42.87 ppm; *m/e* calcd 208.1252, obsd 208.1256.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.81

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Diels–Alder Reactions of *trans*-1-Methoxy-3-trimethylsilyloxy-1,3-butadiene

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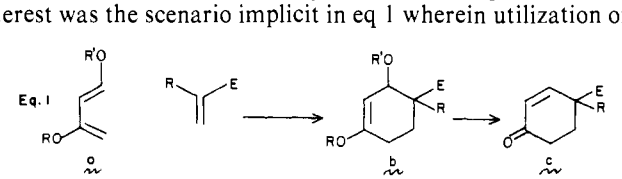
Abstract: Enol silylation of *trans*-4-methoxybut-3-en-2-one affords *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (**1**). This compound has been demonstrated to be a valuable diene in Diels–Alder reactions. These processes provide new and effective routes to aromatic and cyclohexenone systems. The pathways by which the intermediate 3-methoxy-1-silyloxycyclohexenes are transformed to cyclohexenones are considered.

The Diels–Alder cycloaddition has proven to be one of the more reliable reactions in preparative organic chemistry.[1] Its virtually[1,2] perfect cis stereospecificity, its relatively predictable endo selectivity,[1,3] and its excellent regioselectivity,[1,4] particularly with dienes and dienophiles of complementary polarity, have all been used to advantage.[5] Considerable improvements have been realized via recourse to Lewis acid catalysis[6,7] and high pressures.[8]

In embarking on our study in 1974,[9a-d] we noted the relatively modest functionalities which had been incorporated into the dienic components of the cycloaddition. Of particular interest was the scenario implicit in eq 1 wherein utilization of



diene a would eventually afford the 4-substituted cyclohexenone c via adduct b.

A Russian group[10] had, in fact, reported the preparation of 1,3-diethoxybutadiene, through the cracking of the bis acetal of formylacetone. We had experienced some difficulties in carrying out this pyrolysis in a manner consistent with survival of the highly acid-labile product.

This suggested to us what was probably the main reason for the underutilization of functionalized alkoxydienes in Diels–Alder reactions. The primary route to enol ethers involves the cracking of acetals—a relatively troublesome process.[11a-c]

Fortunately, an alternative which is simple and, above all, more amenable to adaptation by nonspecialized laboratories presented itself. Largely as a result of the pioneering studies of Stork[12a] and House,[12b,c] the value of trimethylsilyl (Me_3Si) enol ethers as enolate equivalents had become apparent.[13,14] Both 1-trimethylsilyloxy- and 2-trimethylsilyloxy-1,3-butadiene had been prepared by enol silylation of their α,β-unsaturated carbonyl precursors (crotonaldehyde and methyl vinyl ketone, respectively).[15a,b] Moreover, Frainnet[15a] had described in each case an example of a Diels–Alder reaction of each of these TMSO butadienes.[16a-f]

It was found that the readily (and commercially) available vinylogous ester *trans*-4-methoxybut-3-en-2-one could be

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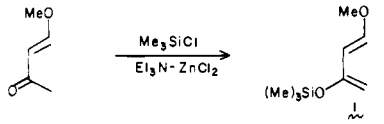
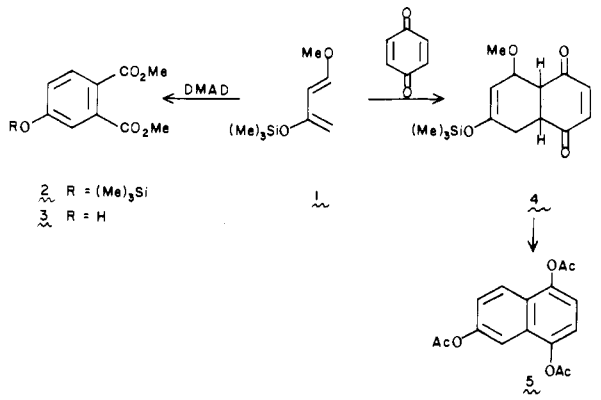
readily converted to the mixed vinylogous ketene acetal **1** in 50–70% isolated yield. This enol silylation could be carried out very simply with triethylamine[12b] in the presence of anhydrous zinc chloride.[17a] With compound **1** available in copious quantity,[17b] we soon found that we had at our disposal a versatile and valuable diene for Diels–Alder reactions, designed to produce, eventually, cyclohexenones or aromatic products. In this paper we describe the cycloaddition reactions of compound **1** with a variety of dienophiles and the hydrolytic transformations of the products so obtained. In subsequent papers in this series, we describe (1) the chemistry of more functionalized versions of compound **1**[18a] and (2) the applications to this methodology pursuant to the total synthesis of various natural products.[18b-c]



