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SYNTHESIS AND CHARACTERIZATION OF ALL FOUR ISOMERS OF METHYL 2,4-DECADIENOATE FOR AN INVESTIGATION OF THE PHEROMONE COMPONENTS OF *Pityogenes chalcographus*

PETER BÆCKSTRÖM, ULLA JACOBSSON, TORBJÖRN NORIN* and C. RIKARD UNELIUS

Department of Organic Chemistry, Royal Institute of Technology
S-100 44 Stockholm, Sweden

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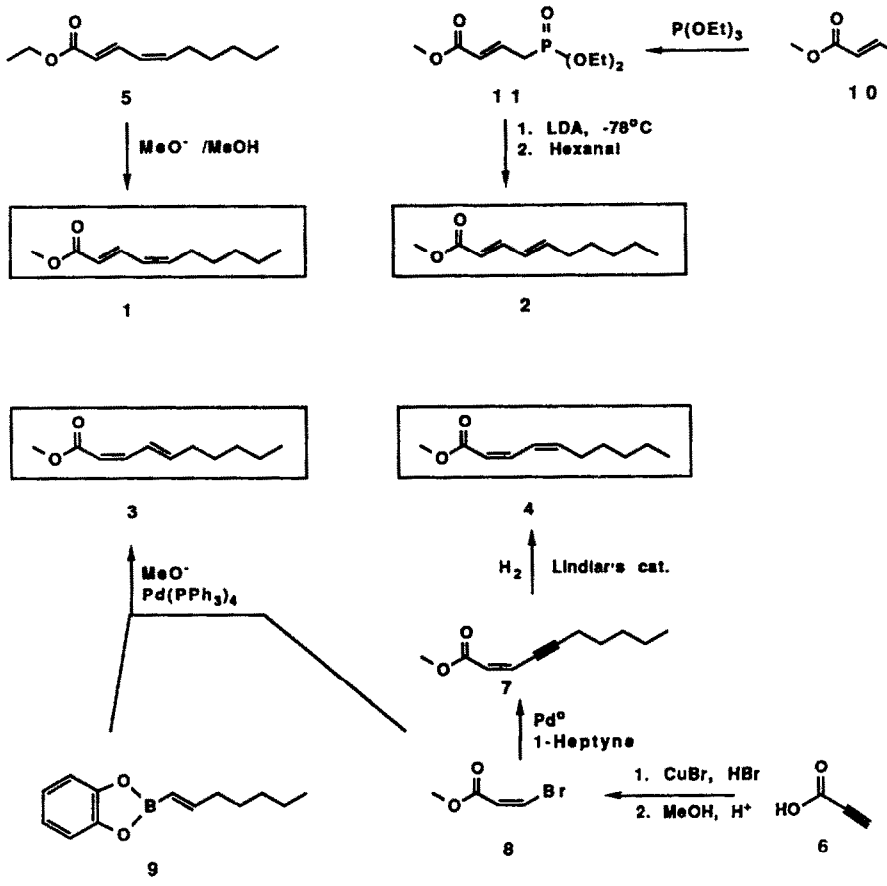
Abstract – Methyl (2*E*,4*Z*)-2,4-decadienoate (**1**), an important pheromone component of *Pityogenes chalcographus*, and its three geometrical isomers (**2-4**) have been synthesized and obtained in >99 % isomeric purity. Urea inclusion complexes were used in the final purification procedures. Spectroscopic data (MS, ^{1}H and ^{13}C NMR) of all four isomers are discussed. A photoisomerization study of the decadienoates is presented.

