and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: ^{1}H NMR spectra for compounds **2b**, **13b**, **13c**, **14**, **1c**, (2*S*)-2-hydroxy-1-(1-methylbicyclo[2.2.1]hept-5-en-2-yl)propan-1-one (major exo isomer), **4d**, **3d**, **3c**, **4c**, (2*S*)-1-(bicyclo[2.2.1]hept-5-en-2-yl)-2-hydroxypropan-1-one (minor exo isomer), (2*S*)-1-(bicyclo[2.2.1]hept-5-en-2-yl)-2-hydroxypropan-1-one (major exo isomer), **6b**, **3e**, **4e**, (2*S*)-1-(1,5-dimethylbicyclo[2.2.1]hept-5-en-2-yl)-2-hydroxypropan-1-one (major exo isomer), **8c**, **8c**·HCl (impure specimen), **5c**, and *ent*-**5c**, and X-ray crystallographic data for **10** (34 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.

Thermolysis of 2-Benzylidenebenzocyclobutenols†

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The thermolysis of a series of 2-benzylidenebenzocyclobuten-1-ols has been studied. Whenever comparisons can be made, the rate of opening of the benzocyclobutene ring was slower for these compounds than the corresponding 2-ones. The intermediate vinylallenes underwent a variety of electrocyclization reactions which depended on the nature of the additional substituent at C-1. 10-Benzylideneanthrone and 4-benzylidene-1-tetralones, respectively, were obtained when this substituent was phenyl or vinyl. 1-(Alkynylphenyl)-2-benzylidenebenzocylobuten-1-ols were converted to mixtures of 4-benzylidene-1,4-naphthoquinonemethides, 2,3-dibenzylidene-1-indanones, and 10-phenylbenzo[b]fluoroeneone.

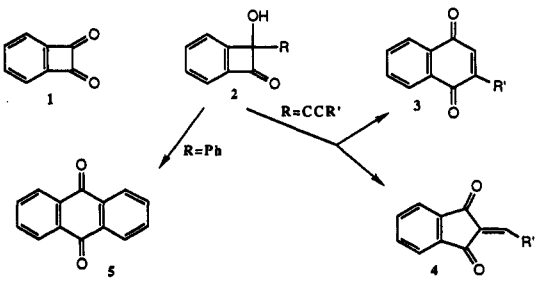
Introduction

Cyclobutene-1,2-diones and their derivatives have gained much attention during the past decade as versatile intermediates in organic synthesis mainly due to the work of Moore and Liebeskind.[1,2] Somewhat less attention has been paid to the benzocyclobutenedione analogs **1**. Nevertheless, these compounds have been used effectively as precursors to naphthoquinones, anthraquinones, and 2-alkylidene-1,2-indandiones. For example, as shown in Scheme I, thermolysis of adducts **2**, formed from **1** and alkynyl or aryl anions, respectively, proceeds readily to yield **3**, **4**, and **5**.[1] Ring expansion of **1** to naphthoquinones via metal carbonyl complexes has also been reported.[2]

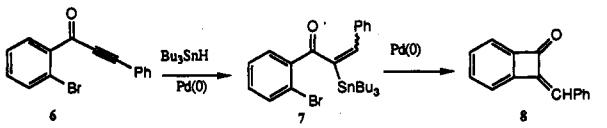
Recently, we have reported a convenient one-pot preparation of benzylidenecyclobutenones **8** starting with alkynones **6**.[3] Palladium-mediated regioselective addition of tributyltin hydride to **6** followed by intramolecular Stille coupling of the intermediate arylbromide–vinylstannane **7** gave **8** as a mixture of *E*/*Z* isomers about the exocyclic double bond in approximately 50% isolated yield. (Scheme II). Furthermore, this methodology enabled us to prepare derivatives of **8** with predictable substitution patterns in the aromatic ring. Methylenebenzocyclobutenones, of which **8** is a representative, have proven surprisingly difficult to prepare. For example, 2-methylenebenzocyclobutene has been prepared in low yield by Trahanovsky[4a] via flash vacuum pyrolysis of 3-[(benzoyloxy)methyl]benzofuran and 2-(carbethoxyethylidene)benzocyclobutenone was obtained by Cava[4b] from the dione and (carbethoxymethylene)triphenylphosphorane; Wittig reactions did not yield the simple alkylidene analogues.

