Chemistry of Natural Compounds and Bioorganic Chemistry

Synthesis of (7*Z*,9*Z*)-dodecadienyl acetate, a component of sex pheromones of the leafrollers *Epinotia* and *Eucosma*, using conjugated diynols

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Two analogous routes to the title pheromones were elaborated based on organocuprate cross-coupling of *Z,Z*-dienic electrophiles, (2*Z*,4*Z*)-1-acetoxy-2,4-heptadiene (**6**) and (3*Z*,5*Z*)-1-bromoctadiene (**8**), with ω-*tert*-butoxy-1-chloropentane and -butane, respectively. Optimal conditions for the reduction of 2,4-heptadiyn-1-ol and 3,5-octadiyn-1-ol to the respective *Z,Z*-alkadienols as precursors for the electrophiles were found. Treatment of diynols with activated zinc in aqueous alcohol provided high geometrical purity of the product (≥94 %). In both cases, copper-catalyzed cross-coupling afforded 1-*tert*-butoxy-7,9-dodecadiene (four stereoisomers), acetolysis of which gave the target pheromone contaminated by stereoisomers. In the case of allylic electrophile **6**, the reaction occurred with the loss of the initial configurational purity, whereas the use of homoallylic bromide **8** ensured almost complete retention of the configuration of the double bonds and obtaining the target pheromone of 87 % configurational purity.

Key words: 2,4- and 3,5-alkadiyn-1-ols, *cis*-reduction; (2*Z*,4*Z*)- 1-acetoxy-2,4-heptadiene; (3*Z*,5*Z*)-1-bromo-3,5-octadiene; organocuprate cross-coupling, stereoselectivity; (7*Z*,9*Z*)-dodecadienyl acetate, synthesis.

Conjugated α,δ-disubstituted dienes with *cis*- or *trans*-configuration of the double bonds are characteristic components of sex pheromones of several species of *Lepidoptera* belonging to the *Lasiocampidae*, *Tortricidae*, *Bombycidae*, and *Noctuidae* families. (7*Z*,9*Z*)-7,9-Dodecadienyl acetate (*Z,Z*-**1**), a pheromone or a component of the pheromone composition of leafrollers of the *Epinotia* (forest pest)[1] genus and the *Eucosma*

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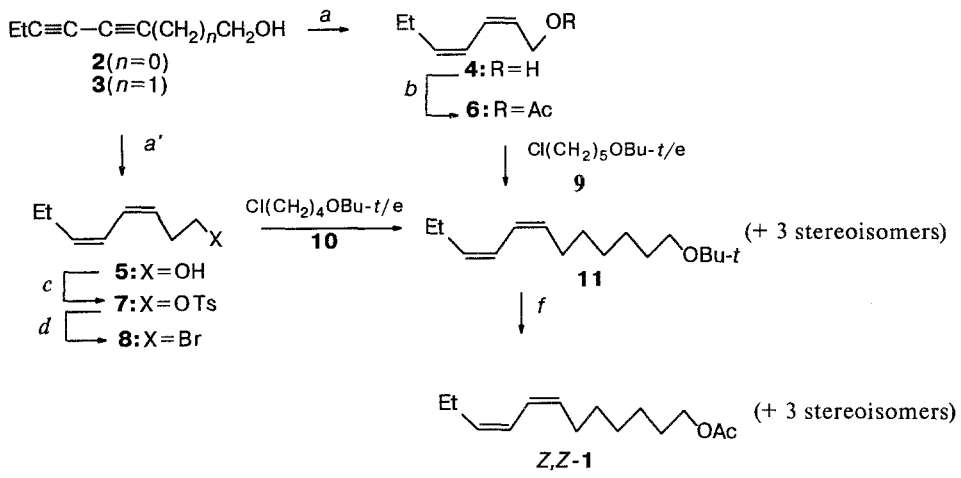
Scheme 1



Reagents and conditions: *a*. Zn(Cu)/*i*-PrOH—H_2O, ~90°C (bath); *a'*. Same as *a*, 130—140°C (bath); *b*. Ac_2O—NEt_3—DMAP; *c*. TsCl/ Et_2O/ KOH(solid); *d*. LiBr/DMF; *e*. Mg/THF, then Li_2CuCl_4; *f*. Ac_2O—$FeCl_3$/ Et_2O.

womonana (sunflower pest)[2] genus, also falls in this category.

