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Article

Synthesis of Acyclic Insect Pheromones from Cycloalkanones via Acetylenic Lactones

Jaswant Rai Mahajan,* Inês Sabioni Resck

Departamento de Química, Universidade de Brasilia, 70.910-900 Brasilia - DF, Brazil

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A Fig. 1 descreve um método geral para preparação de feromônios de insetos.

Vários componentes de feromônios de insetos, junto de seus isômeros geométricos e/ou posicionais, foram preparados a partir de Z-lactonas **2a-d**, que são facilmente acessíveis pela hidrogenação estereosseletiva (Lindlar Pd, H_2) dos precursores acetilênicos **1a-d**, sendo estes já sintetizados a partir de cicloalcanonas. A isomerização de acetatos de Z-alquenilas **6a-d** aos respectivos esteres de E-alquenilas **8a-d**, foi realizada tanto pela técnica catalítica ($NaNO_2$, HNO_3, Δ) como pelo método de inversão química (NBS, TFA; NaI, DMF, Δ). O álcool (E)-6-decenílico (**7b**) foi também preparado diretamente do ester acetilênico (**15b**) pela redução, em trans, com hidreto de lítio-alumínio ($LiAlH_4$), por refluxo em diglima. Os acetatos de decila (**18**) e hexadecila (**19**), componentes dos feromônios de mariposa do nabo (*Agrotis segetum*; turnip moth) e da borboleta *Lycorea ceres ceres,* respectivamente, foram obtidos pela hidrogenação catalítica (Pd, H_2) dos acetatos de Z-alquenilas correspondentes.

Figure 1 describes a general method for the preparation of insect pheromones.

Several members of the title compounds, along with their geometric and/or positional isomers, have been prepared from Z-lactones **2a-d**, which are easily available from the corresponding acetylenic lactones **1a-d**, prepared earlier from cycloalkanones. The Z to E isomerization of alkenyl acetates **6a-d** to **8a-d** was carried out both by a catalytic technique ($NaNO_2$, HNO_3, Δ) and the chemical inversion procedure (NBS, TFA; NaI, DMF, Δ). (E)-6-Decenyl alcohol (**7b**) was also prepared from the acetylenic ester **15b** by the trans reduction with $LiAlH_4$ in refluxing diglyme. decyl acetate (**18**) and hexadecyl acetate (**19**), pheromone components of the turnip moth (*Agrotis segetum*) and the male butterfly *Lycorea ceres ceres*, respectively, were obtained by the catalytic hydrogenation (Pd, H_2) of the corresponding Z-alkenyl acetates.

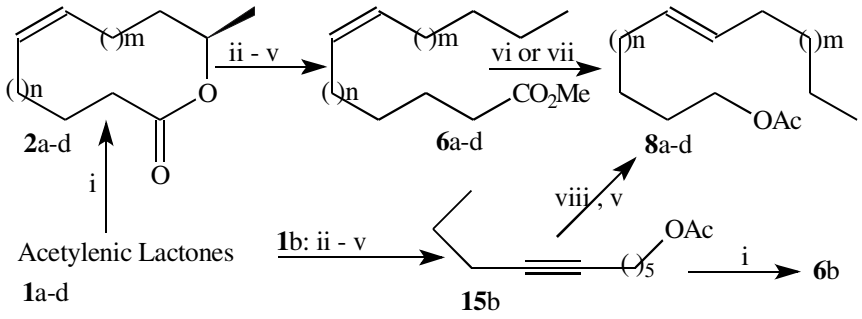
Keywords: *insect pheromones, Z-lactones, acetylenic lactones, cycloalkanones*

Introduction

Pheromones are an important and a rapidly growing class of biologically active organic compounds. A large proportion of pheromones isolated from a variety of insects exemplifies diversely functionallized acyclic compounds, which have been synthesized by several routes[1-3]. While earlier methodologies employed for the construction of the acyclic skeleton involved mainly the acetylenic chemistry and olefin formation by the Wittig or related reactions[1]. More recently, there has been an increasing emphasis on the use of diverse methods for improved isomeric purity of the E or Z product and for those leading to the optically active pheromones[2,3].

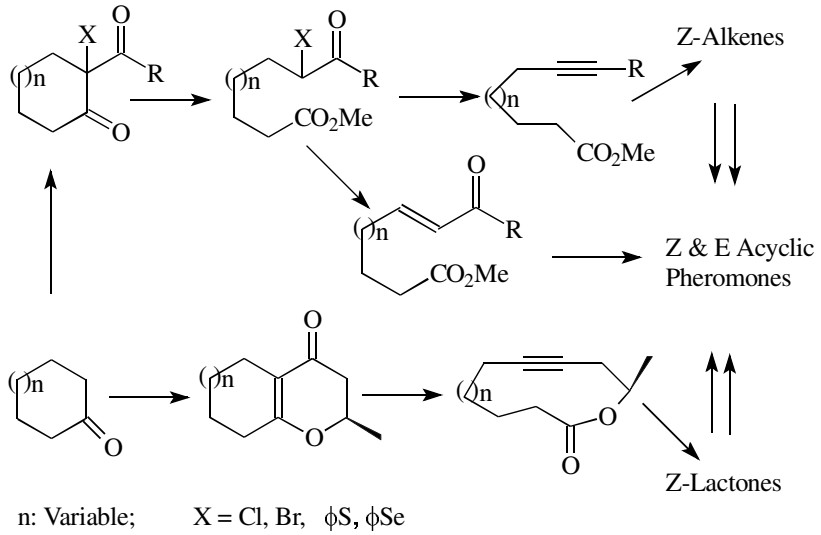
We have recently initiated a different approach to these acyclic compounds by the systematic elaboration of cycloalkanones, where the variable size of the starting ketone is exploited to generate the triple or the double bond of the desired product in a regiospecific and stereoselective manner[4] (Scheme 1).