In view of the work summarized in Scheme I, it became apparent that our compounds could lead to a regiospecific entry into similar ring systems if the benzylidene moiety could be shown to function as a masked carbonyl functionality. Thus, Scheme III was considered as a potential

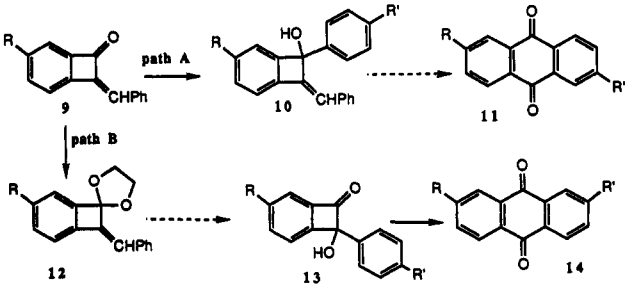
Scheme I



Scheme II



Scheme III



route to a set of regioisomeric anthraquinones. In path A, reaction of **9** with an aryllithium would yield the car-

† This paper is dedicated to the memory of our colleague Jean-Louis Roustan.

‡ Holder of NSERC PGS Scholarship, 1991–93.

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binol adduct **10**, which would then be subjected to oxidative cleavage of the benzylidene group and then thermolyzed to **11**. Alternatively (path B), **9** could first be ketalized to **12** followed by oxidative cleavage and condensation to **13**; thermolysis would then yield the regioisomeric anthraquinone **14**.

In the event, as will be described, the expected equivalence of the benzylidene group in **8** or derivatives thereof to a carbonyl group was found to be only partly valid. In particular, the oxidative conversion of the benzylidene group, when exo to the four-membered ring, to a carbonyl group was much more difficult than expected. Additionally, the benzylidenebenzocyclobutenes proved to be more stable thermally than the corresponding benzocyclobutenones. The higher temperatures required to generate the intermediate vinylallenes tended to lead to a greater variety of products, either directly or upon transformation of the initially formed materials. These features detract from the synthetic utility envisaged for the benzlidenebenzocyclobutenones. Nevertheless, a comparison of the reactivity of derivatives of **8** and **3** is helpful in understanding substituent effects in the ring opening of benzocyclobutenols.

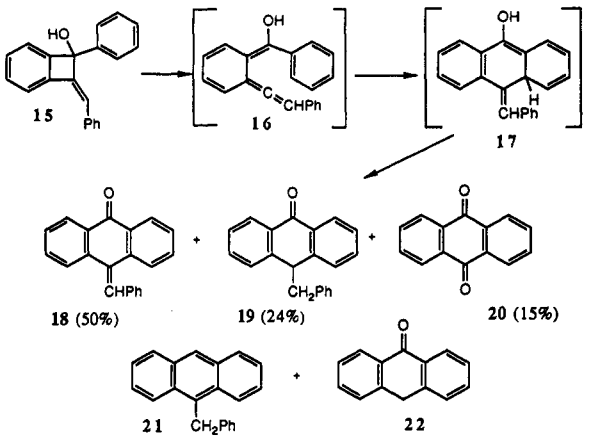
Results and Discussion

The benzocyclobutenol **10** (R = R′ = H) and ketals **12** (R = H, OMe, R′ = H) were readily prepared (vide infra); however, the oxidative cleavage of the benzylidene group in these compounds has proven thus far to be quite problematic. Ozonolysis or permanganate or periodate/permanganate oxidations yielded mainly products resulting from scission of the cyclobutene ring and only traces of the desired ketones.[5] Similar difficulties have been encountered in cleaving methylenecyclobutane to cyclobutanone with the maximum yield of cyclobutanone being 30%.[6]

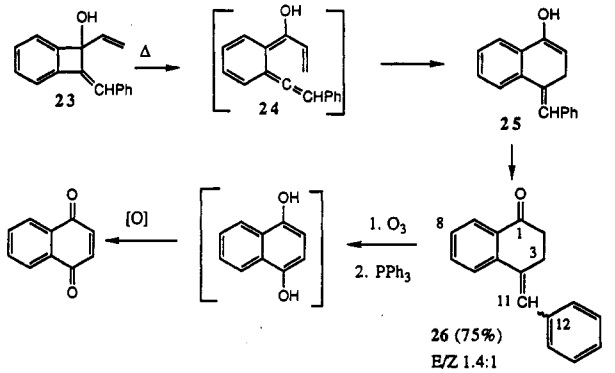
In order to circumvent this problem, at least partially, we explored the possibility of removing the benzylidene group after ring expansion had occurred. This would allow access to one of the isomers resulting from a ring expansion, e.g., **11**, and also enable us to compare the reactivity of **10** vs **2**.

