112. Stereoselective Syntheses of the Isomeric 5,10-Pentadecadienals

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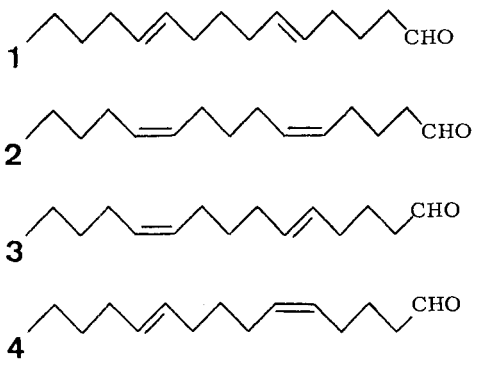
Summary

The four isomeric 5,10-pentadecadienals **1**, **2**, **3** and **4** were prepared by stereoselective routes from acetylenic precursors. Two of them, **2** and **4**, were also made by *Wittig* reaction from 2-hydroxytetrahydropyran (**29**). 2-Hydroxytetrahydropyran (**29**) yields *(Z)*-5-alkenols efficiently by *Wittig* reaction, and *(Z)*-4-hexenol was similarly made from 2-hydroxytetrahydrofuran (**66**).

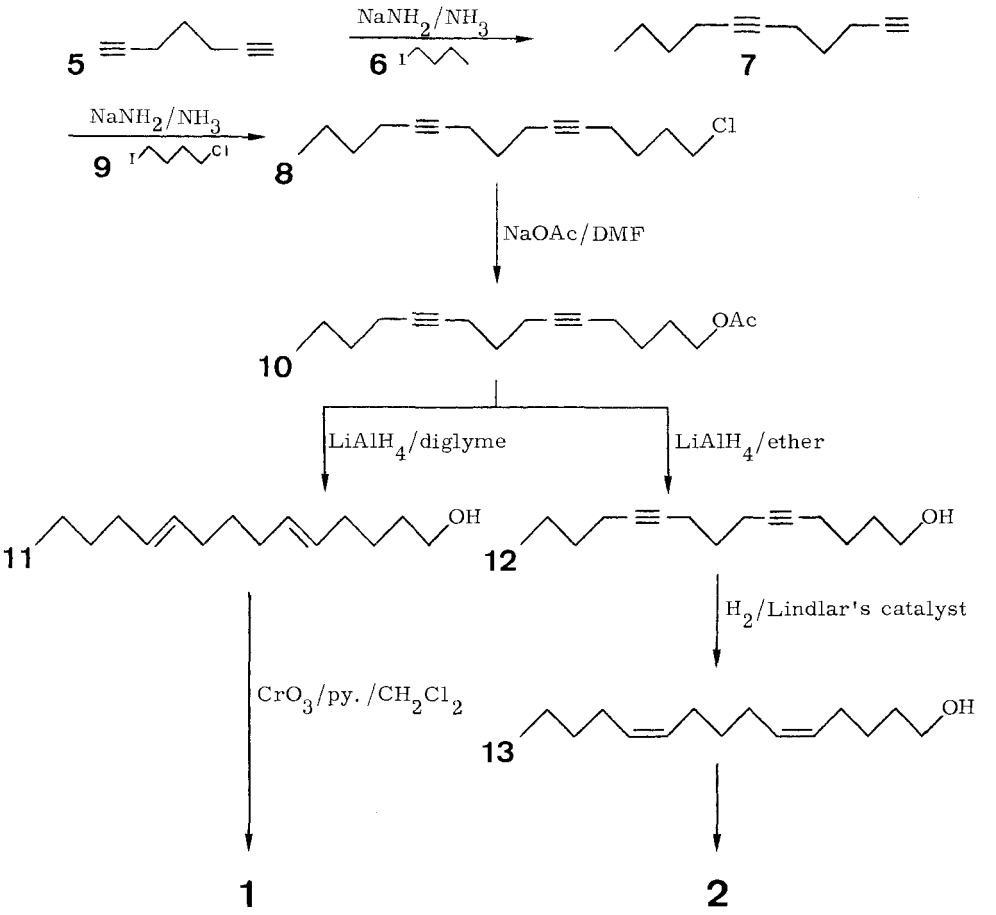
Efficient methods for the regio- and stereoselective construction of unsaturated aliphatic compounds are highly desirable since a large number of insect pheromones as well as flavouring and perfume chemicals have been found which belong to this group.



In this publication some earlier results from our laboratory[1]) will be complemented by the synthesis of the four possible isomeric 5,10-pentadecadienals. One of these isomers is believed to participate in the agreeable odour of turpentine oil from the European silver fir (*Abies pectinata* D.C., Ger. 'Edeltanne') [2].

The C_{15} precursor **8** of both the all-*trans* **1** and the all-*cis* compound **2** was readily accessible from commercially available 1,6-heptadiyne (**5**) *via* two alkylation reactions. The disodium derivative of **5** in liquid ammonia was allowed to react

[1]) See *e.g.* [1].



with butyl iodide (**6**) to yield **7**. A subsequent analogous alkylation with 1-iodo-4-chlorobutane (**9**) [3] gave chloride **8** in 30% yield based on **5**.

The acetate **10**, accessible by the reaction of **8** with sodium acetate in dimethyl formamide, was directly reduced by lithium aluminium hydride in diglyme[2]) to *(E,E)*-5,10-pentadecadien-1-ol (**11**) (90% yield). The same reaction of acetate **10** in ethyl ether as solvent stopped at the level of the corresponding diynol **12**. Catalytic hydrogenation of **12** using *Lindlar's* catalyst led to *(Z,Z)*-5,10-pentadecadien-1-ol (**13**).

A less specific route to *(Z,Z)*-5,10-pentadecadien-1-ol (**13**) utilized a two-fold carbonyl *Wittig* olefination, 2-hydroxytetrahydropyran (**29**) [5] functioning as the bifunctional C_5 building block common to both steps. Firstly, reaction between pentyltriphenylphosphonium bromide (**30**) [6] and 2-hydroxytetrahydropyran (**29**) in the presence of sodium methylsulfinylmethide [7] yielded *(Z)*-5-decen-1-ol (**28**)

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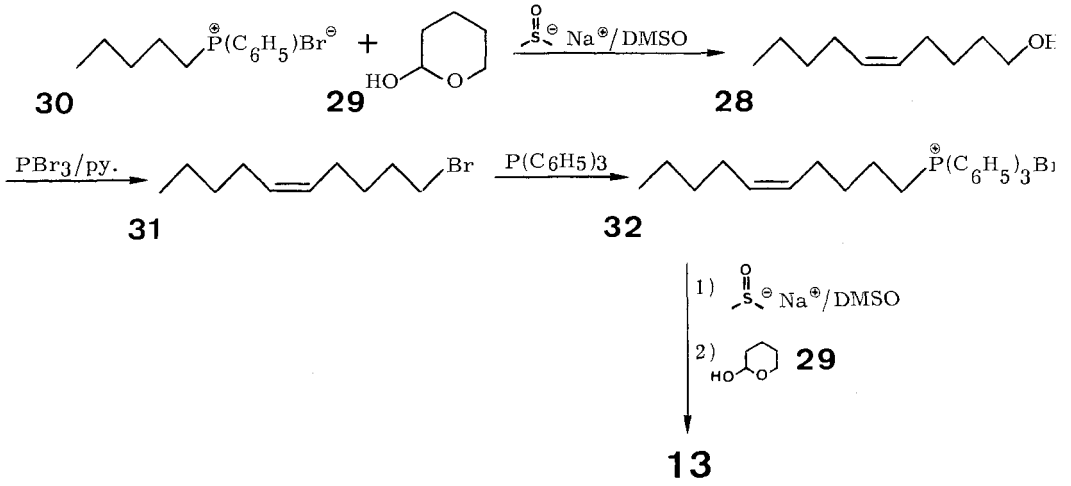
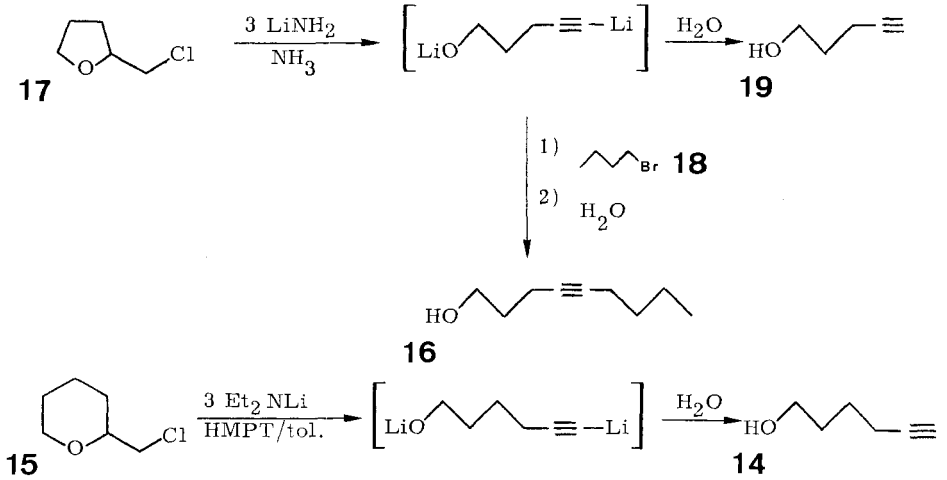
[2]) Acetylenic hydrocarbons in THF and/or diglyme as solvent(s) are known to be reduced by $LiAlH_4$ to the corresponding *E*-olefin. With toluene as solvent, the saturated hydrocarbons are formed [4].

