was added $NaBH_4$ (0.50 g, 13.5 mmol), and the suspension was stirred at ambient temperature for 5 h. The product was poured into ice–water, stirred for 10 min, and worked up conventionally to provide the crude product which was purified by chromatography on silica gel. Elution with benzene provided **17a**: 340 mg (95%); mp 130 °C (lit.[45] mp 131–132 °C); NMR (60 MHz) δ 3.05 (s, 3, H_7), 3.25 (s, 3, H_{12}), 3.90 (s, 3, OCH_3), 7.05–8.50 (m, 9, aromatic).

3-Hydroxy-7,12-dimethylbenz[*a*]anthracene (17b). Treatment of **17a** (1.5 g, 5.24 mmol) with lithium thiomethoxide (1 g, 18.5 mmol) in dry dimethylformamide (50 mL) at reflux for 4 h afforded **17b** (1.35 g, 95%) which was purified by passage through a short column of Florisil. A sample crystallized from benzene–hexane (1:1) melted at 169 °C (lit.[45] mp 167–168 °C): NMR (60 MHz) δ 3.05 (s, 3, H_7), 3.30 (s, 3, H_{12}), 7.00–8.50 (m, 9, aromatic).

Oxidation of 1,2-Dihydroxyphenanthrene. A solution of 1,2-diacetoxyphenanthrene (294 mg, 1 mmol) in THF (5 mL) was added to a solution of sodium methoxide (180 mg, 3.3 mmol) in methanol (10 mL), and heated at reflux for 10 min. Workup gave 1,2-dihydroxyphenanthrene which was oxidized directly with $FeCl_3$·$6H_2O$ (2 g, 8 mmol) in dilute (5%) hydrochloric acid (10 mL). The product which separated was immediately washed with water, dried, and chromatographed on silica gel to provide phenanthrene-1,2-dione: 135 mg (63%); mp 207–212 °C (lit.[55] mp 216 °C).

Acknowledgment. This investigation was supported by Grant No. CA 11968 and CA 14599 and Research Contract No. CP 033385 from the National Cancer Institute, DHEW.

Registry No. 1, 655-04-9; 2, 573-12-6; 3, 4733-11-3; 4, 4841-37-6; 5, 60917-41-1; 6, 569-20-0; 7, 74877-24-0; 8, 74877-25-1; 9, 65199-11-3; 10, 70092-13-6; 11, 71964-73-3; 12, 68162-13-0; 13, 60968-10-7; 14, 37994-80-2; 15, 63216-11-5; 16, 66240-01-5; 17a, 66240-02-6; 17b, 57266-83-8; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; naphthalene-1,2-dione, 524-42-5; naphthalene-1,4-dione, 130-15-4; 2-hydroxyanthracene, 613-14-9; 2-hydroxyphenanthrene, 605-55-0; 3-hydroxyphenanthrene, 605-87-8; 3-hydroxybenz[*a*]anthracene, 4834-35-9; 8-hydroxybenzo[*a*]pyrene, 13345-26-1; 4-hydroxy-7,12-dimethylbenz[*a*]anthracene, 14760-53-3; *trans*-1,2-dihydroxy-1,2-dihydronaphthalene, 771-16-4; *trans*-1,2-dihydroxy-1,2,3,4-tetrahydronaphthalene, 14211-53-1; 1,2-diacetoxyanthracene, 74877-26-2; 1,2-diacetoxyphenanthrene, 19551-05-4; *trans*-3,4-dihydroxy-1,2,3,4-tetrahydrophenanthrene, 60967-97-7; 3,4-diacetoxy-7,12-dimethylbenz[*a*]anthracene, 74893-01-9; 3-methoxy-BA, 69847-25-2.

An Approach to Angularly Functionalized Methylhydrindane Systems[1]

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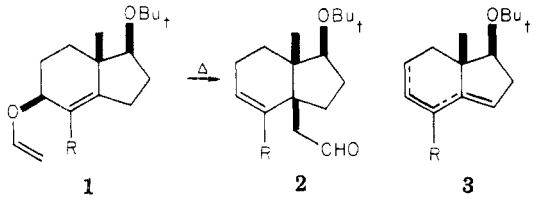
A new version of the Claisen rearrangement utilizing a diosphenol has been developed. This modification attaches an allyl group to the ring juncture of the methylhydrindane system, and other hindered centers, with the retention of the oxygen function on the ring itself.

In recent years a wide variety of natural products have been reported which possess a tricyclic, fused-ring system with a quaternary carbon common to all three rings and approaches toward the preparation of this ring system have been reported by this laboratory.[3,4] In connection with studies directed toward control of the stereochemistry of the quaternary center, the utility of the stereospecific Claisen rearrangement to introduce a functionalized angular group was evaluated.[3] For example, the stereospecific attachment of an acetaldehyde unit to a ring juncture with cis stereochemistry, i.e., 1 to 2, was achieved, and subsequently this reaction sequence was utilized by Boeckman and co-workers[5a] to prepare the natural product gascardic acid (4).[5b,6] The general utility of this thermal rearrangement reaction appears to be limited, however, by irreproducible yields (dienes such as 3 are always found



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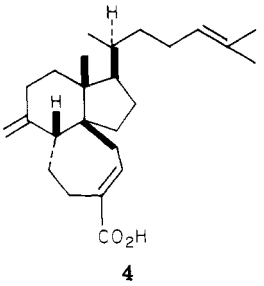

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(1) This work was supported by National Science Foundation Grant CHE-7804811 and by the Hoffmann-La Roche Foundation.

