decoupling of the fully coupled measurement obtained from a pulse routine that produces some nuclear Overhauser enhancement. The pulse width (H_1 field) in typical experiments was 2–25 σ, where a 42-μs pulse is equivalent to a 90° pulse. Acquisition times were between 0.3–0.8 s with pulse delays of 0–9 s depending on the experiment. The total number of transients for a suitable signal to noise ratio for each absorption varied from 100 to 7000 passes. The radio frequency was 25.16 MHz with the absorption referenced from 5% enriched external Me_4Si.

Acknowledgment. The National Institutes of Health are gratefully acknowledged for their support of this work.

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Studies on Terpenes. 5. Synthesis of (+)-Hinesol and (+)-10-Epihinesol

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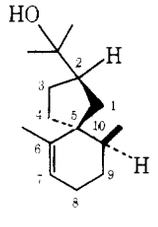
Received December 1, 1977

(−)-β-Pinene was converted into 9-methyl-6-carboethoxymethyl-7-oxatricyclo[4.3.0.0^{3,9}]nonane (**12**, R = H) which was homologated to the ester **15**. The ester **15** was rearranged to the diacetate **16** which on further elaboration gave **31**. Fragmentation of **31** as outlined (**9** → **10**) gave the spiro[4.5]decane **32**, which was readily transformed into a mixture of (+)-hinesol and 10-epihinesol. The synthesis correlates (−)-β-pinene with (+)-hinesol.

Since the revision of the structures of the vetivane sesquiterpenes[3] from hydroazulenes to spiro[4.5]decane skeletal types,[4] many syntheses of this unusual class of terpenes have been reported.[5] Only one synthesis of optically active spiro[4.5]decanes has been described.[6] Here we report the synthesis of (+)-hinesol (**1**)[23] from (−)-β-pinene as part of our



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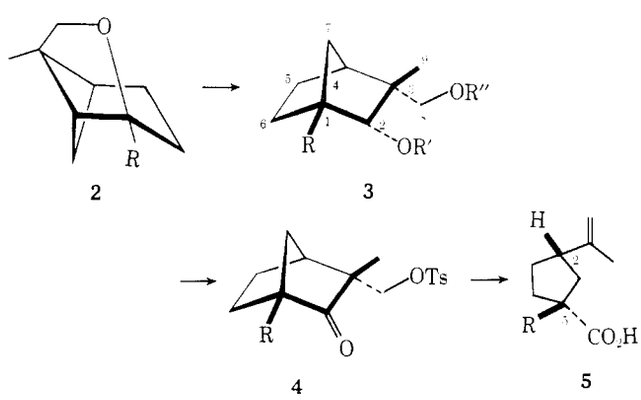
general program that led to the conversion of (−)-β-pinene into grandisol.[7]

The overall strategy of our approach was established by the observation that certain 7-oxatricyclo[4.3.0.0^{3,9}]nonane derivatives **2** can be rearranged to 8-substituted 1,3,3-trimethylnorbornane derivatives **3**. Subsequent fragmentation of the compound **4** to a cyclopentane derivative **5** provides a simple, yet effective way of establishing the correct absolute configuration at C-2 and C-5 in hinesol.[7,8] Scheme I summarizes this strategy. To provide a synthesis of (+)-hinesol (**1**) the substituent R in **2** must be capable of being elaborated to eventually become part of the cyclohexene ring of **1**.

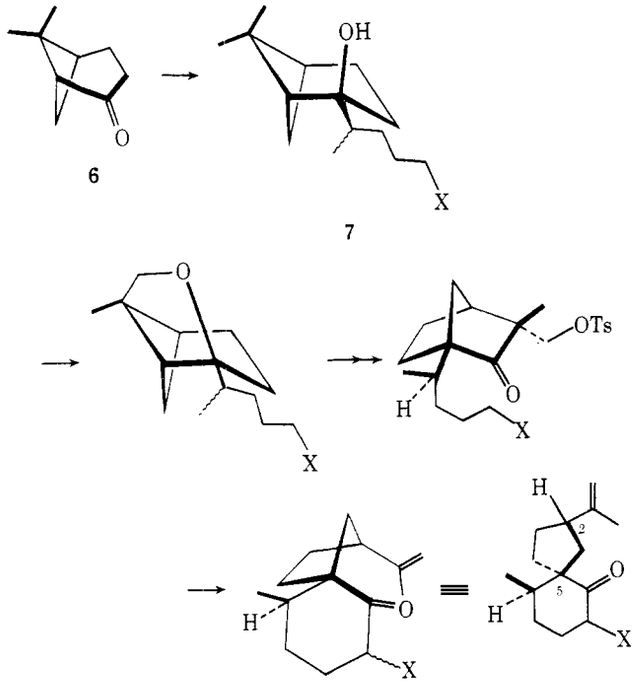
The standard method of preparing 7-oxatricyclo[4.3.0.0^{3,9}]nonane derivatives[8,9] **2** involves the addition of Grignard reagents or organolithiums to (+)-nopinone (**6**) and subsequent intramolecular oxidation of the resulting products **7** to the ethers **2**. All attempts to introduce a suitable R group that contained all the requisite carbon atoms, namely a C_5 unit, were unsuccessful.[10] Extension of Scheme I to the spe-

Scheme I



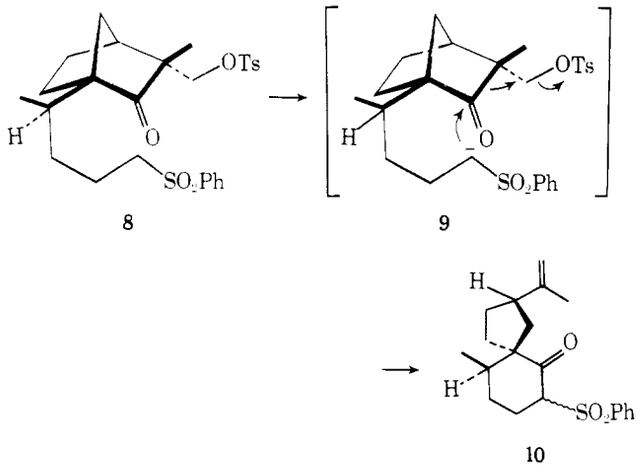
2 3 4 5

Scheme II

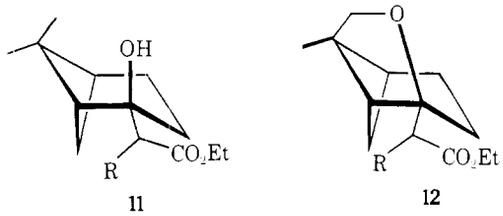


cific case where R is a group that can eventually provide (+)-hinesol is outlined in Scheme II.