(isomeric purity 93% by GC.) which was again transformed into a phosphonium bromide (**32**). The analogous *Wittig* reaction of **32** with **29** proved to be, contrary to our expectation, much less stereoselective, giving a mixture 10:5:1 of *(Z, Z)*-isomer **13**, *(E, Z)*-isomer **23** and *(E, E)*-isomer **11** in 36% yield.



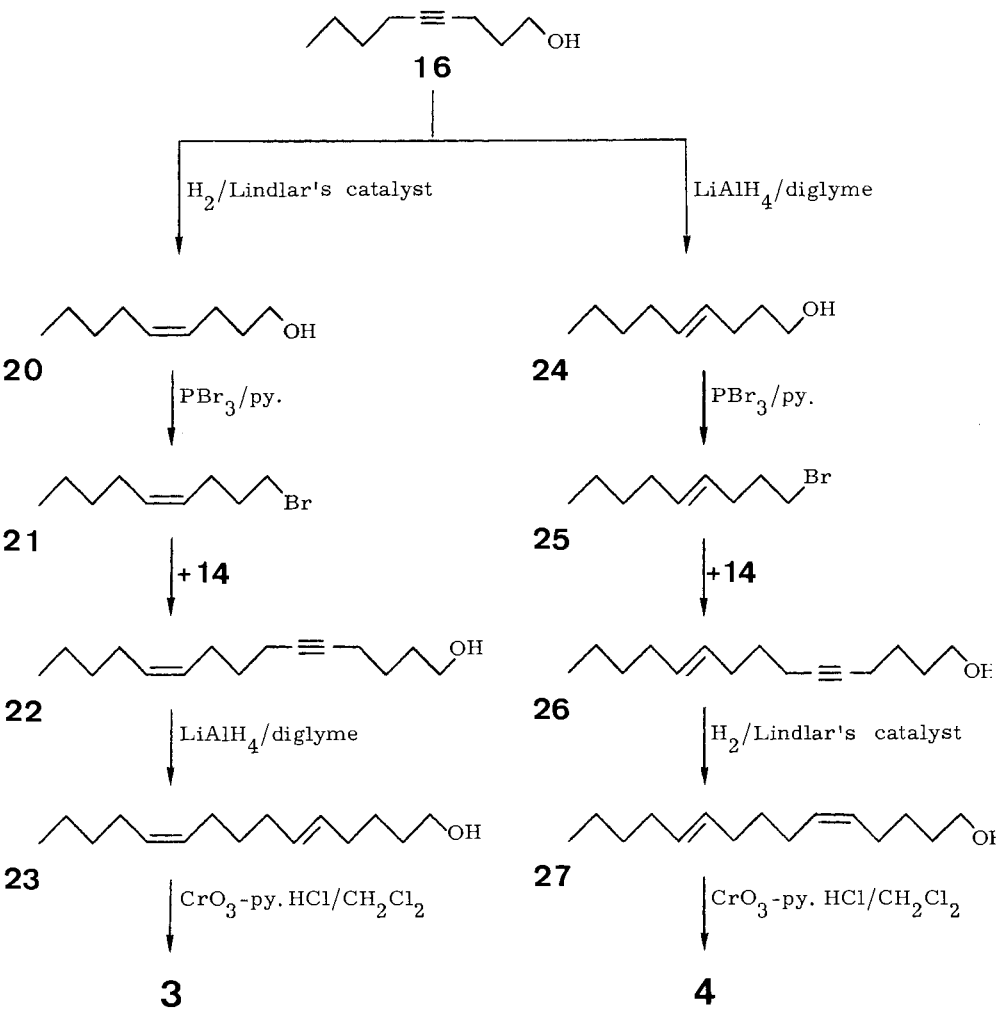
Oxidation of the alcohols **11** and **13** with CrO_3/pyridine complex in methylene chloride [8] finally led to the desired aldehydes **1** and **2** in over 80% yield.

For the preparation of the remaining two C_{15} aldehydes **3** and **4**, 4-nonyn-1-ol (**16**) and 5-hexyn-1-ol (**14**) were used as intermediates for both aldehydes. Nonynol **16** was prepared by alkylation with 1-bromobutane (**18**) of the 4-pentin-1-ol (**19**) dilithium derivative which is formed from 2-chloromethyltetrahydrofuran (**17**) [9] with three equivalents of lithium amide in liquid ammonia. In one step, without isolation of **19**, nonynol **16** is thus obtained directly from **17** (60%). The transformation of **17** into **19** is an example of a most remarkable and useful eliminative



cleavage of cyclic ethers with an α-chloromethyl group giving terminal acetylene alcohols [10]. This reaction has a certain resemblance to the formation of 4-penten-1-ol by reaction of **17** with sodium in ether [11], a general method for the synthesis of 4-alken-1-ols [12].

The second building block of this route, namely 5-hexyn-1-ol **(14)**[3]) was available in over 70% yield from 2-chloromethyltetrahydropyran **(15)** by reaction with lithium diethylamide [13] in HMPT/toluene 1:1. In principle, this eliminative cleavage of **15** to **14** is identical to the transformation of **17** to **19**. In the case of the six-membered ring opening, however, the hypothetical dilithium intermediate of **14** could not be alkylated *in situ* (with **21** or **25**) and only 5-hexyn-1-ol **(14)** was isolated

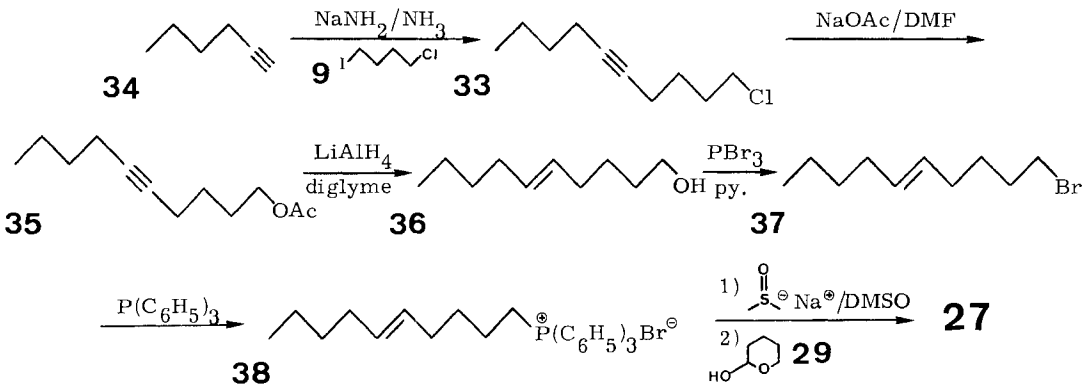


[3]) The method for making 5-hexyn-1-ol reported by *Brandsma* [14] gave in our hands *via* triple-bond migration exclusively the isomeric 4-hexyn-1-ol.

after hydrolysis. On the other hand, opening of **15** to **14** using $LiNH_2$ in liq. ammonia gave a very low yield in our hands, notwithstanding the 80% yield reported [10].

The acetylenic alcohol **16** was transformed by partial reduction either into *(Z)*-4-nonenol **(20)** or *(E)*-4-nonenol **(24)**. Reaction of the corresponding bromides **21** and **25** with the dilithium derivative of 5-hexyn-1-ol **(14)** furnished the desired C_{15} compounds **22** and **26**. The overall yield of *(E)*-10-pentadecen-5-yn-1-ol **(26)** from **16** with respect to *(Z)*-10-pentadecen-5-yn-1-ol **(22)** is unsatisfactory, but the reaction conditions have not yet been optimized. Lithium aluminium hydride reduction of **22** gave a 91% yield of *(E, Z)*-5, 10-pentadecadien-1-ol **(23)** and catalytic hydrogenation of **26** quantitatively furnished the stereoisomeric *(Z, E)*-5, 10-pentadecadien-1-ol **(27)**.

Alcohol **27** is also accessible *via* a *Wittig* reaction using the phosphonium salt **38**, δ-lactol **29** and sodium methylsulfinylmethide in DMSO.