In this opening survey study, we were more interested in establishing the general viability of Diels–Alder reactions of **1** than in optimizing yields or in determining the minimum conditions necessary for cycloaddition. Our findings are described below.

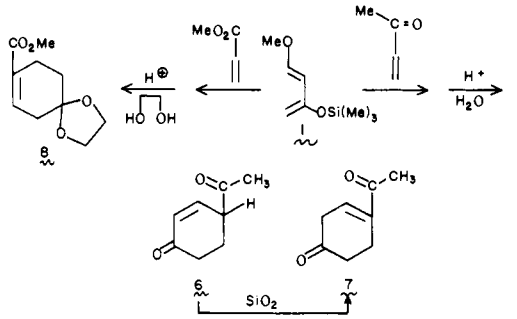
Results

(1) Use of Compound 1 in Aromatic Synthesis. Two cases were examined. Cycloaddition of compound **1** with dimethyl acetylenedicarboxylate was conducted in benzene under reflux. After 5 h, the adduct, which was not examined, was treated with aqueous acid to afford a 79% yield of the known **3**.[19a] Cycloaddition of **1** with *p*-benzoquinone was carried out at room temperature for 30 min in ethanol.[19b] Several attempts to isolate adduct **4** in pure form were unsuccessful, presumably because of β-elimination of methanol and disproportionation of the resultant dihydronaphthoquinone derivative.[20a] Accordingly, the resultant system acylated with pyridine and acetic anhydride to afford an 87% yield of **5**.[20b] Several additional examples of aromatic synthesis were examined with derivatives of **1** and will be described in the next paper of this series.[18a]

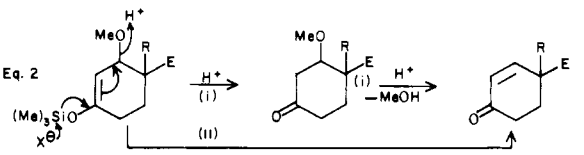


(2) Diels–Alder Cycloaddition of Compound 1 with Activated Monosubstituted Ethylenes. It will be recognized that, with dienophiles where R = H in product c of eq 1, the eventual disposition of the double bond in the enolizable β-dicarbonyl system may well be uncertain. Cycloaddition of **1** with methyl vinyl ketone was carried out in benzene under reflux for 20 h. The adduct was treated with dilute aqueous HCl. The crude product appeared, by NMR analysis, to be ca. a 1:1 mixture of **6** and **7**. In an attempt to separate the mixture, the material was subjected to silica gel chromatography, resulting in a clear conversion of **6** → **7**. Thus, there was isolated, in 86% yield, a mixture where the ratio of **7**:**6** was ca. 8:1. Catalytic hydrogenation of the double bond afforded 4-acetylcyclohexanone.

Cycloaddition of **1** with methyl acrylate was conducted under similar conditions. In this case, to demonstrate another dimension of the method, the adduct was treated with ethylene glycol in the presence of *p*-toluenesulfonic acid. There was thus isolated an 85% yield of **8**. This substance was to serve as the dienophile for another Diels–Alder reaction with **1** (vide infra).

