

SYNTHESES OF PURE (9Z,11Z), (9E,11E), (9E,11Z), AND (9Z,11E)-9,11-HEXADECADIENALS— POSSIBLE CANDIDATE PHEROMONES

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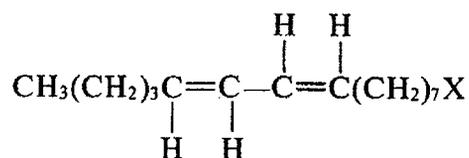
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Abstract—The title compounds were prepared by six different routes, and recommendations are given for the more convenient procedures in laboratory-scale syntheses. Modifications in the literature preparations of the 9E,11E and 9E,11Z isomers are described. Baseline separation of a prepared mixture of all four isomers of the (9Z,11Z), (9E,11E), (9E,11Z), and (9Z,11E)-9,11-hexadecadienals was achieved using GC methods with standard capillary columns. [¹³C]NMR spectroscopy of the *alkene* carbon atoms clearly differentiates between the Z,Z, E,E and either E,Z or Z,E isomers of the precursor dienols and thus of the dienals.

Key Words—(9z,11Z), (9E,11E), (9E,11Z), and (9Z,11E)-9,11-Hexadecadienals, (9E)-hexadecen-11-yn-1-yl acetate, syntheses, aldehydes, ester, conjugated dienes, dienals.

INTRODUCTION

Although the syntheses of insect pheromones having a conjugated diene structure have been well described (Henrick, 1977; Henrick et al., 1982), it is less common (Bestmann et al., 1981; Chisholm et al., 1981) for all four isomers of a single conjugated diene to be prepared in one laboratory using an excellent published procedure regardless of the authors' favorite method. In a program designed for field testing studies on a variety of moth species of the order Lepidoptera, it was essential to quickly prepare stereochemically pure, gram quantities of each of the four isomers of the (9Z,11Z), (9E,11E), (9E,11Z), and (9Z,11E)-9,11-hexadecadienals (I–IV). In fact, compound IV was only recently characterized as a pheromone for *Diatraea saccharatis*



I X = CHO

Ia X = CH₂OH

FIG. 1.

(Carney and Liu, 1983) and III identified, but not fully characterized as a pheromone in *Acrolepiopsis assectella* (Renou et al., 1981).

We (Svirskaya et al., 1980) and Coffelt et al. (1979) had previously shown that pure conjugated *Z,Z* pheromone compounds can be readily obtained by a Cadiot-Chodkiewicz reaction followed by a borane reduction and hence compounds I and Ia (Figure 1) were conveniently prepared in gram quantities. A longer, but possibly commercially more applicable procedure has recently been described for the synthesis of *Z,Z* pheromones (Bishop and Morrow, 1983). The stereoisomers of I (II-IV), however, can be prepared by a wide variety of published procedures. Since we wished to prepare II-IV under the criteria stated above, we selected two literature methods each for the preparation of II-IV.¹

The subsequent availability of all four isomers (I-IV) enabled us to find a simple method of gas-liquid chromatographic (GLC) analysis of the isomers and a simple ¹³C method of structural identification.

METHODS AND MATERIALS

Nuclear magnetic resonance (NMR) spectra for protons were recorded on a Varian EM 360 spectrometer; NMR spectra for carbon were recorded on a Varian FT-80A spectrometer at 20 MHz using deuteriochloroform (CDCl₃) as solvent and tetramethylsilane as the internal standard. Samples used for ¹³C measurements were over 99% pure by GLC analyses.

The analyses of these conjugated diene alcohols and aldehydes by gas chromatography-mass spectrometry were performed on a Pye 204 chromatograph interfaced directly to a VG Micromass 16F single focusing sector mass spectrometer. Fused silica capillary columns were employed. The column