For this purpose, the phosphonium salt **38** was made from alcohol **36** which again was built up from 1-iodo-4-chlorobutane **(9)** and 1-hexyne **(34)** in three steps *via* **33** and **35**. Oxidation of the alcohols **23** and **27** using pyridinium chlorochromate [15] completed the synthesis of the aldehydes **3** and **4**.

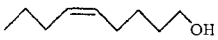
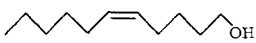
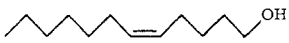
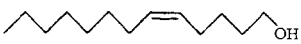
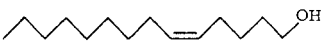
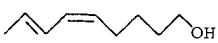
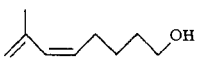
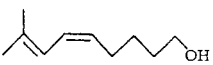
The four 5, 10-pentadecadienals exhibit distinct odour qualities characteristic of each isomer. The *Z, Z*-isomer **2** is fresh, reminiscent of calamus, green in the direction of galbanum, floral, resin-like, dusty with a fatty undertone. The *E, Z*-isomer **3** is very similar to **2** but lacks the freshness. The *E, E*-isomer **1** is dominated by a harsh fatty note. The *Z, E*-isomer **4** strongly resembles the *Z, Z*-isomer **2**; it is, however, much weaker than **2**.

Comparison of the melting points of the oximes, semicarbazones and corresponding carboxylic acids **39**, **40**, **41** and **42** of our synthetic pentadecadienals with the corresponding values reported for the natural aldehyde from European silver fir oil [2] revealed no match at all. Since the fir oil aldehyde was only tentatively assigned a 5, 10-pentadecadienal for lack of material, our results bring into question the correctness of this assignment, making a reinvestigation desirable.

The carbonyl olefination of 2-hydroxytetrahydropyran **29** with phosphorus ylids is a general method for the preparation of 5-alken-1-ols, the yields mainly depending

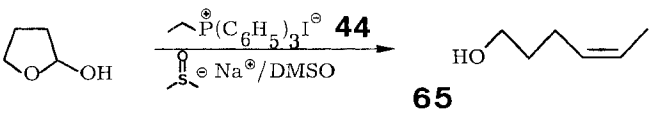
on the substituents of the methylenetriphenylphosphorane (see *Table 1*). Under our reaction conditions, a high *Z*-selectivity was observed in the case of unstabilized ylids. This preference, however, is lost as soon as an additional double bond is in conjugation with the C=P bond of the ylid, and a 1:1 mixture of *Z*- and *E*-isomers results. The only known *Wittig* reaction involving 2-hydroxytetrahydropyran **(29)**, namely its condensation with the resonance-stabilized carbalkoxyalkylidenetriphenylphosphorane, led exclusively to an *E*-double bond [16]. The *Wittig* reaction also

Table 1. Wittig *reaction of 2-hydroxytetrahydropyran* **(29)** *with various phosphonium salts in DMSO/sodium dimethylsulfinylmethide*

Phosphonium salt $R\!\!\smile\!\!P^{\oplus}(C_6H_5)_3Br^{\ominus}$		Product		Yield	
				%	*Z*:*E* ratio
R = H *)	**43**		**54**	39	-
R = CH_3 *)	**44**		**55**	57	86 : 14
R = CH_3–CH_2	**45**		**56**	56	93 : 7
R = CH_3–$(CH_2)_2$	**46**		**57**	65	92 : 8
R = CH_3–$(CH_2)_4$	**47**		**58**	53	98 : 2
R = CH_3–$(CH_2)_5$	**48**		**59**	62	100 : 0
R = CH_3–$(CH_2)_6$	**49**		**60**	51	100 : 0
R = CH_3–$(CH_2)_7$	**50**		**61**	47	100 : 0
R = CH_3–$\underset{H}{\overset{H}{C}}$=$\underset{H}{C}$	**51**		**62**	34	55 : 45
R = $\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!\!=\!\!CH$	**52**		**63**	11	50 : 50
R = $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\!C{=}CH$	**53**		**64**	25	50 : 50

*) The iodide was used instead of the bromide.

lends itself to a one-step preparation of 4-alken-1-ols when 2-hydroxytetrahydrofuran **(66)** is used as the potential carbonyl part. In this way, *(Z)*-4-hexenol **(65)** [17] has been



66 65

obtained in 72% yield and 95% stereoselectivity. An analogous transformation, also *via* γ-lactols, has become most important in prostaglandin syntheses [18] and has also been used for the construction of the *cis*-jasmone side chain [19].

Experimental Part

(with the precious technical assistance of *Hanna Wälchli* and *Pierre-Alain Beney*)

General remarks. – See earlier publications of *G. O.* Additional remarks. Instruments for gas chromatography (GC.): a) using packed 4 mm × 2.5 m glass columns: *Carlo Erba* Fractovap 2200 and *Varian* Aerograph series 1800; b) using capillary columns: *Carlo Erba* GT 450 and *Carlo Erba* Fractovap 2300. Column chromatography. On *Merck* silica gel 0.05–0.2 mm. Bulb distillation with external temperature reading: *Büchi* apparatus, type KR-3. – IR. spectra: *Perkin-Elmer* 720, absorption maxima in cm^{-1}. – MS.: *Atlas* CH_4, inlet temperature ~150°, electron energy ~70 eV, molecular peak (M^+) and fragment ions *(m/e)* with relative peak intensities (base peak = 100%) in brackets. – ^{1}H-NMR. spectra: *Hitachi Perkin-Elmer* R 20 B (60 MHz). – ^{13}C-NMR.: *Bruker* HX 90/15″ operating at 22.63 MHz in the FT mode; chemical shifts (δ) in ppm downfield from tetramethylsilane. Abbreviations for solvents: Diglyme (diethylene glycol dimethyl ether), DMF (dimethylformamide), DMSO (dimethyl sulfoxide), HMPT (hexamethylphosphoric triamide), THF (tetrahydrofuran). Other abbreviations: i.V. = *in vacuo*, RT. = room temperature, anh. = anhydrous, aq. = aqueous.

1. *(E,E)*-**5,10-Pentadecadien-1-al (1).** – a) *1,6-Undecadiyne* **(7).** 1,6-Heptadiyne[4]) **(5)** (9.2 g; 0.1 mol) was added to a suspension of sodamide (freshly prepared from 2.3 g = 0.1 mol of sodium in liq. NH_3 using $Fe(NO)_3$ as catalyst, see *e.g.* [14], in liq. NH_3 (100 ml) at −40°. After stirring for 45 min, butyl iodide **(6)** (17.5 g; 0.1 mol) in 20 ml of anhydrous THF was added, and the resulting mixture was stirred for 1 h at ~ −40°. Then, the cooling bath was removed and the ammonia was allowed to evaporate overnight. The residue was cautiously hydrolysed with water and taken up in ether. The ethereal extract was washed (water), dried (Na_2SO_4), concentrated and distilled at 82°/9 Torr yielding 6.9 g (47%) of 1,6-undecadiyne **7** (pure by GC.)[5]). The yields of several runs varied between 40 and 60%. – IR. (film): 3320, 2950, 2120, 1425. – MS.: M^+ 148 (1), *m/e* 147 (1), 133 (5), 119 (31), 105 (48), 91 (100), 79 (52), 67 (40), 53 (29), 41 (68), 27 (48). – NMR. ($CDCl_3$): 0.90/*t*, *J* = 6/3H($-CH_3$), 2.80 *t*, *J* = 2/1H($-C\equiv CH$).

b) *1-Chloropentadeca-5,10-diyne* **(8).** Alkylation of diyne **7** (10 g; 67.6 mmol) with 1-iodo-4-chlorobutane **(9)** [3] (14.8 g; 67.6 mmol) using sodium amide in liq. NH_3 as described in 1 a) gave 10.2 g (63%) of 1-chloro-5,10-pentadecadiyne **(8)**, b.p. 110°/0.03 Torr. – IR. (film): 2930, 1460, 1440. – MS.: M^+ 238 (< 1), *m/e* 223 (1), 209 (4), 195 (10), 181 (5), 161 (14), 147 (18), 133 (23), 119 (71), 105 (62), 91 (100), 79 (54), 67 (47), 55 (36), 41 (77), 27 (32). – NMR. ($CDCl_3$): 0.90/*t*, *J* = 6/3H($-CH_3$), 3.54/*t*, *J* = 6/2H($-CH_2-Cl$).

c) *1-Acetoxypentadeca-5,10-diyne* **(10).** A solution of chloropentadecadiyne **8** (4.8 g; 0.02 mol) and anhydrous sodium acetate (3.3 g; 0.04 mol) in 60 ml of anhydrous DMF was heated under reflux for 3 h. The cold solution was diluted with water and extracted with hexane. The hexane phase was washed (water), dried (Na_2SO_4), concentrated and distilled at 124–128°/0.3 Torr to give 4.2 g (81%) of 1-acetoxy-pentadeca-5,10-diyne **(10)**. – IR. (film): 2930, 1740, 1460, 1440, 1370, 1250, 1050. – MS.: M^+ 262 (< 1), *m/e* 247 (< 1), 233 (< 1), 219 (3), 201 (1), 191 (1), 173 (9), 159 (19), 145 (25), 131 (45), 117 (42), 105 (33),

[4]) *Chemical Samples Co.*, Columbus (Ohio).

