5-Norbornen-2-ol (6). A mixture of 600 μL (1.49 mmol) of 2.48 M bromodimethylborane in toluene and 585 μL (635 mg, 2.00 mmol) of vinyltributyltin was prepared at 0 °C, stirred at rt for 20 min, treated with 67.2 mg (1.017 mmol) of freshly prepared cyclopentadiene, and stirred at rt for 22 h. A standard oxidation, extraction, and chromatography using 15% EtOAc/petroleum ether as eluent afforded 90.3 mg (81%) of an 84:16 mixture of **6a** and **6b** which exhibited ^1H and ^{13}C NMR spectra identical to commercial material.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of the reaction of Br-9-BBN in CH_2Cl_2 with vinyltributyltin and spectra of vinyl-9-BBN for comparison (4 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.

Exclusive Peri-Selective and Regio- and Stereoselective Cycloaddition Reactions of Benzocycloheptadienones

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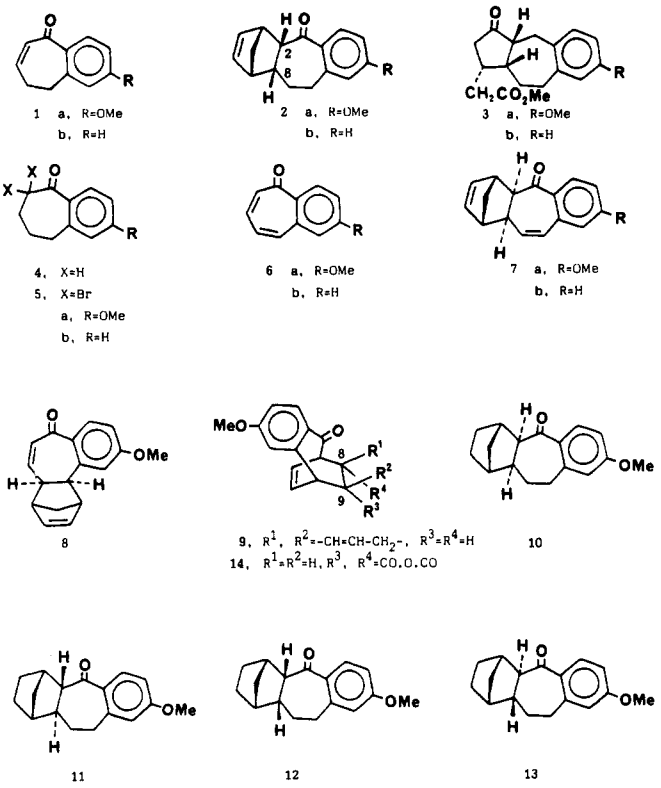
Recently we have shown[1] that the Diels–Alder reaction of benzocycloheptenones **1a,b** with cyclopentadiene under Lewis acid catalysis produces exclusively the endo adducts **2a,b**. These adducts have been transformed to the tricyclic keto esters **3a,b** in an effort directed toward the synthesis of diterpenes bearing the linearly arrayed 5-7-6 tricyclic system. As an extension of this work, we became interested in the cycloaddition of benzocycloheptadienones as this would lead to adducts with an additional functionality in the seven-membered ring that might be required for elaboration to natural products. While the cycloaddition behavior of 2,4-cyclohexadienones[2] has been studied extensively, little is known about the cycloaddition characteristics of cycloheptadienones. Earlier it was reported that 2,4-cycloheptadienones[3] exhibited low dienic reactivity with dienophiles. A recent study[4] using eucarvone has shown that 2,4-cycloheptadienone can exhibit both dienic and dienophilic reactivity toward dienes. Herein, we report the results of our investigation on cycloaddition of benzocycloheptadienones. The cycloaddition reactivity of these species differs from the reported cycloaddition behavior of 2,4-cyclohexadienones and 2,4-cycloheptadienones.

