stirring for 2 h. The cooled reaction mixture was poured into water and extracted with ether. Evaporation of ether followed by chromatographic (silica gel, hexane) separation gave **3** in 45% yield. However, continuous refluxing of the diketone with P_2S_5 for 4 h did not yield **3**.

Synthesis of Dispiro[4.1.4.1]dodecane-6,12-dithione (4).[11] HCl gas was bubbled through a methanolic solution (50 mL) of the diketone (5 g) and zinc chloride (freshly fused, 10 g) at −5 °C for 1 h. H_2S gas was then passed through the solution for 10 h during which the solution turned red. The red solution was poured into water and extracted with ether, the ether was evaporated off, and the resultant dithione was purified by column chromatography (silica gel, hexane); yield 70%.

Interestingly, refluxing the diketone in pyridine with P_2S_5 gave β-dithiolactone **17**.

General Photolysis Procedure. All irradiations were conducted either in methanol or benzene under an N_2 atmosphere at room temperature with a 450-W medium-pressure mercury lamp. Small-scale irradiations (up to 100 mL) were conducted in Pyrex tubes with an external source of irradiation. Large-scale irradiations (250 mL) were conducted in Pyrex immersion wells. Concentration of dithiones varied between 0.008 and 0.05 M. Progress of the reaction was followed by TLC (silica gel, hexane/benzene), and, after about 30–40% completion of the reaction, solvent was evaporated off and the products were characterized by their spectral properties. All irradiations were repeated at least three times, and the required duration of irradiation for 30–40% conversion varied with the thioketones.

Photolysis of 2 in Aerated Solvent. A cyclohexane solution of dithione **2** (0.275 g, 80 mL) was irradiated in a Pyrex vessel for 72 h under aerated conditions. At the end of the irradiation, solvent was distilled off under reduced pressure and the residue that remained was chromatographed (silica gel, hexane) to give the sulfur-incorporation product **7**, disulfide **8**, 2,2,4,4-tetramethyl-3-oxo-1-cyclobutanethione, and the oxygen-trapped product **24** (yield ~10%). **24** had the following spectral properties: IR (CCl_4) 1690 (C=O stretching), 1095 cm^{-1} (C=S stretching); ^1H NMR (CCl_4) δ 1.41 (s, 6 H), 1.84 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 29.61 (q), 34.80 (q), 67.57 (s), 68.21 (s), 206.60 (s), 266.43 (s); mass spectrum (70 eV); M^+ ion at m/e 188.

Quenching and Sensitization Studies. Quenching and sensitization studies were carried out only for 2,2,4,4-tetramethylcyclobutanethione (**1**) and 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (**2**).

Biacetyl (E_T ~ 55 kcal/mol), 2-acetonaphthone (E_T ~59.4), benzil (E_T ~ 53.4), and fluorenone (E_T ~ 53) were used as sensitizers. In a typical experiment, a solution of **1** or **2** (100 mg) and sensitizer (50 mg) in cyclohexane or methanol (25 mL) was irradiated with a 450-W medium-pressure mercury lamp. Selective excitation of the sensitizer was achieved with Corning glass filter CS 7.60. Products were isolated and identified as described earlier for direct excitation.

Quenching studies were carried out with alloocimene (E_T ~ 47 kcal/mol) and cyclooctatetraene (E_T ~ 40 kcal/mol) as quenchers. This was conducted in a merry-go-round apparatus with solutions varying in quencher concentration (0–0.03 M) and fixed thione concentration (0.05 M). The progress of the reaction was followed by UV–vis absorption spectroscopy (disappearance of thione). In both cases linear Stern–Volmer plots were obtained, indicating the involvement of triplet state in the reaction.

Acknowledgment. We are indebted to the Department of Science and Technology and the Department of Atomic Energy, Government of India, for financial support and to Professors N. J. Turro and R. S. H. Liu for mass spectra.

Registry No. **1**, 64273-93-4; **2**, 10181-56-3; **3**, 22502-49-4; **4**, 31934-25-5; **5**, 67230-87-9; **6**, 80472-63-5; **7**, 74835-37-3; **8**, 74835-36-2; **9**, 10181-61-0; **10**, 74835-38-4; **11**, 74835-39-5; **12**, 80472-65-7; **13**, 79606-09-0; **14**, 80472-67-9; **16**, 80472-66-8; **17**, 80472-64-6; **18**, 80472-68-0; **24**, 87533-93-5; 2,2,4,4-tetramethylcyclobutanone, 4298-75-3; dispiro[5.1.5.1]tetradecane-7,14-dione, 950-21-0; 14-oxodispiro[5.1.5.1]tetradecane-7-thione, 22502-48-3; dispiro[4.1.4.1]dodecane-6,12-dione, 5011-61-0.

Asymmetric Induction in the Intramolecular 1,3-Diyl Trapping Reaction through the Use of Menthyl and 8-Phenylmenthyl Esters. An Unexpected Result

R. Daniel Little* and Kevin D. Moeller

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

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Diazenes **4a** and **4b** bearing (−)-menthyl and (−)-8-phenylmenthyl ester units as chiral auxiliaries were prepared and converted into the linearly fused tricyclopentanoid ring system through utilization of the intramolecular 1,3-diyl trapping reaction. The idealized transition state representations **4a**‡ and **4b**‡ were shown to be inadequate, for while they were useful in predicting the observed decrease in the cis,anti to cis,syn ring-fusion product ratio as the size of the ester unit increased, they provided an overly simplified view of the expectations associated with asymmetric induction. In no instance was a synthetically useful *de* value obtained. A brief mechanistic rationale which focuses upon the presumed stepwise nature of the trapping reaction is presented.