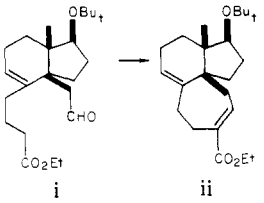
(2) (a) Postdoctoral Fellow, National Research Service Award, National Institute of Health. (b) Postdoctoral Fellow, Swiss National Science Foundation.

(3) Dauben, W. G.; Dietsche, T. J. *J. Org. Chem.* **1972**, *37*, 1212.

(4) Dauben, W. G.; Hart, D. J. *J. Org. Chem.* **1977**, *42*, 3787.

(5) (a) Boeckman, R. K., Jr.; Blum, D. M.; Arthur, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 5060. (b) Boeckman, R. K., Jr.; Blum, D. M.; Arnold, E. U.; Clardy, J. *Tetrahedron. Lett.* **1979**, 4609.

(6) The cyclization of i to ii has been carried out in these laboratories (Dietsche, T. J. Ph.D. Thesis, University of California, Berkeley, 1973).



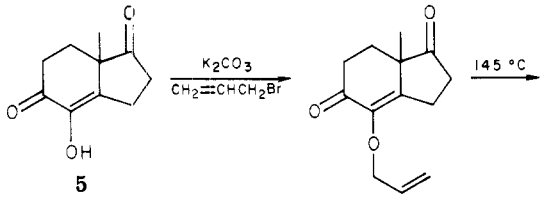
i ii

0022-3263/80/1945-4413$01.00/0

in varying amounts) and by the loss of an oxygen function in the highly substituted ring A.

In this present study, a new version of the Claisen rearrangement utilizing a diosphenol has been developed, a modification which attaches, in high yield, an allyl group to the ring juncture of the methylhydrindane system, and other hindered centers,[7] with the retention of the oxygen function in the ring. Since oxidative fission of an allyl group can produce an acetaldehyde group, this new Claisen rearrangement provides a new route to systems like **2** but which contain two different, and controllable, oxygen functions.

The diosphenol **5**, readily prepared from 2-methyl-1,3-cyclopentanedione and 2-oxo-3-butenyl acetate,[8] was alkylated with allyl bromide to give ether **6** in 84% yield.



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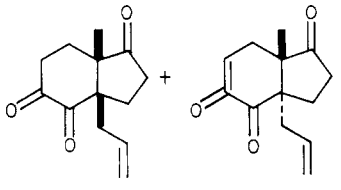

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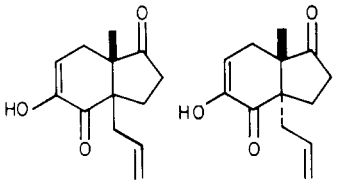
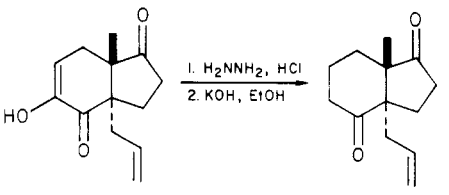


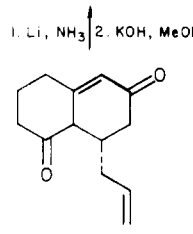
9 10

A solution of ether **6** in 2,6-lutidine was heated at reflux (145 °C) for 6 h to give a 78% yield of angularly allylated diosphenols **9** and **10** in a ratio of 3.2:1, presumably via the triketones **7** and **8**. The diosphenol products were readily separated from any starting material or byproducts by virtue of their solubility in aqueous sodium hydroxide solution[9] and were separated from one another by silica gel chromatography.

A trans ring fusion in the minor isomer **10** was demonstrated by its transformation into diketone **11** which had previously been prepared by Reusch[10] from **12**. Thus, a cis ring fusion was assigned to the major isomer **9**. The related diosphenol allyl ethers **13–15** were prepared to examine what effect (if any) alterations of the nature of the substitution of the oxygen function on the five-membered ring would have on the stereochemical outcome of

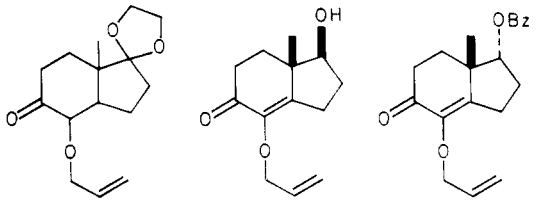


10 11



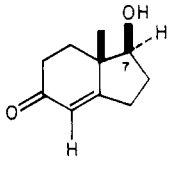
12

the Claisen rearrangement.