INTRODUCTION

Recently it has been found that methyl (2*E*,4*Z*)-2,4-decadienoate (**1**) is a pheromone component of the forest pest *Pityogenes chalcographus*. This insect shows only low attraction towards the previously reported pheromone component chalcogran.[1] However, adding the diene ester **1** to chalcogran causes a 35-fold increase in trap catches of the beetle.[2] Since the behavioural response usually is very sensitive to changes in the stereoisomeric composition of a pheromone, all four geometrical isomers of methyl 2,4-decadienoate **1-4** were prepared in high isomeric purity. An investigation of the biological activity of the isomers is presented in a separate paper.[3]

The methyl and ethyl esters of (2*E*,4*E*)- and (2*E*,4*Z*)-2,4-decadienoic acid are known as important contributors to the flavour of ripe Bartlett pears.[4] Furthermore, the (2*E*,4*Z*)-2,4-decadienoic acid occurs as a glyceride in stillingia oil, which is obtained from the seeds of *Sapium sebiferum* (Chinese tallow tree).[5-7] The conjugated carbonyl-(*E*,*E*)-diene system is also of interest as a synthetic intermediate on the route to some naturally occurring amides, which possess insecticidal properties.[8-12]

Chrombie[7] prepared the four isomers already in 1955 and since then a number of syntheses have been reported for (2*E*,4*E*)-[10-32] and (2*E*,4*Z*)-dienoates.[27-45] To our knowledge, only one practical synthesis of (2*Z*,4*E*)- and (2*Z*,4*Z*)-dienoates



Scheme 1

has been reported. However, the isomeric purity was not specified.[32] None of the published syntheses of the various isomers of 2,4-decadienoates provides products of isomeric purity sufficient for our purpose. We have therefore developed procedures for the preparation of all four isomers in an isomeric purity of more than 99 % and a new synthesis of the (*Z,E*)-isomer.

RESULTS AND DISCUSSION

Syntheses. The (*E,E*)-isomer **2** was prepared starting from methyl crotonate in a way similar to previously described procedures[12–16] (Scheme 1). The isomeric purity, which was 93 %, could be improved to >99 % with the aid of urea inclusion complexes (clathrates).[46–47] The (*E,E*)-isomer was selectively enriched in the clathrate (see Experimental).

Since ethyl (2*E*,4*Z*)-2,4-decadienoate (**5**) is commercially available as an isomeric mixture of 76 % purity, the (*E,Z*)-isomer **1** was prepared simply by transesterification with sodium methoxide in methanol (Scheme 1). The isomeric purity was increased to >99 % with the urea inclusion procedure. The pure (*E,Z*)-isomer was isolated from the mother liquor.

The (*Z,Z*)-isomer **4** was prepared from propiolic acid (**6**) in four steps (Scheme 1). The first three steps were performed according to Heck.[35] The reduction of the enyne ester **7** with hydrogen and Lindlar's catalyst[27] gave the dienoate **4** with an isomeric purity of 87 %. All geometrical isomers were present in the product and preparative GC was used to obtain the pure (>99 %) (*Z,Z*)-isomer.

The (*Z,E*)-isomer **3** was prepared from methyl (*Z*)-3-bromopropenoate (**8**) (Scheme 1). This compound was coupled with (*E*)-1-heptenyl-1,3,2-benzodioxaborole (**9**) (prepared from catecholborane and 1-heptyne) in the presence of $Pd(PPh_3)_4$ and sodium methoxide.[48] The cross-coupling reaction gave the product **3** with 92 % isomeric purity. The contaminating (*E,E*)-isomer could be removed with liquid chromatography or the use of urea inclusion complexes to yield isomerically pure (>99 %) (*Z,E*)-isomer. The possibility of using a vinyl bromide conjugated with a carbonyl function in this type of cross-coupling reaction is of general synthetic interest and has not been reported earlier.

NMR-data. All the ^1H and ^{13}C NMR signals of the four stereoisomers were unambiguously assigned using ^1H-^1H and ^1H-^{13}C two-dimensional correlated spectroscopy (see Table 1 and 2). The β-proton of the (*E,Z*)- and (*E,E*)-isomers and the γ-proton of the (*Z,E*)- and (*Z,Z*)-isomers are influenced by an anisotropic effect due to the vicinity of the ester function and thus the chemical shifts of those protons appear at a very low field (Table 1).