The achievement of asymmetric induction in the synthesis of complex natural products constitutes a noteworthy challenge and objective. During the past decade, considerable progress in this area of research has been recorded.[1] However, with the exception of a few reports,[2] comparatively little progress has been made with respect to the enantioselective construction of the linearly fused tricyclopentanoid ring system. In this paper we describe our efforts to achieve this objective through utilization of the intramolecular 1,3-diyl trapping reaction. As it has thus far been applied, this reaction can be described as one which involves an intramolecular cycloaddition reaction between a cyclopentane-1,3-diyl related to trimethylenemethane and a diylophile which is linked to the five-membered ring by a three-carbon tether. In this way, two

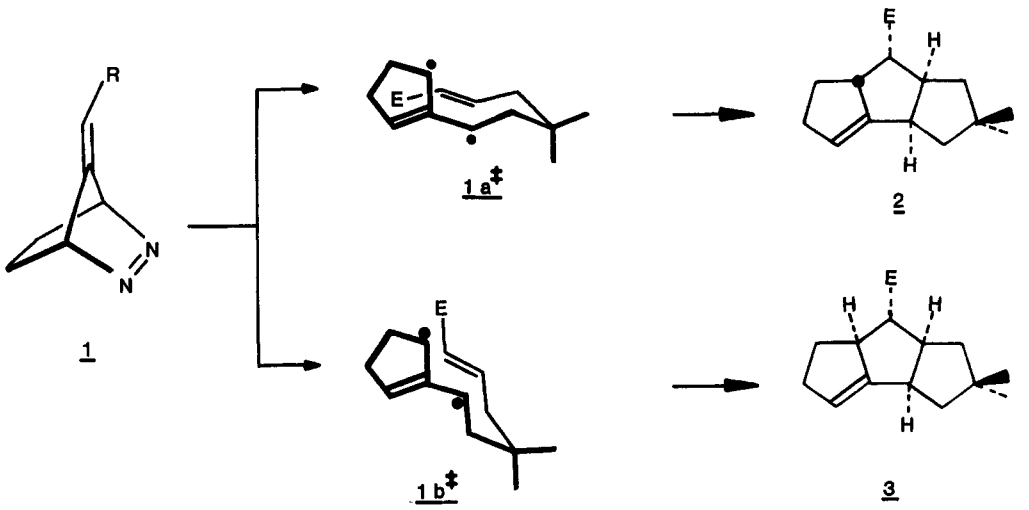
*Alfred P. Sloan Foundation Fellow, 1980–1984.

(1) For example, see: (a) "Asymmetric Reactions and Processes in Chemistry"; Eliel, E. L., Otsuka, S., Ed.; American Chemical Society: Washington, DC, 1982; *ACS Symp. Ser.* 1982, No. 185. (b) "Modern Synthetic Methods, 1980"; Scheffold, R., Ed.; Verlag Chemie: Frankfurt, 1980.

(2) For leading references see: (a) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380. (b) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820–836 and references therein.

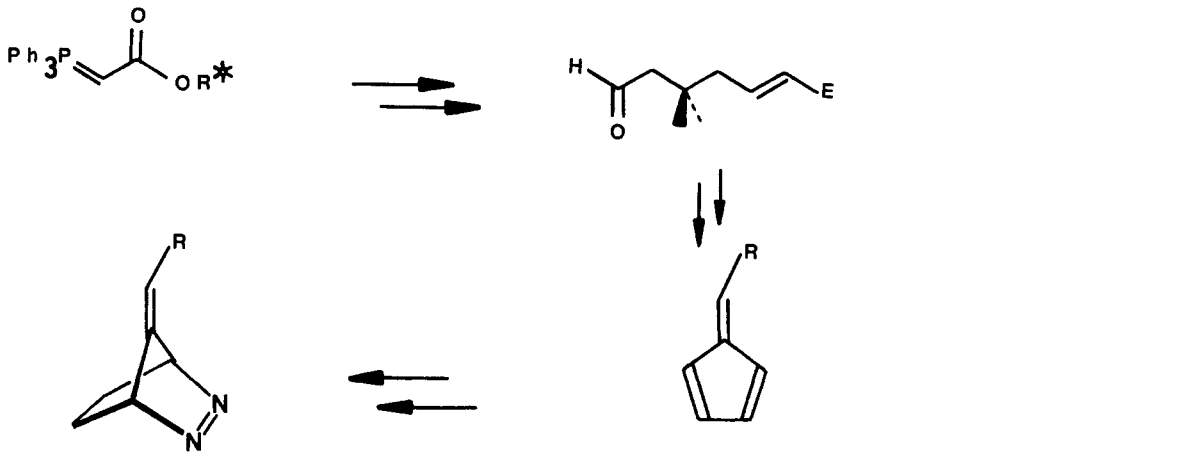
0022-3263/83/1948-4487$01.50/0

Scheme I



R = (E)-$CH_2C(CH_3)_2CH_2CH{=}CHCO_2CH_3$, E = CO_2CH_3

Scheme II



4a, (-)-menthyl ester

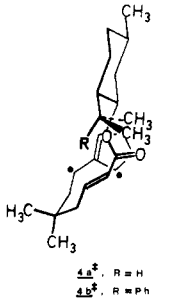
4b, (-)-8-phenylmenthyl ester

R = $CH_2C(Me)_2CH_2CH{=}CHCO_2R^*$

new rings and two new carbon–carbon bonds are formed in a stereoselective fashion.[3]

The Plan

Previously, we have described the results of experiments which lead us to conclude that, of the extended and the folded quasi-chair transition-state representations, **1a**‡ and **1b**‡, **1a**‡ is of lower energy and leads to the stereoselective formation of the cis,anti ring-fused tricyclopentanoid **2**[3c] (Scheme I). From an examination of either of these representations, it is obvious that to achieve asymmetric induction, one must devise a means to influence the direction associated with the approach of the diylophile to the enantiotopic faces of the diyl ring. Of several possibilities, surely the *conceptually most simple* way of achieving the objective is through the use of a chiral ester. An idealized transition-state representation for the a priori lowest energy transition-state conformation leading to the cis,anti ring-fused product is illustrated below for the



4a‡, R = H
4b‡, R = Ph

menthyl and 8-phenylmenthyl esters which were selected for study. Notice that the diyl ring is drawn on the side opposite the large chirality biasing $CRMe_2$ unit. On the basis of this model,[4] it would appear to be reasonable to anticipate that (a) the cis,anti to cis,syn product ratio should decrease as the size of the ester increases, viz., in

(3) (a) Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* **1979**, *101*, 7129–7130. (b) Little, R. D.; Muller, G. W. *Ibid.* **1981**, *103*, 2744–2749. (c) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371–4383. (d) Little, R. D.; Carroll, G. L. *Tetrahedron Lett.* **1981**, *22*, 4389–4392. (e) Little, R. D.; Carroll, G. L.; Petersen, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 928–932.

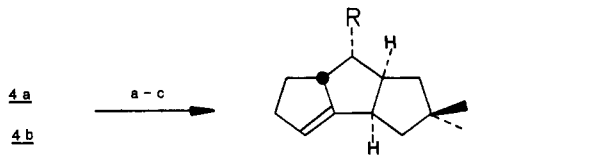
(4) This model is based upon considerations similar to those which are discussed in detail in: "Asymmetric Organic Reactions"; Morrison, J. D.; Mosher, H. S., Eds.; American Chemical Society: Washington, DC, 1976.

the order 8-phenylmenthyl < menthyl < methyl, and that (b) correlated with a decrease in the ring fusion product ratio, there should be an increase in the diasterioselectivity which is associated with the formation of the cis,anti product.

