (1 H, dd, J = 6.1, 13.0 Hz), 2.85 (1 H, dd, J = 5.9, 7.0 Hz), 2.65 (1 H, m), 2.02 (1 H, m); ^{13}C NMR (C_6D_6, 15.04 MHz) δ 169.4, 142.3, 138.1, 128.3, 127.4, 124.9, 124.4, 64.7, 48.9, 31.7, 26.2, 19.2; mass spectrum, m/e (M^+) calcd 186.0678, obsd 186.0681. **4-Oxa-7,8-benzotricyclo[4.3.0.0^{2,9}]-non-7-en-3-one (10)**: mp (ethanol/hexane) 140 °C; IR (KBr, cm^{-1}) 1730, 1390, 1231, 1168, 1090, 1075, 819, 769; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.4–7.0 (4 H, m), 4.68 (1 H, dd, J = 10.6, 1.5 Hz), 4.30 (1 H, dd, J = 10.6, 2.3 Hz), 3.74 (1 H, ddd, J = 7.0, 2.3, 1.5 Hz), 2.84 (2 H, m), 2.13 (1 H, dd, J = 8.5, 7.2 Hz); ^{13}C NMR (Me_2CO-d_6, 15.04 MHz), δ 166.4, 143.1, 142.3, 127.2, 126.9, 124.2, 124.1, 71.6, 40.3, 31.4, 27.3, 22.6; mass spectrum, m/e (M^+) calcd 186.0678, obsd 186.0681.

4-*endo*-(Hydroxymethyl)-2,3-benzobicyclo[3.1.0]hex-2-ene-6-*endo*-carboxylic Acid (12). Lactone **10** (100 mg, 0.54 mmol) in 30 mL of 2% aqueous sodium hydroxide solution was heated on a steam bath for 2 h. The solution was cooled to room temperature, acidified with cold dilute HCl, and immediately extracted with ether (2 × 80 mL). Drying ($MgSO_4$) and removal of the solvent at reduced pressure left **12** (108 mg, 0.54 mmol, 100%) as a crystalline solid: mp 151–153 °C; IR (KBr, cm^{-1}) 3400 (br), 3600–2500 (br), 1710 (s), 1220 (s), 1030 (s); ^1H NMR (Me_2SO-d_6, 100 MHz) δ 7.0 (4 H, m), 3.9–3.5 (4 H, m), 2.9 (1 H, t), 2.2 (1 H, m), 1.9 (1 H, t); mass spectrum, m/e (M^+) calcd 204.0787, obsd 204.0783.

Reclosure of 12. Hydroxy acid **12** (24.5 mg, 0.112 mmol) was dissolved in 2 mL of THF, and a catalytic amount of *p*-toluenesulfonic acid was added. The solution was stirred overnight, and the solvent was removed at reduced pressure. The remaining material was dissolved in ether, and the ether solution was washed sequentially with water and brine. The solution was dried ($MgSO_4$), and the ether was removed at reduced pressure to afford lactone **12** (20 mg, 0.107 mmol, 96%).

Methyl 6-*endo*-(Hydroxymethyl)-3,4-benzobicyclo[3.1.0]-hex-3-ene-2-*exo*-carboxylate (14). Lactone **11** (504 mg, 2.70 mmol) in 100 mL of 2% aqueous sodium hydroxide solution was heated on a steam bath for 1 h. The resulting solution was cooled to room temperature, acidified with dilute HCl, and immediately extracted with ether (2 × 100 mL). The ether was dried ($MgSO_4$) and removed at reduced pressure to afford a crystalline solid which was dissolved in 80 mL of methanol. A catalytic amount of *p*-toluenesulfonic acid was added, and the solution was stirred overnight at room temperature. The methanol was removed at reduced pressure, and the residue was dissolved in ether (80 mL).

