Anal. Calcd for $C_9H_{18}OSi$: C, 63.49; H, 10.67. Found: C, 62.16; H, 10.27. ^1H NMR δ –0.26 ($Si(CH_3)_3$, X), –0.20 ($Si(CH_3)_3$, XVIII), 0.54–2.38 (ring protons), 4.47 (>C*H*OH, XVIII), 5.95 (>C=CCH), XVIII).

3-Methyl-5-(trimethylsilyl)cyclohexan-1-one was obtained in low yield by faithful repetition in all particulars of the reported procedure,[1] and on one occasion none of the desired product was obtained. Still[1] did not silylate 5-methylcyclohex-2-en-1-one (with $(CH_3)_3SiLi$), but he did report no conjugate addition to isophorone. The reasons for these differences have not been established, but the $(CH_3)_3SiLiCu^I$ reagent appears to have certain advantages.[8]

3-Methyl-5-(trimethylsilyl)cyclohexan-1-one (XI and XII) was distilled (92 °C (8 mmHg)).

Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.17; H, 10.95. Found: C, 65.18; H, 11.05. ^1H NMR δ –0.12 ($Si(CH_3)_3$, XI), 0.84 (CH_3, d, J = 7 Hz), 0.94–2.52 (ring protons).

Reductions of Stannyl- and Silylcyclohexanones. Reductions with lithium aluminum hydride (ether, 0 °C) and sodium borohydride (2-propanol solvent) were conducted in the normal way to provide the cyclohexanols in high yields (>90%). These alcohols were examined by ^1H, ^{13}C, ^{119}Sn, and ^{29}Si NMR to provide isomer percentages reported in the text.

3-(Trimethylstannyl)cyclohexanol (IV, V): bp 83 °C (2 mmHg). Anal. Calcd for $C_9H_{20}OSn$: C, 41.07; H, 7.60. Found: C, 41.28; H, 7.75. ^1H NMR δ 0.04 ($Sn(CH_3)_3$, $J_{^{119}Sn-^1H}$ = 51 Hz), 3.4 (CHOH, IV (85%), $w_{1/2}$ = 20 Hz), 3.8 (CHOH, V (15%), $w_{1/2}$ = 12 Hz).

3-Methyl-5-(trimethylstannyl)cyclohexanol (VI–IX): bp 72–74 °C (1 mmHg). Anal. Calcd for $C_{10}H_{22}OSn$: C, 43.22; H, 7.94. Found: C, 43.66; H, 8.09. ^1H NMR δ 0.07 (major), –0.03 ($J_{^{119}Sn-^1H}$ = 49 Hz, $Sn(CH_3)_3$), overlapping CHOH signals from 3.3–3.9 with $w_{1/2}$ characteristic of axial protons.

3-(Trimethylsilyl)cyclohexanol (XIII, XIV): bp 85 °C (2 mmHg) (Kugelrohr). Anal. Calcd for $C_9H_{20}OSi$: C, 62.74; H, 11.71. Found: C, 61.13; H, 10.88. ^1H NMR δ –0.22 ($Si(CH_3)_3$, XIII), –0.12 ($Si(CH_3)_3$, XIV, XVIII), 0.19–2.11 (ring protons), 3.39 (C*H*OH, XIII), 3.91 (C*H*OH, XIV), 4.47 (C*H*OH, XVIII), 5.59 (CH=C<, XVIII).

3-Methyl-5-(trimethylsilyl)cyclohexanol (XV, XVI, XVII): bp 123 °C (8 mmHg) (Kugelrohr). Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.47; H, 11.91. Found: C, 64.62; H, 11.92. ^1H NMR δ –0.24 ($Si(CH_3)_3$, XV), –0.18 ($Si(CH_3)_3$, XVI), 0.78 (CH_3, d, J = 6 Hz, XVI), 0.81 (CH_3, d, J = 7.5 Hz, XV), 0.61–2.16 (ring protons), 3.58 (C*H*OH). The >CHOH region (ca. δ 3.6) is consistent only with axial hydrogens. The more intense CCH_3 doublet is at lower field (δ 0.81), whereas the more intense $Si(CH_3)_3$ signal is at higher field (δ –0.24) with the other observable $Si(CH_3)_3$ signal at δ –0.18. (Ratio ca. 1.4:1). The relative positions of the CCH_3 and $Si(CH_3)_3$ signals for XV and XVI are appropriate for the indicated stereochemistries and conformations. The dominance of XV over XVI (Chart I) is shown in the ^{13}C spectrum by the positions of the CCH_3 and $Si(CH_3)_3$ resonances: both should be to higher field for those of XV than for those of XVI. Signals ascribable to XVII (~6%) were not identified in the ^1H spectrum.

