

## PREPARATION OF (Z) AND (E)-9-DODECENYL ACETATES

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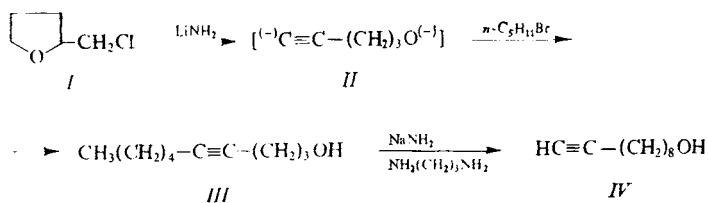
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The sexual pheromones (Z)-9-dodecenyyl acetate (*IXa*) and (E)-9-dodecenyyl acetate (*IXb*) were synthesized using facile preparation of the acetylenic precursor, 9-decyn-1-ol (*IV*), from tetrahydrofurfuryl chloride (*I*). Hydroxyl groups of intermediates in the subsequent steps were protected by the ethoxyethyl group.

Stereoisomeric (Z)- and (E)-9-dodecenyyl acetates (*IXa* and *IXb*, respectively) represent constituents of sexual pheromones of many kinds of harmful insects<sup>1</sup>. Several multistep syntheses of these compounds have been described<sup>2-8</sup>, often starting from less accessible materials.

In the present communication we describe the synthesis based on an advantageous preparation of the acetylenic precursor *IV* from tetrahydrofurfuryl chloride (*I*) (Scheme 1). In the subsequent steps we used the ethoxyethyl group<sup>9</sup> for protection of the hydroxyl; this protecting group can be removed by milder acid hydrolysis than the tetrahydropyranyl group, usually employed in pheromone syntheses.

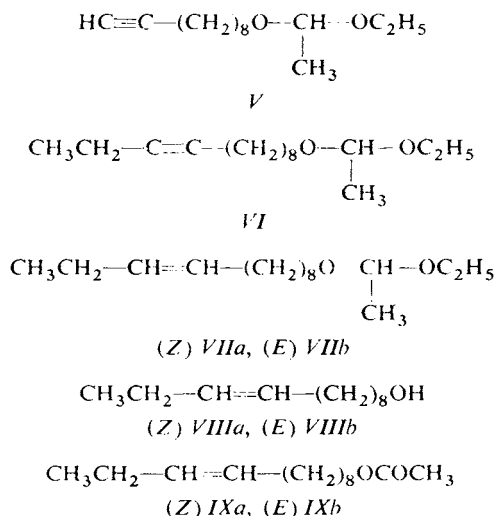


SCHEME 1

Conversion of tetrahydrofurfuryl chloride (*I*) into the dianion *II*, its *in situ* alkylation with alkyl bromide and shift of the triple bond into the terminal position were carried out according to the described methods<sup>10,11</sup>. In our case, the dianion *II* was alkylated with pentyl bromide, affording compound *III* with the triple bond in the middle of the chain. Isomerization with sodium 3-aminopropylamide gave the intermediate *IV* with the terminal triple bond in 32% yield (based on *I*).

The alcohol *IV* reacted with ethyl vinyl ether to give compound *V* which was converted to *VI* by alkylation with ethyl bromide in the presence of lithium amide.

Similarly as in other syntheses of compounds of this type<sup>1,2</sup>, the triple bond in compound *VI* was either hydrogenated over the P2-Ni catalyst under formation of the (Z)-isomer *VIIa* or reduced with sodium in liquid ammonia to afford the (E)-isomer



*VIIb*. In both cases the protecting group was removed with Dowex W-50 (H<sup>+</sup>-form) in methanol and the resulting alcohols *VIIIa* and *VIIIb* were acetylated with acetic anhydride in pyridine to furnish the pheromones *IXa* and *IXb* in the purity 98-9% (Z-isomer) and 99-8% (E-isomer) as determined by gas-liquid chromatography. Yield of the respective Z- and E-isomer was 21% and 22% (related to the starting tetrahydrofurfuryl chloride).

## EXPERIMENTAL

The boiling points are uncorrected. Infrared spectra were measured in tetrachloromethane on a UR-20 spectrophotometer (Zeiss, Jena), mass spectra on an MS 902 spectrometer and <sup>1</sup>H NMR spectra in deuteriochloroform on a Tesla BS 467 (60 MHz) instrument with tetramethylsilane as internal standard. Gas-liquid chromatography (GLC) was performed on an HP 5880 A chromatograph equipped with flame-ionization detector.