The solution was washed with water (20 mL) and dried ($MgSO_4$), and the solvent was removed at reduced pressure to afford **14** (564 mg, 2.56 mmol, 95% crude), which was used without further purification: IR (neat, cm^{-1}) 3700–3100, 1737, 1479, 1460, 1435, 1020, 803, 760; ^1H NMR ($CDCl_3$ 200 MHz) δ 7.4–7.1 (4 H, m), 3.86 (1 H, br s), 3.65 (3 H, s), 3.21 (2 H, AB of ABX, J_{AB} = 11.5 Hz, J_{AX} = 7.8 Hz, J_{BX} = 8.2, ν_A = 637 Hz, ν_B = 647 Hz), 2.71 (1 H, ddd, J = 8.2, 6.1, 2.1 Hz), 2.40 (br singlet, exchangeable), 2.38 (1 H, ddd, J = 8.2, 6.1, 2.1 Hz), 1.55 (1 H, quintet, J = 8.2 Hz); mass spectrum, m/e (M^+) calcd 218.0943, obsd 218.0944.

Tetrahydropyranyl Ether 15. Crude ester **14** (504 mg, 2.56 mmol) was dissolved in 10 mL of dry THF. Dihydropyran (0.71 mL, 7.6 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added, and the solution was stirred at room temperature for 2 h. Dilute aqueous sodium hydroxide solution (1 mL) was added to make the solution slightly alkaline, the THF was removed at reduced pressure, and the residue was taken up in ether (100 mL). The solution was washed with water (10 mL) and dried ($MgSO_4$), and the solvent was removed at reduced pressure to afford **15** (740 mg, 2.43 mmol, 95% crude) as a brown oil (used without further purification): ^1H NMR ($CDCl_3$, 100 MHz) δ 7.4–7.0 (4 H, m), 4.4 (1 H, m), 4.2 (1 H, m), 3.9 (1 H, m), 3.8 (4 H, s), 3.2 (2 H, m), 2.8 (1 H, m), 2.4 (1 H, m), 2.0–1.0 (8 H, m).

Alkylation of THP Ether 15. Crude ether **15** (740 mg, 2.45 mmol) in 10 mL of dry THF was added via syringe to a solution of lithium diisopropylamide in THF/hexane (3.19 mL, 3.1 mmol) at −78 °C. The resulting solution was stirred for 1 h at −78 °C, and methyl iodide (0.31 mL, 4.9 mmol) was added slowly via syringe. The cooling bath was allowed to expire as the solution was stirred overnight. Dilute aqueous sodium dihydrogen phosphate solution (5 mL) was added to quench the excess base, and the solution was acidified with dilute aqueous HCl. After THF removal at reduced pressure, 20 mL of water was added, and the solution was extracted with ether (5 × 30 mL). Drying ($MgSO_4$) and removal of the ether at reduced pressure left **16** (722 mg, 2.43 mmol, 99% crude): ^1H NMR ($CDCl_3$, 100 MHz, partial) δ 7.5–7.1 (4 H, m), 4.4 (1 H, m), 4.2 (1 H, m), 3.7 (s, 3 H), 2.0–1.1 (11 H, m).

6-*exo*-Methyl-4-oxa-7,8-benzotricyclo[4.3.0.0^{2,9}]non-7-en-5-one (17). A solution of 25 mL of methanol, a catalytic amount of *p*-toluenesulfonic acid, and crude **16** (772 mg, 2.44 mol) was stirred 1 h at 0 °C and overnight at room temperature. The solution was diluted with 25 mL of water, the methanol was removed at reduced pressure, and the remaining solution was extracted with ether (5 × 30 mL). The ether was dried ($MgSO_4$) and removed at reduced pressure. Aqueous sodium hydroxide solution (40 mL of 2%) was added to the residue, and the suspension was heated on a steam bath for 1 h. The resulting solution was cooled to room temperature, acidified with dilute HCl, allowed to stand overnight, and extracted with ether (5 × 40 mL). The solution was dried ($MgSO_4$), and the solvent was removed at reduced pressure to yield 414 mg of a slightly discolored solid. Flash chromatography (150 × 30 mm column, 25% ethyl acetate in hexane, 20-mL fractions) afforded **17** (397 mg, 1.97 mmol, 81%) in fractions 5 through 14: mp (ether/hexanes) 72 °C; IR (CH_2Cl_2, cm^{-1}) 1735, 1103, 1026; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.3–7.0 (4 H, m), 4.54 (1 H, dd, J = 13.3, 9.4 Hz), 3.14 (1 H, dd, J = 13.3, 6.7 Hz), 2.88 (1 H, t, J = 6.7 Hz), 2.30 (1 H, dd, J = 6.7, 9.2 Hz), 1.97 (1 H, ddt, J = 6.7, 6.7, 9.2, 9.4 Hz), 1.54 (3 H, s); ^{13}C NMR (C_6D_6, 15.04 MHz) 172.3, 143.3, 141.7, 129.0, 125.5, 124.2, 123.9, 64.6, 51.6, 32.2, 31.1, 24.6, 20.6; UV (CH_3CN), λ_{max} 277 nm (ϵ = 1034 M^{-1} cm^{-1}), 270 (1070); mass spectrum, m/e (M^+) calcd 200.0834, obsd 200.0837.

