1), 124376-17-6; **3d** (isomer 2), 124376-18-7; **4a** (isomer 1), 124289-18-5; **4a** (isomer 2), 124376-40-5; **4a** (isomer 3), 124376-41-6; **4a** (isomer 4), 124376-42-7; **5a** (isomer 1), 124289-09-4; **5a** (isomer 2), 124376-19-8; **5a** (isomer 3), 124376-20-1; **5a** (isomer 4), 124376-21-2; **5b** (isomer 1), 124376-22-3; **5b** (isomer 2), 124376-23-4; **5b** (isomer 3), 124376-24-5; **5b** (isomer 4), 124376-25-6; **5c** (isomer 1), 124376-26-7; **5c** (isomer 2), 124376-27-8; **5c** (isomer 3), 124376-28-9; **5c** (isomer 4), 124376-29-0; **5d** (isomer 1), 124376-30-3; **5d** (isomer 2), 124376-31-4; **5d** (isomer 3), 124376-32-5; **5d** (isomer 4), 124376-33-6; **6a** (isomer 1), 124289-10-7; **6a** (isomer 2), 124376-34-7; **6b** (isomer 1), 124376-35-8; **6b** (isomer 2), 124289-11-8; **6c** (isomer 1), 124376-36-9; **6c** (isomer 2), 124376-37-0; **6d** (isomer 1), 124376-38-1; **6d** (isomer 2), 124376-39-2; **7a**, 124289-12-9; **7b**, 124289-13-0; **7c**, 124289-14-1; **7d**, 124289-15-2; 8, 124289-16-3; **9**, 124289-17-4; $(CH_3)_3SiCH_2MgCl$, 13170-43-9.

Supplementary Material Available: Complete set of NMR data for educts **1a–d** and the diastereomerically pure intermediates **3b**, **5b**, and **6b**, as well as a table with characteristic signals for **3a,c,d** and **5a,c,d** (diastereomeric mixtures) (4 pages). Ordering information is given on any current masthead page.

Unusual Diels–Alder Reactions of Eucarvone[1]

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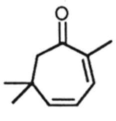
Received August 7, 1989

In continuation of a recent study of Diels–Alder reactions of conjugated, heteroannular dienones,[1b] an investigation of the cycloaddition behavior of a homoannular dienone, i.e., eucarvone (**1**), now has been undertaken.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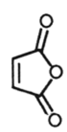
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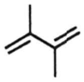
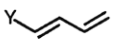
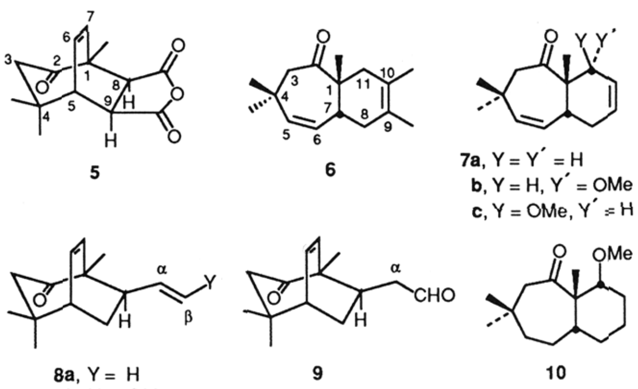

3


4a, Y = H
b, Y = OMe

Whereas the Diels–Alder reactivity of 2,4-cyclohexadienones has been studied extensively,[3] little is known about the reaction characteristics of 2,4-cycloheptadienones. In an early study of the thermal interaction of 2,4-cycloheptadienone with the dienophile *N*-phenylmaleimide the dienone was shown to exhibit low dienic reactivity.[4] It was hoped that an investigation of the reactions of eucarvone (**1**) with maleic anhydride (**2**), 2,3-dimethyl-1,3-butadiene (**3**), 1,3-butadiene (**4a**), and (*E*)-1-methoxy-1,3-butadiene (**4b**) would shed more light on the Diels–Alder reaction behavior of dienones of the 2,4-cycloheptadienone type.

