mass spectrometer (70 eV) to which was interfaced a Pye Unicam Model 104 gas chromotograph. The refractive indexes were determined with a Bausch and Lomb refractometer.

(11) To increase the efficiency of the condensation process, the reaction vessel was cooled (dry ice–acetone bath); and to prevent splattering, the apparatus was tilted slightly to allow the condensing ammonia to run down the walls of the flask.

(12) Normally ca. 10 min elapsed before proceeding with the quenching step, although the time interval does not seem critical.

(13) The NH_4Cl is most conveniently introduced by attaching a glass bulb filled with the salt to a side arm by means of tygon tubing. When the NH_4Cl is to be added, the bulb is raised and tapped gently to smoothly introduce the quenching agent. Should this step start to become violent, the addition and sometimes even the vigorous stirring should be momentarily stopped to avoid an eruption.

(14) During the addition the exothermic reaction was moderated (25–30 °C, internal thermometer) with a water bath.

(15) The temperature was lowered as a precaution to minimize the possibility of competing side reactions. See J. D. Buhler, *J. Org. Chem.*, **38**, 904 (1973).

(16) (*E*)-2-Butenal (crotonaldehyde), which is stabilized with 10% water, was distilled, bp 95–100 °C (760 Torr), just prior to use.

Diels–Alder Reactions of *o*-Benzoquinones. A Route to Derivatives of Δ^2-1-Octalone

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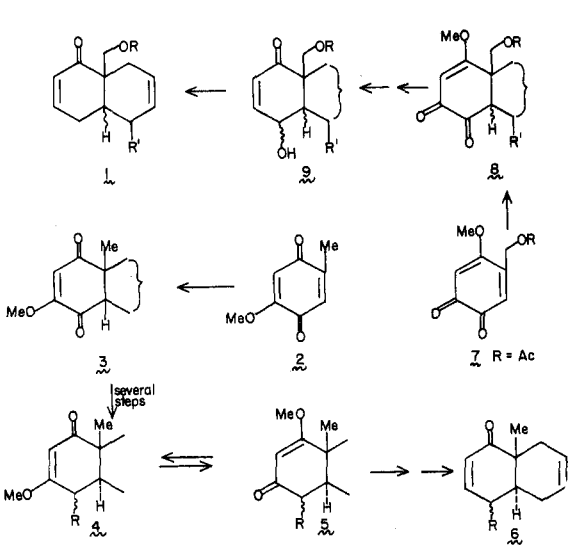
Diels–Alder reactions of 4-methoxy-5-acetoxymethyl-1,2-benzoquinone (**7**) and 4-methoxy-5-methoxymethyl-1,2-benzoquinone (**40**) have been shown to occur smoothly with acyclic dienes. In all cases, cycloaddition occurs at the 5,6 rather than 3,4 double bond. With 1-methoxybutadiene as the diene, regiospecific formation of the 8- rather than 5-methoxy isomer is observed. The applicability of stereospecific "endo" addition has been demonstrated. The adducts produced can be converted in five steps to angularly (**8a**) substituted derivatives of 4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one.

As part of a synthetic study directed at various elemanolide sesquiterpenoids, we had need to develop a simplified route to angularly functionalized hexalones of the type **1**. The known route to such systems, in the angular methyl series, involved equilibration of β-methoxyenones such as **4** with their vinylogous isomers, **5**.[1,2] Reduction affords a β-methoxyallylic alcohol which is unravelled with acid to give **6**.[3,4] System **4** is obtained by the Woodward route,[5] which starts with a Diels–Alder cycloaddition of methoxytoluoquinone **2** with 1,3-butadiene. The cis adduct **3** is epimerized to the trans series, and the C_4 ketone is selectively reduced to give an alcohol.[1] Interconversion of **4** with **5** has been achieved either on the derived tosylate, **4** (R = OTs),[2] or on the reduction product thereof, **4** (R = H). Alternatively the β-diketone, derived from hydrolysis of **4** (R = H), has been converted to a mixture of **4** and **5** (R = H).[1]



Since the stability of **4** vs. **5** is apparently a sensitive and unpredictable function of the nature of the substituents, we preferred to develop an entry to **1** in which such a process is not necessary. If, instead of a *p*-quinone, an *o*-quinone such as **7** is used as the dienophile, an adduct of the type **8** would be produced. Reduction of both carbonyl groups followed by the same type of acidic transformation which is involved in the conversion of **5** → **6** would provide **9** from **8**. Reductive transformation of **9** → **1** could easily be envisaged.

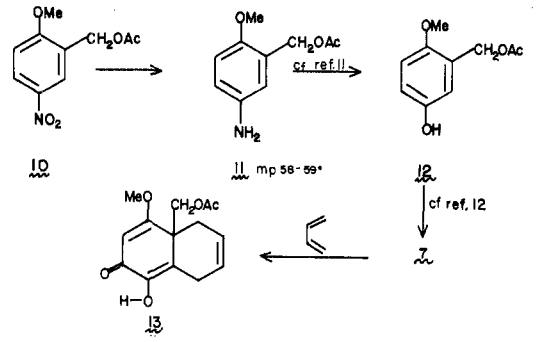
Prior to this investigation, the use of *o*-quinones as dienophiles had received relatively little attention. Of course, Gates and co-workers had utilized a 1,2-napthoquinone as a dienophile in their well-known synthesis of morphine.[6] Ansell had shown[7] that activated *o*-benzoquinones, bearing a 4-cyano or 4-carbomethoxy substituent, were sufficiently activated to react as dienophiles with reactive acyclic dienes such as 2,3-dimethylbutadiene. Subsequent work demonstrated that with simple, nonactivated *o*-quinones,[8] only with massive excesses of 2,3-dimethylbutadiene could Diels–Alder adducts be obtained. Horspool had concluded[9] that the propensity for dimerization and decomposition of simple *o*-quinones is such that Diels–Alder reaction with unactivated dienes was apparently not possible.