Compounds of this type are usually obtained by the Wittig reaction[1—3] or, more stereoselectively, by cross-coupling of vinyl electrophiles with vinyl nucleophiles in the presence of palladium complexes.[4,5] In order to investigate the possibility of stereocontrolled synthesis of stereoisomeric diene pheromones from diynols, specifically, from 2,4-heptadiyn-1-ol (**2**) and 3,5-octadiyn-1-ol (**3**), we evaluated the efficiency and stereoselectivity of organocuprate cross-coupling using *Z,Z*-configured dienes corresponding to diynes **2** and **3** as electrophiles. In this connection, a comparison of two analogous synthetic routes for the preparation of compound *Z,Z*-**1** from compounds **2** or **3** (Scheme 1) was carried out.

The first problem was the stereoselective reduction of diynols. Analysis of the literature data revealed that the most selective *cis*-hydogenation of the triple bonds is achieved with activated zinc in a neutral protic medium. In particular, zinc activated by Cu or by a Cu—Ag pair,[6] and superactive Rieke zinc (from $ZnBr_2$ and K)[7] have been sucessfully used for the partial reduction of propargylic and homopropargylic systems. However, only one example of the transformation of α,γ-diynol into (α*Z*, γ*Z*)-dienol using Rieke zinc[7] is known.

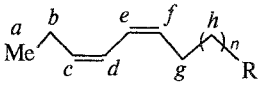
We found that the stereoselective *cis*-reduction of both triple bonds in diynols **2** and **3** by the action of 10 equiv. of Zn/Cu pair in aqueous *i*-PrOH occurs at different rates. The reduction of "propargylic" diynol **2** occurred unexpectedly easily (3.5—4 h at the optimal temperature of 85—90 °C) leading to (2*Z*,4*Z*)-2,4-heptadien-1-ol (**4**) in 53 % yield and with ≥ 93 % selectivity. The reduction of "homopropargylic" diynol **3** in the same system occurred only after 4 h at 130—140 °C (bath temperature) and afforded (3*Z*,5*Z*)-3,5-octadien-1-ol (**5**) in 60 % yield and with selectivity no less than 96 %. GLC and NMR analyses detected no products of more profound reduction or *cis-trans* izomerization of the diene system formed.

Alcohol **4** was smoothly transformed into acetate (**6**) and "homoallylic" bromide (**8**) was obtained from alcohol **5** via the corresponding tosylate (**7**). According to GLC analysis and NMR spectral data, the stereochemical purity of acetate **6** was > 95 % and for bromide **8** it amounted to ≥ 90 %. The *Z,Z*-configuration of compounds **4**,**5**,**6**, and **7** was confirmed by ^1H and ^{13}C NMR spectral data. The presence of two nearly identical coupling constants (J ~ 11.0 Hz) in the region of olefinic protons is characteristic of the ^1H NMR spectra of all of these compounds, which is indicative of the *Z*-configuration of each of the olefinic fragments in diene systems **4**—**7** (Table 1).

In the differential ^1H NOE spectrum the signals for H_d and H_e respond to pre-irradiation of H_c and H_f and *vice versa*. This fact unequivocally points to the *cis*-dispositon of the *c/d* and *e/f* pairs of protons.

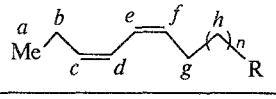
The signals for the carbon atoms in the $-CH_2-CH=CH-CH=CH-CH_2-$ fragment (Table 2) were assigned on the basis of the ^{13}C NMR spectra of compounds **4**—**7** recorded with and without suppression of carbon-proton spin coupling and on the basis of the ^{13}C NMR spectral data of related structures (ref. 8). In *Z,Z*-configured dienes, $^3J_{CH_2,H}$ ~ 9 Hz. This J value is characteristic of olefins with *trans*-position of interacting nuclei, whereas in olefins with the *cis*-position it is ~7 Hz (ref. 9). The same $^3J_{CH_2,H}$ values were also observed for the other *Z,Z*-dienes we obtained.