To test these ideas, we prepared the (−)-menthyl and (−)-8-phenylmenthyl diazenes **4a** and **4b** by utilizing slight modifications of our previously published route to diazene 1 (Scheme II; refer to the Experimental Section for details).[3b]

Results and Discussion

In accord with the expectations set forth above, it was discovered that the cis,anti to cis,syn tricyclopentanoid product ratio was indeed a function of the size of the ester unit. In particular, switching from methyl to menthyl to 8-phenylmenthyl esters led to product ratios of 9:1, 5.6:1, and 3.3:1, respectively. The tricyclopentanoid products from the menthyl and 8-phenylmenthyl runs were then conveniently separated by chromatography, and the diastereoselection achieved in forming the cis,anti tricyclopentanoid was measured by using two independent techniques. In the case of the menthyl ester, capillary column GC analysis indicated a *de* of 5.8 ± 0.9%. This value was confirmed by first forming the Mosher ester derivative of the diastereomers by using the standard sequence of reactions illustrated below[5] and then analyzing the ^{19}F NMR spectrum of the derivatives with the aid of the shift reagent Eu(hfc)$_3$.



5a, R = CO_2(−)-menthyl

5b, R = CO_2(−)-8-phenylmenthyl

8, R = CH_2OH

7, R = $CH_2OCOC(PhCF_3OCH_3)$

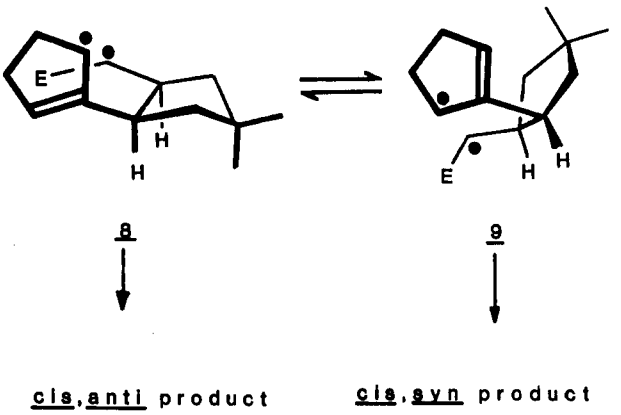
a, THF, reflux; b, LAH, ether;

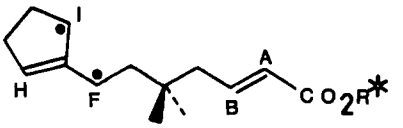
c, (−)-Mosher's acid, DCC, DMAP

While a *de* value of ca. 5% is certainly not acceptable in terms of its applicability to total synthesis, we were nevertheless encouraged by this result and were hopeful that, in accord with the expectations outlined above and in analogy with Diels–Alder and ene reaction chemistry,[6] a switch from menthyl to an 8-phenylmenthyl ester would lead to a sizeable increase in diastereoselection. We were therefore quite suprised to find that while the cis,anti to cis,syn product ratio decreased, the *de* value obtained for the cis,anti product remained low (viz., 5 ± 1%).[7]

Since the chiral auxiliary did not have the effect which was predicted on the basis of the idealized transition-state representation illustrated above, the representation requires modification. The results indicate that the chiral auxiliary plays a reasonably insignificant role in determining the direction of coiling of the acyclic chain, i.e., that is has very little effect in the critical diastereomer selecting portion of the reaction sequence. The experimental observations can be reconciled by suggesting that the trapping reaction proceeds in a stepwise fashion and that 5-EXO,TRIG closure between C_B and C_F occurs prior to bonding between C_A and C_I or C_A and C_H.[8] In this fashion, one can envision the approach of the diylophile to the diyl as occurring when the ester is in a rotational conformation which removes it from the proximity of the reacting centers. Bond formation between centers C_B and C_F leading to the formation of a fixe-membered ring can then occur before much, if any, asymmetric influence of the chiral ester can be achieved. At this point, the diastereoselectivity of the reaction has been determined. However, it is the formation of the second bond between either C_A and C_I or C_A and C_H that determines the cis,anti to cis,syn product ratio. If indeed a stepwise mechanism is correct, then, following formation of the first bond, an equilibrium between diradicals **8** and **9** can occur (Scheme III). As illustrated, the size of the ester, E, should have a marked influence upon the position of the equilibrium and therefore upon the product ratio. It seems clear that a larger ester would favor **9** in the proposed equilibrium and lead to a decrease in the cis,anti to cis,syn ratio as observed.

Scheme III





Concluding Remarks

In previous papers, we have, for the most part, not included commentary regarding the presumed concerted vs. nonconcerted nature of the intramolecular 1,3-diyl trapping reaction. However, it is interesting to note that both the chemistry described above and that associated with our recent efforts to use the trapping reaction in the synthesis of the marine natural product $\Delta^{9,12}$-capnellene can best be described in terms of a stepwise or concerted but nonsynchronous process involving an initial 5-EXO,TRIG closure as above or a 6-ENDO,TRIG closure as was the case with the capnellene chemistry.[3d,e]

(5) (a) Mosher, H. S.; Dull, D. L.; Dale, J. A. *J. Org. Chem.* **1969**, *34*, 2543–2549. (b) Steglich, W.; Bernhard, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 522–524. (c) Ziegler, F. E.; Berger, G. D. *Synth. Commun.* **1979**, *9*, 539–543.

(6) (a) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908–6909. (b) Corey, E. J.; Ensley, H. E.; Parnell, C. A. *J. Org. Chem.* **1978**, *43*, 1610–1612. (c) Roush, W. R.; Gillis, H. R.; Ko, A. I. *J. Am. Chem. Soc.* **1982**, *104*, 2269–2283 and references therein. (d) Oppolzer, W.; Kurth, M.; Reichlin, D.; Moffatt, F. *Tetrahedron Lett.* **1981**, *22*, 2545–2548.

(7) Although we were unable to determine the *de* for the cis,syn isomers using capillary column GC (refer to the Experimental Section for details), ^{19}F NMR showed that there was no significant asymmetric induction, i.e., that the *de* value was very low.

(8) (a) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736, 736–738, 738–741. (b) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground in Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4, pp 162–311. (c) Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1980**, 482.

