phenoxy (*n*-butyl),[19] and 1-pentynyl (*n*-butyl).[20] Alcohols (*S*)-**1** and (*R*)-**3** were prepared from **4b** and **6a** respectively by trichlorosilane cleavage.[21]

Carbamates 4–6. These diastereomers were prepared and separated as previously described.[8] Chromatographic separation of the propargylic carbamate diastereomers is general and facile, increasing in ease for higher members of the series.

(*R*)-1-Heptynyl 3-Acetate (12). To a cold (0 °C) stirred solution of (*R*)-**3** (4 mmol) in diethyl ether (10 mL) was added *n*-butyllithium in hexane (4 mmol). After stirring for 10 min, acetyl chloride (4.2 mmol) was added dropwise and the mixture was stirred for 2 h. The reaction mixture was extracted with 10% $NaHCO_3$ (2 × 10 mL) and dried ($MgSO_4$) and the ether was removed under reduced pressure to afford **12** (95%) as a colorless liquid: NMR (CCl_4) δ 0.9 (triplet, 3, CH_3), 1.4 (multiplet, 4, $CH_2CH_2CH_2CH_3$), 1.7 (multiplet, 2, $HOCHCH_2$), 2.0 (singlet, 3, CO_2CH_3), 2.27 (doublet, 1, C≡CH), 5.2 (dt, 1, HOCH).

Allenes. All allenes were prepared by either (or both) of the procedures described below for the preparation of 1,3-di-*n*-butylallene.

A. Normal Addition. Carbamate **6a,** 1.04 g (3.5 mmol), in diethyl ether (25 mL) was added dropwise over a 10-min period to a stirred solution of di-*n*-butylcuprate (3.5 mmol) in diethyl ether (15 mL) cooled with acetone–dry ice. After being stirred for an additional 7 h at −78 °C, the cooling bath was removed and the reaction mixture was allowed to come to 0 °C, quenched with saturated aqueous NH_4Cl (20 mL), and stirred for 15 min to allow the copper salts to precipitate. The mixture was filtered and the organic layer was separated, washed with saturated aqueous NH_4Cl (20 mL), dried ($MgSO_4$), and concentrated at reduced pressure. Molecular distillation of the residue afforded 0.4 g (76%) of (*S*)-(+)-1,3-di-*n*-butylallene: $[\alpha]^{25}_D$ +54.5° (3.6, $CHCl_3$); IR (film) 1945 cm^{-1} (allene); NMR)ccl$_4$) δ 0.9 (triplet, 6, CH_3), 1.3 (multiplet, 8, $CH_2CH_2CH_2CH_3$), 1.95 (multiplet, 4, C=CCH_2), 4.95 (quintet, 2, HC=C).

B. Inverse Addition. Lithium di-*n*-butylcuprate (3.5 mmol) in diethyl ether (15 mL) cooled to −78 °C was added portionwise over 5 min to cold (−78 °C) stirred solution of carbamate **6a,** 1.08 g (3.5 mmol). The reaction mixture was stirred for 7 h at −78 °C and allene was isolated by a workup identical to that above. (*S*)-(+)-1,3-Di-*n*-butylallene, 0.39 g (74%), $[\alpha]^{25}_D$ +34.7° (5, $CHCl_3$), was obtained.

1,3-Dimethylallene (7). This allene was prepared from **13** as described in Table I. The allene was identical to authentic material by GLPC and gave the same methoxymercuration adduct.[2]

1,3-Diethylallene (8). This allene was prepared in various yields and enantiomeric purities as shown in Table I: IR (film) 1945 cm^{-1} (allene); NMR (CCl_4) δ 1.0 (triplet, 6, CH_3), 2.0 (multiplet, 4, CH_2CH_3), 5.1 (quintet, 2, HC=C).

3,4-Nonadiene (10). This allene was prepared in various yields and enantiomeric purities as shown in Table I: IR (film) 1955 cm^{-1} (allene); NMR (CCl_4) δ 0.97 (triplet, 6, CH_3), 1.32 (multiplet, 4, $CH_2CH_2CH_2CH_3$), 1.9 (multiplet, 4, C=CCH_2), 4.8 (quintet, 2, HC=C).

Acknowledgment. This work has been partially funded by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—(±)-**1,** 65337-13-5; (±)-**2,** 65253-21-6; (±)-**3,** 51586-58-4; (*R*)-**3,** 51703-65-2; (*R*)-1-[1-naphthyl]ethyl isocyanate, 42340-98-7.

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(12) While the origin of this effect cannot be stated with certainty, it may reflect different solution structures for the cuprates.
(13) This small difference between allene enantiomeric purities suggests that structural variation of the chiral amine portion of the carbamate could lead to allenes having still greater enantiomeric purities.
(14) Since the degree of stereospecificity shown by a reaction is a consequence of the energy difference between the diastereomeric transition states, very low activation energies preclude large energy differences between the alternate pathways. When both activation energies are large, the difference between the pathways may be, but is not necessarily, large enough to afford significant stereoselectivity.
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Preparation of *exo*-Tricyclo[3.3.2.0^{2,4}]decan-9-one and Related Compounds

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Synthesis of *exo*-tricyclo[3.3.2.0^{2,4}]decan-9-one (**5**) through efficient (92%) Simmons–Smith reaction of olefinic ketal **4** is described. Efforts to extend this work to ketals **16** and **17** led unexpectedly to selective cyclopropanation anti to the ketal function and formation of **27** and **28,** respectively. Improvements in the preparation of various known intermediates are reported, including a doubling of the yield (to 50%) in oxidation of cycloheptatriene to tropone.

