catalysts which differ by many orders of magnitude in acidity. Examination of Figure 1 shows no such moderate curvature, but even if such an overall trend could be discerned, its significance would be obscured by the changes in catalyst structure required to cover the range of this plot.

Brønsted relations are available for two other aromatic hydrogen exchange reactions, the detritiations of azulene and guaiazulene.[5a] Comparison of these with the present correlation should of course be done on the basis of similar catalysts, preferably of a single structural type, and this effectively limits the examination to relationships based on catalysis by carboxylic acids. The value of α based on all of the carboxylic acid data for trimethoxybenzene is 0.59 ± 0.05, and those for azulene and guaiazulene are 0.61 ± 0.07 and 0.52 ± 0.10, respectively. It must be borne in mind, however, that these correlations use observed detritiation rate constants, which are functions of protonation rate constants, k_1, and intramolecular isotope effects, k_H/k_T: $k_{obsd} = k_1/(1 + k_H/k_T)$.[8a] These isotope effects are known to vary in magnitude in a regular way with changes in catalyst acidity and substrate basicity,[21] and Brønsted exponents based on k_{obsd} will therefore be somewhat different from Brønsted exponents based on k_1. The latter, of course are the quantities of significance in comparisons of different substrates and they can be estimated[8b] as $\alpha = 0.68 \pm 0.06$, 0.67 ± 0.07, and 0.56 ± 0.10 for the carboxylic acid catalyzed detritiation of trimethoxybenzene, azulene, and guaiazulene, respectively. Since the basicity of these substrates[5a,22] increases in this same order, and since proton transfer is expected to be most complete at the transition state of the most weakly basic substrate, this order of Brønsted exponents is quite reasonable.

Experimental Section

Materials. 1,3,5-Trimethoxybenzene-2-*t* was prepared from 2,4,6-trimethoxyphenyllithium and tritiated water by the method already described.[4a] All other materials were obtained commercially in best available grades; reagent-quality substances were used directly and lesser grades were purified by standard methods.

Kinetic Procedure. Appropriate volumes of wholly aqueous buffer and substrate solutions were allowed to equilibrate with a bath operating at 24.62 ± 0.02°; they were then mixed and replaced in the bath. At suitable time intervals, samples were withdrawn by pipet (5 or 10 ml) and were quenched in twice the amount of aqueous alkali needed to neutralize the buffer acid completely. These solutions were then transferred to neoprene-stoppered separatory funnels with Teflon taps (glass-tapped funnels require stopcock grease which, unless renewed frequently, becomes contaminated and leads to erratic results) and were extracted with toluene (15 ml). For runs in bisulfate buffers where the decrease in aromatic radioactivity was being followed, these toluene extracts were dried over calcium chloride and aliquots of dried solution were assayed by liquid scintillation counting in toluene-based counting solution. With all other buffers, exchange was monitored by following the increase in aqueous radioactivity; in these cases, aqueous fractions were separated from original toluene extracts, were washed again with 15-ml portions of toluene, and aliquots of twice-extracted solutions were assayed in Bray's counting solution.[23]

(21) J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1292 (1967).

(22) M. T. Reagan, *ibid.*, **91**, 5506 (1969).

(23) G. A. Bray, *Anal. Biochem.*, **1**, 279 (1960).

A Stereospecific Total Synthesis of α-Santalol

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Abstract: A stereospecific synthetic route to the important constituent of sandalwood oil, α-santalol, from the readily accessible (−)-π-bromotricyclene is outlined. The synthesis illustrates a number of new synthetic methods including (1) chain extension using 3-trimethylsilylpropargyllithium, (2) stereo- and position-specific addition of diisobutylaluminum hydride to the lithium salt of a propargylic alcohol, and (3) stereospecific methoxycarbonylation of a vinylic iodide by nickel carbonyl and sodium methoxide in methanol. The scope of the synthesis as a general route to the structural olefinic unit $RCH_2CH{=}C(CH_3)CH_2OH$ in which H and CH_3 are cis is further illustrated by the case R = n-C_6H_{13}.

The synthesis of α-santalol (**1**), a valuable ingredient in perfumery, is considerably more challenging than that of the parent hydrocarbon α-santalene (**2**),[1] because of the particular geometrical arrangement of substituents about the olefinic linkage. At the outset of this work there were no known synthetic methods capable of generating stereospecifically the type of trisubstituted unsaturated unit which occurs in **1**, *i.e.*, $RCH_2CH{=}C(CH_3)CH_2OH$ with H and CH_3 cis. This fact, together with a wider interest in the development of new stereospecific methods for the synthesis of tri- and tetrasubstituted olefins and the occurrence of the same unsaturated unit in other natural products,[2] led us to study the stereospecific route to α-santalol which forms the subject matter of this paper. The synthesis which is described herein is the second to be reported from these laboratories as a result of recent investigations. The first route[3] involved the conversion of the

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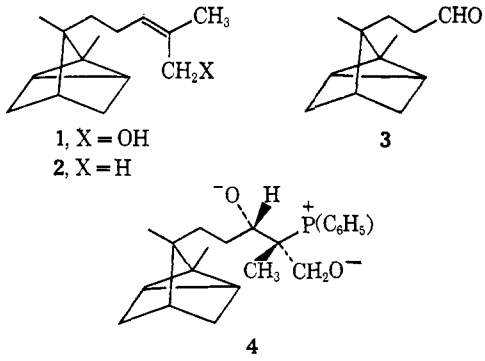
(1) For syntheses of α-santalene see (a) E. J. Corey, S. W. Chow, and R. A. Scherrer, *J. Amer. Chem. Soc.*, **79**, 5773 (1957), and (b) E. J. Corey and M. F. Semmelhack, *ibid.*, **89**, 2755 (1967).

(2) See (a) lanceol: A. Manjarrez, T. Rios, and A. Guzman, *Tetrahedron*, **20**, 333 (1964); (b) valerenic acid: A. Stoll and E. Seebeck, *Justus Liebigs Ann. Chem.*, **603**, 158 (1957); and (c) masticadienonic acid: S. Corsano and E. Mincione, *Tetrahedron Lett.*, 2377 (1965).



1, X = OH
2, X = H

3

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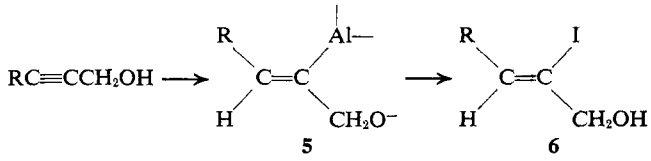
aldehyde **3** to α-santalol in a single step by sequential treatment in tetrahydrofuran with ethylidenetriphenylphosphorane (1 equiv, −78°), *n*-butyllithium (1 equiv, −78°), and paraformaldehyde (excess, 0°). This process occurs *via* the β,β′-dioxido phosphonium derivative **4**.