While the experiments described above have clearly not lead to the desired degree of asymmetric induction, *they have served to help refine our view of the intramolecular diyl trapping reaction* and have served to convince us that an alternative plan to induce asymmetry is required. At the present time, efforts to induce asymmetry by fixing the chirality at one of the carbon atoms of the acylic chain which links the diyl to the diylophile are underway. Details concerning this plan and the results of these efforts will be reported in due course.[9]

Experimental Section

Proton magnetic resonance spectra were recorded on either a Varian T-60, EM-360, FT-80, or XL-100 or a Nicolet NT-300 spectrometer. A Varian CFT-20 was utilized to obtain ^{13}C NMR spectra; both fully decoupled and off-resonance decoupled spectra were recorded. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane (Me_4Si) in δ units, and coupling constants are given in cycles per second (hertz). Unless indicated otherwise, spectra were recorded with $CDCl_3$ as the solvent. Fluorine NMR spectra were recorded by using a Varian XL-100 NMR instrument at 94.1 MHz with a sweep offset of 42 905 Hz. Areas were obtained by integration (plainimeter). Infrared (IR) spectra were recorded by using a Perkin-Elmer 283 spectrometer. Carbon and hydrogen analyses were obtained from Galbraith Laboratories Inc, Knoxville, TN. Rotations were recorded by using a Perkin-Elmer 141 Polarimeter. We thank Professor Thomas Bruice of UCSB for the use of this instrument. A constant temperature was maintained by using a B. Braun Melsingen AG Thermomix 1480-Frigomix system. Medium-pressure liquid chromatography (MPLC) was performed by using a variety of Altex columns packed with E. Merck silica gel 60 (230–400 mesh, ASTM). The identity of the columns which were connected in series is reported for each experiment which called for their use. Gravity flow chromatography was accomplished by using E. Merck silica gel 60 (70–230 mesh, ASTM). Reactions were monitored as a function of time by using TLC (E. Merck silica gel 60F-254 and Baker 250F silica gel glass plates). The solvents used for chromatography were mixed by volume and are reported for each experiment. Column A refers to a 50-m OV-101 fused silica capillary column (J&W Scientific). An HP-5830A GC equipped with an FID detector and an HP 18850 data terminal was used in all cases. The conditions used with column A were as follows: injection temperature 180 °C, FID temperature 300 °C, temperature 1 = 90 °C, time 1 = 1.00 min, rate = 5 °C/min; temperature 2 = 240 °C, time 2 = 25 min. Column B refers to a 12-m OV-101 fused silica capillary column (J&W Scientific). The GC conditions were as follows: injection temperature 190 °C, FID temperature 250 °C, 1 = 80 °C, time 1 = 1.00 min, rate = 5.0 °C/min; temperature 2 = 250, time 2 = 45 min.

Preparation of the (−)-8-phenylmenthyl analogues[10] of the (−)-menthyl esters paralleled the descriptions given below. As a result, *only differences in experimental procedure which are significant with respect their successful repetition are recorded.*

(−)-Menthyl (*E*)-7-Hydroxy-5,5-dimethylhept-2-enoate. Sodium hydride (74 mg of a 50% dispersion, 1.54 mmol) was washed three times with pentane. (Carbomenthoxymethyl)triphenylphosphonium bromide[14,15] (808 mg, 1.54 mmol) was added along with 4.69 mL of acetonitrile. The mixture was allowed to stir for 2 h at room temperature, and then 200 mg (1.54 mmol) of 2-hydroxy-4,4-dimethyltetrahydropyran[3b,c] was added in 1.62 mL of acetonitrile. The reaction mixture was brought to reflux and was allowed to stir there for ca. 20 h. The acetonitrile was then removed in vacuo, and the resulting residue was taken up in ether and stirred for 15 min. The phosphine oxide was filtered and the oil which remained was purified by MPLC (15 × 250 and 15 × 1000 mm columns, 40% ether in pentane) with silica gel to provide 294 mg of two alcohols (63%) in a 9.6:1 trans/cis ratio: TLC (trans) R_f 0.25 (40% ether in pentane); $[\alpha]^{20}_D$ −60° (*c* 1.85, ether); TLC (cis) R_f 0.30 [40% ether in Skelly Solve F (UV and *p*-anisaldehyde active)].

The spectral data for the cis isomer were as follows: ^1H NMR (60 MHz) 6.25 (1 H, dt, J = 12, 7, β to ester), 5.75 (1 H, dt, J = 12, $J_{allylic}$ = 0.5, α to ester), 4.7 (1 H, m, menthyl methine α to ester), 3.7 (2 H, t, J = 8, α to OH), 2.6 (2 H, dd, J = 7, $J_{allylic}$ = 0.5, γ to ester), 1.0 (6 H, s, *gem*-methyls), 0.85 (6 H, d, J = 9, isopropyl), 0.75 (3 H, d, J = 7, methyl). For the trans alcohol: IR (neat, NaCl) 3400, 2960, 2930, 2880, 1710, 1650, 990 cm^{-1}; ^1H NMR (300 MHz) 6.95 (1 H, dt, J = 8, 15, H β to ester), 5.8 (1 H, dt, J = 15, $J_{allylic}$ = 1, proton α to ester), 4.75 (1 H, m, CO_2CH), 3.7 (2 H, t, J = 6, α to OH), 2.15 (2 H, dd, J = 8, $J_{allylic}$ = 1, γ to ester), 1.05 (6 H, s, *gem*-methyls), 0.9 (6 H, d, J = 8, menthyl isopropyl), 0.75 (3 H, d, J = 7, menthyl methyl); ^{13}C NMR (20 MHz) 165.9 (C_9), 145.6 (C_7), 123.9 (C_8), 73.9 (C_{10}), 59.2 (C_1), 47.0, 45.0, 44.2, 30.9, 34.2, 33.0, 31.2, 27.2 (C_4 and C_5), 26.4, 23.7, 21.8, 20.4, 16.5. Anal. Calcd for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04. Found: C, 73.44; H, 10.82.

