Decumulation of Allenes Drives the Cope Ring Expansion to 1,5-Cyclodecadienes

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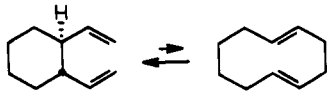
Wharton and Johnson have shown that the Cope equilibrium strongly favors *trans*-1,2-divinylcyclohexane **1** over 1,5-cyclodecadiene **2** ($\Delta G°$ = 8.5 kcal mol^{-1} at 40 °C; $K_{EQ} = 1.3 \times 10^{-6}$).[1] However, a favorable combination of several alkyl substituent and fused ring effects can partially compensate for the transannular strain that destabilizes **2**. Derivatives of **2** as well as **1** can be observed in equilibrium in several cases,[2] and complete conversion to the 10-membered ring isomer is reported in the Cope rearrangement of *epi*-isolinderalactone to neolinderalactone,[3] as well as in a number of oxy-Cope analogs.[4,5] The anionic oxy-Cope technique is the method of choice, and has been widely used in synthesis of cyclodecanones and other medium sized rings.[5] Ring expansion is driven by the dominant thermodynamic effect of a single functional group conversion, but at the cost of strongly basic conditions (sodium or potassium alkoxides and enolates).



1 **2**

We have been interested in the possibility that a simple change in carbon hybridization might also make a dominant thermodynamic contribution in the Cope ring expansion. Thus, replacement of one of the vinyl groups in Wharton's system by an allenyl group was expected to destabilize the 6-membered ring (**5** or **6**) relative to the 10-membered isomer (**7** or **8**). The corresponding Cope rearrangement of 1,2,6-heptatriene is known to be exothermic due to the "decumulation" of the allene subunit to a conjugated 1,3-diene fragment CH_2=CHC(R)=CH_2 (R = allyl),[6ab] but the heat of reaction was not reported.[6,7a] The $\Delta H°$ for decumulation in a relevant example can be estimated as ca. −13 kcal mol^{-1} by comparing $\Delta H_f°$ values for 3-methylbutadiene ($\Delta H_f°$ = 30.9 kcal mol^{-1}) and isoprene ($\Delta H_f°$ = 18.0 kcal mol^{-1}).[7b] Since the $S_f°$ values for these isomers nearly cancel,[7c] the $\Delta G°$ of decumulation should be in the range of −12 to −13 kcal mol^{-1}. Other C_5H_8 allenes and conjugated dienes differ in $\Delta H_f°$ by 8.4–15.6 kcal mol^{-1},[7b,c] and these numbers can be regarded as the extreme limits for likely values of $\Delta H°$ for allene vs. conjugated diene isomers. Thus, decumulation may or may not be enough to compensate for the estimated strain energy of 1,5-cyclodecadiene derivatives (ca. 12 kcal mol^{-1} for **2**),[1] depending on the influence of a medium ring environment on the $\Delta G_f°$ contributions from conjugation, substituent effects, and conformational effects. Definitive experiments have now been performed, and we can report that decumulation is indeed sufficient to drive the Cope ring expansion. Ten-membered rings can be obtained in useful equilibrium ratios by Cope rearrangement of 1-allenyl-2-vinylcyclohexanes (80–130 °C).

Isomeric propargyl acetates **3** and **4** were converted into the allenes **5** and **6** by the method of Inanaga *et al.* (SmI_2/Pd[PPh_3]$_4$).[8,9] When the cis-isomer **5** was heated

3 (cis; X= CH_2) **5** (cis; X= CH_2)
4 (trans; X= CH_2) **6** (trans; X= CH_2)
10 (trans; XX= C_6H_4) **11** (trans; XX= C_6H_4)

to 90° or above in deuterobenzene, rearrangement occurred smoothly to give complete (≥99%) conversion into an isomeric product identified as *Z,E*-2-methyl-3-methylene-1,5-cyclodecadiene (**7**) by ^{1}H NMR (5% NOE between C_2-Me and C_1-H; $J_{5,6}$ = 15.8 Hz) and ^{13}C NMR evidence. As expected for the flexible *Z,E*-1,5-cyclodecadiene, the ring environment was achiral on the NMR time scale at room temperature due to rapid interconversion of conformers.