Thus, phenylcarbinol **15** was prepared in 96% yield by treating **8*E*** with phenyllithium at −78 °C. When **15** was refluxed for 16 h in decalin the major product obtained was 10-benzylideneanthrone (**18**) in 40–65% yields (GC estimation). Variable amounts of 10-benzylanthrone (**19**), anthraquinone (**20**), 9-benzylanthracene (**21**), and anthrone (**22**) were also formed. Isolation of these products via chromatography was impractical due to overlapping R_f's in a number of solvent systems and the known instability of **18** to silica gel.[7] However, it was possible to isolate **18** and **20** by fractional crystallization. The remaining products were identified by comparison of GC–MS data with those from either authentic materials or reports in the literature. The mechanism for the formation of these materials is unclear at the present time, although the intermediacy of **16** and **17** is proposed. Free-radical involvement is unlikely since addition of 2,6-di-*tert*-butylphenol had no significant effect on the outcome of the thermolysis. It should be noted that ring opening of **2** (R = Ph) occurs at 160 °C (refluxing xylene) within 20 min[1f] compared to 16 h at 190 °c for **15**.

Scheme IV



Scheme V



Ozonolysis of **18** gave **20** in essentially quantitatively yield as judged by GC analysis. In principle, this shows that the benzylidene group in **15** can serve as a masked carbonyl functionality via a thermolysis–oxidation procedure.

The tertiary alcohol **23**, obtained in 88% yield from **8*E*** and vinylmagnesium bromide, required heating in refluxing decalin (190 °C) for 30 min for conversion to a 1.4:1 mixture (as judged by integration of the high-field portion of the ^{1}H NMR spectrum) of (*E*)- and (*Z*)-4-benzylidene-1-tetralones, **26** in 75% yield. Using a combination of 2-D NMR experiments such as COSY(H–H), HETCOR(C–H, one-bond correlation) and FLOCK[8] (C–H, mainly three-bond correlation), it was possible to assign the carbon and proton shifts for each isomer, as shown in Table I (see Experimental Section). Inspection of the NOESY allowed identification of the minor component as the *Z*-isomer since a correlation was found between H-3 and H-11 in the *Z* isomer. In refluxing xylene, the reaction was 90% complete (80% isolated products) by NMR after 28 h. This contrasts with the 30 min at 110 °C required to transform 1-vinylbenzocyclobuten-1-ol into 1-tetralone[9] and again illustrates the greater difficulty in generating the allenyl analogs of *o*-quinodimethane, e.g., **24**. Interestingly, the initial cyclization product **25** undergoes preferential ketonization to **26** rather than aromatization

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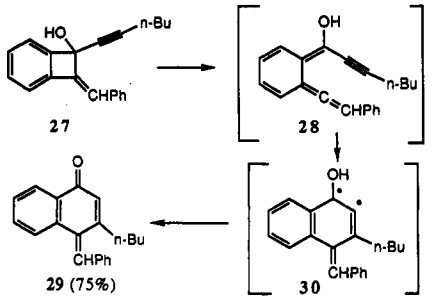
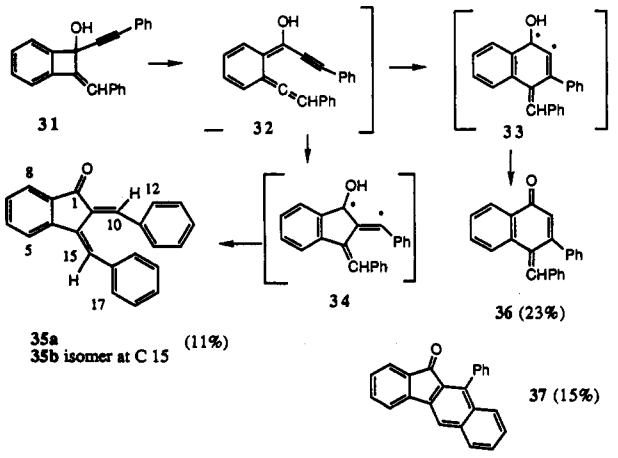
(9) Hickman, D.; Wallace, T. W.; Wardleworth, J. M. *Tetrahedron Lett.* **1991**, *32*, 619.

Scheme VI



Scheme VII

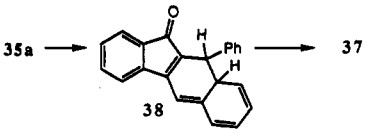


to 4-benzyl-1-naphthol. (Scheme V). Ozonolysis of **26** gave 1,4-naphthaquinone in near quantitative yield presumably via in situ oxidation of the initially formed 1,4-dihydroxynaphthalene.