NMR Spectra. ^{13}C NMR spectra were obtained at 25.05 MHz (JEOL FX-100) for $CDCl_3$ solutions, and chemical shifts are referenced to the center peak of the $CDCl_3$ triplet at 77.00 ppm. ^{119}Sn and ^{29}Si NMR spectra were recorded at 37.08 and 19.79 MHz, respectively (JEOL FX-100). The ^{29}Si spectra were obtained by a polarization transfer technique (INEPT) as described by Doddrell et al.[18] The ^{119}Sn and ^{29}Si chemical shifts are relative to internal $(CH_3)_4Sn$ and $(CH_3)_4Si$, respectively, and positive shifts are to lower field. ^1H NMR spectra were recorded for $CDCl_3$ solutions at 100 MHz (JEOL PS-100) and 300 MHz (Bruker CXP-300) with $CHCl_3$ (7.24 ppm) as internal reference.

Acknowledgment. This research was funded in part by the Australian Research Grants Committee.

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Registry No. I, 63831-50-5; II, 82569-82-2; III, 82569-83-3; IV, 82521-58-2; V, 82521-59-3; VI, 82521-60-6; VII, 82570-82-9; VIII, 82569-84-4; IX, 82570-83-0; X, 7531-60-4; XI, 82521-61-7; XII, 82521-62-8; XIII, 7452-98-4; XIV, 7452-99-5; XV, 82521-63-9; XVI, 82569-85-5; XVII, 82569-86-6; XVIII, 82521-64-0; $(CH_3)_3SnLi$, 17946-71-3; $(CH_3)_3SiLi$, 18000-27-6; 2-cyclohexen-1-one, 930-68-7; 5-methyl-2-cyclohexen-1-one, 7214-50-8; 3-(trimethylsilyl)-1-[trimethylsilyl)oxy]-1-cyclohexene, 55942-21-7.

Syntheses of the Stereoisomers of the Sex Pheromones of the Southern Corn Rootworm and Lesser Tea Tortrix

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Assignments of stereostructure and precise composition of insect sex pheromones are often necessarily made by physiological evaluation of candidate synthetics.[1] Generally the amount of isolate available for structure assignment is less than 0.1 mg, and for chiral materials the difficulty in configuration assignment is often compounded by asymmetric centers remotely situated from spectrally useful functionality. Although the stereoisomers of a pheromonal enantiomer frequently act only as diluents in bioassays of racemic mixtures, the enantiomer of the Japanese beetle sex pheromone inhibits male response to the active stereoisomer at the 1% level.[2] In addition, at least one case is known of an insect sex pheromone that is a nonracemic mixture of stereoisomers on the basis of identification of the natural ratio directly.[3] Despite dramatic accomplishments in asymmetric synthesis by induction of asymmetry[4] and the often clever means by which these have been applied in the cause of insect chemistry, ultimate purification of either key intermediates or final products must be achieved by some form of kinetic resolution in order to obtain unambiquous biological data. We report here the synthesis of the stereoisomers of two insect sex pheromones from readily available 10-undecenoic acid. The key steps involved a facile purification of crystalline diastereomeric amides followed by N-hydroxyethylation of the amides as a ploy to render the purified amides susceptible to mild acid hydrolysis.

Stereochemically undefined structures have been assigned to the sex pheromones of the southern corn rootworm, *Diabrotica undecimpunctata* howardi Barber,[5] and the lesser tea tortrix, *Adoxophyes* spp.[6] The structure assigned the pheromone of the former insect (a beetle) is 10-methyl-2-tridecanone (1, Scheme I). The latter insect, a moth, employs a pheromone blend containing 10-methyl-1-dodecanol acetate (2) as a minor component.