We have already reported our preliminary results on the conversion of cyclohexanone, involving the transformation of an α-chloroketone function into an acetylenic linkage ($RCHClCOR \rightarrow RC{\equiv}CR$), to both the Z and E series of C_9 pheromones[5]. A recent publication[6] described the preparation of Z and E macrolides from the acetylenic lactones[7] **1a-d**, whilst we report their transformation into several



a: m = n = 1; b-d: m = 0; b: n = 2; c: n = 4; d: n = 8. i-viii: 90-95% crude yields, see text.

Figure 1.



Scheme 1. General Strategies for the Synthesis of Acyclic Pheromones from Cycloalkanones.

members of the title compounds and their geometric or positional isomers, as illustrated in Scheme 2.

Results and Discussion

Methanolysis of the Z-lactones[6] 2a-d gave the corresponding hydroxy-esters 3a-d, which on mesylation[8] furnished the respective mesylates 4a-d. Lithium aluminum hydride reduction of the latter in ether afforded the Z-alkenols 5a-d, which were acetylated to the corresponding acetates 6a-d. Of these, (Z)-5-decenyl acetate (6a) is the pheromone component of the turnip moth (*Agrotis segetum*)[3], while (Z)-8-dodecenyl acetate (6c) constitutes the sex pheromone of the oriental fruit moth (*Grapholita molesta*)[3]. These two compounds have been synthesized earlier[3].

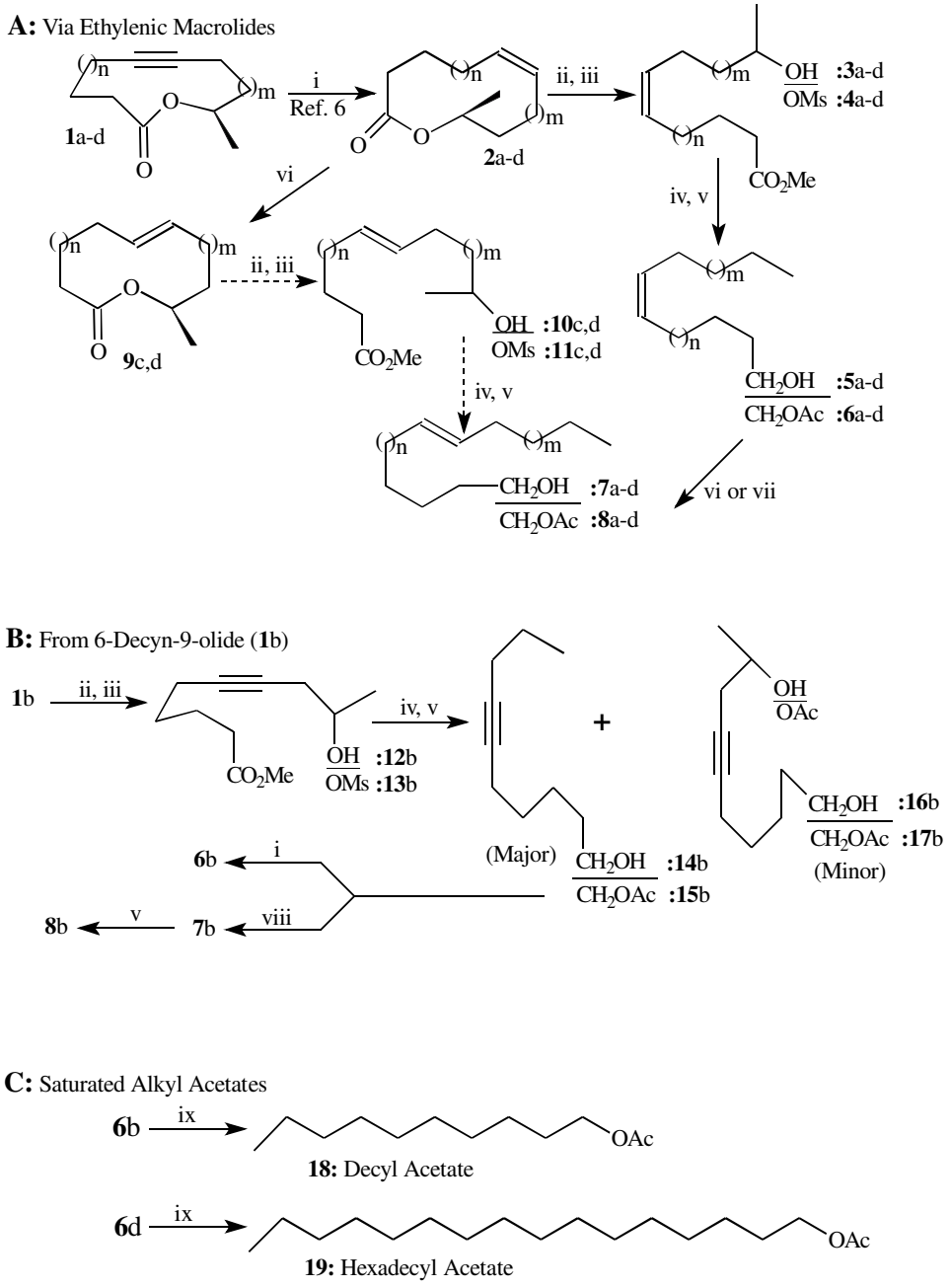
Both the catalytic isomerization ($NaNO_2$, HNO_3)[9] and the chemical inversion (TFA, NBS; NaI, DMF, Δ)[10] of the Z alkenyl acetates **6a-d** worked well with these acyclic compounds, leading to the corresponding E acetates **8a-d** in good (90-95%) yield. Nevertheless, the catalytic technique[9] (2M $NaNO_2$, 2M HNO_3 , 70-75 °C, 1 h) is far more convenient and economical. Among the E compounds **8a-d**, only (E)-8-dodecenyl acetate (**8c**) is a minor component of the pheromone of the oriental fruit fly (*Grapholita molesta*), mentioned earlier[3].