### 4-Decyn-1-ol (*III*) (ref.<sup>13</sup>)

Tetrahydrofurfuryl chloride (*I*; 120.6 g; 1 mol), pre-cooled to -33°C, was added dropwise to a suspension of lithium amide<sup>14</sup> prepared from 23.0 g of lithium and 3.300 ml of liquid ammonia. After stirring for 3.5 h, 1-bromopentane (151.1 g; 1 mol) in tetrahydrofuran (170 ml; pre-cooled to -33°C) was added dropwise and stirring was continued for 3 h. Ammonia was

evaporated on standing overnight, the residue was decomposed with saturated solution of ammonium chloride and extracted with ether ( $4 \times 500$  ml). The ethereal extracts were dried over magnesium sulfate, the solvent was evaporated and the residue was distilled, affording 93.4 g (61%) of the product, b.p.  $75-80^\circ\text{C}/0.03$  kPa. For  $\text{C}_{10}\text{H}_{18}\text{O}$  (154.2) calculated: 77.87% C, 11.76% H; found: 77.61% C, 11.56% H. Mass spectrum,  $m/z$  (%): 97 (100), 79 (90), 83 (76), 67 (68), 98 (61), 81 (54), 41 (53), 55 (41), 68 (39), 77 (37), 54 (37), 84 (34), 80 (29), 70 (27), 93 (27), 91 (25), 69 (24), 39 (24), 53 (23), 111 (22), 95 (22), 107 (17), 82 (15), 65 (15),  $M_{154} < 10\%$ .

#### 8-Decyn-1-ol (IV) (ref.<sup>15</sup>)

1,3-Diaminopropane (500 ml) was added dropwise to a stirred suspension of sodium amide<sup>14</sup> prepared from 22.4 g of sodium and 850 ml of liquid ammonia. Ammonia was evaporated with stirring, the mixture was heated to  $80^\circ\text{C}$  and 4-decyn-1-ol (III; 50.0 g; 0.324 mol) was added dropwise. After stirring at  $80^\circ\text{C}$  for 6 h, the cold mixture was decomposed with water, extracted with ether ( $4 \times 500$  ml) and the ethereal extracts were washed successively with dilute (1:4) hydrochloric acid, water, saturated solution of sodium hydrogen carbonate and brine. Drying over magnesium sulfate, evaporation of the solvent and distillation gave 26.0 g (52%) of the product, b.p.  $78-79^\circ\text{C}/0.07$  kPa. For  $\text{C}_{10}\text{H}_{18}\text{O}$  (154.2) calculated: 77.87% C, 11.76% H; found: 77.60% C, 11.59% H. IR Spectrum:  $\text{CH}_2\text{OH}$  3 635, 1 056  $\text{cm}^{-1}$ ;  $\text{C}\equiv\text{CH}$  3 315, 2 120  $\text{cm}^{-1}$ . Mass spectrum,  $m/z$  (%): 79 (100), 55 (95), 81 (93), 67 (88), 41 (80), 95 (65), 93 (53), 68 (40), 54 (40), 39 (35), 82 (35), 80 (35), 107 (28), 69 (28), 94 (25), 53 (25), 43 (25), 77 (23), 91 (20), 97 (20), 121 (18), 108 (18), 91 (18), 96 (15), 56 (15),  $M_{154} < 5\%$ .

