$C_{5'}H$), 4.03 (q, 1, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 6.0 Hz, $C_{3'}H$), 4.17 (q, 1, $C_{2'}H$), 4.73 (t, 1, $J_{4',5'}$ = 6.0 Hz, $C_{4'}H$), 5.90 (d, 1, $J_{1',2'}$ = 5.2 Hz, $C_{1'}H$), 7.30 (s, 2, NH_2), 8.16 (s, 1, C_2), and 8.37 ppm (s, 1, C_8); ^{13}C NMR (D_2O) 28.78 (C-5'), 31.44 (C-γ), 34.56 (C-β), 54.76 (C-α), 73.24 (C-3'), 74.52 (C-2'), 84.0 (C-4'), 88.37 (C-1'), 119.18 (C-5), 140.55 (C-8), 149.25 (C-4), 153.38 (C-2), 155.88 (C-6), and 174.83 ppm (COO^-).

Reaction of **2** with L-homocysteine thiolactone hydrochloride in 2 N sodium hydroxide or with L-homocystine in sodium and liquid ammonia was described above for 5'-chloro-5'-deoxyadenosine and examination of the reaction mixtures by paper chromatography showed only **3** and no condensation products. From these reaction mixtures **3** could be isolated in approximately 50% yield.

9-(5-Methyl-2-furyl)adenine (3). 9-(3,5-Dichloro-2,3,5-trideoxy-β-D-*threo*-pentofuranosyl)adenine (**2**, 500 mg, 1.64 mmol) was suspended in a mixture of 6 N sodium hydroxide (2.7 mL) and ethanol (5.3 mL) and stirred at 70 °C for 10 min. During this time the reactant dissolved and a new precipitate formed. The reaction mixture was stored at 4 °C overnight to yield 204 mg (58%) of **3**. Recrystallization from ethanol provided **3** as colorless needles: mp 235–236 °C (mp 205–215 °C dec when heated slowly) (lit.[6] 236–237 °C); $[\alpha]^{22}_D$ 0°; UV λ_{max} (pH 1) 252 nm (ϵ 21.3 × 10^3); UV λ_{max} (pH 7) 252 nm (ϵ 19.3 × 10^3); UV λ_{max} (pH 11) 251 nm (ϵ 18.8 × 10^3); ^1H NMR (270 MHz) (Me_2SO-d_6) 2.34 (s, 3, $C_{5'}H$), 6.32 (s, 1, $C_{3'}H$), 6.60 (d, 1, $J_{2',3'}$ = 3.0 Hz, $C_{2'}H$), 7.47 (s, 2, NH_2), 8.21 (s, 1, C_2H), and 8.40 ppm (s, 1, C_8H); ^1H NMR (80 MHz) (Me_2SO-d_6) 2.34 (q, 3, $J_{2',5'}$ = 0.30 Hz, $J_{3',5'}$ = 1.1 Hz, $C_{5'}H$), 6.30 (oct, 1, $J_{2',3'}$ = 3.1 Hz, $C_{3'}H$), 6.59 (q, 1, $C_{2'}H$, 7.40 (s, 2, NH_2), 8.21 (s, 1, C_2H), and 8.38 ppm (s, 1, C_8H); ^{13}C NMR (Me_2SO-d_6) 17.00 (C-5'), 105.90 and 111.33 (C-2' and C-3'), 121.90 (C-5), 142.66 (C-8 and C-4'), 152.81 (C-1'), 152.98 (C-4), 157.19 (C-2), and 159.81 ppm (C-6).