We expected that the enophilic powers of a 4-methoxy-*o*-quinone should be sharply reduced since cycloaddition would necessitate dissipation of the vinylogous ester resonance of the starting material. That such an effect is likely to be important is suggested by the specific dienophilicity of the 5,6 rather than 2,3 double bond of *p*-quinone **2**.[5] Furthermore, Ansell had shown that 4-methoxy-1,2-benzoquinone reacts with 2,3-dimethylbutadiene exclusively at the 5,6 rather than the 3,4 double bond,[8] presumably for the same reason. If the *enophilicity* of a system such as **7** is diminished in line with the curtailment of its *dienophilicity* at the 3,4 double bond, the possibilities of realizing cycloaddition reactions of the 5,6 double bond with a wide variety of dienes becomes more promising. This expectation has been realized in practice.

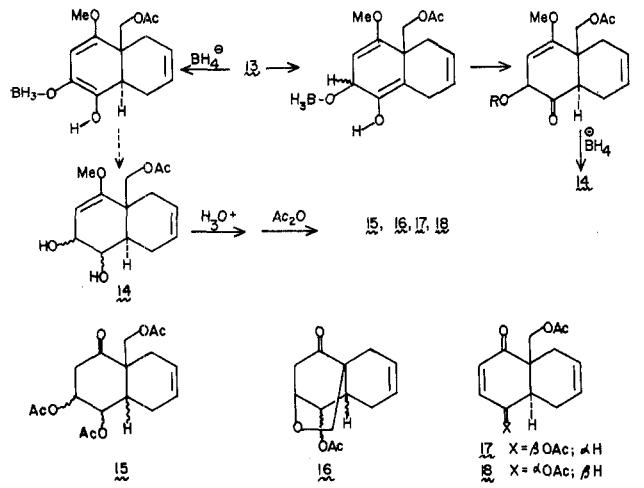
Results

The synthesis of specific compound **7** (R = OAc) started with the commercially available *p*-nitroanisole. This was

converted by known steps[10a] (chloromethylation followed by acetolysis) into the anisole derivative, **10**, and thence by steps which we have previously described into compound **7**.[10b] Heating compound **7** with 1,3-butadiene at 105 °C for 5 h gives a 63% yield of adduct **13**, mp 150–151 °C, whose structure was proven as previously described.[10b]



The existence of **13** as a diosphenol precluded systematic synthesis of both the cis- and trans-fused hexalones along the lines of the Woodward synthesis through the use of kinetic (cis) and equilbrated (trans) Diels–Alder adducts.[5] Treatment of **13** with excess sodium borohydride gave a crude tetrahydro product, **14**, which was submitted directly to the action of aqueous acid and the resultant mixture was acetylated (pyridine–Ac_2O). Chromatography of this material on silica gel



gave a mixture of keto triacetate **15** (4%), bridged ether **16** (0.50%), and the epimeric enone diacetates **17** and **18** (45% combined). While careful chromatography enabled the separation of **17** from **18** (see Experimental Section), the combined material was used for further elaboration.

Although at this point the configuration at C_{4a} was not known, subsequent transformations will show that both **17** and **18** are trans fused. The gross schematics of the sodium borohydride reduction are not known with certainty. One possibility is that reduction occurs first at C_1 through spectroscopically undetected quantities of C_1 keto tautomer. While precedent suggests that a β-methoxyenone is not reduced by sodium borohydride,[1,5] the proximity of the alkoxyborane at C_1 may facilitate intramolecular reduction at C_2. Alternatively, reduction may commence with conjugate addition to C_{8a}. While such conjugate additions to Δ^4-3-ketodecalones with sodium borohydride are not common, an accelerating effect of the hydrogen bond (in **13**) on such a reaction cannot be ruled out.

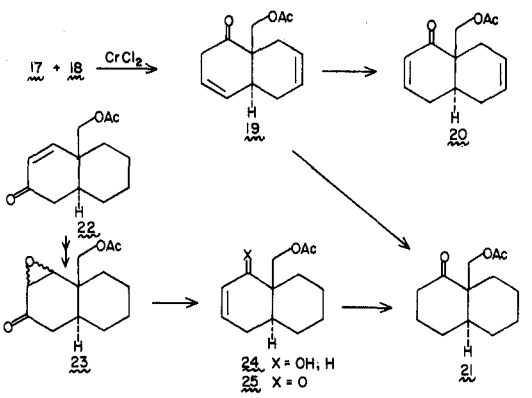
An alternative sequence starts with direct reduction at C_2 (either through a proximate alkoxyborane or because of the special accelerating effect of the diosphenol linkage). After reduction of C_2, the Δ^1-enol ketonizes and the resultant 2-hydroxy-1-ketone is further reduced with sodium borohydride to give diol **14**.

Compound **15** must be derived by competitive cleavage of the enol ether of **14** by the aqueous acid to give the 3ε,4ε-dihydroxy-1-ketone rather than Δ^2-en-1-one. The conditions for the enol ether cleavage apparently suffice to cleave the angular ester. The hydroxymethyl function cyclizes in an intramolecular Michael reaction to give **16** to a small extent. It should be noted that the junction stereochemistry in **15** and **16** has not been proven.

Reaction of the mixture of **17** and **18** with excess chromous chloride for 1 h afforded a 44% yield of β,γ-unsaturated ketone **19**. While the starting ratio of epimers was ca. 1:1, the recovered enone diacetate was virtually pure 4α-acetoxy epimer **18** (ca. 25%). These results indicate that the β epimer **17**, in which the acetoxy group is axial, is reductively cleaved by chromous chloride substantially faster than the α epimer, in which the acetoxy group is equatorial. This relative order of reductive cleavage can be rationalized on the basis of superior overlap of the departing axial acetoxy group with the π system on the enone. A similar trend has been noted in the conceptually related reductive debromination of the α-bromo ketones with zinc.[13] When **18** was resubmitted to reduction with chromous chloride, additional small amounts of **19** were obtained. Other products, which were not characterized, were noted on TLC analysis.

The isomerization of **19** → **20** was achieved (86%) by the action of aqueous HCl in THF. While the overall yield of **20** from **13** is only 15%, the directness of the method and the feasibility of entering the trans series via a Diels–Alder reaction, without recourse to cis → trans epimerization, are attractive features of the o-quinone route.

