

STEREISOIMERS AND ANALOGS OF 14-METHYL-1-OCTADECENE, SEX PHEROMONE OF PEACH LEAFMINER MOTH, *Lyonetia clerkella*, L.¹

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Abstract—The synthesis of the enantiomeric 14-methyl-1-octadecenes in >99% EE is described. Enantiomeric 2-methyl-1-hexanols were intermediates in the synthesis. The 1-alkene had been previously identified as the sex pheromone of the peach leafminer moth. Several closely related structures that have Δ_{12} unsaturation are also described.

Key Words—Chirality, alkenes, synthesis, branched hydrocarbons, diastereomeric amides, resolution, enantiomers, optical purity, olefin inversion.

INTRODUCTION

The peach leafminer, *Lyonetia clerkella* L., is one of Japan's most serious orchard pests (Naruse, 1978). Because larval damage occurs within the leaves, the larvae are not exposed to the usual contact sprays. This results in an emphasis on spray timing, a situation wherein optimal effectiveness of conventional insecticides is compressed into a short time window with attendant un-

¹Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

certainties. The situation might be relieved if one could monitor the adult moth population. This could be done by use of a pheromone lure trap. The sex pheromone of the female peach leafminer moth then became the subject of an investigation that led to the isolation and identification of 14-methyl-1-octadecene from female rinses (Sugie et al., 1984). About 100 ng of this compound can be obtained per female moth, and traps baited with 100 μ g of the synthetic alkene were as attractive as the crude extract of 40 females.

Assignment of absolute configuration of the pheromone by inference using candidate synthetics remained. This report describes synthetic details for the preparation of the enantiomers of 14-methyl-1-octadecene each >99.6% pure (99.2% EE). The route chosen also allows generation of analogs that have the same stereocenter with a slight structural alteration adjacent to that center to employ as probes for the effect of selected physicochemical variables on the biological activity. In this initial trial, we opted to place unsaturation at the 12,13-position because we were of the opinion that such an alteration of the pheromone structure would constitute minimal perturbation. Since this research was initiated, a synthesis of 14-methyl-1-octadecene has been reported (Mori and Kato, 1985).

METHODS AND MATERIALS

Gas-liquid chromatography (GLC) was performed with a Varian 2400 instrument (flame ionization detection, He carrier) using the following columns: column A, cholesterol *p*-chlorocinnamate (0.25 mm \times 11 m) and column B, Durabond I (0.25 mm \times 31 m) operated at temperatures as indicated. Infrared (IR) data were obtained with a Perkin Elmer model 467 spectrophotometer (3% solutions in CCl_4), and nuclear magnetic resonance (NMR) data were obtained with a Nicolet 300-MHz FTNMR spectrometer (1% solutions in CDCl_3). Mass spectral data were obtained with a Finnigan model 3200 mass spectrometer in either electron impact or chemical ionization (isobutane) operating mode. The mass spectrometer was equipped with a GLC inlet (Varian model 1400) served by an OV-101 column (0.25 mm \times 31 m). Melting points were obtained with a Fisher-Johns hot-stage apparatus and are uncorrected.

2-Methylhexanoic Acid. The acid was synthesized by alkylation of the dilithio anion of propanoic acid with *n*-butyl bromide by the general method of Pfeffer and Silbert (1970) (Figure 1). The yield of the racemic acid from 0.20 mol of propanoic acid was 94.4%: bp 70–73°C (0.05 mm); IR (CCl_4) 1706 cm^{-1} ; (CDCl_3) 0.89 (bt, 3H, CH_3R); 1.18 (d, 3H, CH_3CH); 1.25 (CH_2 envelope); 10.15 (s, 1H, CO_2H) ppm (prior lit. Creger, 1970).