The group X must be capable of supporting an adjacent negative charge, and for this purpose we chose the phenylsulfonyl group (X = SO_2Ph) for the following reasons: it is stable to oxidation; and it can be removed under mild conditions that do not reduce carbonyl groups. The overall strategy outlined in Scheme II can be extended to the specific objective of synthesizing **8** and examining its conversion via the anion **9** into **10**. Since we had to build the five-carbon side chain

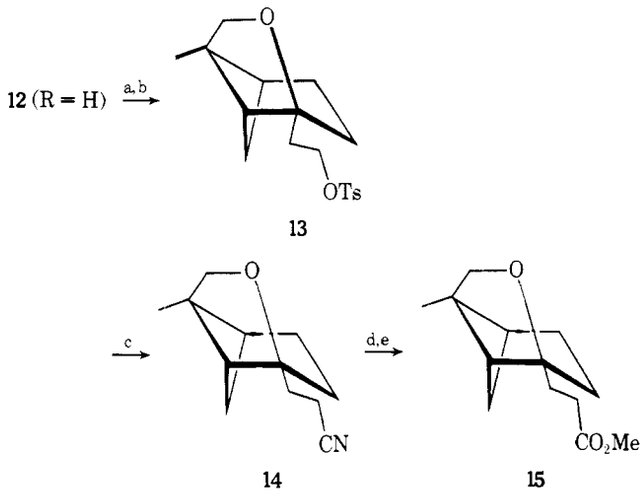


stepwise, a suitable starting material is **11** (R = H), which is conveniently prepared by a Reformatsky reaction on (+)-nopinone using ethyl bromoacetate.[11] Intramolecular oxidation (I_2/HgO/$h\nu$) of **11** (R = H) gave the required ether **12** (R



= H)[9] in excellent yields. Efforts to introduce the *sec*-methyl group at the eventual C-10 by the Reformatsky reaction between (+)-nopinone (**6**) and ethyl α-bromopropionate gave the β-hydroxy ester **11** (R = Me), but treatment of **11** (R = Me) with I_2/HgO/$h\nu$ gave mainly radical fragmentation to (+)-nopinone with only small amounts of the ether **12** (R = Me) being present.

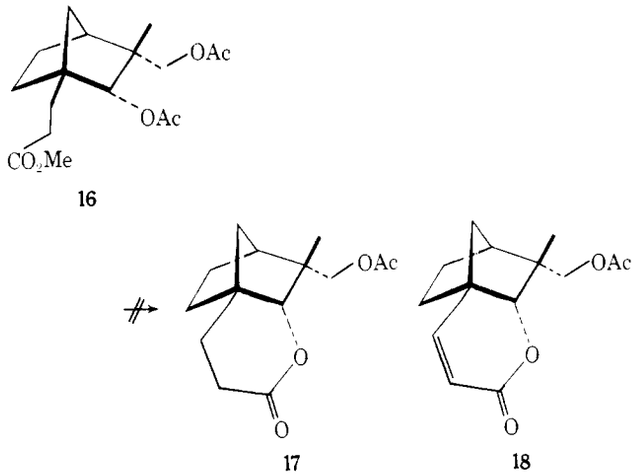
Scheme III



(a) $LiAlH_4$/THF (68–82%); (b) TsCl/pyridine (74–98%); (c) NaCN/Me_2SO (78–91%);[12] (d) NaOH/H_2O/EtOH (73–98%);[13] (e) MeOH/resin IR-120(H) (80–91%).

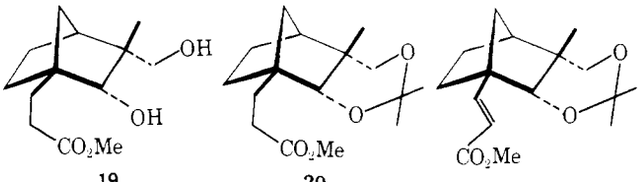
The ether **12** (R = H) was converted into the homologous ester via standard procedures (Scheme III). The cited yields represent the low end and high end of a number of preparations, both on a small and large scale.

When the ester **15** was exposed to BF_3·OEt_2 at 0 °C in acetic anhydride the rearranged ester diacetate **16** was formed in excellent yield (90–100%).[8] All efforts to convert **16** into the lactone **17** were unsuccessful. The lactone **17** might have provided a stereospecific method of introducing the methyl

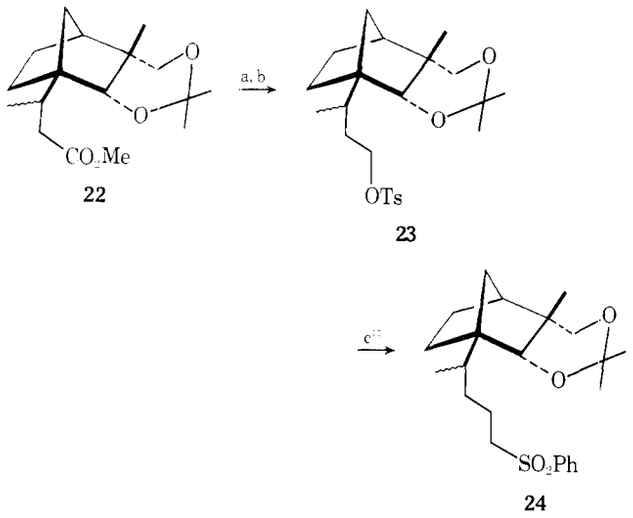


group at C-10 via conjugate addition (Me_2CuLi) to the dehydro lactone **18** (exo approach).

Hydrolysis of the diacetate **16** using sodium methoxide in methanol gave the ester diol **19** in mediocre yield (49%), whereas treatment of the diacetate **16** with methanolic sulfuric acid gave **19** in 96% yield. The 1,3-dihydroxy system in **19** was protected as the acetonide derivative **20**,[14] which was con-

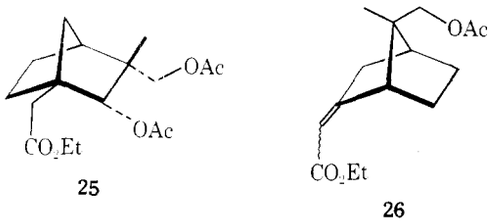


Scheme IV



(a) $LiAlH_4$/THF (94–100%); (b) TsCl/pyridine (95–100%); (c) $PhSO_2Me/NaH/Me_2SO$ (68–69%).

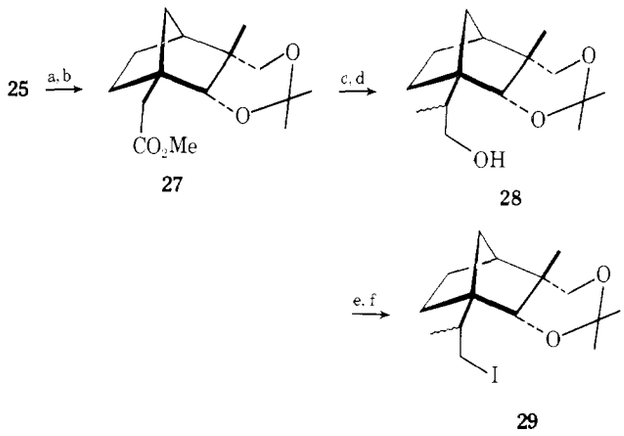
verted into the α,β-unsaturated ester **21** using LDA/$(PhSe)_2/NaIO_4$.[15] The only product formed in this dehydrogenation sequence was the trans isomer (96%). The α,β-unsaturated ester **21**, on treatment with dimethylcopperlithium[16] in ether, gave **22** as a 1:1 mixture of epimers at C-10 as judged from the relative intensities of the NMR signals for the methyl group (C-10) at τ 9.1 and 9.05 (J = 6 Hz). All attempts to separate the epimers were unsuccessful. The ester **22** was converted into the sulfone **24** by the sequence of reactions outlined in Scheme IV. While the above described route to **24** is efficient in terms of yield for each individual step, resulting in an overall yield from **11** (R = H) to **24** of 26.5%, the number of stages is large, namely 14. Consequently we sought a shorter route from **11** (R = H) to **24**. The cyclic ether **12** (R = H) was reacted with acetic anhydride/boron trifluoride etherate at 0 °C for 15 min to give the rearranged product **25**.



Longer reaction times led to further rearrangement resulting in **26**. The diacetate **25** was converted through the sequence of reactions in Scheme V into **29**. The iodide **29** was treated with lithium wire in pentane at reflux followed by 1-pentynylcopper/2HMPT,[18] and the resulting complex was treated with phenyl vinyl sulfone[19] to give **24**, albeit in low yield (5–10%). This low yield could not be increased despite many efforts and modifications. Consequently, while the number of stages through the sequence from **11** (R = H) to **24** is only eight, the overall yield is 2.5%, largely because of the last step.