We would like to stress here that the alternative route to these E alkenyl acetates **8a-d**, through the respective transformations of the E lactones (dashed arrows in Scheme 2-A), is rather limited and less attractive, because the Z to E isomerization works better in the acyclic compounds as compared with the cyclic ones (lactones), as discussed elsewhere[6].

Another path was tested with the opening of the acetylenic lactone **1b**. However, reduction of the mesiloxy-ester **13b**, with $LiAlH_4$ in ether, required a much lower initial reaction temperature (-100 °C as compared with the usual -15 °C), but still gave a mixture of the desired alcohol **14b** and the unwanted diol **16b**. The latter could be separated by column chromatography of the corresponding acetates **15b** and **17b**. Despite this drawback, this path has the advantage of leading to both the Z and E isomers directly from the acetylenic precursor. Thus, semi-hydrogenation (H_2, Lindlar cat.) of **15b** furnished (Z)-6-decenyl acetate (**6b**), while its trans reduction with $LiAlH_4$ in refluxing diglyme[11] gave

directly (E)-6-decen-1-ol (**7b**), which was converted into the respective acetate **8b** (Scheme 2-B).

Apart from furnishing the acetylenic intermediates as well as both the Z and E alkenyl alcohols and their esters, the present methodology also opens an access to the saturated pheromones, either by the full hydrogenation of the unsaturated precursores or by the systematic elaboration of the saturated lactones. We chose to prepare decyl acetate (**18**) and hexadecyl acetate (**19**), pheromone components of the turnip moth (*Agrotis segetum*)[12] and the male butterfly *Lycorea ceres ceres*[13], respectively, from the corresponding Z-alkenyl acetates (Scheme 2-C).



a: m = n = 1; b: m = o, n = 2; c: m = 0, n = 4; d: m = 0, n = 8

Scheme 2. Preparation of Z & E Pheromones from Acetylenic Lactones. *Reagents*: i) Lindlar cat., H_2; ii) MeOH, MeONa, reflux, 20-24 h; iii) MsCl, Et_3N, CH_2Cl_2, -15 °C, 3 h; iv) $LiAlH_4$, ether, -15 °C to reflux, 14-16 h; v) Ac_2O, Py (cat.), 80-90 °C, 3 h; vi) $NaNO_2$, HNO_3, 70-75 °C, 1 h; vii) NBS, TFA, 0 °C, 30 min; NaI, DMF, 90 °C, 20-22 h; viii) $LiAlH_4$, diglyme, reflux, 24 h; ix) Pd-C, H_2. All reactions gave 90-95% crude yields (see Experimental).

The infrared and 90 MHz ^{1}H NMR spectra do not clearly differentiate between the Z and E alkenyl acetates (**6a-d / 8a-d**). Consequently, we resorted to their 200/50 MHz ^{1}H- and ^{13}C- spectra (PND, DEPT, ^{1}H x ^{1}H and ^{1}H x ^{13}C COSY, etc.), where the most evident distinguishing feature, as expected, was the chemical shift of the allylic carbon atoms, which are 4 to 6 ppm upfield in the Z compounds as compared with the respective atoms in the E isomers (Tables 1 and 2)[14]. Moreover, close examination of the olefinic carbon atoms in the PND spectra revealed that all the E alkenyl acetates (**8a-d**) were contaminated with 5-10% of the corresponding Z isomer, while only the (Z)-8-dodecenyl acetate (**6c**) and (Z)-12-hexadecenyl acetate (**6d**) contained 5-10% of the respective E compound, as also present in the precursor Z-lactones[6] **2c,d**.

Experimental

Reagent grade chemicals and solvents were used as received from the commercial suppliers, unless noted otherwise. All reactions were monitored routinely by thin layer chromatography (TLC: silica gel, revealed by I_2 vapours). Organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure on a rotary evaporator. IR spectra of all liquid samples were recorded on a Nicolet 5ZDX-FT spectrometer as neat films. Routine ^{1}H-NMR spectra, reported in the experimental text, were obtained on a Varian EM-390 (90 MHz) instrument as CCl_4 solutions, while the high resolution ^{1}H- and ^{13}C- spectra (PND, DEPT, ^{1}Hx^{1}H and ^{1}Hx^{13}C COSY, etc.) for the Z- and E-alkenyl acetates (Tables 1 and 2) were recorded in $CDCl_3$ on a Bruker AC-200 (200/50 MHz) spectrometer. Bransonic ultrasonic cleaner (Model 1210 or 2210; 47 ± 6 KHz) was used to conduct the semi-hydrogenations. Temperatures in the short path distillations refer to the air bath. Other experimental details are given below.

*Methanolysis of Z-Lactones **2a-d**. General procedure*

A solution of **2a-d** (5 mmol) in MeOH (20 ml), containing NaOMe (10 mL, 0.13 mM) and protected with a $CaCl_2$ tube, was refluxed (N_2) for 20-24 h. After evaporating excess of the solvent, distilled water (20 ml) was added and the mixture extracted with ethyl acetate (3 x 30 ml). The combined extract was washed with water (20 ml) and brine (2 x 20 mL). Drying and evaporation of the solvent furnished the crude hydroxy-esters **3a-d** as yellowish liquids (~4.5 mmol; ~90%), practically pure by TLC , which were used in the next step, after the usual spectral identification.

*Methyl (Z)-9-Hydroxy-5-decenoate **3a***

IR (ν): 3419, 1739, 1245, 1220, 1202, 1128 cm^{-1}. ^{1}H-NMR (δ): 1.16 (d, J = 6 Hz, 3H, CH_3), 1.2-1.9 (m, 4H, $2CH_2$), 1.9-2,5 (m, 6H, $3CH_2$), 3,49 (s, 1H, OH), 3.6-3.9 (m, 4H, containing a singlet at 3.65, OCH_3 and CH), 5.15-5.65 (m, 2H, olefinic).