As part of a study of the photochemistry of tricyclic ketones we required *exo*-tricyclo[3.3.2.0^{2,4}]decan-9-one (**5**). In this report we describe convenient preparation of this substance along with other related synthetic transformations. Many of the compounds involved have been recorded previously, but we were able to make material improvements in some earlier preparations, provide two stereochemical assignments, and also uncover two examples of the Simmons–Smith reaction that specifically furnish an unexpected stereoisomer. There have been recent publications in related

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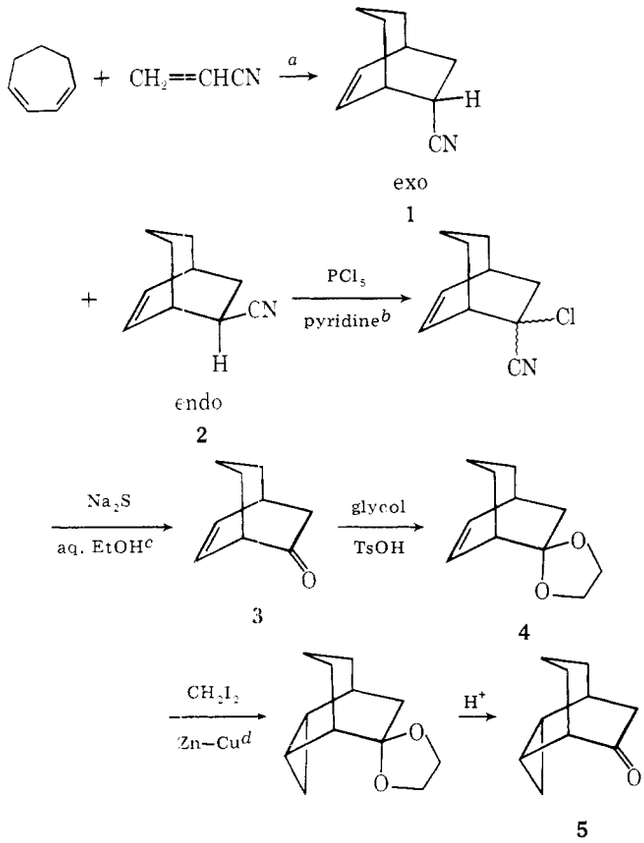
Scheme I

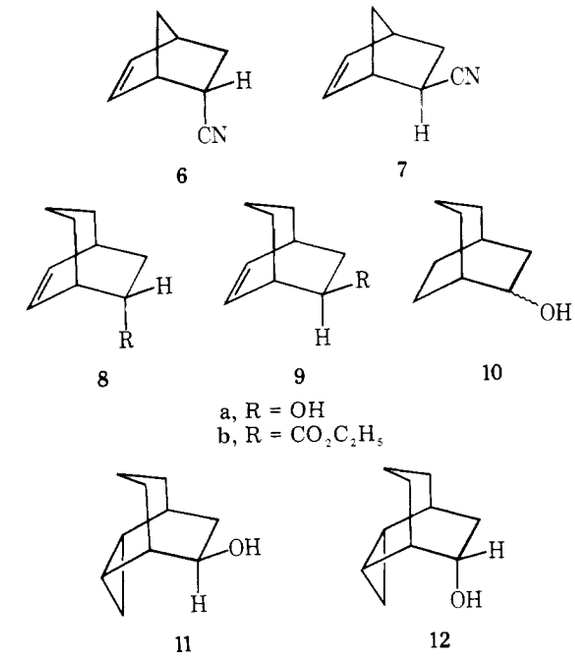


^{a} Reference 3. ^{b} Reference 6. ^{c} Reference 12. ^{d} References 14 and 19.

areas,[1,2] and our observations may be of some general interest. The preparation of **5** is summarized in Scheme I, and only those steps requiring specific comment are discussed below.

We have separated and characterized the two diastereomeric Diels–Alder adducts **1** and **2**, previously known only as a mixture,[3] and assigned their stereochemistry on the basis of differences in their NMR spectra. The olefinic resonance in one (assigned as **2**) appears at δ 6.32 (m, 2 H), while in the other (assigned as **1**) the two protons are shifted downfield and separated, 6.42 and 6.52 (dd, $J_1 = J_2 = 8$ Hz, 1 H, for each signal). A similar spectral difference is seen in the related *endo*- and *exo*-5-norbornene-2-carbonitriles (**6** and **7**, respectively), where the olefinic protons of **6** appear downfield ~0.1 ppm relative to their positions in **7**.[4] In support of this assignment for **1** and **2** is the further observation that the proton α to the cyano group resonates at 2.96 in **1** and at 2.76 in **2**. In the related alcohols the carbinyl proton of **8a** appears 0.17 ppm downfield from that of **9a**. Studies of other bicyclic systems have shown that the relative chemical shift of such protons in epimers is a useful and reliable indication of stereochemistry.[5]

Previous work had shown that for the alcohols **8a** and **9a**, the ethyl esters **8b** and **9b**, and the saturated alcohols **10** the exo isomer (as **8a** and **8b**) is the more stable in each case.[6,7] Attempts to confirm the configurational assignment of **1** and **2** by base-catalyzed equilibration were thwarted, however, since the observed equilibrium mixture contained 50 ± 1% of each isomer. It has been suggested that the controlling factor in determining the relative stability of the two isomers of **10** is the sizable interaction of the hydroxyl group of the endo isomer with hydrogens of the trimethylene bridge.[7] In models it is clear that such interactions in **2** should be much less severe than in **9a** or **9b** because of the cylindrical symmetry of the cyano group. One final point of interest in **1** and **2** concerns

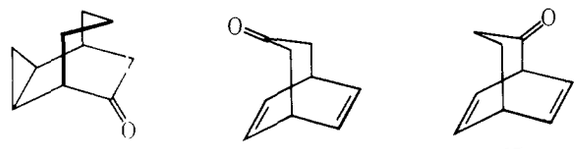


the applicability of the Alder–Stein rules[8] to the Diels–Alder reaction in which they are formed. Alder previously pointed out[9] that the rules worked poorly for the addition of cyclic dienes to acrylonitrile, since the reaction with cyclopentadiene gave **6** and **7** in the ratio 60:40,[10] and since the two adducts with 1,3-cyclohexadiene were formed in essentially equal amounts. This trend is continued in the reaction of acrylonitrile with 1,3-cycloheptadiene; the configurational assignment made above leads to the conclusion that the epimer predicted by the Alder–Stein rules (**1**) is actually the minor product in this case (**1:2** ~ 35:65).