The *trans*-isomer **6** rearranged more slowly, and the experiment was difficult to monitor. When **6** was heated

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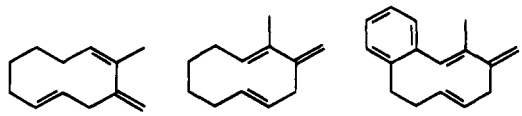

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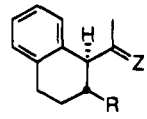
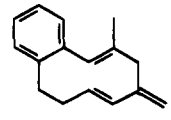
at 130 °C (C_6D_6), absorptions due to **8** increased in intensity until a ratio of 86:14 **8**:**6** was established. GLPC or HPLC conditions that separate **6** from the product **8** were not found, and ^{1}H NMR analysis was complicated by coalescence phenomena. Signals were sufficiently resolved at 57 °C to assay the product ratio and to confirm the presence of the *trans*-disubstituted double bond (J_{trans} = 15.6 Hz), non-equivalent terminal C=CH_2 protons, and the doubly allylic CH_2 group. This evidence is consistent with structure **8**, but analogs were desired that could be purified. To this end, two closely related benzo-fused cyclodecadienes **9** and **10** were prepared from the allenylcyclohexane derivatives **11** and **14**. Allene **11** was obtained from **10**[10] by the Inanaga method while the isomer **14** was prepared via protodesilylation of the propargyl silane **12** with trifluoroacetic acid,[11,12] followed by Lombardo olefination of **13**.[13]





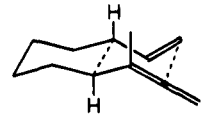
12 R= C≡CCH_2SiMe_2Ph
Z= O
13 R= CH=C=CH2, Z= O
14 R= CH=C=CH2, Z= CH2

15

Heating **11** or **14** as before afforded 95% or 98% conversion, respectively, to the corresponding 10-membered rings **9** or **15**. Both the allene **11** and its Cope product **9** were obtained with <5% cross-contamination by chromatography on analytical scale, and heating either isomer at 133° ($C_6D_5CD_3$) produced the same equilibrium ratio, 95:5 of **9**:**11**. The *E,E*-diene geometry of **9** was established by ^{1}H NMR methods (NOE; vicinal J_{trans} = 15.8 Hz). The NMR spectrum indicated a chiral ring environment and showed no signs of coalescence up to 80 °C.

In the case of **14**, thermolysis at 130 °C ($C_6D_5CD_3$) produced an equilibrium mixture of **15** and **14** in a ratio of 98:2. The room temperature ^{1}H NMR spectrum of **15** indicated a chiral ring environment (non-equivalent CH_2 groups), but the benzylic CH_2 signals simplified to an apparent triplet at 70 °C, probably due to rapid interconversion by rotamers of the nearby *E*-disubstituted alkene (J_{trans} = 16.2 Hz). The doubly allylic CH_2 group was observed as a pair of doublets (J_{AB} = 11.8 Hz) at room temperature that merged into a broad absorption at 70 °C (partial coalescence).

Each of the ring expansions is stereospecific, within the limits of NMR assay, and the stereochemistry corresponds to the usual preference for chair-like transition states. Thus, the *Z,E*-cyclodecadiene **7** results from rearrangement of **5** via geometry **17**, and products from the trans 1-allenyl-2-vinylcyclohexane derivatives arise via transition structures based on **16**. In the most facile



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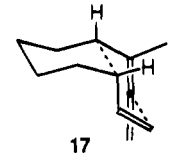

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reaction (**5** to **7**), the rearrangement obeys first order kinetics and the activation parameters (E_a = 26.5 ± 0.3 kcal mol^{-1}; ΔH^* = 25.7 ± 0.3 kcal mol^{-1}; ΔS^* = −11 ± 1 eu) are similar to those of an acyclic analog (1,2,6-heptatriene; E_a = 28.5 kcal mol^{-1}).[6b] Compared to the divinyl analog **1** (E_a = 31.6 kcal mol^{-1}),[1] **5** rearranges with a lower activation energy, presumably because some fraction of the thermodynamic advantage of decumulation is felt in the transition state. There is no evidence for a non-concerted mechanism or other unusual behavior.