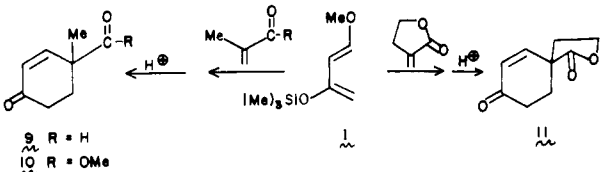


In these cases, we have not dealt explicitly with the issue of the elimination of methanol. In neither case was any β-methoxy ketone isolated. Clearly, two possibilities can be entertained. In one formulation (path i), the methanol is eliminated from the β-methoxy ketone. Alternatively (path ii), the methanol is eliminated concurrently with the hydrolytic conversion of the silyl enol ether to the ketone. We shall return to this matter in the context of dienophiles where the question was probed experimentally.



(3) Diels–Alder Cycloadditions of Compound 1 with Activated 1,1-Disubstituted Ethylenes. Three cases were examined. Cycloaddition of **1** with methacrolein occurred in benzene under reflux. After 18 h, workup with 4:1 THF–0.005 N aqueous HCl (hereafter referred to as "standard conditions") afforded a 71% yield of 4-methyl-4-formylcyclohexenone (**9**). In a similar fashion, cycloaddition with methyl methacrylate afforded a 65% yield of 4-methyl-4-carbomethoxycyclohexenone (**10**).

An example of spiroannelation[21a] is seen in the reaction of **1** with α-methylenebutyrolactone.[21b] Workup, as before, provided a 50% yield of **11**. Under these standard conditions, intermediate β-methoxy ketones were not isolated and only traces were suggested by NMR analysis of the crude reaction mixture.

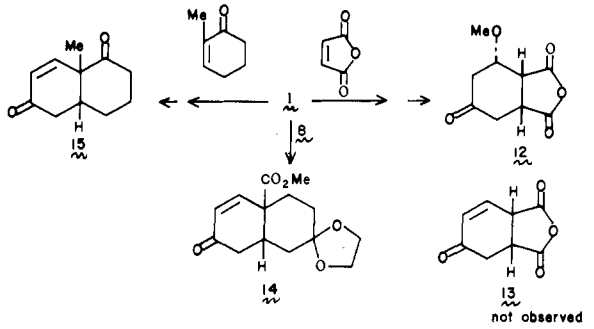


(4) Diels–Alder Cycloadditions of Compound 1 with Activated Vicinally Substituted Ethylenes. Four cases were examined. Cycloaddition of **1** with maleic anhydride occurred rapidly at room temperature. Hydrolysis as before afforded the methoxyanhydride **12**. In this case, there was no indication of the formation of enone **13**. *Thus, it is seen that the hydrolytic disposition of adducts such as b in eq 1 is a function of structural features elsewhere in the molecule.*

The stereochemistry of **12** may be surmised from the prin-

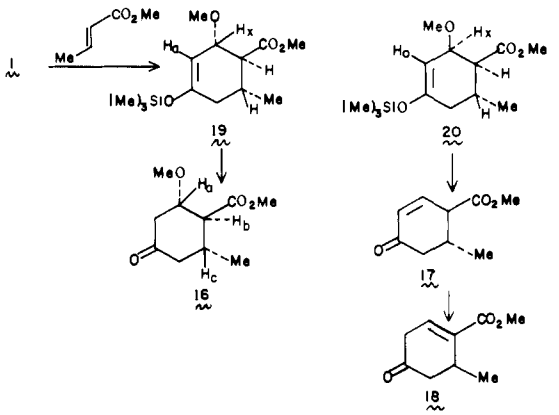
ciple of endo addition but was, in fact, established rigorously by NMR analysis. These results will be described in the paper which follows, in conjunction with a study of substituted versions of compound **1**.[18a]

The cycloadditions of two activated cyclohexene substrates were examined. Reaction of compound **8** (prepared as described above) with **1** was conducted in xylene in a sealed tube at 175–185 °C. Hydrolysis, under the standard conditions, afforded (60–70%) the octalindione monoketal, **14.** In this case, only traces of β-methoxy ketone could be detected. A similar



result was obtained from cycloaddition of **1** with 2-methylcyclohexenone (xylene-sealed tube, 200 °C). Again the major product (50–60%) was the octalindione **15.** Again, only traces of β-methoxy ketone could be detected in the crude reaction mixture.