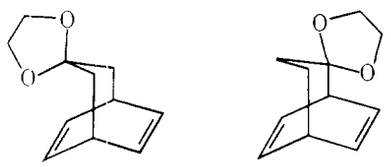
The mixture of nitriles **1** and **2** was converted to ketone **3**[6] through chlorination with phosphorus pentachloride[11] and subsequent hydrolysis in aqueous alcoholic sodium sulfide.[12] In our hands these more recently developed conditions for hydrolysis of the chloronitrile were preferable to the previously employed[6] potassium hydroxide in aqueous dimethyl sulfoxide. In line with observations in related systems,[1,13,14] neither **3** nor the major alcohol formed on its reduction under a variety of conditions, **9a**,[6] was reactive in the Simmons–Smith reaction. Even under forcing conditions, for example, **9a** yielded only a minute amount of **11**.[15] Only in **8a** can the hydroxyl group facilitate cyclopropanation,[14,16,17] and indeed **8a**[6] did react satisfactorily to form **12**. Unfortunately, however, this unsaturated alcohol is not readily available from **3**.[6] A useful solution to this practical problem involved conversion of **3** to its ethylene ketal **4**, which underwent smooth, stereoselective cyclopropanation in 92% yield on treatment with a large excess of zinc–copper couple and methylene iodide.[18] The specific procedure used, which is very convenient since it requires only commercially available zinc–copper, was based on earlier, detailed studies.[19]

Reduction of tricyclic ketone **5** with sodium in alcohol or with lithium aluminum hydride in ether furnished **11** and **12** in the ratio ~3:1, and this correlation provides proof that the inefficient cyclopropanation of **9a** mentioned above proceeds by exo attack.

The efficacious Simmons–Smith reaction of **4**, along with the earlier observations noted above, suggested that an appropriate functional group located on the three-carbon bridge would direct and accelerate cyclopropanation of a bicyclo[3.2.2]nonene from the endo side and thus provide a synthetic approach to the tricyclic ketone **13**. This reasoning led to our preparation of the two isomeric bicyclononenones **14** and **15**, ketones previously described by Baker,[21] and explo-



13 14 15

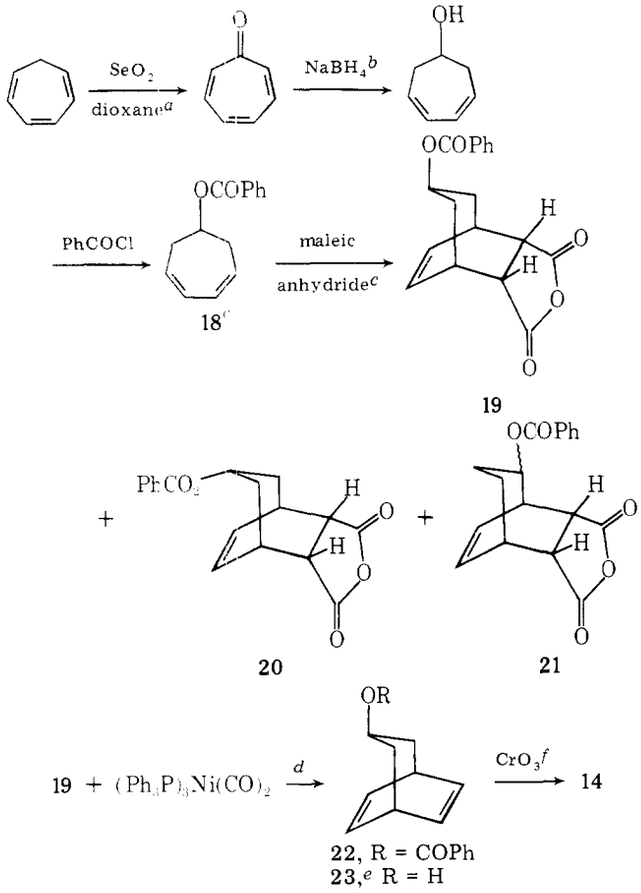


16 17

ration of the Simmons–Smith reaction with the derived ketals **16** and **17**. Preparation of these compounds is shown in Scheme II and makes use of intermediates reported by Baker[21] and others as indicated. Again, only those transformations requiring special comment are discussed below.

The selenium dioxide oxidation of cycloheptatriene to tropone was originally reported to give a 25% yield,[22] and this or a lower yield has been obtained subsequently by others.[21,23] We have reliably obtained a 50% yield in this transformation through use of purified dioxane as solvent, vigorous stirring, and careful control of the reaction temperature at 90 ± 0.5 °C for 21 h; the improvement in yield should enhance the value of this convenient one-step preparation of tropone. We have confirmed the interesting observation first made by Baker[21] that addition of maleic anhydride to **18** furnishes not only the expected adducts **19** and **20**, but also the isomeric adduct **21**. Transformation of one of these adducts (**19**) to dienone **14** is

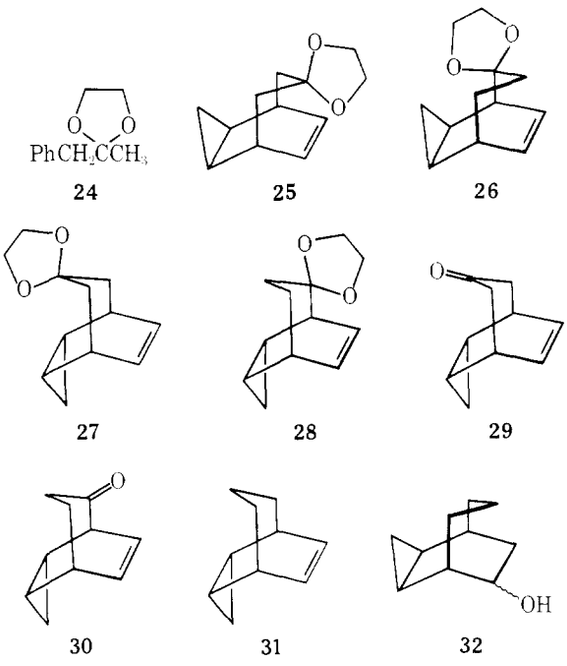
Scheme II



[a] References 21, 22, and 23; see text. [b] Reference 23. [c] Reference 21. [d] Reference 24. [e] From saponification of **22**. [f] Reference 26.

illustrated in Scheme II. For preparative purposes these reactions were also performed on the mixture **19–21** to give both **14** and **15**. Various of the individual steps were carried out on purified materials derived from one or the other of the individual benzoates **19–21**, and the resulting intermediates were identical with those found by Baker.[21] In place of the previously used[21] electrolytic oxidative bisdecarboxylation of these ester anhydrides **19–21**, we found it advantageous to treat them with dicarbonylbis(triphenylphosphine)nickel,[24] a procedure which yielded 92–97% of the desired diene benzoates (as **22**) on a 5-g scale. Ketalization of **14** required particular attention; either excessive acid or prolonged reaction times led to increasing amounts of the ketal of phenylacetone (**24**), through opening of the bicyclic system and aromatization. Mild conditions, either with a quite limited amount of *p*-toluenesulfonic acid or alternatively with pyridinium chloride as catalyst, gave ketal **16** as desired. As is mechanistically reasonable, no similar problem was encountered in ketalization of **15**.