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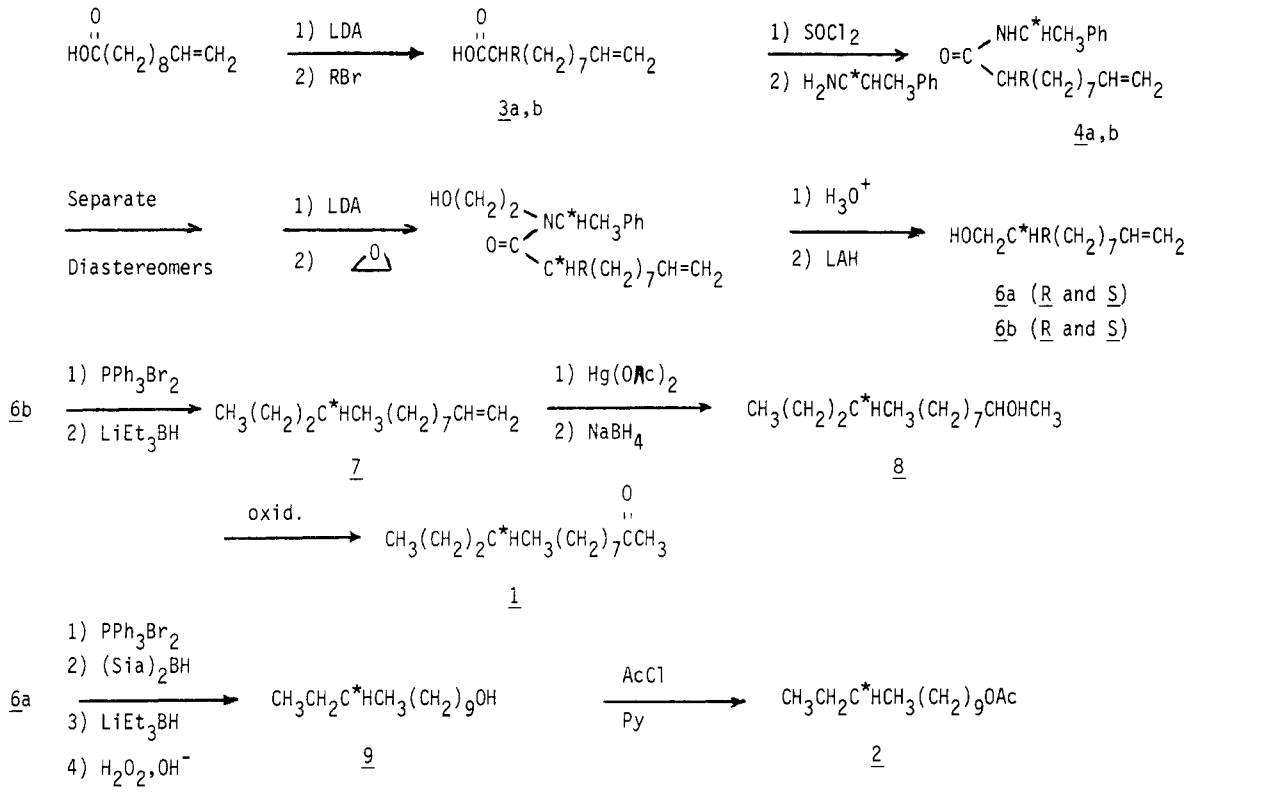
Scheme I



Pheromones of this structural type can be readily prepared from 10-undecenoic acid by (1) α-alkylation, (2) reduction of carboxyl to methyl, and (3) functionalization of the terminal double bond. Thus undecenoic acid was deprotonated with 2 equiv. of lithium diisopropylamide (LDA) in THF and then alkylated with either ethyl bromide or *n*-propyl bromide by the method of Pfeffer and Silbert.[7] The resulting α-alkylated acids **3** were converted to amides **4** of (*S*)-and (*R*)-α-methylbenzylamine. The α-methylbenzylamides, **4**, were readily purified by four-fold recrystallization from ethanol, providing *R**,*S** diastereomers in at least 99.6% purity and in 35–40% theoretical yield. Alternatively, these amides are quite readily purified by HPLC.

At this point one is faced with the difficult task of cleaving the amide linkage while preserving the configuration of the asymmetric carbon of the acid residue. In an initial study we reported a synthesis of **2** and indicated that none of the several mild methods for amide cleavage succeeded for α-methylbenzyl amides.[8,9] However, amides of β-hydroxy amines such as prolinol and ephedrine are known to undergo facile hydrolysis involving a transfer of the acyl group from nitrogen to oxygen.[10] For amides of short-chain acids brief reflux in 1 N HCl was sufficient;[11] for longer chain acids one can employ a two-phase system of hexane and concentrated HCl (reflux time is a little longer).[8,12] It is also useful to know that such amides proceed to amino esters in THF containing 1 equiv of $HClO_4$, at room temperature in 5–6 h. The α-methylbenzylamides could be labilized to hydrolysis, therefore, by N-alkylation to **5a,b** by using the sequence (1) LDA and (2) ethylene oxide. No problem was encountered during deprotonation of the amide with respect to carbon configuration. The N-anion defused the carbonyl group's capacity to render the α-H acidic, and excess LDA was discharged with the excess ethylene oxide employed. The N-hydroxyethylated amides **5** can then be treated so as to yield either the corresponding amino esters (as perchlorate salts) or the acids by complete hydrolysis. Either type of product can be reduced to the carbinol **6** with $LiAlH_4$ although it should be noted that the amino esters revert easily to the hydroxy amides. On one occasion the process of neutralization of an amino ester perchlorate followed directly by $LiAlH_4$ treatment yielded the N-hydroxyethylated tertiary amine related to the *N*-hydroxyethyl amide.