The cycloaddition of **1** with *trans*-methyl crotonate was carried out in toluene under reflux. Workup in the usual way afforded a 2:1 mixture of β-methoxy ketone **16** and enone **17.** After chromatographic separation on silica gel, there was obtained pure **16** and a ca. 1:1 mixture of **17** and **18.**



The stereochemistry of **16,** which is seen to correspond to the exo addition of **1** with respect to the ester function, was ascertained from the NMR coupling constants (J_{ab} = 9.5, J_{bc} = 10.5 Hz) of the indicated methine protons.

In a separate experiment, the cycloaddition was carried out as before, but the hydrolysis step was deleted. Chromatography of the crude adduct on silica gel afforded ca. a 2:1 mixture of epimers **19** and **20.** The assignments of **19** and **20** rest on the couplings of the respective vinylic protons (δH_a in **19** 4.94; δH_a in **20** 5.11) with the adjacent methine proton (J_{ax} in **19** = 2, J_{ax} in **20** = 6 Hz).

Thus, it seems reasonable to conclude that the equatorial methoxyl in **19** survives the "standard" workup conditions, while the axial methoxyl in **20** suffers elimination, leading to **17** and eventually to **17** + **18.** Parenthetically, we note that the predominant formation of exo adduct **19** need occasion little surprise. Thus the breakdown of the endo principle in the case of substituted acrylic dienophiles was already well recognized[3] and considered.[4]

(5) The Hydrolysis Step. The sequence of events by which the enone is produced (see possibilities in eq 2) was examined closely in the methyl methacrylate case leading to **10.** As indicated above, when the hydrolysis of the adduct **21** was carried under the "standard conditions", the preponderant product was enone **10.** It was of interest to examine the consequences of employing more strongly acidic conditions for this hydrolysis. When 4:1 THF–2 N aqueous HCl was employed, there was obtained a 72:28 ratio of enone **10**:β-methoxy ketone **22.** While apparently a single compound, the relative stereochemistry of **22** is left unassigned. At an intermediate acid level, 0.1 N aqueous HCl, the ratio of **10**:**22** was ca. 88:12.

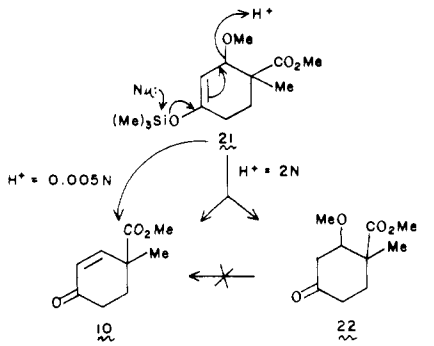
When compound **22** was resubjected to the "standard conditions" (4:1 THF–0.005 N HCl) it suffered no conversion to **10.** *Accordingly, at least in this case and presumably in all the cases, the elimination of methanol does not arise from a methoxy ketone intermediate, but is produced as part of the same process wherein the silyl enol ether is converted to the ketone (path (ii), eq 2).* It is recognized that the direct conversion of **21** to **10** amounts, in essence, to an oxy vinylog of the well-known[22] processes where β-hetero-substituted silanes suffer deheterosilylation to produce olefins. It is also analogous to the conversion of β-alkoxy allylic alcohols to enones, whose mechanism has been shown[23] to correspond to that of the alkoxy analogue of path (ii).