Prior studies have encountered other reactions where decumulation plays a major role in driving sigmatropic rearrangements.[14,15] Neutral and anionic allenyl oxy-Cope ring expansions have also been reported.[4c] However, the magnitude of the allene driving force has not attracted much attention. The *E,E*-cyclodecadiene derivatives **8**, **9**, and **15** are favored at equilibrium by ΔG° = 1.5−3.0 kcal mol^{-1}, and the less strained *Z,E*-analog **7** is favored by >3 kcal mol^{-1} relative to **5**. These values are in the expected range, based on the estimated strain of *E,E*-1,5-cyclodecadiene (ca. 12 kcal mol^{-1}),[1] the conversion of a mono-substituted into a disubstituted alkene (2.5 kcal mol^{-1}), and the free energy advantage of decumulation (>10 kcal mol^{-1}). The decumulation effect is not as dominant as the pK_a change from sodium or potassium alkoxides to enolates (ca. 3−4 pK_a units in ether solvents) that drives the anionic oxy-Cope rearrangement,[4-6] partly because of the temperature difference. However, our results demonstrate that a single neutral substituent is quite capable of providing the necessary driving force for Cope ring expansion. Studies are planned to evaluate modified cumulenes and other potentially dominant substituents.

Experimental Section

***cis*-1-(1,2-Butadien-3-yl)-2-vinylcyclohexane (5).** According to the published procedure, a THF solution of **3**[8] (135 mg, 0.61 mmol), 2-propanol (50 μL), and $Pd(PPh_3)_4$ (43 mg) was treated with SmI_2/ THF (0.1 M, 13.0 mL).[9] The mixture was stirred at 50 °C for 3 h and was then diluted with 2.5 mL pentane. The entire reaction was filtered over a pad of Celite and the Celite pad was washed with 1 mL pentane. THF was removed from the pentane phase by washing 6× with water and the organic phase was evaporated at reduced pressure, kept cold by the evaporation of pentane to minimize loss of the volatile

(10) (a) **10** and **11** were prepared according to ref 8 and 9, starting from 1-acetyl-3,4-dihydronapthalene (ref 10b). (b) Subba Rao, G. S. R.; Sundar, N. S. *J. Chem. Soc., Perkin Trans. 1* **1982**, 875.

(11) **12** was obtained as a *cis/trans* mixture from 1-acetyl-3,4-dihydronapthalene (ref 10b) by 1,4-addition of $Et_2AlC{\equiv}CCH_2SiMe_2Ph$: Hooz, J.; Layton, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 7320. Equilibration to the *trans* isomer occurred under protodesilylation conditions.

(12) (a) 3 equiv CF_3CO_2H in CH_2Cl_2, 3 h at room temperature; 59% **13** and 16% recovered **12** after chromatography. (b) Peterson, P. E.; Flood, T. *J. Org. Chem.* **1980**, *45*, 5006. Pornet, J.; Damour, D.; Miginiac, L. *J. Organomet. Chem.* **1987**, *319*, 333−343.

(13) 70% yield after 2 h at 0 °C: Lombardo, L. *Org. Synth. Coll. Vol. XIII.* **1993**, 386.

(14) Huntsman, W. D. In *The Chemistry of Ketenes, Allenes, and Related Compounds*, Patai, S. Ed., Wiley & Sons: New York, NY, 1980; Part II, Chapter 15.

(15) Frey, H. M.; Ellis, R. J. *J. Chem. Soc.* **1965**, 4770. Heingartner, H.; Zsindely, J.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2924. Okamura, W. H.; Reischl, W. *J. Am. Chem. Soc.* **1982**, *104*, 6115. Okamura, W. H.; Enas, J. D.; Palenzuela, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 1355.

product. The hydrocarbon was purified by flash chromatography on silica gel (10 × 1 cm), pentane eluent (43.6 mg, 48% yield); analytical TLC on silica gel, hexane, R_f = 0.73; GLPC (Packard Becker 409 gas chromatograph) equipped with Alltech, Helilflex, AT-1 (formerly RSL-150) capillary column, 30 m × 0.25 mm × 0.25 μm film thickness; flow = 1.5 mL/min nitrogen, t_R = 4.17 min, oven temperature = 120 °C; molecular ion calcd for $C_{12}H_{18}$ 162.14085; found *m/e* = 162.1411, error = 2 ppm; M − 15, 147.1189, error = 10 ppm; IR (CCl_4, cm^{-1}) 1957, =C=; 3075, =CH; 2854, CH; 200 MHz NMR ($CDCl_3$, ppm) δ 6.00 (1 H, ddd, *J* = 16.8, 10.9, 7.8 Hz) 5.08 (1 H, ddd, *J* = 10.9, 2.2, 1.2 Hz) 5.02 (1 H, ddd, *J* = 16.8, 2.2, 1.2 Hz) 4.72−4.57 (2 H, m) 2.49−2.43 (2 H, m) 1.89−1.03 (9 H, m) 1.61 (3 H, td, *J* = 3.3, 0.6 Hz); ^{13}C NMR (125 MHz, {H}, $CDCl_3$, ppm) δ 207.4, 138.8, 115.0, 101.6, 75.1, 43.5, 40.6, 32.2, 27.3, 26.4, 21.8, 17.9.