General empirical rules for assigning ^{13}C NMR shifts of alkyl-substituted diene systems have been suggested by Rossi *et al.*[49] and Ando *et al.*[50–51] based on extensive shift calculations. To some extent our data fit the suggested shift ranges, but the presence of the ester function causes discrepancies. Thus, these empirical rules have to be used with great caution when applied to diene systems where the substituents are other than alkyl groups. On the other hand, the use

Table 1. ^1H NMR shift data (ppm) of the diene esters **1-4**.

	α	β	γ	δ	allyl
E,E	5.79	7.30	6.16	6.16	2.26
E,Z	5.89	7.63	6.13	5.89	2.31
Z,E	5.58	6.56	7.37	6.09	2.21
Z,Z	5.67	6.94	7.27	5.92	2.27

Table 2. ^{13}C NMR shift data (ppm) of the diene esters **1-4**.

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	MeO
E,E	167.0	118.5	144.8	128.0	144.2	33.1	28.6	31.6	22.7	14.2	51.3
E,Z	166.9	120.5	139.2	126.1	141.1	28.4	29.3	31.6	22.7	14.2	51.3
Z,E	166.4	114.9	145.1	126.7	145.4	33.2	28.8	31.7	22.8	14.3	51.1
Z,Z	166.4	116.8	138.6	124.2	141.3	27.8	29.3	31.7	22.8	14.3	51.2

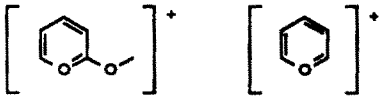
Table 3. Isomerization of methyl 2,4-decadienoates. The numbers show the ratio between the isomers in the mixture (%).

	E,E	*E,Z*	*Z,E*	*Z,Z*
a) Irradiation without iodine				
Starting mixture *E,E*	92	7	1	0
Starting mixture *Z,Z*	2	7	4	87
Final equilibrium mixture[a]	39	22	27	12
b) Irradiation with iodine				
Iodine + starting mixture *E,E*	92	7	1	0
Iodine + starting mixture *E,Z*	11	89	0	0
Iodine + equilibrium mix. from a)	39	22	27	12
Final equilibrium mixture[a]	81	11	7	1

[a] The final equilibrium mixture was reached after 6-8 h.

of various pulse-techniques available on modern NMR spectrometers offers a fast and safe route to unambiguous assignments.

MS-data. Generally the base peak in the mass spectra of most methyl esters is *m/z* 74 (arising from a McLafferty rearrangement). The spectra of the methyl decadienoates **1-4** show very small intensities of this ion. Instead the dominant peaks are *m/z* 111 and 81. We believe that this is due to the formation of the pyrylium fragments shown below.[52] These ions can easily be formed



from the isomers with the α-β double bond in (*Z*)-configuration. In accordance with this, the *m/z* 111 ion is more dominant in the spectra of the (2*Z*,4*E*)- and (2*Z*,4*Z*)-isomers.

Isomerization. Chrombie reported[7] that no isomerization occurred when methyl 2,4-decadienoates were subjected to irradiation (with UV-light from Hanovia lamps in glass or quartz tubes) in the presence of iodine. Repeating these experiments under very similar conditions revealed that extensive isomerization occurred both by direct irradiation and by irradiation with iodine present. The proportions of the four geometrical isomers in the equilibrium mixtures are strongly influenced by the presence of iodine (Table 3); the (*E,E*)-isomer being favoured by iodine.

EXPERIMENTAL

All reactions of air- and water-sensitive materials were performed under inert conditions (N_2 or Ar). Liquid chromatography was performed on silica gel, Merck

60 (0.040–0.063 mm), dry-packed in 15 or 25 mm inner diameter (i.d.) glass columns. Gradient elution with hexane and increasing amounts of ethyl acetate (unless otherwise stated) was performed as described by Baeckström *et al.*[53] TLC was performed on silica gel (Merck 60, HF precoated aluminum foil) using 20 % ethyl acetate in hexane as the eluent. The plates were developed with vanilline and sulphuric acid in ethanol. NMR spectra were recorded in $CDCl_3$ on Bruker WP 200 and AM 400 spectrometers. Standard Bruker microprograms were used to perform the DEPT, ^1H-^1H and ^1H-^{13}C COSY experiments. Analytical GC was performed on a PYE Unicam 204 instrument with an FID detector using a 25 m cross-bound Chrompack (Cp wax 57 CB) fused silica capillary column. The elution order of the decadienoates was (*Z,E*), (*E,Z*), (*Z,Z*) and (*E,E*). Mass spectra (70 eV) were recorded on a Finnigan 4021 GC/MS instrument supplied with a Superox FA fused silica capillary column.