[5]) 5% Carbowax 20M on chromosorb W 80–100 mesh.

91 (63), 79 (41), 67 (30), 55 (23), 43 (100), 27 (16). – NMR. ($CDCl_3$): 0.90/*t*, J=6/3H ($-CH_3$), 2.03/*s*/3H($-COCH_3$), 4.07/*t*, J=6/2H($-CH_2-O$).

d) (E,E)-*5,10-pentadecadien-1-ol* (**11**). A solution of acetate (**10**) (1.3 g; 0.005 mol) in diglyme (10 ml) was gradually added to a well stirred suspension of lithium aluminium hydride (1.2 g; 0.03 mol) in diglyme (50 ml). After stirring under reflux for 10 h the mixture was carefully hydrolysed with ice/water under external cooling. The organic layer was separated, dried (Na_2SO_4), concentrated and distilled at 112°/0.05 Torr giving 1.0 g (89%) of *(E,E)*-5,10-pentadecadien-1-ol (**11**). – IR. (film): 3330, 2930, 1460, 1440, 1070, 980. – MS.: M^+ 224 (1), *m/e* 206, 191, 178, 163 (<1), 149 (3), 135 (9), 121 (10), 110 (25), 95 (45), 81 (76), 67 (100), 55 (96), 41 (91), 29 (29). – NMR. ($CDCl_3$): 0.88/*t*, J=6/3H($-CH_3$), 3.60/*t*, J=6/2H($-CH_2-O$), 5.37/*m*/4H($-CH=CH-$).

e) *Aldehyde* **1**. Chromium trioxide (9 g; 0.09 mol) was added, in small portions and with vigorous stirring, to a solution of pyridine (15 g; 0.19 mol) and methylene chloride (225 ml) [8]. After the addition, stirring was continued for 15 min and then a solution of alcohol **9** (3.2 g; 0.014 mol) in methylene chloride (10 ml) was added dropwise. The mixture was stirred at RT. for 5 h and then decomposed with ice/water. The layers were separated, and the aqueous phase was reextracted twice with methylene chloride (100 ml each portion). The combined organic extracts were washed (water), dried (Na_2SO_4), concentrated and distilled at 103°/0.05 Torr to give 2.7 g (85%) of aldehyde **1**, semicarbazone m.p. 69–70°, oxime m.p. 44–45°. – IR. (film): 2930, 2725, 1730, 1460, 1440, 980. – MS.: M^+ 222 (1), *m/e* 205 (1), 193 (<1), 178 (3), 161 (1), 149 (3), 135 (5), 121 (13), 110 (25), 95 (39), 80 (89), 67 (92), 55 (100), 41 (95), 29 (33). – NMR. ($CDCl_3$): 0.89/*t*, J=6/3H($-CH_3$), 5.38/*m*/4H($-CH=CH-$), 9.72/*t*, J=1.5/1H($-CHO$). For ^{13}C-NMR. see *Table 2*.

2. *(Z,Z)*-5,10-Pentadecadien-1-al (2). – a) *5,10-Pentadecadiyn-1-ol* (**12**). A solution of acetate **10** (3.2 g; 0.012 mol) in ether (20 ml) was added dropwise to a vigorously stirred suspension of lithium aluminium hydride (0.6 g; 0.016 mol) in ether (100 ml). After having been heated under reflux for 30 min the mixture was hydrolysed with ice/water and extracted with ether. The ethereal phase was dried (Na_2SO_4), concentrated and distilled at 118°/0.05 Torr giving 2.8 g (96%) of alcohol **12**. – IR. (film): 3350, 2930, 1460, 1440, 1340, 1070. – MS.: M^+ 220 (<1), *m/e* 205 (<1), 191 (1), 177 (18), 161 (9), 145 (12), 131 (31), 119 (56), 105 (51), 91 (100), 79 (68), 67 (50), 55 (43), 41 (73), 27 (30). – NMR. ($CDCl_3$): 0.90/*t*, J=6/3H($-CH_3$), 3.62/*t*, J=6/2H($-CH_2-O$).

b) (Z,Z)-*5,10-Pentadecadien-1-ol* (**13**). A solution of alcohol **12** (5 g) in methanol (100 ml) was hydrogenated over *Lindlar's* catalyst under atmospheric pressure at RT. After the up-take of two mol.-equiv. of hydrogen the catalyst was filtered off and the filtrate concentrated and distilled at 110°/0.05 Torr giving ~5 g (~100%) of *Z,Z*-pentadecadienol **13**. – IR. (film): 3330, 2930, 1460, 1070, 740. – MS.: M^+ 224 (<1), *m/e* 206, 192, 178, 163 (<1), 149 (3), 135 (10), 121 (8), 110 (19), 95 (44), 81 (76), 67 (100), 55 (93), 41 (88), 29 (28). – NMR. ($CDCl_3$): 0.89/*t*, J=6/3H($-CH_3$), 3.60/*t*, J=6/2H($-CH_2-O$), 5.35/*m*/4H($-CH=CH-$).

c) *Aldehyde* **2**. Dienol **13** (2.2 g; 9.8 mmol) was oxidized, as described in experiment 1 e), to give 1.8 g (82%) of aldehyde **2**, b.p. 98°/0.03 Torr. Semicarbazone and oxime were both non-crystalline. – IR. (film): 2930, 2720, 1730, 1460, 730. – MS.: M^+ 222 (1), *m/e* 205 (1), 193 (<1), 178 (3), 161 (2), 148 (3), 135 (5), 121 (13), 110 (20), 95 (41), 80 (80), 67 (89), 55 (97), 41 (100), 29 (35). – NMR. ($CDCl_3$): 0.90/*t*, J=6/3H($-CH_3$), 5.37/*m*/4H($-CH=CH-$), 9.75/*t*, J=1.5/1H($-CHO$). For ^{13}C-NMR. *see Table 2*.

3. *(E,Z)*-5,10-Pentadecadien-1-al (3). – a) *5-Hexyn-1-ol* (**14**). Granulated lithium[6]) (14 g; 2 mol) was added in portions to a solution of diethylamine (146 g; 2 mol) in a mixture (500 ml) of HMPT/toluene 1:1, the whole reaction being under nitrogen. The temperature during the addition (for 1 h) stayed at 45–50°. Then the reaction mixture was stirred at 60° until all lithium had disappeared (8–10 h) and a deep red solution was obtained. A solution of 2-chloromethyltetrahydropyran (**15**)[7]) (67.25 g; 0.5 mol) in anhydrous toluene (50 ml) was added at 20–25° (external cooling necessary). The resulting mixture was stirred at RT. for 24 h, then poured on to ice/water and extracted 3 times with ether. The etheral extract was washed (ice-cold, aq. 10% HCl- and aq. 6% $NaHCO_3$-solution, brine), dried (Na_2SO_4) and distilled through a 30 cm *Vigreux* column giving 35.2 g (72%) of pure 5-hexyn-1-ol (**14**), b.p. 72–75°/10 Torr. – IR. (film): 3330, 3290, 2950, 2140, 1070. – MS.: M^+ 98 (1), *m/e* 97 (10), 79 (69),

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[6]) *Metallgesellschaft*, Frankfurt am Main.

[7]) In contrast to the published procedure [10] for 2-chloromethyltetrahydropyran (**15**) (giving very low yield in our hands), we added the thionylchloride dropwise at 60° and obtained a 84% yield.

Table 2. *^{13}C-NMR. shift values (δ in ppm downfield from tetramethylsilane) of the four 5,10-pentadecadienals* **1**, **2**, **3** *and* **4**

Carbonatom[a])	1	5,6,10,11	2	13	8	4,7	9,12	3,14	15
Compound	202.9	129.1 130.1	43.3	32.3	29.6	31.8 (2)[b])		22.1	14.1
1		130.6 131.8				31.9 (2)[b])		22.3	
	202.4	128.5 129.3	43.3	32.0	29.8	26.6 (3)[b])		22.2	14.0
2		130.3 131.0				26.2		22.4	
	202.5	129.1 129.5	43.2	32.2	29.6	32.0 (2)[b])	26.7	22.0	14.0
3		130.2 131.7					27.0	22.3	
	202.2	128.4 129.8	43.3	32.2	29.6	26.5	31.8	22.2 (2)[b])	13.9
4		130.8 131.1				26.7	32.2		

[a]) Numbering:

$$\overset{15}{CH_3}-\overset{14}{CH_2}-\overset{13}{CH_2}-\overset{12}{CH_2}-\overset{11}{CH}=\overset{10}{CH}-\overset{9}{CH_2}-\overset{8}{CH_2}-\overset{7}{CH_2}-\overset{6}{CH}=\overset{5}{CH}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CHO}$$

[b]) Number of carbon atoms > 1 per signal.