13 14 15

The ketal ether **13** was prepared by ketalization and alkylation or vice versa, both routes in low yield,[11] and the thermal rearrangement of **13** proceeded more slowly than that in the case of **6** and produced the cis and trans angularly allylated diosphenols in a ratio of 3:1. The stereochemistry was established by convertiong **9** and **10** to the two isomers. The 7β-alcohol **14** was prepared by sodium borohydride reduction of **5** followed by allylation or vice versa. The 7β configuration of the hydroxyl group in **14** was assigned by comparison of its ^{1}H NMR spectrum to that of the known alcohol **16**.[12] In **16** the C-7 proton was



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found at δ 3.86 (dd, J = 7, 10 Hz) and the angular methyl group resonated at δ 1.17. In **14**, the C-7 proton was found at δ 3.86 (dd, J = 8, 10 Hz) and the angular methyl group resonated at δ 1.16. The rearrangement of **14** in boiling 2,6-lutidine proceeded at a comparable rate to **6** and gave, in 60% yield, the cis and trans angularly allylated diosphenols in a ratio of 3.5:1. The stereochemical assignments

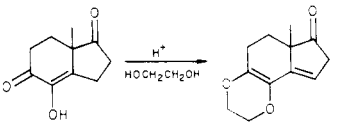
(7) Ponaras, A. A., to be published.

(8) Baggaley, K. H.; Brooks, S. G.; Green, J.; Redman, B. T. *J. Chem. Soc. C* **1971**, 2671.

(9) Diosphenols have a pK_a of about 11: Schwarzenbach, G.; Wittwer, C. *Helv. Chim. Acta* **1947**, *30*, 663.

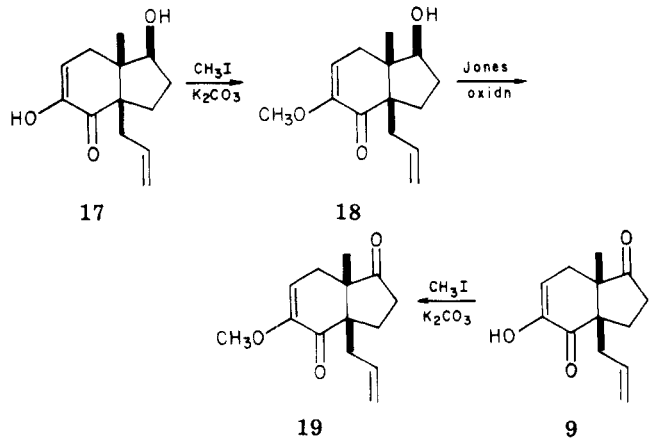
(10) Reusch, W., private communication, Michigan State University. We are grateful to Professor Reusch for a sample of 11. The stereochemical assignment was made by analogy to the result obtained with the related angularly methylated diketone (Grimm, K.; Venkataramani, P. S.; Reusch, W. *J. Am. Chem. Soc.* **1971**, *93*, 269).

(11) The diosphenol array is destroyed under acid ketalization conditions at a rate comparable to the ketalization of the cyclopentanone. Related studies (Robinson, C. H.; Milewich, L. *J. Org. Chem.* **1971**, *36*, 1812 and references therein) suggest the following reaction of the diosphenol under the reaction conditions.



(12) (a) Boyce, C. B.; Whitehurst, J. S. *J. Chem. Soc.* **1960**, 4547. (b) Hajos, Z. G.; Parrish, D. R.; Oliveto, E. P. *Tetrahedron* **1968**, *24*, 2039.

were made by direct chemical correlation with **9** and **10**. For example, the major isomer **17** was methylated to **18** which was oxidized with Jones reagent to yield **19**; methylation of **9** yielded **19**. The trans isomers were correlated in a simlar manner.



The 7a-benzoate **15** was synthesized by alcohol inversion[13] modified by using benzoic acid. Under the standard reaction conditions **15** yielded the cis and trans angularly alkylated diosphenol benzoates in a ratio of 3:1. The stereochemistry assignments were made by conversion to the previously prepared **19** and its related trans isomer.

The thermal rearrangements of **13–15** indicate that functional group alterations at C-7 have little effect on the stereochemical outcome of this type of Claisen rearrangement; approximately a 3:1 cis/trans ratio is obtained in the four methylhydrindane systems examined.

Experimental Section

2-(Allyloxy)-6-methylbicyclo[4.3.0]non-1-ene-3,7-dione (6). A mixture of 35.4 g (0.197 mol) of 2-hydroxy-6-methylbicyclo-[4.3.0]non-1-ene-3,7-dione **5**,[3] 48.3 g (0.399 mol) of 3-bromopropene and 56.0 g (0.405 mol) of anhydrous potassium carbonate in 300 mL of acetone was heated under reflux in a nitrogen atmosphere for 20 h. The mixture was cooled, poured into 800 mL of water, and extracted with 800 mL of ether. The organic layer was washed twice with 400 mL of 5% aqueous potassium hydroxide and with 400 mL of saturated aqueous sodium chloride solution and dried ($MgSO_4$), and the solvent was removed by rotary evaporation to give a brown oil. This oil was filtered through 200 g of silica gel, eluting with a 4:1 hexane–ethyl acetate solution. The solvent was removed by rotary evaporation to give 36.5 g (84%) of a pale yellow oil: IR (film) 1744, 1674 cm^{-1}; NMR ($CDCl_3$) δ 1.32 (s, 3), 1.5–3.4 (m, 8), 4.38 (d, 2, J = 6 Hz), 5.0–5.5 (m, 2), 5.6–6.4 (m, 1); mass spectrum (70 eV), m/e 220 (parent).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.76; H, 7.30.