Catalytic hydrogenation of **19** gave a tetrahydro product, **21**. The same compound was synthesized by a five-step sequence starting with the known *trans*-acetoxymethyloctalone **22**.[14a,b] Epoxidation of **22** with alkaline hydrogen peroxide followed by acetylation with pyridine–acetic anhydride gave **23**. Treatment of **23** with hydrazine hydrate[15] afforded allylic alcohol **24** which, upon oxidation with activated MnO_2, was converted into **25**. Catalytic hydrogenation of **25** gave **21**. These transformations establish the trans stereochemistry of **21** and hence of its precursors **14**, **17**, **18**, **19**, and **20**.



With the objective of incorporating oxygen functionality into the scheme, the Diels–Alder reaction of o-quinone **7** with 1-methoxybutadiene was examined. On the basis of analogies discussed above, it seemed likely that cycloaddition could again occur at the 5,6 double bond. We further reasoned that of the two carbonyl groups in **7**, the C_1 center would be the more electrophilic since C_2 is part of a vinylogous ester system. Accordingly, "intial" bond formation in the cycloaddition was expected to occur between C_5 of the o-quinone and C_4 of the diene. Such an alignment would lead to adduct **27**. A similar trend was noted in our laboratory in the cycloaddition of the electronically related p-quinone **26** with the same diene

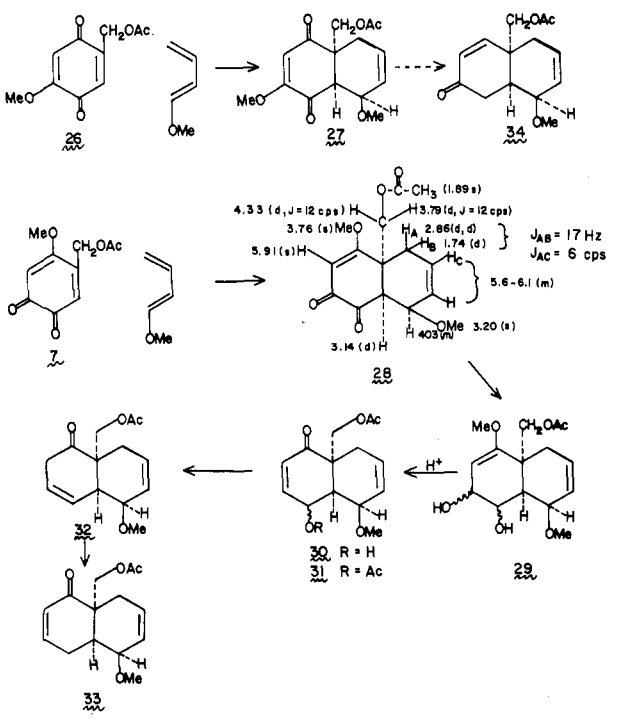
to give **27** as the sole detectable product.[14b] It will be recognized that such an alignment requires "initial" bond formation between the termini of the diene and the *more hindered* carbon of the quinone.

Reaction of **7** with 1-methoxybutadiene in methanol[16] occurred quickly under reflux. After 120 min there was obtained in 81% yield a crystalline 1:1 adduct whose structure and stereochemistry correspond to structure **28**. *Unlike the case of* **13**, *this adduct exists entirely in the* α*-diketo form.* At 250 MHz ($CDCl_3$) all the protons may be assigned and are shown in the figure in parts per million (δ) from Me_4Si. Particularly noteworthy are the absence of any exchangeable hydrogens and the appearance of a doublet, δ 3.14, J = 8 Hz, which is due to the hydrogen at C_{8a} coupled to the hydrogen at C_8. The latter is seen as a multiplet, $h_{1/2}$ = 14 Hz. While the stereochemistry indicated in **28** would have been expected on the basis of the cis–endo rules governing Diels–Alder reactions,[17] the correctness of the assignment will be rigorously established.

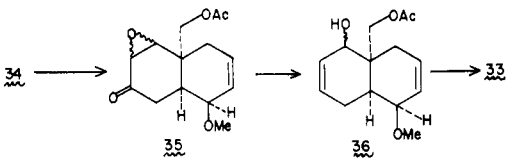
In our hands, all attempts to achieve epimerization of **28** were to no avail. Use of mild conditions ($NaHCO_3$–MeOH) gave recovery of starting material and more forcing conditions (NaOMe–MeOH) afforded intractable mixtures. Similar failures were recorded in attempted epimerizations of **27**.[14b] The definition of the structural factors which cause complete enolization in the case of **13** while exclusively favoring the α-diketone form in **28** must await further experiments with other 1-substituted butadienes.

While the 1-methoxybutadiene Diels–Alder reaction did not provide access to the trans series, a route analogous to that used to convert **13** → **20** was used with excellent success to convert **28** → **33**. Reaction of **28** with sodium borohydride gave a tetrahydro product (see discussion above for the conversion of **13** → **14**), **29**, mp 75–80 °C, which on treatment with aqueous acid gave in 97% crude recovery the alcohol **30**. Acetylation of **30** with pyridine and acetic anhydride gave (80% yield) the crystalline enone diacetate **31**, mp 81–82 °C.

Treatment of **31** with chromous chloride gave a quantitative recovery of β,γ-unsaturated isomer **32** which was isomerized with aqueous HCl–THF. The crude product was acetylated and the conjugated enone, **33**, mp 85–86 °C, was obtained in 85% yield after purification.



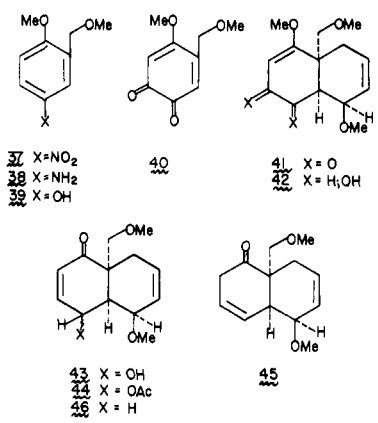
The stereochemistry of **33** (and therefore, the stereochemistry at C_{4a} and C_5 of its precursors, **28** → **32**) was confirmed by alternate synthesis. Previously[14b] we have described the synthesis of the Δ^1-3-enone **34** via the *p*-quinone Diels–Alder adduct **27** using the conventional methods of transformation. The relative stereochemistry of **34** had been established unequivocally.[14b] Epoxidation of **34** with alkaline hydrogen peroxide afforded (39%) **35**. The stereochemistry of the epoxide linkage in **35** is not known. A Wharton reaction[15] on **35** gave an allylic alcohol **36**, which, without purification, was oxidized by Corey's reagent[18] to give compound **33** (39%,



two steps). The infrared and NMR spectra as well as the melting point of **33** thus obtained were identical with those of the same compound derived from the *o*-quinone. Thus it is seen that the direct route via **7** is a considerably more expeditious pathway to **33** than is the *p*-quinone route via **26** in that no enone transposition is required.