Diels–Alder Reaction Products. In accord with expectation, eucarvone (**1**) behaved as a diene in its conversion into adduct **5** (Chart I) in 48% yield on thermal treatment with maleic anhydride (**2**) and as a dienophile in its thermal and aluminum chloride catalyzed[5] cycloadditions with 2,3-dimethyl-1,3-butadiene (**3**), leading to adduct **6** in 50% (by GC analysis) and 87% yield, respectively. On the other hand, eucarvone (**1**) acted surprisingly as both dienophile and diene toward the butadienes **4**. This aluminum chloride induced reaction with 1,3-butadiene (**4a**) produced a 1.6:1 mixture of adducts **7a** and **8a** in 85% yield (by GC analysis). Thermal reaction with (*E*)-1-methoxy-1,3-butadiene (**4b**) afforded a 3.4:2:1 mixture of adducts **7b**, **8b**, and **7c** in 47% yield (by GC analysis), and Yb(fod)$_3$-promoted[6] reaction with diene **4b** gave a 3.3:1.2:1 mixture of the same products in 66% yield (by GC analysis).

Chart I



5

6

7a, Y = Y′ = H
b, Y = H, Y′ = OMe
c, Y = OMe, Y′ = H

8a, Y = H
b, Y = OMe

9

10

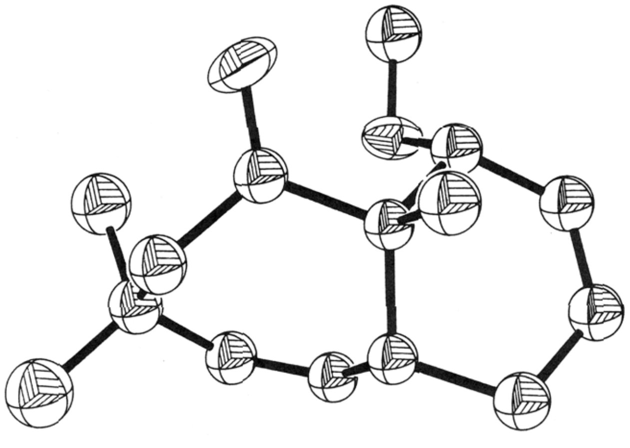


Figure 1. ORTEP drawing of structure **7b**.

Acid hydrolysis of enol ether **8b** furnished aldehyde **9** (97%), and hydrogenation of diene **7b** led nearly quantitatively to perhydrobenzosuberone **10**.

The structure assignment of compounds **5–10** was based on their NMR spectral analysis and the single-crystal X-ray crystallographic analysis of Diels–Alder adduct **7b**. Examination of hydrogen chemical shifts by COSY NMR experiments yielded hydrogen connectivities, which, in turn, determined the position of the vinyl side chains of compounds **8**. The H(5)–H(9)–H(8) coupling characteristics of bicycles **5** and **8** revealed these substances to possess endo stereochemistry. Thus, for example, ketones **5** and **8a** showed $J_{H(5)-H(9-exo)}$ and $J_{H(8)-H(9-exo)}$ values of <1

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[1] (a) Part 18 of the series: Diels–Alder Reactions of Cycloalkenones. (b) For part 17: see Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.*, in press.

[2] (a) University of California. (b) Università di Perugia.

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[5] (a) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056. (b) Fringuelli, F.; Pizzo, F.: Taticchi, A.; Wenkert, E. *Ibid.* **1983**, *48*, 2802.

[6] Fringuelli, F.; Minuti, L.; Radics, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1988**, *53*, 4607.

0022-3263/90/1955-1366$02.50/0

and 9–10 Hz, respectively. The carbonyl absorption of >1700 cm^{-1} in the infrared spectra of ketones **6**, **7**, and **10** indicated the absence of ketone conjugation in the dienones **6** and **7**, thus determining the site of cycloaddition on the dienophilic eucarvone (**1**) and settling the structures of ketones **6** and **7a**. COSY-based hydrogen connectivity analysis of ethers **7b** and **7c** showed their methoxy groups to be C(11) attached. The stereochemistry of the methoxy function of ether **7c** was derived from ^{13}C NMR spectroscopy. Thus, whereas the carbon shifts of the geminal methyl groups of bicycle **7c** were the same as those of models **6** and **7a**, the angular methyl function of ether **7c** was shielded by >5 ppm compared with the same methyl group in these models. This γ effect was indicative of a cis relationship between the methoxy and angular methyl groups of ether **7c**. This observation was in accord with structure **7b** and **7c** for the two isomeric ethers. Finally, the structure depicted in formula **7b** was confirmed by a single-crystal X-ray crystallographic analysis of the substance (Figure 1).