Treatment of **8*E*** with 1-lithiohexyne at −78 °C followed by quenching at room temperature afforded alkynol **27** in 80% yield. Thermolysis of this adduct was carried out in refluxing decalin for 1.75 h and gave a 2:1 *Z*:*E* isomeric mixture of 3-*n*-butyl-4-benzylidenenaphthoquinonemethides **29** in 75% isolated yield. The identification of these structures rests primarily on the IR absorption at 1640 cm^{-1}, which is typical[10] of a *p*-quinonemethide moiety, and analysis of the ^1H NMR spectrum, which showed two characteristic singlets for each isomer. Irradiation of the methylene protons adjacent to the ring (δ = 2.23) in the minor isomer led to NOE enhancement of the singlet at δ = 6.43 and the aromatic protons at δ7.3, thus establishing the *E* isomer as the minor constituent. The formation of **29** is rationalized as involving ring opening to the vinylallene **28** followed by ring closure to the diradical **30**. Intramolecular hydrogen atom transfer yields **29**. The formation of **29** is expected based on the observations by Moore[1c] concerning the thermolysis of 4-alkynyl-4-hydroxycyclobutenones.

In contrast, thermolysis of the phenyl-substituted alcohol **31** afforded the four isomeric products shown in Scheme VII. One of these, **36** (23%), was shown to be a 3:1 *Z*:*E* mixture of 3-phenyl-4-benzylidenenaphthoquinonemethides. Their structure assignment was based on IR and NMR arguments made for the analogous isomeric mixture **29**. In this case, the identification of the *E* isomer as the minor component was accomplished by inspection of the NOESY, which showed a correlation between the benzylidene hydrogen at δ = 7.95 and the nearest hydrogen on the naphthaquinonemethide skeleton at δ = 8.10.

Scheme VIII



The isomeric pair of 2,3-dibenzylideneindan-1-ones **35a** and **35b** can be rationalized as arising from an alternate cyclization of **32** to the diradical **33** followed by hydrogen transfer. This path becomes competitive with cyclization to **34** since phenyl is a good radical stabilizer.[1c] It was possible to isolate **35a** and characterize it by its IR spectrum which showed an absorption at 1703 cm^{-1} characteristic of 2-alkylidene-1-indanones[2d] and full assignment the hydrogen and carbon resonances by means of the same 2-D NMR techniques used for the isomeric mixture **26**. These results are summarized in Table II (see Experimental Section). The stereochemical assignment at the vinyl carbon 15 was unambiguous due to a clear NOE enhancement of H-5 upon irradiation of H-15. However, NOE techniques proved to be futile for similar assignment at C-10 because the shifts of H-12 and H-17 are too close. This problem was resolved by addition of the shift reagent $Eu(fod)_3$, which selectively deshielded H-10 by 1.6 ppm and H-8 by 0.6 ppm while the rest of the hydrogens were affected by only 0.1–0.3 ppm. This is possible only with the assigned stereochemistry at C-10 assuming that the shift reagent coordinates with the carbonyl functionality. Isolation of the isomer **35b** by chromatography was not possible. 2-Alkylidene-1,3-indanediones have proved to be quite unstable to silica gel[2e] and it is possible that **35b** is more sensitive than **35a** and decomposes partially upon attempted purification. Some of the crude fractions suggest that this material may be present since they show an IR absorption at 1704 cm^{-1} expected for this structure.

Finally, the formation of the tetracyclic product **37**, characterized by MS, IR, and NMR evidence as well as comparison with the reported mp, can be rationalized as resulting from a 6π cyclization of **35a** involving both the exocyclic C–C double bonds and 2π electrons of the phenyl group which is part of the 3-benzylidene group followed by in situ oxidation of the intermediate **38** to **37**. Not unexpectedly **35a** undergoes slow conversion to **37**, even upon standing in air at room temperature (Scheme VIII).

Experimental Section

General. Solvents for the extractions and chromatographic purifications were routinely distilled prior to use. Reagent-grade decalin kept over 4A molecular sieves was used without prior distillation. ^1H and ^{13}C spectra were obtained either on a Varian XL-300 or a Gemini-200 spectrometer. Two-dimensional NMR experiments were run on the Varian XL-300 instrument. The FLOCK pulse sequence was optimized for 7.5 Hz, yielding mainly three-bond C–H correlations for the compounds under study. For inseparable mixtures, ^{13}C shifts were assigned to each component based on quantitative ^{13}C experiments, using a 90° pulse and a delay of 80 s.

2-Benzylidene-1-phenylbenzocyclobuten-1-ol (15). *n*-BuLi (2.15 M in hexanes, 1.5 mL, 3.23 mmol) was added to a solution of bromobenzene (0.55 g, 3.5 mmol) in 5 mL of THF at −78 °C. The solution was stirred at −78 °C for 15 min, and then a solution of **8*E***[3] (180 mg, 0.88 mmol) in 15 mL of THF, precooled to −78 °C, was added via cannula over 15 min. The mixture was stirred for an additional 30 min at −78 °C, quenched by dropwise addition of saturated NH_4Cl, warmed to rt, extracted into ether, dried over $MgSO_4$, and evaporated. Purification of the remaining brown oil by flash chromatography (1:1 hexanes–CH_2Cl_2) gave **15** (241 mg,

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(11) *Merk Index*, 10th ed.; Merck: Rahway, NJ, 1983; p 6247.