Although α-santalol has been synthesized previously using standard methods, the approaches which have been used are either of low or unspecified stereoselectivity with low or unstated yields.[4-7]

The starting point for the synthetic plan to be outlined here was the observation that propargylic alcohols undergo reaction with lithium aluminum hydride–aluminum chloride (ratio 60:1) in ether to give an intermediate (presumably the vinylaluminum derivative **5**) which yields stereospecifically a 2-iodinated *trans*-allylic alcohol (**6**) as major product upon reaction with iodine.[8,9] The transformation of hydroxymethyl and



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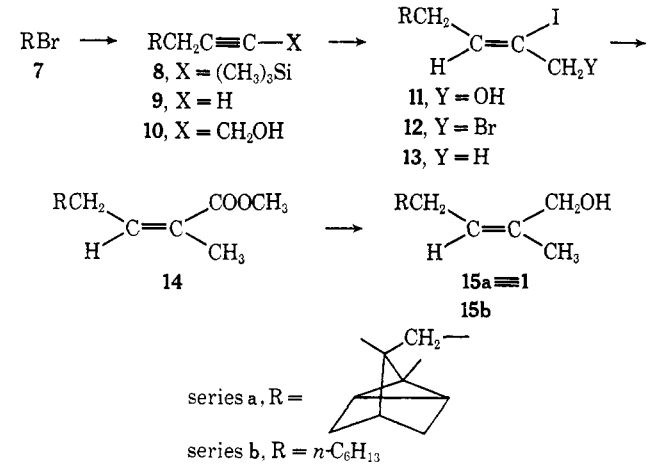
iodo groups in **6** to methyl and hydroxymethyl, respectively, would constitute a sequence which could be applied to the synthesis of α-santalol *via* a propargylic intermediate. This possibility suggested the synthetic approach outlined in Chart I.

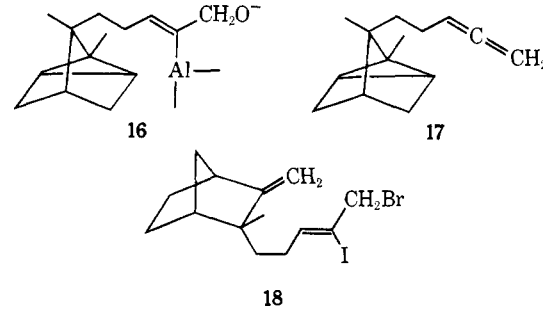
(−)-π-Bromotricyclene (**7a**)[1a,10] (from (+)-α-bromocamphor[1a]) was treated with lithio-1-trimethylsilylpropyne[11] to form the tricyclic acetylene derivative **8a** in 77% yield.[12] Silver(I) promoted desilylation[11,13]

Chart I



of **8a** and subsequent treatment of the resulting silver acetylide with potassium cyanide produced the terminal acetylene **9a** (88% yield) which was converted *via* the lithium derivative to the propargylic alcohol **10a** (90% yield) by reaction with paraformaldehyde.

The propargylic alcohol **10a** was then converted to the 2-iodinated allylic alcohol **11a** by a new modification of the previously described reduction procedure[8] which has the advantage of being easily reproducible and of avoiding formation of 3-iodinated allylic alcohol as a by-product.[9] A solution of the propargylic alcohol **10a** in ether at −20° was treated with *n*-butyllithium (1 equiv) followed by diisobutylaluminum hydride (3 equiv, first at −20°, then at 35° for 48 hr) to effect trans hydroalumination and was then treated with ethyl acetate (2 equiv at 0° to decompose excess hydride) and iodine (9 equiv at −78° for 10 min to iodinate the vinylic aluminum containing intermediate **16**). Isolation of the product chromatographically afforded the desired alcohol **11a** in 70% yield. Neither the position isomers of **11a** with iodine at C-3 nor the stereoisomer of **11a** with respect to the olefinic linkage could be detected chromatographically or by nmr analysis. The other product which was isolated was the terminal allene **17** which arises by elimination of aluminum alkoxide from **16**.[14] The iodo alcohol **11a** yielded the corresponding mesylate by reaction with *n*-



16 17

18

butyllithium followed by mesyl chloride, and this in turn was converted to the corresponding bromide **12a**

(3) E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226 (1970).

(4) R. G. Lewis, D. H. Gustafson, and W. F. Erman, *Tetrahedron Lett.*, 401 (1967).

(5) S. Y. Kamat, K. K. Chakravarti, and S. C. Bhattacharyya, *Tetrahedron*, **23**, 4487 (1967).

(6) V. M. Sathe, K. K. Chakravarti, M. V. Kadival, and S. C. Bhattacharyya, *Indian J. Chem.*, **4**, 393 (1966).

(7) J. Colonge, G. Descotes, Y. Bahurel, and A. Menet, *Bull. Soc. Chim. Fr.*, 374 (1966).

(8) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 4245 (1967), and references cited therein.

(9) Subsequent to the preliminary studies[8] it has been found that the lithium aluminum hydride–aluminum chloride reagent usually produces appreciable amounts of 3-iodo-*trans*-allylic alcohols in addition to the 2-iodo alcohols **6**; see J. A. Katzenellenbogen, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1969.

(10) The corresponding iodide (levorotatory) [E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Amer. Chem. Soc.*, **81**, 6305 (1959)] could also be used.

(11) E. J. Corey and H. A. Kirst, *Tetrahedron Lett.*, 5041 (1968).

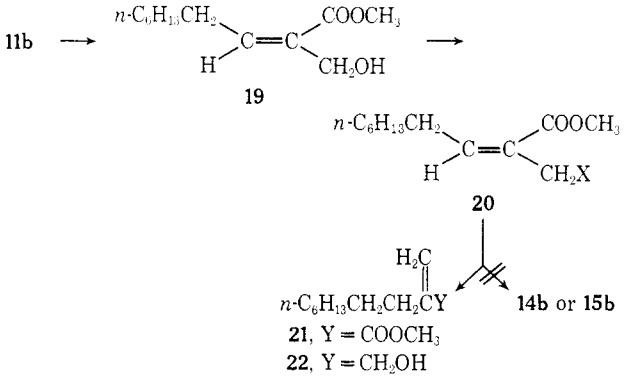
(12) This useful new route to acetylenes has also been employed in these laboratories in the syntheses of the insect juvenile hormone from Cecropia [E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Amer. Chem. Soc.*, **90**, 5618 (1968)] and sirenin, the Allomyces sperm attractant [E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *ibid.*, **91**, 4318 (1969)].

(13) H. M. Schmidt and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **86**, 1138 (1967).