Preparation and Resolution of Diastereomeric Amides, 2. Both (R)- and (S)- α -methylbenzylamines were purified by recrystallization of monotartrate salts from ethanol and analyzed for configurational purity as the first step of a

resolution procedure that has been previously described (Sonnet, 1984). Acid **1** was converted to its acid halide with SOCl_2 and DMF catalyst in anhydrous ether. The acid halide was allowed to react with (R)- or (S)- α -methylbenzylamine in CH_2Cl_2 with 1.1 equivalent of triethylamine. The amides were recrystallized four to five times from aqueous ethanol using charcoal treatment during first recrystallization. The yields of purified R^*S^* diastereomers was 40% of theoretical and each diastereomer was 99.6% pure. Analysis by GLC: col A (120°C) $\alpha = 1.098$, R^*R^* diastereomer eluted first; col B (150°C) = 1.077, R^*R^* diastereomer eluted first also; mp (R^*S^*): $98\text{--}99^\circ\text{C}$; IR (CCl_4) 3460 , 1680 cm^{-1} ; NMR (CDCl_3) $\delta 0.89$ (bt, 3H, CH_3R), 1.11 (d, 3H, $J = 6.9\text{ Hz}$, $\text{CH}_3\text{CHC}=\text{O}$), 1.49 (d, 3H, $J = 6.9\text{ Hz}$, CH_3CHN), 2.14 (sextuplet, 1H, $J = 6.9\text{ Hz}$, CH_3CHCH_2), 5.15 (p, 1H, $J = 7.1\text{ Hz}$, CH_3CHNH), 7.2 (5H, aryl H) ppm; CI-MS (m/e) 234 ($M+1$).

(R)- and (S)-2-Methyl-1-hexanol, **3**. Diastereomerically pure amide **2** (7.1 g, 30.5 mmol) was added via Gooch tubing in portions to a reaction mixture consisting of lithium diisopropylamide (LDA) (45 mmol) in tetrahydrofuran (THF) (75 ml) under nitrogen and cooled to 0°C . The resulting mixture was stirred for ca. 0.25 hr without external cooling. The reaction mixture was then cooled to -30°C , and ethylene oxide (3.0 ml, 60 mmol) was injected. Hexamethylphosphoric triamide (HMPT) (16 ml) was injected, and the resulting mixture was stirred at ambient temperature overnight. The reaction mixture was worked up with 2 N HCl (100 ml) and ether in the usual manner. The crude *N*-2-hydroxyethylated amide was dissolved in THF (40 ml) containing 2 equiv conc. HCl and heated under reflux for 1.5 hr, at which time GLC analysis indicated absence of the starting material, i.e., transacylation to the aminoester was complete. The mixture was stripped of solvent and heated briefly in benzene to drive off residual water. After the benzene had been removed, the residue was dissolved in dry THF (20 ml) and 2–2.5 g of solid LAH were added. The mixture was stirred under reflux for 1 hr and then worked up with aqueous NaOH and ether. The ethereal layer was suction filtered through Celite accompanied by further ether washes of flask and precipitate. The combined ethereal layer was washed with 2 N HCl, H_2O ($2\times$) and dried (MgSO_4). Distillation of the crude product gave 3.1 g of **3** (88%): bp $84\text{--}101^\circ\text{C}/30\text{ mm}$; IR (CCl_4) 3560 cm^{-1} ; NMR (CDCl_3) $\delta 0.90$ (m's, 6H, CH_3R and CH_3CH), $1.1\text{--}2.0$ (m's, ca. 6H), 3.41 and 3.51 (2d of d's, ABX, 2H, CHCH_2OH) ppm; (*R*) $[\alpha]_D^{25}$, -9.3° (c, 8.10, CHCl_3); (*S*) $[\alpha]_D^{25}$, $+8.7^\circ$ (c, 8.15, CHCl_3).