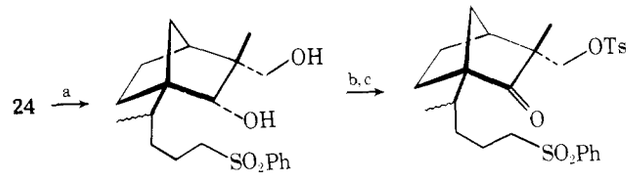
The acetonide **24** was hydrolyzed to the diol **30** and converted into the keto tosylate **31** (Scheme VI). The keto tosylate **31** was treated with sodium hydride in Me_2SO at room temperature to give the β-keto sulfone **32** (65%) and a product **33** formed in approximately 5% yield. If the above fragmentation reaction was carried out at higher temperatures (~50 °C), the yield of the product **33** increased to at least 20%. It is essential in this reaction that all traces of water are scrupulously removed, otherwise the carboxylic acid **34** is formed. Other combinations of base systems, such as LDA/THF, t-BuOK/

Scheme V



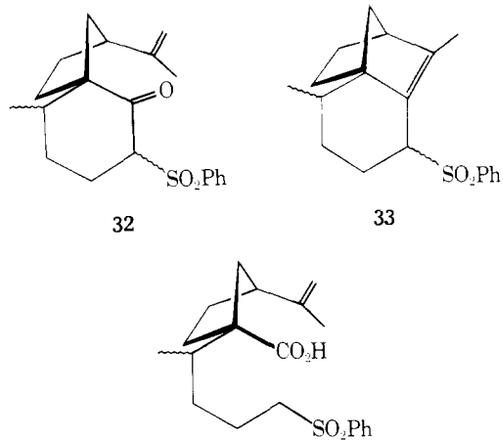
(a) $MeOH/H_2SO_4$ (95%); (b) acetone/$CuSO_4/H_2SO_4$ (77%); (c) LDA/THF/MeI (82%); (d) $LiAlH_4$/THF, −70 °C (67%); (e) $MeSO_2Cl$/pyridine (92%); (f) NaI/MEK (91%).

Scheme VI



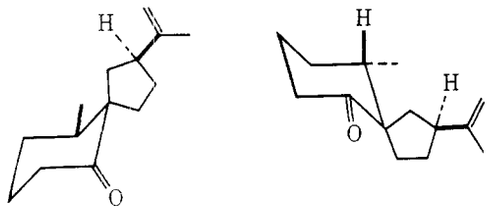
(a) 6 N HCl/$CHCl_3$/dioxane (4:1) (55–79%); (b) TsCl/pyridine (94–100%); (c) CrO_3/2 pyridine/CH_2Cl_2 (75–98%).

THF, and t-BuOK/t-BuOH, reacted with the keto tosylate **31** to give a complex mixture which contained very little of the β-keto sulfone **32**. The NMR spectrum of **32** displays two



distinct doublets for the epimeric methyl groups (τ 9.22 and 9.03, J = 6 Hz) and two well-separated singlets (τ 8.32 and 8.43) for the isopropenylmethyl group. All attempts to separate the epimers of **32** were unsuccessful. The β-keto sulfone **32** was treated with aluminum amalgam[20] in aqueous THF to give the ketone **35** (70–90%). The NMR spectrum of **35** shows a singlet at τ 5.28 corresponding to the vinylic protons, and a pair of overlapping doublets (J = 6 Hz) at about τ 9, corresponding to the epimeric methyl groups at C-10. In the presence of tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]europium (III), the NMR spectrum shows two well separated singlets of equal intensity, corresponding to the vinylic protons. The two overlapping doublets, also of equal intensity, are shifted downfield (τ 8.7).

The mixture of ketones **35** was reacted with methylmagnesium iodide to give the tertiary alcohol **36** (74–97%), which



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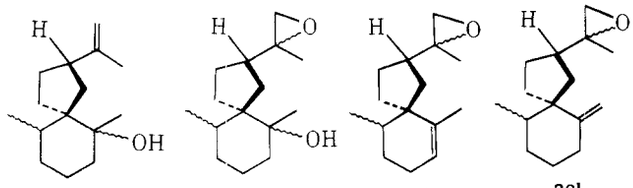
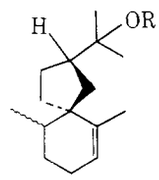
was converted into the epoxide **37** (88%) using *m*-chloroperbenzoic acid. The epoxidation was carried out in the presence of sodium bicarbonate to prevent possible acid-catalyzed formation of byproducts because of the proximity of the hydroxyl group and epoxide group.[21] Indeed, in the absence of sodium bicarbonate a large number of products were formed, whereas in the presence of this base the transformation to the epoxide **37** took place cleanly. Dehydration of **37** using the Burgess reagent[22] gave a mixture and endo- (**38a**) and exocyclic (**38b**) olefin isomers in an average ratio at 1.6:1. The



36 **37** **38a** **38b**

exocyclic isomer **38b** can be converted into the endocyclic isomer by treatment with *p*-toluenesulfonic acid in benzene, resulting in an overall yield of 44%. Reduction of **38a** with lithium aluminum hydride gave an alcohol whose spectral properties are compatible with the structure **39** (R = H), namely (+)-hinesol and its C-10 epimer.[23] (The specific rotation of **39** as 1:1 epimers is +35.4°, confirming the dextrorotatory form of the product. The literature values[3,4,5] are −40.2 and −47.8°.) Since the acetates of **39** (R = H) and its 10-epimer are known[5] and separable (VPC), this constitutes a synthesis of optically active (+)-hinesol and 10-epihinesol.



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This synthesis correlates (+)-hinesol (**39**, R = H) with (−)-β-pinene, and utilizes two novel key rearrangements, **15** → **16** and **31** → **32**, to achieve this synthesis.

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded for Nujol mulls or liquid films on Pye Unicam SP200 and Perkin-Elmer 257 instruments. Ultraviolet spectra were measured on a Pye Unicam SP800 spectrometer, and NMR spectra were recorded with a Varian T-60 spectrometer for solutions in [^{2}H]chloroform using Me_4Si as an internal standard unless otherwise indicated. Mass spectra were run on an AEI MS-9 high-resolution instrument. Optical rotations were measured as solutions in given solvents on a Perkin-Elmer 141 polarimeter. Analytical preparative GLC was performed by a Perkin-Elmer F11 and a Pye 105 instrument, respectively. Solvents were purified and dried by standard techniques. Light petroleum refers to the fraction, bp 40–60 °C.

9-Methyl-6-carboethoxymethyl-7-oxatricyclo[4.3.0.0^{3,9}]nonane (12, R = H). Ethyl nopinolacetate **11** (R = H) (1.0 g) in dry carbon tetrachloride (30 mL) at −10 °C was treated with yellow mercuric oxide (3 g dried under vacuum at 80 °C), followed by iodine (1.3 g). The mixture was irradiated (tungsten lamp, 750 W) under a stream of N_2 and slowly warmed to room temperature. After 48 h the above mixture was filtered and the filtrate was washed with saturated aqueous sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The crude product was purified by passing through alumina (G3, 15 g) and eluting with light petroleum/ethyl acetate (9:1) to give the pure ether **12** (R = H) (0.7 g; 70%):[9] IR 1740, 1205, 1175, and 1055 cm^{-1}; NMR τ 8.76 (3 H, t, *J* = 7 Hz), 8.73 (3 H, s), 7.43 (2 H, s), 6.18, 6.64 (2 H, ABq, *J* = 9 Hz), and 5.87 (2 H, q, *J* = 7 Hz). For this and subsequent NMR data only diagnostic signals are reported.