Methyl (2*E*,4*Z*)-2,4-decadienoate (1). Commercial ethyl (2*E*,4*Z*)-2,4-decadienoate (5) was obtained from IFF (International Flavours and Fragrances) and the purity was 76.5 % (by GC). Apart from some polymerized material, the contaminants were ethyl (2*E*,4*E*)-2,4-decadienoate (4.6 %), methyl (2*E*,4*Z*)-2,4-decadienoate (7.1 %) and ethyl (3E,5E)-3,5-decadienoate (10.9 %). The latter compound can be formed by treatment of **5** with a strong base.[54–55] The commercial ethyl ester (4.68 g, 23.88 mmol) was dissolved in methanol (200 ml) without prior purification. Sodium methoxide in methanol (24 ml, 0.5 M) was added at 0 °C. The reaction mixture was stirred overnight in darkness at room temperature and then neutralized with saturated ammonium chloride. The product was extracted with several portions of hexane and the combined organic phases were dried ($MgSO_4$) and concentrated. Chromatography yielded 82.5 % of the methyl (*E,Z*)-ester. The purity was 85.2 % with 4.7 % of the (*E,E*)-isomer and 10.2 % of the methyl (3E,5E)-3,5-isomer. MS (*m/z*): 182 (23%, M^+), 111 (100), 81 (85), 79 (42), 67 (57), 66 (36), 59 (36), 55 (39), 41 (72), 39 (42), 29 (58). ^1H NMR: δ 7.66–7.53 (dd, 1H, $J_{\beta-\gamma} = 11.5$ Hz, $J_{\beta-\alpha} = 15.0$ Hz), 6.10 (t, 1H, $J_{\gamma-\beta} = 11.5$ Hz, $J_{\gamma-\delta} = 11.0$ Hz), 5.85 (m, 2H), 3.73 (s, 3H), 2.28 (q, 2H), 1.43–1.25 (m, 6H), 0.88 (t, 3H).

Urea inclusion complexes. In a typical experiment 2.52 g (13.8 mmol) of the impure methyl decadienoate 85 % of the (*E,Z*)-isomer was mixed with a hot solution of urea (5 g, 83.2 mmol) in methanol (25 ml). The resulting solution was allowed to cool to room temperature before leaving it in the refrigerator overnight. The resulting crystals were rapidly filtered off and the mother liquor was mixed with silica gel. The methanol was evaporated and the impregnated silica gel was applied on top of a dry-packed silica gel column. Gradient elution gave 0.91 g of the (*E,Z*)-isomer and its isomeric purity was 99.2 %. The clathrate was dissolved in brine and extracted with ether. Drying and concentration gave 1.27 g of a mixture containing 72.4 % of the (*E,Z*)-isomer together with 8.7 % of the (*E,E*)-isomer and 16.4 % of the (3E,5E)-3,5-isomer.

Methyl 2(*E*)-4-bromo-2-butenoate (10). Methyl crotonate (35.0 g, 350 mmol), N-bromosuccinimide (37.4 g, 210 mmol) and azaisobutyronitrile (100 mg, 0.61 mmol) were refluxed in carbon tetrachloride for 3 h. The succinimide was filtered off and subsequently washed with CCl_4. The organic phase was washed

with water, dried ($MgSO_4$) and concentrated. Distillation yielded 26.9 g (73.9 %) of product. ^{1}H NMR: δ 7.03–6.92 (dt, 1H, J = 15.4 Hz), 6.01 (d, 1H, J = 15.4 Hz), 3.98 (dd, 2H, J_{allylic} = 1.1 Hz), 3.74 (s, 3H).

