SYNTHESES OF SOME *cis* MONO-OLEFINIC INSECT SEX PHEROMONES

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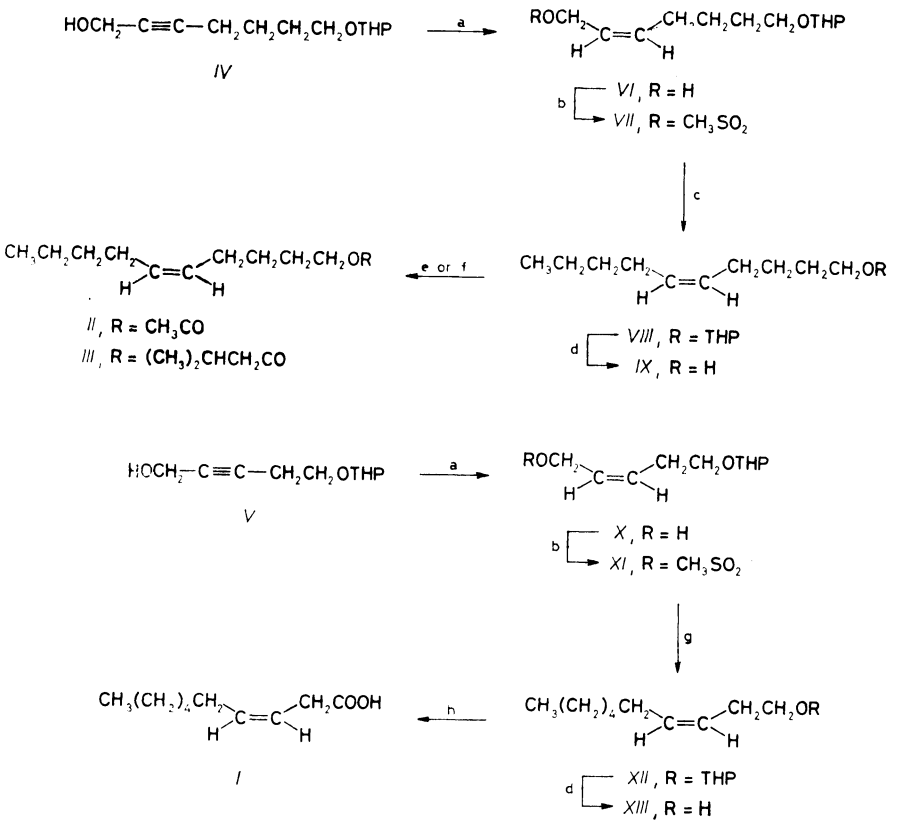
A convenient synthesis of *cis* mono-olefinic pheromone components *I*, *II*, and *III* has been achieved starting from (*Z*)-5-(2-tetrahydropyranyloxy)-pent-2-yn-1-ol (*V*) and (*Z*)-7-(2-tetrahydropyranyloxy)-hept-2-yn-1-ol (*IV*), both of which have been obtained from a common intermediate, viz. the dianion of prop-2-yn-1-ol.

Cis mono-olefinic compounds form an important class of insect sex pheromones. Among them we can find such compounds as (*Z*)-3-decenoic acid (*I*) of beetle genus *Anthrenus flavipes*[1], (*Z*)-5-decen-1-yl acetate (*II*) of male turnip moth (*Agrotis segetum*)[2], (*Z*)-5-decen-1-yl isovalerate (*III*) of female pine emperor moth (*Nadaurelia cytherea* FABR.)[3]. Compound *II* has also been identified as the sex pheromone component of other insect species[4]. Literature[3,5–10] records several syntheses of these pheromone components. We now report an alternative synthetic approach leading to *I*, *II*, and *III* (Scheme 1) via the known alkynols *V* and *IV* which in turn were prepared[11] from the dianion of prop-2-yn-1-ol and 2-bromo-1-(2-tetrahydropyranyloxy)ethane or 4-bromo-1-(2-tetrahydropyranlyoxy)butane.