Chart I



Results and Discussion

Benzocycloheptadienones **6a,b** were prepared by bromination of the benzosuberones **4a,b** followed by dehydrobromination of the resulting dibromo derivatives **5a,b**. Refluxing a benzene or toluene solution of the dienone **6a** in the presence of cyclopentadiene failed to produce any adduct. On the other hand, when a solution of **6a** in THF was allowed to react with cyclopentadiene in the presence of $BF_3{\cdot}Et_2O$ at 0–5 °C for 20 h, a single crystalline compound, mp 113 °C, was obtained in 75% yield. The structural and stereochemical assignment of this adduct was made by spectral analysis as well as by chemical transformation. On the basis of previous findings[2-4] on cycloaddition behavior of cyclohexadienones and cycloheptadienones, one can expect three exo, endo pairs of adducts, **7**, **8**, and **9** (only the exo isomer is shown). Of these three possibilities, the formation of compound **8** bearing the conjugated enone functionality can be excluded by examination of the ^{13}C NMR spectrum, which showed the presence of four olefinic methines at δ 132.04, 132.68, 133.09, and 136.13, much lower than the chemical shift (δ 150 ppm) for the β-carbon of a cyclic conjugated ketone. The cycloadduct from **6a** was hydrogenated, and the resulting product, on treatment with methanolic sodium methoxide, was found to undergo epimerization. This observation clearly excludes the possibility of formation of the compound **9** and at the same time suggests **7a** to be the structure of the adduct as its hydrogenation product **10** could be epimerized to produce **11**. Thus, during cycloaddition **6a** behaved as a dienophile involving the α,β-double bond. It is interesting to note that 2,4-cyclohexadienone[2a] behaved as a diene in its reaction with cyclopentadiene.

The stereochemical assignment of the cycloadduct **7a** was made by comparison of the coupling constants of the protons at C_2 and C_8 with those reported for the C_2, C_3

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protons of the norbornene derivatives. In contrast to our previous findings[1] that the endo adducts **2a,b** exhibited $J_{2,8}$ = 10.5 Hz and $J_{2,1}$ = 3 Hz, the adduct **7a** showed the presence of two doublets at δ 3.51 and 3.58 attributed to either of the C_2 and C_8 protons ($J_{2,8}$ = 6.5 Hz and $J_{2,1}$ = 0 Hz). This observation clearly indicates that the protons at C_2, C_8 in the adduct **7a** are endo-syn, and hence **7a** possesses an exo configuration. The observed coupling constants for the C_2, C_8 protons of **7a** are also in good agreement with the reported[5] coupling constants ($J_{2\text{-}endo,3\text{-}endo}$ = 6–7 Hz and $J_{1,2\text{-}endo}$ = 0–2 Hz) for the *exo*-norbornene derivatives. The exo stereochemical assignment of **7a** was further substantiated by chemical transformation. Catalytic hydrogenation of **2a** afforded the ketone **12** which was found to be different (by ^{1}H NMR and GC analyses) from the ketone **10** obtained by hydrogenation of **7a**. Similarly the *trans*-ketones **11** and **13** obtained by epimerization of the respective *cis*-ketones **10** and **12** differed spectroscopically and had different retention times by GC. Reaction of the benzocycloheptadienone **6b** with cyclopentadiene under identical condition gave similarly the exo adduct **7b** in 75% yield. Thus, the cycloaddition of benzocycloheptadienones **6a,b** with cyclopentadiene is totally peri-selective, regioselective, and exo diastereoselective. Benzocycloheptadienone **6a** failed to undergo cycloaddition with isoprene under thermal and catalyzed conditions. On the other hand **6a** behaved as a diene, in accord with literature precedence,[3,4] in reaction with maleic anhydride to produce the endo adduct **14** in 87% yield. The endo configuration was assigned from comparison of the coupling constants ($J_{8,9}$ = 8 Hz and $J_{1,8\text{ or }5,9}$ < 1 Hz) with those reported[4] for an analogous compound.