[5'-^{2}H,8-^{2}H]-9-(5-Methyl-2-furyl)adenine (4). **2** (500 mg, 1.64 mmol) was suspended in a mixture of 7.5 N sodium deuterioxide (2.1 mL) and deuterioethanol (5.9 mL) and heated at 70 °C for 10 min. The reaction mixture was worked up as described above to yield 185 mg (52%) of crystalline **4**: mp 235–236 °C; ^1H NMR (80 MHz) (Me_2SO-d_6) 2.34 (m, 2, $C_{5'}H$), 6.30 (sx, 1, $J_{2',3'}$ = 3.1 Hz, $J_{3',5'}$ = 1.1 Hz, $C_{3'}H$), 6.59 (d, 1, $C_{2'}H$), 7.40 (s, 2, NH_2), 8.21 (s, 1, C_2H); ^{13}C NMR (Me_2SO-d_6) 16.61 (t, $J_{C\text{-}^2H}$ = 20.0 Hz, C-5'), 105.94 and 111.43 (C-2' and C-3'), 122.06 (C-5), 142.90 (C-4'), 153.08 (C-1'), 153.18 (C-4), 157.40 (C-2), and 160.08 ppm (C-6).

Acknowledgments. The authors thank Drs. J. M. Wood and R. L. Thrift of the Freshwater Biological Institute for the 270-MHz ^1H NMR spectra and Dr. N. A. Matwiyoff of the Los Alamos Scientific Laboratory for the use of the Varian XL-100 spectrometer.

Registry No.—**2**, 63162-55-0; **3**, 6979-90-4; **4**, 64784-77-6; L-homocysteine thiolactone hydrochloride, 31828-68-9; 5'-chloro-5'-deoxyadenosine, 892-48-8; *S*-adenosyl-L-homocysteine, 979-92-0; L-homocystine, 626-72-2.

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Synthesis of Methyl Arylmethyl 2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropylphosphonates as Potential Insecticides

Jack R. Reid* and Robert S. Marmor

Lorillard, A Division of Loews Theatres, Inc., Greensboro, North Carolina 27420

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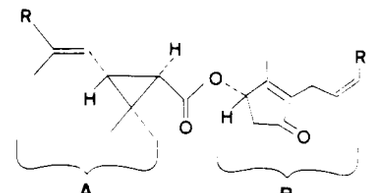
The interest generated by the insecticidal properties and low mammalian toxicity of the extracts of pyrethrum flowers has prompted many detailed investigations into the chemical nature of the chrysanthemate esters.[1-3] The esters **1** have been isolated and synthesized along with numerous synthetic analogues. Many of the previous investigations have dealt with a modification of the 2-methyl-1-propenyl group attached to the acid functionality A[5,6] or the replacement of the cyclopentenone alcohol moiety B by other suitable alcohols.[4] Many of these synthetic analogues exhibit enhanced insecticidal activity and a lowered rate of degradation when compared to the natural materials.[7] A heteroatom modification of the carboxylic function has not been reported. We now report the successful synthesis of compounds related to the chrysanthemate esters **1** in which the carboxylic function has been replaced by a phosphonic function.



1

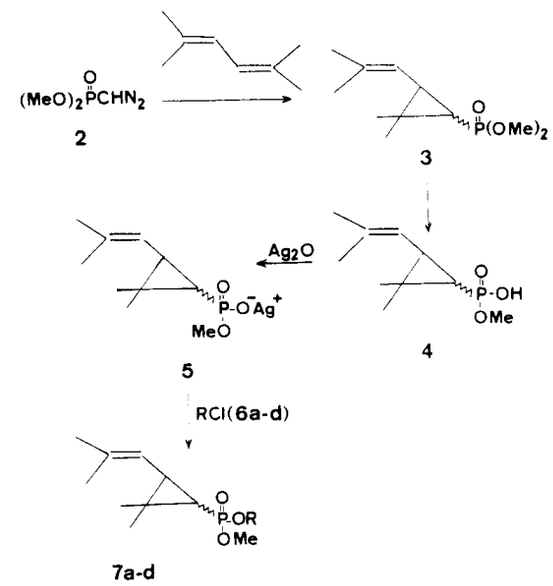
R=Me, $COOCH_3$
R'=Me, Et, $CH{=}CH_2$

The synthesis of ethyl chrysanthemate by Staudinger[9] was accomplished by the reaction of ethyl diazoacetate and 2,5-dimethyl-2,4-hexadiene. The availability of dimethyl diazomethylphosphonate[8] prompted us to attempt the synthesis of the phosphonochrysanthemates using a similar procedure.