96%) as a colorless oil: ^{1}H NMR δ 2.93 (1 H, s), 6.46 (1 H, s), 7.2–7.7 (14 H, m); ^{13}C NMR δ 119.69, 121.81, 122.14, 125.84, 127.45, 127.58, 127.82, 128.26, 128.55, 130.17, 136.69, 141.86, 144.07, 148.40, 153.75; IR (CH_2Cl_2) 3574, 1046 cm^{-1}; MS (*m/e*, int) 284 (M^+, 100), 207 (32), 178 (32), 150 (10), 105 (20), 51 (27); HRMS for $C_{21}H_{16}O$ calcd 284.1201, found 284.1176.

Thermolysis of 15. A solution of **15** (66 mg, 0.23 mmol) was refluxed in 10 mL of decalin under Ar. After 16 h, a GC sample indicated the disappearance of starting material and formation of **18** (50%), **19** (24%), and **20** (15%). The solvent was removed by washing with hexanes over a plug of silica gel. Chromatography of the residue was unsuccessful in separating the components due to overlapping R_f's in various combinations of hexanes, CH_2Cl_2, ether, ethyl acetate, toluene, and CCl_4. Fractional crystallization using hexanes/CH_2Cl yielded small quantities of sufficiently pure materials in the following order: **anthraquinone (20)** as white needles [^{1}H NMR δ 8.29 (4 H, m), 7.78 (4 H, m); IR (CH_2Cl_2) 1675 cm^{-1}; MS (*m/e*, int) 208 (M^+, 100), 180 (97), 152 (77), 76 (54)]; **benzylideneanthrone (18)** as a yellowish solid [mp 128 °C (lit.[12] mp 127 °C); ^{1}H NMR δ 8.28 (1 H, d, *J* = 8 Hz), 8.24 (1 H, d, *J* = 8 Hz), 7.64 (1 H, td, *J* = 8, 1.5 Hz), 7.57 (1 H, s), 7.54–7.46 (2 H, m), 7.40 (1 H, td, *J* = 8, 1 Hz), 7.34–7.25 (5 H, m), 7.22 (1 H, td, *J* = 8, 1.5 Hz); IR (CH_2Cl_2) 1660, 1602 cm^{-1}; MS (*m/e*, int) 282 (M^+, 83), 281 (100), 252 (57)]; **benzylanthrone (19)** [identified by comparison of the MS (*m/e*, int) 284 (M^+, 22), 193 (100), 165 (37), 91 (56) (obtained from a GC–MS) with the reported[14] cleavage pattern. In other runs compounds **21** and **22** were also obtained in yields of up to 35% and 14%, respectively, as estimated by GC]; **9-benzylanthracene (21)** [identified by GC–MS and comparison of the reported[15] cleavage pattern, MS (*m/e*, int) 268 (M^+, 100), 191 (50)]; and **anthrone (22)** [identified by GC–MS and comparison with an authentic sample, MS (*m/e*, int) 194 (M^+, 100), 165 (83)].

2-Benzylidene-1-vinylbenzocyclobuten-1-ol (23). Vinylmagnesium bromide (1 M in hexanes, 2.8 mL, 2.8 mmol) was added to a solution of **8*E*** (308 mg, 1.50 mmol) in 10 mL of THF at −78 °C. The solution was stirred at −78 °C for 45 min and then allowed to warm to rt over 30 min. Saturated NH_4Cl was then added and the mixture extracted with ether (2 × 20 mL), dried over $MgSO_4$, and evaporated to give **23** (308 mg, 88%) as a colorless glassy residue: ^{1}H NMR δ 2.64 (1 H, s), 5.22 (1 H, dd, *J* = 10.5, 1.5 Hz), 5.53 (1 H, dd, *J* = 17.2, 1.5 Hz), 6.14 (1 H, dd, *J* = 17.7, 10.5 Hz), 6.44 (1 H, s), 7.25–7.45 (6 H, m), 7.5–7.6 (3 H, m); IR (CH_2Cl_2) 3579, 1079, 992, 930 cm^{-1}; MS (*m/e*, int) 234 (M^+, 73), 233 (48), 215 (70), 202 (50), 178 (66), 157 (50), 131 (99), 119 (100); HRMS calcd for $C_{17}H_{14}O$ 234.1045, found 234.1047.