Although the hydrolytic cleavage of *N*-alkyl amides via hydroxyethylated derivatives was successfully applied to preparing the configurationally pure acids that we sought, the chiral amines were recovered as *N*-(hydroxyethyl)-α-methylbenzylamines. These were not successfully recycled in the process for preparing acids. Even though the N-hydroxyethylated amides were crystalline, we were unable to affect resolution of those diastereomers vis crystallization.

The alcohols **6a,b** constitute the last opportunity to conveniently analyze for configurational purity. Jones oxidation gave the acids **3** from which the amides **4** were again prepared for GLC analysis with care taken to avoid diastereomer fractionation. Each alcohol was ≥99.6% pure.

In order to complete the synthesis of the ketones (*R*)-**1** and (*S*)-**1**, the configurationally pure alcohols **6b** were first converted to bromides by using $PPh_3{\cdot}Br_2$ and then reduced with $LiEt_3BH$. The usual oxidative workup[13] provided not only the expected alkenes **7** but also the primary alcohol 10-methyl-1-tridecanol.[14] The alkenes **7**

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were separated by column chromatography from the by-product alcohols, hydroxymercurated, reduced with $NaBH_4$ to give the secondary alcohols **8**, and then oxidized to the target ketones **1**.

The acetates **2** could be obtained in similar fashion. Bromides were prepared from the alcohols **6a** and then hydroborated with excess disiamylborane. The hydroboration miture was treated directly with excess $LiEt_3BH$ and, after 12 h at ambient temperature, the mixtures were worked up oxidatively. Acetylation of the alcohols produced the desired acetates **2**.

In summary, fractional crystallization of diastereomeric amides is a useful process for obtaining acids of high configurational purity. In the present instance the acids prepared were employed in synthesizing two insect sex pheromones in configurational purity sufficient to allow unambiguous biological (insect behavioral) assay. Efforts to reracemize the amides that were recovered from the crystallization and to develop a cleavage technique allowing the chiral auxiliary to be recycled have thus far been unsuccessful.

Experimental Section

Gas–liquid chromatography was performed with Varian 1400 and 2400 instruments by using the following columns: column A, Ultrabond II (3.2 mm × 1.5 m); column B, SE-54 (0.25 mm × 15 m); column C, OV-1 (0.25 mm × 31 m) operated at temperatures as indicated. High-performance liquid chromatography was conducted with an analytical column of 5-μm Lichrosorb Si-60 (6.3 mm × 25 cm). Mass spectral data were obtained with a Finnigan Model 3200 chamical-ionization mass spectrometer that was equipped with a chromatographic inlet (Varian Model 1400) served by a 3% OV-101 column (3.2 cm × 1.5 m) by using either methane or isobutane as the reagent gas. Infrared data were recorded with a Nicolet 7199-FT-IR system as CCl_4 solutions, and ^1H NMR data were obtained with a Nicolet 300-MHz FT NMR spectrometer ($CDCl_3$). Methoxy(trifluoromethyl)phenylacetic acid was obtained from Aldrich Chemical Co. and converted to the acid chloride;[8] (*R*)- and (*S*)-α-methylbenzylamines were purchased from Fluka Tridom Chemical Corp. and purified as tartrate salts (see text) by using column A to analyze the amines as MTPA amides[15] (150 °C, $\alpha = 1.14$, *R*S** eluted first; each diastereomer was ≥99.7% pure).

(±)-2-Alkyl-10-undecenoic Acids (3). The preparation of 2-ethyl- and 2-*n*-propylundecenoic acids followed the general procedure of Pfeffer and Silbert.[7] The 2-ethylated acid **3a** was obtained in 95.2% yield (<5% unalkylated) from 10-undecenoic acid: bp 125–227 °C (0.01 mm).[9] The 2-*n*-propylated acid **3b** was obtained in 98.5% yield (<5% unalkylated): bp 116–120 °C (0.005 mm); IR 1705 (C=O), 990, 910 cm^{-1} ($CH=CH_2$); NMR δ 0.88 (t, 3 H, CH_3CH_2), 2.05 (m, 2 H, $CH_2C=$), 2.36 (m, 1 H, $CHCO_2H$), 4.95 and 5.80 (m, 3 H, $CH=CH_2$); CIMS of methyl ester, *m/e* 241 (P + 1).