Dimethyl diazomethylphosphonate (**2**) was treated with an excess of 2,5-dimethyl-2,4-hexadiene in methylene chloride in the presence of copper powder to give dimethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropylphosphonate (**3**). Although the cis/trans structural isomers could be separated by gas chromatography, no attempt was made to use the individual structural or optical isomers for our initial investigations. The esters which we chose to prepare were the phosphorus analogues of the chrysanthemate esters reported to have high insecticidal properties.

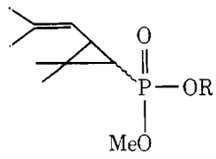
The diester **3** was selectively saponified to yield monomethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropylphosphonic acid (**4**). This acid was converted into its silver salt, silver methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-

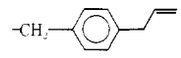
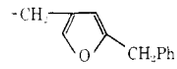
Scheme I



0022-3263/78/1943-0999$01.00/0

Table I



Compd	Registry no.	R	Yield, %	Bp, °C (mm)
7a	64771-44-4	$-CH_2-C_6H_4$-3-OPh	22	170–190 (0.05)
7b	64771-45-5	$-CH_2-C_6H_2$-2,4,6-Me_3	27	110–125 (0.05)
7c	64771-46-6		14	140–141 (0.01)
7d	64771-47-7		2	196–200 (0.001)

cyclopropylphosphonate (**5**), by reacting it with freshly prepared silver oxide in subdued light. The silver salt **5** was a white semicrystalline solid which rapidly turned brown upon exposure to light. Reaction of the appropriate arylmethyl alcohols with the sodium and potassium salts of this acid, or with the corresponding pyrophosphate made by reaction with dicyclohexylcarbodiimide,[10] all failed. The desired esters **7** were successfully prepared by the reaction of the silver salt **5** with the desired arylmethyl chlorides, **6**, which were prepared from the reaction of the alcohol with thionyl chloride in pyridine.[11] These alcohols were prepared by literature methods.[12–14] The entire sequence is shown in Scheme I. Chromatographic workup followed by a vacuum distillation afforded the desired phosphonic esters **7**.

The yields in the reaction of the silver salt **5** with the corresponding arylmethyl chloride **6** along with the boiling points of the diester products **7** are listed in Table I.

Preliminary tests of esters **7a–d** for their toxicity to houseflies (*Musca domestica*) and cigarette beetles (*Lasioderma serricorne*) by the general method of Bull and Ridgeway[16] have indicated greatly decreased insecticidal activity compared to their carboxylic ester counterparts. It is not known whether this initially observed low activity is a result of metabolism and transport differences from the carboxylic ester systems or the loss of the specific spatial orientation required for maximum insecticidal activities.

Experimental Section

All melting points and boiling points are uncorrected. Solvents and commercial reagents were purified by conventional methods. ^1H NMR spectra were recorded at 60 MHz with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded using a Perkin-Elmer Model 621 infrared spectrophotometer. Mass spectra were obtained from a CEC type 21-104 mass spectrometer at a 70-eV ionizing voltage.

Combustion analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. All compounds analyzed within ±0.40% of the calculated values for carbon, hydrogen, and phosphorus except compound **7d**. This compound was extremely sensitive to light and air and was too unstable for an accurate combustion analysis. The stability was somewhat improved by dissolving the compound in acetone.

The IR, ^1H NMR, and mass spectra of all compounds agree with those expected for the proposed structures.