6-*endo*-(Hydroxymethyl)-2-*exo*-methyl-3,4-benzobicyclo[3.1.0]hex-3-ene-2-*endo*-carboxylic Acid. Lactone **17** (100 mg, 0.50 mmol) was added to 20 mL of 2% aqueous sodium hydroxide solution and heated on a steam bath for 2 h. The solution was cooled to room temperature, acidified with cold dilute HCl, and immediately extracted with ether (2 × 50 mL). The solution was dried ($MgSO_4$), and the solvent was removed at reduced pressure to afford hydroxy acid (116 mg, 99%): mp 146–148 °C; IR (KBr, cm^{-1}) 3500–3300 (br), 3400–2600 (br), 1710 (s); ^1H NMR (Me_2CO-d_6, 100 MHz) δ 7.4–7.1 (4 H, m), 3.40 (1 H, br), 3.20 (1 H, dd), 2.87 (1 H, dd), 2.65 (1 H, dd), 1.95 (1 H, dd), 1.55 (3 H, s), 1.55 (1 H, m); mass spectrum, m/e (M^+) calcd 218.0939, obsd 218.0944.

2-*exo*-Methyl-3,4-benzobicyclo[3.1.0]hex-3-ene-2-*endo*,6-*endo*-dicarboxylic Acid (18). Lactone **17** (0.46 g, 2.28 mmol) was dissolved in 5 mL of 2 N aqueous NaOH. Potassium permanganate (2 g, 12.6 mmol) was added, and the solution was stirred overnight. After acidification with dilute HCl, the solution was thoroughly extracted with ether. The ether was filtered, dried ($MgSO_4$), and removed at reduced pressure to yield **18** (0.50 g, 2.14 mmol, crude yield 94%) as a white solid: mp (ethanol/hexane) 203–205 °C; IR (KBr, cm^{-1}) 3600–2400, 1710, 1650; ^1H NMR (Me_2CO-d_6, 200 MHz) δ 7.6–7.0 (4 H, m), 3.07 (1 H, dd, J = 6.2, 8.5 Hz), 2.27 (1 H, dd, J = 6.2, 7.8 Hz), 2.13 (1 H, dd, J = 8.5, 7.8 Hz), 1.55 (3 H, s); mass spectrum, m/e (M^+) calcd 232.0732, obsd 232.0736. The diacid was difficult to purify, but the procedure gave material of sufficient purity for subsequent transformations.

Dimethyl 2-*exo*-Methyl-3,4-benzobicyclo[3.1.0]hex-3-ene-2-*endo*,6-*endo*-dicarboxylate (20). A solution of diacid **18** (55.0 mg, 0.237 mmol) in 20 mL of ether was stirred at 0 °C, and an ethereal solution of diazomethane was added slowly until a yellow color persisted. After 1 h of stirring at 0 °C, excess diazomethane was quenched with dilute ethereal acetic acid. The resulting solution was washed with water (2 × 10 mL) and dried ($MgSO_4$). Removal of the solvent at reduced pressure and preparative TLC of the resultant material afforded **20** (54.4 mg, 0.209 mmol, 88%) as a white solid: mp 99–100 °C; IR (CH_2Cl_2, cm^{-1}) 1735 (s), 1435 (s), 1205 (s); NMR ($CDCl_3$, 200 MHz) δ 7.6–6.2 (4 H, m), 3.68 (3 H, s), 3.28 (3 H, s), 2.97 (1 H, dd, J = 7, 8 Hz), 2.24 (1 H, dd, J = 7, 8 Hz), 2.08 (1 H, t, J = 8 Hz), 1.64 (3 H, s); mass spectrum, m/e (M^+) calcd 260.0144, obsd 260.0150.