*Methyl (Z)-9-Hydroxy-6-decenoate **3b***

IR (ν): 3496, 1740, 1261, 1209, 1120 cm^{-1}. ^{1}H-NMR (δ): 1.12 (d, J = 6 Hz, 3H, CH_3), 1.2-1.9 (m, 4H, $2CH_2$), 1.9-3.0 (m, 7H, $3CH_2$ and OH) , 3.5-3.9 (m, 4H, containing a singlet at 3.62, OCH_3 and CH), 5.2-5.7 (m, 2H, olefinic).

*Methyl (Z)-11-Hydroxy-8-dodecenoate **3c***

IR (ν): 3425, 1740, 1254, 1201, 1119 cm^{-1}. ^{1}H-NMR (δ): 1.13 (d, J = 6 HZ , 3H, CH_3), 1.2-1.9 (m, 8H, $4CH_2$), 1.9-2.5 (m, 6H, $3CH_2$), 3.3 (s, 1H, OH), 3.6-4.1 (m, 4H, containing a singlet at 3.62, OCH_3 and CH), 5.3-5.7 (m, 2H, olefinic).

*Methyl (Z)-15-Hydroxy-12-hexadecenoate **3d***

IR (ν): 3435, 1740, 1253, 1208, 1120 cm^{-1} . ^{1}H-NMR (δ): 1.16 (d, J = 7 Hz, 3H, CH_3), 1.2-1.9 (m, 16H, $8CH_2$), 1.9-2.5 (m, 6H, $3CH_2$), 2.77 (s, 1H, OH), 3.6-4.0 (m, 4H, containing a singlet at 3.63, OCH_3 and CH), 5.25-5.65 (m, 2H, olefinic).

*Mesylation of the Hydroxy-Esters **3a-d**. General procedure*

To a stirred solution of the hydroxy-ester **3**a-d (4.5 mmol) and triethylamine (0,95 mL, 690 mg, 6.83 mmol) in CH_2Cl_2 (20 mL), cooled to -15 °C and under anhydrous conditions, was added slowly a solution of H_3CSO_2Cl (0.4 mL, 592 mg, 5.17 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h, when it was diluted with more CH_2Cl_2 (50 mL) and washed with water (3 x 20 mL) and brine (20 mL). Drying and evaporation of solvent gave yellowish, viscous liquids **4a-d** (4.0-4.3 mmol; 90-95%), showing one spot on TLC plates. A rapid passage through a small column of Florisil (3-5 g), in CH_2Cl_2 (20-30 mL), afforded purer samples which were characterized by their spectra and subsequently reduced with $LiAlH_4$.

*Methyl (Z)-9-Mesyloxy-5-decenoate **4a***

IR (ν): 1736, 1354, 1174 cm^{-1}. ^{1}H-NMR (δ): 1.38 (d, J ~ 6 Hz, 3H, CH_3), 1.4-1.9 (m, 4H, $2CH_2$), 1.9-2.5 (m, 6H, $3CH_2$), 3.0 (s, 3H, SO_3CH_3), 3.62 (s, 3H, OCH_3), 4,75 (sextet, J ~ 6 Hz, 1H, CH), 5.2-5.6 (m, 2H, olefinic).

*Methyl (Z)-9-Mesyloxy-6-decenoate **4b***

IR (ν): 1737, 1355, 1207, 1177 cm^{-1}. ^{1}H-NMR (δ): 1.1-1.9 (m, 7H, containing a doublet at 1.39, J ~ 6 Hz, CH_3 and $2CH_2$), 1.9-2.7 (m, 6H, $3CH_2$), 2.97 (s, 3H, SO_3CH_3), 3.63 (s, 3H, OCH_3), 4.75 (sextet, J ~ 6 Hz, 1H, CH), 5.2-5.8 (m, 2H, olefinic).

*Methyl (Z)-11-Mesyloxy-8-dodecenoate **4c***

IR (ν): 1737, 1357, 1253, 1176 cm^{-1}. ^{1}H-NMR (δ): 1.1-1.9 (m, 11H, containing a doublet at 1.4, J ~ 6 Hz, CH_3 and $4CH_2$), 1.9-2.7 (m, 6H, $3CH_2$), 2.95 (s, 3H, SO_3CH_3), 3.63 (s, 3H, OCH_3), 4,75 (sextet, J ~ 6 Hz, 1H, CH), 5.2-5.8 (m, 2H, olefinic).

*Methyl (Z)-15-Mesyloxy-12-hexadecenoate **4d***

IR (ν): 1738, 1358, 1252, 1176 cm^{-1}. ^{1}H-NMR (δ): 1.1-1.9 (m, 19H, containing a doublet at 1.37, J ~ 7 Hz, CH_3 and 8 CH_2), 1.9-2.7 (m, 6H, $3CH_2$), 2.97 (s, 3H, SO_3CH_3), 3.6(s, 3H, OCH_3), 4.75 (sextet, J ~ 6 Hz, 1H, CH), 5.2-5.8 (m, 2H, olefinic).

*Reduction of Mesyloxy-esters **4a-d**. General procedure*

To a stirred suspension of $LiAlH_4$ (608-646 mg, 16-17 mmol) in ether (40-50 mL), cooled to -15 °C, was added dropwise a solution of the mesyloxy-ester **4a-d** (4.0-4.3 mmol) in the same solvent (10 mL). The reaction mixture was stirred until it attained r. t. (2-3 h), when it was gently refluxed for 14-16 h. After cooling, it was carefully decomposed with small pieces of ice and extracted with ethyl acetate (3 x 30 mL), the combined extract being successively washed with dil. HCl (20 mL), satd. solution of $NaHCO_3$ (20 mL) and brine (20 mL). Drying and evaporation furnished yellowish liquids (3.6-3.8 mmol; 90-95%), which were acetylated after spectral characterization.