Cyclopropanation of ketals **16** and **17** proceeded to give products originally presumed to be the endo cyclopropanes **25** and **26** respectively. This view was reinforced by the finding that the alcohol **23** failed to undergo the Simmons–Smith reaction under comparable conditions. This latter result seemed reasonable, since the expected dominant conformation of **23** holds the hydroxyl group equatorial and away from both double bonds, as shown. In the reactive ketals, however, the two half-chair conformations of the three-carbon bridge are



equivalent, and one of the double bonds will always have a nearby oxygen atom to facilitate cyclopropanation. The apparent wisdom of these considerations notwithstanding, the Simmons–Smith products from **16** and **17** were shown unequivocally to be **27** and **28** by conversion of each ketal to tricyclic ketone **5**. Ketones **29** and **30** obtained from the ketals underwent Wolff–Kishner reduction to give the same hydrocarbon **31**. A control experiment showed that **30** was thermally stable at 195–200 °C in diethylene glycol, thus ruling out the possibility that the configuration of the three-membered ring was inverted in the course of the Wolff–Kishner reduction. Hydroboration[25] of **31** yielded **11** selectively and **11** was oxidized to **5** using chromic oxide in pyridine.[26] The formal possibility that it is the Simmons–Smith reaction of **4** rather than that of **16** and **17** that leads to the unanticipated stereochemical result may be dismissed on the

basis of the spectroscopic properties of various intermediates. A striking example is the large downfield chemical shift of the methylene protons of the cyclopropane ring of **12** and of the ethylene ketal of **5** in comparison with their position in **11**.[27] No such difference in NMR spectra would be expected for the two epimers represented in **32**.

We conclude then that, although **16** and **17** show reactivity in the Simmons–Smith reaction greater than that expected for unactivated simple olefins, they are exceptional in that the stereochemistry of this process is not that required by intramolecular assistance of the sort seen in **4** and in earlier work by others.[1,14,16,17] It appears that the relative positions of the ketal grouping and double bond in both **16** and **17** are such that this sort of intramolecular assistance in cyclopropanation is unfavorable; the observed enhanced reactivity may be due to a directive effect of the second double bond or to intermolecular assistance, but further information is needed to explain this behavior of **16** and **17** satisfactorily. For the present our observations provide a cautionary note on assignment of stereochemistry solely on the basis of stereoselective Simmons–Smith cyclopropanation.

Experimental Section

Materials and Equipment. All analytical and preparative VPC separations were performed on a Varian Aerograph Model 920 single-column gas chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas at ~65 lb pressure. Injection port and detector temperatures were kept constant at 200–210 and 210–220 °C, respectively. Chromatograms were recorded with a Servo Writer II (Texas Instruments, Inc.) operating at a constant speed of 8 in./h. The following columns were used: A, 16 g of 20% Carbowax 20M, 5 ft; B, 33 g of 20% DEGS, 11 ft; C, 25% QF-1, 10 ft; D, 28 g of SILAR 10-C, 10 ft. All columns were constructed of standard aluminum tubing having $^3/_{16}$-in. i.d. Chromosorb P, mesh 60/80, was used as the solid support in all, except in column C, where chromosorb W, mesh 45/60, was employed. Yields were determined either by weighing the collected fractions or by weighing cutout traces of the peaks. Retention times were measured at the interval between the injection point and the maximum of a given peak. VPC data are reported as follows: retention time in minutes, column temperature in degrees centigrade, flow rate in milliliters per minute. NMR spectra were obtained on a Varian T-60A (60 MHz), or on a Varian HR-220 (220 MHz) spectrometer operating in either continuous wave mode or in Fourier Transform (FT) mode. NMR spectra were recorded in CCl_4 solution containing ~1% tetramethylsilane (Me_4Si) as an internal reference (0 ppm). Infrared spectra (CCl_4 solution) were recorded on a Perkin-Elmer Model 621 grating infrared spectrophotometer. A mass spectrum was obtained on a Du Pont 21-492 double-focusing mass spectrometer with a resolution of 10^4 with an AEI DS-30 data system. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus. Melting points are corrected, and boiling points are reported uncorrected. Solutions were dried over anhydrous Na_2SO_4 or $MgSO_4$. Exceptions to the above are noted.

***exo*- and *endo*-6-Cyanobicyclo[3.2.2]non-8-ene (1 and 2).** A mixture of the epimeric nitriles was prepared in 78% yield as described by Alder.[3] VPC analysis of a crude sample on column A (182 °C, 167 mL/min) indicated two products which were isolated and identified as the following: *endo*-8-cyanobicyclo[3.2.2]non-6-ene (**2**) (14 min, 51%): mp 65.5–67.0 °C; IR 3045 (m), 2933 (s), 2879 (m), 2864 (m), 2243 (m), 1646 (w), 1472 (m), 1465 (m), 1455 (m), 1448 (m), 942 (w), 933 (m), 721 (m), 708 (s), 660 (w) cm^{-1}; NMR (220 MHz) δ 1.44–1.75 (m, 4 H), 1.75–2.08 (m, 3 H), 2.20 (ddd, J = 13.5, 12, 6.5 Hz, 1 H), 2.54 (m, 1 H), 2.67 (m, 1 H), 2.76 (ddd, J = 12, 10, 6 Hz, 1 H), 6.32 (m, 2 H); *exo*-8-cyanobicyclo[3.2.2]non-6-ene (**1**) (20 min, 27%): mp 57.5–58.5 °C; IR 3046 (m), 2935 (s), 2860 (m), 2242 (m), 1654 (w), 1466 (w), 1452 (m), 1448 (m), 941 (m), 713 (s) cm^{-1}; NMR (220 MHz) δ 1.30–1.73 (m, 6 H), 1.98 (ddd, J = 14, 5, 5 Hz, 1 H), 2.21 (ddd, J = 14, 10, 1.5 Hz, 1 H), 2.56 (m, 1 H), 2.78 (m, 1 H), 2.96 (ddd, J = 10, 5, 1.5 Hz, 1 H), 6.42 (dd, J = 8, 8 Hz, 1 H), 6.52 (dd, J = 8, 8 Hz, 1 H).