The change in endo diastereoselectivity to exo diastereoselectivity in going from **1** to **6** during cycloaddition with cyclopentadiene is noteworthy. The stereoselectivities observed in the Diels–Alder reactions have been shown to originate generally from secondary orbital interactions[6] between the nonbonding π-orbitals of the diene and the dienophile. Recent investigations by Houk et al.[7a] Fox et al.,[7b] and Singleton et al.[7c] have suggested that in the Diels–Alder reactions of cyclopentadiene and its analogues secondary orbital effects, if present, are small and that steric effects are the major factor that controls the stereoselectivity. Thus, the endo selectivity observed in reaction of **1** possibly originates from destabilization of the exo transition state through some interference involving the methylene hydrogens of cyclopentadiene with the dienophile's C_6 (C_7) hydrogens (from Dreiding model). This steric interference is diminished to an appreciable extent in the exo transition state in cycloaddition of **6**, and the exo adduct **7** is thus formed exclusively.

Experimental Section

Melting points were measured in open capillary tubes in sulfuric acid bath and are uncorrected. The organic extracts were dried over anhydrous Na_2SO_4. Column chromatography was performed on silica gel (60–120 mesh). Gas chromatographic analyses were performed on a Shimadzu GC9A instrument on an OV-17 column (2 m × 3 mm) using N_2 as carrier gas.

3′-Methoxy-6,7-benzocyclohepta-2,4-dien-1-one (6a). To the benzosuberone **4a** (1.9 g, 10 mmol) in Et_2O (190 mL) was added Br_2 (3.2 g, 20 mmol) at 0–5 °C. The reaction mixture after stirring for 2.5 h at 0–5 °C was poured into ice-cold H_2O. The Et_2O layer was separated, washed with saturated aqueous $NaHCO_3$, and dried. Removal of solvent afforded the dibromo ketone **5a** (3.2 g, 90%) as a semisolid mass: ^{1}H NMR (60 MHz) δ 1.66–2.33 (m, 2), 2.73 (t, J = 6 Hz, 4), 3.83 (s, 3, OMe), 6.46–6.86 (m, 2), and 7.36 (d, J = 8 Hz, 1). A solution of the dibromo ketone **5a** (3.2 g, 9.2 mmol) in DMF (16 mL) was heated with powdered LiCl (4.23 g, 100 mmol) and Li_2CO_3 (3.84 g, 51 mmol) at 130–135 °C under magnetic stirring for 2.5 h. The reaction mixture was diluted with H_2O (50 mL). The undissolved salt was filtered out. The solid residue was washed several times with Et_2O. The filtrate was extracted with Et_2O (3 × 50 mL). The combined Et_2O extracts were washed with H_2O (3 × 15 mL) and dried. Removal of the solvent afforded a liquid which was sublimed to give **6a** (1.6 g, 86% from **4a**): bp 140 °C (0.01 mm) (bath temperature); mp 77 °C; IR 1635 (m), 1605 (m), and 1570 (s) cm^{-1}; UV λ_{max} 231.5 and 276.6 nm (EtOH, ε 20 692 and 28 249); ^{1}H NMR (60 MHz) δ 3.9 (s, 3, OMe), 6.2–7.25 (m, 6, olefinic and ArH) and 8.33 (d, 1, J = 8 Hz, ArH). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.08; H, 5.32.

6,7-Benzocyclohepta-2,4-dien-1-one (6b). Via the above procedure, the benzosuberone **4b** (1.6 g, 10 mmol) was converted to the dienone **6b**[8] (1.1 g, 71%): bp 85 °C (0.1 mm) (bath temperature); IR 1640 (m), 1605 (m), 1585 (s) cm^{-1}; UV λ_{max} 227.8 and 267 (EtOH, ε 29 621 and 10 567); ^{1}H NMR (60 MHz) δ 6.33–7.93 (m, 7 H) and 8.46 (dd, J = 8 and 2 Hz, 1). Anal. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16; Found: C, 84.41; H, 5.48.