Organocuprate cross-coupling of acetate **6** and bromide **8** with Grignard reagents prepared from their complementary ω-*tert*-butoxy-1-chloroalkanes (from compounds (**9**) and (**10**), respectively) was carried out under conditions similar to those we found earlier for

Table 1. NMR spectra of conjugated *Z,Z*-dienes  (δ, $J_{H,H}$/Hz)

Diene	Proton signals							
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
1 (*n*=1, R=$(CH_2)_4OAc$)*	0.98 t (7.6)	2.05 q.d (7.6,7.6)	5.39 d.t (11.2,7.6)	6.19 d.d (11.2,11.0)	6.21 d.d (11.2,10.8)	5.43 d.t (10.8,7.6)	2.05 — 2.25 m	4.05 t (7.0)
4 (*n*=0,R=OH)	1.00 t (7.5)	2.15 q.d.d (7.5,7.5,1.5)	5.53 d.t.d (11.7,7.5,1.0)	6.10 d.d.t.d (11.7,10.8,1.5,1.4)	6.25 d.d.t.d (11.9,10.7,1.6,1.0)	5.45 d.t.d (11.9,7.0,1.4)	4.23 d.d (7.0,1.6)	—
5 (*n*=1,R=OH)	0.98 t (7.6)	2.16 q.d.d (7.6,7.6,1.3)	5.47 d.t.d (11.2,7.6,1.2)	6.20 d.d.t.d (11.2,10.6,1.2,1.2)	6.39 d.d.t.d (11.2,10.6,1.2,1.2)	5.45 d.t.d (11.2,6.6,1.2)	2.42 t.d.d (6.6,6.6,1.2)	3.64 t (6.6)
6 (*n*=0,R=OAc)	0.94 t (7.6)	2.14 q.d.d (7.6,7.6,1.8)	5.53 d.t.d (11.9,7.6,1.1)	6.15 d.d.t.d (11.9,11.0,1.8,1.1)	6.38 d.d.t.d (11.9,11.0,1.5,1.1)	5.47 d.t.d (11.9,7.0,1.8)	4.67 d.d (7.0,1.5)	—
7 (*n*=1,R=OTs)	0.99 t (7.6)	2.16 q.d.d (7.5,7.5,1.6)	5.50 d.t.d (11.9,7.5,1.0)	6.08 d.d.t.d (11.9,11.0,1.6,1.1)	6.33 d.d.t.d (11.9,11.0,1.7,1.0)	5.28 d.t.d (11.9,7.0,1.1)	2.53 t.d.d (7.0,7.0,1.7)	4.04 t (7.0)

* The signals for the R group have standard values.

TTable 2. ^{13}C NMR spectra of conjugated *Z,Z*-dienes  (δ, $^3J_{CH_2,H}$/Hz)

Diene	Carbon* signals							
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
1 (*n*=1, R=$(CH_2)_4OAc$)	14.0	20.7 (9.3)	133.4	123.0	123.7	131.5	**	—
4 (*n*=0,R=OH)	13.8	20.5 (9.3)	129.6	122.2	124.8	135.3	58.1 (9.5)	—
5 (*n*=1,R=OH)	13.9	20.7 (9.0)	127.0	122.7	125.8	134.4	30.9 (9.4)	61.9
6 (*n*=0,R=OAc)	14.0	20.9 (9.2)	127.4	122.1	124.0	136.6	60.3 (9.4)	—
7 (*n*=1,R=OTs)	14.1	20.9 (9.2)	126.8	122.2	124.1	135.6	27.3 (9.3)	69.6

* The signals for the R group have standard values. ** Not identified.