Since such mechanisms must compete with the rapid hydrolysis of a silyl enol ether to a ketone, one can qualitatively explain the effect of acid on the ratio of **10**:**22,** arising from **21.** Under more strongly acidic conditions there is apparently more hydrolysis independent of elimination. Conceivably, under the weaker acid conditions, desilylation requires protonation of the allylic methoxyl group.

Furthermore, it seems reasonable that the concerted pathway would be favored on stereoelectronic grounds[22] by the presence of an axial methoxyl. *This would tend to explain why crotonate adduct* **20** *undergoes conversion to enone* **17** (*cf. eq 2, path (ii)*), *while in the case of its epimer* **19,** *where an axial conformation for the methoxyl would be energetically difficult, the identical hydrolytic treatment affords* **16** (*cf. eq 2, step (i)*).

The failure of the maleic anhydride adduct to give any detectable enone **13** under the standard conditions may be ascribed to the instability associated with introduction of addition trigonal centers in the fused ring system, thus disfavoring desilylative β-elimination (path (ii)) relative to simple hydrolysis (path (i)).

In summary, it is seen that diene **1** reacts with a broad range of dienophiles to provide entries to a variety of aromatic and cyclohexenone derivatives. We note that, in the intervening years since our original communications concerning compound **1**,[9a,b] the value of siloxy dienes in synthesis and total synthesis has become widely recognized.[24-26] In addition to its original application in our laboratory toward the total synthesis of vernolepin,[27] such functionalized dienes have served us well in the total syntheses of prephenic acid,[18d] griseofulvin,[18e] and pentalenolactone.[18f] These total syntheses will be described in forthcoming papers in this series.



Experimental Section[28]

Preparation of Dimethyl 4-Hydroxyphthalate (3). A solution of diene **1** (224 mg, 1.3 mmol) and dimethyl acetylenedicarboxylate (142 mg, 1 mmol) in benzene (3 mL) was heated under reflux for 5 h. After evaporation of the volatiles, the residue was treated with 2 mL of 0.1 N aqueous HCl–THF at room temperature for 30 min. The mixture was poured into 15 mL of 5% sodium bicarbonate. The aqueous system was extracted with 3 × 20 mL of chloroform. The organic phase was dried over anhydrous magnesium sulfate. Evaporation of the volatiles left a residue which was triturated with cold ether to afford 166 mg (79%) of compound **3:** mp 106–107 °C (lit.[19a] 107–108 °C); λ_{max} ($CHCl_3$) 5.80 μ; δ($CDCl_3$) 3.83 (s, 3), 3.88 (s, 3), 6.88 (dd, J_1 = 8, J_2 = 2 Hz, 1), 6.98 (br s, 1), 7.72 (br d, J = 8 Hz, 1) ppm; *m/e* 210 (P).

Preparation of 1,4,6-Triacetoxynaphthalene (5). A solution of diene **1** (516 mg, 3 mmol) and *p*-benzoquinone (216 mg, 2 mmol) in ethanol (4 mL) was stirred at room temperature for 30 min. During this time, the color changed from orange-red to yellow. To this solution was added acetic anhydride (10 mL) and pyridine (1 drop) and stirring was continued for 16 h at room temperature and 1 h at 80 °C. After cooling 5 mL of methanol was added and the mixture was poured into 20 mL of brine. The aqueous system was extracted with 3 × 20 mL of ether. The organic layer was washed, successively, with 5% aqueous sodium bicarbonate, 0.1 N HCl, and brine. Evaporation of the volatiles from the dried ($MgSO_4$) organic phase afforded a residue which was chromatographed on 30 g of silica gel. Elution with 9% ether in benzene afforded 524 mg (87%) of compound **5**: mp 92–93 °C (lit.[20b] 94–95 °C); λ_{max} ($CHCl_3$) 5.79 μ; δ ($CDCl_3$) 2.33 (s, 3), 2.43 (s, 6), 7.23 (br s, 2), 7.32 (dd, J_1 = 9, J_2 = 2 Hz, 1), 7.60 (d, J = 2 Hz, 1), 7.92 (d, J = 9 Hz, 1) ppm; *m/e* (P) 302.0804 (calcd, 302.0790).