***cis*- and *trans*-1-Allyl-3-hydroxy-6-methylbicyclo[4.3.0]-non-3-ene-2,7-diones (9 and 10).** A solution of 25.3 g (0.115 mol) of 2-(allyloxy)-6-methylbicyclo[4.3.0]non-3-ene-3,7-dione (**6**) in 100 mL of distilled 2,6-lutidine was heated under reflux in a nitrogen atmosphere for 6.5 h. The cooled solution was poured into 400 mL of ether and extracted with two 120-mL portions of 5% aqueous potassium hydroxide solution, 120 mL of water, and 120 mL of saturated aqueous sodium chloride solution. The combined aqueous layers were washed with carbon tetrachloride (3 × 10 mL), acidified with concentrated hydrochloric acid, saturated with ammonium sulfate, and extracted with three 120-mL portions of chloroform. The organic layer was dried ($MgSO_4$) and concentrated to give 25.0 g of a brown semisolid, which was crystallized from two volumes of methanol to give 12.6 g of tan crystals, pure cis isomer by TLC analysis and NMR. A 405-mg portion of this material was recrystallized from chloroform/hexane to give 275 mg of white prisms: mp 128.5–129.5 °C; UV max (95% ethanol) 276 nm (ϵ 5760) (addition of concentrated potassium hydroxide solution shifts the UV max to 328 nm); IR ($CHCl_3$) 3520, 1742, 1679, 1646, 1414 cm^{-1}; NMR ($CDCl_3$) δ 1.11 (s, 3), 1.5–3.1 (m, 8), 4.7–5.8 (m, 3), 6.03 (dd, 1, J = 3.5, 6); mass spectrum (70 eV), m/e 220 (parent).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.86; H, 7.27.

The material obtained from the methanol recrystallization mother liquor was chromatographed on 250 g of silica gel, using 85:15 hexane–ethyl acetate, to afford an additional 2.2 g (overall yield 58.5%) of the cis isomer, followed by 4.6 g (18%) of the trans isomer, which was recrystallized from methanol to give white prisms: mp 118–119 °C; UV max (95% ethanol) 274 nm (ϵ 4930) (addition of concentrated potassium hydroxide solution shifts the UV max to 327 nm); IR ($CHCl_3$) 3520, 1744, 1684, 1404 cm^{-1}; NMR ($CDCl_3$) δ 1.16 (s, 3), 1.7–3.0 (m, 8), 4.8–5.9 (m, 3), 5.94 (dd, 1, J = 3.2, 6); mass spectrum (70 eV), m/e 220 (parent).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.76; H, 7.29.

***trans*-1-Allyl-6-methylbicyclo[4.3.0]nonane-2,7-dione (11).** A solution of *trans*-1-allyl-3-hydroxy-6-methylbicyclo[4.3.0]non-3-ene-2,7-dione (**10**) (706 mg, 3.4 mmol), 64% aqueous hydrazine (1 mL, 20 mmol), and hydrazine dihydrochloride (354 mg, 3.4 mol) in 34 mL of methanol was heated at reflux under nitrogen for 30 min. The cooled solution was poured into 170 mL of saturated aqueous sodium chloride solution and extracted with ethyl acetate (2 × 170 mL). The dried extracts were evaporated, giving 637 mg of the crude monohydrazone (IR 1682, 1737 cm^{-1}; TLC, no starting material). This material was dissolved in 34 mL of 95% ethanol in a 100-mL round-bottomed flask and the flask was repeatedly evacuated and filled with nitrogen. A 3.4-mL portion of 20% aqueous potassium hydroxide solution was injected and the red solution was heated at reflux under nitrogen for 45 min. The cooled solution was poured into 170 mL of water and extracted with ether (2 × 170 mL). The extracts were washed with aqueous sodium chloride solution, dried, and evaporated to give 0.4 g of an oil. This material was chromatographed on silica gel to afford 160 mg (24%) of **11** as a solid. The solid was recrystallized first from methanol, then petroleum ether, and then, again, methanol, to yield a pure sample: mp 101.0–102.5 °C; IR 1710, 1740 cm^{-1}; NMR ($CDCl_3$) δ 0.96 (s, 3), 1.2–3.0 (m, 12), 4.7–5.0 (m, 1), 5.17 (s, 1), 5.20–6.00 (m, 1); NMR ($CDCl_3/C_6H_6$, 1:1) δ 0.71 (s, 3), 1.4–2.8 (m, 12), 4.6–4.9 (m, 1), 5.00 (s, 1), 5.1–5.8 (m, 1). A sample kindly supplied by Professor Reusch[10] has mp 99–100 °C, mixture mp 99.5–102.0 °C, and all spectra were superimposable.