Equilibration of **1** with a catalytic amount of potassium *tert*-butoxide in THF[28] and subsequent VPC analysis on column A gave equal amounts of **1** and **2** (50 ± 1%).

Bicyclo[3.2.2]non-8-en-6-one (3). A solution of 6-chloro-6-cyanobicyclo[3.2.2]non-8-ene (22.5 g, 124 mmol),[6] $Na_2S{\cdot}9H_2O$ (44.7 g, 186 mmol), and 95% aqueous ethanol (150 mL) was heated at reflux for 17 h.[12] The cooled orange mixture was added to water (200 mL) and extracted with 100 mL of ether (8×). The combined ether extracts were washed with brine and dried. Concentration, followed by sublimation at 115–150 °C (17 mm), gave 8.0 g (47%) of a white solid. The physical and spectroscopic characteristics of **3** were the same as those reported.[6]

***exo*- and *endo*-Bicyclo[3.2.2]non-8-en-6-ol (8a and 9a).** Reduction of **3** (1.00 g, 7.36 mmol) with sodium (7.50 g, 326 mmol), in dry, absolute ethanol (100 mL) and purification by sublimation (aspirator) gave 957 mg (96%) of a white solid. VPC of a crude sample on column A (150 °C, 122 mL/min) indicated complete conversion and two products which were isolated and identified on the basis of their previously reported IR spectra.[6] For *exo*-bicyclo[3.2.2]non-8-en-6-ol (**8a**) (30 min, 35%): NMR (220 MHz) δ 1.22–1.67 (m, 8 H), 2.25 (dd, J = 14.6, 8.2 Hz, 1 H), 2.40 (m, 2 H), 4.08 (d, J = 8.1 Hz, 1 H), 6.00 (dd, J = 8.0, 8.0 Hz, 1 H), 6.19 (dd, J = 8.0, 8.0 Hz, 1 H). For *endo*-bicyclo[3.2.2]non-8-en-6-ol (**9a**) (37 min, 61%): NMR (220 MHz) δ 1.23–1.68 (m, 5 H), 1.68–1.93 (m, 3 H), 2.24 (ddd, J = 14, 10, 7 Hz, 1 H), 2.42 (m, 2 H), 3.91 (ddd, J = 10, 5, 5 Hz, 1 H), 5.92 (m, 2 H).

Bicyclo[3.2.2]non-8-en-6-one Ethylene Acetal (4). A mixture of **3** (4.91 g, 361 mmol), ethylene glycol (10 mL), and *p*-toluenesulfonic acid monohydrate (292 mg) in benzene (200 mL) was heated at reflux with continuous removal of water. Fresh acid (187 mg) was added after 20 h and heating continued for 30 additional h. The mixture was worked up in the usual fashion and distilled to give 6.50 g (100%) of a colorless liquid, bp 77–79 °C (0.80–0.85 mm). A sample purified further by VPC on column A had the following properties: IR 3042 (m), 2929 (s), 2875 (s), 1648 (w), 1446 (m), 1380 (m), 1360 (m), 1198 (m), 1135 (s), 1105 (s), 1039 (s), 967 (m), 948 (m), 844 (m), 712 (s) cm^{-1}; NMR (60 MHz), δ 0.958–2.69 with major absorptions at 1.56, 1.96, 2.29 (m, 10 H), 3.76 (br s, 4 H), 5.91 (m, 2 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.17; H, 8.97.

General Cyclopropanation Procedure. All Simmons–Smith reactions were carried out as reported in the literature,[14] except that a large excess of diiodomethane (Aldrich) and a zinc–copper couple (Ventron-Alfa) were used.[19] In a typical run, a mixture of zinc–copper couple (5–6 equiv) and a few crystals of iodine in anhydrous ether was heated at reflux for ~0.5 h. At the end of this period, a solution of the olefinic compound (1 equiv) and diiodomethane (3–4 equiv) in a small amount of anhydrous ether was added dropwise over 0.5 h. The mixture was heated for 24–48 h, cooled to 0–5 °C, and quenched with saturated aqueous NH_4Cl. The two layers were separated, and the aqueous layer was extracted with ether (3–4×). The combined ether extracts were washed with 10% aqueous Na_2CO_3 and with brine. After drying and concentration, the crude product was purified by distillation or by preparative VPC.

***exo*-Tricyclo[3.3.2.0^{2,4}]decan-*exo*-9-ol (12).** Treatment of **8a** (50 mg, 362 mmol) with diiodomethane (292 mg, 1.09 mmol) and zinc–copper couple (142 mg, 2.17 mmol) in ether (5 mL) for 21 h and purification of the crude product by VPC on column A gave 23 mg (42%) of a white solid: mp 157–161 °C (sealed tube); IR 3620 (m), 3384 (br, s), 3082 (w), 3006 (s), 2923 (s), 1468 (m), 1465 (m), 1448 (m), 1322 (w), 1182 (m), 1086 (w), 1071 (w), 1061 (m), 1033 (s), 1011 (s), 940 (m) cm^{-1}; NMR (220 MHz) δ 0.438 (ddd, J = 8.5, 8.5, 5.5 Hz, 1 H), 0.784 (dddd, J = 13, 8.5, 4.5, 2 Hz, 1 H), 0.903 (dddd, J = 13, 8.5, 4.5, 1.5 Hz, 1 H), 1.26 (ddd, J = 5.5, 4.5, 4.5 Hz, 1 H), 1.32–1.97 (m, 9 H), 2.11 (m, 1 H), 2.23 (m, 1 H), 3.90 (dddd, J = 8, 4, 4, 2 Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.71; H, 10.61.