The method was also extended to produce hexalone **46** bearing an angular methoxymethyl group. The starting material was the known[10a] 2-methoxymethyl-4-nitroanisole **37**. This was converted to the crude aniline derivative **38** and thence to the crystalline phenol **39**, mp 79–80 °C (56% for the two steps). Oxidation of **39** with Fremy's salt[12] gave a quantitative yield of *o*-quinone **40**, mp 134.5–136°C.

As before, Diels–Alder cycloaddition of **40** with 1-methoxybutadiene gave a single identifiable crystalline (76%) 1:1



adduct, mp 157.5–158.5 °C. On the basis of the strong similarity of its spectra with those of **28**, structure **41** is safely assigned to this adduct. Reduction of **41** with sodium borohydride gave a tetrahydro product **42** (100%), mp 145–145.5 °C, which, upon treatment with acid, gave a virtually quantitative yield of enone alcohol **43**. Acetylation of **43** (pyridine–acetic anhydride) gave (99%) a crystalline acetate, **44**, mp 67.5–68 °C. Reductive cleavage with chromous chloride followed by isomerization (HCl–THF) of the β,γ isomer **45** gave **46**, mp 52–53 °C (70%, two steps).

It has thus been demonstrated that 4-methoxy-*o*-quinones are viable dienophiles for Diels–Alder reactions with acyclic dienes. In this connection it must, however, be noted that we have recently found[10b] that 4-methoxy-5-methyl-1,2-benzoquinone reacts anomalously with 1,3-butadiene to give a spirodecane derivative. The definition of structural features favoring "normal" vs. "abnormal" Diels–Alder reactions of 5-alkylated 4-methoxy-1,2-benzoquinones remains to be achieved. The delineation of the structural features which favor diosphenolic (cf. **13**) as opposed to α-diketonic

(cf. 28 and 41) character in the "normal" adducts is also of importance in providing stereochemical control over the manipulation of these compounds. These issues, as well as the exploitation of the now easily accessible substitution patterns embodied in compounds **20**, **33**, and **46**, are currently being studied.

Experimental Section[19]

Reaction of 3-Methoxy-4-acetoxymethyl-1,2-benzoquinone (7) with 1,3-Butadiene. Formation of *dl*-1-Hydroxy-4-methoxy-4a-acetoxymethyl-4a,5-dihydronaphthalen-2(8*H*)-one (13). A solution of 1 g of quinone **7**,[10b] 19 ml of 1,3-butadiene, and 12 ml of benzene was heated in a sealed tube at 105 °C for 5 h. The color changed from red to light yellow. Evaporation of the volatiles left a semisolid residue which, upon trituration with ether, afforded 718 mg of **13** as a white solid. Treatment of the mother liquors with ether–hexane gave an additional 76 mg of **13** (63%): mp 150–151 °C; λ_{max} ($CHCl_3$) 3.85, 5.74, 6.15 μ; λ_{max} (EtOH) 250 (ϵ nm 10 500), 297 (2500); δ ($CDCl_3$, 250 MHz) 1.89 (s, 3), 2.18 (d, J = 18 Hz, 1), 2.30 (d, d, J = 18, 5 Hz, 1), 2.82 (br d, J = 21 Hz, 1) 3.46 (d, J = 21 Hz), 3.76 (s, 3), 4.35 (d, J = 10 Hz, 1) 4.47 (d, J = 10 Hz, 1), 5.4–6.0 (m, 3 containing a singlet at 5.72, ca. 1), 6.67 ppm (s, 1, exchangeable with D_2O); *m/e* 264 (parent).

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.53; H, 6.04.

Direct Conversion of Compound 13 to Keto Triacetate 15, Bridged Ether 16, and Dienone Diacetates 17 and 18. To a solution of sodium borohydride (1.00 g, 0.027 mol) in 50 ml of absolute ethanol stirred at 0 °C was added adduct **13** (3.30 g, 0.0125 mol) as a solid. The system was stirred for 15 min at 0 °C and for 4 h at room temperature. The mixture was added to aqueous KCl and extracted thoroughly with chloroform. Evaporation of the volatiles left a semisolid residue which was redissolved in 25 ml of chloroform and this solution was stirred with 50 ml of 10% aqueous HCl. To the aqueous phase, after separation of the layers, was added solid KCl till saturation, and this was reextracted with chloroform. The combined chloroform layers were dried over sodium sulfate. Evaporation of the volatiles at the water pump left a residue of 2.29 g which was stirred overnight with 30 ml of acetic anhydride containing ca. 0.5 ml of pyridine. Evaporation of this solution by warming at the water pump left a residue of 2.2 g which was chromatographed on 130 g of silica gel. Elution with 4:1 hexane–ethyl acetate gave 16 mg (0.5%) of **16**, 1.57 g (45%) of a mixture of **17** and **18**, and 180 mg (4%) of **15**. Although the separation of **17** and **18** was not complete and the mixture was used in the next step, early fractions gave essentially pure **17** and later fractions gave essentially pure **18**.

For **16**: λ_{max} ($CHCl_3$) 5.81, 5.85 μ; δ ($CDCl_3$) 1.2–3.0 (m, 10 containing a singlet, ca. 3 at 2.03), 3.60 (d, J = 10 Hz, 1) 4.30 (d, J = 10 Hz, 1), 4.35 (d, d, J = 5, J_2 = 2 Hz, 1), 4.88 (d, d, J_1 = 5, J_2 = 1 Hz, 1), 5.6–5.8 ppm (m, 2); *m/e* 236 (parent).