70 (87), 57 (48), 41 (77), 39 (87), 31 (100). – NMR. ($CDCl_3$): 1.4→1.9/*m*/4H($-CH_2-CH_2-$), 1.97/*t*, *J* = 3/1H($-C\equiv CH$), 2.1→2.4/*m*/2H($-CH_2-C\equiv C-$), 3.63/*t* (br.), *J* = 6/2H($-CH_2-O$).

b) *4-Nonyn-1-ol* (**16**). 2-Chloromethyltetrahydrofuran **17** (114.5 g; 0.95 mol) was added to a suspension of lithium amide (freshly prepared from 21.4 g = 3.05 mol of lithium in liq. NH_3 using $Fe(NO_3)_3$ as catalyst, see *e.g.* [14]) in liquid ammonia (1 l). The reaction mixture was stirred under reflux (−33°) for 3½ h. A solution of 1-bromobutane **18** (155 g; 1.15 mol) in anhydrous THF (200 ml) was added and the ammonia was allowed to evaporate overnight. The residue was decomposed by addition of aq. 20% NH_4Cl-solution at 0° and subsequent stirring at 20° for 2 h. The product was extracted with hexane (3 times), washed (brine, 5 times), dried (Na_2SO_4) and distilled from a *Widmer* apparatus (20 cm column) at 102–105°/9 Torr. 76.9 g (58%) of 4-nonyn-1-ol (**16**) (85% pure by GC.[4])) was obtained. For the spectral data a sample was further purified by GC. – IR. (film): 3330, 2930, 1470, 1440, 1060. – MS.: M^+ 140 (1), *m/e* 122 (1), 107 (13), 97 (66), 83 (75), 79 (95), 67 (91), 55 (88), 54 (76), 41 (100). – NMR. ($CDCl_3$): 0.90/*t*, *J* = 6/3H($-CH_3$), 3.71/*t*, *J* = 6/2H($-CH_2-O-$).

c) (Z)-*4-Nonen-1-ol* (**20**). 4-Nonyn-1-ol (**16**) (40 g; 85% pure) in ethanol (350 ml) was hydrogenated over *Lindlar's* catalyst (100 mg) under atmospheric pressure and at RT. After up-take of one mol.-equiv. of hydrogen, the mixture was filtered through celite, concentrated and chromatographed on silica gel (400 g) using hexane/ether 9:1. The pure fractions were distilled through a 10 cm *Vigreux* column at 95–97°/10 Torr giving 30.9 g (76.8%) of *(Z)*-4-nonen-1-ol (**20**) (pure by GC.)[4]). – IR. (film): 3320, 2920, 1470, 1460, 1070, 720. – MS.: M^+ 142 (< 1), *m/e* 124 (9), 109 (1), 95 (36), 81 (84), 68 (73), 55 (79), 41 (100), 27 (44). – NMR. ($CDCl_3$): 0.89/*t*, *J* = 6/3H($-CH_3$), 3.59/*t*, *J* = 7/2H($-CH_2-O-$), 5.35/*m*/2H($-CH=CH-$).

d) (Z)-*1-Bromo-4-nonen* (**21**). *(Z)*-4-nonen-1-ol (**20**) (29.82 g; 0.21 mol) was added dropwise to a cooled (−30°), stirred mixture of PBr_3 (21.7 g; 0.08 mol), anh. pyridine (1.5 g) and anh. ether (100 ml). After having been stirred at −30° for 1 h and at RT. for 5 h the reaction mixture is poured onto ice and extracted 3 times with ether. The etheral extract was washed (aq. 6% $NaHCO_3$-solution, brine), dried (Na_2SO_4), concentrated and distilled through a *Vigreux* column (10 cm long) at 91–94°/10 Torr giving 29.1 g (67.6%) of bromide **21**. – IR. (film): 2950, 1460, 1440, 1250, 720. – MS.: M^+ 204, 206 (8), *m/e*

162–164 (9), 148–150 (20), 135 (8), 121 (2), 107–109 (4), 95 (13), 83 (40), 69 (75), 55 (100), 41 (78). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 3.39/*t*, J = 6/2H($-CH_2-$Br), 5.39/*m*/2H($-$CH=CH$-$).

e) (*Z*)-*10-Pentadecen-5-yn-1-ol* (**22**). A solution of 5-hexyn-1-ol (**14**) (13.72 g; 0.14 mol) in anh. THF (20 ml) was added to a suspension of lithium amide (freshly prepared from 2.1 g = 0.3 mol lithium in liq. NH_3 using $Fe(NO_3)_3$ as catalyst) in liquid ammonia (200 ml) and the reaction mixture was stirred 3 h at reflux (– 33°). Bromononene **21** (28.7 g; 0.14 mol) in anh. THF (30 ml) was added and the mixture was stirred under reflux (– 33°) for 3 h. After the ammonia had been evaporated overnight the residue was decomposed at 0° with aq. 6% NH_4Cl-solution and extracted 3 times with ether. The ethereal extract was washed (aq. 10% HCl- and aq. 6% $NaHCO_3$-solution brine), dried ($MgSO_4$), concentrated and distilled through a 10 cm long *Vigreux* column giving 18.4 g (59%) of pure (by GC.)[4]) pentadecenynol **22**, b.p. 114–119°/0.2 Torr. – IR. (film): 3330, 2930, 1460, 1440, 1060, 730. – MS.: M^+ 222 (< 1), *m/e* 179 (1), 161 (8), 149 (33), 133 (18), 119 (25), 107 (36), 91 (65), 79 (81), 67 (79), 55 (75), 41 (100), 29 (34). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 3.60/*t*, J = 6/2H($-CH_2-$O), 5.33/*m*/2H($-$CH=CH$-$).

f) (E,Z)-*5,10-Pentadecadien-1-ol* (**23**). Alcohol **22** (17.76 g; 0.08 mol) was added dropwise to a vigorously stirred suspension of lithium aluminium hydride (9.5 g; 0.25 mol) in anh. diglyme (300 ml). After having been heated under reflux for 11½ h the mixture was treated with ethyl acetate (25 ml) (to destroy the excess of hydride), poured onto ice, acidified with aq. 10% HCl-solution and extracted 3 times with ether. The ethereal extract was washed (aq. 6% $NaHCO_3$-solution brine), dried (Na_2SO_4), concentrated and chromatographed on silica gel (400 g) using hexane/ether 8:2. The pure fractions were bulb-distilled at 126–127°/0.7 Torr to give 13.7 g (76.5%) of pure (by GC.)[4]) **23**. – IR. (film): 3360, 2950, 1450, 1430, 1050, 960, 710. – MS.: M^+ 224 (2), *m/e* 149 (4), 135 (12), 121 (10), 110 (30), 95 (50), 81 (83), 67 (100), 55 (91), 41 (84), 29 (25). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 3.61/*t*, J = 6/2H($-CH_2-$O$-$), 5.34/*m*/4H(2×$-$CH=CH$-$).

g) *Aldehyde* **3**. A solution of alcohol **23** (13.0 g; 0.058 mol) in methylene chloride (20 ml) was added dropwise to a stirred suspension of pyridinium chlorochromate [15] (18.74 g; 0.087 mol) in methylene chloride. After having been stirred at RT. for 15 h the reaction mixture was diluted with ether (100 ml) and then filtered through a column filled with silica gel (100 g). Abudant elution with ether gave, after bulb distillation at 120–130°/0.01 Torr, 9.3 g (72%) pure (by capillary GC.)[8]) aldehyde **3**, semicarbazone m.p. 45–55° (semicrystalline, could not be recrystallized). – IR. (film): 2940, 2725, 1720, 1450, 960, 710. – MS.: M^+ 222 (1), *m/e* 204 (1), 178 (5), 161 (2), 148 (3), 135 (7), 124 (16), 110 (29), 95 (43), 80 (100), 67 (90), 55 (95), 41 (91), 29 (29). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 5.34/*m*/4H (2×$-$CH=CH$-$), 9.75/*t*, J = 1.5/1H($-$CHO). For ^{13}C-NMR. see *Table 2*.