Discussion. It is noteworthy that the cycloadditions, with eucarvone (**1**) acting as dienophile, i.e., reactions leading to adducts **6** and **7**, are site-selective, inasmuch as they involve the dienone only at its α,β double bond, and preponderantly exo diastereoselective, in view of the ca. 3:1 **7b**/**7c** ratio. The Diels–Alder reactions leading to adducts **8**, i.e., those implicating eucarvone (**1**) as diene and dienes **4** as dienophiles, appear to be cycloadditions of inverse electron demand[7] involving the LUMO of dienes **4** and the HOMO of eucarvone (**1**). They are regioselective (in the case of the reaction of diene **4b**) and endo diastereoselective. Whereas both endo and exo transition states may have stabilizing secondary orbital interactions[7,8] of comparable magnitude (with eucarvone's incipiently forming β,γ double bond in the former transition state and with eucarvone's keto group in the latter excited state), the exo transition state suffers from destabilizing, nonbonding, steric interaction between the unbonded vinyl group of dienes **4** with the eucarvone methylene function. Finally, the steric factor may be responsible also for the lack of cycloaddition of eucarvone (**1**) and diene **3** in an inverse electron demand mode, since steric interference would be present in both endo and exo transition states. Thus the competition of the dienophilic and dienic character of eucarvone in reactions with dienes may depend strongly on the diene structure.

Experimental Section

Melting points were taken on a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra of $CHCl_3$ solutions were recorded on a Perkin-Elmer 257 spectrophotometer. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained on a Nicolet QE-300 spectrometer, operating in the Fourier transform mode at 300 and 75.5 MHz, respectively. The carbon shifts are in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. Mass spectra were observed on a Hewlett-Packard 5970 GC-MS instrument, calibrated with perfluorotributylamine for 70-eV operations. Analytical GC was carried out with Carlo Erba HRGC-5160 (with 30-m, 0.32-mm-diameter SP-2340 fused silica capillary column and with an "on column" injection system) and Hewlett-Packard 5880A (with 30-m, 0.25-mm-diameter SPB-5 capillary column and with an "on column" injection system) gas chromatographs. Absorption chromatography was executed on 0.040–0.063-mm, 230–400 mesh ASTM Merck silica gel. All operations involving the preparation of the starting reaction mixtures for both thermal and catalyzed Diels–Alder reactions were performed in a drybox, and the subsequent reactions monitored by GC.

Maleic Anhydride Adduct 5. A solution of 2.00 g (13.8 mmol) of eucarvone (**1**)[9] and 1.40 g (14.3 mmol) of maleic anhydride (**2**) in 42 mL of dry toluene was refluxed for 70 h. Vacuum distillation of the solvent and crystallization of the residue from ethyl acetate provided 1.60 g (48%) of colorless, crystalline anhydride **5**: mp 165–166 °C; IR C=O 1790 (s), 1711 (s) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.01, 1.13 (s, 3 each, C-4 methyls), 1.34 (s, 3, C-1 Me), 2.16 (dd, 1, J = 13, 1 Hz, H-3), 2.71 (br d, 1, J = 13 Hz, H-3), 2.74 (br d, 1, J = 7 Hz, H-5), 3.92 (d, 1, J = 9 Hz, H-8), 4.02 (dd, 1, J = 9, 1 Hz, H-9), 5.72 (d, 1, J = 9 *Hz*, H-7), 6.24 (dd, 1, J = 9, 7 Hz, H-6); ^{13}C NMR (DMSO-d_6) δ 18.7 (1-Me), 26.1 (4-Me), 29.0 (4-Me), 39.7 (C-4), 43.6 (C-9), 44.9 (C-5), 47.4 (C-8), 49.2 (C-1), 53.9 (C-3), 132.8 (C-7), 135.0 (C-6), 171.2 (C=O), 174.5 (C=O), 202.7 (C-2); MS, *m/e* 248 (M^+, 1), 133 (45), 119 (24), 92 (base), 91 (46), 56 (50).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.71; H, 6.50. Found: C 67.82; H, 6.50.

***cis*-1β,4,4,9,10-Pentamethylbicyclo[5.4.0]undeca-5,9-dien-2-one (6).** A solution of 750 mg (5.0 mmol) of eucarvone (**1**), 2.46 g (30.0 mmol) of 2,3-dimethyl-1,3-butadiene (**3**), and 30 mg of hydroquinone was degassed, sealed in a tube under vacuum, and heated at 170 °C for 30 h. The usual workup[5a] provided ketone **6** (see below) in 50% yield (by GC analysis).