(14) Prolonged reaction time for the hydroalumination step leads to increased formation of allene at the expense of **11a**. Allene formation was also favored by the use of higher temperatures or hydrocarbon solvents.

by reaction with lithium bromide in ether.[15a] The use of phosphorus tribromide in ether[15b] was unsatisfactory for the synthesis of **12a** from **11a**, since cleavage of the tricyclic skeleton occurred with formation of the β-santalene derivative **18** (*cf.* ref 7). Reduction of **12a** with sodium borohydride in dimethyl sulfoxide[16] afforded smoothly the vinylic iodide **13a** (96%). Reaction of **13a** with nickel carbonyl–sodium methoxide in methanol afforded *stereospecifically* in 73% yield the methyl ester **14a**[17] which by reduction with aluminum hydride[18] gave α-santalol (**1** ≡ **15a**) in 100% yield. The infrared and nmr spectra of the synthetic product were identical with those obtained[3,4] for α-santalol, and the odors of the synthetic and natural compounds were also the same.

The stereospecific construction of the unit RCH_2-$CH{=}C(CH_3)CH_2OH$ having methyl and hydrogen cis about the olefinic linkage was also demonstrated for a simple aliphatic case. Starting with 2-decyn-1-ol (**10b**, Chart I) and using a series of reactions generally paralleling those used for the synthesis of α-santalol, 2-methyl-*cis*-2-decen-1-ol (**15b**) was obtained stereospecifically and efficiently *via* the intermediates (in sequence) **11b** to **14b**. A potentially shorter route for the synthesis of **15b** from **10b** was also studied, but with disappointing results. This consisted of (1) methoxycarbonylation[17] to **11b** to form the hydroxy ester **19**, (2) conversion of **19** to **20**, X = OSO_3^-[19] or Br,[15] and (3) hydride reduction of **20**. Unexpectedly, the hydride reduction of **20** under a variety of conditions



and with a number of different hydride reagents (*e.g.*, lithium aluminum hydride, lithium borohydride, sodium borohydride, aluminum hydride, diborane) led predominantly to the unsaturated ester **21** or alcohol **22** which would result from SN2′ or Michael-type addition of hydride β to the carbonyl group.

Experimental Section

General. The concentration of commercial *n*-butyllithium (Foote Mineral Co.) was determined by titration with 2-butanol in xylene using 1,10-phenanthroline as indicator.[20] Diisobutylaluminum hydride (caution: pyrophoric!) was transferred from a lecture bottle (Alfa Inorganics, Inc.) into a dry flask under argon and used neat. All reactions involving nickel carbonyl (toxic vapors!) were performed in a well-ventilated hood, and nickel carbonyl (Matheson Co.) was removed from a lecture bottle as needed. Lithium aluminum hydride solutions were prepared by stirring the crude hydride in ether overnight under argon and filtering the mixture through a pad of Celite 545 and glass wool in a Schlenk tube under argon. Paraformaldehyde was dried for several days over phosphorus pentoxide *in vacuo*, and lithium bromide was dried *in vacuo* overnight at 110°. 2-Decyn-1-ol (Farchan Research Laboratories) was distilled before use. Methanesulfonyl chloride and ethyl acetate were distilled from phosphorus pentoxide; *N,N,N′,N′*-tetramethylethylenediamine (TMED), dimethyl sulfoxide (DMSO), and hexamethylphosphoric triamide (HMPA) were distilled from calcium hydride (the latter two under reduced pressure); tetrahydrofuran (THF) and diglyme were distilled from lithium aluminum hydride under argon. Diethyl ether (Mallinckrodt AR anhydrous grade) and hexane (Fisher ACS grade) were used without further purification. The basic sodium thiosulfate solution used was 1 *M* in thiosulfate and 2.2 *M* in sodium hydroxide. Anhydrous magnesium sulfate was used as drying agent for all solutions. All boiling points are uncorrected.

Infrared spectra were recorded for carbon tetrachloride solutions with a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance (nmr) spectra were determined using deuteriochloroform as solvent with Varian A-60 or T-60 spectrometers, and data are reported as τ in parts per million downfield from tetramethylsilane (internal standard, τ 10). Optical rotations were measured using chloroform as solvent with a Perkin-Elmer Model 141 polarimeter. Mass spectra and exact mass measurements were determined using an AEI Model MS-9 double focusing spectrometer at 70 eV. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark, and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Analytical thin layer chromatography (tlc) was carried out using Merck precoated, glass-backed silica gel F-254 plates (0.25 mm), visualized by either ultraviolet illumination or spraying with 2–10% phosphomolybdic acid in dilute ethanolic sulfuric acid followed by heating to 150°. Preparative tlc was carried out with 20-cm square glass plates coated with Merck silica gel PF-254 (2 mm). F&M Model 810 and 5750 research gas chromatographs (nitrogen carrier gas, 30 ml/min. dual flame ionization detector) were used for analytical gas–liquid phase chromatography (glpc), and a Model 300 chromatograph (helium carrier gas, 60–80 ml/min, thermal conductivity detector) was used for preparative glpc; retention times are abbreviated as t_r. The glpc columns used are designated as: column A, 10 ft × 0.125 in., 3% OV-17 on 60–80 mesh Gaschrom Q; column B, 3 ft × 0.125 in., 5% SE-30 on 80–100 mesh Gaschrom Q; column C, 10 ft × 0.125 in., 5% SE-30 on 80–100 mesh Gaschrom Q; column D, 20 ft × 0.125 in., 10% SE-30 on 60–80 mesh Diatoport S Hi-Pak; column E, 3 ft × 0.125 in., 5% Carbowax 20M + 2% KOH on 80–100 mesh Chromosorb W (acid-washed, dimethylchlorosilanized); column F, 16 ft × 0.125 in., 10% LAC-728 on 80–100 mesh Diatoport S; column G, 10 ft × 0.25 in., 5% SE-30 on 60–80 mesh Diatoport S; column H, 10 ft × 0.25 in., 5% Carbowax 20M + 2% KOH on 60–80 mesh Diatoport S.

1-Trimethylsilylpropyne.[11] Trimethylchlorosilane (56 ml, 0.44 mmol) was added to a suspension of propynyllithium[21] (21.2 g, 0.46 mmol) in anhydrous diglyme (250 ml) at 0° with vigorous (Hershberg) stirring, and the mixture was stirred at 0° for 10 hr, filtered, and slowly distilled through a 30-cm Vigreux column to yield 43.7 g (89%) of 1-trimethylsilylpropyne: bp 97–100° [lit.[22] bp 99–100°]; ir 2188 (s, C≡C), 1248 (s, Me_3Si), 1028 (s), 845 cm^{-1} (vs, Me_3Si); nmr τ 9.87 (s, 9) and 8.13 (s, 3).

1-Trimethylsilyl-3-(π-tricyclyl)propyne (8a). *n*-Butyllithium (28.0 mmol, 22.2 ml of a 1.26 *M* solution) in pentane under argon was freed of solvent *in vacuo* at 20°. The residue was cooled to −15° (Dry Ice–acetone bath), and anhydrous argon-flushed ether (50 ml), TMED (4.30 ml, 28.0 mmol), and 1-trimethylsilylpropyne (4.32 ml, 28.0 mmol) were successively added.[11] After stirring at −15° for 4 hr, the solution was treated successively at −20° with (−)-π-bromotricyclene[1a] (3.00 g, 14.0 mmol, $[\alpha]^{25}D$ −10.5°) and anhydrous HMPA (30 ml).[23] After 6 hr at −20°, the reaction

(15) (a) See G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Lett.*, 1393 (1969); (b) J. M. Osbond, *J. Chem. Soc.*, 5270 (1961).