Thermolysis of 23. A solution of **23** (65 mg, 0.28 mmol) in 10 mL of decalin was refluxed under N_2 for 30 min. TLC indicated completion of the reaction, and the mixture was washed on a plug of silic (70–230 mesh, 12 g) with 150 mL of hexanes. An orange band was eluted out with ether (25 mL), and the residue was chromatographed on a Chromatotron plate (2 mm, 20:1 hexanes–EtOAc) to yield **4-benzylidenetetralone (26)** as a white solid consisting of a 1.4:1 *E*/*Z* mixture (50 mg, 75% yield): ^{1}H and ^{13}C NMR (see Table I); IR (CH_2Cl_2) 1682 cm^{-1}; MS (*m/z*, int) 234 (100), 191 (40), 91 (60); HRMS calcd for $C_{17}H_{14}O$ 234.1045, found 234.1046.

Ozonolysis of 26. A solution of **26** (74 mg, 0.32 mmol) in CH_2Cl_2 (5 mL)/MeOH (0.5 mL) was placed in a gas bubbler and cooled to −78 °C. Ozone was bubbled through for 3 min, at which time the solution was deep blue. A solution of triphenylphosphine (92 mg, 0.35 mmol) in 1 mL of CH_2Cl_2 was then added and the mixture stirred at −78 °C for 5 min and then allowed to warm to rt, evaporated, and purified on a Chromatotron plate (2 mm, 10:1 hexanes/EtOAc) to yield **naphthoquinone** (48 mg, 95%) as a yellow solid: mp 127–128 °C (lit.[11] mp 126 °C); ^{1}H NMR δ 6.95 (2 H, s), 7.73 (2 H, dd, *J* = 5.7, 3.4 Hz), 8.06 (2 H, dd, *J* = 5.8, 3.3 Hz); ^{13}C NMR δ 126.39, 131.88, 133.90, 136.64, 184.98;

Table I. ^{13}C and ^{1}H NMR Assignments and FLOCK Correlations for 26*E*/*Z*

	^{13}C		^{1}H		C–H corr	
position	*E*	*Z*	*E*[a]	*Z*[a]	*E*	*Z*
1	127.08	127.14	8.04d	8.03d	3	
2	128.10	128.67	7.39c	7.27c	4	4
3	133.79	132.32	7.56t	7.20c	1, 4	1
4	124.85	128.11	7.70d	7.30c	2	
5	142.61	140.48			11, 19	11
6	131.24	132.52			2, 4	2, 4
7	197.61	197.98				
8	38.84	40.09	2.68t	2.82c	9	9
9	27.19	35.63	3.09t	2.82c	8, 11	8, 11
10	137.05	136.99			8, 9	8, 9
11	127.50	127.18	7.17s	6.72s	9	9
12	137.05	136.99			14	14
13	129.12	130.33	7.20c	7.32c	11, 13	11, 13
14	128.40	128.32	7.21c	7.40c	14	14
15	127.28	127.19	7.3c	7.3c	13	

[a] c = centered at, d = doublet, s = singlet, t = triplet.

IR (CH_2Cl_2) 1669, 1599 cm^{-1}; MS 158 (M^+, 100), 130 (47), 104 (64), 102 (59), 76 (61), 50 (39); HRMS calcd for $C_{10}H_6O_2$ 158.0368, found 158.0359.

2-Benzylidene-1-(1-hexynyl)benzocyclobuten-1-ol (27). *n*-BuLi (2.15 M in hexanes, 1.5 mL, 3.2 mmol) was added to a solution of 1-hexyne (0.33 g, 4.0 mmol) in 10 mL of THF at −78 °C, and the mixture was stirred for 25 min. A solution of **8*E*** (186 mg, 0.90 mmol) in THF (5 mL), precooled to −78 °C, was added via cannula over 15 min, and the resulting mixture was stirred at −78 °C for 6 h, quenched with saturated NH_4Cl (5 mL), and then allowed to warm to rt, extracted with ether (25 mL), and dried over $MgSO_4$. The evaporated residue was purified on a Chromatotron plate (2 mm, 1:1 hexanes/CH_2Cl_2) to yield **27** (183 mg, 71%) as a colorless oil: ^{1}H NMR δ 0.87 (t, 3 H), 1.3–1.6 (m, 4 H), 2.24 (t, 2 H), 2.71 (s, 1 H), 6.62 (s, 1 H), 7.25–7.47 (m, 6 H), 7.5–7.6 (m, 3 H); IR (CH_2Cl_2) 3570, 2233 cm^{-1}; MS (*m/e*, int) 288 (M^+, 10), 231 (100), 215 (39), 202 (48); HRMS calcd for $C_{21}H_{20}O$ 288.1514, found 288.1523.