A solution of 750 mg (5.0 mmol) of eucarvone (**1**) in 2 mL of dry toluene was added slowly to a suspension of 330 mg (2.5 mmol) of anhydrous aluminum chloride in 25 mL of dry toluene, and the mixture stirred at room temperature for 40 min. A solution of 2.46 g (30.0 mmol) of diene **3** in 20 mL of dry toluene was added, and the reaction mixture stirred at 45 °C for 2.5 h. The usual workup,[5a] chromatography of the crude product, and elution with 9:1 hexane–ether afforded 950 mg (87%) of colorless, crystalline ketone **6**: mp 44–45 °C (hexane); IR C=O 1700 (s), C=C 1650 (m) cm^{-1}; ^{1}H NMR δ 1.02, 1.03, 1.14 (s, 3 each, methyls), 1.62 (s, 6, 9-Me, 10-Me), 1.84 (d, 1, J = 18 Hz, H-11), 1.90 (d, 1, J = 18 Hz, H-8), 2.00 (dd, 1, J = 11, 1 Hz, H-3), 2.12 (br d, 1, J = 18 Hz, H-11), 2.35 (br d, 1, J = 18 Hz, H-8), 3.00 (br s, 1, H-7), 3.40 (d, 1, J = 11 Hz, H-3), 5.11 (dd, 1, J = 12, 4 Hz, H-6), 5.18 (br d, 1, J = 12 Hz, H-5); ^{13}C NMR δ 18.9 (9-Me or 10-Me), 19.2 (10-Me or 9-Me), 23.1 (1-Me), 30.2 (4-Me), 31.4 (4-Me), 35.0 (C-8), 36.0 (C-11), 36.4 (C-7), 37.5 (C-4), 50.1 (C-3), 51.5 (C-1), 121.3 (C-8 or C-9), 124.3 (C-9 or C-8), 131.9 (C-6), 138.7 (C-5), 216.3 (C-2); MS, *m/e* 232 (M^+, 65), 189 (94), 159 (62), 133 (59), 121 (44), 119 (84), 108 (58), 107 (base), 105 (68), 91 (99), 79 (60), 77 (61), 67 (53), 55 (51), 53 (44).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.69; H, 10.42. Found: C, 82.80; H, 10.39.

Ketones 7a and 8a. The $AlCl_3$-catalyzed reaction of eucarvone (**1**) and 1,3-butadiene (**4a**) followed the procedure of the above acid-induced preparation of ketone **6**. A 1:0.9:6 **1**–$AlCl_3$–**4a** mixture in 100 mL of dry toluene, based on 3.00 g (20.2 mmol) of eucarvone (**1**), was heated at 45 °C for 20 h. The usual workup[5a] gave a crude product, whose chromatography on 200 g of silica gel and elution with 4:1 hexane–ethyl acetate led to 3.47 g (85%) of a 1.6:1 **7a**–**8a** mixture (by GC analysis). Cooling a hexane solution of the mixture to −10 °C caused precipitation of a solid, whose filtration yielded 1.50 g (37%) of colorless, crystalline *cis*-1β,4,4-trimethylbicyclo[5.4.0]undecan-5,9-dien-2-one (**7a**): mp 39–40 °C (hexane); IR olefinic CH 3015 (w), C=O 1700 (s), C=C 1655 (w) cm^{-1}; ^{1}H NMR δ 1.01 (s, 3, 4-Me), 1.07 (s, 3, 1-Me), 1.15 (s, 3, 4-Me), 2.00 (d, 1, J = 11 Hz, H-3), 2.0–2.5 (m, 4, C-8 and C-11 Hs), 3.06 (br d, 1, J = 5Hz, H-7), 3.41 (d, 1, J = 11 Hz, H-3), 5.19 (s, 2, H-5, H-6), 5.5–5.7 (m, 2, H-9, H-10); ^{13}C NMR δ 22.6 (1-Me), 28.3 (C-11), 29.4 (C-8), 29.9 (4-Me), 31.1 (4-Me), 35.2 (C-7), 37.2 (C-4), 49.6 (C-3), 50.4 (C-1), 122.7 (C-10), 125.5 (C-9), 131.2 (C-6), 138.5 (C-5), 215.7 (C-2); MS, *m/e* 204 (M^+, 33), 171 (39), 161 (base), 160 (62), 147 (27), 145 (41), 133 (26), 131 (30), 119 (34), 107 (45), 105 (60), 93 (31), 91 (75), 79 (43), 77 (45).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.15; H, 9.85.