In subsequent runs on a 25-g scale the ether **12** (R = H) was obtained in 100% crude yield, sufficiently pure for the next stage.

9-Methyl-6-(2′-toluene-*p*-sulfonyloxyethyl)-7-oxatricyclo-[4.3.0.0^{3,9}]nonane (13). The ether **12** (R = H) was reduced with lithium aluminum hydride to give (1*R*,3*S*,6*S*,9*S*)-9-methyl-6-(2′-hydroxyethyl)-7-oxatricyclo[4.3.0.0^{3,9}]nonane; bp 100 °C (5 × 10^{-4} mm); $[\alpha]^{21}_D$ +9.9° (*c* 2.8 in $CHCl_3$); IR 3445 and 1045 cm^{-1}; NMR τ 8.72 (3 H, s), 6.25, 6.62 (2 H, ABq, *J* = 9 Hz), and 6.1–6.45 (3 H, m). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.05; H, 9.85.

The above alcohol (16.3 g, 0.089 mol) in dry pyridine (240 mL) at 0 °C was treated with *p*-toluenesulfonyl chloride (46 g, 2.7 equiv). The mixture was stirred at 0 °C for 18 h and poured into ice–water. Workup in the conventional manner gave the tosylate **13** (29.4 g; 98%); mp 66–69 °C (from light petroleum–ether); $[\alpha]^{20.5}_D$ +4.2° (*c* 2.2 in $CHCl_3$); IR 1600, 1370, 1185, 1045, 985, 860, and 680 cm^{-1}; NMR τ 8.77 (3 H, s), 7.54 (3 H, s), 6.18, 6.68 (2 H, ABq, *J* = 9 Hz), 5.84 (2 H, t, *J* = 7 Hz), and 2.17, 2.62 (4 H, AA′BB′, *J* = 8 Hz). Anal. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53. Found: C, 64.32; H, 7.32; S, 9.53.

9-Methyl-6-(2′-cyanoethyl)-7-oxatricyclo[4.3.0.0^{3,9}]nonane (14). The tosylate **13** (3 g, 8.9 mmol) in dry dimethyl sulfoxide (30 mL) was treated with sodium cyanide (0.66 g, 1.5 equiv) and the mixture was stirred for 15 h at 60 °C under N_2. Workup in the usual way gave the cyanide **14** (1.55 g; 91%); bp 100 °C (5 × 10^{-4} mm); $[\alpha]^{20.5}_D$ +16.0° (*c* 2.3 in $CHCl_3$); IR 2265 and 1045 cm^{-1}; NMR τ 8.75 (3 H, s), 7.57 (2 H, t, *J* = 6 Hz), and 6.18, 6.62 (2 H, ABq, *J* = 9 Hz). Anal. Calcd for $C_{12}H_{17}ON$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.12; H, 8.80; N, 7.14.

9-Methyl-6-(2′-carbomethoxyethyl)-7-oxatricyclo[4.3.0.0^{3,9}]-nonane (15). The nitrile **14** (12 g, 0.063 mol) in ethanol (170 mL) and 10 N aqueous sodium hydroxide (170 mL) was stirred under reflux for 20 h. Workup gave the corresponding acid (12.9 g; 98%): bp 140 °C (5 × 10^{-4} mm); $[\alpha]^{20}_D$ +2.0° (*c* 2.7 in $CHCl_3$); IR 3040, 2700, 1735, and 1030 cm^{-1}; NMR τ 8.72 (3 H, s), 7.54 (2 H, t, *J* = 6 Hz), 6.12, 6.60 (2 H, ABq, *J* = 9 Hz), and −0.37 (1 H, s). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.42; H, 8.43. The crude acid (13.6 g, 0.065 mol) in dry methanol (320 mL) was treated with 'Amberlite' resin IR-120(H) (41 g) under reflux for 5 h. The mixture was filtered and the filtrate was evaporated to give the ester **15** (14.3 g) which was passed through a column of neutral alumina (G3, 100 g) and washed with light petroleum/ethyl acetate (5:2) to afford the pure ester **15** (13.15 g; 91%); bp 90 °C (5 × 10^{-4} mm); $[\alpha]^{22}_D$ +3.9° (*c* 2.7 in $CHCl_3$); IR 1740 and 1030 cm^{-1}; NMR τ 8.74 (3 H, s), 7.57 (2 H, t, *J* = 7 Hz), 6.14, 6.62 (2 H, ABq, *J* = 9 Hz), and 6.31 (3 H, s). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.45; H, 8.91.

1-(2′-Carbomethoxyethyl)-2α-acetoxy-3β-methyl-3α-acetoxymethylnorbornane (16). The ester **15** (12 g, 0.053 mol) in acetic anhydride (128 mL) at 0 °C was treated with BF_3·OEt_2 (22.9 mL). The mixture was stirred for 19 h at 0 °C. Workup by pouring the above mixture into water (400 mL), extraction with chloroform (3 × 100 mL), washing with saturated aqueous sodium hydrogen carbonate, drying (Na_2SO_4), and evaporation gave the diacetate **16** (17.5 g, 100%): bp 140 °C (5 × 10^{-4} mm); $[\alpha]^{24.5}_D$ +33.6° (*c* 3.8 in $CHCl_3$); IR 1750, 1730, 1430, 1370, 1240, and 1045 cm^{-1}; NMR τ 8.85 (3 H, s), 7.97 (3 H, s), 7.95 (3 H, s), 6.32 (3 H, s), 5.88, 6.16 (2 H, ABq, *J* = 11 Hz), and 5.33 (1 H, s). Anal. Calcd for $C_{17}H_{26}O_6$: C, 62.56; H, 8.03. Found: C, 62.60; H, 7.97.

1-(2′-Carbomethoxyethyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane (19). The diacetate **16** (18.6 g) in dry methanol (190 mL) was treated with concentrated sulfuric acid (3.2 mL) and the mixture was heated at reflux for 4 h. Workup in the conventional manner gave the diol **19** (13.3 g, 96%); bp 140–150 °C (5 × 10^{-4} mm); $[\alpha]^{24}_D$ −19.0° (*c* 2.4 in $CHCl_3$); IR 3470, 1730, 1065, and 1020 cm^{-1}; NMR τ 8.9 (3 H, s), 7.59 (2 H, t, *J* = 7 Hz), 6.8 (2 H, br s), 6.51 (1 H, s), 6.02, 6.62 (2 H, ABq, *J* = 11 Hz), and 6.3 (3 H, s). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.54; H, 8.91.

1-(2′-Carbomethoxyethyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (20). The crude diol **19** (13.2 g) in dry acetone (200 mL) was treated with anhydrous

cupric sulfate (6.6 g) and concentrated sulfuric acid (0.25 mL). The mixture was stirred at room temperature for 1 h, filtered, and diluted with water. Extraction with dichloromethane, drying (Na_2SO_4), and evaporation gave an oil which was purified by chromatography over alumina (G3), eluting with light petroleum/ethyl acetate (13:1), to give the acetonide **20** (11.6 g; 75%); bp 90–98 °C (5×10^{-4} mm); $[\alpha]^{22.5}_D$ +23.4° (*c* 3.3 in $CHCl_3$); IR 1740, 1225, 1085, and 1030 cm^{-1}; NMR τ 8.85 (3 H, s), 8.68 (6 H, s), 6.71 (1 H, s), 6.20, 6.90 (2 H, ABq, J = 11 Hz), and 6.30 (3 H, s). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 68.02; H, 9.28.