Methyl 2(*E*)-4-diethylphosphonate-2-butenoate (11). The brominated methyl crotonate (9.0 g, 50.3 mmol) was added dropwise to triethylphosphite (9.2 g, 55.3 mmol) at 120 °C. The mixture was stirred for 30 min while the ethyl bromide formed was distilled off. The reaction mixture was allowed to cool and then diluted with methylene chloride followed by addition of silica gel (50 g). The methylene chloride was evaporated and the gel was put on a column. Gradient chromatography (increasing amounts of methanol in methylene chloride) gave 91.1 % of product. ^{1}H NMR: δ 6.87 (m, 1H, J = 15.5 Hz, J_{H-P} = 7.4 Hz, 5.97 (dd, 1H, J = 15.5 Hz, J_{H-P} = 4.9 Hz), 4.10 (m, 4H), 3.73 (s, 3H), 2.73 (dd, 2H, J_{H-P} = 22.8 Hz), 1.28 (t, 6H).

Methyl (2*E*,4*E*)-2,4-decadienoate (2). Lithium diisopropylamine (9.0 mmol) was prepared by carefully adding *n*-butyllithium to diisopropylamine in THF at 0 °C. After stirring for one hour the temperature was decreased to -78 °C. The phosphonate ester **11** (2.0 g 8.47 mmol) was added and the colour turned from light brown to yellow. After addition of hexanal (875 mg, 8.75 mmol) the solution was stirred at -78 °C for 1 h and then allowed to warm to room temperature. The reaction mixture was washed with brine (100 ml) and 10 % aqueous ammonium chloride (30 ml). The combined aqueous phases were then extracted with hexane (100 ml) and ether (100 ml). The combined organic phases were washed with 10 % aqueous ammonium chloride (50 ml). Drying ($MgSO_4$), concentration and chromatography yielded 37.3 % of product. The product contained 7 % of the (*E*,*Z*)-isomer. Pure (>99 %) (*E*,*E*)-isomer was obtained *via* urea inclusion complexes (see above). The (*E*,*E*)-isomer was selectively enriched in the clathrate. MS (*m*/*z*): 182 (12%, M^+), 111 (98), 81 (75), 67 (52), 66 (45), 59 (49), 55 (46), 53 (49), 41 (100), 39 (70), 29 (93). ^{1}H NMR: δ 7.34–7.21 (m, 1H), 6.16 (m, 2H), 5.79 (d, 2H, J = 15.3 Hz), 3.74 (s, 3H), 2.17 (q, 2H), 1.56–1.12 (m, 6H), 0.89 (t, 3H).

Methyl (*Z*)-3-Bromopropenoate (8). Propiolic acid (**6**) was brominated with HBr in the presence of CuBr and subsequently esterified with acidic methanol according to a literature procedure.[35] ^{1}H NMR: δ 7.03 (d, 1H, J = 8.3 Hz), 6.65 (d, 1H, J = 8.3 Hz), 3.78 (s, 3H).

(*E*)-1-Heptenyl-1,3,2-benzodioxaborole (9). 1-Heptyne (1.2 g, 12.5 mmol) and commercial catecholborane (Fluka) (1.5 g, 12.5 mmol) were mixed and heated at 70 °C for 1 h. The reaction mixture was distilled in a bulb-to-bulb apparatus. The expected product was collected at 250 μbar, 120 °C. The product was kept in the freezer as a 1 M solution in toluene.