Thermolysis of 27. The acetylenic alcohol **27** (47.2 mg, 0.16 mmol) was refluxed in 3 mL of decalin for 1.75 h, when the reaction was judged complete by TLC. The reaction mixture was washed on a silica plug (15 g) with hexanes (400 mL). Elution with ether yielded the **4-benzylidene-3-butyl-1,4-naphthoquinonemethides (29)** (35.4 mg, 75%) as a brown oil (2:1 *Z*/*E* mixture): ^{1}H NMR (*Z*) δ 8.11 (1 H, d, *J* = 8 Hz), 7.51 (1 H, d, *J* = 8.3 Hz), 7.46 (1 H, s), 7.13 (1 H, t, *J* = 7.3 Hz), 6.41 (1 H, s), 2.73 (2 H, t), 1.68 (2 H, m), 1.42 (2 H, m), 0.95 (3 H, t); (*E*) 8.16 (1 H, d, *J* = 7 Hz), 7.94 (1 H, d, *J* = 8.2 Hz), 7.80 (1 H, s), 7.57 (1 H, t, *J* = 8.3 Hz), 6.43 (1 H, s), 2.23 (2 H, t), 1.25 (2 H, m), 0.85 (2 H, m), 0.63 (3 H, t); (overlapping) δ 7.40–7.25 (m); ^{13}C NMR (*Z* + 2 double int. of *E*) δ 185.24, 156.17, 137.23, 136.06, 135.51, 132.18, 132.07, 129.95, 129.43, 128.87 (×2), 128.74, 128.56, 128.32, 128.17, 126.02, 125.89, 33.09, 31.65, 22.67, 13.89; (*E*) δ 185.24, 156.25, 139.83, 137.41, 136.65, 132.53, 131.71, 130.52, 128.93, 128.23, 127.54, 126.06, 122.66, 35.10, 31.95, 22.14, 13.55; IR (CH_2Cl_2) 1641 cm^{-1}; MS (*m/e*, int) 288 (65), 207 (38), 181 (100), 105 (30), 91 (43); HRMS calcd for $C_{21}H_{20}O$ 288.1514, found 288.1511.

2-Benzylidene-1-(1-phenylethynyl)benzocyclobuten-1-ol (31). Phenylacetylene (130 μL, 1.22 mmol) was added to a solution of *n*-BuLi (2.35 M in hexanes, 0.50 mL, 1.18 mmol) at −78 °C. The mixture was stirred for 45 min followed by addition of **8*E*** (125 mg, 0.61 mmol) in 5 mL THF, precooled to −78 °C. The mixture was stirred at −78 °C for 1.5 h and then allowed to warm to rt for 30 min. The resulting brownish solution was poured into a vigorously stirred mixture of ether (40 mL) and saturated NH_4Cl (10 mL), which turned yellowish after a few minutes. The organic phase was separated, dried and evaporated and then purified on a 2-mm Chromatotron plate (2 mm, 3:1 hexanes/ethyl acetate) to yield **31** (158.3 mg, 85%) as a brown oil: ^{1}H NMR δ 2.92 (1 H, s), 6.72 (1 H, s), 7.2–7.6 (14 H, m); ^{13}C NMR δ 84.59, 88.23, 119.94, 121.24, 122.16, 122.41, 127.71, 127.98, 128.25, 128.56, 128.62, 130.23, 130.62, 131.93, 136.39, 143.57, 145.89, 151.42; MS (*m/e*, int) 308 (M^+, 78), 307 (94), 231 (100), 202 (41); HRMS calcd for $C_{23}H_{16}O$ 308.1201, found 308.1117.

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Table II. ^{13}C and ^{1}H Assignments and FLOCK Correlations for 35a

position	^{13}C	$^{1}H^{a}$	C–H corr
1	124.08	7.89d	3
2	134.71	7.42t	4
3	128.02	7.65t	1
4	120.01	7.89d	
5	149.98		3, 11
6	134.02		2, 4
7	187.2		
8	135.48		11
9	130.59		10
10	135.48	7.74s	17
11	125.31	7.31s	13
12	136.35		14
13	129.43	7.00c	11, 13
14	127.15	6.80c	14
15	127.5	6.91t	13
16	135.28		18
17	130.49	7.08d	10, 17, 19
18	127.04	6.83c	18
19	128.43	7.00c	17

[a] c = centered at, d = doublet, t = triplet.

Thermolysis of 31. A solution of acetylenic alcohol 31 (169 mg, 0.55 mmol) in 20 mL of decalin was refluxed for 2 h, at which time the reaction was judged to be complete by TLC. The mixture was washed with hexanes (400 mL) over a plug of silica (20 g) and then eluted with ether (100 mL), CH_2Cl_2 (100 mL), and EtOAc (100 mL). The combined eluents were chromatographed on a Chromatotron plate (2 mm, 3:1 hexanes/CH_2Cl_2 → pure CH_2Cl_2). The following fractions were obtained:

(*E*,*Z*)-2,3-Dibenzylidene-1-indanone (35a) (18.6 mg, 11%): ^{1}H and ^{13}C NMR (see Table II); IR (CH_2Cl_2) 1703, 1615 cm^{-1}; MS (*m*/*e*) 308 (M^+, 100), 307 (43), 306 (33), 231 (54), 202 (38), 138 (23); HRMS calcd for $C_{23}H_{16}O$ 308.1201, found 308.1210.