For **17**: λ_{max} ($CHCl_3$) 5.79, 5.96 μ; δ ($CDCl_3$) 2.08 (s, 3), 2.2–2.9 (m, 8 containing a singlet, ca. 3, at 2.20), 4.2 (d, J = 12 Hz, 1), 4.75 (d, J = 12 Hz, 1), 5.5 (t, J = 5 Hz, 1), 5.6–5.8 (m, 2), 6.18 ppm (d, J = 10, 5 Hz, 1); *m/e* 278 (parent).

For **18**: λ_{max} ($CHCl_3$) 5.81, 5.96 μ; δ ($CDCl_3$) 1.8–3.0 (m, 11 containing 2, ca. 3 H singlets at 2.10 and 2.25), 4.20 (d, J = 12 Hz, 1), 4.53 (d, J = 12 Hz, 1), 5.4–5.9 (m, 3), 6.15 (d, d, J = 10, 1 Hz), 6.85 ppm (d, d, J = 10, 1 Hz, 1); *m/e* 278 (paret).

For **15**: λ_{max} ($CHCl_3$) 5.80, 5.96 μ; δ ($CDCl_3$ 2.00 (s, 3), 2.15 ppm (s, 6); *m/e* 338 (parent).

Preparation of *dl-trans*-8a-Acetoxymethyl-4a,5,8,8a-tetrahydronaphthalen-1(2*H*)-one (19). To a solution of 1.00 g (3.6 mol) of the mixture of **17** and **18** in 40 ml of acetone under an atmosphere of carbon dioxide was added 80 ml of 0.86 M aqueous chromous chloride.[20] After 1 h at room temperature, the liquid was decanted and extracted with chloroform. The chloroform extracts were dried over sodium sulfate and concentrated at the water pump to give a residue of 800 mg which was chromatographed on 40 g of silica gel. Elution with 9:1 hexane–ethyl acetate afforded 340 mg of **19** followed by 347 mg of essentially pure **18**. Resubmission of **18** to the same reaction afforded an additional 50 mg of **19** (50% combined).

19: λ_{max} ($CHCl_3$) 5.78, 5.85 μ; δ ($CDCl_3$) 2.00 (s, 3), 2.10–2.50 (m, 4), 2.5–2.7 (m, 1), 2.8–3.2 (m, 4), 4.23 (d, J = 11 Hz, 1), 4.52 (d, J = 11 Hz, 1), 5.4–6.0 ppm (m, 4); *m/e* 220 (parent).

Formation of *dl-trans*-8a-Acetoxymethyl-4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one (20). To a solution of **19** (600 mg, 2.73 mmol) in 8 ml of tetrahydrofuran was added ca. 0.2 ml of concentrated HCl. The reaction mixture was stirred at room temperature under nitrogen for 12 h. To this was added 12 ml of ether and the solution dried over anhydrous sodium sulfate. The residue, left after evaporation of the volatiles at the water pump, was chromatographed on 30 g of silica gel. Elution with 9:1 hexane–ethyl acetate afforded 515 mg (86%) of **20**: mp 38–39 °C; λ_{max} ($CHCl_3$) 5.80, 6.95 μ; δ ($CDCl_3$) 1.95 (s, 3), 2.0–2.5 (m, 7), 4.15 (d, J = 11 Hz, 1), 4.40 (d, J = 11 Hz, 1), 5.5–5.7 (m, 2), 6.0 (d, t, J_d = 10, J_t = 1 Hz), 6.8 ppm (d, t, J_d = 10, J_t = 2.3 Hz); *m/e* 220 (parent).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.05; H, 7.29.

Epoxidation of 22. Formation of *dl-trans*-4a-Acetoxymethyl-3ϵ,4ϵ-oxido-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2-(1*H*)-one (23). A solution of 444 mg (2 mmol) of **22**[14b] in 5 ml of methanol containing 0.6 ml of 30% aqueous hydrogen peroxide and 0.17 ml of 6 N aqueous sodium hydroxide was stirred for 3 h at room temperature. After dilution with aqueous saturated potassium chloride, the system was extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated at the water pump. The mixture was stirred overnight with 10 ml of acetic anhydride containing 0.5 ml of pyridine. The volatiles were removed at the water pump to afford 460 mg (97%) of **23**: λ_{max} ($CHCl_3$) 5.78, 5.84 μ; *m/e* 238 (parent).

Formation of *dl-trans*-8a-Acetoxymethyl-1ϵ-hydroxy-1,4,4a,5,6,7,8,8a-octahydronaphthalene (24). To a solution of **23** (404 mg, 1.7 mmo) in 6 ml of ethanol containing 0.02 ml of acetic acid was added 0.350 ml (7 mmol) of hydrazine hydrate. Evolution of a gas was noted. The solution was stirred for 35 min at room temperature. Dilution with water, extraction with chloroform, drying the chloroform over sodium sulfate, and evaporation of the volatiles at the water pump left a residue which was chromatographed on 27 g of silica gel. Elution with 9:1 chloroform–acetone afforded 130 mg (34%) of **24** as an oil: λ_{max} ($CHCl_3$) 2.80, 5.79 μ; *m/e* 181 (parent − 43).

Oxidation of 24. Formation of *dl-trans*-8a-Acetoxymethyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4*H*)-one (25). A solution of **24** (112 mg, 0.05 mmol) in 10 ml of chloroform was heated under reflux for 17 h with 1 g of activated manganese dioxide. The residue, obtained after filtration and evaporation of the volatiles at the water pump, was purified by preparative TLC (silica gel) using 2:1 hexane–ethyl acetate to afford 88 mg (79%) of **25**: λ_{max} ($CHCl_3$) 5.79, 5.96 μ; *m/e* 224 (parent).

Catalytic Hydrogenation of 25. Formation of *dl-trans*-8a-Acetoxymethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1(2*H*)-one (21). A solution of 18 mg of compound **25** in 1 ml of ethanol was stirred over 10 mg of 10% palladium on charcoal under 1 atm of hydrogen at room temperature for 4 h. After filtration and evaporation of the volatiles at the water pump, the residue (18 mg) was purified by preparative TLC using 2:1 hexane–ethyl acetate for elution to give 14 mg (78%) of **21**: λ_{max} ($CHCl_3$) 5.79, 5.84 μ; δ ($CDCl_3$) 1.1–2.8 (m, 18 containing s, ca. 3 at 1.98), 4.53 ppm (br s, 2); *m/e* 224 (parent).