***exo*-Tricyclo[3.3.2.0^{2,4}]decan-9-one Ethylene Acetal.** A mixture of **4** (2.96 g, 16.4 mmol), diiodomethane (12.9 g, 48.2 mmol), and zinc–copper couple (6.31 g, 96.5 mmol) in ether (40 mL) was treated as described above. Microdistillation gave 2.93 g (92%) of a colorless liquid: bp 106–110 °C (1.4 mm). An analytical sample purified by VPC on column A had the following characteristics: IR 3090 (w), 3014 (m), 3001 (m), 2954 (s), 2931 (s), 2900 (s), 2880 (s), 2856 (m), 1466 (m), 1447 (m), 1437 (m), 1371 (m), 1127 (s), 1108 (s), 1072 (m), 1057 (s), 1043 (m), 1031 (m), 1016 (w), 985 (m) cm^{-1}; NMR (60 MHz, with $CHCl_3$ as internal reference) δ 0.346 (m, 1 H), 0.942 (m, 3 H), 1.27–2.40 with d, J = 4 Hz at 1.72 (m, 10 H), 3.77 (br s, 4 H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.43. Found: C, 74.14; H, 9.50.

Bicyclo[3.2.2]non-8-en-6-one tosylhydrazone was prepared in 90% yield according to a procedure of Cope:[29] mp 195–198 °C (dec); IR ($CHCl_3$) 3294 (w), 3220 (w), 3022 (m), 2937 (s), 2860 (m), 1632 (w), 1598 (w), 1388 (m), 1335 (m), 1166 (s), 1092 (m), 812 (m), 658 (m), 545 (m) cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 0.933–2.02 with major absorption at 1.52 (m, 6 H), 2.02–2.82 with s at 2.42 (m, 7 H), 3.08 (m, 1 H), 6.05 (m, 2 H), 7.22 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.14; H, 6.62; N, 9.21. Found: C, 63.18; H, 6.76; N, 9.24.

Tropone. The procedure used for the preparation of **14** was essentially that of Radlick[22] with the following modifications: Spectral grade dioxane (Scintrex Reagent from J. T. Baker), cycloheptatriene (43.0 g, 97% from Aldrich), and a freshly opened bottle of selenium dioxide (55.0 g, from MCB) were used. The mixture was thermostated at 90 ± 0.5 °C (oil bath) with vigorous stirring for 21 h. Distillation on a simple head gave a small amount of cycloheptatriene and 24.1 g (50%) of a pale yellow liquid: bp 110 °C (11 mm) [lit.[14] bp 91–92 °C (4 mm)]. The yield was found to be reproducible on this scale.

3-Benzoyloxybicyclo[3.2.2]nona-6,8-diene (22). Anhydride **19** (5.00 g, 16.0 mmol)[21] was treated with dicarbonylbis(triphenylphosphine)nickel (20.5 g, 32.1 mmol) in dry diglyme (200 mL) at vigorous reflux for 65 h.[24] The cooled, black mixture was concentrated in vacuo, diluted with chloroform (200 mL), and filtered through Celite. Chloroform was removed and the yellow-green residue was diluted with pentane (1000 mL) to precipitate unreacted starting material and/or impurities. The solution was filtered, and the filtrate was washed with 200 mL of water (3×), dried, and concentrated. The yellow semisolid was dissolved in a small amount of 7:3 (v:v) petroleum ether/benzene and chromatographed over a 44 × 4 (i.d.) cm silica gel (activity I, 260 g) column to give 17.8 g (87% recovery) of the catalyst (eluted with 1500 mL of 7:3 petroleum ether/benzene) and a white solid (eluted with 1500 mL of benzene) which after drying at 40 °C (0.1 mm) weighed 3.55 g (92%); the melting point and spectral characteristics were the same with those reported for **22**.[21] In another run using twice the amount of catalyst indicated above while keeping the other reagents constant, a 97% yield of **22** was realized.

In similar fashion mixtures of **19** and the isomeric 2-benzoate anhydride yielded **22** and the 2-benzoate diene. Purification of the latter product by preparative VPC gave material identical with that previously reported.[21]

Bicyclo[3.2.2]nona-6,8-dien-3-one Ethylene Acetal (16). Ketone **14** obtained by hydrolysis of **22** and subsequent oxidation[21] was ketalized with minimal rearrangement by treatment (3.44 g, 25.6 mmol) with ethylene glycol (10 mL) using pyridinium chloride (304 mg) as catalyst[30] in benzene (75 mL) for 39 h. Distillation gave 3.76 g of a colorless liquid (82%): bp 64–65 °C (0.40 mm). VPC on column A (150 °C, 109 mL/min) revealed three peaks identified as starting **14** (30 min, 4.4%), **24** (35 min, 8.1%), and **16** (54 min, 70%). For **16:** IR (CS_2) 3047 (m), 2947 (s), 2928 (s), 2873 (m), 1610 (w), 1372 (m), 1361 (w), 1157 (m), 1101 (s), 1068 (m), 1058 (m), 948 (m), 780 (s) cm^{-1}; NMR (60 MHz) δ 1.72, (d, J = 4 Hz, 4 H), 3.02 (m, 2 H), 3.69 (s, 4 H), 6.15 (m, 4 H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.25; H, 7.98.

Ketalization was also carried out successfully using very small amounts of *p*-toluenesulfonic acid and by controlling the reaction period. However, use of ordinary conditions and amounts of this acid led to a 78% yield of **24**, acid hydrolysis of which gave phenylacetone.

Bicyclo[3.2.2]nona-6,8-dien-2-one Ethylene Acetal (17). A 52:48 mixture of **14** and **15**[21] (3.32 g, 24.7 mmol) was treated with ethylene glycol (7.0 mL) and *p*-toluenesulfonic acid (203 mg) in benzene (150 mL) for 24 h. Concentration of the solution gave 3.89 g (88%) of a viscous oil. VPC on column D (150 °C, 71 mL/min) indicated **24** (51 min, 48%) and **17** (82 min, 40%). For **17:** IR (CS_2) 3045 (m), 2955 (s), 2926 (s), 2873 (s), 1609 (w), 1372 (m), 1352 (m), 1296 (m), 1282 (m), 1222 (m), 1129 (m), 1098 (s), 1067 (s), 1055 (m), 1033 (m), 950 (s), 909 (m), 895 (m), 725 (s), 693 (m), 671 (m), 658 (m) cm^{-1}; NMR (60 MHz) δ 1.28–1.97 (m, 4 H), 2.88 (m, 2 H), 3.75 (br s, 4 H), 6.08 (m, 4 H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.12; H, 7.87.