2-(Allyloxy)-7,7-(ethylenedioxy)-6-methylbicyclo[4.3.0]-non-1-en-3-one (13). A mixture of 1.30 g (7.2 mmol) of **5**, 6.2 g (100 mmol) of ethylene glycol, and 63 mg (0.5 mmol) of oxalic acid dihydrate in 100 mL of toluene was heated to reflux under a Dean–Stark trap for 16 h. The cooled mixture was poured into 200 mL of ether and washed with 10 mL of 20% aqueous potassium bicarbonate solution. The organic layer was extracted with two 100-mL portions of 5% aqueous potassium hydroxide solution. The combined aqueous layers were neutralized with 18 mL of concentrated hydrochloric acid, saturated with ammonium sulfate, and extracted with two 100-mL portions of chloroform. The chloroform extract was dried and concentrated to give 0.76 g of an oil whose NMR spectrum in benzene established it as a 2:1 molar mixture of **5** (36%) and 2-hydroxy-7,7-(ethylenedioxy)-6-methylbicyclo[4.3.0]non-1-en-3-one. This later compound was separated by chromatography on neutral alumina: IR (film) 3430, 1689, 1654 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (s, 3), 1.4–2.9 (m, 8), 3.94 (s, 4), 5.93 (br s, 1); mass spectrum (70 eV), m/e 224 (parent).

A 40-mg portion (0.23 mmol) of the pure ketal was allylated, using the procedure described for the preparation of **6**, to give 27 mg (44%) of **13** as an oil: IR (film) 1674 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 3), 1.4–2.9 (m, 8), 3.94 (s, 4), 4.38 (d, 2, J = 5.5), 5.0–5.4 (m, 2), 5.5–6.3 (m, 1).

2-(Allyloxy)-7β-hydroxy-6β-methylbicyclo[4.3.0]non-1-en-3-one (14). A. By Reduction of 6. To a stirred solution of 16.1 g (73 mmol) of dione **6** in 50 mL of 95% ethanol at 0 °C was added, dropwise during 15 min, 120 mL of a solution of 0.70 g (18.5 mmol) of sodium borohydride in ethanol–water (2:1). The mixture was stirred at 0 °C for 10 min, warmed to room tem-

(13) Bose, A. K.; Lal, B.; Hoffman, W. A.; Manhas, M. S. *Tetrahedron Lett.* **1973**, 1619.

perature, and poured into 500 mL of aqueous saturated sodium chloride solution. The mixture was acidified with 2 mL of concentrated hydrochloric acid and extracted with three 100-mL portions of chloroform. The organic layers were washed with aqueous saturated sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to give 14.7 g (90.5%) of a yellow oil: UV max (95% ethanol) 258 (ϵ 8670); IR (film) 3460, 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.16 (s, 3), 1.5–2.8 (m, 9), 3.86 (dd, 2, J = 8, 10 Hz), 4.36 (d, 2, J = 5.5 Hz), 5.0–5.4 (m, 2), 5.6–6.3 (m, 1); mass spectrum (70 eV), m/e 222 (parent).

The alcohol **14** was further characterized as its benzoate, prepared in the usual manner with benzoyl chloride in pyridine at room temperature in 81% yield: white solid; mp 67–68 °C; IR (film) 3060, 1710, 1665 cm^{-1}; 180-MHz NMR ($CDCl_3$) δ 1.33 (s, 3), 1.9–2.8 (m, 8), 4.43 (dm, 2, J = 5.5Hz), 5.0–5.4 (m, 3), 5.8–6.1 (m, 1), 7.4–7.7 (m, 3), 8.0–8.1 (m, 2).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.45; H, 6.78.

B. By Reduction of 5 Followed by Etherification. To a suspension of 18.0 g (100 mmol) of diosphenol **5** in 75 mL of 95% ethanol was added 25 mL of 20% aqueous potassium hydroxide solution. To the resulting deep amber solution at −10 °C was added 2.0 g (51 mmol) of sodium borohydride. The mixture was stirred at 15 °C for 20 min and poured into 400 mL of aqueous saturated sodium chloride solution. A 12.5-mL portion of concentrated hydrochloric acid was cautiously added and the mixture was extracted with three 400-mL portions of chloroform. The organic layers were dried ($MgSO_4$) and the solvent was removed by rotary evaporation to give 18.0 g (99%) of 2,7β-dihydroxy-6β-methylbicyclo[4.3.0]non-1-en-3-one as an oil: IR (film) 3430, 1733, 1686, 1652 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (s, 3), 1.5–3.2 (m, 9), 3.85 (dd, 1, J = 7.5, 10Hz); mass spectrum (70 eV), m/e 182 (parent).

This diol was characterized as its diacetate, prepared in the usual manner with acetic anhydride in pyridine at room temperature: mp 82–84 °C; IR ($CHCl_3$) 1764, 1743, 1679 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (s, 3), 1.7–2.8 (m, 8), 2.06, 2.18 (2 s, 6), 4.82 (m, 1); mass spectrum (70 eV), m/e 266 (parent), 164 (base).

Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.06; H, 6.77.

A 10-g portion (55 mol) of this diol was allylated, using the procedure used for the preparation of **6**, to give 9.4 g (77%) of **14**.