4. *(Z,E)*-**5,10-Pentadecadien-1-al** (**4**). – a) (E)-*4-Nonen-1-ol* (**24**). Nonynol **16** (35 g; 0.25 mol) was added with stirring to a suspension of lithium aluminium hydride (9.5 g; 0.25 mol) in anh. diglyme (300 ml). The mixture was heated under reflux for 11½ h, cooled to RT., treated with ethyl acetate (25 ml), poured onto ice, acidified with ice-cold aqueous 10% HCl-solution and extracted 3 times with ether. The etheral extract was washed (aq. 6% $NaHCO_3$-solution and brine), dried (Na_2SO_4), concentrated and distilled through a *Vigreux* column (30 cm) giving 33.3 g (94%) of alcohol **24**, 85% pure (by GC.). Redistillation using a *Fischer* column MS 300 (~ 40 theoretical plates) led to 24.2 g of pure **24**, b.p. 94–95°/10 Torr. – IR. (film): 3320, 2940, 1070, 980. – MS.: M^+ 142 (1), *m/e* 124 (18), 109 (2), 95 (41), 81 (100), 68 (88), 55 (91), 41 (100), 27 (38). – NMR. ($CDCl_3$): 0.88/*t*, J = 6/3H($-CH_3$), 3.60/*t*, J = 6/2H($-CH_2-$O$-$), 5.39/*m*/2H($-$CH=CH$-$).

b) (E)-*1-Bromo-4-nonen* (**25**). Alcohol **24** (22.72 g; 0.16 mol) was transformed into 14.4 g (44%) pure bromide **25**, using the method described in experiment 3 d). – IR. (film): 2950, 1735, 1460, 1430, 1240, 965. – MS.: M^+ 204–206 (10), *m/e* 162–164 (9), 148–150 (18), 135 (7), 124 (2), 107–109 (3), 95 (14), 81 (40), 69 (61), 55 (100), 41 (78). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 3.39/*t*, J = 6/2H($-CH_2$Br), 5.41/*m*/2H($-$CH=CH$-$).

c) (E)-*10-Pentadecen-5-yn-1-ol* (**26**). Hexynol **14** (6.86 g; 0.07 mol) and bromide **25** (14.35 g; 0.07 mol) were condensed as described in experiment 3 e). The crude product (93% pure by GC.)[4]) was chromatographed on silica gel (250 g), using hexan/ether 7:3 as solvent. The pure fractions were bulb-distilled at 130°/0.2 Torr giving 5.3 g (34%) of pure **26**. – IR. (film): 3360, 2950, 1450, 1430, 1060, 960. – MS.: M^+ 222 (< 1), *m/e* 204 (1), 191 (2), 179 (4), 161 (12), 149 (44), 133 (23), 119 (31), 107 (44), 91 (70),

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[8]) UCON HB 5100/50 m.

79 (86), 67 (91), 55 (89), 41 (100), 29 (34). - NMR. ($CDCl_3$): 0.87/*t*, J=6/3H(−CH_3), 3.62/*t*, J=6/2H(−CH_2−O−), 5.39/*m*/2H(−CH=CH−).

d) (Z,E)-*5,10-Pentadecadien-1-ol* (**27**). Alcohol **26** (5 g; 0.0225 mol) in ethanol (50 ml) was hydrogenated over *Lindlar's* catalyst (50 mg) under atmospheric pressure at RT. After the up-take of one equivalent of hydrogen the mixture is filtered over celite, concentrated and bulb-distilled at 160°/0.1 Torr giving 4.9 g (97%) of alcohol **27**, 92% pure (by GC.)[4]). This material was further purified by counter-current distribution (*Desaga* apparatus, type MVS-RO-700 with 200 segments) furnishing 0.8 g of pure (>99.5% by GC.)[4]) alcohol **27**. - IR. (film): 3330, 2940, 1460, 1440, 1080, 980, 740. - MS.: M^+ 224 (1), *m/e* 163 (19), 149 (4), 136 (24), 121 (10), 107 (81), 95 (45), 81 (79), 67 (100), 55 (96), 41 (100), 29 (28). - NMR. ($CDCl_3$): 0.89/*t*, J=6/3H(−CH_3), 3.60/*t*, J=6/2H(−CH_2−O−), 5.35/*m*/4H(2×−CH=CH−).

e) *Aldehyde* **4**. Alcohol **27** (700 mg; 3.1 mmol) was oxidized with pyridinium chlorochromate (1.08 g; 5 mmol) as described in section 3 g). Bulb distillation of the crude product at 130°/0.01 Torr gave 573 mg (83%) of aldehyde **4**. Semicarbazone and oxime were both non-crystalline. - IR. (film): 2950, 2740, 1725, 1460, 1440, 970, 720. - MS.: M^+ 222 (1), *m/e* 205 (2), 178 (4), 161 (3), 147 (4), 135 (7), 124 (15), 110 (27), 95 (47), 80 (91), 67 (88), 55 (100), 41 (87), 29 (27). - NMR. ($CDCl_3$): 0.88/*t*, J=6/3H(−CH_3), 5.37/*m*/4H(2×−CH=CH−), 9.75/*t*, J=1.5/1H(−CHO). For ^{13}C-NMR. see *Table 2*.

5. Routes to alcohols *13* and *27* using a *Wittig* reaction. - a) (Z)-*5-Decen-1-ol* (**28**) via *a* Wittig *reaction with 2-hydroxytetrahydropyran* (**29**). Sodium hydride as a 50% dispersion in mineral oil (24 g; 0.5 mol) was washed with several portions of pentane in an argon atmosphere, and anh. DMSO was added [7]. The mixture was, with efficient stirring, slowly heated up to 75° in order to keep hydrogen gas evolution under control. After cessation of the gas evolution stirring was continued at 75° for 10 min, and then the solution was cooled to RT. This solution was slowly added to a solution of phosphonium salt (**30**) [6] (0.375 mol) in anh. DMSO. In an exothermic reaction a deep-red solution was obtained. After stirring at RT. for 30 min 2-hydroxytetrahydropyran (**29**) [5] (25.05 g; 0.116 mol) in anh. DMSO (50 ml) was added (exothermic reaction) and stirring was continued at 20° for 2 h. The mixture was poured onto crushed ice and extracted 3 times with hexane. The extracts were washed (aq. 10% H_2SO_4-solution, saturated $NaHCO_3$-solution, and water), dried (Na_2SO_4), concentrated and distilled i.V., giving 31.4 g (81%) of *(Z)*-5-decen-1-ol (**28**), b.p. 109–111°/10 Torr. Since the product obtained had a repellent sulfuric odour, it was purified by stirring with *Raney* Ni (~ 10–15% by weight) in methanol at RT. for 2 h. After filtration and distillation the desulfurized compound (29.4 g; 76%) was obtained (purity by GC.)[9]): 93% *Z* and 7% *E*. - IR. (film): 3320, 3000, 2920, 1650, 1450, 1060, 710. - MS.: M^+ 156 (<1), *m/e* 138 (10), 110 (20), 95 (53), 81 (74), 67 (98), 55 (100), 41 (89), 27 (35). - NMR. ($CDCl_3$): 0.89/*t*, J=6/3H(−CH_3), 3.59/*t*, J=6/2H(−CH_2−O), 5.36/*m*/2H(−CH=CH−).

b) (Z)-*1-Bromo-5-decen* (**31**). Alcohol **28** (93% isomerically pure by GC.)[8]) was transformed into the bromide by the method described in section 3 d) (43% yield), b.p. 110–140°/10 Torr. - IR. (film): 3000, 2910, 1450, 1245, 730. - MS.: M^+ 218–220 (5), *m/e* 162–164 (5), 148–150 (13), 135 (8), 109 (4), 97 (24), 83 (33), 69 (46), 55 (100), 41 (55), 27 (16). - NMR. ($CDCl_3$): 0.88/*t*, J=6/3H(−CH_3), 3.38/*t*, J=6/2H(−CH_2−Br), 5.35/*m*/2H(−CH=CH−).

c) (Z)-*5-Decenyltriphenylphosphonium bromide* (**32**). Bromide **31** (18.6 g; 0.085 mol) was added to a solution of triphenyl phosphine (22.2 g; 0.085 mol) in anh. xylene (50 ml) and heated under reflux for 5 h. The mixture was concentrated and then vigorously shaken with hexane at 50° followed by decantation (two portions of 50 ml each). The remaining viscous residue was dried i.V. (0.05 Torr) at RT. for 1 night giving 34 g (83%) of **32**, a pale yellow viscous material.

d) (Z,Z)-*5,10-Pentadecadien-1-ol* (**13**) *and its isomers* **23** *and* **11**. Phosphonium salt **32** and 2-hydroxytetrahydropyran (**29**) were allowed to react by the method described in experiment 5 a) giving a mixture (38% yield) of **13** (63%), **23** (31%) and **11** (6%) (by GC.)[6]).

e) *1-Chloro-5-decyne* (**33**). 1-Hexyne (**34**)[3]) (41 g; 0.5 mol) was alkylated with 1-iodo-4-chlorobutane (**9**) (109.3 g; 0.5 mol) using sodium amide (0.5 mol) in liq. NH_3 (500 ml) and anh. THF (100 ml) by the procedure described in section 1 b). 56.5 g (64%) of 1-chloro-5-decyne (**33**) was obtained, b.p. 87–103°/10 Torr. - IR. (film): 2950, 1460, 1440, 740. - MS.: M^+ 172 (<1), *m/e* 157 (3), 143 (3), 130 (7), 109 (7), 95 (77), 81 (100), 67 (97), 55 (88), 41 (68), 27 (45). - NMR. ($CDCl_3$): 0.90/*t*, J=6/3H(−CH_3), 3.56/*t*, J=6/2H(−CH_2−Cl).