1,12-Dodecanediol Monotetrahydropyranyl Ether, **4**. The diol (7.0 g, 34.6 mmol) was dissolved with warming in 1,2-dichloroethane (DCE) (70 ml). A crystal of *p*-toluenesulfonic acid was added, and then dihydropyran (3.3 ml) was added dropwise. After 0.25 hr, the mixture was stripped and triturated with hexane. The mixture was suctioned filtered, and the recovered solid diol was treated again with DCE and a proportional amount of dihydropyran. The product mixture was again stripped of DCE, slurried with hexane, and filtered. The

combined filtrate from both reactions was freed of solvent and chromatographed on silica gel (60–120 mesh, 30 g) eluting with 200 ml of 5% ether–hexane [bistetrahydropyranyl ether (THP) and some mono-THP] and 300 ml of 10% ether. GLC analysis: col A (200°C) compound (R_f min), diol (1), mono-THP (2.2), bis-THP (9.5). In this fashion **4** (2.7 g, 27.3%) was obtained containing ca. 3% of diol and no bis-THP; the recovered materials may, of course, be recycled, although no effort was made to optimize yields. Thin-layer chromatography (silica gel, 30% ether–hexane): R_f 0.16 mono-THP, 0.5 bis-THP; IR (CCl_4) 3560, 1050 cm^{-1} ; NMR (CDCl_3) δ 1.25 (CH_2 envelope), 3.5 (m, 6H, CH_2O), 4.09 (m, 1H, OCHO) ppm.

(*R*)- and (*S*)-14-Methyl-12-(*Z*)-octadecen-1-ol, THF Ether, **5**. The diol-mono-THP, **4**, (4.71 g, 16.5 mmol) was added to a stirred mixture of pyridinium chlorochromate (5.3 g, 24.7 mmol) and NaOAc (5.3 g) in CH_2Cl_2 (30 ml) that was cooled in an ice bath. The resulting mixture was stirred at room temperature for 2 hr. Ether (150 ml) was added, and the mixture was passed through Florisil (10 g). The eluant was concentrated and then chromatographed on silica gel (25 g) eluting with 5% ether–hexane. Concentration of the eluant provided crude aldehyde (GLC 90%, col A 200°C, R_f 1.6 min, principal contaminant was the starting alcohol).

The required phosphonium salt (Figure 1) was prepared from (*R*)- and (*S*)-2-methyl-1-hexanol by first converting the alcohol to a bromide. Triphenylphosphine dibromide (25 mmol) was prepared in the usual way in CH_2Cl_2 adding bromine to triphenylphosphine at 0–25°C. The alcohol (3.0 g, 20.8 mmol) was added with 1–2 ml CH_2Cl_2 rinse, and the mixture was stirred at ambient temperature for 16 hr. After a few drops of methanol had been added to consume unreacted dibromide, the mixture was concentrated on a flash evaporator. The residue was triturated with hexane several times, and the hexane solution was concentrated. The crude bromide was then passed through silica gel (20 g) with hexane. The eluant was concentrated, and the bromide thus obtained was treated with triphenylphosphine (5.7 g, 21.8 mmol) and NaI (8.2 g, 54.6 mmol) in acetonitrile (25 ml) under reflux for 64 hr. The solvent was removed, and the crude product was triturated several times with DCE (phosphonium iodide is soluble). The triturate was concentrated and washed with ether. The residual oil was slurried in heptane and the solvent removed by rotary evaporation (to remove traces of DCE). The yield of crude oily salt was near quantitative.

The oil (ca. 20.8 mmol of phosphonium iodide) was dissolved in dry THF (25 ml) under nitrogen. The mixture was cooled (ca. 0°C) and *n*-butyllithium (1 equiv) was injected to generate the ylid. The mixture was cooled (–78°C) and HMPT (2 equiv) was injected. The aldehyde prepared above from **4** (2.6 g, 9.1 mmol) was added and the mixture was stirred at –78°C for 1 hr and for another 1 hr without external cooling. The product was worked up with water and hexane in the usual manner. The crude product was chromatographed on silica gel (30 g) eluting with 100 ml each of hexane, 1% then 2% ethyl acetate–

hexane. The product, **5**, was obtained: 2.23 g (67% yield from alcohol **4**); GLC Col B (250°C) $k' = 2.27$, containing 8% *E* isomer $k' = 2.40$, $\alpha = 1.057$; TLC (5% ethyl acetate-hexane $R_f = 0.28$); IR (CCl₄) 1050 cm⁻¹; NMR (CDCl₃) δ 0.88 (m's, 6H, CH₃R and CH₃CH), 1.25 (CH₂ envelope), 1.6 (m, ca. 3H, allylic CH), 3.5 (m, ca. 4H, CH₂O), 4.1 (m, ca. 1H, OCHO), 5.34 (m, 2H, HC=CH) ppm.