Catalytic Hydrogenation of 19. Formation of 21. A solution of 70 mg of **19** in 2 ml of ethanol was stirred over 10 mg of 10% palladium in charcoal under 1 atm of hydrogen. Filtration and evaporation of the volatiles at the water pump left a residue of 67 mg (96%) of **21** identical in all respects with a sample obtained from the experiments described above.

Preparation of *dl*-4aα-Acetoxymethyl-8aα-4,8β-dimethoxy-1,2,4a,5,8,8a-hexahydronapthalene-1,2-dione (28). To a solution of 2.00 g (9.50 mmol) of o-quinone **7** in 65 ml of absolute methanol was added 1.60 g (19.0 mmol) of 1-methoxy-1,3-butadiene. The orange solution was heated under reflux for 2 h under N_2. During this time the color turned light yellow. The mixture was cooled and evaporated to an oil to which 5 ml of benzene was added. The benzene solution was cooled in an ice bath and hexane was slowly added until crystallization appeared to be complete. The crystalline solid was filtered and washed with small amounts of ice-cold ether to afford 2.27 g (81%) of adduct **28** as a tan, crystalline solid: mp 157–158 °C; λ_{max} ($CHCl_3$) 6.25 μ; δ ($CDCl_3$) see structure **28** in text.

Anal. Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16. Found: C, 61.34; H, 5.99.

Reduction of 28. Formation of Tetrahydro Product 29. To a solution of 1.00 g (3.40 mmol) of **28** in 5 ml of dry tetrahydrofuran and 5 ml of absolute ethanol at 0 °C was added, with stirring, 257 mg (6.59 mmol) of $NaBH_4$. The solution slowly became homogeneous and was stirred under N_2 at 0 °C for 15 min. Stirring was continued at room temperature for an additional 4 h. The solution was poured into 15 ml of saturated KCl and 3 ml of water. The aqueous solution was extracted with 4 × 50 ml of ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford 1.01 g (100%) of **29** as a yellow oil which became a crystalline mass: mp 75–80 °C; λ_{max} ($CHCl_3$) 2.85, 5.84, 6.08 μ; *m/e* 298 (parent).

Formation of *dl*-4aα-8aα-Acetoxymethyl-4ϵ-hydroxy-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one (30). To a vigorously stirred solution of 1.10 g (3.7 mmol) of **29** in 3.5 ml of methylene chloride was added 10 ml of 10% (w/v) H_2SO_4. After 1 h, the phases were separated and the aqueous layer was extracted with 4 × 20 ml of methylene chloride. The combined methylene chloride extracts were dried over anhydrous Na_2SO_4 and evaporated to yield 955 mg (87%) of **30** as a clear oil: λ_{max} ($CHCl_3$) 2.85, 5.75, 5.95 μ; *m/e* 266 (parent).

Formation of 4aα-8aα-Acetoxymethyl-4ϵ-acetoxy-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one (31). A solution of 0.950 g (3.60 mmol) of enone alcohol **30**, 3.0 ml of acetic anhydride, and 3.0 ml of pyridine was stirred at ambience for 12 h. The volatiles were removed in vacuo. The residual yellow oil was chromatographed on 20 g of silica gel. Elution with 3:2 benzene–ethyl acetate afforded 880 mg (80%) of crystalline enone diacetate: mp 81–82 °C (R_f 0.48, 3:2 benzene–ethyl acetate); λ_{max} ($CDCl_3$) 5.76, 5.94 μ; δ ($CDCl_3$) 1.83 (d, J = 21 Hz, 1), 2.01 (s, 3), 2.04 (s, 3), 2.62 (d, J = 21 Hz, 1), 2.99 (t, J = 7 Hz), 3.37 (s, 3), 3.92 (m, 1), 4.15 (d, J = 12 Hz), 4.50 (d, J = 12 Hz), 5.78 (m, 3), 6.10 (d, J = 11 Hz, 1), 6.86 ppm (d, d, J = 11, 5 Hz, 1).

Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.35; H, 6.39.

Formation of *dl*-4aα-8aα-Acetoxymethyl-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(2*H*)-one (32). To a solution of 500 mg (1.60 mmol) of enone diacetate **31** in 16 ml of acetone under CO_2 was added 60 ml of 0.86 M $CrCl_2$[20] in water. The solution was stirred under CO_2 for 1 h, then extracted with 5 × 60 ml of ether. The combined ether extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield 406 mg (100%) of β,γ-unsaturated ketone **32** [λ_{max} (neat) 5.76, 584 μ] as a yellow oil used directly in the next step.

Formation of *dl*-4aα-8aα-Acetoxymethyl-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one (33). A solution of compound **32** (405 mg, 1.6 mmol) of β,γ isomer in 1.8 ml of tetrahydrofuran containing 0.03 ml of concentrated HCl was stirred at room temperature for 48 h. The volatiles were removed in vacuo. The yellow oily residue was dissolved in 2 ml of acetic anhydride and 2 ml of pyridine. The solution was stirred for 12 h at room temperature. The residue, obtained upon evaporation of the volatiles in vacuo, was chromatographed on 12 g of silicic acid. Elution with 3:2 benzene–ethyl acetate afforded 340 mg (84%) of **33** as a colorless oil which crystallized (mp 85–86 °C) on standing: λ_{max} ($CHCl_3$) 5.77, 598 μ; δ ($CDCl_3$) 1.8–3.0 (m, 8 containing s, ca. 3 at 2.0), 3.4 (s, 3), 3.9 (m, 1), 4.2 (d, J = 11 Hz, 1), 4.5 (d, J = 11 Hz, 1), 5.8 (br s, 2), 6.0 (d, t, J_d = 11, J_t = 2 Hz, 1), 6.8–7.3 ppm (m, 1).

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.27; H, 7.24.