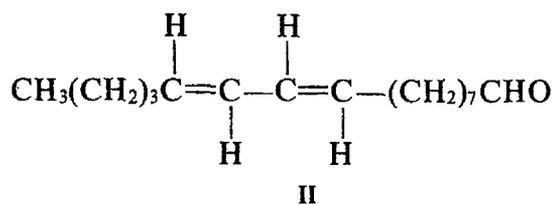
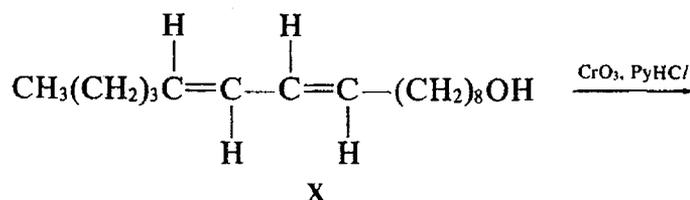
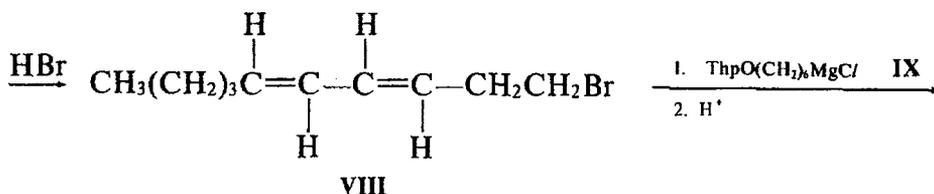
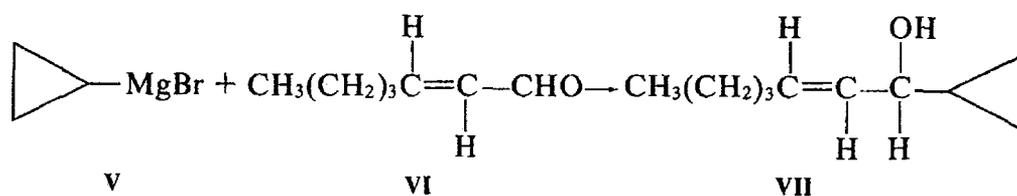
¹We have not attempted the palladium catalyzed cross-coupling reaction between an alkenylborane and an alkenyl halide (Miyaura et al., 1983, and references therein).

used for the separation of the isomeric alcohols was 60 m \times 0.25 mm *ID* coated with DBI701 having a film thickness of 0.25 μ m, while that for the isomeric aldehydes was 60 m \times 0.25 mm *ID* coated with SE30 with a film thickness of 0.25 μ m. The temperature programming conditions were 140–200°C at 6°C/min for the aldehydes. For the diene alcohols the temperature was held at 120°C for 4 min and programmed to 200°C at 8°/min. On both columns the order of elution of the diene alcohols and aldehydes were *Z,E*, *E,Z*, *Z,Z*, and *E,E*. Computer-acquired mass spectral data were recorded, through a VG2025 data system interfaced to the GC-MS system, at an ionizing energy of 70 eV in the EI mode at an ion source temperature of 200°C and a scan rate of 1.5 sec/decade. Infrared (IR) spectra were recorded on a Unicam SP 1000 IR spectrophotometer as neat films between NaCl disks. Silica gel was used for all thin- and preparative layer chromatography (TLC) and column chromatography unless otherwise specified. All glassware for reactions involving organometallics was oven-dried, cooled, and kept under argon during reaction. The reagents and reaction mixtures, containing organoboron, organolithium, and Grignard reagents were transferred via syringe and carried out under an argon atmosphere, using dry and pure solvents. Solvents were removed on a rotary evaporator. An aliquot (1 ml) of the prepared dialkylborane was hydrolyzed and analyzed for hydride concentration (Brown et al., 1977). All melting and boiling points are uncorrected. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, and by Organic Microanalyses, Montreal, Quebec. The reaction schemes are shown in Schemes 1–3.

(*E*)-7-Cyclopropyl-5-hepten-7-ol (7). Compound VII was prepared from (*E*)-2-heptenal (6) (Svirskaya et al., 1980) according to the reaction sequence of Descoins and Henrick (1972) and Mori (1974) using a procedure originally devised by Julia et al. (1960).

Thus 7.0 g of VI reacted with cyclopropylmagnesium bromide (prepared from 9.8 g of cyclopropylbromide) to give 6.0 g of VII (bp 55–62°C/0.1 mm) in 63% yield. NMR: δ 5.75–5.4 (m, 2H), 4.01 (s, 1H), 3.6–3.3 (m, 1H), 1.78–1.1 (m, 4H), 0.88 (t, 3H, $J = 6$ Hz), 0.6–0.1 (m, 5H).