Syntheses of Diastereomerically Pure Amides 4. The carboxylic acids, **3** (1 equiv) were converted to acid halides with $SOCl_2$ (1.2 equiv) and DMF (0.12 equiv) in anhydrous Et_2O.[16a] The reaction mixtures were concentrated on a flash evaporator, the residues were taken up in hexane and filtered through Na_2SO_4, and the filtrates were again concentrated. The crude acid halides were then added as solutions in CH_2Cl_2 to cooled, stirred solutions containing 1.1 equiv each of one of the α-methylbenzylamines and Et_3N in CH_2Cl_2 (ice bath). The resulting mixtures were stirred at ambient temperature for 2 h and then worked up in the usual manner to yield the solid amides quantitatively. Recrystallization from ethanol (8 mL/g of amide) gave material close to 95% *R*,S**. Two or three further recrystallizations gave amide ≥99.9% pure in three of four cases, ≥99.6% pure for **4b** (R_{acid},S_{amine}). Purifications were monitored by using GLC (column B, 210 °C). GLC for **4a**: $k_{S^*,S^{*\prime}}$, 10.45; $k_{R^*,S^{*\prime}}$, 11.18; α, 1.07; *R*, 2.0. GLC for **4b**: $k_{S^*,S^{*\prime}}$, 13.00; $k_{R^*,S^{*\prime}}$, 13.64, α, 1.05; *R*, 1.4[17,18] Yields of purified amides (*R*,S**) were 32–40% of theoretical: IR 3460, 1688 (amide I), 990, 910 ($CH=CH_2$); NMR δ 0.88 (brt, 3 H, CH_3CH_2), 1.67 (d, 3 H, CH_3CHN)), 2.04 (m, 2 H, $CH_2C=$), 4.9 and 5.7 (m, 3 H, $CH_2=CH$), 5.31 (9, 1 H, CH_3CHN), 7.3 (m, 5 H, aryl H); CIMS, *m/e* 316 (**4a**, p + 1), 330 (**4b**, P + 1); HPLC (2% THF/20% EtOAc/78% hexane) for **4a**, $\alpha = 1.45$, $R = 3.08$ at 1 mL/min, *R*,S** eluted first. (*R*,S**)-**4a**, mp 98–99 °C (ethanol). (*R*,R**)-**4a**, mp 56–57 °C (ethanol). (*R*,S**) **4b**, mp 91–92 °C (ethanol); *R*R** isomer not determined.

Hydroxyethylated Amides 5. In a typical preparation the amide (7.0 g, 22.2 mmol) was dried over P_2O_5 in vacuo for 16 h and then added at one time to a solution of LDA that had been prepared with diisopropylamine (4.8 mL, 33 mmol) and commercial 1.55 M *n*-butyllithium (22 mL) in THF (50 mL) under nitrogen and maintained at 0–5 °C. The mixture was stirred without external cooling for 20 min and then cooled again to 0–5 °C. Ethylene oxide (2 mL, 40 mmol) was injected, and the mixture was then stirred at ambient temperature overnight. The reaction was worked up with 100 mL of 1 N HCl and washed with hexane (3 × 50 mL). The organic phase was washed twice with H_2O and dried ($MgSO_4$). Removal of solvent gave 7.9 g of crude crystalline product containing ca. 3% of unalkylated amide (98% yield). **5a**: mp 72–74 °C (hexane); IR 3540, 1630 (H-bonded amide I), 990, 910 cm^{-1} ($CH=CH_2$); NMR δ 0.90 (t, 3 H, CH_3CH_2), 1.66 (d, 3 H, CH_3CHN), 2.04 (m, 2 H, $CH_2C=$), 3.21 (brt, 2 H, NCH_2CH_2), 3.51 (m, 3 H, OCH_2CH_2 and $RR'CHC=O$), 4.9 and 5.8 (m, 3 H, $CH=CH_2$), 5.30 (q, 1 H, CH_3CHN), 7.3 (m, 5 H, aryl H); CIMS, *m/e* 360 (P + 1), 316 (P + 1 − C_2H_4O). **5b**: crude mp 72–80 °C; IR and NMR essentially the same as for **5a**, CIMS, *m/e* 374 (P + 1), 340 (P + 1 − C_2H_4O).