(16) (a) R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Lett.*, 3495 (1969); (b) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969).

(17) E. J. Corey and L. S. Hegedus, *J. Amer. Chem. Soc.*, **91**, 1233 (1969).

(18) M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).

(19) E. J. Corey and K. Achiwa, *Tetrahedron Lett.*, 1837 (1969); *J. Org. Chem.*, **34**, 3667 (1969).

(20) S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

(21) Foote Mineral Co.

(22) A. D. Petrov, L. L. Shchukovskaya, and Y. P. Egorov, *Dokl. Akad. Nauk SSSR*, **93**, 293 (1953); *Chem. Abstr.*, **48**, 13616 (1954).

(23) Addition of HMPA is unnecessary with unhindered alkyl halides.[11]

mixture was poured into cold 3 *N* hydrochloric acid, and the product was extracted with ether and dried. The crude product was distilled through a 30-cm Holtzmann column to yield 2.65 g (77%) of **8a**: bp 74–76° (0.02 mm); ir 2160 (s, C≡C), 1255 (s, Me_3Si), 847 cm^{-1} (vs, Me_3Si); nmr[24] τ 9.87 (s, 9, Me_3Si); mass spectrum parent *m/e* 246. Glpc analysis (column F, 190°) indicated the product was about 95% pure (t_r 5.8 min). An analytical sample was obtained by preparative glpc (column G, 140°): $[\alpha]^{23}D$ +31.7° (*c* 3.6).

Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 78.22; H, 10.58.

The acetylenic silane **8a** could also be prepared by the above procedure from 3-trimethylsilylpropargyllithium and 0.6 equiv of (−)-π-iodotricyclene[10] ($[\alpha]^{24}D$ −26.4° (*c* 3.1)) in ether–HMPA at −25° for 1.5 hr.

3-(π-Tricyclyl)propyne (9a). The acetylenic silane **8a** (2.57 g, 11.5 mmol) in ethanol (12 ml) was added over a 15-min period to a solution of silver nitrate (2.60 g, 15.3 mmol) in ethanol (18 ml) and water (6 ml) at room temperature with vigorous (Hershberg) stirring, immediately forming a dense white precipitate.[13] After stirring for 15 min, potassium cyanide (4.9 g, 75 mmol) in water (10 ml) was added, quickly dissolving most of the precipitate, and the mixture was stirred for 4 hr. The mixture was poured into water, and the product was extracted with petroleum ether and dried. The crude product was distilled under reduced pressure to yield 1.60 g (88%) of **9a**: bp 86–89° (12 mm); ir 3290 (m, acetylenic CH), 2123 cm^{-1} (w, C≡C); nmr[24] τ 8.13–7.69 (complex pattern, 3, overlapping CH_2—C≡C*H*); mass spectrum parent *m/e* 174. Glpc analysis (column F, 190°) showed the product was greater than 98% pure (t_r 5.5 min). An analytical sample was obtained by preparative glpc (column G, 100°): $[\alpha]^{23}D$ +32.8° (*c* 2.7).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.59; H, 10.49.

4-(π-Tricyclyl)-2-butyn-1-ol (10a). *n*-Butyllithium (8.85 mmol, 7.0 ml of a 1.26 *M* solution) in pentane was added dropwise to the terminal acetylene **9a** (1.54 g, 8.85 mmol) in anhydrous THF (25 ml) at −78° under argon, and the resulting yellow solution was stirred at −78° for 30 min. A suspension of dry paraformaldehyde (530 mg, 17.7 mmol) in anhydrous THF (5 ml) was added,[25] and the mixture was allowed to warm to room temperature over a 30-min period. The colorless solution was stirred for 1 hr at room temperature and then poured into saturated sodium chloride solution; the product was extracted with ether and dried. The crude product was distilled *in vacuo* to yield 1.62 g (90%) of **10a**: bp 103–105° (0.03 mm); $[\alpha]^{24}D$ +34.5° (*c* 4.5); ir 3730 and 3480 (m, OH), 2315 and 2252 (w, C≡C), 1010 cm^{-1} (s, C—O stretch); nmr[24] τ 7.34 (broad s, 1, OH), 5.77 (t, 2, *J* = 2 Hz, CH_2O); mass spectrum parent *m/e* 204 (weak, <1%), 189 (parent − 15). The compound exhibited a single spot (R_f 0.47) on tlc (3:1 petroleum ether–ether, two developments) and a single peak (t_r 7.3 min) on glpc analysis (column E, 200°).

Mol wt Calcd for $C_{14}H_{20}O$: 204.1514. Found: 204.1496 (high-resolution mass spectrometry).

2-Iodo-4-(π-tricyclyl)-*trans*-2-buten-1-ol (11a). The propargylic alcohol **10a** (1.55 g, 7.60 mmol) in anhydrous ether (7 ml) at −20° under argon was treated successively with *n*-butyllithium (7.60 mmol, 6.00 ml of a 1.26 *M* solution) and diisobutylaluminum hydride (4.05 ml, 22.8 mmol), and the colorless solution was heated at 35° for 48 hr. Excess hydride was decomposed with anhydrous ethyl acetate (1.5 ml, 15 mmol) at 0°. Iodine (17.3 g, 68.4 mmol) in ether (100 ml) was added at −78°, and the mixture was stirred at −78° for 10–15 min. The mixture was poured into basic sodium thiosulfate solution, and the product was extracted with ether and dried. After evaporation of solvent, the crude product was dissolved in petroleum ether and chromatographed on basic alumina II (70 g, 40 × 2 cm diameter column); the column was eluted with petroleum ether (200 ml), 5:1 petroleum ether–ether (120 ml), and ether (200 ml). Evaporation of the ether fraction yielded 1.77 g (70%) of **11a**: ir 3520 and 3380 (m, OH), 1647 cm^{-1} (m, C=C); nmr[24] τ 6.88 (broad s, 1, OH), 5.78 (s, 2, CH_2O), 4.10 (t, 1, *J* = 7 Hz, CH=C); mass spectrum parent *m/e* 332. Tlc analysis (3:1 petroleum ether–ether, two developments) showed a single spot (R_f 0.52). A sample was purified by preparative tlc (4:1 petroleum ether–ether, three developments) followed by evaporative distillation at 130° (0.01 mm): $[\alpha]^{23}D$ −2.9° (*c* 4.4).

Mol wt Calcd for $C_{14}H_{21}IO$: 332.0639. Found: 332.0637 (high-resolution mass spectrometry).