(*1*)-(−)-Menthyl (*E*)-7-Oxo-5,5-dimethylhept-2-enoate. Pyridinium dichromate (434 mg, 1.24 mmol) and 257 mg (0.83 mmol) of the trans alcohol prepared as described above were dissolved in 1.66 mL of methylene chloride, and the mixture was then stirred at room temperature for ca. 5 h. The reaction was monitored by TLC until complete. The solution was then diluted with ether, and the solid was removed in vacuo to afford 207 mg of a yellow oil which was chromatographed on 45 g of silica gel (25-mm-diameter column) with 5% ether in pentane to afford the pure aldehyde: 178 mg (69%); TLC R_f of 0.14 [5% ether in Skelly Solve F (UV and *p*-anisaldehyde active)]; IR (neat, NaCl) 2920, 2820, 1720, 1710, 1650, 970 cm^{-1}; ^1H NMR (80 MHz) 9.7 (1 H, t, J = 2, CHO), 6.9 (1 H, dt, J = 16, 8, β to ester), 5.8 (1 H, dt, J = 16, $J_{allylic}$ = 1, α to ester), 4.7 (1 H, m, menthyl methine alpha to ester), 2.3 (2 H, d, J = 2, α to aldehyde), 2.2 (2 H, dd, J = 1, 8, γ to ester), 1.15 (6 H, s, *gem*-methyls), 0.9 (6 H, d, J = 8, isopropyl methyls), 0.75 (3 H, d, J = 7, menthyl methyl); $[\alpha]^{20}_D$ −58° (*c* 2.9, ether). Anal. Calcd for $C_{19}H_{32}O_3$: C, 73.98; H, 10.46. Found: C, 73.92; H, 10.62.

6-[(−)-(*E*)-5-(Carbomenthyloxy)-2,2-dimethyl-4-pentenyl]fulvene. To a cold 0 °C solution of 1.44 g (4.6 mmol) of the aldehyde prepared as described above and 774 mg (11.7 mmol) of cyclopentadiene in 8.3 mL of methanol was added, dropwise, a solution of 518 mg (7.0 mmol) of diethylamine in 6.8 mL of methanol. The resulting mixture was warmed to room temperature and was allowed to stir for 1.5 h. The course of the reaction was monitored by TLC until the aldehyde disappeared. At that point the solution was cooled to 0 °C, and 0.94 mL of glacial acetic acid was added dropwise. Most of the solvent was then removed in vacuo, and the residue was taken up in water and extracted three times with ether. The combined organic layers were washed with saturated sodium bicarbonate and brine, dried over $MgSO_4$, and concentrated in vacuo to afford a bright yellow oil which was immediately chromatographed on silica gel (ca. 60 g, 25-mm-diameter column) with 5% ether in Skellysolve F. This gave rise to 1.62 g (97%) of the desired fulvene (average yield over three runs of 81%): TLC R_f 0.5 [10% ether in Skelly Solve F (UV and *p*-anisaldehyde active)]; IR (NaCl, neat) 3100, 3080, 3040, 2930, 2870, 1720, 1645, 1460 cm^{-1}; ^1H NMR (80 MHz) 6.9 (1 H, dt, J = 16, 8, β to ester), 6.6–6.05 (5 H, m, fulvene ring protons), 5.9 (1 H, dt, J = 16, $J_{allylic}$ = 1 H, α to ester), 4.7 (1 H, m, menthyl methine α to ester unit), 2.4 (2 H, d, J = 7.5, methylene α to fulvene), 2.15 (2 H, dd, J = 8, $J_{allylic}$ = 1, methylenes γ to ester unit), 1.0 (6 H, s, *gem*-methyls), 0.9 (6 H, d, J = 7, isopropyl methyls), 0.75 (3 H, d, J = 7, menthyl methyl).

N,N′-Bis[(2,2,2-trichloroethoxy)carbonyl]-7-[(*E*)-6-(carbomenthoxy)-3,3-dimethylhex-5-enylidene]-2,3-diazabicyclo[2.2.1]heptane. To a stirred solution of bis(2,2,2-trichloroethyl)

(9) Ongoing research with Mr. Keith Stone of UCSB.

(10) We are grateful to Professor U. Schoelkopf for providing us with a detailed experimental procedure for the preparation of (−)-8-phenylmenthol.

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(15) Roush, W. R.; Gillis, H. R.; Ko, A. I. *J. Am. Chem. Soc.* **1982**, *104*, 2269–2283. We will be pleased to furnish full experimental and spectral details for the preparation of the (−)-menthyl and (−)-8-phenylmenthyl phosphonium salts upon request from an interested reader.

azodicarboxylate[12] (1.55 g, 4.1 mmol) in 11.7 mL of ether was added at 0 °C 1.45 g (4.1 mmol) of the fulvene prepared as described above, dissolved in 1.4 mL of ether over a period of 15 min. The course of the reaction was monitored by TLC for the loss of the fulvene, and when the reaction was complete, the mixture was simply concentrated in vacuo. The crude Diels–Alder product was then added to a round-bottomed flask precooled to 0 °C and containing *freshly prepared* dipotassium azodicarboxylate[11] (3.99 g, 20.4 mmol) and 5.4 mL of dry dichloromethane. To the resulting stirred solution was added slowly over a 30-min period 2.63 mL of glacial acetic acid in 12 mL of dichloromethane. The solution was allowed to stir for another 2 h after the addition was complete. The mixture was then filtered, the solid washed with ether, and the mixture concentrated. The resulting residue was chromatographed on 160 g of silica gel (30 mm diameter × 30 cm Vycor column) with 20% ether in Skellysolve F. An 82% yield (2.47 g) of a colorless, extremely viscous oil (subject to foaming during removal of the last traces of solvent) was obtained: TLC R_f 0.20 [20% ether in Skellysolve F (UV and *p*-anisaldehyde active)]; IR (NaCl, neat) 2950, 2920, 2870, 1780–1700, 1650, 1450, 990 cm^{-1}; ^1H NMR (60 MHz) 6.9 (1 H, dt, J = 8, 16, vinyl β to ester), 5.75 (1 H, dt, J = 16, $J_{allylic}$ = 1, vinyl α to ester), 5.45 (2 H, apparent t, J = 7, one vinyl plus one bridgehead), 5.0–4.55 (6 H, br m, 4 H from trichloroethyl units plus menthyl methine α to ester unit plus one bridgehead), 2.25–1.9 (4 H, m, methylene), 0.95 (3 H, d, J = 8, methyl on menthyl ring). $[\alpha]^{20}_D$ −21° (*c* 1.84, EtOH). Anal. Calcd for $C_{30}H_{42}O_6N_2Cl_6$: C, 48.73; H, 5.73; N, 3.79. Found: C, 48.49; H, 5.95; N, 3.49.