4′-Methoxy-*exo*-4,5-benzotricyclo[7.2.1.0^{2,8}]dodeca-5,10-dien-3-one (7a). To an ice-cold solution of the dienone **6a** (500 mg, 3 mmol) in anhydrous THF (8 mL) were added successively cyclopentadiene (8 mL) and BF_3·Et_2O (0.95 mL, 7.92 mmol). The clear solution thus obtained was kept in the refrigerator for ca. 20 h. The reaction mixture was diluted with Et_2O (50 mL), and the resulting solution was washed with saturated aqueous $NaHCO_3$ and brine and dried. Removal of solvent followed by chromatography of the residual mass afforded **7a** (500 mg, 75%): mp 113 °C; IR 1660 (s), 1630 (w), 1595 (s) cm^{-1}; UV λ_{max} 211.6, 230.4, and 286.9 nm (EtOH, ε 10 435, 12 244, and 11 755); ^{1}H NMR (200 MHz) δ ($CDCl_3$) 2.04–2.24 (m, 1), 2.60–2.84 (m, 1), 3.06 (m, 1), 3.33 (m, 1), 3.51 (br d, J = 6.5 Hz, 1), 3.58 (br d, J = 6.5 Hz, 1), 3.83 (s, 3), 5.54 (dd, J = 5.6 and 2 Hz, 1), 5.70 (dd, J = 5.6 and 2 Hz, 1), 6.12 (t, J = 8 Hz, 1), 6.50 (t, J = 8 Hz, 1), 6.75 (d, J = 2.6 Hz, 1), 6.78 (dd, J = 8.7 and 2.6 Hz, 1), and 8.06 (d, J = 8.8 Hz, 1); ^{13}C{^{1}H} NMR (25 MHz) δ ($CDCl_3$) 40.71 (t), 42.76 (d), 48.84 (d), 49.61 (d), 55.34 (d), 56.27 (d), 112.09 (d), 112.96 (d), 125.25 (s), 128.06 (d), 132.04 (d), 132.68 (d), 133.09 (d), 136.13 (d), 150.23 (s), 163.1 (s), 194.46 (s). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.59; H, 6.39.

***exo*-4,5-Benzotricyclo[7.2.1.0^{2,8}]dodeca-5,10-dien-3-one (7b).** The enone **6b** (310 mg, 2 mmol) in THF (5 mL) was allowed to react with cyclopentadiene (5 mL) in the presence of BF_3·Et_2O (0.782 mL, 6.4 mmol) under the above conditions to afford **7b** (330 mg, 75%): mp 87 °C; IR 1660 (s), 1630 (w), 1595 (s) cm^{-1}; ^{1}H NMR (100 MHz) δ ($CDCl_3$) 1.96–2.48 (m, 1), 2.52–3.48 (m, 3), 3.62 (t, J = 6.5 Hz, 2), 5.44–5.96 (m, 2), 6.12 (t, J = 8 Hz, 1), 6.56 (t, J = 8 Hz, 1), 7.12–7.80 (m, 3), and 8.10 (dd, J = 8 and 2 Hz, 1). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.53; H, 6.45.

4′-Methoxy-*exo*-4,5-benzotricyclo[7.2.1.0^{2,8}]dodecan-3-one (10). A solution of the enone **7a** (250 mg, 1 mmol) in EtOH (20 mL) was stirred under an H_2 atmosphere in the presence of 10% Pd–C (40 mg) for 1 h. The catalyst was filtered off, and the solvent was removed to afford **10** (250 mg, 95%): IR 1660 (s), 1595 (s) cm^{-1}; t_R (250 °C) 4.3 min; ^{1}H NMR (60 MHz) δ 1.16–2.46 (m, 12), 2.56–3.16 (m, 2), 3.86 (s, 3), 6.61 (d, J = 2 Hz, 1), 6.81 (dd, J = 8 and 2 Hz, 1), and 8.03 (d, J = 8 Hz, 1). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.23; H, 8.12.