Methyl (2*Z*,4*E*)-2,4-decadienoate (3). Methyl (*Z*)-3-bromopropenoate (**8**) (300 mg, 1.82 mmol), $Pd(PPh_3)_4$ (63 mg, 0.05 mmol) and toluene (3 ml) were mixed under argon atmosphere. (*E*)-1-Heptenyl-1,3,2-benzodioxaborole (**9**) (3 ml, 1M, 3 mmol) and sodium methoxide (1.1 ml, 2 M, 2.2 mmol) were added *via* a hypodermic syringe. The reaction mixture was stirred for 45 min at 40 °C and then at room temperature overnight. Saturated aqueous NH_4Cl was added and

the product extracted with ether. Drying ($MgSO_4$), concentration and chromatography yielded 256 mg (77.3 %) of product. Notably, the first chromatography tube contained 3 mg of >98 % pure (*E,Z*)-isomer. The isomeric purity of the other combined fractions was 92 % with 7 % of the (*E,E*)-isomer. The urea inclusion procedure increased the isomeric purity to >99 %. MS (*m/z*): 182 (15%, M^+), 111 (100), 81 (32), 79 (26), 67 (25), 66 (17), 59 (16), 55 (19), 41 (35), 39 (20), 29 (29). ^{1}H NMR: δ 7.38 (m, 1H), 6.56 (t, 1H, $J_{\beta-\alpha}$ = 11.5 Hz, $J_{\beta-\gamma}$ = 11.5 Hz), 6.08 (m, 1H, $J_{\delta-\gamma}$ = 15 Hz), 5.57 (d, 1H, $J_{\alpha-\beta}$ = 11.5 Hz), 3.73 (s, 3H), 2.21 (q, 2H), 1.48–1.26 (m, 6H), 0.90 (t, 3H).

Methyl (*Z*)-2-decen-4-ynoate (7). A mixture of methyl (*Z*)-3-bromopropenoate (8) (1.0 g, 6.1 mmol), distilled 1-heptyne (2.7 g, 28.2 mmol), $Pd(OAc)_2$ (101 mg, 0.45 mmol), triphenylphosphine (237 mg, 0.904 mmol) and distilled triethylamine (18 ml) was stirred under argon atmosphere for 24 h. Water (25 ml) was added and the mixture was extracted with ether (3 x 25 ml). The combined ether extracts were dried ($MgSO_4$), concentrated *in vacuo* and finally chromatographed on silica gel. A fraction containing 3.58 g (88 %) was >99 % pure by GC-analysis. ^{1}H NMR: δ 6.16 (dt, 1H, J = 11.4 Hz, J = 2.2 Hz), 6.02 (d, 1H, J = 11.4 Hz), 3.76 (s, 1H), 2.45 (t, 2H, J = 2.2 Hz, J_{CH_2} = 7.1 Hz), 1.64–1.32 (m, 6H), 0.91 (t, 3H).

Methyl (2*Z*,4*Z*)-2,4-decadienoate (4). Methyl (*Z*)-2-decen-4-ynoate (7) (100 mg, 0.556 mmol), hexane (5 ml), quinoline (0.1 ml) and Lindlar's catalyst (20 mg) were mixed in a three-necked flask. Hydrogen atmosphere was established and hydrogen uptake was measured by means of a gas buret. When 12.5 ml (0.56 mmol) hydrogen had been consumed the reaction mixture was filtered and chromatographed. The isomeric purity of the product was 87 %. Preparative GC was used to obtain the pure (>99 %) (*Z,Z*)-isomer. MS (*m/z*): 182 (15%, M^+), 111 (100), 81 (35), 79 (29), 67 (28), 66 (17), 55 (20), 53 (17), 41 (36), 39 (21), 29 (28). ^{1}H NMR: δ 7.27 (t, 1H, J = 11.5 Hz), 6.94 (t, 1H, J = 11.5 Hz), 5.98–5.84 (m, 1H), 5.67 (d, 1H, J = 11.5 Hz), 3.72 (s, 3H), 2.35–2.20 (m, 2H), 1.50–1.27 (m, 6H), 0.89 (t, 3H).

Isomerization experiments. The photoisomerizations were carried out in a Rayonet reactor equipped with 16 RPR 300 nm lamps. The methyl decadienoates (4 mg) in pentane (1 ml) with or without a crystal of iodine were kept in the reactor in an NMR-tube (borosilicate glass). Aliquots for GC-analysis were withdrawn at intervals until the isomeric ratio was constant. The equilibrium mixture was reached after 6-8 h. The results are presented in Table 3.

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