1-(2′-Carbomethoxy-(*E*)-ethenyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (21). Diisopropylamine (0.36 g) in dry tetrahydrofuran (3 mL) under N_2 at −78 °C was treated with 2.1 M *n*-butyllithium in hexane (1.7 mL) followed by a solution of the acetonide **20** (0.5 g) in dry tetrahydrofuran (3 mL). The mixture was stirred at −78 °C for 20 min and a solution of diphenyl diselenide (0.66 g) in dry tetrahydrofuran (3 mL) was added. The solution was stirred at −78 °C for 30 min and allowed to warm to 20 °C over a period of 2 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride and extracted twice with ethyl acetate. The ethyl acetate extracts were washed successively with 1 N hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and saturated aqueous sodium chloride, dried (Na_2SO_4), and evaporated. The residue was dissolved in tetrahydrofuran and treated dropwise at 20 °C with sodium periodate (0.76 g) in methanol–water (50 mL, 7:3). After 0.5 h the mixture was poured into saturated aqueous sodium hydrogen carbonate and extracted with ether. The ether extracts were washed with water and 1 N hydrochloric acid, dried (Na_2SO_4), and evaporated. The residual yellow oil was purified by chromatography over silica gel, eluting with light petroleum/ethyl acetate (13:1), to give the unsaturated ester **21** (0.35 g; 71%): $[\alpha]^{23}_D$ +49.4° (*c* 2.4 in $CHCl_3$); IR 1725, 1650, 1220, 1090, 1030, 985, and 855 cm^{-1}; NMR τ 8.82 (3 H, s), 8.65 (6 H, s), 6.52 (1 H, s), 6.88, 6.20 (2 H, ABq, J = 11 Hz), 6.25 (3 H, s), 4.18, 2.84 (2 H, ABq, J = 16 Hz). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.44. Scaling the reaction up to 4 g gave a 96% yield of the unsaturated ester **21**, but beyond this scale the yield dropped.

1-(1′-Methyl-2′-carbomethoxyethyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (22). Ethereal methyllithium (36.3 mL, 1.9 M) was added to a slurry of cuprous iodide (7.0 g) in dry ether (60 mL) under argon at 0 °C. After stirring the mixture at 0 °C for 30 min, the unsaturated ester **21** (1.0 g) in dry ether (20 mL) was added and the mixture was stirred at 0 °C for a further 3 h. Workup in the usual way followed by chromatography over silica gel, eluting with light petroleum/ethyl acetate, gave 95% yield of ester **22**: $[\alpha]^{18}_D$ +27.6° (*c* 2.0 in $CHCl_3$); IR 1735, 1220, and 1080 cm^{-1}; NMR τ 9 1 and 9.05 (3 H, 2 d, J = 6 Hz), 8.91 (3 H, s), 8.74 (3 H, s), 8.73 (3 H, s), 6.71 and 6.66 (1 H, 2 s), 6.14, 6.84 (2 H, ABq, J = 11 Hz), and 6.4 (3 H, s). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 69.22; H, 9.49.

1-(1′-Methyl-3′-toluene-*p*-sulfonyloxypropyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (23). The ester **22** (4.05 g) in dry tetrahydrofuran (40 mL) was treated with lithium aluminum hydride (2.4 g) in the usual way. Workup gave the alcohol (3.55 g; 97%): $[\alpha]^{23}_D$ +26.2° (*c* 2.0 in $CHCl_3$); IR 3350, 1220, and 1080 cm^{-1}; NMR τ 9.06 (3 H, d, J = 6 Hz), 8.87 (3 H, s), 8.68 (6 H, s), 6.61 (1 H, s), 6.15, 6.91 (2 H, J = 11 Hz), and 6.28–6.51 (3 H, m). Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.51. Found: C, 71.38; H, 10.64. The crude alcohol was converted into the tosylate **23** (95%) in the usual way. It has: $[\alpha]^{24}_D$ + 16.7° (*c* 2.2 in $CHCl_3$); IR 1590, 1360, 1220, 1170, 1080, and 935 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 8.90 (3 H, s), 8.72 (6 H, s), 7.53 (3 H, s), 6.75 and 6.67 (1 H, 2 s), 6.00, 6.98 (2 H, ABq, J = 11 Hz), 5.91 (2 H, t, J = 6 Hz), and 2.42 (4 H, ABq, J = 8 Hz). Anal. Calcd for $C_{23}H_{34}O_5S$: C, 65.37; H, 8.11. Found: C, 65.66; H, 7.96.

1-(1′-Methyl-4′-phenylsulfonylbutyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (24). To a slurry of sodium hydride (10.5 equiv from 2.2 g of 60% dispersion in mineral oil) in dimethyl sulfoxide (26 mL) under argon was added methyl phenyl sulfone (1.3 g) in dimethyl sulfoxide (26 mL). The above mixture was stirred at room temperature for 10 min and the tosylate **23** (2.2 g) in dimethyl sulfoxide (44 mL) was added. After stirring at room temperature for 15 h the mixture was poured into dilute hydrochloric acid (100 mL, 6 N) and extracted with chloroform. The extract was washed with saturated aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated to give the crude product. Chromatography over silica gel, eluting with light petroleum/ethyl acetate (13:1), gave the pure sulfone **24** (1.45 g; 69%): $[\alpha]^{23}_D$ +18.0° (*c* 2.1 in $CHCl_3$); IR 1300, 1220, 1140, and 1080 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 8.90 (3 H, s), 8.72 (6 H, s), 6.95 (2 H, t, J = 7 Hz), 6.70 (1 H, s), 6.20, 6.86 (2 H, ABq, J = 11 Hz), and 1.9–2.5 (5 H, m). Anal. Calcd for $C_{23}H_{34}O_4S$: C, 67.94; H, 8.43; S, 7.89. Found: C, 68.22; H, 8.19; S, 7.30.

1-Carboethoxymethyl-2α-acetoxy-3β-methyl-3α-acetoxymethylnorbornane (25). The ether **12** (R = H) (0.5 g) was treated with acetic anhydride (10 mL) at 0 °C, followed by boron trifluoride etherate (0.5 mL). After 15 min at 0 °C, water (30 mL) was added to the above mixture. Extraction with ether, washing with saturated aqueous sodium hydrogen carbonate, drying (Na_2SO_4), and evaporation gave the diacetate **25** (76%): IR 1730, 1370, 1240, and 1040 cm^{-1}; NMR τ 8.86 (3 H, s), 8.76 (3 H, t, J = 8 Hz), 8.04 (3 H, s), 8.02 (3 H, s), 7.65 (2 H, s), 6.00 (4 H, q), 5.35 (1 H, b s); MS 326.39 for $C_{17}H_{26}O_6$.

If the above reaction is run for longer times (~1 h) the product **26** is formed: IR 1740, 1710, 1650, 1240, 1200, and 1040 cm^{-1}; NMR τ 8.98 (3 H, s), 8.73 (3 H, t, J = 8 Hz), 7.94 (3 H, s), 6.13 (2 H, s), 5.86 (2 H, q, J = 8 Hz), 4.32 (1 H, b s).

1-Carbomethoxymethyl-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (27). The diacetate **25** (0.30 g) in methanol (4 mL) was treated with concentrated sulfuric acid (3 drops). The mixture was heated at reflux for 3 h and worked up in the usual way to give the diol (100%): IR 3420, 1710, 1435, 1355, 1200, 1070, and 1020 cm^{-1}; NMR τ 8.86 (3 H, s), 8.25 (2 H, b s), 7.92 (2 H, s), 6.36 (1 H, s), 6.30 (3 H, s), 6.75, 6.18 (2 H, q, J = 11 Hz).