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(9) Corey, E. J.; Burke, H. J. *J. Am. Chem. Soc.* **1956**, *78*, 174.

Evaporation of the filtrate, chromatography of the residue on silica gel impregnated with 20% silver nitrate, and elution with 33:1 hexane–ethyl acetate gave 600 mg (15%) of colorless, liquid 1,4,4-trimethyl-9-*endo*-vinylbicyclo[3.2.2]non-6-en-2-one (**8a**): IR C=O 1705 (s), C=C 1652 (w) cm^{-1}; ^{1}H NMR δ 1.01, 1.06, 1.07 (s, 3 each, methyls), 1.42 (ddd, 1, J = 14, 5, 5 Hz, H-9), 2.21 (br dd, 1, J = 8, 5 Hz, H-5), 2.29 (dd, 1, J = 13, 1, Hz, H-3), 2.45 (dd, 1, J = 14, 10 Hz, H-9), 2.52 (d, 1, J = 13 Hz, H-3), 2.61 (ddd, 1, J = 10, 10, 5 Hz, H-8), 4.8–5.0 (m, 2, olefinic CH$_2$), 5.49 (ddd, 1, J = 17, 10, 10 Hz, α-H), 5.58 (d, 1, J = 9 Hz, H-7), 6.27 (dd, 1, J = 9, 8 Hz, H-6); ^{13}C NMR δ 20.4 (1-Me), 27.8 (4-Me), 29.8 (4-Me), 30.3 (C-9), 39.3 (C-4), 42.9 (C-5), 47.2 (C-8), 50.6 (C-1), 54.1 (C-3), 113.5 (β-C) 132.1 (C-7), 135.9 (C-6), 141.6 (α-C), 208.8 (C-2); MS, *m/e* 204 (M$^+$, 31), 160 (36), 159 (31), 148 (25), 145 (34), 133 (25), 120 (22), 119 (base), 105 (60), 92 (20), 91 (44), 77 (23).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.36; H, 9.90.

Ketones 7b, 7c, and 8b. The cycloaddition of eucarvone (**1**) and (*E*)-1-methoxy-1,3-butadiene (**4b**) was carried out (heating at 180 °C for 60 h) in the same manner as the above thermal **1–4a** reaction, leading to a 3.4:2:1 **7b–8b–7c** adduct mixture in 47% yield (by GC analysis).

11α-Methoxy-1β,4,4-trimethylbicyclo[5.4.0]undeca-5,9-dien-2-one (7b): mp 74–75 °C (C_6H_{14}-EtOAc); IR olefinic CH 3010 (w), C=O 1702 (s), C=C 1650 (w) cm^{-1}; ^{1}H NMR δ 1.04, 1.11, 1.12 (s, 3 each, methyls), 2.13 (d, 1, J = 11 Hz, H-3), 2.18 (dd, 1, J = 17, 5 Hz, H-8), 2.39 (dm, 1, J = 11 Hz, H-8), 3.22 (br s, 1, H-7), 3.36 (s, 3, OMe), 3.47 (d, 1, J = 11 Hz, H-3), 3.77 (br d, 1, J = 4 Hz, H-11), 5.20 (dd, 1, J = 12, 2 Hz, H-5), 5.27 (dd, 1, J = 12, 3 Hz, H-6), 5.80 (ddd, 1, J = 10, 5, 2 Hz, H-9), 5.9–6.0 (m, 1, H-10); ^{13}C NMR δ 23.6 (1-Me), 27.6 (4-Me), 29.5 (C-8), 31.6 (4-Me), 33.5 (C-7), 37.2 (C-4), 51.0 (C-3), 55.9 (C-1), 58.3 (OMe), 78.6 (C-11), 124.9 (C-10), 125.6 (C-9), 129.4 (C-6), 137.6 (C-5), 214.2 (C-2); MS, *m/e* 234 (M$^+$, 1), 91 (18), 84 (base), 69 (22).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.90; H, 9.50.