(3*E*,5*E*)-3,5-Decadienyl bromide (VIII). To (*E*)-7-cyclopropyl-5-hepten-7-ol (VII) (6.0 g) at 0°C was added 15 ml of 48% HBr in one portion (Julia et al., 1960). The reaction mixture was stirred at 0° for 15 min and extracted with hexane. The extract was washed, dried, and the solvent was evaporated. The crude product VIII (7.5 g) was chromatographed on a silica gel column using hexane as eluant to give 5.4 g of pure bromide VIII in 65% yield. IR: 980 cm^{-1} . NMR: δ 6.3–5.32 (m, 4H), 3.61 (t, 2H, $J = 8$ Hz), 2.71 (t, 2H, $J = 9$ Hz), 2.32–1.95 (m, 2H), 1.58–1.18 (m, 4H), 0.9 (t, 3H, $J = 5$ Hz). Anal: calcd. for $\text{C}_{10}\text{H}_{17}\text{Br}$: C, 55.31; H, 7.89; Br, 36.80; found: C, 55.00; H, 7.94; Br, 36.81.



SCHEME 1.

(9*E*,11*E*)-9,11-Hexadecadien-1-ol (X). The solution of cooled (5°C) 6-tetrahydropyranyloxy-1-hexyl magnesium chloride (IX) (prepared from 8.8 g of 1-chloro-6-tetrahydropyranyloxyhexane) was added dropwise to 5.0 g of cooled (-10°C) bromide VIII using dilithium tetrachlorocuprate as a catalyst (Tamura and Kochi, 1971; Descoins and Henrick, 1972). The reaction was stirred for 3 hr at -5 to 5°C and after work-up and column chromatography on silica yielded 4.0 g of (9*E*,11*E*)-9,11-hexadecadien-1-ol (X). Recrystallization from ether-hexane gave 3.5 g of pure X, mp 34-35°C in 65% yield. Product X is >99.5% pure by GC analysis (column 1) and by [¹³C]NMR (Table 2). IR (Nujol): 3360, 980 cm⁻¹. NMR: δ 6.24-5.18 (m, 4H), 3.62 (t, 2H, *J* = 8 Hz), 2.34-1.9 (m, 4H), 1.84 (s, 1H), 2.72-1.08 (m, 16H), 0.89 (t, 3H,

$J = 5$ Hz). Anal: calcd. for $C_{16}H_{30}O$: C, 80.60, H, 12.68; found C, 80.54, H, 12.64.

(9*E*,11*E*)-9,11-Hexadecadienal (II). Oxidation of 3.0 g of X as previously described (Svirskaya et al., 1980) yielded 2.4 g of (9*E*,11*E*)-9,11-hexadecadienal (II) in 80–85% yield. Even though alcohol X was >99% stereochemically pure, product II was contaminated with 5–10% of the isomeric *E,Z* and *Z,E* isomers (Henrick, 1977) as shown by GC analysis. Chromatography on silica and elution with ether–benzene (1:19) (fume hood) gave pure II, (bp 120–125°C/0.01 mm, Kugelrohr distillation), in the middle fraction in 80–85% yield. IR: 1750, 980 cm^{-1} . NMR: δ 9.85 (t, 1H, $J = 2$ Hz), 6.35–5.35 (m, 4H), 2.62–1.8 (m, 4H), 1.8–1.1 (m, 16H), 0.85 (t, 3H, $J = 7$ Hz). Anal: calcd. for $C_{16}H_{28}O$: C, 81.29, H, 11.94; found C, 80.84, H, 12.24.

(*E*)-9-Hexadecen-11-yn-1-ol (XV). Compound XV was prepared by some minor but important modifications of the method of Negishi et al. (1973). and hence the procedure is reproduced in full below.