7-[(*E*)-6-(Carbomenthyloxy)-3,3-dimethylhex-5-enylidene]-2,3-diazabicyclo[2.2.1]hept-2-ene. The carbamate described above (770 mg, 1.05 mmol), 1.45 g of freshly prepared zinc–copper couple,[13] and 6.5 mL of methyl alcohol were added to a round-bottomed flask, and the contents were stirred under argon at room temperature for 45 min. The course of the reaction was monitored by TLC for the disappearance of the carbamate. When the reaction was complete, the couple which remained was filtered and washed with dichloromethane. To the filtrate, precooled to 0 °C, was added 1.028 g (3.5 mmol) of potassium ferricyanide dissolved in 8.2 mL of water. The mixture was allowed to stir for 15 min, during which time a yellow-orange solid formed. The resulting mixture was taken up in 100 mL of ether and 100 mL of brine. The layers were separated, and the aqueous layer was extracted six times with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was immediately chromatographed on 60 g of silica gel (25-mm-diameter column) with 30% ether in Skellysolve F to afford 235 mg (58%) of the pure diazene (the reaction sequence has been repeated numerous times; yields range from 50% to 80% for the two steps): TLC R_f 0.2 [40% ether in Skellysolve F (UV and *p*-anisaldehyde active)]; IR (neat, NaCl) 2950, 2920, 2860, 1710, 1650, 1460, 1450, 985 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) 6.9 (1 H, dt, J = 16, 8, vinyl β to ester), 5.7 (1 H, dt, J = 16, $J_{allylic}$ = 1, vinyl α to ester), 5.25 and 5.15 (2 H, 2 m, bridgeheads), 5.15 (1 H, t buried under bridgehead, J = 8, C_8 vinyl H), 2.0 (2 H, dd, J = 8, $J_{allylic}$ = 1, methylene γ to ester), 1.85 (2 H, d, J = 8, methylene α to C_8 vinyl), 0.9 (6 H, d, J = 6, isopropyl methyls), 0.85 (6 H, s, *gem*-methyls), 0.80 (3 H, d, J = 7, methyl).

Menthyl (3aα,6aβ,7α,7aα)-2,3,3a,5,6,6a,7,7a-Octahydro-2,2-dimethyl-1*H*-cyclopenta[*a*]pentalene-7-carboxylate. To 80 mg (0.2 mmol) of the diazene prepared as described above was added 1.04 mL of acetonitrile. The mixture was refluxed for 5 h and cooled to room temperature, and the solvent was removed in vacuo to afford 67 mg of a pale yellow oil. The crude reaction mixture was analyzed by gas chromatography and showed a 5.6:1 ratio of the cis,anti to cis,syn tricyclopentanoid. The material was then chromatographed on 15 g of silica gel (10-mm glass column) with 2% ether in Skellysolve F to afford 52 mg of a mixed fraction and 10 mg of pure cis,anti tricyclopentanoid (total yield 83%). The mixed fractions were rechromatographed to afford pure cis,anti and cis,syn tricyclopentanoids. The cis,anti tricyclopentanoid displayed an optical rotation of $[\alpha]^{20}_{Na}$ −36° (*c* 2.1, EtOH). The TLC R_f was 0.43 for the cis,anti and 0.52 for the cis,syn isomer with 5% ether in pentane (UV, PMA, and *p*-anisaldehyde active). Capillary column B indicated retention times of 46.72 and 46.93 min for the cis,anti diasteriomers while the cis,syn isomers appeared as a single sharp peak at 47.57 min. For the cis,syn isomer: IR (neat, NaCl) 2950, 2920, 2880, 1730, 1460; ^1H NMR (80 MHz) 5.2 (1 H, t, J = 2, vinyl), 4.65 (1 H, m, menthyl methine α to ester), 3.2 (2 H, m, allylic bridgehead), 2.5 (2 H, m, allylic methylene), 1.05 and 0.9 (6 H, 2 s, tricyclopentanoid ring methyls), 0.85 (6 H, d, J = 8, menthyl isopropyl), 0.70 (3 H, d, J = 8, menthyl methyl). This material was taken on to form the Mosher ester derivative. However, we were unable to determine the *de* using capillary column GC (vide supra). For the cis,anti isomer: IR (neat, NaCl) 3050, 2940, 2860, 1720, 1450 cm^{-1}; ^1H NMR (80 MHz) 5.14 (1 H, m, vinyl), 4.55 (1 H, m, menthyl methine α to ester), 3.1 (3 H, m, ring junction protons), 2.5 (3 H, br d, J = 9, allylic plus methine α to ester), 1.01 (3 H, s, one methyl of geminate methyl pair), 0.9 (3 H, s, one methyl of geminate methyl pair), 0.86 (6 H, d, J = 7, isopropyl), 0.74 (3 H, d, J = 8, menthyl methyl); ^{13}C NMR 174.26 (CO_2R), 155.11 (s, vinyl), 117.35 (d, vinyl), 73.97 (d, COOC), 57.07, 52.15, 51.71, 47.88, 47.48, 47.02, 41.25, 41.07, 40.23, 37.22, 34.32, 31.38, 28.42, 26.36, 26.21, 25.81, 25.78, 23.18, 21.87, 20.23, 15.95. Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.40; H, 10.68. Found: C, 80.52; H, 10.57.

(3aα,6aβ,7α,7aα)-2,3,3a,5,6,6a,7,7a-Octahydro-7-(hydroxymethyl)-2,2-dimethyl-1*H*-cyclopenta[*a*]pentalene. To a stirred suspension of lithium aluminum hydride (9.7 mg, 0.25 mmol) in 0.42 mL of ether at room temperature was added dropwise a solution of the cis,anti tricyclopentanoid ester prepared as described above (45 mg, 0.13 mmol) dissolved in 1.32 mL of ether. The course of the reaction was monitored by TLC. After 45 min the reaction mixture was cooled to 0 °C, and the intermediate was quenched with 1.21 mL of 5% HCl. The organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford material which was chromatographed on 15 g of silica gel (10-mm-diameter column) with 20% ether in pentane. A 97% yield of the desired tricyclopentanoid was obtained. Its spectral data were in complete agreement with those previously reported.[3b]