Partial catalytic hydrogenation of *IV* over Lindlar's catalyst[12] in hexane–ethanol yielded *VI* which, after conversion[13] to the corresponding mesylate *VII*, was coupled with propylmagnesium bromide in the presence of dilithium tetrachlorocuprate[14] to yield *VIII*. Deprotection of *VIII* was achieved using *p*-toluenesulfonic acid monohydrate in methanol[15] to generate the alcohol *IX* which furnished the esters *II* and *III* on treatment with acetic anhydride-pyridine[16] and isovaleryl chloride[10] respectively.

By an analogous sequence of reactions compound *V* was converted into alcohol *XIII* which upon oxidation with pyridinium dichromate[17] in anhydrous N,N-dimethylformamide afforded the acid *I*. The spectral data (IR, ^{1}H NMR) of the synthetic samples were found to be in agreement with the reported values[1,3].



SCHEME 1

a H_2/Lindlar catalyst, hexane–ethanol; b methanesulfonyl chloride, triethylamine; c propylmagnesium bromide, dilithium tetrachlorocuprate, tetrahydrofuran; d *p*-toluenesulfonic acid monohydrate, methanol; e acetic anhydride, pyridine; f isovaleryl chloride, pyridine; g pentylmagnesium bromide, dilithium tetrachlorocuprate, tetrahydrofuran; h pyridinium dichromate, N,N-dimethylformamide

EXPERIMENTAL

Boiling points are uncorrected. IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer (wavenumbers in cm^{-1}) and ^1H NMR spectra on a Varian EM-390 (90 MHz) spectrometer in carbon tetrachloride using tetramethylsilane as internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants (J) in Hz. Silica gel (Acme, 60—80 mesh) was used for column chromatography. Unless stated otherwise, organic extracts were dried over anhydrous sodium sulfate.

(*Z*)-7-(2-Tetrahydropyranyloxy)-hept-2-en-1-ol (*VI*)

The alkynol ether *IV* (5·0 g, 24 mmol) was hydrogenated over Lindlar's catalyst (200 mg) poisoned with quinoline (2 drops) in hexane–ethanol (2 : 1, 20 ml). When one equivalent of hydrogen (pressure 276 kPa) was consumed, the catalyst was filtered off and the solvent removed under reduced pressure to afford *VI*; yield, 4·64 g (92%). IR spectrum (neat): 3 400 (OH); 1 640, 725 (*cis* double bond). ^{1}H NMR spectrum: 5·3–5·8 m, 2 H (2 × H—C=); 4·6 s, 1 H (H-2 of tetrahydropyranyloxy group); 4·2 s, 1 H (OH); 4·0 s, 2 H (CH_2OH); 3·3–3·8 m, 4 H (CH_2O, 2 × H-6 of tetrahydropyranyloxy group); 2·4 m, 2 H (CH_2—CH=); 1·4–1·7 m, 10 H (5 × CH_2). For $C_{12}H_{22}O_3$ (214·3) calculated: 67·26% C, 10·35% H; found 67·26% C, 10·27% H.

(*Z*)-1-(2-Tetrahydropyranyloxy)-dec-5-ene (*VIII*)

To a solution of alcohol *VI* (3·5 g, 16 mmol) and triethylamine (2·99 ml, 24 mmol) in dry dichloromethane (30 ml) at 0°C, methanesulfonyl chloride (1·51 ml, 20 mmol) was added and the mixture was stirred for 3 h. The reaction mixture was poured in water and the product was extracted with ether. The organic phase was washed successively with 5% hydrochloric acid, 5% sodium hydrogen carbonate solution, water, and dried. The solvent was removed under reduced pressure to give mesylate *VII* (3·43 g, 72%) which was used directly for the subsequent reaction.