Epoxidation of the Conjugated Double Bond of 34. Formation of *dl*-4aα-Acetoxymethyl-8aα-3,4ϵ-oxido-8β-methoxy-3,4,4a,5,8,8a-hexahydronaphalen-2(1*H*)-one (35). A solution of enone **34**[14b] (140 mg, 0.56 mmol) in 0.7 ml of methanol, 25 ml of 30% aqueous hydrogen peroxide, and 60 μl of 6 N aqueous sodium hydroxide was stirred for 2 h under nitrogen at room temperature. Dilution with 3 ml of water was followed by extraction with 5 × 10 ml of ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous sodium sulfate. A residue of 97 mg, left upon evaporation of the volatiles in vacuo, was dissolved in 1 ml of acetic anhydride and 1 ml of pyridine. The solution was stirred for 12 h at room temperature. The volatiles were evaporated in vacuo and the residue was submitted to preparative TLC using 9:1 chloroform–acetone for elution. A fraction of 58 mg (39%) of epoxy ketone **35** was obtained as a clear, viscous oil: λ_{max} ($CHCl_3$) 5.75, 5.82 μ; δ ($CDCl_3$) 2.1 (s, 3), 3.3 (s, 3), 4.1 (d, J = 11.5 Hz, 1), 4.3 (d, J = 11.5 Hz, 1), 5.7 (br s, 2).

Formation of *dl*-4aα-8aα-Acetoxymethyl-1ϵ-hydroxy-5β-methoxy-1,4,4a,5,8,8a-hexahydronaphthalene (36). To a solution of 40 mg (0.15 mmol) of enone **35** in 0.5 ml of absolute methanol was added 24 mg (3 equiv) of hydrazine hydrate in 0.5 ml of absolute methanol immediately followed by 20 μl of glacial acetic acid. The reaction became exothermic and the mixture turned yellow as gas was evolved. After 1 h of stirring under N_2 at ambience, the reaction mixture had turned somewhat lighter in color. Water (2.0 ml) was added and this was extracted with 3 × 10 ml of ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford an oil which was chromatographed on 4 g of silicic acid. Elution with 9:1 chloroform–acetone as an eluent gave 20 mg (53%) of the allylic alcohol **3** as an oil: λ_{max} ($CHCl_3$) 2.81, 5.76 μ; δ ($CDCl_3$) 1.4–2.7 (complex, 5), 2.1 (s, 3), 3.4 (s, 3), 3.4–4.2 (m, 3), 4.3 (s, 2), 5.6 (s, 2), 5.9 ppm (s, 2).

Oxidation of 36. Formation of 33. To a suspension of 23 mg (0.11 mmol, 1.52 equiv) of pyridinium chlorochromate[18] in 1.0 ml of methylene chloride was added a solution of 18 mg (0.071 mmol) of allylic alcohol **36** in 1 ml of methylene chloride. After 3 h, the solution was rapidly filtered through a plug of 1 g of Florisil using 100 ml of methylene chloride as an eluent. The collected methylene chloride was evaporated in vacuo to an oil which easily crystallized to afford 13 mg (73%) of enone **33**, mp 85–86 °C (mixture melting point, no depression) whose infrared and NMR spectra were identical with those of compound **33** prepared via the *o*-quinone route.

Preparation of 2-Methoxymethyl-4-aminoanisole (38). To a vigorously stirred suspension of 2-methoxymethyl-4-nitroanisole (**37**, 6.54 g, 0.033 mol) in 327 ml of 5% aqueous HCl was added 12 g of zinc dust. Stirring was continued for 30 min whereupon 15 ml of concentrated HCl and 10 g of zinc dust were added. Vigorous stirring was continued for an additional 30 min. The aqueous solution was filtered. After basification with solid potassium carbonate, the system was extracted with 4 × 150 ml of chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate. Evaporation of the volatiles afforded 4.92 g (89%) of **38** as a dark oil: λ_{max} ($CHCl_3$) 2.95, 3.01, 6.17 μ; δ ($CDCl_3$) 3.4 (s, 3), 3.5 (s, 2), 3.8 (s, 3), 4.5 (s, 2), 6.5–6.9 ppm (m, 3).

Preparation of 3-Methoxymethyl-4-methoxyphenol (39). To 2.0 l. of 0.1 M H_2SO_4 was added 11.44 g (68.5 mmol) of **38**. The solution was cooled to 0 °C and a solution of 5.06 g of $NaNO_2$ in 200 ml of water was added with stirring. After 10 min, 3.40 l. of 1.5 M $Cu(NO_3)_2$·$6H_2O$ was added immediately followed by 12.00 g of Cu_2O. The solution was heated to 50 °C with stirring and maintained at that temperature for 30 min. A gas was evolved during this time and the solution became green. The aqueous system was extracted with 6 × 1 l. of chloroform. The combined chloroform extracts were dried over anhydrous $MgSO_4$ and evaporated to yield a black solid residue. The solid was dissolved in 1:1 ether–hexane with heat (steam bath) and allowed to crystallize slowly to afford 7.84 g (69%) of phenol **39**: mp 79–80 °C; λ_{max} ($CHCl_3$) 2.70, 2.94, 3.27 μ; δ ($CDCl_3$) 3.4 (s, 3), 3.8 (s, 3), 4.5 (s, 2), 3.5 (br s, 1), 6.6–7.0 ppm (m, 3).

Formation of 4-Methoxy-5-methoxymethyl-1,2-benzoquinone (40). To a solution of 1.40 ml of 1/6 M KH_2PO_4 in 1.40 l. of water at 0 °C was added 28 g of Fremy's salt.[12] A solution of 4.74 g (28.2 mmol) of phenol **39** in 15 ml of chloroform was added with vigorous stirring. After 30 min, the orange solution was extracted wih 6 × 200 ml of chloroform. The combined chloroform extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford a dark red solid, which upon washing with 4 × 20 ml of ether and filtration gave 5.12 g (100%) of the *o*-quinone **40** as a bright red solid: mp 134.5–136 °C; λ_{max} ($CHCl_3$) 5.98 (br), 6.23 μ; δ ($CDCl_3$) 3.5 (s, 3), 3.9 (s, 3), 4.3 (d, J = 2.2 Hz, 2), 5.8 (s, 1), 6.5 ppm (t, J = 2.2 Hz, 1).

Anal. Calcd for $C_9H_{10}O_4$: *m/e* 182.05791. Found: *m/e* 182.05794.