***exo*-Tricyclo[3.3.2.0^{2,4}]dec-9-en-7-one Ethylene Acetal (27).** A mixture of **16** (413 mg, 2.32 mmol), diiodomethane (2.48 g, 9.27 mmol), and zinc–copper couple (0.91 g, 14 mmol) in ether (15 mL) was heated at reflux for 24 h. VPC on column A (initial column temperature 150 °C, raised to 170 °C after 90 min, 109 mL/min) showed three peaks, two of which were identified as **24** (35 min, 7.1%) and **27** (77 min, 68%); the third (127 min, 25%) remains unidentified. Preparative VPC gave 193 mg (43%) of **27:** IR (CS_2) 3074 (w), 3037 (m), 3002 (m), 2970 (m), 2943 (s), 2916 (s), 2871 (m), 1154 (m), 1113 (s), 1094 (s), 1052 (m), 1029 (s), 828 (s), 764 (m), 752 (m) cm^{-1}; NMR (60 MHz) δ 0–0.583 (m, 2 H), 1.10 (m, 2 H), 1.88 (d, J = 4 Hz, 4 H), 2.55 (m, 2 H), 3.78 (br s, 4 H), 5.66 (m, 2 H).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.21.

***exo*-Tricyclo[3.3.2.0^{2,4}]dec-9-en-7-one (29).** Hydrolysis of **27** (30.5 mg, 0.159 mmol) with an equivolume solution of 10% aqueous HCl–methanol, followed by preparative VPC on column A, gave 14.5 mg (62%) of a white solid: mp 46–49 °C (sealed tube); IR (CS_2) 3077 (w), 3042 (m), 3007 (s), 2912 (s), 1698 (s), 1411 (m), 1385 (m), 1327 (m), 1191 (m), 1153 (m), 1032 (s), 1028 (s), 829 (s), 814 (w), 779 (m), 722 (m) cm^{-1}; NMR (60 MHz) δ 0.062–0.612 (m, 2 H), 1.14 (m, 2 H), 2.51 (m, 4 H), 2.71 (m, 2 H), 5.84 (m, 2 H).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.81; H, 8.16.

***exo*-Tricyclo[3.3.2.0^{2,4}]dec-9-en-6-one Ethylene Acetal (28).** Cyclopropanation of **17** (430 mg, 2.41 mmol) was carried out as for **16.** An analytical sample purified by VPC on column A had the following properties: IR (CS_2) 3076 (w), 3041 (m), 3003 (m), 2953 (m), 2912 (s), 2874 (s), 1290 (m), 1115 (s), 1100 (s), 1088 (s), 1061 (s), 1043 (m), 1034 (m), 956 (s), 881 (m), 827 (m), 740 (m), 719 (m) cm^{-1}; NMR (60 MHz) δ 0.117–0.617 (m, 2 H), 0.617–1.38 (m, 2 H), 1.38–2.28 (m, 4 H), 2.53 (m, 2 H), 3.83 (br s, 4 H), 5.60 (m, 2 H).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.00; H, 8.24.

***exo*-Tricyclo[3.3.2.0^{2,4}]dec-9-en-6-one (30).** Crude **28** was hydrolyzed to give (after purification by VPC on column A) 266 mg of a white solid (74%, based on **17**): mp 33–35 °C (sealed tube); IR (CS_2) 3076 (w), 3042 (m), 3004 (m), 2952 (m), 2922 (s), 2859 (m), 1701 (s), 1412 (m), 1226 (m), 1160 (m), 1151 (m), 1032 (m), 1027 (m), 889 (m), 881 (m), 727 (m), 722 (m), 702 (s) cm^{-1}; NMR (60 MHz) δ 0.500 (m, 2 H), 1.18 (m, 2 H), 2.00 (m, 2 H), 2.65 (m, 3 H), 3.10 (m, 1 H), 5.75 (m, 2 H).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.02; H, 8.15.

***exo*-Tricyclo[3.3.2.0^{2,4}]dec-9-ene. (31). A. From 29.** The modified Wolff–Kishner reduction[31] of **29** (231 mg, 1.56 mmol), followed by VPC purification on column A, gave 180 mg of a white solid (86%): mp 78–80.5 °C (sealed tube); IR (CS_2) 3073 (w), 3033 (m), 3000 (s), 2915 (s), 2851 (s), 1652 (w), 1432 (w), 1384 (m), 1323 (m), 1108 (w), 1094 (w), 1059 (m), 1040 (w), 1027 (m), 923 (m), 875 (m), 831 (m), 748 (m), 726 (w), 713 (s), cm^{-1}; NMR (60 MHz) δ 0.012–0.595 (m, 2 H), 0.920 (m, 2 H), 1.48 (m, 6 H), 2.50 (m, 2 H), 5.50 (m, 2 H).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.42; H, 10.38.

B. From 30. Similar treatment of **30** (241 mg, 1.63 mmol) and purification gave 162 mg of **31** (74%). In a control experiment, no change was observed in **30** after heating it in diethylene glycol at 195–200 °C for 1.5 h.