*(Z)-5-Decenol **5a***

IR (ν): 3336, 1056 cm^{-1}. ^{1}H-NMR (δ): 0.94 (deformed t, 3H, CH_3), 1.1-1.8 (m, 8H, $4CH_2$), 1.8-2.4 (m, 4H, $2CH_2$), 3.56 (t, J = 6 Hz, 2H, CH_2O), 4.5 (br. s, 1H, OH), 5.15-5.60 (m, 2H, olefinic).

*(Z)-6-Decenol **5b***

IR (ν): 3338, 1054 cm^{-1}. ^{1}H-NMR (δ): 0.88 (t, J = 7 Hz, 3H, CH_3), 1.1-1.8 (m, 8H, $4CH_2$), 1.8-2.3 (m, 4H, $2CH_2$), 3.5 (t, J = 6 Hz, 2H, CH_2O), 3.8 (br. s, 1H, OH), 5.1-5.5 (m, 2H, olefinic).

*(Z)-8-Dodecenol **5c***

IR (ν): 3332, 1058 cm^{-1}. ^{1}H-NMR (δ): 0.90 (t, J = 7 Hz, 3H, CH_3), 1.1-1.8 (m, 12H, $6CH_2$), 1.8-2.3 (m, 4H, $2CH_2$), 3.52 (t, J = 6 Hz, 2H, CH_2O), 4.0 (br. s, 1H, OH), 5.15-5.55 (m, 2H, olefinic).

*(Z)-12-Hexadecenol **5d***

IR (ν): 3334, 1056 cm^{-1}. ^{1}H-NMR (δ): 0.92 (t, J~7 Hz, 3H, CH_3), 1.1-1.8 (m, 20H, $10CH_2$), 1.8-2.3 (m, 4H, $2CH_2$), 3.52 (t, J = 6 Hz, 2H, CH_2), 3.93 (br. s, OH), 5.1-5.5 (m, 2H, olefinic).

*Acetylation of Z-Alkenols **5a-d**. General procedure*

A solution of **5a-d** (3.6-3.8 mmol) in acetic anhydride (3.2-3.4 mL, 3.5-3.7 g, 34-36 mmol), containing 6-7 drops of pyridine and protected with a $CaCl_2$ tube, was heated on a water bath (80-90 °C) for 3 h, after which water (15-20 mL) was added and the cooled reaction mixture extracted with hexane (3 x 30 mL). The combined extract was washed with dil. HCl (10 mL), satd. solution of $NaHCO_3$ (10 mL), and brine (20 mL). Drying and evaporation gave the desired acetates **6a-d**, as colorless liquids, possessing pleasant odor. Short path distillation (**6a-c**: 110-120 °C/5 Torr; **6d**: 110-120 °C/0.5 Torr) furnished the pure samples in 85-90% yield.

*(Z)-5-Decenyl Acetate[3] **6a***

Colorless liquid (641 mg; ~90% yield). IR (ν): 1745, 1234 cm^{-1}. ^{1}H-NMR (δ): 0,9 (deformed t, J ~ 6 Hz, 3H, CH_3), 1.1-1.8 (m, 8H, $4CH_2$), 1.8-2.5 (m, 7H, containing a singlet at 1.96, AcO and $2CH_2$), 4,0 (t, J = 6 Hz, 2H, CH_2O), 5.15-5.55 (m, 2H, olefinic).

*(Z)-6-Decenyl Acetate **6b***

Colorless liquid (652mg; 90%). IR (ν): 1743, 1236 cm^{-1}. ^{1}H-NMR (δ): 0.92 (t, J ~ 6 Hz, 3H, CH_3), 1.1-1.9 (m, ~10H, $5CH_2$), 1.9-2.4 (m, ~5H, containing a singlet at 2.0, AcO and CH_2), 4,0 (t, J = 6 Hz, 2H, CH_2O), 5.1-5.6 (m, 2H, olefinic).

*(Z)-8-Dodecenyl Acetate[3] **6c***

Colorless liquid (691mg; 85%). IR (ν): 1743, 1240 cm^{-1}. ^{1}H-NMR (δ): 1.0 (t, J = 6 Hz, 3H, CH_3), 1.2-1.8 (m, ~12H, $6CH_2$), 1.8-2.5 (m, ~7H, containing a singlet at 2.05, AcO and $2CH_2$), 4,05 (t, J = 6 Hz, 2H, CH_2O), 5.2-5.6 (m, 2H, olefinic).

*(Z)-12-Hexadecenyl Acetate **6d***

Colorless liquid (873 mg; 86%). IR (ν): 1743, 1237 cm^{-1}. ^{1}H-NMR (δ): 0.89 (t, J ~ 7 Hz, 3H, CH_3), 1.1-1.8 (m, 20H, $10CH_2$), 1.8-2.6 (m, 7H, having a singlet at 1.95, AcO and $2CH_2$), 4,0 (t, J ~ 7 Hz, 2H, CH_2O), 5.15-5.60 (m, 2H, olefinic).

200/50 MHz spectra of these acetates are shown in Table 1.

*Catalytic Isomerization of Z Acetates **6a-d** into E Isomers **8a-d**. General procedure*

Sodium nitrite solution (2M, 0.1mL) and 2M HNO_3 (0.2 mL) were added to the Z acetate **6a-d** (1 mmol), kept under N_2 atmosphere. The resulting yellowish mixture was stirred vigorously and heated to 70-75 °C for 1 h. After cooling and dilution with water (10 mL), it was extracted with hexane (3 x 20 mL), the combined extract being washed

Table 1. ^{13}C- and ^{1}H- spectra# of Z-Alkenyl Acetates **6a-d**.