To a solution of propylmagnesium bromide (prepared from 1-bromopropane (1·80 g, 15 mmol) and magnesium turnings (0·35 g)) in tetrahydrofuran (15 ml), the mesylate *VII* (3·43 g, 12 mmol) in tetrahydrofuran (15 ml) was added at −10°C. The mixture was stirred for 1 h and then 0·1M solution of dilithium tetrachlorocuprate in tetrahydrofuran (3 ml) was added. Stirring was continued at −10°C for another 3 h, the mixture was left overnight and then decomposed with saturated aqueous ammonium chloride. The product was extracted with ether, the extract was washed with brine and dried. Evaporation of the solvent followed by purification by column chromatography on silica gel (35 g), eluting with petroleum ether–ether (9 : 1), afforded *VIII*; yield, 1·54 g (55%). IR spectrum (neat): 1 650, 920, 875, 800, 725. ^{1}H NMR spectrum: 5·4 to 5·8 m, 2 H (2 × H—C=); 4·6 s, 1 H (H-2 of tetrahydropyranyloxy group); 3·3–3·8 m, 4 H (2 × CH_2O); 2·2 m, 4 H (CH_2—CH=); 1·3–1·7 m, 14 H (7 × CH_2); 0·9 t, 3 H (CH_3). For $C_{15}H_{28}O_2$ (240·4) calculated: 74·95% C, 11·74% H; found: 74·95% C, 11·61% H.

(*Z*)-5-Decen-1-ol (*IX*)

p-Toluenesulfonic acid monohydrate (100 mg) was added to a solution of the compound *VIII* (1·54 g, 6 mmol) in methanol (20 ml) and the mixture was stirred at room temperature for 6 h. Methanol was distilled off under reduced pressure. The residue was diluted with water, the product was extracted with ether, the extract was washed with 5% solution of sodium hydrogen carbonate, water, brine and dried. Evaporation of the solvent and vacuum distillation yielded the carbinol *IX*; 0·85 g (85%), b.p. 106–107°C/1·33–1·60 kPa. IR spectrum (neat): 3 400, 2 950, 1 650, 725, 705. ^{1}H NMR spectrum: 5·2–5·7 m, 2 H (2 × H—C=); 3·9 s, 1 H (OH); 3·7 t, 2 H (CH_2OH); 2·3 m, 4 H (CH_2—CH=); 1·3–1·8 m, 8 H (4 × CH_2); 0·9 t, 3 H (CH_3). For $C_{10}H_{20}O$ (156·3) calculated: 76·86% C, 12·90% H; found: 76·90% C, 12·80% H.

(*Z*)-5-(2-Tetrahydropyranyloxy)-pent-2-en-1-ol (*X*)

The compound *X* was prepared from *V* (4·0 g, 22 mmol) using the Lindlar's catalyst (200 mg) in hexane–ethanol (2 : 1, 20 ml) as reported for preparation of *VI*; yield, 3·82 g (94%) of compound *X*. IR spectrum (neat): 3 400, 1 650, 730, 700. ^{1}H NMR spectrum: 5·4–5·8 m, 2 H (2 × H—C=); 4·6 s, 1 H; 4·2 s, 2 H (CH_2OH); 3·8 s, 1 H (OH); 3·3–3·7 m, 4 H (2 × CH_2O);

2·4 t, 2 H (CH_2—C=C); 1·3—1·7 m, 6 H (3 × CH_2). For $C_{10}H_{18}O_3$ (186·3) calculated: 64·49% C, 9·74% H; found: 64·48% C, 9·65% H.

(*Z*)-1-(2-Tetrahydropyranyloxy)-dec-3-ene (*XII*)

Compound *XII* was prepared by reaction of pentylmagnesium bromide (prepared from 1-bromopentane (2·48 ml, 20 mmol) and magnesium turnings (0·48 g) in tetrahydrofuran (25 ml)) and mesylate *XI* (prepared from alcohol *X* (3·82 g, 20 mmol)) as reported for compound *VIII*; yield, 2·2 g, (55%). IR spectrum (neat): 3 420, 1 640, 730. ^{1}H NMR spectrum: 5·3—5·7 m, 2 H (2 × H—C=); 4·6 s, 1 H; 3·3—3·7 m, 4 H (2 × CH_2O); 2·1—2·5 m, 4 H (CH_2—CH=); 1·2—1·7 m, 14 H (7 × CH_2); 0·9 t, 3 H (CH_3). For $C_{15}H_{28}O_2$ (240·2) calculated: 74·95% C, 11·74% H; found: 74·95% C, 11·63% H.