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[9]) 10% TCEP on chromosorb W 60–80 mesh.

f) *1-Acetoxy-5-decyne* (**35**). Chloride **33** (56 g; 0.325 mol) and anhydrous sodium acetate (53.4 g; 0.65 mol) in anh. DMF were allowed to react as described in section 1 c) giving 49.3 g (77%) of acetate **35**, b.p. 118–121°/10 Torr. – IR. (film): 2920, 1735, 1470, 1450, 1430, 1360, 1240, 1050. – MS.: M^+ 196 (0), *m/e* 181 (1), 153 (3), 140 (2), 121 (2), 107 (8), 93 (37), 79 (62), 67 (18), 54 (18), 43 (100), 27 (74). – NMR. ($CDCl_3$): 0.90/*t*, J = 6/3H($-CH_3$), 2.05/*s*/3H($-OCOCH_3$), 4.08/*t*, J = 6/2H($-CH_2-OAc$).

g) (E)-*5-Decen-1-ol* (**36**). Acetate **35** (48.0 g, 0.245 mol) was reduced with lithium aluminium hydride (9.5 g; 0.25 mol) in diglyme (350 ml) by the method described in section 1 d) giving 33 g (86%) of alcohol **36**, b.p. 113–118°/11 Torr. – IR. (film): 3320, 2920, 1450, 1060, 970. – MS.: M^+ 156 (< 1), *m/e* 138 (7), 123 (1), 110 (18), 95 (45), 81 (73), 67 (91), 55 (100), 41 (80), 31 (27), 29 (32). – NMR. ($CDCl_3$): 0.90/*t*, J = 6/3H($-CH_3$), 3.62/*t*, J = 6/2H($-CH_2-O-$), 5.40/*m*/2H($-CH=CH-$).

h) *Bromide* **37**. Alcohol **36** was transformed into the bromide **37** in 38% yield using the method described in section 3 d), b.p. 107–110°/10 Torr. – IR. (film): 2930, 1460, 1440, 1260, 980, 750. MS.: M^+ 218–220 (6), *m/e* 162–164 (6), 148–150 (15), 135 (8), 109 (4), 97 (26), 83 (35), 69 (50), 55 (100), 41 (59), 27 (17). – NMR. ($CDCl_3$): 0.90/*t*, J = 6/3H($-CH_3$), 3.42/*t*, J = 6/2H($-CH_2-Br$), 5.43/*m*/2H($-CH=CH-$).

i) (E)-*5-Decenyltriphenylphosphonium bromide* (**38**). Bromide **37** (10.95 g; 0.05 mol) and triphenylphosphine (13.1 g; 0.05 mol) were heated at 120° for 5 h. The cold reaction mixture was extracted 3 times with hexane and the viscous residue was dried i.V. (0.05 Torr) at RT. overnight giving 24 g of **38**, a viscous, yellowish oil.

k) (Z,E)-*5,10-Pentadecadien-1-ol* (**27**). Phosphonium salt **38** and 2-hydroxytetrahydropyran (**29**) were allowed to react by the method described in experiment 5 a) giving alcohol **27** (17% yield, isomeric purity: 94% **27** and 6% **11** by GC.)[6]).

6. The four isomeric 5,10-pentadecadienoic acids. – They were prepared by Ag_2O oxidation [20], of the corresponding aldehydes in ~quant. yield. In all cases their purity was better than 99% by GC.[4]), and they could not be obtained in a crystalline form.

a) (E,E)-*5,10-pentadecadienoic acid* (**39**). – IR. (film): 2400–3400 (broad), 2940, 1700, 1450, 1430, 1410, 1240, 960. – MS.: M^+ 238 (7), *m/e* 205 (7), 181 (2), 168 (4), 149 (7), 140 (24), 121 (10), 110 (30), 95 (44), 81 (100), 67 (86), 55 (93), 41 (98), 29 (31). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 5.39/*m*/4H($-CH=CH-$), 11.23/*s*/1H($-COOH$).

b) (Z,Z)-*5,10-pentadecadienoic acid* (**40**). – IR. (film): 2400–3400 (br.), 2940, 1700, 1450, 1430, 1410, 1230, 710. – MS.: M^+ 238 (5), *m/e* 205 (2), 178 (2), 168 (3), 149 (6), 140 (19), 121 (8), 110 (24), 95 (46), 81 (100), 67 (87), 55 (96), 41 (100), 29 (35). – NMR. ($CDCl_3$): 0.88/*t*, J = 6/3H($-CH_3$), 5.36/*m*/4H($-CH=CH-$), 11.22/*s*/1H($-COOH$).

c) (E,Z)-*5,10-pentadecadienoic acid* (**41**). – IR. (film): 2400–3400 (br.), 2940, 1710, 1460, 1440, 1420, 1250, 980, 730. – MS.: M^+ 238 (6), *m/e* 205 (1), 181 (1), 168 (3), 149 (5), 140 (21), 121 (8), 110 (24), 95 (41), 81 (100), 67 (80), 55 (81), 41 (88), 29 (30). – NMR. ($CDCl_3$): 0.89/*t*, J = 6/3H($-CH_3$), 5.41/*m*/4H($-CH=CH-$), 10.38/*s* (narrow)/1H($-COOH$).

d) (Z,E)-*5,10-pentadecadienoic acid* (**42**). – IR. (film): 2400–3400 (br.), 2950, 1710, 1460, 1440, 1410, 1240, 965, 710. – MS.: M^+ 238 (2), *m/e* 205 (1), 194 (12), 176 (11), 165 (2), 149 (11), 134 (52), 121 (27), 110 (28), 95 (72), 81 (98), 67 (93), 55 (100), 41 (93), 29 (32). – NMR. ($CDCl_3$): 0.88/*t*, J = 6/3H($-CH_3$), 5.39/*m*/4H($-CH=CH-$), 11.07/*s*/1H($-COOH$).

7. *Wittig* reaction of 2-hydroxytetrahydropyran (29) with further phosphonium salts in DMSO/sodium dimethylsulfinylmethide. – a) *The non-commercial phosphonium salts* were prepared as described in the reference given: $R(C_6H_5)_3P^{\oplus}I^{\ominus}$ (R = methyl: **43** [21], R = ethyl: **44** [21]), $R(C_6H_5)_3P^{\oplus}Br^{\ominus}$ (R = propyl: **45** [16], R = butyl: **46** [22], R = hexyl: **47** [23], R = heptyl: **48** [23], R = octyl: **49** [24], R = *(E)*-2-butenyl: **51** [25], R = 2-methylpropenyl: **52** [26], R = 3-methyl-2-butenyl: **53** [27]).

b) *Nonyltriphenylphosphonium bromide* (**50**). Nonyl bromide (87 g; 0.42 mol) and triphenylphosphine (104.8 g; 0.4 mol) were heated at 100° for 8 h. The cold mixture was extracted by shaking with hexane and dried i.V. (0.05 Torr) at RT. for 1 night giving 151.8 g of an amorphous viscous material.

c) *The* Wittig *reaction of 2-hydroxytetrahydropyran* (**29**) *with various ylids in DMSO.* Application of the general method described in experiment 5 a) to various phosphonium salts led to the results summarized in *Table 1.* Boiling points and spectral data of the compounds prepared are given in the following.

5-Hexen-1-ol (**54**) (for solubility reasons continuous extraction with hexane for 50 h was used), b.p. 58°/10 Torr. – IR. (film): 3330, 3080, 2940, 1645, 1460, 1440, 1080, 1000, 920. – MS.: M^+ 100 (< 1), *m/e* 82 (32), 67 (100), 54 (100), 41 (89), 31 (81). – NMR. ($CDCl_3$): 1.2→1.8/*m*/4H($-CH_2-CH_2-$),

1.8→2.4/*m*/2H(allyl. CH_2–), 3.60/*t*, *J*=6/2H(–CH_2–O–), 4.8→5.3/*m*/2H(–C=CH_2), 5.5→6.2/*m*/1H(–C*H*=CH_2).

(Z)-*5-Hepten-1-ol* (**55**) (86% *Z*, 14% *E*), b.p. 88–91°/11 Torr. – IR. (film): 3350, 2960, 1650, 1450, 1430, 1050, 960 *(trans)*, 690 *(cis)*. – MS.: M^+ 114 (3), *m/e* 96 (23), 81 (75), 68 (100), 55 (71), 41 (61), 31 (39). – NMR. ($CDCl_3$): 1.60/*d*, *J*=6/3H(allyl. CH_3), 3.61/*t*, *J*=6/2H(–CH_2–O–), 5.43/*m*/2H(–CH=CH–).