2-Ethyl- and 2-Propyl-10-undecen-1-ol (6a,b). In a typical reaction the diastereomerically pure N-hydroxyethylamide (7.0 g, 19.5 mmol) was dissolved in THF (140 mL) containing 70% $HClO_4$ (15.4 mL, 10 equiv), and H_2O was added to saturation. The solution was heated under reflux overnight (8 h was sufficient). The mixture was cooled, diluted with 200 mL of brine, and extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was washed with two 50-mL portions of brine and dried ($MgSO_4$). Removal of the solvent yielded the enantiomerically pure acid that was directly reduced to the carbinol **6** by addition in THF (15 mL) to a cooled (0–5 °C) stirred suspension of $LiAlH_4$ (2 g) in THF (40 mL). The resulting mixture was stirred 2–3 h, allowing the bath to achieve room temperature, and was then heated under reflux overnight. The mixture was worked up in the usual manner, employing 1.25 N NaOH, ether, and Celite filtration. The filtrate was washed with 50 mL each of 2 N HCl and H_2O. The ethereal layer was dried ($MgSO_4$), concentrated, and distilled: giving 3.26 g (84.5%) of **6a** [*R* or *S*; bp 100–103 °C (0.1 mm)] identical with material previously characterized.[8] **6b** (*R* or *S*): bp 82–87 °C (0.02 mm); IR 3640 (OH), 990, 910 cm^{-1} ($CH=CH_2$); NMR δ 0.91 (brt, 3 H, CH_3CH_2), 2.04 (m, 2 H, $CH_2C=$), 3.54 (d, 2 H, $J = 5.5$ Hz, $CHCH_2OH$), 5.0 and 5.8 (m, 3 H, $CH=CH_2$); CIMS, *m/e* 213 (P + 1), 211 (P − 1), 195 (P + 1 − H_2O), 193 (P − 1 − H_2O).

Basification of the aqueous phase and extraction with ether followed by drying (Na_2SO_4) and removal of solvent allowed recovery of N-hydroxyethylated α-methylbenzylamines. Distillation provided product: 2.0 g (63%); bp 80–81 °C (0.10 mm).

Determination of the Enantiomeric Purity of Carbinols 6. The carbinols **6** were oxidized with Jones reagent[16b] to the acids and converted subsequently via acid halides (vide supra) to the amides of an enantiomerically pure α-methylbenzylamine in the

(14) Prompted by these observations and related control experiments, as well as by the result of experiments underway in the laboratories of Professor H. C. Brown at Purdue University, Dr. Clinton Lanc of Aldrich Boranes, Inc., determined that aged (ca. 6 months) solutions of Super-Hydride contained about 25% each of $LiEt_2BH_2$ and $LiEt_4B$. This agreed well with the 20–25% yields of alcohols we obtained by reducing haloalkenes such as **7** or by reducing alkyl halides in the presence of alkenes. Evidently, as halogen replacement proceeds and Et_3B is produced, hydride is exchanged from $LiEt_2BH_2$ to produce Et_2BH which then hydroborates the double bond.

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(17) Ettre, L. S. *J. Gas Chromatogr.* **1963**, *1*, 36.

(18) The stereochemistry of the acid residue has been assigned by using the knowledge of the configurational bias induced in alkylations of chiral amide enolates. See ref 9 and also: Sonnet, P. E.; Heath, R. R. *J. Chromatogr.* **1982**, *238* (1), 40.

usual manner.[19] Analyses were identical with those described above.