The diol (3.5 g) in acetone (60 mL) was treated with anhydrous cupric sulfate (2.0 g) and concentrated sulfurate acid (3 drops). After stirring the above mixture at room temperature for 1.5 h, workup gave the acetonide **27** (77%): IR 1730, 1370, 1220, 1080, and 1025 cm^{-1}; NMR τ 8.88 (3 H, s), 8.75 (6 H, s), 7.55 (2 H, s), 6.98, 6.27 (2 H, q, J = 11 Hz), 6.45 (1 H, s), 6.35 (3 H, s); MS 268.34 for $C_{15}H_{24}O_4$.

1-(2′-Methyl-2′-hydroxyethyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (28). The ester **27** (0.30 g) was added to a solution of lithium diisopropylamide (prepared from diisopropylamine (0.31 mL) and *n*-butyllithium (1 mL) in dry tetrahydrofuran (5 mL) under N_2 at −78 °C). The solution was stirred for 20 min at −78 °C and methyl iodide (0.1 mL) was added. The reaction was quenched and worked up in the usual way to give the methylated product (82%): IR 1730, 1460, 1370, 1220, and 1080 cm^{-1}; NMR τ 8.85 (3 H, s), 8.79 (3 H, s), 8.70 (6 H, s), 8.45 (1 H, q, J = 5.5 Hz), 6.35 (3 H, s), 6.88, 6.15 (2 H, ABq, J = 11 Hz); MS 282.35 for $C_{16}H_{26}O_4$. The methylated ester (0.245 g) in dry tetrahydrofuran (2 mL) was added dropwise to a slurry of lithium aluminum hydride (0.158 g) in dry tetrahydrofuran (5.2 mL) at −78 °C. The mixture was allowed to warm to room temperature over 2 h and worked up the usual way to give the alcohol **28** (67%): IR 3550–3100, 1220, 1075, and 875 cm^{-1}; NMR τ 9.12 (3 H, d, J = 8 Hz), 8.94 (3 H, d, J = 8 Hz), 8.80 (3 H, s), 8.62 (6 H, s), 7.95 (1 H, s, exchange by D_2O), 6.15, 6.80 (2 H, ABq, J = 11 Hz), 6.53 (2 H, d, J = 8 Hz). The alcohol **28** was converted into the iodide **29** without purification.

1-(1′-Methyl-2′-iodoethyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane Isopropylidene Acetal (29) and Its Conversion into 24. The alcohol **28** (0.139 g) in dry pyridine (1 mL) was treated with methanesulfonyl chloride (0.03 mL) at 0 °C. The reaction was quenched with ice water and worked up in the usual way to give the mesylate (92%): IR 1465, 1355, 1220, 1175, and 950 cm^{-1}; MS 342.43 for $C_{16}H_{28}O_5S$.

The mesylate (0.062 g) in methyl ethyl ketone (3 mL) and sodium iodide (0.1423 g) was heated at reflux for 4 h, quenched with water, and worked up in the usual way to give the iodide **29** (91%): IR 1460–1450, 1370, 1265, 1220, 1070, 1025, and 875 cm^{-1}; NMR τ 8.9 (3 H, d), 8.80 (3 H, s), 8.68 (6 H, s), 7.08 (2 H, d), 5.7 (3 H, m). MS 364.24 for $C_{15}H_{25}O_2I$, 237.34 for ($M^{+\cdot}$ − I).

The iodide **29** (0.20 g) in dry pentane (10 mL) containing lithium wire (2 equiv) under argon was heated at reflux for 5 h. Dry ether (5 mL) was added and the mixture was stirred at room temperature overnight. Addition at −78 °C of 1-pentynylcopper[18] (0.078 g) and hexamethylphosphoric triamide (0.2 mL) gave a homogeneous solution which was treated with phenyl vinyl sulfone[19] (0.103 g). After stirring at −78 °C for 1 h and warming to room temperature the reaction was worked up by quenching in saturated aqueous ammonium chloride, extraction with ether, drying (Na_2SO_4), and evaporation. The resulting dark oil was chromatographed over alumina, eluting with ethyl acetate/light petroleum (1:9), to give the sulfone **24** (8%): IR, NMR, MS, and TLC identical with an authentic sample.

1-(1′-Methyl-4′-phenylsulfonylbutyl)-2α-hydroxy-3β-methyl-3α-hydroxymethylnorbornane (30). The sulfone **24** (210 mg) in chloroform (4 mL) and dioxane (1 mL) was stirred vigorously with 6 N hydrochloric acid (10 mL) for 4 h at room temperature. The organic layer was then separated and the aqueous layer was diluted with water and extracted with chloroform. The combined chloroform ex-

tracts were washed with water, dried (Na_2SO_4), and evaporated to give a viscous oil. Passing this through a silica gel column and washing with petrol/ethyl acetate (4:3) gave the diol **30** (150 mg; 79%): $[\alpha]^{19}_D$ −3.0° (*c* 1.0 in chloroform); IR 3490, 1300, and 1140 cm^{-1}; NMR τ 9.11 (3 H, d, J = 6 Hz), 8.94 (3 H, s), 7.3–7.9 (2 H, br), 6.92 (2 H, t, J = 7 Hz), 6.37 (1 H, s), 6.68, 6.06 (2 H, ABq, J = 10 Hz), and 1.9–2.5 (5 H, m). Anal. Calcd for $C_{20}H_{30}O_4S$: C, 65.54; H, 8.25. Found: C, 66.87; H, 7.97.

The diol **30** was also obtained in a large-scale preparation directly from tosylate **23** in 68% yield when the latter was subjected to the alkylation described earlier.

1-(1′-Methyl-4′-phenylsulfonylbutyl)-2-oxo-3β-methyl-3α-toluene-*p*-sulfonyloxymethylnorbornane (31). A mixture of the diol **30** (5.1 g) in dry pyridine (100 mL) and *p*-toluenesulfonyl chloride (5.4 g) was stirred overnight at 0 °C, then poured into ice and extracted with chloroform. The chloroform extracts were washed with 6 N hydrochloric acid and water and dried (Na_2SO_4). Evaporation of chloroform gave the tosylate (6.8 g; 94%): $[\alpha]^{22.5}_D$ +9.5° (*c* 2.2 in chloroform); IR 3540, 1590, 1350, 1300, 1170, 1140, and 950 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 9.02 (3 H, s), 7.55 (3 H, s), 7.3 (1 H, br), 6.94 (2 H, t, J = 7 Hz), 6.40 (1 H, s), 6.0 (2 H, s), 2.10, 2.68 (4 H, AA′BB′, J = 8 Hz), and 1.9–2.5 (5 H, m). The product was used without any purification.

To chromium trioxide (0.24 g, 6 equiv, dried in vacuum at room temperature) in dichloromethane (6 mL) was added pyridine (0.37 mL, 12 equiv). After stirring for 15 min at room temperature the mixture was treated with the above tosylate (0.2 g) in dichloromethane (3 mL). After stirring for 20 min further the mixture was decanted and the residue was washed with more solvent. The combined dichloromethane solutions were washed successively with 3 N sodium hydroxide, 2 N hydrochloric acid, saturated sodium hydrogen carbonate, and saturated sodium chloride, then dried (Na_2SO_4) and evaporated to give a thick oil. Filtration of this oil through a silica gel column using petrol/ethyl acetate (5:2, 1:1) as eluent gave the keto tosylate **31** (165 mg; 83%): $[\alpha]^{20}_D$ −26.1° (*c* 0.9 in chloroform); IR 1730, 1590, 1360, 1300, 1170, and 1140 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 8.99 (3 H, s), 7.55 (3 H, s), 6.94 (2 H, t, J = 7 Hz), 6.13 (2 H, s), 2.10, 2.66 (4 H, AA′BB′, J = 8 Hz), and 1.98–2.53 (5 H, m). Anal. Calcd for $C_{27}H_{34}O_6S_2$: C, 62.52; H, 6.61. Found: C, 62.69; H, 6.89.