***trans*-1-(1,2-Butadien-3-yl)-2-vinylcyclohexane (6).** Analytical TLC on silica gel, hexane, R_f = 0.65: molecular ion calcd for $C_{12}H_{18}$ 162.14085; found *m/e* = 162.1408, error = 0 ppm; M − 15, 147.1187, error = 9 ppm; IR (CCl_4, cm^{-1}) 1958, =C=; 2854, CH; 200 MHz NMR ($CDCl_3$, ppm) δ 5.71 (1 H, ddd, *J* = 17.2, 10.3, 10.3 Hz) 4.95 (1 H, ddd, *J* = 17.2, 2.0, 1.0 Hz) 4.90 (1 H, ddd, *J* = 10.3, 2.0, 0.7 Hz) 4.55 (2 H, q, *J* = 3.2 Hz) 2.05−1.86 (2 H, m) 1.84−1.59 (6 H, m) 1.71−1.22 (2 H, m) 1.62 (3 H, dd, *J* = 3.3, 3.3 Hz); ^{13}C NMR (125 MHz, {H}, $CDCl_3$, ppm) δ 207.0, 143.4, 113.3, 101.9, 74.3, 47.4, 45.8, 33.3, 32.2, 26.6, 26.1, 16.8.

***trans*-1-(1,2-Butadien-3-yl)-2-vinyl-3,4-dihydronaphthalene (11):** molecular ion calcd for $C_{16}H_{18}$ 210.14085; found *m/e* = 210.1407, error = 1 ppm; M − vinyl, 183.1173, error = 0 ppm; base peak = 129 amu; IR (CCl_4, cm^{-1}) 1959, =C=; 3075, =CH; 270 MHz NMR ($CDCl_3$, ppm) δ 7.40 (1 H, d, *J* = 7.0 Hz) 7.09 (1 H, ddd, *J* = 7.0, 7.0, 2.0 Hz) 7.04 (1 H, ddd, *J* = 7.0, 7.0, 2.0 Hz) 6.95 (1 H, d, *J* = 7.0 Hz) 5.81 (1 H, ddd, *J* = 17.7, 10.5, 7.5 Hz) 5.02 (1 H, dd, *J* = 17.7, 2.0 Hz) 5.00 (1 H, dd, *J* = 10.5, 2.0 Hz) 4.65 (1 H, dq, *J* = 10.5, 3.2 Hz) 4.57 (1 H, dq, *J* = 9.4, 3.2 Hz) 3.40 (1 H, d, *J* = 9.7 Hz) 2.63 (1 H, ddd, *J* = 16.5, 11.3, 5.7 Hz) 2.58 (1 H, ddd, *J* = 16.5, 8.3, 4.7 Hz) 2.31 (1 H, dddd, *J* = 9.7, 9.3, 7.5, 2.9 Hz) 1.82 (1 H, dddd, *J* = 11.9, 9.3, 11.3, 4.7 Hz) 1.5 (3 H, t, *J* = 3.2 Hz) 1.44 (1 H, dddd, *J* = 11.9, 8.3, 5.7, 2.9 Hz).