A dry 500-ml flask, equipped with a thermometer, a condenser, a magnetic stirrer, and a septum inlet was flushed with argon. In the flask was placed 14.7 g (75 mmol) of 9-decynyl acetate (XI) in 20 ml of tetrahydrofuran (THF). Disiamylborane, 75 mmol at $-50^{\circ}C$, prepared by the method of Brown et al. (1977), was added dropwise by a syringe. The stirring was continued for 3 hr ($-50^{\circ}C$ for 1 hr, $-30^{\circ}C$ for 1 hr, and then $0^{\circ}C$ for 1 hr), and the solution of disiamyl[(*E*)-9-decenylnylacetate]borane (XII) was recooled to $-78^{\circ}C$. To this solution was added, by a syringe, cooled ($-50^{\circ}C$) lithium hexyne (XIII), freshly prepared from 6.15 g (75 mmol) of 1-hexyne in 15 ml THF and 63.75 ml (75 mmol) of *n*-BuLi. The resulting light yellow solution was stirred for 2.5 hr ($-78^{\circ}C$ for 1 hr, $-50^{\circ}C$ for 1 hr, and $0^{\circ}C$ for 0.5 hr) and recooled again to $-78^{\circ}C$. Iodine (20.64 g, 80 mmol) in 50 ml THF was added dropwise at $-78^{\circ}C$, and the resulting brown solution containing a white suspension was stirred for 1 hr at -78° to $-50^{\circ}C$ and allowed to warm to room temperature. To this solution 60 ml of 3 M sodium hydroxide was added, and the stirring was continued for 0.5 hr. The mixture was extracted with ether and washed with a saturated solution of sodium thiosulfate, water, and dried over $MgSO_4$. The solvent was evaporated, and the product was taken up in 50 ml of a methanol–THF (1:1) solution. The reaction mixture was oxidized and hydrolyzed by H_2O_2 at 30–40°C. The mixture was stirred for 1 hr at 30–40°C and for 0.5–1 hr at room temperature. The usual work-up gave 22 g of crude product, which was distilled through a short-path distillation column. The fraction with bp 120–180°C/0.01 mm (14.2 g) was separated on a silica gel column using hexane, followed by a hexane–benzene (1:1) mixture as eluants. Further elution with benzene, followed by ether–benzene (1:19) yielded the product XV which contained 9% of a

saturated alcohol. A second column chromatography and distillation gave XV (>98% pure) in 61% yield (10.8 g) bp 120–122°C/0.01 mm. IR: 3350, 1060, 950, 720 cm^{-1} . NMR: δ 6.35–5.61 (m, 1H), 5.55–5.14 (m, 1H), 3.64 (t, 2H, $J = 7$ Hz), 2.28 (s, 1H), 2.5–1.8 (m, 4H), 1.8–1.1 (m, 16H), 0.86 (t, 3H, $J = 7$ Hz). Anal: calcd. for $\text{C}_{16}\text{H}_{28}\text{O}$: C, 81.29, H, 11.94; found C, 80.91, H, 12.06.

(9E,11Z)-9,11-Hexadecadien-1-ol XVI. Reduction of enyne XV (5.0 g) with disiamylborane as described (Negishi et al. 1973) gave, upon column chromatography and distillation, 4.4 g (87% yield) of (9E,11Z)-9,11-hexadecadien-1-ol XVI, bp 118–120°C/0.01 mm Lit. (Bestmann et al., 1977), bp 115–116°C/0.01 mm. GC analysis (column I) showed that XVI was 97.3% pure and contained 2.5% of the Z,E and 0.2% of the Z,Z isomers respectively.

(9E,11Z)-9,11-Hexadecadienal (III). Compound III, prepared by oxidation of XVI as for II, was obtained in 80% yield (bp 135–142°C/0.02 mm, Kugelrohr distillation). IR: 1730, 985, 950, 735 cm^{-1} . NMR: δ 9.85 (t, 1H, $J = 2$ Hz), 6.6–5.1 (m, 4H), 2.6–1.9 (m, 4H), 1.9–1.1 (m, 16H), 0.9 (t, 3H, $J = 6$ Hz). Anal: calcd. for $\text{C}_{16}\text{H}_{28}\text{O}$: C, 81.29, H, 11.94; found C, 80.80, H, 12.06.

(9Z,11E)-9,11-Hexadecadienal(IV). Compound IV was prepared by the method of Zweifel and Backlund (1977) as shown in Scheme 3 and by the method of Bestmann (1976) for the precursor XXI. The Wittig procedure of Bestmann (1976) gave IV in low yield but high purity, and the data recorded for IV were those prepared by the Wittig procedure.

Thus, oxidation (Svirskaya et al., 1980) of XXI (3.7 g) via Bestmann et al. (1976) gave, after column chromatography and distillation, 2.0 g of pure (9Z,11E)-9,11-hexadecadienal (IV) (bp 130–140°C/0.01 mm, Kugelrohr distillation) as a colorless liquid in 77% yield. IR: 2720, 1730, 985, 950, 735 cm^{-1} . MS: 236 (M^+), 95, 81, 67 (100). NMR: δ 9.82–9.70 (m, 1H), 6.60–6.05 (m, 4H), 2.60–1.10 (m, 20H), 0.90 (t, 3H, $J = 6$ Hz). Anal: calcd. for $\text{C}_{16}\text{H}_{28}\text{O}$: C, 81.35, H, 11.86; found C, 81.38, H, 11.97.