2-(Allyloxy)-7α-(benzoyloxy)-6-methylbicyclo[4.3.0]non-1-en-3-one (15). A mixture of 1.0 g (4.5 mmol) of the alcohol **14**, 1.3 g (5 mmol) of triphenylphosphine, 0.6 g (5 mmol) of benzoic acid, and 0.9 g (5 mmol) of diethyl azodicarboxylate in 16 mL of toluene was heated under reflux for 15 min. The solvent was removed by rotary evaporation and the mixture was chromatographed on 250 g of silica gel, using 9:1 hexane–ethyl acetate, to give 221 mg (15%) of an oil: IR (film) 3050, 1710, 1670 cm^{-1}; 180-MHz NMR ($CDCl_3$) δ 1.31 (s, 3), 1.7–3.1 (m, 8), 4.47 (dm, 2, J = 5 Hz), 5.2–5.4 (m, 3), 5.9–6.2 (m, 1), 7.4–7.8 (m, 3), 7.9–8.1 (m, 2).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.54; H, 6.76.

A second chromatography fraction contained 730 mg (73%) of recovered alcohol **14**.

Thermal Rearrangement of 2-(Allyloxy)-7α-(benzoyloxy)-6β-methylbicyclo[4.3.0]non-1-en-3-one (15). By use of the procedure described for the preparation of **9** and **10**, 198 mg (0.61 mmol) of the α-allyloxy enone **15** was thermally rearranged to give 162 mg (82%) of a 3:1 mixture of cis-fused and trans-fused diosphenols: 180-MHz NMR ($CDCl_3$) δ 1.08 and 1.15 (2 s, 3) in a 1:3 ratio, 1.5–2.9 (m, 8), 4.9–6.1 (m, 5), 7.3–8.1 (m, 5).

This crude mixture of diosphenols (162 mg, 0.5 mmol) was methylated, using the procedure for the preparation of **18**, to give 90 mg (53%) of a 3:1 mixture of *cis*- and *trans*-1-allyl-7α-(benzoyloxy)-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-ones: NMR ($CDCl_3$) δ 1.07 and 1.13 (2 s, 3) in a 1:3 ratio, 1.5–3.0 (m, 8), 3.30 and 3.61 (2 s, 3) in a 3:1 ratio, 4.8–6.0 (m, 5), 7.3–8.1 (m, 5).

Without purification, 79 mg (0.23 mmol) of this mixture of benzoates in 2 mL of methanol was treated with 5 mL of 5% aqueous potassium hydroxide solution at 60 °C for 40 min to give after the usual workup 36 mg (65%) of a 3:1 mixture of *cis*- and *trans*-1-allyl-7α-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-ones: NMR ($CDCl_3$) δ 0.88 and 0.98 (2 s, 3) in a 1:3 ratio, 1.5–3.0 (m, 8), 3.58 and 3.62 (2 s, 3) in a 3:1 ratio, 4.0 (m, 1), 4.8–6.0 (m, 4).

A 32-mg (0.14 mmol) portion of this crude mixture of alcohols was oxidized with Jones reagent, using the procedure for preparation of **19** (method B), to give 19 mg (59%) of a 3:1 mixture of *cis*- and *trans*-1-allyl-3-methoxy-6-methylbicyclo[4.3.0]non-3-ene-2,7-diones. These products were found identical by NMR and TLC with **19** and its trans-fused isomer prepared independently by another route.

In full completion of the correlation experiments, the same sequence of Claisen rearrangement, methylation, saponification, and Jones oxidation was carried out with the benzoate of the β-alcohol **14** to give, with similar yields as for the α series, a 3:1 mixture of the cis-dione **19** and its trans-fused isomer, *trans*-1-allyl-3-methoxy-6-methylbicyclo[4.3.0]non-3-ene-2,7-dione.

***cis*- and *trans*-1-Allyl-3,7β-dihydroxy-6β-methylbicyclo[4.3.0]non-3-en-2-ones (17 and its Trans-Fused Isomer).** The thermal rearrangement of 5.0 g (22.5 mmol) of 2-(allyloxy)-7β-hydroxy-6β-methylbicyclo[4.3.0]non-1-en-3-one (**14**) was carried out under the same conditions as used for the preparation of **9** and **10** (12 h). The crude product was chromatographed on silica gel to give 2.32 g (46.5%) of the cis-fused isomer **17**, followed by 0.67 g (13.2%) of the trans-fused isomer.

Cis-fused isomer **17**: white crystals; mp 82–84 °C (benzene/isopentane); UV max (95% ethanol) 271 (ϵ 5670) (addition of concentrated potassium hydroxide solution shifts the UV max to 322 nm); IR (film) 3445, 1675, 1653 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (s, 3), 1.2–2.8 (m, 8), 4.05 (m, 1), 4.7–5.6 (m, 3), 5.82 (dd, 1, J = 4, 5.5 Hz); mass spectrum (70 eV), m/e 222 (parent), 137 (base).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.15; H, 7.88.

The diacetate of **17** has mp 88–93 °C.

Trans-fused isomer: oil, IR (film) 3450, 1689, 1679, 1647 cm^{-1}; NMR ($CDCl_3$) δ 1.01 (s, 3), 1.3–2.7 (m, 8), 4.36 (m, 1), 4.7–5.8 (m, 3), 5.88 (dd, 1, J = 3.5, 5.5 Hz); mass spectrum (70 eV), m/e 222 (parent), 137 (base).