The petroleum ether eluent was evaporated under reduced pressure and separated by preparative tlc (petroleum ether) to yield 371 mg (26%) of 4-(π-tricyclyl)-1,2-butadiene (**17**): $[\alpha]^{23}D$ +28.6° (*c* 4.6); ir 1960 (m, allene), 846 cm^{-1} (s, allene); nmr[24] τ 5.48, 5.45, 5.42, 5.40, 5.37, 5.31, 5.27, 5.25 (m, 2, C=C=CH_2), 5.10, 5.00, 4.86, 4.78 (m, 1, *CH*=C=CH_2); mass spectrum parent *m/e* 188 (vw, <1%), 149 (parent − CH=C=CH_2); tlc R_f 0.62 (petroleum ether).

Mesylate of 2-Iodo-4-(π-tricyclyl)-*trans*-2-buten-1-ol. The iodo alcohol **11a** (1.00 g, 3.01 mmol) in anhydrous ether (6 ml) at −50° under argon was treated successively with *n*-butyllithium (3.01 mmol, 2.40 ml of a 1.26 *M* solution) in pentane and methanesulfonyl chloride (0.25 ml, 3.16 mmol) in ether (0.2 ml), and the mixture was allowed to warm to −10° over a 30-min period, forming a white precipitate near −10°. After stirring for an additional 30 min at −10°, the mixture was poured into cold sodium bicarbonate solution, and the product was extracted with ether and dried. Evaporation of solvent under reduced pressure gave a quantitative yield of the desired mesylate, essentially pure by nmr analysis: ir 1650 (w, C=C), 1370 and 1178 (vs, $-SO_2$—O–), 968 (s), 941 cm^{-1} (vs); nmr[24] τ 6.93 (s, 3, CH_3–SO_2), 5.12 (s, 2, CH_2O), 3.88 (t, 1, *J* = 7 Hz, CH=C); tlc R_f 0.55 (3:1 petroleum ether–ether, two developments).

1-Bromo-2-iodo-4-(π-tricyclyl)-*trans*-2-butene (12a). The mesylate of **11a** (1.24 g, 3.01 mmol) in ether (15 ml) was treated with anhydrous lithium bromide (393 mg, 4.51 mmol) at room temperature for 7 hr; the mixture was extracted with saturated sodium chloride solution and dried. Evaporation of solvent under reduced pressure yielded 1.16 g (98%) of **12a**, pure by nmr analysis: ir 1634 cm^{-1} (m, C=C); nmr[24] τ 5.64 (s, 2, CH_2Br), 4.01 (t, 1, *J* = 7 Hz, CH=C); tlc R_f 0.60 (petroleum ether, two developments).

2-Iodo-4-(π-tricyclyl)-*trans*-2-buten-1-ol (11a) and PBr_3. The iodo alcohol **11a** (180 mg, 0.54 mmol) in anhydrous ether (1 ml) was treated with phosphorus tribromide (20.5 μl, 0.217 mmol) in the dark at 0° for 22 hr,[15b] and the mixture was extracted with cold sodium bicarbonate solution and dried. Evaporation of solvent under reduced pressure yielded 130 mg (61%) of a 4:1 mixture (nmr analysis) of the iodobromides **12a** and **18**, respectively; tlc analysis (petroleum ether, two developments) showed two components with R_f values of 0.60 and 0.46, respectively. The mixture was separated by preparative tlc (petroleum ether) to yield 75 mg of **12a** and 31 mg of **18**. The β-santalene derivative **18** was identified by its spectra: ir 1658 and 1634 (m, C=C), 882 cm^{-1} (s, C=CH_2); nmr τ 8.95 (s, 3, CH_3), 9.17, 8.88, 8.68, 8.41, 8.22, 7.91, 7.30 (maxima of complex pattern, 12, ring and methylene protons), 5.65 (s, 2, CH_2Br), 5.50 and 5.24 (two s, 2, C=CH_2), 4.01 (t, 1, *J* = 7 Hz, CH=C).[26]

2-Iodo-4-(π-tricyclyl)-*trans*-2-butene (13a). The iodobromide **12a** (1.16 g, 2.94 mmol) in anhydrous DMSO (5 ml) was slowly added to sodium borohydride (222 mg, 5.88 mmol) in anhydrous DMSO (30 ml) at 18° (water bath) under argon during a 1-hr period, and the colorless solution was stirred for an additional hour at 18°.[16,27] The mixture was slowly added to cold 3 *N* hydrochloric acid, and the product was extracted with petroleum ether and dried. Evaporation of solvent yielded 891 mg (96%) of **13a**: ir 1653 cm^{-1} (w, C=C); nmr[24] τ 7.52 (d, 3, *J* = 1.5 Hz, CH_3—C=C), 4.58 (t of q, 1, J_t = 7 Hz, J_q = 1.5 Hz, CH=C); mass spectrum parent *m/e* 316. Tlc analysis (petroleum ether, two developments) showed a single spot (R_f 0.60); glpc analysis (column B, 120°) showed a single peak (t_r 7.4 min). A sample was purified by preparative glpc (column G, 185°): $[\alpha]^{24}D$ −4.6° (*c* 0.5).

Mol wt Calcd for $C_{14}H_{21}I$: 316.0690. Found: 316.0700 (high-resolution mass spectrometry).

Methyl α-Santalate (14a). Nickel carbonyl (2.33 ml, 18.0 mmol) and the vinyl iodide **13a** (944 mg, 3.0 mmol) were added successively to sodium methoxide (486 mg, 9.0 mmol) in anhydrous methanol (15 ml) at room temperature under argon, and the solution was heated at 40–45° for 10 hr under an efficient water-cooled condenser, giving a deep red solution after several minutes;[17] the reaction

(24) The tricyclic skeleton (R group of series a, Chart I) of α-santalol and all of the intermediates leading to it exhibited essentially the same nmr absorptions: τ 9.18 (s, 3, CH_3), 9.00 (s, 3, CH_3), 9.15 (sh), 9.05 (sh), 8.87, 8.71, 8.67, 8.58, 8.54, 8.45, 8.30 (complex pattern, 9, ring and methylene protons), and 8.15–7.65 (complex pattern, 2, allylic protons).

(25) A. Schaap, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **84**, 1200 (1965).

(26) The spectra obtained for **18** showed all the characteristic bands of the β-santalene unit as described for β-santalene itself by M. F. Semmelhack, Ph.D. Thesis, Harvard University, 1967.