Mosher Ester Derivative of (3aα,6aβ,7α,7aα)-2,3,3a,5,6,6a,7,7a-Octahydro-7-(hydroxymethyl)-2,2-dimethyl-1*H*-cyclopenta[*a*]pentalene. To a solution of 45 mg (0.19 mmol) of Mosher's acid[5a] in 1.0 mL of dry dichloromethane were added 0.002 g (0.016 mmol) of 4-(dimethylamino)pyridine and 36 mg (0.17 mmol) of the tricyclopentanoid alcohol prepared as described above. The mixture was cooled to 0 °C, and 70 mg (0.26 mmol) of DCC was added. The reaction mixture was allowed to warm to room temperature where it was stirred until the alcohol was no longer evident by TLC analysis (ca. 16 h). When the reaction was complete, the dicyclohexylurea byproduct was filtered out and washed with ether, and the filtrate was concentrated in vacuo. The material was then taken up in ether and washed twice with 0.5 N HCl and saturated sodium bicarbonate. The organic layer was the dried over $MgSO_4$ and concentrated in vacuo to afford an oil which was chromatographed on 15 g of silica gel (10-mm-diameter Vycor column) with 1% ether in Skellysolve F. A total of 67 mg (90%) of the desired product was isolated. The conditions which were used for the cis,syn tricyclopentanoid were identical with those described above: TLC (cis,anti) R_f 0.21 [1% ether in pentane (UV, PMA, and *p*-anisaldehyde active)]; IR (neat, NaCl) 3050, 2950, 2920, 2860, 1745, 1450 cm^{-1}; ^1H NMR (300 MHz) 7.55 and 7.39 (5 H, m, aromatic), 5.18 (1 H, br s, vinyl), 4.25 and 3.95 (2 H, 2 m, methylene α to ester unit), 3.53 (3 H, s, OMe), 3.55 (2 H, m, allylic bridgeheads), 2.85 (1 H, m, methine β to ester alkyl oxygen), 2.65 (1 H, t, J = 6, nonallylic bridgehead), 2.45 (2 H, m, allylic methylene), 0.98 (6 H, s, *gem*-methyls), 0.87 and 0.85 (4 H, 2 s, methylenes α to *gem*-methyls).

(*E*)-(−)-8-Phenylmenthyl 7-Hydroxy-5,5-dimethylhept-2-enoate. The solution was allowed to reflux for 16.5 h and afforded a crude yellow oil which was purified on silica gel by using gradient elution (40–60% ether in Skellysolve F). A 71% yield of a 4.4:1 mixture of trans to cis alcohols was obtained. Occasionally, mixed fractions of alcohols were obtained; this material could be taken on to the next step, after which the isomers were readily separated by using chromatography: TLC R_f 0.23 [40% ether in Skellysolve F (*p*-anisaldehyde active)]; $[\alpha]^{20}_D$ 2.96° (*c* 1.25, ether), 2.7 (*c* 0.95, ether); IR (NaCl) 3420, 3080, 3050, 3020, 2950, 2920, 2860, 1705, 1440 cm^{-1}; ^1H NMR (80 MHz) 7.18 (5 H, m, Ar), 6.6 (1 H, dt, J = 16, 8, beta vinyl), 5.25 (1 H, dt, J = 16, $J_{allylic}$ = 1, vinyl α to carbonyl), 4.8 (1 H, m, methine of 8-phenylmenthyl), 3.7 (2 H, t, J = 8, methylene α to OH), 2.15–0.75 (7 H, m, cyclohexyl ring

protons), 1.98 (2 H, dd, J = 8, $J_{allylic}$ = 1, allylic methylenes), 1.3 and 1.21 (6 H, 2 s, methyls β to Ar), 0.98 (6 H, s, *gem*-methyls), 0.8 (3 H, d, J = 6, cyclohexyl ring methyl); ^{13}C NMR (20 MHz) 165.38 (s, carbonyl), 151.33 (s, Ar), 145.06 (d), 127.78, 125.38, 124.78, 124.10 (Ar and alpha vinyl carbon), 74.15 (d), 59.42 (t, α to OH), 50.60 (t, allylic methylene), 45.12, 44.36, 41.72, 39.74, 34.56, 33.04, 31.12, 27.22, 26.67, 25.55, 21.64. Anal. Calcd for $C_{25}H_{38}O_3$: C, 77.67; H, 9.91. Found: C, 77.57; H, 10.16.

(*E*)-(−)-8-Phenylmenthyl 7-Oxo-5,5-dimethylhept-2-enoate. After 9.5 h, the crude product was a thick black oil which was purified by chromatography on silica gel with 10% ether in Skellysolve F. A 60% yield of the pure colorless aldehyde was obtained: TLC R_f 0.21 [10% ether in Skelly Solve F (UV and *p*-anisaldehyde active)]; $[\alpha]^{20}_D$ +1.3° (*c* 1.7, ether); IR (neat, NaCl) 3080, 3060, 3020, 1710, 1650, 1450 cm^{-1}; ^{1}H NMR (60 MHz) 9.7 (1 H, t, J = 4, aldehyde), 7.18 (5 H, m, Ar), 6.55 (1 H, dt, J = 16, 8, β vinyl), 5.25 (1 H, dt, J = 16, $J_{allylic}$ = 1, vinyl α to ester), 4.85 (1 H, m, 8-phenylmenthyl methine), 2.25 (2 H, d, J = 4, methylene α to CHO), 2.1 (2 H, dd, J = 8, $J_{allylic}$ = 1, methylene γ to ester), ca. 2.0–0.8 (m, cyclohexyl ring protons), 1.35 and 1.12 (6 H, 2 s, methyls β to Ar), 1.05 (6 H, s, *gem*-methyls), 0.85 (3 H, d, J = 7, cyclohexyl ring methyl). Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44. Found: C, 78.27; H, 9.28.

6-[(*E*)-(−)-5-[(8-Phenylcarbomenthyl)oxy]-2,2-dimethyl-4-pentenyl]fulvene. After 3 h, a bright yellow oil was obtained and purified by chromatography on silica gel with 5% ether in Skellysolve F to afford an 87% yield of the desired product: TLC R_f 0.23 [5% ether in Skellysolve F (UV and *p*-anisaldehyde active); IR (neat, NaCl) 3080, 3060, 3020, 2960, 2920, 2820, 1710, 1640, 1600, 1470 cm^{-1}; ^{1}H NMR (60 MHz) 7.2 (5 H, m, Ar), 6.7 (1 H, buried dt, J = 15, 8, β vinyl), 6.6–6.2 (5 H, m, fulvene ring protons), 5.3 (1 H, dt, J = 15, 1, α vinyl), 4.85 (1 H, m, 8-phenylmenthyl methine), 2.4 (2 H, d, J = 8, methylenes α to fulvene), 2.15 (2 H, dt, J = 8, 1, methylenes γ to ester), 2.0–0.7 (m, cyclohexyl ring protons), 1.35 and 1.25 (6 H, 2 s, methyls β to Ar), 1.0 (6 H, s, *gem*-methyls), 0.9 (3 H, d, J = 8, methyl on cyclohexyl ring).