1-Acetyl-2-(1,2-propadien-2-yl)-3,4-dihydronaphthalene (13). A CH_2Cl_2 solution of **12** (25 mg, 0.072 mmol of a *cis*/*trans* mixture)[11] was treated with 3 equiv trifluoroacetic acid at 25 °C (5 h under a nitrogen). The resulting dark solution was quenched with water and extracted into ether, washed with 1 N NaOH, 2 × 500 μL and 1 × 500 μL water, and dried over $MgSO_4$. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (10 × 1 cm), 1:16 acetone/hexane eluent (9.0 mg, 59% yield). Starting material **12**, 15% yield, was also recovered from the column in a later fraction that closely followed **13**; analytical TLC on silica gel, chloroform, R_f = 0.56; GLPC, Hewlett Packard 5890 equipped with an Hp-1 capillary column (methyl silicone gum) 10 m × 0.53 mm × 2.65 μm film thickness, 8.45 mL/min flow, nitrogen carrier gas, t_R = 10.60 min, >98% *trans* isomer: molecular ion calcd for $C_{15}H_{16}O$ 212.12010; found *m/e* = 212.1203, error = 1 ppm; M − 15, 197.0986, error = 10 ppm; base peak = 141 amu; IR (CCl_4, cm^{-1}) 1956, =C=; 1708, C=O; 200 MHz NMR ($CDCl_3$, ppm) δ 7.20−7.08 (3 H, m) 7.01−6.93 (1 H, m) 5.15 (1 H, ddd, *J* = 6.6 Hz) 4.74 (1 H, ddd, *J* = 10.5, 6.6, 2.3 Hz) 4.78 (1 H, ddd, *J* = 10.5, 6.6, 2.6 Hz) 3.69 (1 H, d, *J* = 9.0 Hz) 2.95−2.83 (2 H, m) 2.81−2.66 (1 H, m) 2.16−2.05 (1 H, m) 2.11 (3 H, s) 1.62 (1 H, dddd, *J* = 13.3, 10.3, 9.2, 6.7 Hz). ^{13}C NMR (125 MHz {H}, $CDCl_3$, ppm) δ 209.7, 207.7, 136.5, 132.7, 129.5, 128.4, 126.9, 126.2, 96.1, 92.8, 59.9, 36.5, 28.6, 27.9, 27.6.

1-(2-Propenyl)-2-(1,2-propadien-2-yl)-3,4-dihydronaphthalene (14). The Lombardo reagent,[13] 1 mL of a stock solution (prepared on the same scale as the published procedure and stored in a reagent vessel at −5 °C), was added to a THF solution of 200 μL of **13** (16.9 mg, 0.08 mmol). After 2 h at 0 °C, the contents of the reaction vessel were diluted with pentane (2 mL) and cautiously quenched with 500 μL of 2 g/mL $NaHCO_3$ slurry. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (10 × 1 cm), hexane eluent to give **14** (11.8 mg, 0.056 mmol, 70% yield) Analytical TLC on silica gel, hexane, R_f = 0.38; molecular ion calcd for $C_{16}H_{18}$ 210.14085; found *m/e* = 210.1412, error = 2 ppm; M − 15, 195.1170, error = 2 ppm; IR (CCl_4, cm^{-1}) 1955, =C=; 3074, =CH; 2841, CH; 500 MHz NMR (C_6D_6, ppm) δ 7.24−6.95 (4 H, m) 5.22 (1 H, ddd, *J* = 6.7, 6.7, 6.7 Hz) 4.99 (1 H, dq, *J* = 2.3, 1.3 Hz) 4.85 (1 H, d, *J* = 2.3 Hz) 4.73 (1 H, dd, *J* = 10.3, 6.7 Hz) 4.72 (1 H, dt, *J* = 10.3, 6.7 Hz) 3.28 (1 H, d, *J* = 9.7 Hz) 2.69−2.58 (2 H, m) 2.39−2.31 (1 H, m) 1.97 (1 H, dddd, *J* = 8.7, 4.4, 3.3, 12.1 Hz) 1.53−1.44 (1 H, m) 1.48 (3 H, s); ^{13}C NMR (125 MHz, {H}, DEPT135, C_6D_6, ppm) δ 213.7 s, 152.0 s, 142.7 s, 142.2 s, 134.7 d, 134.4 d, 131.8 d, 131.7 d, 121.3 t, 99.7 d, 81.5 t, 60.1 d, 42.4 q, 35.0 t, 34.0 t, 24.1 d.

Thermal Ring Expansions. An NMR tube containing a C_6D_6 or $C_6D_5CD_3$ solution of the six-membered ring starting material was frozen in a bath of liquid N_2. The space above the frozen solvent was partially evacuated (0.5 torr). The pressure was then equalized by closing off the vacuum line, allowing the sample to slowly thaw, and then bleeding N_2 into the sample head space. Freeze-pump-thaw cycles were repeated until there was no visible evolution of dissolved gas. The open end of the tube was sealed under vacuum and the samples were thermolyzed in a filings bath contained in a 7 × 7 × 13 cm^3 insulated aluminum block heated with a temperature controller. In the case of the kinetic experiments to determine the activation parameters, the samples were completely submerged in a thermostated, vigorously agitated, insulated silicone oil bath.