#### 1-(1-Ethoxyethyloxy)-8-decyne (V)

Ethyl vinyl ether (21.5 g; 0.297 mol) was added dropwise with stirring to 8-decyn-1-ol (IV; 25.5 g; 0.165 mol) and *p*-toluenesulfonic acid (40 mg) in ether (150 ml). After stirring for 4 h at  $0-5^\circ\text{C}$ , powdered potassium hydroxide (1 g) and water (2 ml) were added. The mixture was diluted with ether (100 ml), washed with saturated solution of sodium hydrogen carbonate, brine and dried over potassium carbonate. Evaporation of the solvent and distillation gave 33.8 g (91%) of the title compound, b.p.  $82-83^\circ\text{C}/0.01$  kPa. For  $\text{C}_{14}\text{H}_{26}\text{O}_2$  (226.3) calculated: 74.29% C, 11.59% H; found: 74.47% C, 11.74% H. IR Spectrum:  $\text{C}\equiv\text{CH}$  3 315, 2 120  $\text{cm}^{-1}$ ;  $\text{O}-\text{CH}-\text{O}$  1 138, 1 105, 1 090, 1 064  $\text{cm}^{-1}$ . Mass spectrum,  $m/z$  (%): 73 (100), 81 (98), 45 (98), 95 (93), 211 (61), 55 (49), 67 (42), 75 (39), 41 (39), 79 (24), 69 (24), 74 (17), 93 (15), 43 (15), 39 (15). <sup>1</sup>H NMR Spectrum ( $\delta$ ): 1.05–1.57 (overlap 6 H,  $2 \times \text{CH}_3$ , 12 H,  $6 \times \text{CH}_2$ ), 1.90 (t, 1 H,  $\text{HC}\equiv\text{C}$ ), 2.15 (t, 2 H,  $\text{CH}_2(\text{C}\equiv\text{C})$ ), 3.25–3.75 (m, 4 H,  $2 \times \text{CH}_2(\text{O})$ ), 4.65 (q, 1 H,  $\text{O}-\text{CH}-\text{O}$ ).

#### 1-(1-Ethoxyethyloxy)-9-dodecyne (VI)

Compound V (50.0 g; 0.221 mol) in tetrahydrofuran (100 ml) was added to a suspension of lithium amide<sup>15</sup>, prepared from 1.84 g of lithium in 390 ml of liquid ammonia. After stirring for 1 h, 1-bromoethane (28.0 g; 0.265 mol) in tetrahydrofuran (150 ml) was added dropwise and stirring was continued for 3 h. Ammonia was evaporated on standing overnight and the residue was decomposed with water (1 000 ml). The mixture was extracted with ether ( $4 \times 500$  ml), the ethereal extracts were washed with brine and dried over potassium carbonate. Evaporation of solvents and distillation gave 50.5 g (90%) of the product, b.p.  $110-112^\circ\text{C}/0.03$  kPa. For  $\text{C}_{16}\text{H}_{30}\text{O}_2$  (254.4) calculated: 75.54% C, 11.89% H; found: 75.70% C, 11.63% H. IR Spectrum:  $\text{O}-\text{CH}-\text{O}$  1 139, 1 106, 1 090, 1 065  $\text{cm}^{-1}$ . Mass spectrum,  $m/z$  (%): 73 (100), 45 (70), 109 (28), 81 (28), 95 (28), 67 (30), 41 (33), 55 (30), 239 (13),  $M_{254} < 10\%$ . <sup>1</sup>H NMR Spectrum ( $\delta$ ): 0.87 to 1.63 (overlap 12 H,  $6 \times \text{CH}_2$ , 9 H,  $3 \times \text{CH}_3$ ), 1.88–2.27 (m, 4 H,  $2 \times \text{CH}_2(\text{C}\equiv\text{C})$ ), 3.17 to 3.76 (m, 4 H,  $2 \times \text{CH}_2(\text{O})$ ), 4.65 (q, 1 H,  $\text{O}-\text{CH}-\text{O}$ ).

## 1-(1-Ethoxyethyloxy)-(Z)-9-dodecene (VIIa)

1,2-Diaminoethane (3.2 g) and compound VI (3.5 g; 0.014 mol) were added to a suspension of P2-Ni (prepared<sup>16</sup> from 1.98 g of nickel acetate) in ethanol (90 ml). The mixture was hydrogenated until the hydrogen consumption ceased (30 min). The catalyst was filtered, ethanol evaporated and the residue partitioned between water and ether. The combined ethereal extracts were dried over potassium carbonate and taken down, yielding 3.04 g (86%) of the product. For  $C_{16}H_{32}O_2$  (256.4) calculated: 74.94% C, 12.58% H; found: 74.81% C, 12.45% H. IR Spectrum: (Z) CH=CH 3 070, 3 005, 1 663, 723  $cm^{-1}$ ; O—CH—O 1 137, 1 103, 1 090, 1 064  $cm^{-1}$ . <sup>1</sup>H NMR Spectrum ( $\delta$ ): 0.77—1.53 (overlap 12 H, 6  $\times$  CH<sub>2</sub>, 9 H, 3  $\times$  CH<sub>3</sub>), 1.70—2.20 (m, 4 H, 2  $\times$  CH<sub>2</sub>(C=C)), 3.13—3.76 (m, 4 H, 2  $\times$  CH<sub>2</sub>(O)), 4.65 (q, 1 H, O—CH—O), 5.18—5.40 (m, 2 H, CH=CH).