***N*,*N*′-Bis[(2,2,2-trichloroethoxy)carbonyl]-7-[(*E*)-6-[(8-phenylcarbomenthyl)oxy]-3,3-dimethyl-5-hexenylidene]-2,3-diazabicyclo[2.2.1]heptane.** Unlike the menthyl case described previously, the dipotassium azodicarboxylate was not freshly prepared prior to use, and, as a result, the hydrogenation needed to be repeated three times before it was complete. An 83% yield of pure material was obtained after chromatography on silica gel with 20% ether in Skellysolve F. The product was a colorless oil which foamed upon removal of the last of the solvent to afford a white solid; the material turned to a sticky gluelike material at 55 °C, and at 70 °C, the material became even more viscous and changed its appearance. A solid was not obtained after recooling the material to room temperature. As a result, a melting point could not be obtained: TLC R_f 0.20 [20% ether in Skellysolve F (UV and *p*-anisaldehyde active)]; $[\alpha]^{20}_D$ +7.3° (*c* 1.06, EtOH for the mixture of diasteriomers); IR (KBr) 2950, 2920, 2860, 1710, 1440 cm^{-1}; ^{1}H NMR (60 MHz) 7.27 (5 H, m, Ar), 6.6 (1 H, dt, J = 8, 15, β vinyl), 5.4 (1 H, t, J = 8, C_8 vinyl), 5.25 (1 H, dt, J = 15, 1, α vinyl), 5.0–4.6 (7 H, m, bridgeheads, carbamate methylenes, 8-phenylmenthyl methine), 2.0–0.85 (m, cyclohexyl ring protons), 1.31 and 1.23 (6 H, 2 s, methyls β to Ar), 0.85 (6 H, s, *gem*-methyls). Anal. Calcd for $C_{36}H_{46}N_2O_6Cl_6$: C, 53.02; H, 5.69; N, 3.44. Found: C, 53.26; H, 5.86; N, 3.44.

7-[(*E*)-6-[(8-Phenylcarbomenthyl)oxy]-3,3-dimethylhex-5-enylidene]-2,3-diazabicyclo[2.2.1]hept-2-ene. Unlike the menthyl case described previously, the zinc–copper couple reduction did not proceed satisfactorily at room temperature but did go to completion in ca. 2 h at reflux. After oxidation with potassium ferricyanide, the crude product was chromatographed on silica gel with 25% ether in Skellysolve F. A 50% yield (two steps) of the pure diazene was obtained: TLC R_f 0.24 [25% ether in Skellysolve F (UV and *p*-anisaldehyde active)]; IR (neat, NaCl) 3080, 3060, 3020, 2960, 2920, 2880, 1710, 1660, 1680, 1600, 1445 cm^{-1}; ^{1}H NMR (300 MHz) 7.27 (5 H, m, aromatic), 6.6 (1 H, dt, J = 15, 8, vinyl β to ester), 5.45–5.0 (4 H, m, vinyl α to ester, C_8 vinyl, bridgeheads), 4.85 (1 H, m, COOCH), 1.9 (2 H, dt, J = 8, 1, methylene), 1.8 (2 H, d, J = 8, methylene), 3.5 and 2.5 (6 H, 2 s, methyls β to Ph), 0.85 (6 H, s, *gem*-methyls).

(−)-8-Phenylmenthyl (3aα,6aβ,7α,7aα)-2,3,3a,5,6,6a,7,7a-Octahydro-2,2-dimethyl-1*H*-cyclopenta[*a*]pentalene-7-carboxylate. The reaction mixture was allowed to reflux for 5 h, and after removal of the solvent and chromatography on silica gel with 3% ether in Skellysolve F, and 84% yield of the two tricyclopentanoids was obtained in a 3.3:1 cis,anti to cis,syn ratio: TLC R_f for the cis,anti form 0.20 and for the cis,syn form 0.30 [2% ether in Skellysolve F (UV and *p*-anisaldehyde active)]; $[\alpha]^{20}_D$ −1.25° (*c* 2, EtOH; cis,anti). Capillary column GC analysis (column B, retention times of 40.53 and 42.21 min) indicated a 5% ± 1% *de* while ^{19}F NMR indicated a 7% ± 6% *de*. Both the cis,anti and the cis,syn tricyclopentanoids were converted to the Mosher ester derivatives by using the procedures described above. The spectral data were in complete accord with those previously reported. For cis,syn isomer: IR (neat, NaCl) 3080, 3050, 3020, 2940, 2920, 2950, 1740, 1600, 1450 cm^{-1}; ^{1}H NMR (100 MHz) 7.26 (5 H, br s, Ar), 5.14 (1 H, br s, vinyl), 4.82 (1 H, m, 8-phenylmenthyl methine), 3.05 (2 H, m, allylic bridgeheads), 2.50 (2 H, m, allylic methylenes), 1.32 and 1.24 (6 H, 2 s, methyls β to Ar), 1.04 and 0.93 (6 H, 2 s, *gem*-methyls), 0.86 (3 H, d, J = 6, methyl on cyclohexyl ring), ca. 2.0–0.83 (m, ring protons). For cis,anti isomer: IR (neat, NaCl) 3090, 3060, 3020, 2940, 2860, 1725, 1600, 1460, 1440 cm^{-1}; ^{1}H NMR (100 MHz) 7.26 (5 H, m, Ar), 5.17 (1 H, m, vinyl), 4.79 (1 H, m, 8-phenylmenthyl methine), 3.4–0.8 (ring protons), 1.02 and 0.86 (6 H, 2 s, *gem*-methyls), 0.85 (3 H, d, J = 8, methyl on cyclohexyl ring); four peaks are observed for the methyls located β to the Ar unit at δ 1.34, 1.30, 1.23, 1.21; these signals are most likely due to diasteriomers; ^{13}C NMR 157.0 (s, ester carbonyl carbon), 155.2 (d, vinyl), 127.92 (d, Ar), 125.56, 125.38, 125.17, 124.94 (Ar), 117.51, and 117.04 (2 d, vinyl carbon of diasteriomers), 74.67 and 73.99 (2 d, methine α to ester), 51.77, 51.60, 51.39, 50.51, 49.68, 47.94, 47.58, 47.39, 42.46, 42.07, 41.05, 40.01, 37.43, 37.01, 34.64, 31.37, 29.67, 28.12, 27.03, 26.23, 26.18, 25.0, 21.79. Anal. Calcd for $C_{30}H_{42}O_2$: C, 82.90; H, 9.74. Found: C, 81.10; H, 9.89.

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