Formation of 4-Acetylcyclohex-2-en-3-one (6) and 4-Acetylcyclohex-3-en-2-one (7). A solution of compound **1** (2.60 g, 15 mmol) and methyl vinyl ketone (700 mg, 10 mmol) in 5 mL of benzene was heated under reflux for 20 h. After cooling to room temperature, this solution was stirred rapidly with 20 mL of 4:1 THF–0.1 N aqueous HCl for 30 min at room temperature. The mixture was poured into 20 mL of 5% aqueous sodium bicarbonate and extracted with 3 × 20 mL of chloroform. Evaporation of the volatiles from the dried ($MgSO_4$) organic phase afforded a residue which was chromatographed on 10 g of silica gel. Elution with 4% ether in benzene afforded 197 mg (71%) of an 8:1 mixture of **7:6:** for **7** δ ($CDCl_3$) 3.0–3.2 (m, 2), 6.8–7.0 (m, 1); for **6** δ 3.4 (d, J = 8 Hz, 1), 6.1 (dd, J_1 = 8, J_2 = 2 Hz) ppm. The ratio of **7:6** prior to chromatography was ca. 1:1.

Preparation of 4-Carbomethoxycyclohex-3-en-2-one Ethylene Ketal (8). A solution of diene **1** (3.8 g, 23 mmol) and methyl acrylate (1.72 g, 20 mmol) in 5 mL of benzene was heated under reflux for 24 h. To the solution was added a solution of ethylene glycol (2 g) and *p*-toluenesulfonic acid (200 mg) in 15 mL of benzene. The resultant system was heated under reflux for 6 h with continuous separation of water. The benzene solution was washed with 20 mL of 5% aqueous sodium bicarbonate and then with brine. Evaporation of the volatiles from the dried ($MgSO_4$) organic phase left a residue which was chromatographed on 200 g of silica gel. Elution with 8% ethyl acetate in benzene afforded 3.38 g (85%) of compound **8:** mp (ether) 40–41 °C; λ_{max} ($CHCl_3$) 5.87, 6.07 μ; δ ($CDCl_3$) 1.6–2.7 (m, 6), 3.70 (s, 3), 3.99 (s, 4), 6.8 (m, 1) ppm; *m/e* (P) 198.0879 (calcd, 198.0892).

Cycloaddition of 8 with 1. Formation of Octalindione Monoketal 14. A solution of diene **1** (900 mg, 5 mmol) and compound **8** (198 mg, 1 mmol) in 0.5 mL of xylene was heated at 175–185 °C in a sealed tube for 40 h. After cooling to room temperature, the solution was treated with 10 mL of 4:1 THF–0.005 N HCl at 0 °C for 10 min and poured into 10 mL of 5% aqueous sodium bicarbonate. The aqueous system was extracted with 5 × 20 mL of chloroform. Evaporation of the volatiles of the dried ($MgSO_4$) organic phase left a residue which was chromatographed on 20 g of silica gel. Elution with 8% ethyl acetate in benzene afforded 172 mg (65%) of compound **14:** λ_{max} ($CHCl_3$) 5.79, 5.95 μ; δ ($CDCl_3$) 1.3–3.1 (m, 9), 3.76 (s, 3), 3.96 (s, 4), 6.08 (d, J = 10 Hz, 1), 6.70 (d, J = 10 Hz, 1) ppm; *m/e* (P) 266.1147 (calcd, 266.1154).