(27) It is very important to perform the addition slowly with external cooling to prevent decomposition.

was followed by tlc analysis (50:1 petroleum ether–ether, visualized by ultraviolet light). When complete, the reaction was quenched with iodine in methanol at room temperature until the iodine color remained for 15 min. The reaction was poured into basic sodium thiosulfate solution, and the product was extracted with ether and dried. The crude product was purified by evaporative distillation at 110° (0.01 mm) to yield 540 mg (73%) of methyl α-santalate: ir 1725 (s, C=O), 1650 cm^{-1} (w, C=C); nmr[24] τ 8.13 (d, 3, J = 1.2 Hz, CH_3—C=C), 6.27 (s, 3, OCH_3), 4.07 (t of q, 1, J_t = 7.5 Hz, J_q = 1.2 Hz, CH=C); mass spectrum parent m/e 248. Tlc analysis (50:1 petroleum ether–ether) showed a single spot (R_f 0.30; glpc analysis (column C, 160°) showed a single peak (t_r 6.5 min). A sample was purified by preparative tlc (50:1 petroleum ether–ether, two developments) followed by evaporative distillation at 110° (0.03 mm): $[\alpha]^{23}D$ +6.1° (c 1.9).

Mol wt Calcd for $C_{16}H_{24}O_2$: 248.1776. Found: 248.1777 (high-resolution mass spectrometry).

α-Santalol (1). Lithium aluminum hydride (1.67 mmol, 1.20 ml of a 1.4 M solution) in ether was added to anhydrous aluminum chloride (74 mg, 0.557 mmol) in ether (6 ml) at 0° under argon, immediately forming a white precipitate. After 15 min at 0°, methyl α-santalate (207 mg, 0.833 mmol) in ether (0.5 ml) was added. After 30 min at 0°, the mixture was poured into cold dilute acid, and the product was extracted with ether and dried. Evaporation of solvent under reduced pressure yielded 183 mg (100%) of α-santalol: ir 3730 and 3280 (m, OH), 3085 (w), 2995 and 2925 (s, CH), 1675 (vw, C=C), 1456 (s), 1374 (m), 1316 (w), 1285 (w), 1258 (w), 1163 (w), 1096 (w), 1079 (m), 1033 (m), 997 (s, C—O), 969 (w), 934 (w), 905 (w), 875 (m), 849 cm^{-1} (m); nmr[24] τ 8.23 (d, 3, J = 1.2 Hz, CH_3—C=C), 7.21 (s, 1, OH), 5.90 (s, 2, CH_2O), 4.73 (unresolved t, 1, J = 7 Hz, CH=C);[28a,b] mass spectrum parent m/e 220. Tlc analysis (3:1 petroleum ether–ether, two developments) showed a single spot (R_f 0.47), and glpc analysis (column E, 175°) showed a single peak (t_r 7.7 min).[28b] A sample was purified by preparative tlc (4:1 petroleum ether–ether, two developments) followed by evaporative distillation at 80° (0.02 mm): $[\alpha]^{23}D$ +17.5° (c 3.3) (lit. natural[29] +17.0°; synthetic[4] +18.33°).

Mol wt Calcd for $C_{15}H_{24}O$: 220.1827. Found: 220.1828 (high-resolution mass spectrometry).

***trans*-2-Iodo-2-decen-1-ol (11B).** n-Butyllithium (6.50 mmol, 5.5 ml of a 1.18 M solution) and diisobutylaluminum hydride (3.5 ml, 19.5 mmol) were successively added to 2-decyn-1-ol (1.01 g, 6.50 mmol) in anhydrous ether (6 ml) at −20° under argon, and the colorless solution was heated at 35° for 50 hr. Hydrolysis of an aliquot yielded exclusively *trans*-2-decen-1-ol, identical with an authentic sample[30] and different from *cis*-2-decen-1-ol[31] with regard to infrared and nmr spectra and glpc analysis as the trimethylsilyl ether.[32] The reaction was quenched with anhydrous ethyl acetate (1.3 ml, 13.0 mmol) at 0° and with iodine (14.8 g, 58.5 mmol) in ether (75 ml) at −78°, and the product was isolated chromatographically as described above, yielding 1.22 g (67%) of *trans*-2-iodo-2-decen-1-ol, identical in all respects with an authentic sample:[8] ir 3560 and 3390 (m, OH), 1650 cm^{-1} (w, C=C); nmr[33] τ 6.80 (s, 1, OH), 5.76 (d, 2, J = 1.2 Hz, CH_2O), 4.08 (t of t, 1, J = 7 and 1.2 Hz, CH=C). Tlc analysis (3:1 petroleum ether–ether, two developments) showed a single compound (R_f 0.55) with no trace of the isomeric *trans*-3-iodo-2-decen-1-ol (R_f 0.49).[9]

***trans*-2-Bromo-2-decen-1-ol.** The reduction was carried out exactly as described above for the iodo alcohol **11b** except a cold (0°) solution of bromine (3.2 ml, 58.5 mmol) in ether (50 ml) was added at −78° instead of iodine. After chromatography 1.14 g (75%) of *trans*-2-bromo-2-decen-1-ol was obtained: ir 3720 and 3450 (m, OH), 1664 cm^{-1} (w, C=C); nmr[33] τ 6.70 (broad s, 1, OH), 5.79 (broad s, 2, CH_2O), 4.00 (t of t, 1, J = 7 and 1.5 Hz, CH=C); mass spectrum parent m/e 234, 236 (doublet). Tlc analysis (3:1 petroleum ether–ether, two developments) showed a single spot with R_f 0.55, identical with that of *trans*-2-iodo-2-decen-1-ol. An analytical sample was obtained by preparative glpc (column G, 135°).

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.07; H, 8.14; Br, 33.98. Found: C, 50.89; H, 8.09; Br, 34.45.

Mesylate of *trans*-2-Iodo-2-decen-1-ol. *trans*-2-Iodo-2-decen-1-ol (390 mg, 1.38 mmol) in ether (3 ml) was treated successively with n-butyllithium (1.38 mmol, 1.1 ml of a 1.26 M solution) in pentane and methanesulfonyl chloride (113 μl, 1.45 mmol) in ether (50 μl) as described above, yielding 492 mg (98%) of the desired mesylate: ir 1645 (w, C=C), 1366 and 1176 (vs, $-SO_2$–O), 972 (s), 941 cm^{-1} (vs); nmr[33] τ 6.93 (s, 3, CH_3—SO_2), 5.11 (d, 2, J = 1 Hz, CH_2O), 3.88 (t of t, 1, J = 6.5 and 1 Hz, CH=C); tlc R_f 0.57 (3:1 petroleum ether–ether, two developments).

1-Bromo-2-iodo-*trans*-2-decene. A. From Mesylate of *trans*-2-Iodo-2-decen-1-ol. The mesylate of *trans*-2-iodo-2-decen-1-ol (39 mg, 0.108 mmol) in ether (0.5 ml) was treated with lithium bromide (12 mg, 0.135 mmol) as described above to yield 37 mg (100%) of *trans*-1-bromo-2-iodo-2-decene: ir 1634 cm^{-1} (m, C=C); nmr[33] τ 5.66 (s, 2, CH_2Br), 4.03 (t, 1, J = 7 Hz, CH=C).