## 1-(1-Ethoxyethyloxy)-(E)-9-dodecene (VIIb)

Compound VI (35.0 g; 0.137 mol) in ether (650 ml) was added dropwise to a solution of sodium (8.05 g) in liquid ammonia (2 000 ml). The mixture was stirred for 7 h, set aside for 12 h to let the ammonia evaporate, mixed with ether (1 000 ml) and decomposed with water (1 000 ml). The ethereal layer was separated and the aqueous one extracted with ether (3  $\times$  500 ml). The combined ethereal solutions were washed with brine and dried over potassium carbonate. Evaporation of the solvent and distillation afforded 32.6 g (93%) of the product, b.p. 101—105°C/0.01 kPa. For  $C_{16}H_{32}O_2$  (256.4) calculated: 74.94% C, 12.58% H; found: 75.07% C, 12.93% H. IR Spectrum: (E) CH=CH 3 030, 967  $cm^{-1}$ ; O—CH—O 1 137, 1 103, 1 090, 1 064  $cm^{-1}$ . Mass spectrum,  $m/z$  (%): 73 (100), 45 (53), 69 (35), 55 (35), 41 (35), 68 (20), 81 (18), 67 (18), 97 (18), 82 (13), M 256 < 10%. <sup>1</sup>H NMR Spectrum ( $\delta$ ): 0.80—1.52 (overlap 12 H, 6  $\times$  CH<sub>2</sub>, 9 H, 3  $\times$  CH<sub>3</sub>), 1.68—2.13 (m, 4 H, 2  $\times$  CH<sub>2</sub>(C=C)), 3.13—3.80 (m, 4 H, 2  $\times$  CH<sub>2</sub>(O)), 4.65 (q, 1 H, O—CH—O), 5.30—5.48 (m, 2 H, CH=CH).

(Z)-9-Dodecen-1-ol (VIIIa) (ref.<sup>17</sup>) and (E)-9-Dodecen-1-ol (VIIIb) (ref.<sup>18</sup>)

Dowex W-50 (H<sup>+</sup>-form; 0.50 g; washed with methanol) was added to a solution of the isomer VIIa or VIIb (3.00 g; 0.012 mol) in methanol (50 ml). After stirring for 6 h, the ion-exchanger was filtered off, the filtrate was taken down and the residue was dried at 0.01 kPa for 4 h. According to TLC (Merck Kieselgel GF<sub>254</sub>, light petroleum—ethyl acetate (9 : 1)), the crude product (2.20 g, 99%) contained neither the starting VII nor any other impurity and was used directly in the acetylation.

(Z)-9-Dodecenyl Acetate (IXa) (ref.<sup>17</sup>) and (E)-9-Dodecenyl Acetate (IXb) (ref.<sup>18</sup>)

Pyridine (1.02 g; 0.013 mol), followed by acetic anhydride (1.33 g; 0.013 mol), was added to the alcohol VIIIa or VIIIb (2.00 g; 0.011 mol). The mixture was set aside for 24 h at room temperature, diluted with ether (50 ml), washed successively with dilute hydrochloric acid (1 : 4, 3  $\times$  20 ml), water, saturated solution of sodium hydrogen carbonate and brine, and dried over magnesium sulfate. The solvent was evaporated and the residue distilled, affording 2.38 g (96%) of IXa, b.p. 70—80°C/0.07 kPa, or 2.35 g (94%) of IXb, b.p. 80—82°C/0.07 kPa. IR Spectrum: IXa (Z) CH=CH 3 070, 3 010, 1 656, 723  $cm^{-1}$ ; OCOCH<sub>3</sub> 1 743, 1 243  $cm^{-1}$ ; IXb (E) CH=CH 3 025, 966  $cm^{-1}$ ; OCOCH<sub>3</sub> 1 739, 1 241  $cm^{-1}$ . Purity: (Z) 98.9%, (E) 99.8% (GLC, 25 capillary column, internal diameter 0.3 mm, SE-54).

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