6-*exo*-Methyl-4-oxa-7,8-benzotricyclo[4.3.0.0^{2,9}]non-7-ene-3,5-dione (19). Diacid **18** (9.7 mg, 0.042 mmol) was dissolved in 1 mL of dry benzene and cooled to 10 °C. Oxalyl chloride (0.10 mL, 1.1 mmol) was added slowly via syringe. The cooling bath was removed, and stirring was continued for 4 h. Solvents were removed at reduced pressure to yield anhydride **19** as a white solid which was recrystallized from ether/hexane (7.6 mg, 0.036 mmol, 85%): mp (ether/hexane) 109 °C; IR (CH_2Cl_2, cm^{-1}) 1806, 1761, 1040, 975; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.4–7.0 (4 H, m), 3.20 (1 H, dd, J = 6.2, 8.1 Hz), 2.62 (2 H, m), 1.80 (3 H, s); ^{13}C NMR (C_6D_6, 15.04 MHz) δ 169.8, 163.7, 143.7, 140.7, 129.2, 128.2, 125.0, 123.8, 52.3, 34.2, 32.5, 27.0, 21.9; UV (CH_3CN) λ_{max} 277 nm (ϵ = 509 M^{-1} cm^{-1}), 269 (571); mass spectrum, m/e (M^+) calcd 214.0627, obsd 214.0610. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.88; H, 4.70. Found: C, 72.64; H, 4.91.

3,4-Benzobicyclo[3.1.0]hex-3-ene-2-*exo*,6-*endo*-dicarboxylic Acid (21). Hydroxy acid **13** (110 mg, 0.54 mmol) was dissolved in 5 mL of acetone and cooled to 0 °C. Jones reagent (3 equiv) was added dropwise, and the resulting solution was stirred for 30 min at 0 °C at which time the bath was removed and stirring continued for 2 h. The excess reagent was quenched with isopropyl alcohol, and the solvents were removed at reduced pressure. Water was added to the resulting material, which was then extracted thoroughly with ether. The combined extracts were washed with brine and dried ($MgSO_4$), and the solvent was removed at reduced pressure to yield **21** (105 mg, 0.48 mmol, crude yield 89%) as a slightly discolored solid: IR (CH_2Cl_2, cm^{-1}) 3400–2400, 1716, 1703; ^1H NMR (Me_2CO-d_6, 200 MHz), δ 7.4–7.0 (4 H, m), 4.6 (1 H, broadened singlet), 3.05 (1 H, dd), 2.70 (1 H, dd), 2.20 (1 H, dd).

Dimethyl 3,4-Benzobicyclo[3.1.0]hex-3-ene-2-*exo*,6-*endo*-dicarboxylate (22). An ethereal solution of diacid **21** was cooled to 0 °C, and an ethereal solution of diazomethane was added slowly until the yellow color of diazomethane persisted. The solution was allowed to stand for 30 min and then quenched with ethereal acetic acid. The resulting solution was washed sequentially with dilute aqueous sodium hydroxide and brine and dried (Na_2SO_4). Solvent removal at reduced pressure afforded **22** as a yellow oil which was crystallized from hexane at −20 °C (no yield was obtained): mp (hexane) 80 °C; IR (KBr, cm^{-1}) 1732, 1720, 1438, 1278, 1210, 1192, 1179, 1160, 1142, 810, 761, 750; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.5–7.1 (4 H, m), 4.50 (1 H, br s), 3.75 (3 H, s), 3.40 (3 H, s), 3.08 (1 H, ddd, J = 8.6, 6.3, 1.2 Hz), 2.71 (1 H, ddd, J = 7.9, 6.3, 0.9 Hz), 2.16 (1 H, ddd, J = 8.6, 7.9, 0.4 Hz); mass spectrum, m/e (M^+) calcd 246.0892, obsd 246.0893.