B. From *trans*-2-Iodo-2-decen-1-ol and PBr_3. *trans*-2-Iodo-2-decen-1-ol (309 mg, 1.09 mmol) in anhydrous ether (2 ml) was treated with phosphorus tribromide (37 μl, 0.39 mmol) at 0° for 24 hr in the dark;[15b] the reaction was quenched in cold sodium bicarbonate solution, and the product was extracted with ether and dried. Evaporation of solvent gave 302 mg (80%) of 1-bromo-2-iodo-*trans*-2-decene.

C. From *trans*-2-Iodo-2-decen-1-ol and PBr_3 in the Presence of CaH_2.[34] Phosphorus tribromide (23 μl, 0.24 mmol) was added to a mixture of *trans*-2-iodo-2-decen-1-ol (169 mg, 0.60 mmol) and calcium hydride (25 mg, 0.60 mmol) in hexane (1 ml) at room temperature, causing immediate gas evolution. After stirring at 22° for 13 hr, the mixture was poured into water, and the product was extracted with ether and dried. Evaporation of solvent under reduced pressure yielded 140 mg (74%) of *trans*-1-bromo-2-iodo-2-decene, pure by nmr analysis.

1,2-Dibromo-*trans*-2-decene. Following procedure B outlined above, *trans*-2-bromo-2-decen-1-ol (250 mg, 1.06 mmol) in ether (2 ml) was treated with phosphorus tribromide (38 μl, 0.40 mmol) to yield 264 mg (83%) of 1,2-dibromo-*trans*-2-decene: ir 1645 cm^{-1} (m, C=C); nmr[33] τ 5.75 (s, 2, CH_2Br), 3.87 (t, 1, J = 7 Hz, CH=C).

***trans*-2-Iodo-2-decene.** *trans*-1-Bromo-2-iodo-2-decene (271 mg, 0.785 mmol) in anhydrous DMSO (3 ml) was added over a 30-min period to sodium borohydride (60 mg, 1.57 mmol) in DMSO (9 ml) as described above, yielding 196 mg (94%) of *trans*-2-iodo-2-decene: ir 1658 cm^{-1} (w, C=C); nmr[33] τ 7.53 (d, 3, J = 1.5 Hz, CH_3—C=C), 4.59 (t of q, 1, J_t = 7 Hz, J_q = 1.5 Hz, CH=C); tlc R_f 0.78 (50:1 petroleum ether–ether). Glpc analysis (column D, 200°) showed a single peak (t_r 9.6 min).[35]

***trans*-2-Bromo-2-decene.** *trans*-1,2-Dibromo-2-decene (201 mg, 0.674 mmol) in DMSO (4 ml) was slowly added to sodium borohydride (51 mg, 1.35 mmol) in DMSO (6 ml) as described above to yield 150 mg (100%) of *trans*-2-bromo-2-decene: ir 1667 cm^{-1} (w, C=C); nmr[33] τ 7.73 (d, 3, J = 1.5 Hz, CH_3—C=C), 4.40 (t of q, 1, J_t = 6.5 Hz, J_q = 1.5 Hz, CH=C). Glpc analysis (column D, 180°) showed a single peak (t_r 9.6 min).[35]

Methyl 2-Methyl-*cis*-2-decenoate. Neat nickel carbonyl (0.16 ml, 1.24 mmol) and *trans*-2-iodo-2-decene (55 mg, 0.217 mmol) in methanol (0.25 ml) were added successively to sodium methoxide (34 mg, 0.62 mmol) in anhydrous methanol (1 ml) at room temperature under argon, and the solution was heated at 40° for 2 hr, slowly turning deep red;[17] tlc analysis (50:1 petroleum ether–ether, ultraviolet visualization) at this point indicated the reaction was complete.[36] Iodine in methanol was added at room temperature until the iodine color remained for 15 min; the mixture was poured into basic sodium thiosulfate solution, and the product was extracted with ether and dried. Evaporation of solvent under reduced pressure yielded 42 mg (100%) of methyl 2-methyl-*cis*-2-decenoate: ir 1724 (s, C=O),

(28) (a) Identical with published data and different from that for CH_3 and H *trans*;[4] (b) identical with a sample previously synthesized.[3]

(29) V. Herout, V. Jarolim, and J. Pliva, *Collect. Czech. Chem. Commun.*, 22, 773 (1957).

(30) Prepared by lithium aluminum hydride reduction of 2-decyn-1-ol.

(31) Prepared by hydrogenation of 2-decyn-1-ol with 5% palladium on barium sulfate in pyridine as outlined in L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 566. See also F. Bohlmann, U. Niedballa, and J. Schneider, *Chem. Ber.*, 98, 3010 (1965).

(32) The trimethylsilyl ethers were prepared by treating the alcohol in a small volume of ether with excess bis(trimethylsilyl)acetamide (Aldrich Chemical Co.) and were successfully separated by glpc (column A, 110°) with retention times of 9.6 (cis) and 10.2 min (trans).

(33) The n-C_7H_{15} group exhibited essentially the same nmr absorptions in all of the compounds described: τ 9.12 (t, 3, J = 5 Hz, CH_3–CH_2–), 8.73 (broad s, 10, CH_3—$(CH_2)_5$–), 7.85–8.00 (broad, t, 2, J = 7 Hz, CH_2—C=C).

(34) Attempted application of this procedure to **11a** led to new unidentified rearrangement products.

(35) *cis*- and *trans*-2-chloro-2-nonene have been cleanly separated with this column: E. J. Corey, J. I. Shulman, and H. Yamamoto, *Tetrahedron Lett.*, 447 (1970).

(36) 2-Bromo-2-decene failed to react within 30 hr at 50°.

1653 cm^{-1} (w, C=C); nmr[33] τ 8.10 (d, 3, J = 1 Hz, CH_3—C=C), 6.27 (s, 3, OCH_3), 4.07 (t of q, 1, J_t = 7 Hz, J_q = 1 Hz, CH=C);[37] mass spectrum parent *m/e* 198. Tlc analysis (50:1 petroleum ether–ether) showed a single spot (R_f 0.28); glpc analysis (column B, 100°) showed a single peak (t_r 4.5 min).[39] An analytical sample was obtained by preparative glpc (column G, 150°).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.19. Found: C, 72.58; H, 11.14.