Preparation of *dl*-4aα-Methoxymethyl-8aα-4,8β-dimethoxy-1,2,4a,5,8,8a-hexahydronaphthalene-1,2-dione (41). To a suspension of 5.00 g (27.5 mmol) of **40** in 200 ml of absolute methanol was added 6.00 g (71.4 mmol) of 1-methoxy-1,3-butadiene. The reaction mixture became homogeneous upon refluxing and slowly turned from red to yellow in color over a period of 9 h. Another 3 g (35.7 mmol) of 1-methoxy-1,3-butadiene was added and reflux was continued for an additional 3 h. Evaporation of the volatiles in vacuo gave a semicrystalline solid which was washed with 100 ml of ether to give 5.52 g (76%) of **41** as a white solid: mp 157.5–158.5 °C; λ_{max} ($CHCl_3$) 5.75, 5.99, 6.25 μ; δ ($CDCl_3$) 1.5–3.2 (complex, 3), 3.1–3.3 (m, 7 containing a singlet, ca. 2 at 3.2), 3.4 (d, J = 9 Hz, 1), 3.8 (s, 3), 4.0 (m, 1), 5.9 ppm (m, 3).

Reduction of 41 with Sodium Borohydride. Formation of Tetrahydro Product 42. To a suspension of 266 mg (1 mmol) of adduct **41** in 4 ml of absolute ethanol at 0 °C was added 65 mg (1.67 mmol) of $NaBH_4$. After stirring under N_2 at 0 °C for 15 min the solution was homogeneous. The solution was stirred at ambient temperature under N_2 for 4 h. The reaction mixture was poured into 25 ml of saturated KCl and 10 ml of water and extracted with 4 × 50 ml of ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford 270 mg (100%) of an oil which crystallized on standing to give **42**: mp 145–145.5 °C; λ_{max} ($CHCl_3$) 2.76, 6.04 μ; *m/e* 270 (parent).

Anal. Calcd for $C_{14}H_{22}O_5$: *m/e* 270.146725. Found: *m/e* 270.146342.

Formation of *dl*-4aα-8aα-Methoxymethyl-4ϵ-hydroxy-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one (43). To a solution of 270 mg (1 mmol) of diol **42** in 5 ml of methylene chloride was added 15 ml of 10% H_2SO_4 (w/v) with vigorous stirring. The two-phase system was stirred vigorously under N_2 for 40 min at room temperature. The layers were separated and the aqueous phase was

extracted with 4 × 50 ml of methylene chloride. The combined methylene chloride extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to give 235 mg (99%) of **43** as an oil which could be crystallized by cooling: mp 54–55 °C; λ_{max} ($CHCl_3$) 2.71, 5.94 μ; δ ($CDCl_3$) 1.6–3.4 (complex, m, 11 containing 2 ca. 3 H singlets at 3.30 and 3.50), 3.8 (d, J = 10 Hz, 1), 4.2 (m, 1), 4.6 (br s, 1), 5.9 (s, 2), 6.1 (d, J_{AB} = 11 Hz, 1), 6.9 ppm (d, d, J_{BA} = 11, , J_{BX} = 5 Hz, 1).

Acetylation of 43. Formation of *dl*-4aα-8aα-Methoxymethyl-4ϵ-acetoxy-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1-(4*H*)-one (44). A solution of 235 mg of **43** in 12 ml of acetic anhydride on 5 ml of pyridine was stirred at room temperature under nitrogen for 20 h. The volatiles were removed by pumping in vacuo to afford 273 mg (99%) of enone acetate **44** as an oil which slowly crystallized in the cold: mp 67.5–68 °C; λ_{max} ($CHCl_3$) 5.79, 5.96 μ; δ ($CDCl_3$) 1.5–3.4 (complex, m, 13 containing 3, ca. 3 H singlets at 2.0, 3.3, and 3.4), 3.7–4.1 (m, 2), 5.8 (m, 3), 6.1 (d, J_{AB} = 10.5 Hz, 1), 6.8 ppm (d, d, J_{BA} = 10.5 J_{BX} = 4.5 Hz, 1).

Anal. Calcd for $C_{15}H_{20}O_5$: *m/e* 280.13107. Found: *m/e* 280.13100.

Conversion of 44 to *dl*-4aα-8aα-Methoxymethyl-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(2*H*)-one (45). To a solution of 0.525 g (1.88 mmol) of acetoxy enone **44** in 40 ml of acetone under CO_2 was added with stirring 90 ml of 0.86 M chromous chloride[20] solution. The mixture was stirred under CO_2 for 45 min whereupon it was extracted with 3 × 100 ml of ether. The combined ether extracts were dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford an oil which was chromatographed on 60 g of silica gel. Elution with 15% ethyl acetate in hexane gave 309 mg (75%) of **45** as an oil (R_f 0.67, 3:2 benzene–ethyl acetate): λ_{max} ($CHCl_3$) 5.77 μ; δ ($CDCl_3$) 1.1–2.6 (m, 3), 3.0 (m, 2), 3.1–1.40 (complex, 3), 3.35 (s, 3), 3.37 (s, 3), 5.4–6.1 ppm (m, 4).

Isomerization of 45. Formation of *dl*-4aα-8aα-Methoxymethyl-5β-methoxy-4a,5,8,8a-tetrahydronaphthalen-1(4*H*)-one (46). To a solution of 123 mg (0.55 mmol) of **45** in 2.5 ml of tetrahydrofuran was added 0.1 ml of concentrated HCl. The reaction mixture was stirred at room temperature under N_2 for 44 h. Analysis by TLC showed the reaction to be complete at this time. The volatiles were removed in vacuo and the residual yellow oil chromatographed on 10 g of silica gel. Elution with 5% ethyl acetate in hexane aafforded 115 mg (94%) of **46** as a crystalline solid: mp 52–53 °C; λ_{max} ($CHCl_3$) 6.00 μ; δ ($CDCl_3$) 1.3–2.6 (complex, 5), 3.0–3.5 (complex, m, 7, containing 2, ca. 3 H singlets at 3.3 and 3.4), 3.9–4.3 (m, 2), 5.8 (s, 2), 6.0 (d, t, J_d = 10, J_t = 2 Hz, 1), 7.0 ppm (d, t, J_d = 10, J_t = 4 Hz, 1); *m/e* 222 (parent).

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