2-Oxo-3,4-benzobicyclo[3.1.0]hex-3-ene-6-*endo*-carboxylic Acid (23). Hydroxy acid **13** (0.50 g, 2.29 mmol) and potassium permanganate (2.0 g, 12.6 mmol) were stirred 18 h in 20 mL of

2 N aqueous sodium hydroxide. The solution was acidified with dilute hydrochloric acid and extracted thoroughly with ether. The solution was dried ($MgSO_4$) and filtered, and the solvent was removed at reduced pressure to afford a solid which was recrystallized from acetone to yield **23** (0.27 g, 1.3 mmol, 59%): mp 205 °C; IR ($CHCl_3$, cm^{-1}) 3600–2800, 1715, 1698, 1420, 1167; ^1H NMR (Me_2CO-d_6, 200 MHz) δ 11.3 (1 H, br), 7.4–7.0 (4 H, m), 3.44 (1 H, dd, J = 8.6, 6.0 Hz), 2.84 (1 H, t, J = 8.6 Hz), 2.64 (1 H, dd, J = 8.6, 6.0 Hz).

Methyl 2-Oxo-3,4-benzobicyclo[3.1.0]hex-3-ene-6-*endo*-carboxylate (24). Keto acid **23** was esterified as described for **22**. Recrystallization of the solid product from ether afforded pure **24** (no yield was obtained): mp 104 °C; IR ($CHCl_3$, cm^{-1}) 1735, 1712, 1605, 1200, 1161; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.6–7.2 (4 H, m), 3.39 (3 H, s), 3.30 (1 H, X of ABX, $J_{AX} = J_{BX}$ = 7.3 Hz), 2.68 (2 H, AB of ABX, J_{AB} = 7.3 Hz); ^{13}C NMR (C_6D_6, 15.04 MHz) δ 197.7, 167.8, 146.7, 137.4, 133.2, 125.9, 123.2, 51.7, 41.4, 31.4, and 28.7 (one aromatic carbon is obscured by solvent); mass spectrum, m/e (M^+) calcd 202.0630, obsd 202.0638.

4-Oxa-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (25). Keto acid **23** (118 mg, 0.631 mmol) was dissolved in 10 mL of dry THF, and the solution was cooled to −40 °C. Methyllithium (1.2 mL of a 1.05 M solution, 1.26 mmol) was added dropwise and stirring was continued for 2 h at −40 °C. The cooling bath was allowed to expire, and the solution was stirred at room temperature for 8 h. Acidification of the solution with dilute hydrochloric acid and extraction with ether followed by drying ($MgSO_4$) and removal of the ether at reduced pressure afforded a solid product. The solid was dissolved in 5 mL of acetone and cooled to 0 °C. A solution of triethylamine (97 μL, 0.69 mmol) and methyl chloroformate (59 μL, 0.76 mmol) in 1 mL of acetone was added dropwise via syringe. Stirring was continued for 90 min at 0 °C and 30 min at room temperature. The acetone was removed at reduced pressure, and ether was added. The ether solution was washed sequentially with water and brine and dried (Na_2SO_4) and the solvent removed at reduced pressure to yield a yellow oil which was subjected to flash chromatography (15 × 3 cm column, 30% acetone in hexanes v/v). Slightly yellow **25** was eluted in 10-mL fractions 5 through 10. Removal of the solvent at reduced pressure afforded **25** (50 mg, 0.27 mmol, 42%): mp (ether/hexane) 103 °C; IR ($CDCl_3$, cm^{-1}) 1757, 1255, 998; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.4–7.1 (4 H, m), 3.35 (1 H, t, J = 6.0), 2.97 (1 H, dd, J = 6.0, 8.0 Hz), 2.75 (1 H, dd, J = 6.0, 8.0 Hz), 1.93 (3 H, s); ^{13}C NMR (C_6D_6, 15.04 MHz) δ 170.8, 146.7, 140.7, 129.2, 127.1, 125.1, 121.1, 91.6, 45.0, 39.4, 33.4, 18.9; mass spectrum, m/e (M^+) calcd 186.0681, obsd 186.0681.