RESULTS AND DISCUSSION

(9Z,11Z)-9,11-Hexadecadienal (I). Compound I had been previously prepared (Svirskaya et al., 1980). In this study larger quantities of high stereochemical purity were easily prepared in good yield (Table I).

(9E,11E)-9,11-Hexadecadienal (II). Compound II, previously unknown, was prepared via the cyclopropyl derivative VII by methods previously described (Descoins and Henrick, 1972; Mori, 1974). We found these methods mostly satisfactory for the preparation of the E,E isomer II, both with regard to overall yield and stereochemical purity (Table I). We did find,

TABLE I. SYNTHETIC YIELDS AND STEREOCHEMICAL PURITY OF GEOMETRICAL ISOMERS OF 9,11-HEXADECADIENOL

Method of preparation	Isomer (%)					Overall yield (%) ^c
	1a (Z,Z)	10 (E,E)	16 (E,Z)	21 (Z,E)		
1. Svirskaya et al. (1980)	>99		0.2	0.2		33 (from XI, Ac = H)
2. Descoins and Henrick (1972)		>99				20 (from VI)
3. Negishi and Yoshida (1973)		99				3 ^b
4. Negishi et al. (1973)	1.8		98.2			7 (from XI)
5. Modified Negishi and Abramovitch (1977) (this work)	0.1	0.3	99	0.3		42 (from XI)
6. Zweifel and Backlund (1978)	3.1	15.5	81.5			28 (from XI)
7. Modified Zweifel and Backlund (1978) (this work)	0.2	2.5	97.3			16 (from XI)
8. Zweifel and Backlund (1978)		3.9		77.3		28 (from XVIII)
9. Bestmann et al. (1976, 1981)	0.2		0.1	99		14 ^d

^aThe yields quoted are those of the purest products obtained after all chromatographic and distillation procedures were performed. Chromatographic and distillation fractions containing less pure compounds are not included in this calculation. Pure aldehydes 1-IV were obtained in isolated yields of 80-85% and having >99% purity by oxidation and chromatography of Ia, X, XVI, and XXI, respectively, and the yields quoted are the overall yields of 1-IV.

^bFrom 1-bromo-1-hexyne.

^cAn impurity accounts for 18.8% of this mixture and may be the E,Z isomer.

^dFrom 9-bromononan-1-yl acetate.

however, that in the coupling reaction of VIII with IX to produce X both VIII and IX should be kept cool and the temperature of the reaction mixture should not be allowed to rise during the course of the reaction. On the other hand attempts to prepare II via the xylborane, 1-bromoheptyne, and 9-decyn-1-yl tetrahydropyranyl ether (Negishi and Yoshida, 1973) gave very low yields (Table 1). Although *E,E* isomers such as II can be prepared by thiophenol-catalyzed isomerization (Henrick et al., 1975), we have found this procedure tedious and malodorous and prefer the definitive synthesis described above.

(9E,11Z)-9,11-Hexadecadienal (III). Compound III was prepared by our modified method of Negishi, et al. (1973) as well as by the published routes. Our modified version gave slightly higher yields and a significantly purer product (Table 1). As noted by Henrick et al. (1982) the original procedure of Negishi was difficult to follow, but we found it to be an excellent route as modified herein. In addition, III was prepared via the one-step procedure described (Zweifel and Backlund, 1978) in Scheme 3, and this latter procedure is definitely poorer in terms of yield and stereochemical purity of the product (Table 1). Henrick et al. (1982) note, however, that good yields are obtained in this latter procedure by using tri-*n*-butyltin chloride instead of boron trifluoride etherate as used herein.

(9Z,11E)-9,11-Hexadecadienal (IV). Compound IV, previously unknown, was prepared by the one-step procedure of Zweifel and Backlund (1978) in modest yield and barely acceptable stereochemical purity (Table 1). In addition, IV was prepared via a Wittig route previously described by Bestmann et al. (1981). This latter route in our hands afforded IV in high stereochemical purity but low chemical yield in the key Wittig reaction (Table 1). We would recommend that IV be prepared by our modified version of the method of Negishi et al. (1973) and Negishi and Abramovitch (1977).