Large-scale preparations of **31** afforded in 75–98% yields the crude material, which required no further treatment.

(2*S*,5*R*)-2-Isopropenyl-6-oxo-7-phenylsulfonyl-10-methylspiro[4.5]decane (32). The keto tosylate **31** (0.95 g) in dimethyl sulfoxide (30 mL) was added dropwise to a slurry of sodium hydride (10 equiv, from 0.76 g of 60% dispersion in oil) in dimethyl sulfoxide (20 mL) under argon at 40 °C. The mixture was stirred at 40–50 °C for 1 h. Excess sodium hydride was destroyed by adding water and the resulting mixture was acidified with 6 N hydrochloric acid and extracted with chloroform. The chloroform extracts were washed with water, dried (Na_2SO_4), and evaporated. The resulting residue was chromatographed (silica gel column) into three fractions. Fraction 1 (eluted with petrol/ethyl acetate, 6:1) consisted of a crystalline byproduct **33** (26 mg); mp 89 °C; IR 1600, 1300, 1280, 1140, 1080, and 730 cm^{-1}; NMR τ 9.11 (3 H, d, J = 7 Hz), 8.87 (3 H, s), 5.75–6.1 (1 H, m), and 2.0–2.6 (5 H, m); M^+· *m/e* 316, 219, 218, 286, 256, 175 (M^+· − SO_2Ph; calcd for $C_{13}H_{19}^+$), 147, 145, 105, 91, 77, 55, 41, 32. Fraction 2 (eluted with petrol/ethyl acetate, 5:2) gave the major product **32** (253 mg of viscous oil, 40%); $[\alpha]^{22.5}_D$ −26.1° (*c* 0.16 in chloroform); IR 1710, 1635, 1300, 1140, and 880 cm^{-1}; NMR τ 9.22 and 9.03 (3 H, 2 d, J = 6 Hz), 8.43 and 8.32 (3 H, 2 s), 5.55–6.1 (1 H, m), 5.37 (2 H, s), and 1.8–2.6 (5 H, m); M^+ *m/e* 346 (M^+ − SO_2Ph), 205, 187, 107. Anal. Calcd for $C_{20}H_{26}O_3S$: C, 69.33; H, 7.56. Found: C, 69.37; H, 7.55. Fraction 3 (eluted with petrol/ethyl acetate, 5:2) consisted of the byproduct **34** (63 mg of oil): IR 3250, 3070, 1720, 1640, 1300, 1145, and 890 cm^{-1}; NMR (CCl_4) 9.11 (3 H, d, J = 6 Hz), 8.32 (3 H, s), 7.03 (2 H, t, J = 7 Hz), 5.32 (2 H, s), 2.0–2.6 (5 H, m), and −0.57 (1 H, s). The compound **32** may be obtained in 65% yield on a larger scale.

(2*S*,5*R*)-2-Isopropenyl-6-oxo-10-methylspiro[4.5]decane (35). The sulfone **32** (1.035 g) in tetrahydrofuran (40 mL) was treated with aluminum amalgam[20] and the mixture was heated at reflux for 3 h then filtered. The filtrate containing some added ether was washed with water and saturated sodium chloride and concentrated. The crude residual mixture was chromatographed on a column of silica gel; elution with petrol/ethyl acetate (6.5:0.5) gave the ketone **35** (480 mg; 90% based on reacted starting material): $[\alpha]^{21.5}_D$ −4.8° (*c* 0.25 in chloroform); IR 1705, 1640, and 890 cm^{-1}; NMR τ 9.09 and 9.04 (3 H, 2 d, J = 6 Hz), 8.27 (3 H, s), 7.58 (2 H, br t, J = 7 Hz), and 5.28 (2 H, s); M^+· *m/e* 206, 191 (M^+· − CH_3), 163, 135, 125, 107, 93, 82, 57. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; 10.75. Found: C, 81.41; H, 10.81.

GLC analysis at 150 °C showed a single peak, retention time 4.5 min. Multiple TLC using petrol/ethyl acetate solvent gave a single spot of **35.**

The NMR spectrum in the presence of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) (1.2 equiv) shows signals at τ 5.16 and 5.3 (2 H, s), 8.67 and 8.69 (3 H, 2 d, 2-Hz separation, J = 6 Hz). With 0.08 equiv of shift reagent, 4.5-Hz separation between the two doublets is observed; the separation decreases (more overlapping) with increasing concentration of the shift reagent.

(2*S*,5*R*)-2-Isopropenyl-6-hydroxy-6,10-dimethylspiro[4.5]decane (36). The ketone **35** (245 mg) in dry ether (25 mL) was added dropwise to a freshly prepared ether solution of methylmagnesium iodide (8.5 equiv). After 15–20 min of stirring at room temperature, the mixture was worked up in the usual way to give the crude product. Chromatography over neutral alumina (grade 1), eluting light with petroleum/ethyl acetate (13:1), gave the pure alcohol **36** (viscous oil, 195 mg; 74%): $[\alpha]^{19}_D$ −10.5° (*c* 0.2 in chloroform); IR 3450, 1640, and 890 cm^{-1}; NMR τ 9.12 (3 H, d, J = 6 Hz), 8.77 and 8.82 (3 H, 2 s), 8.25 (3 H, s), 7.7 (1 H, br), and 5.31 (2 H, s). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 80.94; H, 11.66. Multiple TLC developed with petrol–ethyl acetate solvent system gave a single spot of **36.**

(2*S*,5*R*)-2-(1′,2′-Epoxy-1′-methylethyl)-6-hydroxy-6,10-dimethylspiro[4.5]decane (37). The olefin **36** (55 mg) in dichloromethane was treated with 85% *m*-chloroperbenzoic acid (55 mg, 1.1 equiv of peracid) in dichloromethane. After 0.5 h at room temperature, the excess peracid was then destroyed by addition of 10% aqueous sodium sulfite. The resulting mixture was washed successively with saturated sodium hydrogen carbonate, water, and saturated aqueous sodium chloride and then dried (Na_2SO_4) and the solvent was evaporated. The residue was passed through a column of silica gel and eluted with petrol/ethyl acetate (6:1, 5.5:1.5) to yield a colorless viscous liquid **37** (52 mg, 88%): $[\alpha]^{24}_D$ −0.8° (*c* 0.25 in chloroform); IR 3450, 1460, 1370, 1045, 975, and 915 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 8.85 and 8.8 (3 H, 2 s), 8.7 and 8.63 (3 H, 2 s) and 6–7.6 (2 H, m). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.66; H, 11.06.

For subsequent preparation of epoxide **37,** the following condition was used. Olefin **36** (220 mg) in tetrahydrofuran (13 mL) was stirred at room temperature and added with sodium bicarbonate (129 mg), followed by 85% *m*-chloroperbenzoic acid (583 mg, 2.9 equiv of peracid) in tetrahydrofuran (6 mL) dropwise. After addition the mixture was stirred for 3 h, then poured into 2 N sodium hydroxide (20 mL) and ether (10 mL). The aqueous layer was separated and the organic layer was washed with another 20 mL of 2 N sodium hydroxide, then water and saturated brine. Drying (Na_2SO_4) and removal of solvent from the organic solution gave the epoxide **37** as a viscous colorless oil (236 mg; 100%).