9-*endo*-[(*E*)-β-Methoxyvinyl]-1,4,4-trimethylbicyclo[3.2.2]non-6-en-2-one (8b): colorless liquid; IR olefinic CH 3030 (w), C=O 1685 (s), C=C 1648 (m) cm^{-1}; ^{1}H NMR δ 1.08 (s, 3, 4-Me), 1.10 (s, 3, 4-Me), 1.25 (s, 3, 1-Me), 1.48 (ddd, 1, J = 14, 5, 4 Hz, H-9), 2.26 (br dd, 1, J = 8, 5 Hz, H-5), 2.5–2.6 (m, 3, H-3, H-8, H-9), 2.69 (d, 1, J = 13 Hz, H-3), 3.52 (s, 3, OMe), 4.54 (dd, 1, J = 13, 10 Hz, α-H), 5.72 (d, 1, J = 9 Hz, H-7), 6.27 (d, 1, J = 13 Hz, β-H), 6.36 (dd, 1, J = 9, 8 Hz, H-6); ^{13}C NMR δ 21.2 (1-Me), 28.3 (4-Me), 29.3 (4-Me), 32.3 (C-9), 39.3 (C-4), 41.8 (C-8), 43.1 (C-5), 52.0 (C-1), 54.6 (C-3), 55.9 (OMe), 107.5 (α-C), 132.7 (C-7), 136.0 (C-6), 146.6 (β-C), 210.7 (C-2); MS, *m/e* 234 (M$^+$, 9), 84 (base), 69 (18).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.80; H, 9.45.

11β-Methoxy-1β,4,4-trimethylbicyclo[5.4.0]undeca-5,9-dien-2-one (7c): colorless liquid; IR C=O 1710 (s), C=C 1670 (m) cm^{-1}; ^{1}H NMR δ 1.11, 1.12, 1.14 (s, 3 each, methyls), 1.99 (dm, 1, J = 19 Hz, H-8), 2.33 (d, 1, J = 11 Hz, H-3), 2.46 (dm, 1, J = 19 Hz, H-8), 2.9–3.0 (m, 1, H-7), 3.01 (d, 1, J = 11 Hz, H-3), 3.45 (s, 3, OMe), 3.92 (br s, 1, H-11), 5.27 (dd, 1, J = 12, 5 Hz, H-6), 5.33 (d, 1, J = 12 Hz, H-5), 5.6–5.7 (m, 2, H-9, H-10); ^{13}C NMR δ 17.4 (1-Me), 29.0 (C-8), 29.3 (4-Me), 31.3 (4-Me), 37.1 (C-4 or C-7), 37.3 (C-7 or C-4), 50.9 (C-3), 55.8 (C-1), 57.2 (OMe), 76.8 (C-11), 125.3 (C-10), 127.0 (C-9), 130.7 (C-6), 139.8 (C-5), 213.7 (C-2); MS, *m/e* 234 (M$^+$, 1), 84 (base), 69 (30).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47. Found: C, 76.92; H, 9.48.

A solution of 2.80 g (18.9 mmol) of eucarvone (**1**) in 20 mL of dry toluene was added to a solution of 9.90 g (9.4 mmol) of Yb(fod)$_3$ in 40 mL of dry toluene, and the mixture stirred under nitrogen at room temperature for 40 min. A solution of 9.42 g (112 mmol) of (*E*)-1-methoxy-1,3-butadiene (**4b**) in 23 mL of dry toluene was added, the heating tube degassed and sealed, and the solution heated at 110 °C for 168 h. The cooled mixture was poured into ice water, and the aqueous layer extracted with ether. The toluene and ether solutions were combined, washed with 10% sodium bicarbonate solution, dried (Na$_2$SO$_4$), and evaporated under vacuum. Chromatography of the residue, a 3.3:1.2:1 **7b–8b–7c** mixture (66%, by GC analysis), on 220 g of silica gel and elution with 9:1 hexane–ethyl acetate afforded 1.55 g (35%) of ketone **7b**, 400 mg (9%) of enol ether **8b**, and 300 mg (7%) of ketone **7c**.