***exo*-Tricyclo[3.3.2.0^{2,4}]decan-*endo*-9-ol (11). A. From 31.** Hydroboration of **31** (742 mg, 5.53 mmol) with diborane in THF[25] gave 0.80 g of a white solid. A small sample (purified by VPC on column A) and a large excess of bis(trimethylsilyl) acetamide were sealed in a tube and heated at 75–78 °C (oil bath) for 40 h. The cooled tube was unsealed; the solution was shaken with water (~10 min) and extracted with ether (4×). The combined ether extracts were washed with water and brine, and dried. Removal of ether gave a viscous oil which was purified by VPC on column B and subsequently hydrolyzed. An analytical sample purified by VPC on column B had the following characteristics: mp 177–179 °C (sealed tube); IR 3620 (m), 3418 (br, s), 3078 (w), 3007 (s), 2929 (s), 1469 (m), 1461 (m), 1447 (m), 1217 (w), 1085 (s), 1071 (s), 1061 (m), 1025 (m), 1009 (s), 994 (m), 946 (m) cm^{-1}; NMR (220 MHz) δ 0.379 (m, 2 H), 0.902 (m, 2 H), 1.19–2.10 (m, 9 H), 1.83 (m, 2 H), 3.76 (ddd, J = 10, 6, 4, Hz, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.77; H, 10.58.

B. From 9a. A mixture of **9a** (102 mg, 0.738 mmol), diiodomethane (592 mg, 2.21 mmol), and zinc–copper couple (289 mg, 4.42 mmol) in ether (10 mL) was heated at reflux for 63 h. Preparative VPC on column A (168 °C, 162 mL/min) gave 19 mg of two unidentified products A (9.4 min) and B (10 min), 24 mg of starting **8b** (16 min) and 4.9 mg (5.7% yield, based on unrecovered **9a**) of a white solid (33 min). The IR and NMR spectra of the latter, were identical with those of **11** described above.

***exo*-Tricyclo[3.3.2.0^{2,4}]decan-9-one (5). A. From its Ethylene Acetal.** The acetal (2.90 g, 14.9 mmol) was hydrolyzed with 10% aqueous HCl–methanol solution. Preparative VPC on column A gave 2.09 g of a white solid (93%): mp 141–142 °C; IR 3072 (w), 3009 (m), 2929 (s), 2862 (m), 1717 (s), 1461 (m), 1443 (m), 1412 (m), 1380 (w), 1342 (w), 1313 (w), 1214 (m), 1187 (w), 1088 (m), 1024 (m) cm^{-1}; NMR (220 MHz, $CHCl_3$ as internal reference) δ 0.329 (m, 1 H), 0.471 (ddd, J = 8, 8, 6.5 Hz, 1 H), 1.06 (m, 2 H), 1.23–2.16 with d, J = 4 Hz, at 1.93 (m, 8 H), 2.34 (m, 1 H), 2.65 (m, 1 H); mass spectrum m/e 150.1026 (M^+, calcd for $C_{10}H_{14}O$, 150.1044).

B. From 12. Oxidation[26] of **12** (279 mg, 1.83 mmol) followed by VPC isolation on column A gave 212 mg of a white solid (77%) which had identical melting point and spectral characteristics with those of **5** described above.

C. From 11. Similarly, crude **11** (0.80 g) from hydroboration of **31** was oxidized[27] to 664 mg of **5** (80%, based on **31**).

Reduction of 5. A. With Sodium in Ethanol. Ketone **5** (196 mg, 1.30 mmol) was reduced with sodium (1.34 g, 58.2 mmol) in dry, absolute ethanol (15 mL), as described above for **3**. The crude sample was purified by VPC on column A to give 167 mg (one peak) of **11** and **12** (84%), treatment of which with bis(trimethylsilyl) acetamide (see above) gave a viscous liquid. VPC on column B (110 °C, 71 mL/min) indicated two products, A (50 min, 76%) and B (54 min, 24%). Each product was isolated and hydrolyzed to the corresponding alcohol. The IR spectra of the alcohols from A and B were identical with those of **11** and **12**, respectively.

B. With Lithium Aluminum Hydride. Ketone **5** (188 mg, 1.25 mmol) was reduced with excess lithium aluminum hydride in ether to give a white solid which after purification by VPC on column A weighed 144 mg (76%). Analysis via the trimethylsilyl ethers as described above indicated **11** (73%) and **12** (27%).

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Registry No.—**1**, 65311-25-3; **2**, 65375-83-9; **3**, 29415-86-9; **4**, 65311-26-4; **5**, 65311-27-5; **8a**, 29577-00-2; **8b**, 23217-50-7; **9a**, 30365-09-4; **11**, 65311-28-6; **12**, 65375-84-0; **14**, 26788-91-0; **15**, 26760-27-0; **16**, 65311-29-7; **17**, 65311-30-0; **19**, 63072-75-3; **22**, 65311-31-1; **24**, 4362-18-9; **27**, 65311-32-2; **28**, 65311-33-3; **29**, 65366-49-6; **30**, 65311-34-4; **31**, 65311-35-5; 6-chloro-6-cyanobicyclo[3.2.2]non-8-ene, 29415-85-8; ethylene glycol, 107-21-1; *exo*-tricyclo[3.3.2.0^{2,4}]decan-9-one ethylene acetal, 65311-36-6; bicyclo[3.2.2]non-8-en-6-one tosylhydrazone, 65311-37-7; tropone, 539-80-0; cycloheptatriene, 544-25-2.

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Stereoselective Total Syntheses of the Fungitoxic Hydroquinones (±)-Zonarol and (±)-Isozonarol

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Stereoselective and regioselective total syntheses of two naturally occuring fungitoxic hydroquinones (±)-zonarol (**1b**) and (±)-isozonarol (**2b**) are described. The key features of these syntheses are: (a) the dehydration of tertiary alcohol **6** to alkene **7** without rearrangement utilizing dimethyl sulfoxide at 155 °C; (b) the conjugate addition of 2,5-dimethoxyphenylmagnesium bromide Grignard reagent to enone **9b**; and (c) ether cleavage of compounds **1a** and **2a** utilizing lithium *n*-butyl mercaptide in hexamethylphosphoric triamide at 150 °C for 24 h to afford the respective natural products.

The two naturally occurring fungitoxic hydroquinones zonarol (**1b**) and isozonarol (**2b**) were isolated from brown seaweed *Dictopteris undulata* found in the Pacific Ocean near Southern California and the Gulf of California.[1-3] The structure and absolute stereochemistry of these merosesquiterpenoids[4] were rigorously defined by degradation and spectroscopy.[1-3] These two marine natural products were found to be active against the following pathogenic fungi: *Phytophthora cinnamoni, Rhizoctonia solani, Sclerotinia sclerotiorum,* and *Sclerotium rolfsii.*[1] We wish to report,

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