(*R*)- and (*S*)-14-Methyl-12-(*Z*)-octadecen-1-yl Bromide, **6**. The protected alkenol **5** (1.73 g, 4.7 mmol) was added to a solution of triphenylphosphine dibromide (5.7 mmol) in CH₂Cl₂ (15 ml). After 1 hr, the solvent was removed by rotary evaporation, and the crude product was triturated with hexane several times. The hexane solution was concentrated and filtered through silice gel (15 g) with hexane. The solvent was removed providing 0.80 g (50%) of the (*Z*)-alkenyl bromide **6**: GLC col A (170°C) $R_t = 5.0$ min, *E* isomer ca. 6% $R_t = 6.2$ min, $\alpha = 1.03$; NMR (CDCl₃) 0.89 (m's, ca. 6H, overlapped CH₃R and CH₃CH), 1.27 (CH₂ envelope), 1.58 (bs, 3H, allylic CH₂, CH), and 3.41 (t, 2H, $J = 7.9$ Hz, CH₂CH₂Br) ppm; CI-MS (m/e) 345, 347 (M+1).

(*R*)- and (*S*)-14-Methyl-1-(*Z*)-12-octadecadiene, **7**. A solution of LDA was prepared with butyllithium (2.5 mmol) and diisopropylamine (4 mmol) in THF (10 ml) under nitrogen at 0–5°C. The (*Z*)-alkenyl bromide **6** (3 mmol) was added in ca. 1 ml of hexane. After 10 min, the elimination was complete and the product was worked up with hexane and 2 N HCl. The crude diene was purified by argentation column chromatography. A CH₃CN (50 ml) solution of AgNO₃ (2 g) was prepared. Silica gel (60–120 mesh, 10 g) was added and swirled gently for 0.25 hr. The silica gel was collected by filtration and washed with dry benzene. The gel was then dried over P₂O₅ in vacuo. A column of this material was made up in hexane and employed repeatedly in this procedure. Retention volumes and GLC retention data for the various compounds are tabulated below (Table 1). More efficient chromatography is possible, but the required separation was affected in this manner.

Pure (*R*)- and (*S*)-*Z*-diene **7** were obtained: IR (CCl₄) 910 cm⁻¹, NMR (CDCl₃) δ 0.90 (m, ca. 6H, overlapped CH₃'s), 1.27 (CH₂ envelopes) 2.03 (m, 5H, allylic CH), 4.9–5.8 (5H, vinyl H); CI-MS (m/e) 265 (M+1).

(*R*)- and (*S*)-14-Methyl-1-(*E*)-12-Octadecadiene, **8**. Diene **7** (140 mg,

TABLE 1.

Compound	k_s col B (190°C)	R_v (ml) ^a
(<i>E</i>)-Diene, 7	2.50	70–85
(<i>Z</i>)-Diene, 8	2.36	80–120
1-Alkene, 10	3.68	60–110
Alkane, 11	3.97	20–40

^aRetention volume using AgNO₃ column chromatography and a flow rate of 1 drop/1–2 sec.

0.53 mmol) was added to a solution of metachloroperbenzoic acid (0.25 g, >2 equiv) in CH_2Cl_2 (5 ml). The mixture was allowed to stand at ambient temperature overnight. The crude bis epoxide was obtained by removing the solvent. A suspension of 3 equiv of triphenylphosphine dibromide in 10 ml of benzene was prepared. The bis epoxide was added thereto with 1–2 ml of benzene, and the resultant mixture was stirred at ambient temperature overnight. The crude tetrabromide was obtained by concentrating the product mixture and triturating the residue with hexane. The hexane was removed, and the product was debrominated by allowing it to react for 2 hr in propanoic acid to which an excess of powdered, activated, zinc had been added (0–5°C). The mixture was worked up with H_2O and hexane. The organic phase was washed to neutrality with aqueous NaHCO_3 , and the extract was dried (MgSO_4). Removal of the solvent was followed by column chromatography on silica gel (1–2 g) with hexane. The dienes **8** were obtained in ca. 70% yield containing 3–7% *Z* isomer. Passage through the AgNO_3 column provided samples containing no more than 3% *Z*: IR (CCl_4) 965, 910 cm^{-1} ; CI-MS (*m/e*) 265 ($\text{M}+1$).