(2*S*,5*R*)-2-(1′,2′-Epoxy-1′-methylethyl)-6,10-dimethylspiro[4.5]dec-6-ene (38a). (Carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester[22] (1.3 g, 5 equiv) was added to a stirred solution of alcohol **36** (236 mg) in benzene (33 mL) and the mixture was stirred at room temperature for 3 h. Workup by washing repeatedly with water, drying (Na_2SO_4), and evaporation gave the residue (~0.5 g), still containing some of the inner salt. Chromatography over silica gel (23 g), eluting with light petroleum, gave 40 mg (18%) of the exocyclic olefin isomer **38b:** IR 1635, 1450, 1370, and 885 cm^{-1}; NMR τ 9.17 (3 H, d, J = 6 Hz), 8.74 (3 H, s), 7.15–7.92 (2 H, m), and 4.25–5.5 (2 H, m). Elution with light petroleum/ethyl acetate (95:5) gave 57 mg (26%) of the endocyclic olefin isomer **38a:** IR 1640, 1450, 1370, and 890 cm^{-1}; NMR τ 9.13 (3 H, d, J = 6 Hz), 8.73 (3 H, s), 8.35 (3 H, br s), 7.7 (2 H, m), and 4.67 (1 H, m). Treatment of **38b** in benzene with a catalytic amount of *p*-toluenesulfonic acid at room temperature gave **38a** in quantitative yield.

Hinesol (39, R = H). The epoxide **38a** (36 mg) in dry ether (2 mL) was added dropwise to an ice-cooled slurry of lithium aluminum hydride (90 mg) in dry ether (2 mL). The mixture was stirred for 6 h, then worked up with saturated ammonium chloride. Ether extraction gave 25 mg of the crude product which was purified by a chromatography over neutral alumina (grade 1). Elution with petrol/ethyl acetate (6:1, 5.5:1.5) gave 11 mg (30%) of the alcohol **39** (R = H) as a liquid which failed to crystallize upon prolonged cooling: $[\alpha]^{25}_D$ +35.4° (*c* 0.5 in chloroform); IR 3345, 1630, 1445, 1365, 1230, 1130, 1025, 885, and 795 cm^{-1}; NMR τ 9.05 (3 H, d, J = 6 Hz), 8.75 (6 H, s), 8.36 (3 H, br s), 6.45 (1 H, br s), and 4.70 (1 H, m); *m/e* 222 (M^+·), 207 (M^+· − CH_3), 204 (M^+· − H_2O), 189, 163, 121, 107, 95, 93, 81, 55. TLC of this alcohol **39** (R = H) on a silica gel plate impregnated with 20% silver nitrate and developed with 0.5% glacial acetic acid in chloroform did not give a satisfactory separation of the epimeric mixture (a slightly elongated spot was obtained).

Hinesol Acetate (39, R = Ac). The alcohol **39** (R = H) (~10 mg) and sodium acetate (40 mg) were dissolved in acetic anhydride (0.5 mL) and the mixture was heated at reflux for 3 h. The cooled mixture

was stirred at room temperature for 1 h with saturated sodium bicarbonate (4 mL) and ether (3 mL). The crude acetate **39** (R = Ac) (15 mg) was isolated by ether extraction as a light yellow oil: IR 1735, 1655, 1445, 1365, 1230, 1030, 880, and 800 cm^{-1}; NMR τ 9.15 (3 H, d, J = 6 Hz), 8.66 (6 H, s), 8.16 (3 H, br s), 7.96 (3 H, s), and 4.74 (1 H, m). TLC of the acetate **39** (R = Ac) on a silica gel plate impregnated with 20% silver nitrate, developed with petrol/ethyl acetate (13:1) or 0.5% glacial acetic acid in chloroform, gave a slight elongation of the spot. Analytical GLC using the usual columns was unsatisfactory. The above acetate **39** (R = Ac) had IR and NMR spectra in agreement with literature values.

Acknowledgment. We thank Professor J. A. Marshall for supplying spectra of authentic (±)-hinesol.

Registry No.—**11,** 65354-38-3; **12,** 23971-53-1; **13,** 65338-83-2; **13** alcohol, 65338-84-3; **14,** 65338-85-4; **15,** 58698-24-1; **15** acid, 65338-86-5; **16,** 58698-25-2; **19,** 58698-26-3; **20,** 58700-62-2; **21,** 58700-63-3; **22** isomer 1, 65378-09-8; **22** isomer 2, 65378-10-1; **23,** 65338-87-6; **23** alcohol, 65338-88-7; **24,** 58698-28-5; **25,** 65338-89-8; **25** diol, 65338-90-1; **26,** 65338-91-2; **27,** 65338-92-3; **28,** 65338-75-2; **28** mesylate, 65338-76-3; **29,** 65338-77-4; **30,** 65338-78-5; **30** 3-tosylate, 65366-44-1; **31,** 58698-29-6; **32,** 58698-30-9; **33,** 65338-79-6; **34,** 65338-80-9; (10*R*)-**35,** 65378-05-4; (10*S*)-**35,** 65378-06-5; **36,** 65338-81-0; **37,** 58700-60-0; **38a,** 58700-61-1; **387,** 65338-82-1; (+)-hinesol, 59331-07-6; 10-epihinesol, 59331-08-7; (+)-hinesol acetate, 65378-07-6; (+)-10-epihinesol acetate, 65378-08-7; *p*-toluenesulfonyl chloride, 98-59-9; acetic anhydride, 108-24-7; acetone, 67-64-1; methyllithium, 917-54-4; methyl phenyl sulfone, 3112-85-4; methyl iodide, 74-88-4.

References and Notes

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(23) (+)-Hinesol is the mirror image of the natural isomer; see ref 8 for a discussion of the relevant stereochemical relationships.

Photochemical Transformations. 21. Photochemical and Thermal Methanolyses of Two Epimeric Bridged Polycyclic Bromides[1]

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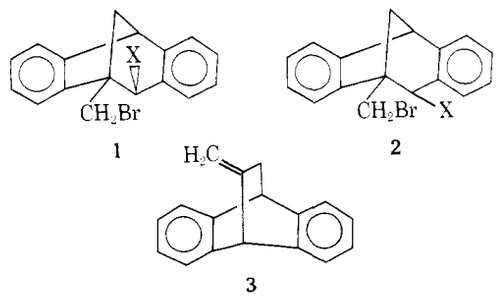
Received May 20, 1977

Addition of bromine to 7-methylenedibenzobicyclo[2.2.2]octadiene (**3**) gave a mixture of the epimeric 5-bromomethyl-4-bromodibenzobicyclo[3.2.1]octadienes (**1**-Br and **2**-Br). The dibromides suffer methanolysis in THF–methanol solutions in the dark at 60 °C and upon direct irradiation at room temperature to form the corresponding 4-methyl ethers (**1**-OCH_3 and **2**-OCH_3). The solvolyses are neither stereoselective nor stereoconvergent, although in all cases the exo ether (**1**-OCH_3) is the principal solvolysis product. Plausible rationalizations of the product differences are discussed.

Photoinduced solvolyses of a number of benzyl derivatives have been reported;[2] these have been shown to proceed through benzylic cation intermediates. It seemed to us that an interesting question is whether cationic intermediates, otherwise identical, but produced on the one hand from an electronically excited species and on the other hand from a ground-state species, would be different enough to note experimentally. Obviously, any differences could be noted only if bimolecular capture occurred more rapidly than unimolecular relaxation processes.

As one test, we decided to investigate the epimeric 5-bromomethyl-4-bromo-2,3;6,7-dibenzobicyclo[3.2.1]octadienes (**1**-Br and **2**-Br). These offered the additional possibility that the two epimers might show differences among themselves, and in addition, we needed to have a system whose



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