The trans-fused isomer was further characterized as its diacetate: mp 73.5–75 °C (diisopropyl ether/hexane); UV max (95% ethanol) 240 (ϵ 5350); IR ($CHCl_3$) 1759, 1733, 1707, 1652 cm^{-1}; NMR ($CDCl_3$) δ 1.04 (s, 3), 1.3–2.6 (m, 6), 2.04 (s, 3), 2.17 (s, 3), 4.7–6.0 (m, 3), 6.25 (m, 1); mass spectrum (70 eV), m/e 306 (parent).

Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.78; H, 7.22.

***cis*-1-Allyl-7,7-(ethylenedioxy)-3-hydroxy-6-methylbicyclo[4.3.0]non-3-en-2-one (Monoketal of 9).** A mixture of 11.0 g (50 mmol) of *cis*-diosphenol **9**, 31 g (500 mmol) of ethylene glycol, and 950 mg (5 mmol) of *p*-toluenesulfonic acid in 500 mL of benzene was heated under reflux, using a Dean–Stark trap, for 2 h. The trap was replaced by a Soxhlet extractor containing calcium hydride in the thimble and the mixture was heated to reflux for 8 h. The mixture was cooled, poured into 500 mL of ether, and washed with 1 L of 1% aqueous potassium bicarbonate solution and 1 L of water. The organic layer was extracted with two 500-mL portions of 5% aqueous potassium hydroxide solution. The aqueous layer was partially neutralized with 80 mL of concentrated hydrochloric acid, saturated with ammonium sulfate, and extracted with two 500-mL portions of chloroform. The organic layer was dried ($MgSO_4$) and concentrated to give 7.4 g of a partly crystalline residue as a 3:4 mixture of ketal and unreacted **9** (by NMR). The mixture was dissolved in a small volume of warm chloroform and chromatographed through 148 g of Woelm alumina (neutral, activity II), using hexane–ethyl acetate (9:1). The first 300 mL of solvent gave 2.13 g of crystalline ketal containing about 15% **9** by NMR. The next 600 mL of solvent gave 1.79 g of a 1:1 mixture of ketal and **9**. Finally, 600 mL of chloroform–methanol (4:1) gave 2.24 g of crystalline recovered **9**. Pure ketal could be obtained by recrystallization from methanol of the first chromatography fraction: mp 107.5–111 °C; UV max (95% ethanol) 272 (ϵ 5700) (addition of concentrated potassium hydroxide solution shifts the UV max to 322 nm); IR ($CHCl_3$) 3500, 1694, 1655 cm^{-1}; NMR ($CDCl_3$) δ 1.11 (s, 3), 1.4–2.7 (m, 8), 3.71 (m, 4), 4.7–5.6 (m, 3), 5.74 (dd, 1, J = 3.5, 5 Hz); mass spectrum (70 eV), m/e 264 (parent), 99 (base).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.12; H, 7.59.

***trans*-1-Allyl-7,7-(ethylenedioxy)-3-hydroxy-6-methylbicyclo[4.3.0]non-3-en-2-one (Monoketal of 10).** A mixture of 2.20 g (10 mmol) of *trans*-diosphenol **10**, 6.2 g (100 mmol) of ethylene glycol, and 95 mg (0.5 mmol) of *p*-toluenesulfonic acid in 100 mL of benzene was heated under reflux with a Dean–Stark trap for 12 h. The mixture was worked up in the same manner as the cis-fused isomer to give 2.3 g of diosphenols as a 3:1 mixture of ketal and **10**. The mixture was chromatographed on 230 g of silica gel to give 1.42 g (54%) of an oil: IR (film) 3480, 1684, 1646 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (s, 3), 1.4–3.0 (m, 8), 3.8 (m, 4), 4.7–5.7 (m, 3), 5.78 (dd, 1, J = 3, 6 Hz); mass spectrum (70 eV), m/e 264 (parent), 99 (base).

***cis*- and *trans*-Allyl-7,7-(ethylenedioxy)-3-hydroxy-6-methylbicyclo[4.3.0]non-3-en-2-one.** The procedure for the preparation of **9** and **10** was used with 27 mg (0.1 mmol) of 2-(allyloxy)-7,7-(ethylenedioxy)-6-methylbicyclo[4.3.0]non-1-en-3-one (**13**) to give 13 mg (50%) of an oil as a 3:1 mixture of the cis- and trans-fused isomers (by NMR) which had been separately prepared by ketalization of **9** and **10**, respectively.

Further confirmation of the 3:1 ratio of cis and trans isomers was obtained by hydrolyzing the above reaction product with aqueous hydrochloric acid which gave a 3:1 mixture by NMR of diosphenols **9** and **10**.

***cis*-1-Allyl-7β-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one (18).** A mixture of 1.16 g (5.2 mmol) of *cis*-1-allyl-3,7β-dihydroxy-6β-methylbicyclo[4.3.0]non-3-en-2-one (**17**), 1.5 g (11 mmol) of anhydrous potassium carbonate, and 1.2 mL (19 mmol) of methyl iodide in 12 mL of acetone was heated under reflux in a nitrogen atmosphere for 12 h. The cooled solution was poured into 50 mL of water and extracted with three 20-mL portions of ether. The organic layer was washed with 20 mL of 5% aqueous potassium hydroxide, dried ($MgSO_4$), and concentrated to give 1.0 g of yellow oil. This oil was rapidly chromatographed on silica gel to give 657 mg (54%) of colorless oil: IR (film) 3480, 1744, 1675, 1644 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (s, 3), 1.1–2.6 (m, 8), 3.56 (s, 3), 3.97 (m, 1), 4.7–5.2 (m, 2), 5.2–5.9 (m, 1), 5.58 (t, 1, J = 2.5 Hz).