Dimethyl Diazomethylphosphonate (2). Dimethyl diazomethylphosphonate (**2**) was prepared in 44% yield by the method of Seyferth and Marmor.[8] *Caution:* the product is potentially carcinogenic and explosive!

Dimethyl 2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropylphosphonate (3). A solution of 150 mL of freshly distilled 2,5-dimethyl-2,4-hexadiene and 50 mL of methylene chloride was stirred under nitrogen with 7.60 g (120 mg-atoms) of copper powder. To this was added 7.50 g (50 mmol) of dimethyl diazomethylphosphonate (**2**) dissolved in 25 mL of methylene chloride. The suspension was stirred vigorously for a total of 8 days. Solvent and excess 2,5-dimethyl-2,4-hexadiene were removed by bulb-to-bulb vacuum distillation at room temperature. The residue was taken up in 100 mL of benzene,[17] filtered from the copper powder and concentrated on the rotary evaporator. Upon distillation 6.45 g (56%) of product **3** was recovered as a clear colorless oil: bp 76–77°C (0.15 mm); mass spectrum M^+ *m/e* 232 (6), 123 (100); ^1H NMR ($CHCl_3$-*d*) δ 0.52 (1 H, d of d, *J* = 7, 2 Hz), 1.1–1.6 (7 H, m), 1.73 (6 H, s), 3.72 (6 H, d, *p*-OCH_3, *J* = 11 Hz), 4.92 (1 H, d, C=CH, *J* = 7 Hz); IR (NaCl–neat liquid) 2960, 2860, 1360, 1250, 1070–1030, 820, 790 cm^{-1}. Anal. Calcd for $C_{11}H_{21}O_3P$: C, 56.88; H, 9.11; P, 13.34. Found: C, 57.22; H, 9.24; P, 12.96.

Silver Methyl 2,2-Dimethyl-3-(2-methylpropenyl)cyclopropylphosphonate (5). A mixture of 1.20 g (5 mmol) of **3**, 220 mg (5 mmol) of sodium hydroxide, 10 mL of methanol, and 25 mL of water was refluxed vigorously for 24 h. The clear solution was treated with 2.0 g of Baker 50W-X12 ion-exchange resin (H^+ form) and diluted with water, and the oil formed was dissolved in methanol and filtered. The mono acid **4** was deposited as a clear colorless oil upon evaporation of the water and methanol. It was characterized by the preparation of the anilinium salt in 70% yield, mp 89.5–93 °C, as white microfine needles (hexane). Anal. Calcd for $C_{16}H_{26}NO_3P$: C, 61.72; H, 8.42; N, 4.50. Found: C, 61.36; H, 8.60; N, 4.33.

A solution of 1.09 g of **5** (5 mmol) in 200 mL of acetronitrile and 50 mL of water was mixed with 2.40 g (10 mmol) of silver oxide, which was freshly prepared by the general method of Willstätter and Pfannenstiel.[15] The mixture was refluxed in darkness 30 min, filtered hot, and evaporated to dryness in a foil-covered flask. The product amounted to 1.52 g (93%) of white solid **5**, which rapidly turned brown upon exposure to light and air. It was used immediately without further purification.

Arylmethyl Chlorides 6a–d. The 2,4,6-trimethylbenzyl chloride was purchased from the Aldrich Chemical Company, Inc. The remaining arylmethyl chlorides were prepared by the general procedure of Frazer,[11] from the corresponding alcohols. *p*-Allylbenzyl alcohol, *m*-phenoxybenzyl alcohol, and 2-benzyl-4-furfuryl alcohol were prepared by literature methods.[12–14]

General Procedure for the Preparation of Methyl Arylmethyl 2,2-Dimethyl-3-(2-methylpropenyl)cyclopropylphosphonates (7). To 1.52 g (4.7 mmol) of the silver salt **5** in 250.0 mL of dry acetonitrile was added 6.0 mmol of the appropriate arylmethyl chloride **6**. The suspension was refluxed with stirring in a foil-covered flask under nitrogen for at least 2 h. The silver chloride was filtered from the cooled solution and the solvent was evaporated to yield an oily residue.