Compound:	**6a**		**6b**		**6c**		**6d**	
C-	δC	δH	δC	δH	δC	δH	δC	δH
ACO:	170.93	-	170.88	-	~171.0	-	171.06	-
CH_3	20.79	1.96s	20.85	1.97s	20.72	2.05s	20.84	1.98s
1	64.24	3.98t	64.43	3.97t	64.39	4.05t	64.53	4.00t
2	28.03	1.5-1.7	28.39	1.5-1.7	28.44	1.5-1.7	28.51	1.56m
3	25.85	1.2-1.4	25.42	1.2-1.4	25.73	1.2-1.5	25.82	1.1-1.4
4	26.55*	1.99m	29.21	1.2-1.4	29.12	1.2-1.5	29.19[i]	1.1-1.4
5	128.85[i]	5.26m	26.90*	1.8-2.0	28.99	1.2-1.5	29.66[i]	1.1-1.4
6	130.34[i]	5.28m	129.83	5.1-5.4	28.99	1.2-1.5	29.46[i]	1.1-1.4
7	26.76*	1.93m	129.40	5.1-5.4	26.99*	1.9-2.1	29.46[i]	1.1-1.4
8	31.75	1.1-1.3	29.21*	1.8-2.0	129.72	5.2-5.5	29.46[i]	1.1-1.4
9	22-18	1.1-1.3	22.75	1.2-1.4	129.52	5.2-5.5	29.66[i]	1.1-1.4
10	13.80	0.82t	13.66	0.82t	29.49*	1.9-2.1	29.19[i]	1.1-1.4
11	-	-	-	-	22.73	1.2-1.5	27.12*	1.9-2.0
12	-	-	-	-	13.61	0.90t	129.96	5.3t
13	-	-	-	-	-	-	129.48	5.3t
14	-	-	-	-	-	-	29.19*	1.9-2.0
15	-	-	-	-	-	-	22.79	1.1-1.4
16	-	-	-	-	-	-	13.69	0.85t

#: Based on PND, DEPT, ^{1}H x ^{1}H and ^{1}H x ^{13}C COSY Spectra at 200/50 MHz in $CDCl_3$.
*: Allylic C; i: Interchangeable assignment; s, m, t : Usual multiplicity of peaks.

with satd. soln. of $NaHCO_3$ (10 mL) and brine (10 mL). Drying and evaporation gave yellowish liquids in 95-100% yield. Short path distillation (**8a-c**: 110-120 °C/5 Torr; **8d**: 110-120 °C/0.5 Torr) afforded colorless liquids (90-95%).

*(E)-5-Decenyl Acetate **8a***

IR (ν): 1744, 1240, 970 cm^{-1}. ^{1}H-NMR (δ): 0.90 (deformed t, J ~ 6 Hz, 3H, CH_3), 1.1-1.9 (m, 8H, $4CH_2$), 1.9-2.3 (m, 7H, having a singlet at 2.03, AcO and $2CH_2$), 4.0 (t, J = 6 Hz, 2H, CH_2O), 5.15-5.65 (m, 2H, olefinic).

*(E)-6-Decenyl Acetate **8b***

IR (ν): 1743, 1238, 969 cm^{-1}. ^{1}H-NMR (δ): 0.86 (t, J ~ 7 Hz, 3H, CH_3), 1.1-1.8 (m, 8H, $2CH_2$), 1.8-2.3 (m, 7H, showing a singlet at 1.95, AcO and $2CH_2$), 3.98 (t, J ~ 6 Hz, 2H, CH_2O), 5.1-5.6 (m, 2H, olefinic).

*(E)-8-Dodecenyl Acetate[3] **8c***

IR (ν): 1743, 1240, 969 cm^{-1}. ^{1}H-NMR (δ): 0.94 (t, J ~ 7 Hz, 3H, CH_3), 1.20-1.85 (m, 12H, $6CH_2$), 1.85-2.5 (m, 7H, having a singlet at 2.02, AcO and $2CH_2$), 4.04 (t, J = 6 Hz, 2H, CH_2)), 5.2-5.6 (m, 2H, olefinic).

*(E)-12-Hexadecenyl Acetate **8d***

IR (ν): 1743, 1238, 967 cm^{-1}. ^{1}H-NMR (δ): 0.88 (deformed t, 3H, CH_3), 1.1-1.8 (m, 20H, $10CH_2$), 1.8-2.6 (m, 7H, having a singlet at 1.97, AcO and $2CH_2$), 4.0 (t, J = 6 Hz, 2H, CH_2O), 5.15-5.65 (m, 2H, olefinic).

Higher field spectra of these acetates are shown in Table 2.

*Chemical Inversion of Z Acetates (**6a-d**) to E Isomers (**8a-d**). General procedure*

Compound **6a-d** (0.5 mmol) was added slowly to a cold (0 °C) and stirred solution of NBS (107 mg, 0.6 mmol) in TFA (0.75 mL, 1.1 g, 9.74 mmol), protected with a drying tube. After stirring for 30 min, the reaction mixture was diluted with water (10 mL) and extracted with hexane (3 x 10 mL), the extract being washed with water (5 x 10 mL) and brine (10 mL). Usual work-up furnished the crude adducts, in almost quantitative yield, showing characteristic absorptions around 1785 and 1740 cm^{-1}.

The crude product dissolved in DMF (2 mL) and containing NaI (338 mg, 2.25 mmol) was heated at 90 °C for 20-22 h. After cooling, a dil. solution of $NaHSO_3$ (10 mL) was added and the whole extracted with hexane (3 x 10 mL). Usual work-up gave brown liquids, which on short path distillation furnished the E acetates **8a-d**, in

Table 2. ^{13}C- and ^{1}H- spectra# of E-Alkenyl Acetates **8a-d**.