Photolysis of 25. A solution of lactone **25** (10 mg, 0.05 mmol) and CD_3CN (0.5 mL) was placed in a 5-mm o.d. quartz tube and deoxygenated by purging with a slow stream of nitrogen. The tube was then placed in the cavity of a Rayonet photochemical reactor and irradiated at 254 nm. After 16 h of irradiation, ca. 50% conversion to 1-methylnaphthalene was observed by ^1H NMR. No other products were observed.

Photolysis of 19. A solution of anhydride **19** (10 mg, 0.05 mmol) and CD_3CN (0.5 mL) was placed in a 5-mm o.d. quartz tube and deoxygenated by purging with a slow stream of nitrogen. The tube was then placed in the cavity of a Rayonet photochemical reactor and irradiated at 254 nm. After 20 min of irradiation, ca. 4% conversion to **25** was observed by ^1H NMR. A trace of 1-methylnaphthalene was observable by capillary GC. No other products were observed. Photolysis for 16 h resulted in 30% conversion to lactone **25**, and a trace of (ca. 1%) of 1-methylnaphthalene was observable by ^1H NMR. No other products were observed.

Solution Thermolysis of 25. A solution of lactone **25** (10 mg, 0.05 mmol) and solvent (0.5 mL) was sealed in a 5-mm o.d. Pyrex tube and heated in a silicone oil bath. The tube was then opened and its contents were analyzed by ^1H NMR. If necessary, the tube was resealed for further thermolysis. In both Me_2CO-d_6 and C_6D_6 **25** was found to be stable at temperatures below 200 °C. Lactone **25** was found to decompose to unidentifiable products over a period of several hours at 200 °C.

Vapor-Phase Thermolysis of 25. A sample of lactone **25** was sublimed (90 °C, 0.2 mmHg) through a 300 °C Pyrex tube (20 cm × 1.5 cm) packed loosely with quartz wool. The pyrolysate consisted of a yellow oil which was collected in a cold trap at −78 °C. Analysis by ^1H NMR showed 1-methylnaphthalene to be the sole identifiable product (ca. 30%).

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Synthesis of Stereoisomeric 4,9a-Dimethylhydrodicyclopenta[*a*,*d*]cycloocten-1-ones Related to the Ophiobolins and Ceroplastins via Annelative Ring Expansion of Hydrindene Precursors

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Synthesis of several stereoisomeric ketones possessing the tricyclic 5-8-5 nucleus characteristic of the ophiobolin and ceroplastin sesterterpenes is described. Hydrindenebutenolides **15a,b** and **16a,b** bearing epimeric butenyl and (*E*)-pentenyl side chains were prepared from *trans*-hydrindanone **6** via the bromo Vilsmeier reaction, Grignard addition, and lithiation–carboxylation and were separated by chromatography. Sensitized irradiation of **15a,b** and **16a,b** effected intramolecular [2 + 2] cycloaddition to tetracyclic lactones **17a,b**, **20a,b** and **21a,b**. The corresponding keto acids underwent reductive cleavage of the cyclobutane ring with lithium–ammonia to form 5-8-5 keto esters **19** or acids **25**, **35**, and **40**. Iododecarboxylation followed by removal of iodine by either reductive replacement or dehydroiodination afforded a stereoisomeric series of dodecahydro-4,9a-dimethyldicyclopenta-[*a*,*d*]cyclooctan-1-ones (**27**, **28**, **30**, **37**, and **43**) and decahydro-4,9a-dimethyldicyclopenta[*a*,*d*]cyclooct-4(or 5)-en-1-ones (**29**, **38**, and **39a**, and **42**). The anti or syn relationship of the C-3a/C-9a (C-6/C-11 by ophiobolane numbering) substituents and the complete stereochemistry of the anti 5-8-5 ketones were established through an X-ray crystal analysis of one iodo ketone (**26c**) and various interconversions. The stereochemistry of reactions at C-8 and C-2, A/B ring fusion equilibrations, and the conformation of various 5-8-5 ketones are discussed.

The ophiobolins (e.g., ophiobolin F, **1**)[1] and the ceroplastins (e.g., ceroplastol I, **2**)[2] comprise two families of naturally occurring sesterterpenes that have in common a tricyclic dicyclopenta[*a*,*d*]cyclooctene nucleus bearing

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