The residue was chromatographed on a silica gel column, using benzene,[17] until the excess chloride was completely eluted. The silica gel was extracted with hot ethyl acetate and filtered. The extract was evaporated and the residue fractionally vacuum distilled to afford the pure esters **7**. A listing of boiling points and yields can be found in Table I.

Acknowledgments. The authors are grateful to Mrs. Margie Scott and Mrs. Rebecca Wright for their technical assistance.

Registry No.—**2**, 27491-70-9; **3**, 64771-48-8; 4 aniline salt, 64771-50-2; **5**, 64771-51-3; 2,5-dimethyl-2,4-hexadiene, 764-13-6; *p*-allylbenzyl chloride, 36875-10-2; *m*-phenoxybenzyl chloride, 53874-66-1; 2-benzyl-4-furfuryl chloride, 33486-19-0; 2,4,6-trimethylbenzyl chloride, 1585-16-6.

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(17) *Caution:* suspected carcinogen.

New Synthesis of 3,7-Dimethylpentadec-2-yl Acetate Sex Pheromone of the Pine Sawfly *Neodiprion lecontei*

Pierre Place, Marie-Louise Roumestant, and Jacques Gore*

ERA CNRS No. 611, Département de Chimie Organique, Universite Claude Bernard, 69621 Villeurbanne, France

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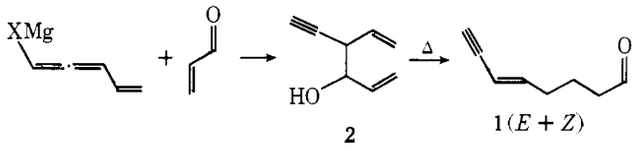
Recently,[1] we published a two-step synthetic sequence for aldehydes **1** by (i) the reaction of vinylallenic Grignard reagents with $\alpha\beta$-ethylenic ketones and (ii) the oxy-Cope transposition in refluxing diglyme of the resulting 4-ethynyl hexa-1,5-dien-3-ols **2** (Scheme I).

We report here an application of this sequence in the synthesis of the title pheromone **3** (*dl*), the structure of which was demonstrated by Coppel and co-workers in 1976.[2] A seven-step synthesis of **3** from 2,6-dimethylcyclohexanone was proposed very recently.[3]

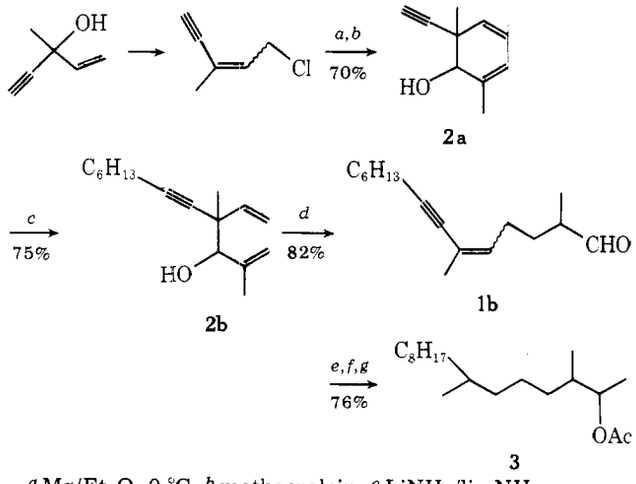
5-Chloro-3-methylpent-3-en-1-yne is readily prepared from 3-methylpent-4-en-1-yn-3-ol.[4] Its vinylallenic Grignard reagent reacts with methacrolein leading to alcohol **2a** which is easily alkylated by *n*-hexyl bromide using lithium amide in liquid ammonia. Heating of **2b** for 2 h in refluxing diglyme gives the fairly unstable aldehyde **1b**. After hydrogenation of **1b** the synthesis of **3** is terminated as outlined in Scheme II by reaction of methylmagnesium iodide with the corresponding saturated aldehyde. The overall yield from alcohol **2a** to the pheromone (identified by comparison of its spectra with those previously described) is 47%.