10-Methyl-1-tridecene (7, *R* and *S*). The carbinol 6 (*R* or *S*; 4.23 g, 19.95 mmol) was added at one time to a cooled (0–5 °C) solution of PPh_3Br_2 (from 6.3 g, 24 mmol, of PPh_3 and 3.85 g, 24 mmol, of Br_2) in CH_2Cl_2 (40 mL). The resulting mixture was allowed to stir without external cooling for 2 h. Methanol (1 mL) was added to discharge the excess PPh_3Br_2, and the solvent was stripped. The residue was triturated with hexane and filtered. The filtrate was concentrated, and the oily residue was then filtered through silica gel (10 g) with pentane (100 mL). Removal of the solvent gave the crude alkyl bromide (>95% GLC pure) quantitatively. Foaming prevented distillation: IR 3080, 990, 910 cm^{-1} ($CH{=}CH_2$); NMR δ 0.89 (brt, 3 H, CH_3CH_2), 2.05 (m, 2 H, $CH_2C{=}$), 3.43 (d, 2 H, J = 6.9, $CHCH_2Br$), 4.9 and 5.8 (m, 3 H, $CH{=}CH_2$); CIMS, m/e 195 (P + 1 - Br). The crude bromide (4.9 g, 17.8 mmol) was treated with commercial $LiEt_3BH$ (38 mL of a 0.95 M solution) in THF (20 mL) of 0–5 °C for 0.5 h and then without external cooling for another 1.5 h to ensure completion. The mixture was worked up oxidatively with 3 N NaOH (14 mL) and 30% H_2O_2 (14 mL) in the usual way.[13] Extraction with pentane, drying ($MgSO_4$), and concentrating provided a mixture (ca. 4:1) of the alkene 7 and an alcohol, 10-methyl-1-tridecanol. These were separated by chromatography on silica gel (10 g), the alkene eluting with pentene (foaming again rpevented distillation): 2.75 g (70% yield from **6b**); IR 3080, 990, 910 cm^{-1} ($CH{=}CH_2$); NMR δ 0.87 and 0.88 (overlapped d and t, 3 H each, CH_3CH_2 and CH_3CH), 2.04 (m, 2 H, $CH_2C{=}$), 4.9 and 5.8 (m, 3 H, $CH{=}CH_2$), CIMS, m/e 197 (P + 1). Elution with 1:1 EtOAc/hexane gave the alcohol byproduct (identical with a sample prepared by hydroborating–oxidizing racemic 7 (1.05 g, 20%): bp 98–100 °C (0.1 mm); IR 3640 cm^{-1}; NMR δ 0.85 (d, 3 H, J = 7 Hz, CH_3CH), 0.88 (t, 3 H, J = 7 Hz, CH_3CH_2), 3.64 (t, 2 H, J = 6.8 Hz, CH_2CH_2OH); CIMS, m/e 214 (P + 1), 197 (P + 1 - 18).

10-Methyl-2-tridecanol (8, *R* and *S*). The alkene 7 (*R* or *S*, 0.97 g, 4.95 mmol) in THF (9 mL) was added dropwise to a stirred, cooled (0–5 °C) solution of $Hg(OAc)_2$ (1.84 g, 5.4 mmol) in H_2O (9 mL). The resulting mixture was stirred for 1.5 h beyond discharge of its yellow color. To the mixture was added 3.0 N NaOH (17 mL) and then]7 mL of 3.0 N NaOH that was 1.0 N in $NaBH_4$, the latter with ice cooling of the reaction mixture. The final mixture was stirred another 15 min without cooling, diluted with brine, and extracted with hexane. The extract was dried ($MgSO_4$) and concentrated. The residue was distilled to give product: 1.0 g (95%); bp 63–65 °C (0.04 mm); IR 3640 cm^{-1}; NMR δ 3.78 (m, 1 H, CHOH); CIMS, m/e 197 (P + 1 - 18). These alcohols (*R*)- and (*S*)-8 were identical with those prepared by an independent route.[5]

10-Methyl-2-tridecanone (1, *R* and *S*). The alcohol 8 (*R* or *S*; 0.45 g, 2.1 mmol) was dissolved in 5 mL of ether to which was added a solution of $Na_2Cr_2O_7$ (0.4 g, 1.3 mmol) and H_2SO_4 (0.3 mL, 5.0 mmol) in 2 mL or H_2O. The resulting mixture was stirred for 2 h and then worked up in the usual manner. The ketone was distilled bulb-to-bulb to give (*R*)-1 (and (*S*)-1): 0.35 g (78%): bath temperature 180 °C (30 mm); $[\alpha]^{24}_D$ for (*R*)-1 -1.71° (*c* 9.35, $CHCl_3$); IR 1720 cm^{-1}; NMR δ 2.13 (s, 3 H, $CH_3C{=}O$), 2.42 (t, 2 H, J = 7 Hz, $CH_2CH_2C{=}O$); CIMS, m/e 213 (P + 1).

10-Methyl-1-dodecanol (9, *R* and *S*). The alcohol **6a** (*R* or *S*; 3.0 g, 15.1 mmol) was treated with PPh_3Br_2 in CH_2Cl_2 as described for **6b** above. The crude bromides (>95% GLC pure) gave equivalent spectral data and were employed directly for the hydroboration step. A solution of disiamylborane was prepared from 3-methyl-2-butene (3.85 mL, 36.2 mmol) and commercial BH_3·THF (18.1 mL of a 1.0 M solution) in the usual manner.[20] The bromoalkene [(*R*)- or (*S*)-2-ethyl-10-undecen-1-yl bromide, 15.1 mmol] was added dropwise as a solution in THF (5 mL), maintaining the mixture at 0–5 °C for 1 h. Then $LiEt_3BH$ (47.7 mL of a 0.95 M solution) was added at one time and the mixture allowed to stir overnight. The mixture was worked up oxidatively by sequentially adding 3.0 N NaOH (23 mL) and 30% H_2O_2 (23 mL). The mixture was kept at 40 °C for 0.5 h, diluted with H_2O, and extracted with hexane. The extract was dried ($MgSO_4$) and concentrated. The product was distilled through a Vigreaux column to give recovered alkene **6a** [0.25 g (9.1%); bp 50–52 °C (0.025 mm)] and (*R*)- or (*S*)-**9**: 1.73 g (57.7%); bp 84–86 °C (0.04 mm). The alcohols were identical with the racemic alcohol previously reported.[9]