Preparation of 4-Methyl-4-formylcyclohex-2-en-3-one (9). A solution of diene **1** (520 mg, 3 mmol) and methacrolein (140 mg, 2 mmol) in 3 mL of benzene was heated under reflux for 18 h. The volatiles were evaporated. The residue was stirred with 6 mL of 4:1 THF–0.1 N aqueous HCl at room temperature for 30 min. The mixture was poured into 20 mL of 5% aqueous sodium bicarbonate. The aqueous system was extracted with 3 × 20 mL of chloroform. Evaporation of the volatiles of the dried ($MgSO_4$) organic layer afforded a residue which was chromatographed on 10 g of silica gel. Elution with 4% ether in benzene afforded 197 mg (71% yield) of **9** as an oil, bis-2,4-DNP: mp 136–136.5 °C; λ_{max} ($CHCl_3$) 3.66, 5.81, and 6.00 μ; δ ($CDCl_3$) 1.31 (s, 3), 1.7–2.3 (m, 4), 5.94 (d, J = 10 Hz, 1), 6.62 (d, J = 10 Hz, 1), 9.40 (s, 1) ppm; *m/e* 110 (P − CO), 109 (P − CHO).

Preparation of 4-Methyl-4-carbomethoxycyclohex-2-en-3-one (10). A solution of diene **1** (2.06 g, 12 mmol) and methyl methacrylate (300 mg, 3 mol) in 1 mL of benzene was heated in a sealed tube at 95 °C for 22 h. The volatiles were removed at the water pump and the residue (**21**) was treated with 4:1 THF–0.005 N HCl for 30 min at room temperature. The mixture was diluted with chloroform, and the organic phase was washed with brine. Evaporation of the volatiles of the dried ($MgSO_4$) organic phase afforded a residue which was chromatographed on 30 g of silica gel. Elution with 15% ethyl acetate in hexane afforded 330 mg (65%) of enone **10:** λ_{max} ($CHCl_3$) 5.73, 5.90 μ; δ ($CDCl_3$) 1.44 (s, 3), 1.8–2.6 (m, 4), 3.75 (s, 3), 5.95 (d, J = 10 Hz, 1), 6.88 (d, J = 10 Hz, 1) ppm; *m/e* (P) 168.0795 (calcd, 168.0786).

Preparation of 4-Carboxy-4-(2-hydroxy)ethylcyclohex-2-en-1-one γ-Lactone (11). A solution of diene **1** (292 mg, 1.70 mmol) and α-methylenebutyrolactone (55 mg, 0.57 mmol)[21b] in 2 mL of toluene was heated under reflux for 20 h. Workup in the usual way afforded a residue which was chromatographed on 10 g of silica gel. Elution with 1:1 ether–chloroform afforded 47 mg (50%) of **11:** λ_{max} ($CHCl_3$) 5.65, 5.95 μ; δ ($CDCl_3$) 1.9–2.9 (m, 6), 4.4 (m, 2), 6.1 (d, J = 10 Hz, 1), 6.7 (d, J = 10 Hz, 1); *m/e* (P) 166.0620 (calcd, 166.0629).

Preparation of *dl*-8aβ-Methyl-3,4,4aβ,8-tetrahydronaphthalene-1(2*H*),6(5*H*)-dione (15). A solution of compound **1** (940 mg, 5.46 mmol) and 2-methylcyclohexenone (119.7 mg, 1.08 mmol) in 3 mL of xylene was heated in a sealed tube at 195 °C for 50 h. The volatiles were removed under vacuum. The crude residue was treated with 10 mL of 4:1 THF–0.005 N aqueous HCl for 1 h at room temperature. Workup in the usual way afforded a residue which was purified by preparative TLC (Analtech, silica gel plates GF, 1000 μ, elution with 4:1 benzene–ethyl acetate) to afford 101 mg (53%) of enone **15:** mp (ether–hexane) 61–62 °C; λ_{max} ($CHCl_3$) 5.88, 5.95, 6.04 μ; δ ($CDCl_3$) 1.47 (s, 3), 1.6–2.2 (m, 4), 2.2–2.6 (m, 5), 6.00 (d, J = 10 Hz, 1), 6.63 (d, J = 10 Hz, 1) ppm; *m/e* 178 (P).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.10; H, 8.12.