4-Benzylidene-3-phenyl-1,4-naphthoquinonemethides (36) (38.9 mg, 23%) (isolated as 3:1 *Z*/*E* mixture): ^{1}H NMR δ *Z* (major) 8.20 (1 H, d, *J* = 8.4 Hz), 7.63 (1 H, d, *J* = 8.6 Hz), 7.43 (1 H, t, *J* = 7.9 Hz), 7.15 (1 H, s, br), 6.53 (1 H, d, *J* = 0.5 Hz); *E* (minor) 8.25 (1 H, d, *J* = 7.8 Hz), 8.10 (1 H, d, *J* = 7.5 Hz), 7.95 (1 H, d, *J* = 1.5 Hz), 7.67 (1 H, t, *J* = 7.2 Hz), 6.70 (1 H, d, *J* = 1.5 Hz); (overlapping peaks) 7.56–7.46 (m), 7.3–7.2 (m), 7.03–6.92 (m); ^{13}C-NMR δ *Z* (major) 184.98, 156.95, 141.69, 138.45, 136.82, 135.34, 132.93, 132.52, 130.23, 129.36, 129.21, 129.01, 128.79, 128.73, 128.62, 128.53, 128.49, 126.18, 126.10; *E* (minor) 185.25, 152.99, 139.97, 139.22, 138.58, 135.82, 132.04, 130.75, 129.87, 128.32, 127.86, 127.77, 127.73, 127.41, 126.30, 122.71; IR (CH_2Cl_2) 1641, 1600 cm^{-1}; MS (*m*/*e*, int) 308 (M^+, 77), 230 (100), 202 (50), 100 (89); HRMS calcd for $C_{23}H_{16}O$ 308.1201, found 308.1162.

10-Phenylbenzo[*b*]fluorenone (37) (25.4 mg, 15%): mp 218–219 °C (lit.[13] mp 219 °C); ^{1}H NMR δ 7.31 (td, *J* = 7.4, 0.95 Hz), 7.4–7.35 (3 H, m), 7.65–7.49 (7 H, m), 7.75 (1 H, dt, *J* = 7.5, 0.8 Hz), 7.86 (1 H, dt, *J* = 8.1, 0.6 Hz), 7.92 (1 H, s); ^{13}C NMR d 118.67, 120.64, 124.13, 126.76, 127.95, 128.03, 128.62, 128.70, 128.96, 129.15, 129.52, 133.77, 134.64, 135.44, 136.27, 136.60, 138.36, 141.18, 144.0, 192.2; IR (CH_2Cl_2) 1711 cm^{-1}; MS (*m*/*e*, int) 306 (M^+, 100), 305 (77), 276 (38), 138 (39); HRMS calcd for $C_{23}H_{14}O$ 306.1044, found 306.1023.

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Supplementary Material Available: ^{1}H or ^{13}C NMR spectra of **15**, **23**, **26**, **29**, **31**, **35a**, **36**, and **37** (8 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.

Molecular Sieve Controlled Diastereoselectivity: Effect in the Palladium-Catalyzed Cyclization of *cis*-1,2-Divinylcyclohexane with α-Oxygen-Substituted Acids as Chiral Nucleophiles

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Molecular sieves have been shown to improve greatly the stereoselectivity in the palladium(II)-catalyzed reaction of *cis*-1,2-divinylcyclohexane with chiral acids. Reactions run with molecular sieves and derivatives of (*R*)-lactic acids as nucleophiles always yielded products with *S* configuration at the newly formed chiral center in contrast to reactions without molecular sieves that gave products with either *S* or *R* configuration at this chiral center. It appears that this effect has not been observed previously. Only water-containing molecular sieves increased the stereoselectivity. A chiral palladium complex was formed faster in the presence of molecular sieves, but use of this complex as catalyst in the cyclization did not result in increased selectivity. The best stereoselectivity was found for molecular sieves with a high sodium content (Lancaster 13X and 4-Å sieves).

Molecular sieves have recently been shown to greatly improve the stereoselectivity in some titanium-catalyzed reactions such as the Sharpless epoxidation,[1] a Diels–Alder cyclization,[2] a glyoxylate–ene reaction,[3] and the aluminum-catalyzed ene reaction of prochiral aldehydes with alkenes.[4]

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