Purification of I-IV. It is known that oxidation of conjugated dienols with chromate results in some isomerization (Henrick, 1977). In this study, however, we found that simple chromatography on silica of the aldehydes I-IV removes the 5-10% impurities of minor isomers resulting from the oxidation.² In all cases the minor isomers eluted first, along with some of the bulk isomer, and the major isomer was then collected with elution of only 50 ml of solvent. We feel that the major isomer can aggregate, thus ensuring that the conformationally more mobile minor impurities elute first in every case. Thus simple chromatography of these aldehydes can result in very pure final products, albeit with a 15-20% reduction in yield.

GC Analysis of I-IV. Very recently Chisholm et al. (1981) have shown that all four geometrical isomers of 5,7-dodecadienal can be separated on a

²A referee informs us that oxidation of olefinic alcohols using *N*-chlorosuccinimide, dimethyl sulfide, and triethylamine gives aldehydes in good yield without any appreciable isomerization.

0.25 mm ID \times 23 m Supelco SP-2100 glass capillary column. We have achieved a very similar separation of I-IV using the common SE-30 column (column 2) described in Methods and Materials, and the elution order of the isomers is identical to that of Chisholm et al. (1981). The relative retention times (to pentadecane at 11.3 min) of I-IV are 1.82, 1.85, 1.91, and 1.95, respectively. The relative retention times of the corresponding alcohols of I-IV, i.e. Ia, X, XVI, and XXI on column 1 (to pentadecane at 5.3 min.) are 4.24, 4.31, 4.50, and 4.63, and it is from these alcohols that isomer ratios were determined in Table 1.

^{13}C NMR Analysis of Ia, X, XVI, and XXI. Using common correlation principles based on related unsaturated fatty acids (Batchelor et al., 1974; Gunstone et al., 1977) and some pheromones (Rossi et al., 1982; Barabas et al., 1978), it was possible to assign most of the ^{13}C NMR absorption peaks for Ia, X, XVI, and XXI (Table 2). Although Rossi had pointed out that the allylic carbons are characteristic of the geometry about the double bonds, the olefinic carbons can also be characteristic as well. The Z,Z, E,E, and E,Z or Z,E isomers can be readily distinguished from each other by examining the olefin resonances. A note of caution should be added. The hexadienols Ia, X,

TABLE 2. ^{13}C CHEMICAL SHIFTS OF FOUR GEOMETRICAL ISOMERS OF 9,11-HEXADECADIENOL I, X, XVI, AND XXI

Carbon No.	$\delta^{13}\text{C}$ (ppm)			
	Ia (Z,Z)	X (E,E)	XVI (E,Z)	XXI (Z,E)
1.	63.04	63.23	63.05	63.08
2.	32.83	32.99 ^a	32.82	32.90
3.	25.77	25.90	25.90	25.82
4.	29.48	29.59	29.65	29.81
5.	29.48	29.59	29.65	29.53
6.	(29.48) ^b	29.59	29.65	29.53
7.	29.25	29.33	29.28	29.25
8.	27.48	32.74	32.82	27.75
9.	131.99	132.52	(130.07)	(134.66)
10.	123.66	130.56	125.73	128.78
11.	123.66	130.56	(128.68)	125.75
12.	132.06	132.52	(134.57)	(130.01)
13.	27.20	32.43	27.00	32.62
14.	31.88	31.96	31.88	31.68
15.	22.37	22.43	22.35	22.32
16.	13.96	14.05	13.95	13.97

^aAssigned by intensity considerations.

^bAssignments in parentheses are tentative.

XVI, and XXI are compounds in which the olefinic groups are surrounded by aliphatic carbons. In other closely related compounds, the functional groups may be closer to the diene moiety and will affect the clear pattern of shifts described for Ia, X, XVI, and XXI.

The preparation of all four geometrical isomers (I–IV) of a candidate insect pheromone by a total of six different methods has resulted in some improvements in the published methods and has allowed us to recommend preferred methods of synthesis at least within the framework of the methods attempted. Analysis of the products by capillary GC and [¹³C]NMR spectroscopy allows one to readily confirm their identification and monitor their purity.

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