Compound:	**8a**		**8b**		**8c**		**8d**	
C-	δC	δH	δC	δH	δC	δH	δC	δH
AcO:	170.69	-	~171.0		171.06	-	170.51	-
CH_3	20.57	2.02s	20.84	2.04s	20.93	2.05s	20.68	2.01s
1	64.10	4.03t	64.47	4.05t	64.57	4.05t	64.35	4.01t
2	27.79	1.5-1.7	28.36	1.5-1.7	28.52	1.5-1.7	28.46	1.53m
3	25.60	1.4m	25.27	1.1-1.4	25.81	1.1-1.5	25.76	1.2-1.5
4	31.99*	1.9-2.1	29.09	1.1-1.4	29.46	1.1-1.5	29.45[i]	1.2-1.5
5	130.72[i]	5.2-5.5	32.30*	1.8-2.1	29.05	1.1-1.5	29.00[i]	1.2-1.5
6	129.2l[i]	5.2-5.5	130.39	5.3-5.5	28.93	1.1-1.5	29.45[i]	1.2-1.5
7	31.85*	1.9-2.1	129.97	5.3-5.5	32.49*	1.8-2.1	29.00[i]	1.2-1.5
8	31.49	1.2-1.4	34.58*	1.8-2.1	130.36	5.2-5.5	29.45[i]	1.2-1.5
9	21.91	1.2-1.4	22.60	1.1-1.4	130.16	5.2-5.5	29.00[i]	1.2-1.5
10	13.63	0.87t	13.52	0.88t	34.64*	1.8-2.1	29.45[i]	1.2-1.5
11	-	-	-	-	22.63	1.1-1.5	32.45*	1.8-2.1
12	-	-	-	-	13.58	0.88t	129.85	5.2-5.4
13	-	-	-	-	-	-	130.32	5.2-5.4
14	-	-	-	-	-	-	34.55*	1.8-2.1
15	-	-	-	-	-	-	22.57	1.2-1.5
16	-	-	-	-	-	-	13.75	0.85t

#: Based on PND, DEPT, ^{1}H x ^{1}H and ^{1}H x ^{13}C COSY Spectra at 200/50 MHz in $CDCl_3$.
*: Allylic C; i: Interchangeable assignment; s, m, t : Usual multiplicity of signals.

90-95% yield, as colorless liquids, identical (IR and ^{1}H-NMR) with the respective products obtained earlier by the catalytic procedure.

*Methanolysis of the Acetylenic Lactone **1b***

A solution of **1b** (830 mg, 5 mmol) in MeOH (20 mL), containing NaOMe (0.13 mM, 10 mL), was refluxed for 2-3 h, when it was worked-up as described earlier for the methanolysis of Z lactones, obtaining the hydroxy-ester **12b**, a yellowish liquid, in 90% yield (891 mg). IR (ν): 3433, 1739, 1283, 1264, 1216, 1177 cm^{-1}. ^{1}H-NMR (δ): 1.2 (d, J = 6 Hz, 3H, CH_3), 1.3-2.0 (m, 4H, $2CH_2$), 2.0-2.6 (m, 6H ,$3CH_2$), 3.2-4.2 (m, 5H, having a singlet at 3.64, OCH_3, CH,OH).

The crude product (~890 mg) was mesylated with MsCl (0.4 mL, 592 mg, 5.17 mmol) and Et_3N (0.95 mL) in CH_2Cl_2 (30 mL), as described earlier, to obtain the mesyloxy-ester **13**b as a yellowish liquid (1.24 g; 100%). After a quick passage through a small column of Florisil® (3-5 g) in CH_2Cl_2 (20-30 mL), it was characterized by its spectra. IR (ν): 1736, 1354, 1212, 1176 cm^{-1}. ^{1}H-NMR (δ): 1.3-2.0 (m, 7H, showing a doublet at 1.52, J = 6 Hz, CH_3 and $2CH_2$), 2.0-2.5 (m, 4H, $2CH_2$), 2.5-2.8 (m, 2H, CH_2), 3.08 (s, 3H, SO_3CH_3), 3.68 (s, OCH_3), 4.8 (sextet, J = 6 Hz, 1H, CH).

*Reduction of the Mesyloxy-Ester **13b***

A solution of ester **13b** (1.2 g; 4.5 mmol) in anhydrous ether (40 mL) was added slowly to a stirred suspension of $LiAlH_4$ (684 mg, 18 mmol) in ether (10 mL), kept at -100 °C (liquid N_2 and EtOAc). After allowing the reaction mixture to attain r. t. (2-3 h), it was gently refluxed for 14-16 h. Usual work-up, as described in the earlier cases, furnished a yellowish liquid (770 mg), showing two principal spots on TLC plate. Spectral analysis revealed these as the desired alcohol **14b** and unwanted diol **16b**. IR (ν): 3349, 1161, 1073, 1052 cm^{-1}. ^{1}H-NMR (δ): 0,97 (t, J ~ 7 Hz, $\underline{H}_3C$-CH_2), 1.2 (d, J ~ 6 Hz, $\underline{H}_3C$-CH-O) 1.2-2.0 (m, methylenes), 2.0-3.0 (m, methylenes), 3.53 (~t, CH_2O), 3.7-4.0 (m, having a singlet at 3.8, OH and CH).

The above mixture was acetylated with Ac_2O (4.3 mL) and pyridine (8 drops), under the usual conditions, and the resulting product (1.1 g) chromatographed, under reduced pressure,[15] over silica gel 60G (15 g), eluted with hexane-EtOAc (98:2), obtaining the acetylenic monoacetate **15b** (690 mg; 70%) and diacetate **17b** (340 mg; 27%).

*6-Decynyl Acetate **15b** (Colorless liquid)*

IR (ν): 1742,1238 cm^{-1}. ^{1}H-NMR (δ): 0.98 (t, J = 6 Hz, 3H, CH_3), 1.2-1.9 (m, 8H, $4CH_2$), 1.9-2.5 (m, 7H, containing a singlet at 2.0, AcO and $2CH_2$), 4.03 (t, J = 6 Hz, 2H, CH_2O).

*1,9-Diacetoxy-6-decyn **17b** (Colorless liquid)*

IR (ν): 1740, 1242 cm^{-1}. ^{1}H-NMR (δ): 1.32 (t, J = 6 Hz, 3H, CH_3), 1.4-1.9 (m, 6H, $3CH_2$), 1.9-2.7 (m, 10H, showing a singlet at 2.03, 2AcO and $2CH_2$), 4.05 (t, J = 6 Hz, 2H, CH_2O), 4.9 (sextet, J = 6 Hz ,1H, CH).