(*Z*)-3-Decen-1-ol (*XIII*)

Alcohol *XIII* was prepared from THP-ether *XII* (2·07 g, 9 mmol) as reported for *IX*; yield 1·1 g (82%). b.p. 80—81°C/1·33 kPa. IR spectrum (neat): 3 420, 1 640, 730, 705. ^{1}H NMR spectrum: 5·3—5·7 m, 2 H (2 × H—C=); 3·55 t, 2 H (CH_2OH); 3·4 s, 1 H (OH); 2·1—2·4 m, 4 H (CH_2—C=); 1·5—1·8 m, 8 H (4 × CH_2); 0·89 t, 3 H (CH_3). For $C_{10}H_{20}O$ (156·3); calculated: 76·86% C, 12·90% H; found: 76·90% C, 12·81% H.

(*Z*)-3-Decenoic Acid (*I*)

To a solution of pyridinium dichromate (10·92 g, 42 mmol) in N,N-dimethylformamide (15 ml), a solution of *XIII* (1·1 g, 7 mmol) in N,N-dimethylformamide (4 ml) was added at 0°C under nitrogen. The mixture was stirred for 14 h at room temperature and then poured into water, the product was extracted with ether, extract was dried and concentrated. Purification of the crude product afforded 0·8 g (67%) of *I*; b.p. 154—160°C/133 kPa. IR spectrum (neat); 3 450 (OH); 1 730 (C=O); 1 680, 710 (*cis* double bond). ^{1}H NMR spectrum: 8·7 bs, 1 H (COOH); 5·3—5·8 m, 2 H (2 × H—C=); 2·85 d, 2 H (CH_2COO, J = 12); 2·1—2·4 m, 2 H (CH_2—CH=); 1·2—1·5 m, 8 H (4 × CH_2); 0·9 t, 3 H (CH_3). For $C_{10}H_{18}O_2$ (170·3) calculated: 70·55% C, 10·66% H; found: 70·56% C, 10·57% H.

(*Z*)-5-Decen-1-yl Acetate (*II*)

To a solution of alcohol *IX* (0·85 g, 5 mmol) and catalytic amount of dimethylaminopyridine in pyridine (5 ml) cooled at 0°C, acetic anhydride (1·5 ml) was added and the mixture was stirred at room temperature for 3 h. The reaction was quenched by addition of ice and the product was extracted with ethyl acetate. The organic extract was washed successively with 5% hydrochloric acid, water, 5% sodium hydrogen carbonate solution, water, brine, and dried. Evaporation of the solvent and distillation under reduced pressure afforded acetate *II* (0·95 g; 88%), b.p. 102 to 104°C/1·73—1·87 kPa. IR spectrum (neat): 1 720 (C=O); 1 650, 725 (*cis* double bond). ^{1}H NMR spectrum: 5·3—5·7 m, 2 H (2 × H—C=); 4·1 t, 2 H (CH_2OCO); 2·2 m, 4 H (CH_2—C=); 2·1 s, 3 H ($OOCCH_3$); 1·3—1·7 m, 8 H (4 × CH_2); 0·9 t, 3 H (CH_3). For $C_{12}H_{22}O_2$ (198·3) calculated: 72·68% C, 11·18% H; found: 72·70% C, 11·1% H.

(*Z*)-5-Decen-1-yl Isovalerate (*III*)

To a solution of alcohol *IX* (0·25 g, 1·6 mmol) and pyridine (0·155 ml, 1·9 mmol) in dichloromethane (10 ml) at 0°C, isovaleryl chloride (0·235 ml, 1·9 mmol) was added dropwise with

stirring. Stirring was continued at room temperature overnight. The reaction mixture was extracted with ether. The organic phase was washed with 5% hydrochloric acid, 5% sodium hydrogen carbonate solution, brine, and dried. Evaporation and purification of the resulting residue by column chromatography on silica gel (10 g) afforded the liquid ester *III*; yield, 1·46 g (95%). IR spectrum (neat): 1 740 (C=O); 1 650, 730 (*cis* double bond). ^{1}H NMR spectrum: 5·3—5·5 m, 2 H (2 × H—C=); 3·9 t, 2 H (CH_2O); 1·2—2·5 m, 15 H (CH, $COCH_2$, 4 × CH_2, 2 × CH_2—C=); 1·0 t, 3 H (CH_3); 0·98 d, 6 H ($(CH_3)_2CH$). For $C_{15}H_{28}O_2$ (240·3) calculated: 74·95% C, 11·74% H; found: 74·96% C, 11·64% H.

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