4′-Methoxy-*endo*-4,5-benzotricyclo[7.2.1.0^{2,8}]dodecan-3-one (12). The enone **2a** (130 mg, 0.5 mmol) was hydrogenated as above to afford **12** (100 mg, 77%): mp 85 °C; IR 1650 (s), 1600 (s) cm^{-1};

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t_R (250 °C) 4.16 min; ^{1}H NMR (60 MHz) δ 1.05–2.08 (m, 9), 2.25 (br s, 1), 2.55 (br s, 1), 2.81 (m, 1), 2.91–3.28 (m, 2), 3.80 (s, 3), 6.55 (br s, 1.5), 6.70 (d, J = 2 Hz, 0.5), and 7.48 (d, J = 8 Hz, 1). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.35; H, 8.01.

Epimerization of 10 to 11. The ketone **10** (130 mg, 0.5 mmol) was heated under reflux with a solution of NaOMe in MeOH (25 mL, 2%) for 3.5 h. After removing most of the MeOH, the residue was diluted with H_2O (10 mL) and extracted with Et_2O (3 × 15 mL). The Et_2O extract was washed with brine and dried. Removal of solvent followed by column chromatography of the residue afforded **11** (110 mg, 84%): IR 1660 (s), 1600 (s) cm^{-1}; t_R (250 °C) 1.7 min; ^{1}H NMR (60 MHz) δ 1.05–2.65 (m, 12), 3.05 (d, J = 4 Hz, 2), 3.73 (s, 3), 6.43 (m, 1.5), 6.60 (d, J = 2 Hz, 0.5), and 6.91 (d, J = 8 Hz, 1). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.37; H, 7.93.

Epimerization of 12 to 13. Following the above procedure, the ketone **12** (130 mg, 0.5 mmol) was epimerized to give, after column chromatography, the *trans*-ketone **13** (100 mg, 77%): mp 85 °C; IR 1670 (s), 1600 (s) cm^{-1}; t_R (250 °C) 4.03 min; ^{1}H NMR (60 MHz) δ 1.13–2.23 (m, 11), 2.56–3.46 (m, 3), 3.85 (s, 3), 6.65 (m, 1.5), 6.85 (d, J = 2 Hz, 0.5), and 7.98 (d, J = 8 Hz, 1). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.78; H, 8.19.

Cycloaddition of 6a with Maleic Anhydride to 14. A suspension of the dienone **6a** (50 mg, 0.3 mmol) and maleic anhydride (30 mg, 0.3 mmol) in xylene (2 mL) was refluxed for 22 h. In the beginning all of the solid was dissolved, but after 2–3 h refluxing, the adduct started crystallizing out. The crystals were collected by filtration and dried to afford **14** (70 mg, 87%): mp 188 °C; IR 1855, 1775 cm^{-1}; ^{1}H NMR (100 MHz) δ ($CDCl_3$) 3.72 (narrow t, J = 1 Hz, 2), 3.88 (s, 3), 4.16 (br t, J = 8 Hz, 2), 6.32 (t, J = 8 Hz, 1), 6.74 (t, J = 8 Hz, 1), 6.88 (m, 2), and 8.12 (d, J = 8 Hz, 1). Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26. Found: C, 67.13; H, 4.27.

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Metachromins D–H, New Cytotoxic Sesquiterpenoids from the Okinawan Marine Sponge *Hippospongia metachromia*