10-Methyl-1-dodecanol Acetate (2, *R* and *S*). The alcohols **9** (*R* or *S*) were acetylated with Ac_2O in pyridine as previously described.[9] The product acetates were purified by passage through silica gel (20 g/1 g of acetate), eluting with 5% EtOAc/hexane. Bult-to-bulb distillation gave samples of (*R*)-**2** [$[\alpha]^{24}_D$ -5.57° (*c* 21.8, $CHCl_3$)] and **2*S*** [$[\alpha]^{24}_D$ +5.60° (*c* 21.8, $CHCl_3$)]. The previously reported rotation for this acetate prepared from commercial citronellol was 4.85°.[21] It is now clear that bioassays were reported based the basis of ca. 86.6 ee.[22]

Registry No. (*R*)-1, 82621-53-2; (*S*)-1, 82621-54-3; (*R*)-2, 71777-34-9; (*S*)-2, 71777-35-0; (±)-3a, 82621-55-4; (±)-3a acid chloride, 82621-56-5; (±)-3b, 82638-73-1; (±)-3b acid chloride, 82621-57-6; (*R**,*S**)-4a, 82621-58-7; (*R**,*R**)-4a, 82621-59-8; (*R**,*S**)-4b, 825638-74-2; (*R**,*R**)-4b, 82638-75-3; (*R**,*S**)-5a, 82621-60-1; (*R**,*R**)-5a, 82621-61-2; (*R**,*S**)-5b, 82621-62-3; (*R**,*R**)-5b, 82621-63-4; (*R*)-6a, 82621-64-5; (*S*)-6a, 82621-65-6; (*R*)-6b, 82621-66-7; (*S*)-6b, 82621-67-8; (*R*)-7, 82621-68-9; (*S*)-7, 82621-69-0; 8, 82621-70-3; (*R*)-9, 71777-32-7; (*S*)-9, 71777-33-8; (*S*)-α-methylbenzylamine, 2627-86-3; (*R*)-α-methylbenzylamine, 3886-69-9; ethylene oxide, 75-21-8; (*R*)-2-propyl-10-undecen-1-yl bromide, 82621-71-4; (*S*)-2-propyl-10-undecen-1-yl bromide, 82621-72-5; 10-methyl-1-tridecanol, 82621-73-6; (*R*)-2-ethyl-10-undecen-1-yl bromide, 82621-74-7; (*S*)-2-ethyl-10-undecen-1-yl bromide, 82621-74-7; disiamylborane, 1069-54-1; 10-undecenoic acid, 112-38-9.

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Synthesis and Diels–Alder Reactivity of 7-Isopropylidene-2,3,5,6-tetramethylenebicyclo-[2.2.1]heptane (7,7-Dimethyl[2.2.1]hericene)[1]

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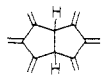
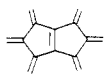
The 2,3,5,6-tetramethylenebicyclo[2.2.*n*]alkanes **1–5** and the 2,3,5,6,7,8-hexamethylenebicyclo[2.2.2]octane (**6**,[2,3] [2.2.2]hericene[1]) have interesting properties. Evidence for transannular interactions between the homoconjugated exocyclic *s-cis*-butadiene functions were found in the

(1) The shortened name [*l.m.n*]hericene is used for bicyclo[*l.m.n*]alkanes with $l + m + n$ methylidene groups,[2,3] after the latin name hericeus for hedgehog. We thank Professor H. Wyler for suggesting us this resemblance. Substituents at the bridgehead atoms are numbered 1 and $l + 2$, those at the exocyclic centers are numbered according to the positions of the connecting atoms, being part of the bicyclic skeleton. This nomenclature appears to us to be shorter than the bicyclo[*l.m.n*]-radialene nomenclature proposed by Hart et al.[4] Accordingly, the following compounds are named as shown. For the [*n*]radialene nomen-



[3.3.0]hericene



1,5-dehydro[3.3.0]hericene

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