Table 3. The dependence of the isomeric composition of 7,9-dodecadienyl acetates on the structure of *Z,Z*-dienic electrophiles used for organocuprate cross-coupling

Dienic electrophile (nucleophile)	Content of *Z,Z*-isomer in the electrophile (%)	Overall yield of **1*** (%)	Content of isomers of **1** (%)			
			Z,Z-**1**	*7E,9Z*-**1**	*7Z,9E*-**1**	*E,E*-**1**
6 (+**9**)	95	48	34.6	29.3	13.7	22.4
8 (+**10**)	~90	36	87.0	6.0	6.0	≤1.0

* Over the two synthetic stages: preparation of the dienic ether **11** and its transformation into acetate **1**.

the synthesis of *7E,9Z*-**1** (ref. 10), the pheromone of the grapevine moth. The ratio of isomers of 1-*tert*-butoxy-7,9-dodecadiene (**11**) thus obtained was evaluated after its transformation into the corresponding acetate **1** by treatment with Ac_2O and $FeCl_3$ according to the known method.[11] Stereoisomeric 7,9-dodecadienyl acetates were identified by GLC (Table 3) and GLC-MS (Table 4). These data are in qualitative agreement with the results reported in the literature[3,12] and with our own results[10] obtained earlier for mixtures of the same compounds in which the *7E,9Z*-isomer predominated.

Though the product of organocuprate cross-coupling contained all of the possible stereoisomers of diene **11** regardless of the structure of the *Z,Z*-dienic electrophile (**6** or **8**), the stereoselectivity of the formation of the target *Z,Z*-isomer depends substantially on the nature of the electrophile (Table 3).

When acetate **6** is used as the electrophile significant stereomutation takes place both at the Δ^4-double bond and, especially, at the allylic Δ^2-double bond, which is reflected in the stereoisomeric composition of the final dodecadienyl acetate. On the other hand, the cross-coupling of homoallylic bromide **8** with chloride **10** under similar conditions provides nearly complete retention of the initial configuration of both double bonds in the final product. The configurational stability of homoallylic electrophiles and the instability of allylic electrophiles in organocuprate cross-coupling reactions has been observed before (see ref. 10 and references cited therein). The content of the target *Z,Z*-**1** is 87 % and its overall yield from diynol **3** is about 20 % over

Table 4. Relative intensity (%) of some daughter ions in the mass spectrum of an isomeric mixture of 7,9-dodecadienyl acetate

m/z	Isomer (t_R/min)			
	Z,E (9.43)	*E,Z* (9.53)	*Z,Z* (10.03)	*E,E* (10.09)
41	51.9	52.1	51.6	50.6
43	100.0	100.0	100.0	100.0
53	11.6	12.2	13.5	11.3
54	6.1	7.2	7.8	5.4
55	35.9	35.7	33.0	36.2
65	4.4	5.9	5.4	3.5
67	89.9	88.6	89.9	90.6
68	18.8	22.4	20.9	18.6
69	7.4	8.6	7.5	8.9
77	9.1	11.5	11.3	9.5
79	56.6	63.8	62.9	60.9
80	16.5	19.7	18.0	18.2
81	24.1	29.0	26.2	25.2
82	31.2	36.3	33.3	35.8
93	23.7	28.3	25.8	26.9
94	12.1	13.8	13.4	13.6
95	26.1	27.8	23.9	31.4
96	13.0	12.0	12.3	10.5
108	5.8	9.4	8.4	7.3
121	12.4	13.9	12.7	13.2
135	8.1	9.8	8.9	9.8
164	3.8	4.9	5.2	2.9
224[M^+]	3.1	4.5	3.2	4.1

Note. Mass-spectral data were obtained on a Finnigan MAT INCOS 50 quadrupole mass spectrometer. The range of scan is 10÷400 mass units; EI-mode at 70 eV (Varian 3400 gas chromatograph; RSL-200 capillary column, l = 30 m, d = 0.25 mm with temperature programming rate 15 deg/min from 35 to 250 °C).

the five synthesis stages. This result is of obvious interest for the preparation of *Z,Z*-diene pheromones.

Experimental

IR spectra were obtained on a UR-20 spectrometer (Carl Zeiss, Jena) in a thin film. Analytical GLC was performed on a Hewlett-Packard 5890A chromatograph with a capillary Ultra-1 column (l = 25 m, d = 0.2 mm, N_2 as the carrier gas, flame-ionization detector, isotherm for 1 min, then temperature programming at the rate of 10 deg/min from 100 to 290 °C; pressure 140 kPa). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument at 300.13 MHz and 75.46 MHz in $CDCl_3$. For other general methods see ref. 10.