Formation of *dl*-3α-Methoxycyclohexanone-4α,5α-dicarboxylic Acid Anhydride (12). Maleic anhydride (98 mg, 1 mmol) was added to diene **1** (344 mg, 2 mmol) without solvent. The system was stirred for 5 min at room temperature and then treated with 3 mL of 4:1 THF–0.1 N HCl at room temperature for 15 min. This was poured into 10 mL of 5% aqueous sodium bicarbonate. The aqueous system was extracted with 5 × 10 mL of chloroform. Evaporation of the volatiles from the dried ($MgSO_4$) organic layer afforded 183 mg (93% yield) of compound **12:** mp 103–104 °C; λ_{max} ($CHCl_3$) 5.40, 5.60 μ; δ ($CDCl_3$) 2.06 (dd, J_1 = 18, J_2 = 1 Hz, 1), 2.7–3.1 (m, 3), 3.32 (s, 3), 3.3–3.8 (m, 2), 4.15–4.35 (m, 1) ppm; *m/e* 198 (P).

Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 54.73; H, 5.10.

Reaction of Diene 1 with *trans*-Methyl Crotonate. Formation of 19 and 20 and Their Hydrolytic Conversion to 16, 17, and 18. A solution of compound **1** (2.85 g, 16.6 mmol) and *trans*-methyl crotonate (508 mg, 5.1 mmol) in 10 mL of toluene was heated under reflux for 54 h. The volatiles were removed in vacuo to afford a residue consisting largely of **19** and **20** (see NMR data in text). This was treated with 4:1 THF–0.005 N aqueous HCl for 1 h at room temperature. The reaction mixture was diluted with ethyl acetate and the organic phase was extracted successively with 5% aqueous sodium bicarbonate and brine and dried over anhydrous sodium sulfate. Evaporation of the volatiles afforded a residue which was chromatographed on 40 g of silica gel. Elution with 3% ether in chloroform afforded 88 mg (10%) of ca. a 1:1 mixture of enones **17** and **18** and 202 mg (20%) of methoxy ketone **16.** For **16:** λ_{max} ($CHCl_3$) 5.82 μ broad; δ ($CDCl_3$) 1.02 (d, J = 6 Hz, 3), 1.9–2.7 (m, 5), 2.7–3.1 (ddd, J_1 = 13.8, J_2 = 5, J_3 = 5 Hz, 1), 3.76 (s, 3) ppm; *m/e* 169 (P − 31), 140 (P − 60).

Isolation of ε-3-Methoxy-4-methyl-4-carbomethoxycyclohexanone (22). A solution of methyl methacrylate (9.0 g, 90 mmol) and diene **1** (8.6 g, 50 mmol) in 15 mL of toluene was heated under reflux for 30 h. The volatiles were removed in vacuo. The residue was diluted

to 64 mL with THF. A 16-mL aliquot of this solution was combined with 4 mL of 2 N aqueous HCl and the system stirred at room temperature for 1 **h**. The reaction mixture was diluted with chloroform and the organic phase was washed successively with 5% aqueous sodium bicarbonate and brine. Evaporation of the volatiles from the dried ($MgSO_4$) organic layer afforded 2.64 g of a crude mixture which was estimated to be 28:72 of **22:10** (vide supra) by NMR integration. Compound **22** can be isolated by chromatography on silica gel and elution with 15% ethyl acetate in hexane: λ_{max} ($CHCl_3$) 5.81 μ br; δ ($CDCl_3$) 1.37 (s, 3), 1.4–2.8 (m, 6), 3.26 (s, 3), 3.64 (s, 3), 3.48 (m, 1) ppm.

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