***cis*-1-Allyl-3-methoxy-6-methylbicyclo[4.3.0]non-3-ene-2,7-dione (19). A. By Methylation of 9.** The *cis*-diosphenol **9** (40 mg, 0.18 mmol) was methylated, using the same conditions as for the preparation of **18**, to yield 38 mg (90%) of dione **19** as a pale yellow oil: UV max (95% ethanol) 272 (ϵ 4,400); IR (film) 1744, 1677, 1642 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (s, 3), 1.6–3.2 (m, 8), 3.55 (s, 3), 4.9–5.4 (m, 2), 5.4–6.1 (m, 1), 5.72 (t, 1, J = 2.5 Hz); mass spectrum (70 eV) m/e 234 (parent), 165 (base).

B. By Jones Oxidation of 18. To a solution of 300 mg (1.28 mmol) of *cis*-1-allyl-7β-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one (**18**) in 6 mL of acetone was added, dropwise, until persistance of a yellow color, a standard solution of the Jones reagent. The mixture was stirred for 2 min, poured into 30 mL of water, and extracted with 30 mL of ether. The organic layer was washed with aqueous saturated sodium chloride solution, dried ($MgSO_4$), and concentrated to give 245 mg (82%) of **19** as an oil.

***trans*-1-Allyl-7β-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one.** By use of the conditions reported for the preparation of **18**, 55 mg (0.25 mmol) of *trans*-1-allyl-3,7β-dihydroxy-6β-methylbicyclo[4.3.0]non-3-en-2-one gave 27 mg (46%) of an oil: NMR ($CDCl_3$) δ 0.96 (s, 3), 1.2–2.6 (m, 9), 3.60 (s, 3), 4.31 (m, 1), 4.7–5.4 (m, 3), 5.51 (dd, 1, J = 3.5, 5 Hz).

***trans*-1-Allyl-3-methoxy-6-methylbicyclo[4.3.0]non-3-ene-2,7-dione. A. By Methylation of 10.** The *trans*-diosphenol **10** (220 mg, 1.0 mmol) was methylated, using the conditions used for the preparation of **18**, to give 186 mg (80%) of a colorless crystalline solid, which was recrystallized from chloroform/hexane: mp 98–99 °C; IR ($CHCl_3$) 1740, 1699, 1620 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (s, 3), 1.6–2.8 (m, 8), 3.64 (s, 3), 4.7–5.5 (m, 3), 5.62 (dd, 1, J = 5.5 Hz).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.69.

B. By Jones Oxidation. *trans*-1-Allyl-7β-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one (27 mg, 0.11 mmol) was oxidized, using the same conditions employed for the preparation of **19** (method B), to give 22 mg (81%) of a crystalline solid, identical with the material prepared via route A.

Registry No. **5**, 33333-03-8; **6**, 74868-94-3; **9**, 74868-95-4; **9** 7-ethylene ketal, 74868-96-5; **10**, 74868-97-6; **10** 7-ethylene ketal, 74868-98-7; **10** monohydrazone, 74878-01-6; **11**, 74868-99-8; **13**, 74869-00-4; **14**, 74869-01-5; **14** benzoate, 74869-02-6; **15**, 74869-03-7; *cis*-**17**, 74869-04-8; *cis*-**17** diacetate ester, 74869-05-9; *trans*-**17**, 74869-06-0; *trans*-**17** diacetate ester, 74869-07-1; *cis*-**18**, 74869-08-2; *trans*-**18**, 74869-09-3; *cis*-**19**, 74869-10-6; *trans*-**19**, 74869-11-7; 3-bromopropene, 106-95-6; 2-hydroxy-7,7-(ethylenedioxy)-6-methylbicyclo[4.3.0]non-1-en-3-one, 74869-12-8; 2,7β-dihydroxy-6b-methylbicyclo[4.3.0]non-1-en-3-one, 74869-13-9; 2,7β-diacetoxy-6b-methylbicyclo[4.3.0]non-1-en-3-one, 74869-14-0; *cis*-1-allyl-7α-(benzoyloxy)-3-hydroxy-6β-methylbicyclo[4.3.0]non-3-en-2-one, 74869-15-1; *trans*-1-allyl-7α-(benzoyloxy)-3-hydroxy-6β-methylbicyclo[4.3.0]non-3-en-2-one, 74869-16-2; *cis*-1-allyl-7α-(benzoyloxy)-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one, 74869-17-3; *trans*-1-allyl-7α-(benzoyloxy)-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one, 74869-18-4; *cis*-1-allyl-7α-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one, 74869-19-5; *trans*-1-allyl-7α-hydroxy-3-methoxy-6β-methylbicyclo[4.3.0]non-3-en-2-one, 74869-20-8.