The starting compounds, 2,4-heptadiyn-1-ol (**2**), 3,5-octadiyn-1-ol (**3**), 1-*tert*-butoxy-5-chloropentane (**9**), and 1-*tert*-butoxy-4-chlorobutane (**10**) are described in ref. 10.

(2*Z*,4*Z*)-2,4-Heptadien-1-ol (4). An aqueous solution of 7.2 g (0.042 mol) of copper (II) chloride dihydrate was added to a suspension of 27.4 g (0.42 mol) of Zn powder in water and the mixture was activated under alkaline conditions.[13] 4.86 g (0.045 mol) of alcohol **2** was added to the reducing reagent thus obtained and the mixture was stirred in 10 mL of aqueous 2-propanol (2 : 1, v/v) at 85—90 °C (bath) until total conversion of the alkynol (GLC monitoring, 3.5—4 h). The metal was removed by filtration and washed with aqueous ethanol, and the filtrate was diluted with a saturated NH_4Cl solution. The product was extracted with ether (4×60 mL), and the extract was washed with brine and dried with $MgSO_4$. The distillation yielded 2.8 g (56 %) of alcohol **4**, b.p. 85—90 °C (15 Torr), n_D^{18} 1.4950, chemical and configurational purity was ≥ 93 % (GLC data), t_R = 3.5 min. IR, ν/cm^{-1}: 3332, 3072, 3012, 2996, 1648, 1584, 1350, 1304, 1164, 1064, 968, 940, 898, 864, 836, 720. UV (EtOH), λ_{max}/nm 235 (ε 21,000).

(2*Z*,4*Z*)-1-Acetoxy-2,4-heptadiene (6). 0.4 mL of Ac_2O, 1.6 mL of triethylamine, and 12 mg of 4-dimethylaminopyridine as a catalyst were added to a mixture of 0.22 g (2 mmol) of alcohol **4** in 10 mL of absolute diethyl ether and the mixture was stirred for 24—30 h at ~20 °C. After the workup of the reaction mixture, 0.28 g (92 %) of acetate **6** was isolated, b.p. 84—85 °C (12 Torr), n_D^{18} 1.4723. Chemical and configurational purity was ≥ 95 % (GLC data), t_R = 5.0 min. IR, ν/cm^{-1}: 1740, 1236, 1028, 724. UV (EtOH), λ_{max}/nm 235 (ε 18,200).

(3*Z*,5*Z*)-3,5-Octadien-1-ol (5) was prepared as described for compound **4** from 5.5 g (0.045 mol) of diacetylenic alcohol **3** in 15 mL of aqueous 2-propanol (2 : 1, v/v) with vigorous boiling for about 4 h (bath temperature, 130—140 °C). Yield 60 %, b.p. 90 °C (18 Torr), n_D^{18} 1.4945. Chemical and configurational purity was ≥ 96 % (GLC data), t_R = 4.5 min. IR, ν/cm^{-1}: 3324, 3024, 1598, 1462, 1048, 916, 866. UV (EtOH), λ_{max}/nm 236 (ε 21,800).

(3*Z*,5*Z*)-3,5-Octadienyl tosylate (7). Powdered KOH 28.0 g (0.5 mol) was added portionwise to a solution of 6.3 g (0.05 mol) of alcohol **6** and 19.0 g (0.1 mol) of toluene-*p*-sulfonyl chloride in 200 mL of absolute diethyl ether at −20 °C over a period of 30 min and the mixture was stirred for 1.5 h until the solution attained room temperature. After the workup of the reaction mixture, a solution of the residue in hexane was filtered through a small Al_2O_3 layer to afford 11.0 g (80 %) of tosylate **7** as an oil, n_D^{16} 1.5355. IR, ν/cm^{-1}: 2968, 1714, 1600, 1596, 1560, 1496, 1360, 1188, 1178, 1098, 976, 916, 816, 772, 664, 554. UV (EtOH), λ_{max}/nm 228 (ε 27,200); 265 (ε 530).