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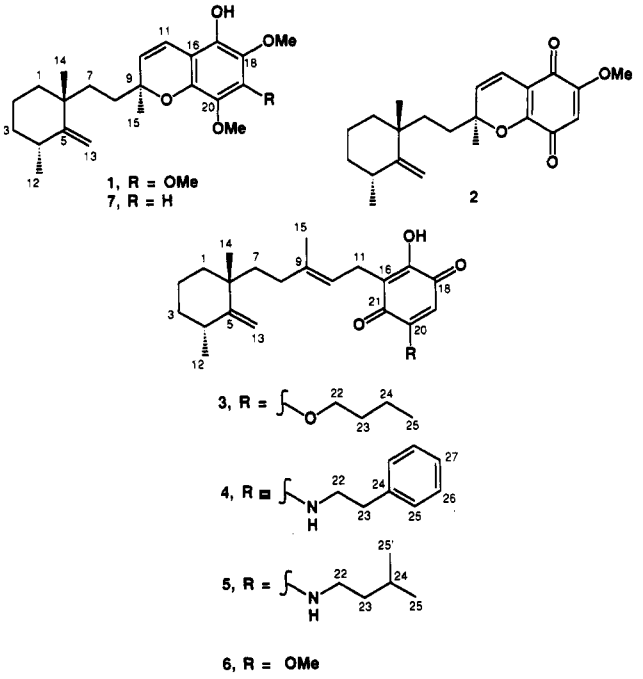
Many terpenoid quinones and phenols from marine sponges have been shown to exhibit interesting biological activities.[2] We have also reported the isolation and structural elucidation of three novel antineoplastic sesquiterpenoids, metachromins A, B, and C, from the Okinawan marine sponge *Hippospongia metachromia*.[3] In our continuing studies on bioactive metabolites from marine organisms,[4] we further examined extracts of the same sponge *H. metachromia* to obtain five new cytotoxic sesquiterpenoids, metachromins D–H (**1**–**5**), together with known related compounds metachromins A (**6**) and B (**7**). In this paper we describe the isolation and structural elucidation of **1**–**5**.



The purple-colored sponge *H. metachromia* was collected at Unten Harbour, Okinawa, and kept frozen until required. The methanolic extract of the sponge was partitioned between EtOAc and H_2O. The EtOAc-soluble fraction was subjected to silica gel column chromatography followed by silica gel TLC to yield metachromins D (**1**, 0.0037%, wet weight), E (**2**, 0.0076%), F (**3**, 0.0026%), G (**4**, 0.0010%), and H (**5**, 0.0013%) together with metachromins A (**6**, 0.17%) and B (**7**, 0.014%).

Metachromin D (**1**), a colorless oil, was shown to have the molecular formula $C_{24}H_{34}O_5$ by HREIMS (m/z 402.2408, M$^+$, Δ +0.2 mmu). The IR spectrum (ν_{max} 3400 cm^{-1}) suggested that **1** possessed hydroxyl group, and the UV absorptions (λ_{max} 226, 280, and 320 nm) were indicative of the presence of a phenol moiety. The ^{1}H NMR spectrum of **1** in $CDCl_3$ showed signals due to a secondary methyl (δ 1.03), two tertiary methyls (δ 1.01 and 1.41), three methoxy groups (δ 3.82, 3.85, and 3.94), an exomethylene (δ 4.69 and 4.76), one singlet deuterium-exchangeable proton (δ 5.58), and two doublet olefinic protons (δ 5.52 and 6.62, J = 10.3 Hz; cis-oriented). These data were reminiscent of a chromenol ring system.[5] The ^{1}H and ^{13}C NMR (Table I) data of **1** were similar to those of metachromin B (**7**), while three methoxy signals (δ_H 3.82, 3.85, and 3.94; δ_C 61.3, 61.4, and 61.5) in place of two methoxy signals (δ_H 3.82 and 3.83; δ_C 56.8 and 58.4) and an aromatic proton signal (δ_H 6.47) in **7** were observed for **1**. Irradiation of a hydroxyl proton (δ 5.53) caused 2.0 and 2.8% NOE of the olefinic proton at δ 6.62 (H-11) and the methoxy protons at δ 3.85 (CH_3O-22), respectively, since the hydroxyl group was attached to C-17. This result was coincident with the HMBC correlations for OH-17/C-16, OH-17/C-18, and H-11/C-17. Thus the structure of metachromin D was concluded to be **1**. Configurations of C-4, C-6, and C-9 in **1** were tentatively assigned as *R*, *R*, and

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