2-Methyl-3-methylene-*Z*,*E*-1,5-cyclodecadiene (7): molecular ion calcd for $C_{12}H_{18}$ 162.14085; found *m/e* = 162.1405, error = 2 ppm; M − 15, 147.1187, error = 9 ppm; IR (CCl_4, cm^{-1}) 2984, =CH; 2854, CH; 500 MHz NMR (C_6D_6, ppm) δ 5.23 (1 H, dt, *J* = 15.8, 6.7 Hz) 5.20 (1 H, dt, *J* = 15.8, 7.0 Hz) 5.13 (1 H, dd, *J* = 7.4, 1.4 Hz) 4.82 (1 H, dq, *J* = 2.6, 1.1 Hz) 4.65 (1 H, t, *J* = 2.6 Hz) 2.68−2.55 (2 H, m) 2.13−1.90 (4 H, m) 1.74 (3 H, dd, *J* = 1.4, 1.1 Hz) 1.52−1.23 (4 H, m). ^{13}C NMR (125 MHz, dept 135, C_6D_6, ppm) δ 149.4 s, 135.1 d, 134.9 s, 127.6 s, 125.2 d, 111.4 t, 39.2 t, 33.3 t, 28.0 t, 28.4 t, 26.1 t, 23.8 q.

1,2-Benzo-4-methyl-5-methylene-*E*,*E*-3,7-cyclodecadiene (9): molecular ion calcd for $C_{16}H_{18}$ 210.14085; found *m/e* = 210.1397, error = 6 ppm; M − 15, 195.1197, error = 11 ppm; base peak = 195 amu; IR (CCl_4, cm^{-1}) 3064, =CH; 2853, CH; NMR (C_6D_6, ppm) δ 7.26 (1 H, d, *J* = 7.4 Hz) 7.14−7.01 (3 H, m) 5.81 (1 H, s) 5.28 (1 H, ddd, *J* = 15.8, 9.7, 6.0 Hz) 4.99 (1 H, dd, *J* = 2.1, 1.3 Hz) 4.85 (1 H, t, *J* = 2.1 Hz) 4.81 (1 H, ddd, *J* = 15.8, 9.4, 6.4 Hz) 3.32 (1 H, ddt, *J* = 17.1, 13.4, 4.1 Hz) 2.72 (1 H, dd, *J* = 13.9, 5.7 Hz) 2.61 (1 H, td, *J* = 13.1, 4.4 Hz) 2.50 (1 H, dd, *J* = 13.9, 9.7 Hz) 2.54 (1 H, dt, *J* = 13.8, 4.4 Hz) 2.17 (1 H, ddt, *J* = 17.1, 12.4, 4.4 Hz) 1.58−1.57 (3 H, m).

1,2-Benzo-4-methyl-6-methylene-*E*,*E*-3,7-cyclodecadiene (15): molecular ion calcd for $C_{16}H_{18}$ 210.14085; found *m/e* = 210.1423, error = 7 ppm; base peak = 116 amu; IR (CCl_4, cm^{-1}) 3074, =CH; 2853, CH; NMR (room temperature, C_6D_6, ppm) δ 7.26 (1 H, d, *J* = 5.9 Hz) 7.19−7.05 (3 H, m) 5.86 (1 H, s) 5.6 (1 H, d, *J* = 16.2 Hz) 5.01−4.97 (1 H, m) 4.94−4.88 (1 H, m) 4.66 (1 H, ddd, *J* = 16.2, 10.3, 6.2 Hz) 2.78 (1 H, d, *J* = 11.8 Hz) 2.56 (1 H, d, *J* = 11.8 Hz) 2.56 (1 H, dd, *J* = 9.7, 4.0 Hz) 2.55−2.50 (1 H, m) 2.29 (1 H, ddt, *J* = 10.3, 12.1, 4.0 Hz) 2.15−1.99 (1 H, m) 1.49 (3 H, s); ^{13}C NMR (125 MHz, {H}, C_6D_6, ppm) δ 147.6, 139.9, 138.3, 138.2, 134.2, 133.3, 131.0, 128.9, 127.2, 126.1, 126.1, 112.9, 50.1, 38.5, 34.2, 16.2.

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Supplementary Material Available: ^1H NMR spectra of **5**, **6**, **7**, **8**, **9**, **11**, **14**, and **15** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.