(*R*)- and (*S*)-14-Methyl-1-Octadecyl Bromide, **9**. The (*R*)- and (*S*)-alkenyl bromides **6** were hydrogenated over PtO_2 in propanoic acid and produced the saturated bromides **9** contaminated with the parent hydrocarbons (ca. 10%). These were not separated at this point: NMR δ 3.40 (t, CH_2Br) ppm and no signals for vinyl H; GLC col A (170°C) for 2.4 min for alkane **11**, 8.0 min for alkyl bromide **9**; CI-MS (*m/e*) 347, 349 ($\text{M}+1$).

(*R*)- and (*S*)-14-Methyl-1-Octadecene, **10**. The bromides **9** were debrominated as described above for dienes **7**. The crude product containing the parent alkane was chromatographed on the AgNO_3 column to give alkane (eluting first): NMR (CDCl_3) δ 0.88 (bt, CH_3R), 1.25 (CH_2 envelope) ppm; EI-MS (*m/e*) 268 ($\text{P}+1$), 267 ($\text{P}-1$), 211 ($\text{C}_{15}\text{H}_{31}$), and 210 ($\text{C}_{15}\text{H}_{30}$), and **10**: IR (CCl_4) 910 and 990 (weak) cm^{-1} ; NMR (CDCl_3) δ 0.89 (m, ca. 6H, overlapped CH_3 's), 1.26 (CH_2 envelope), 2.05 (m, ca. 2H, allylic CH_2), and 4.9–5.8 (m's, 3H, vinyl H); CI-MS (*m/e*) 267 ($\text{M}+1$), 266 (P), 265 ($\text{M}-1$).

RESULTS AND DISCUSSION

The asymmetric center was introduced, as shown in Figure 1, by alkylating the dianion of propionic acid with butyl bromide. The original procedure (Creger, 1970) employed the sodium salt of the acid and reported a 54% yield of 2-methylcaproic acid, **1**. We used the general procedure of Pfeffer and Silbert (1970) involving a dilithio anion to obtain a 94% yield. The acid was converted to amide **2** with either (*R*)- or (*S*)- α -methylbenzylamine to produce a mixture of diastereomers that was resolved easily by several-fold recrystallization from ethanol. The process of purification to a nearly pure (>99.6%) diastereomer was monitored by gas chromatography (Methods and Materials). The purified

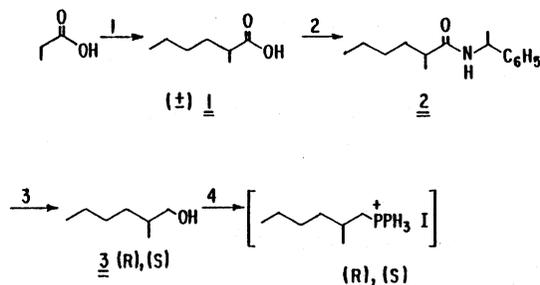


FIG. 1. Synthesis of configurationally pure phosphonium salts: 1. lithium diisopropylamide, butyl bromide; 2. thionyl chloride, (*R*)- or (*S*)- α -methylbenzyl amine; 3. fractional crystallization, amide reductive cleavage (Sonnet, 1984); 4. triphenylphosphine dibromide, then sodium iodide and triphenylphosphine.