Keto Aldehyde 9. Perchloric acid (1.3 mL, 50%) was added slowly to a solution of 50 mg (0.22 mmol) of enol ether **8b** in 13 mL of ether under nitrogen at 0 °C, and the mixture then stirred at room temperature for 2 h. The solution was poured into a mixture of pentane and water, and the aqueous layer extracted with pentane. The combined pentane solutions were washed with water, dried (Na$_2$SO$_4$), and evaporated. The residue was chromatographed and eluted with 20:1 hexane–ethyl acetate, giving 46 mg (98%) of colorless, liquid keto aldehyde **9**: IR olefinic CH 3020 (w), C=O 1718 (s), 1686 (s), C=C 1648 (w) cm^{-1}; ^{1}H NMR δ 1.00, 1.06, 1.17 (s, 3 each, methyls), 1.1–1.3 (m, 2, H-8, H-9), 2.19 (dd, 1, J = 8, 6 Hz, H-5), 2.30 (d, 1, J = 13Hz, H-3), 2.31 (ddd, 1, J = 15, 10, 2 Hz, α-H), 2.4-2.7 (m, 2, H-9, α-H), 2.55 (d, 1, J = 13 Hz, H-3), 5.56 (d, 1, J = 9Hz, H-7), 6.26 (dd, 1, J = 9, 8 Hz, H-6), 9.78 (dd, 1, J = 2, <1 Hz, CHO); ^{13}C NMR δ 19.7 (1-Me), 27.8 (4-Me), 29.3 (4-Me), 30.1 (C-8), 35.3 (C-9), 39.5 (C-4), 42.6 (C-5), 49.3 (α-C), 50.9 (C-1), 54.0 (C-3), 131.7 (C-7), 136.2 (C-6), 202.0 (CHO), 208.5 (C-2); MS, *m/e* 220 (M$^+$, 1), 176 (32), 175 (34), 133 (69), 120 (60), 119 (60), 105 (35), 93 (52), 92 (base), 91 (85), 77 (45).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.20; H, 9.15.

***cis*-11α-Methoxy-1β,4,4-trimethylbicyclo[5.4.0]undecan-2-one (10).** A mixture of 230 mg (0.99 mmol) of ketone **7b** and platinum (preformed on hydrogenation of 230 mg of platinum oxide) in 13 mL of dry ethanol was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered, and the filtrate evaporated. Chromatography of the residue and elution with hexane afforded 230 mg (97%) of colorless liquid ketone **10**: IR C=O 1700 (s) cm^{-1}; ^{1}H NMR δ 0.91, 0.98, 1.00 (s, 3 each, methyls), 1.2–1.9 (m, 10, methylenes), 2.00 (dd, 1, J = 11, 2 Hz, H-3), 2.5–2.7 (m, 1, CH), 2.80 (d, 1, J = 11 Hz, H-3), 3.25 (s, 3, OMe), 3.67 (br s, 1, H-11); ^{13}C NMR δ 15.5 (C-9), 23.7 (C-8), 24.3 (1-Me), 24.3 (4-Me), 29.5 (C-6), 30.5 (C-10), 33.7 (4-Me), 33.9 (C-4), 40.9 (C-7), 45.3 (C-5), 52.9 (C-3), 53.5 (C-1), 57.4 (OMe), 80.4 (C-11), 215.2 (C-2); MS, *m/e* 238 (M$^+$, 6), 223 (48), 153 (49), 125 (47), 95 (86), 93 (55), 83 (47), 81 (45), 79 (51), 71 (base), 69 (42), 67 (62), 55 (92), 53 (41).

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.56; H, 11.00. Found: C, 75.60; H, 10.95.

Acknowledgment. L.M. and A.T. acknowledge gratefully support by the Consiglio Nazionale delle Ricerche and the Ministero della Pubblica Istruzione for the work in Perugia. We are indebted to Dr. R. Chadha for the X-ray analysis.

Registry No. **1**, 503-93-5; **2**, 108-31-6; **3**, 513-81-5; **4a**, 106-99-0; **4b**, 10034-09-0; (±)-**5**, 124562-44-3; (±)-**6**, 124562-45-4; (±)-**7a**, 124562-46-5; (±)-**7b**, 124562-50-1; (±)-**7c**, 124562-51-2; (±)-**8a**, 124562-47-6; (±)-**8b**, 124562-52-3; (±)-**9**, 124562-48-7; (±)-**10**, 124562-49-8.

Synthesis and Reactions of 7-Chloro-7-cyano-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene

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Received April 3, 1989

We have studied a variety of [2 + 2] cycloadditions to acenaphthylene (**1a**) using the heavy-atom solvent effect (HAE) to improve the yield through enhanced triplet excited-state formation of **1a**.[1,2] We discovered that 2-

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(1) Hopkinson, M. J.; Schloman, W. S., Jr.; Plummer, B. F.; Wenkert, E.; Raju, M. *J. Am. Chem. Soc.* **1979**, *101*, 2157, and references therein.

0022-3263/90/1955-1368$02.50/0 © 1990 American Chemical Society