Scheme I



2 $1(E + Z)$

Scheme II



3

[a] Mg/Et_2O, 0 °C. [b] methacrolein. [c] $LiNH_2$/liq NH_3, $C_6H_{13}Br$. [d] diglyme reflux. [e] H_2, Pd/C 5%/AcOEt. [f] CH_3MgI/Et_2O. [g] Ac_2O.

Experimental Section[5]

The starting 3-methylpent-4-en-1-yn-3-ol was kindly provided by Dr. Pesnelle from Sté Roure-Bertrand.

2,4-Dimethyl-4-ethynylhexa-1,5-dien-3-ol (2a). The Grignard reagent of 11.5 g (0.1 mol) of 5-chloropent-3-en-1-yne is prepared and condensed with 7 g (0.1 mol) of methacrolein following published procedure;[1] 10.5 g (70%) of **2a** ($E_{0.2}$ = 47–48°) are obtained: IR (neat liq) 3550, 3450, 3300, 3080, 3060, 3010, 2100, and 1640 cm^{-1}; NMR (CCl_4) δ 1.20 and 1.28 (3 H, 2 s corresponding to threo and erythro isomers 1/1), 1.74 and 1.77 (3 H, 2t, J = 1.5 Hz), 2.30 (1 H, s), 2.52 (1 H, s, exchange with D_2O), 3.81 (1 H, s), 4.7–6.1 (5 H, M); mass spectrum 150 $M^{+\cdot}$ (1), 79 (100). Anal. Calcd: C, 79.95; H, 9.39. Found: C, 79.75; H, 9.71.

2,4-Dimethyl-4-vinyldodec-1-en-5-yn-3-ol (2b). Alcohol **2a** (10.5 g, 0.07 mol) is added after 5 min to a solution cooled to −45 °C of 0.15 mol of lithiumamide in 150 mL of liquid ammonia (freshly prepared from 1.0 g of lithium). *n*-Hexyl bromide (12.5 g, 0.075 mol) is then added after 10 min and the reaction mixture is stirred for 5 h at −45 °C. After addition of 200 mL of ether, ammonia is slowly evaporated. The residue is hydrolyzed by 200 mL of crushed ice and the solution was extracted with ether. The organic layer is washed until neutral and dried over $MgSO_4$. Evaporation of solvent leaves 15 g of crude material which by chromatography over silica gel (eluant petroleum ether–ether 4:1) gives 11.5 g (75%) of **2b** contaminated with about 10% aldehyde **1b**. This aldehyde seems to be formed during purification and complicates isolation of pure **2b** on a large scale: IR (neat liq) 3550, 3450, 3080, 3010, and 1640 cm^{-1}; NMR (CCl_4) δ 0.87 (3 H, t), 1.0–1.6 (11 H, M), 1.75 (3 H, M), 2.0 (1 H, M exchange with D_2O), 2.20 (2 H, M), 3.8 (1 H, broad s), 4.7–6.1 (5 H, M).

2,6-Dimethyltetradec-5-en-7-ynal (1b). A solution of 4.4 g (0.019 mol) of alcohol **2b** (contamined with ~10% of **1b**) in 100 mL of diglyme is refluxed for 2.25 h. After cooling, 400 mL of ether is added; the resulting solution is washed 15 times with 30 mL of water in order to eliminate diglyme and dried over $CaCl_2$. The unstable aldehyde (3.6 g 82%) is purified by chromatography over silica gel (eluent petroleum ether–ether 9:1) after removal of the solvent: IR (neat liq) 3010, 2700, 2220, 1730, 1670, and 1630 cm^{-1}; NMR (CCl_4) δ 0.89 (3 H, t), 1.05 (3 H, d, J = 7 Hz), 1.15–1.70 (13 H, M), 1.80–2.40 (5 H, M), 5.5 (1 H, M), 9.70 (1 H, d, J = 1 Hz); mass spectrum m/e 234 $M^{+\cdot}$ (20), 164 (99), 93 (100).