*R***S**- (asterisks indicate relative stereochemistry) diastereomer was then cleaved by (1) *N*-alkylation with ethylene oxide, and (2) transacylation–reduction (Sonnet, 1984) yielding either (*R*)- or (*S*)-2-methyl-1-hexanol, **3**. This procedure has been shown to afford alcohols of configurational purity equal to that of the diastereomeric amide from which it was derived. The alcohols were then transformed to bromides, and these to triphenylphosphonium iodides in preparation for a Wittig condensation reaction.

The other component for this condensation (Figure 2) was obtained by blocking one hydroxyl group of 1,12-dodecanediol and then oxidizing that alcohol, **4**, to the corresponding aldehyde with pyridinium chlorochromate–sodium acetate. The condensation itself was conducted to maximize the *cis*-olefin

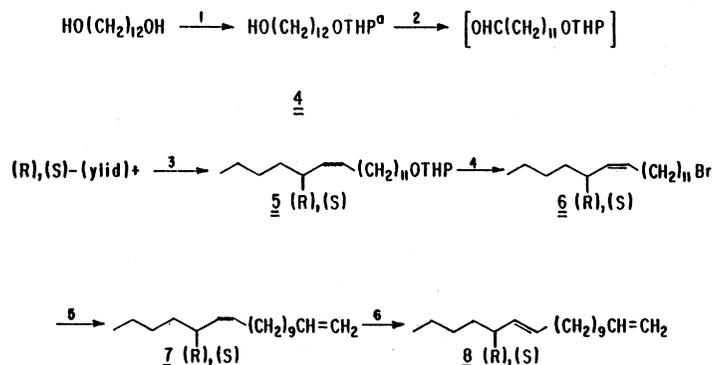


FIG. 2. Synthesis of configurationally pure dienes (^aTHP = 2-tetrahydropyryl): 1. dihydropyran, H⁺; 2. pyridinium chlorochromate, sodium acetate; 3. butyllithium (\rightarrow ylid), procedure for *cis* (Sonnet, 1974); 4. triphenylphosphine dibromide; 5. lithium diisopropylamide; 6. olefin inversion via bisepoxides (Sonnet and Oliver, 1976).

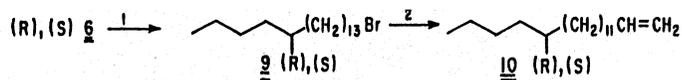


FIG. 3. Synthesis of the enantiomers of the peach leafminer moth sex pheromone: 1. H_2 /platinum oxide; 2. lithium diisopropylamide.

generated by using hexamethylphosphoric triamide as an additive (Sonnet, 1974). Completion of the pheromone synthesis involved conversion of the tetrahydropyranyl ether of the (*R*)- and (*S*)-alkene **5** to a bromide **6** with triphenylphosphine dibromide (Sonnet, 1976). Catalytic hydrogenation of the double bond (Figure 3) was followed by dehydrobromination with lithium diisopropyl amide. The final product, (*R*)- or (*S*)-14-methyl-1-octadecene, **10**, was purified by argentation column chromatography to separate it from the corresponding alkane that had arisen in the catalytic hydrogenation of the alkenyl bromide **6**.

In order to obtain the several stereoisomers of the desired analog, 14-methyl-1,11-octadecadiene, (*R*)- and (*S*)-**6** was dehydrobrominated to the corresponding (*R*)- and (*S*)-*Z*-isomers, **7** (Figure 2). The *E* isomers were prepared by carrying out an inversion via the bisepoxides (Sonnet and Oliver, 1976). The bisepoxides were allowed to react with triphenylphosphine dibromide in benzene producing tetrabromides that are the result of $\text{S}_\text{N}2$ inversions on each oxygenated carbon. Reduction with activated zinc-propionic acid, a *trans*-antiplanar elimination of vicinal halogens, causes net inversion of one of the carbons 12/13 to give the inverted alkene. All of these materials were purified by argentation column chromatography monitored by gas chromatography (Methods and Materials).

CONCLUSION

With these materials in hand we were in a position to measure biological activity versus stereostructure and thereby make the final assignment of pheromone structure. Results of field tests showed that the sex pheromone has the *S* configuration and full details of these studies are published elsewhere (Sugie et al. 1985).

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