(3*Z*,5*Z*)-1-Bromo-3,5-octadiene (8). A mixture of 11.0 g (0.04 mol) of tosylate **7** and 4.6 g (0.053 mol) of LiBr in 80 mL of dry DMF was stirred for 2 h at 50 °C and kept for 12 h at 20—25 °C. After the usual workup, distillation of the residue *in vacuo* afforded 6.5 g (~87 % yield) of bromide **8**, b.p. 90 °C (20—25 Torr), n_D^{18} 1.5110. Purity (GLC analysis) was 90 %. IR, ν/cm^{-1}: 3004, 2992, 2964, 2944, 2932, 1458, 1304, 1264, 1208, 1068, 948, 866, 722, 564. UV (EtOH), λ_{max}/nm: 236 (ε 25,200).

1-*tert*-Butoxy-7,9-dodecadiene (11) was obtained via acetate **6** or bromide **8** (30 mol of each) by treating them with Grignard reagents (prepared from 65 mmol of ω-*tert*-butoxy-1-chloroalkane **9** or **10** and 80 mg-at. of Mg) in THF at −20 °C in the presence of 2.5 mmol Li_2CuCl_4 by the method reported earlier.[10]

A. After the usual workup of the reaction mixture, cross-coupling of **9** with **6** yielded ~4 g of a product with b.p. 110—120 °C (15 Torr), which, according to GLC data, contained 20—25 % of 1,10-di-*tert*-butoxydecane in addition to the four isomeric ethers **11**. The yield of ether **11** was 42—45 %.

B. Cross-coupling of **8** with **10** afforded ether **11** of 85 % chemical purity in a yield of ~56 %. The isomeric composition determined by GLC was as follows (listed are the isomer, its content (in %), and t_R/min): *Z,E*, 5.0, 11.26; *E,Z*, 5.1, 1.35; *Z,Z*, 89.8, 11.44; *E,E*, ≈1, 11.6. IR, ν/cm^{-1}: 2972, 2932, 1462, 1390, 1360, 1232, 1198, 1084, 1020, 878, 724.

(7*Z*,9*Z*)-7,9-Dodecadienyl acetate (1) was synthesized from the speciments of ether **11** using a standard procedure,[11] *i.e.*, by treatment with Ac_2O—$FeCl_3$ in absolute diethyl ether at 20 °C. The stereoisomeric composition of the mixture of acetates was analyzed by GLC (listed are the isomer and t_R/min: *Z,E,* 11.5; *E,Z,* 11.24; *Z,Z,* 11.33; *E,E,* 11.38) and GC-MS (Table 4).

Additional purification of the sample of ether **11** synthesized according to procedure B by flash chromatography on a SiO_2 column yielded 86 % of acetate **1**, b.p. 160 °C (20 Torr), n_D^{18} 1.4685. The content of the major *Z,Z*-isomer was 87 % (Table 3). IR,ν/cm $^{-1}$: 2931, 2884, 2856, 1742, 1462, 1388, 1364, 1238, 1040, 726. UV (EtOH), λ_{max}/nm 235 (ε 25,300).

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New data on the structure of laminaran from *Chorda filum* (L.) Lam. and reserve glucans from other brown algae

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M-chains of highly branched (1→3),(1→6)-β-*D*-glucan (laminaran) isolated previously from the brown alga *Chorda filum* contain 1-glucosylated and 1,6-bis-glucosylated *D*-mannitol residues, as shown by methylation analysis and enzymolysis. The latter structural element is found in laminarans for the first time. Structural investigation of laminarans from six other brown algae shows that the polysaccharides consist predominantly of (1→3)-linked β-*D*-glucopyranose residues with a small number of (1→6)-glycosidic bonds in chains and branching points. Mannitol residues was not detected in laminarans from two *Cystoseira* species.

Key words: brown algae; laminarans, structure.

Laminarans are a class of comparatively low-molecular-weight reserve β-glucans of brown algae consisting of (1→3)-linked β-*D*-glucopyranose residues.[1,2] The majority of laminarans contain polymeric chains of two types: some of them are built only of glucopyranose residues (G-chains), whereas the other are terminated with 1-O-substituted *D*-mannitol residues (M-chains). In addition, some 6-O-branchings in the main chain

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