2-Methyl-*cis*-2-decen-1-ol. Methyl 2-methyl-*cis*-2-decenoate (76 mg, 0.383 mmol) was treated with aluminum hydride as described above to yield 65 mg (100%) of 2-methyl-*cis*-2-decen-1-ol, identical in all respects with an authentic sample:[40] ir 3730 and 3410 (m, OH), 2950 and 2890 (s, CH), 1451 (m), 1372 (m), 1253 (w), 1170 (w), 1096 (m), 996 (s, C—O stretch), 947 (m), 852 cm^{-1} (w); nmr[33] τ 8.22 (d, 3, J = 1 Hz, CH_3—C=C), 7.90 (1, OH), 5.88 (s, 2, CH_2O), 4.71 (t, 1, J = 7.5 Hz, CH=C).[37] Both tlc (5:1 petroleum ether–ether, three developments) and glpc (column E, 150°) analyses showed a single isomer with properties identical with those of the cis isomer (R_f 0.48, t_r 5.5 min) and different from those of the trans isomer (R_f 0.42, t_r 6.1 min).[40]

Methyl 2-Hydroxymethyl-*cis*-2-decenoate (19). Neat nickel carbonyl (0.92 ml, 7.06 mmol) and 2-iodo-*trans*-2-decen-1-ol (500 mg, 1.77 mmol) in a small volume of methanol were successively added to sodium methoxide (144 mg, 2.66 mmol) in anhydrous methanol (10 ml) under argon at 0°, and the mixture was warmed to 25°.[17] After 30 min at 25°, tlc analysis (1:1 hexane–ether) indicated complete consumption of starting material, and the reaction was quenched with iodine in methanol until the iodine color persisted for 15 min. The mixture was poured into dilute acid–saturated sodium chloride solution, and the product was extracted with ether, treated with sodium bisulfite solution, and dried. The crude product was purified by preparative tlc (4:1, 3:1, 2:1 hexane–ether, one development each) to yield 324 mg (85%) of methyl 2-hydroxymethyl-*cis*-2-decenoate: ir (neat) 3330 (m, OH), 1710 (s, C=O), 1653 (m, C=C), 1220 cm^{-1} (s, C—O); nmr (CCl_4) τ 9.13 (t, 3), 8.70 (broad s, 10), 7.54 (t, 2, CH_2—C=C), 6.31 (s, 3, OCH_3), 6.12 (s, 1, OH), 5.91 (s, 2, CH_2O), 4.68 (t, 1, J = 7 Hz, CH=C); mass spectrum parent *m/e* 196 (mol wt − 18). Tlc analysis (1:1 hexane–ether) showed a single spot (R_f 0.50), and glpc analysis of its trimethylsilyl ether[32] (column B, 140°) showed a single peak (t_r 3.7 min).

Methyl 2-Hydroxymethyl-*cis*-2-decenoate with Pyridine–SO_3 and AlH_3. Methyl 2-hydroxymethyl-*cis*-2-decenoate (100 mg, 0.47 mmol) in anhydrous THF (7 ml) was treated with pyridine–sulfur trioxide complex[41] (186 mg, 1.17 mmol) at 0° for 2.5 hr;[19] since tlc analysis (1:1 petroleum ether–ether) indicated incomplete consumption of alcohol, the mixture was treated with additional pyridine–sulfur trioxide complex (62 mg, 0.39 mmol) for 1 hr at 0°, giving complete conversion of alcohol to sulfate. The mixture was treated at −60° with a solution of aluminum hydride, prepared from lithium aluminum hydride (1.88 mmol, 0.94 ml of a 2.0 *M* solution) and aluminum chloride (273 mg, 2.05 mmol) in THF (4 ml). The mixture was stirred at 25° for 18 hr, treated with lithium aluminum hydride (2.0 mmol) at −78°, and stirred at 25° for 1.5 hr.[42] After quenching with methanol (1.5 ml) at −78°, the mixture was poured into dilute acid, and the product was extracted with ether and dried. Evaporation of solvent under reduced pressure yielded 79 mg (99%) of an 8:1 mixture (glpc analysis, column E, 145°) of 2-methylenedecan-1-ol (**22**) and 2-methyl-*cis*-2-decen-1-ol (**15b**) with retention times of 9.1 and 7.9 min, respectively. A pure sample of 2-methylenedecan-1-ol was isolated by preparative glpc (column H, 165°): ir (neat) 2800 (s, OH), 1656 (m, C=C), 1066 (s), 1031 (s), 870 cm^{-1} (s, C=CH_2); nmr τ 9.12 (t, 3), 8.72 (broad s, 12), 7.98 (broad t, 2, CH_2—C=C), 7.70 (broad s, 1, OH), 6.08 (broad s, 2, CH_2O), 5.24 and 5.08 (two s, 2, C=CH_2).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.51; H, 12.84.

Methyl 2-Bromomethyl-*cis*-2-decenoate. Methyl 2-hydroxymethyl-*cis*-2-decenoate (102 mg, 0.477 mmol) in anhydrous ether (1 ml) was treated with phosphorus tribromide (16 μl, 0.17 mmol) in the dark at 0° for 26 hr.[15b] The mixture was extracted with cold sodium bicarbonate solution, dried, and evaporated under reduced pressure to give 128 mg (97%) of methyl 2-bromomethyl-*cis*-2-decenoate: ir 1727 (s, C=O), 1645 cm^{-1} (m, C=C); nmr τ 9.13 (t, 3), 8.69 (broad s, 10), 7.52 (broad t, 2, CH_2—C=C), 6.18 (s, 3, OCH_3), 5.81 (s, 2, CH_2Br), 3.64 (t, 1, J = 7.5 Hz, CH=C).

Methyl 2-Bromomethyl-*cis*-2-decenoate with $NaBH_4$ in DMSO. Methyl 2-bromomethyl-*cis*-2-decenoate (117 mg, 0.42 mmol) in DMSO (2 ml) was slowly added to sodium borohydride (32 mg, 0.84 mmol) in DMSO (3 ml) as described above. After the usual work-up, 83 mg (100%) of product was isolated which showed one major component (t_r 5.4 min, about 75%) and two minor components (t_r 4.5 min, about 10%; t_r 7.4 min, about 15%) by glpc analysis (column B, 100°). The major constituent was separated by preparative glpc (column G, 140°) and identified as methyl 2-methylenedecanoate (**21**): ir 1727 (s, C=O), 1634 (w, C=C), 944 and 910 cm^{-1} (m, C=CH_2); nmr τ 9.10 (t, 3), 8.69 (broad s, 12), 7.67 (broad t, 2, CH_2—C=C), 6.22 (s, 3, OCH_3), 4.44 and 3.83 (two s, 2, C=CH_2); mass spectrum parent *m/e* 198. *Anal.* Calcd for $C_{12}H_{22}O_2$: mol wt, 198.1620. Found: mol wt, 198.1614 (high-resolution mass spectrometry).

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(37) The assignment of cis geometry is supported by published nmr data.[38] No trace of the trans isomer was observed

(38) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, 33, 3382 (1968).

(39) Ethyl 2-methyl-*cis*- and *trans*-2-decenoate[40] were separated under these analytical conditions: cis, R_f 0.44, t_r 7.3 min; trans, R_f 0.33, t_r 10.7 min.

(40) J. A. Katzenellenbogen, Ph.D. Thesis, Harvard University, 1969.

(41) Aldrich Chemical Co.

(42) Treatment of the pyridinium sulfate **20** (X = OSO_3^-) directly with lithium aluminum hydride yielded a new unidentified compound as the principal reaction product (glpc t_r 6.2 min).