*Semi-hydrogenation[6] of 6-Decynyl Acetate (**15b**)*

Compound **15b** (196 mg, 1 mmol), Lindlar catalyst (60 mg) and hexane (10 mL) were put in a pear-shaped flask, which was connected to a balloon filled with H_2 (~500 mL). After the usual purging with H_2 (3 times) the reaction flask was placed in the center of an ultrasound bath and irradiated for 4 h, when there was no more starting alkyne **15b**, as detected by GC analysis (FFAP column, 200 °C). Filtration of the catalyst and evaporation of the solvent gave a colorless liquid, which on short path distillation (110-120 °C/5 Torr) furnished an analytical sample (194 mg; 98%), identical in all respects (TLC, IR, ^{1}H-NMR) with (Z)-6-decenyl acetate (**6b**), prepared earlier by an alternative route.

*Reduction of 6-Decynyl Acetate (**15b**) to (E)-6-Decenyl Alcohol (**7b**)*

A solution of compound **15b** (196 mg, 1 mmol) in diglyme (5 mL) was added dropwise to a magnetically stirred suspension of $LiAlH_4$ (152 mg, 4 mmol) in diglyme (10 mL), cooled to 0 °C. After attaining r. t., the reaction mixture was refluxed gently for 24 h, when it was cooled and decomposed carefully with small pieces of ice. Extraction with hexane (3 x 20 mL) and usual work-up afforded the (E)-6-decenol (**7b**), which was acetylated to the corresponding acetate under the usual conditions descrided earlier. Short path distillation (110-120 °C/5 Torr) gave the pure compound **8b** (190 mg; 95%), identical (TLC, IR, ^{1}H-NMR) with the product obtained earlier by the isomerization of Z isomer **6b**.

*Decyl Acetate[12] (**18**)*

A solution of (Z)-6-decenyl acetate (**6b**: 198 mg, 1 mmol) in hexane (10 mL), containing 10% Pd-C (20-30 mg), was subjected to hydrogenation (2 atm) in a Parr apparatus for 2-3 h, when there was no more of the starting material. Usual work-up furnished the product in a quantitative yield, while short path distillation (110-120 °C/5 Torr) afforded an analytical sample. IR (ν): 1744, 1238 cm^{-1}. ^{1}H-NMR (δ): 0.92 (deformed t, J ~ 6 Hz, 3H, CH_3), 1.1-1.8 (m, 16H, $8CH_2$), 1.97 (s, 3H, AcO), 4.0 (t, J = 6 Hz, 2H, CH_2O).

*Hexadecyl Acetate[13] (**19**)*

Was obtained from (Z)-12-hexadecenyl acetate (6d), exactly in the manner described above. IR (ν): 1744, 1237 cm^{-1}. ^{1}H-NMR (δ): 0.89 (deformed t, 3H, CH_3), 1.28 (~s, 28H, $14CH_2$), 1.97 (s, 3H, OAC), 4.0 (t, J~6 Hz, 2H, CH_2O).

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References

1. a) Rossi, R. *Synthesis* **1977**, 817; b) Henrick, C.A. *Tetrahedron* **1977**, *33*, 1845.
2. Mori, K. *Tetrahedron* **1989**, *45*, 3223.
3. Mori, K. In *The Total Synthesis of Natural Products*, Vol. 9; Apsimon, J.; Ed.; Wiley; New York, 1992, and the pertinent references cited therein.
4. a) Mahajan, J.R. In *Organic Synthesis in Brazil: An Overview*; Comasseto, J.V.; Ferreira, J.T.B.; Ed.; DOT Editoração Eletrônica & Multimídia; São Carlos - SP, 1994; pp 79-87; b) Mahajan, J.R. **ICOS 10**, Bangalore-India, **1994**; *ABSTRACTS*: ISP-27, P 81; c) Mahajan, J.R.; Resck, I.S.; **6th BMOS**, USP-SP, **1994**; *ABSTRACTS*: p 94; d) Mahajan, J.R.; *J. Braz. Chem. Soc*. **1996**, *7*, 297.
5. a) Mahajan, J.R.; Tresvenzol, L.M.F. *J. Braz. Chem. Soc*. **1993**, *4*, 179; b) Mahajan, J.R.; Resck, I.S.; Aspesi, G.H. 17th Annual Meeting of SBQ **1994**; *Abstracts*: QO-041.
6. Mahajan, J.R.; Resck, I.S. *Synth. Commun*. **1996**, *26*, 3809.
7. a) Mahajan, J.R.; Resck, I.S. *J. Chem. Soc., Chem. Commun.* **1993**, 1748; b) Resck, I.S. PhD Thesis **1995**; QUI-IE-UNB.
8. Crossland, R.K.; Servis, K.L. *J. Org. Chem*. **1970**, *35*, 3195.
9. Sonnet, P.E. *J. Org. Chem*. **1974**, *39*, 3793.
10. Sonnet, P.E. *J. Org. Chem.* **1980**, *45*, 154.
11. Schwarz, M.; Graminski, G.F.; Waters, R.M. *J. Org. Chem*. **1986**, *51*, 260.
12. Olsson, A.-M.; Jonsson, J.A.; Thelin, B.; Liljefors, T. *J. Chem. Ecol*. **1983**, *9*, 375.
13. a) Meinwald, J.; Meinwald, Y.C. *J. Am. Chem*. Soc. **1966**, *88*, 1305; b) Meinwald, J.; Meinwald, Y. C.; Wheeler, J.W.; Eisner, T. *Science* **1966**, *151*, 583.
14. Mahajan, J.R.; Resck, I.S.; Braz-Filho, R.; Carvalho, M.G. 5th Meeting of NMR Users (V-AUREMN), Angra dos Reis-RJ, **1995**; *Abstracts:* p 38; *, pp 123-132.*