2,6-Dimethyltetradecanal. Aldehyde **1b** (2 g, 0.085 mol) in 30 mL of ethyl acetate is hydrogenated at ordinary pressure using 5% Pd/C as catalyst. After filtration and evaporation of solvent, 1.88 g (94%) of saturated aldehyde are obtained, pure enough (TLC) to be used without further purification: IR (neat liq) 2700, 1725 cm^{-1}; NMR (CCl_4) δ 0.9 (6 H, M), 1.05 (3 H, D, J = 7 Hz), 1.1–2.4 (20 H, M), 9.62 (1 H, d, J = 1 Hz); mass spectrum m/e 240 $M^{+\cdot}$ (0.5), 57 (100).

3,7-Dimethylpentadec-2-yl acetate (3). The Grignard reagent is prepared from 1.42 g (0.01 mol) of methyl iodide, 0.36 g (0.015 g-atom) of magnesium, and 10 mL of anhydrous ether. To the magnetically stirred solution is added at 0 °C 1.34 g (0.006 mol) of the saturated aldehyde dissolved in 5 mL of ether. After 20 min of stirring at 0 °C, 2 g (0.02 mol) of acetic anhydride in 2 mL of ether is dropped into the mixture which is hydrolyzed by 20 mL of a saturated solution of NH_4Cl 20 min after the end of the addition. The organic layer is separated, washed with 3 × 20 mL of H_2O, and dried over $CaCl_2$. The pheromone is, after removal of the solvent, purified by chromatography over silica gel (eluent: petroleum ether–ether 9:1) and 1.35 g (81%) of **3** is obtained: IR (neat liq) 1735, 1240 (identical to one described (**3**)) cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (9 H, M), 1.0–1.7 (25 H, M), 1.97 (3 H, s), 4.80 (1 H, M); ^{13}C NMR ($CDCl_3$) δ 170.5)s), 74.24 (d), 74.03 (d), 73.95 (d), 24 peaks between 37.6 and 14.1; mass spectrum m/e 298 $M^{+\cdot}$ (0), 255 (5), 254 (11), 238 (33), 116 (14), 87 (45), 44 (55), 43 (100). Anal. Calcd: C, 76.45; H, 12.83. Found: C, 76.03; H, 12.66. All the prominent peaks were also described by Coppel et al.[2]

Registry No.—**1b**, 64682-96-8; *erythro*-**2a**, 64682-97-9; *threo*-**2a**, 64682-98-0; **2b**, 64728-32-1; **3**, 59056-74-5; hexyl bromide, 111-25-1; 2,6-dimethyltetradecanal, 64682-99-1.

References and Notes

(1) (a) M. L. Roumestant, P. Place, and J. Gore, *Tetrahedron Lett.*, 677 (1976); (b) *Tetrahedron*, **33**, 1823 (1977).
(2) D. M. Jewett, F. Matsumura, and H. C. Coppel, *Science*, **192**, 51 (1976).
(3) P. J. Kocienski and J. M. Ansell, *J. Org. Chem.*, **42**, 1102 (1977).
(4) J. P. Dulcere, M. L. Roumestant, and J. Gore, *Bull. Soc. Chim. Fr.*, 1119 (1974).
(5) Infrared spectra were determined using a Perkin-Elmer Model 257; NMR spectra were measured in a Varian Associates Model A-60 or XL-100 spectrometer with solvent as specified. Mass spectra were observed using Varian Associates Model CH-5 spectrometer at 70 eV by direct inlet.

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