(Z)-*5-Octen-1-ol* (**56**) (93% *Z*, 7% *E*), b.p. 32°/0.01 Torr. – IR. (film): 3360, 2960, 1650, 1440, 1060, 960 *(trans)*, 700 *(cis)*. – MS.: M^+ 128 (1), *m/e* 110 (16), 95 (17), 81 (58), 67 (90), 55 (56), 41 (100), 31 (32). – NMR. ($CDCl_3$): 0.95/*t*, *J*=6/3H(–CH_3), 3.60/*t*, *J*=6/2H(–CH_2O–), 5.38/*m*/2H(–CH=CH–).

(Z)-*5-Nonen-1-ol* (**57**) (92% *Z*, 8% *E*), b.p. 50°/0.001 Torr. – IR. (film): 3360, 2960, 1650, 1460, 1060, 965 *(trans)*, 700 *(cis)*. – MS.: M^+ 142 (< 1), *m/e* 124 (11), 109 (2), 95 (56), 81 (74), 67 (90), 55 (86), 41 (100), 31 (50). – NMR. ($CDCl_3$): 0.90/*t*, *J*=6/3H(–CH_3), 3.62/*t*, *J*=6/2H(–CH_2–O–), 5.40/*m*/2H(–CH=CH–).

(Z)-*5-Undecen-1-ol* (**58**) (98% *Z*, 2% *E*), b.p. 63°/0.01 Torr. – IR. (film): 3350, 2950, 1640, 1450, 1060, 710. – MS.: M^+ 170 (< 1), *m/e* 152 (8), 124 (12), 109 (16), 95 (57), 82 (68), 67 (100), 55 (90), 41 (95), 31 (28). – NMR. ($CDCl_3$): 0.89/*t*, *J*=6/3H(–CH_3), 3.62/*t*, *J*=6/2H(–CH_2–O), 5.39/*m*/2H(–CH=CH–).

(Z)-*5-Dodecen-1-ol* (**59**) (~ 100% *Z*), b.p. 81°/0.01 Torr. – IR. (film): 3360, 2950, 1640, 1450, 1060, 720. – MS.: M^+ 184 (0), *m/e* 166 (3), 138 (3), 124 (4), 109 (14), 95 (43), 81 (52), 67 (79), 55 (89), 41 (100), 31 (54). – NMR. ($CDCl_3$): 0.89/*t*, *J*=6/3H(–CH_3), 3.60/*t*, *J*=6/2H(–CH_2O–), 5.38/*m*/2H(–CH=CH–).

(Z)-*5-Tridecen-1-ol* (**60**) (~ 100% *Z*), b.p. 98°/0.05 Torr. – IR. (film): 3360, 2950, 1650, 1460, 1060, 710. – MS.: M^+ 198 (0), *m/e* 180 (4), 152 (5), 137 (1), 124 (9), 109 (13), 95 (40), 82 (74), 67 (80), 55 (100), 41 (97), 31 (34). – NMR. ($CDCl_3$): 0.89/*t*, *J*=6/3H(–CH_3), 3.66/*t*, *J*=6/2H(–CH_2–O–), 5.40/*m*/2H(–CH=CH–).

(Z)-*5-Tetradecen-1-ol* (**61**) (~ 100% Z), b.p. 98°/0.001 Torr. – IR. (film): 3370, 2950, 1640, 1460, 1060, 720. – MS.: M^+ 212 (0), *m/e* 194 (6), 166 (5), 152 (1), 138 (8), 124 (9), 109 (20), 95 (57), 82 (90), 67 (100), 55 (94), 41 (96), 31 (20). – NMR. ($CDCl_3$): 0.89/*t*, *J*=6/3H(–CH_3), 3.62/*t*, *J*=6/2H(–CH_2–O–), 5.40/*m*/2H(–CH=CH–).

(Z,E)- *and* (Z,Z)-*5,7-Nonadien-1-ol* (**62**) (45:55 mixture), b.p. 53–95°/0.01 Torr (bulb distillation). – IR. (film): 3360, 2950, 1640, 1440, 1060, 1020, 980, 940, 910, 810, 710. – MS.: M^+ 140 (9), *m/e* 122 (19), 107 (16), 93–94 (36), 79 (100), 67 (50), 53 (39), 41 (65), 31 (22), 27 (36). – NMR. ($CDCl_3$): 1.1→2.5/*m*/9H(allyl. CH_3 + –CH_2–), 3.62/*t*, *J*=6/2H(–CH_2–O–), 5.1→6.7/*m*/4H(–CH=CH–CH=CH–).

(E)- *and* (Z)-*7-Methyl-5,7-octadien-1-ol* (**63**) (1:1 mixture). – IR. (film): 3360, 3100, 2960, 1640, 1610, 1450, 1430, 1370, 1060, 960, 880. – MS.: M^+ 140 (10), *m/e* 122 (11), 107 (42), 93 (41), 79 (100), 67 (57), 53 (43), 41 (74), 31 (28), 27 (32). For the NMR. spectra the two isomers were separated by GC. Peak I (*Z-Isomer*): NMR. ($CDCl_3$): 1.3→1.8/*m*/4H(–CH_2–CH_2–), 1.87/*m*/3H(H_3C–C(7)), 2.0→2.5/*m*/2H(2 H–C(4)), 3.63/*t*, *J*=6/2H(–CH_2–O–), 4.8→5.1/*m*/2H(2 H–C(8)), 5.39/*dt*, J_1=11, J_2=7/1H(H–C(5)), 5.88/*d*, *J*=11/1H(H–C(6)). – Peak 2 (*E-Isomer*): NMR. ($CDCl_3$): 1.3→1.8/*m*/4H(–CH_2–CH_2–), 1.85/*m*/3H(H_3C–C(7)), 1.9→2.4/*m*/2H(2 H–C(4)), 3.64/*t*, *J*=6/2H(–CH_2–O–), 4.90/*m* fine/2H(2 H–C(8)), 5.65/*dt*, J_1=16, J_2=7/1H(H–C(5)), 6.20/*d*, *J*=16/1H(H–C(6)).

(E)- *and* (Z)-*8-Methyl-5,7-nonadien-1-ol* (**64**) (1:1 mixture), b.p. 78–140°/0.03 Torr (bulb distillation). – IR. (film): 3360, 2950, 1640, 1450, 1430, 1370, 1060, 1030, 980, 950, 860, 730. – MS.: M^+ 154 (34), *m/e* 136 (7), 121 (21), 108 (20), 95 (100), 85 (53), 67 (84), 55 (59), 41 (68), 31 (18). – NMR. ($CDCl_3$): 1.1→2.5/*m*/12H(2 H_3C–C(8), 2 H–C(2), 2 H–C(3) and 2 H–C(4)), 3.62/*t*, *J*=6/2H(–CH_2–O–), 5.1→6.6/*m*/3H(H–C(5), H–C(6) and H–C(7)).

8. *(Z)*-**4-Hexenol (65).** – a) *2-Hydroxytetrahydrofuran* (**66**). Diisobutylaluminium hydride (28.4 g; 0.25 mol) in anh. ether (120 ml) was added dropwise, under nitrogen, to a stirred solution of butyrolactone (17.2 g; 0.2 mol) in anh. ether (150 ml) at −75°. After stirring at −75° for 4 h, methanol (50 ml) was added. After the mixture had been stirred at −75° for 1 h it was poured on to crushed ice (violent reaction!) and the non-soluble parts were removed by filtration through a sintered glass funnel (G-3). The filtrate was acidified with aq. 10% HCl-solution (pH 5) and extracted 3 times with ether. The ethereal extract was washed (brine), dried (Na_2SO_4), concentrated and distilled through a *Vigreux* column (5 cm) giving 4.7 g (27%) of 2-hydroxytetrahydrofuran (**66**), b.p. 51°/11 Torr. – IR. (film): 3420, 2980, 1720, 1460, 1360, 1270, 1180, 1120, 1060, 1030, 990, 920, 850. – MS.: M^+ 88 (< 1),

m/e 87 (3), 71 (55), 57 (25), 42 (100), 31 (33). – NMR. ($CDCl_3$): 1.95/*m*/4H($-CH_2-CH_2-$), 3.6-4.3/*m*/2H($-CH_2-O$), 5.6/narrow *m*/1H($-O-CH-O$).

b) (Z)-*4-Hexenol* **65**. 2-Hydroxytetrahydrofuran (**66**) (4.4 g; 0.05 mol), ethyltriphenylphosphonium iodide (**44**) (31.3 g; 0.075 mol) and sodium dimethylsulfinylmethide (0.1 mol) in DMSO (170 ml) were allowed to react as described in experiment 5 a). Hydrolysis followed by pentane extraction (3 times) gave 3.6 g (72%) of *(Z)*-4-hexen-1-ol (**65**), b.p. 59°/9 Torr, isomeric purity by GC.[4]): 95% *Z*, 5% *E*. – IR. (film): 3340, 1650, 695. – MS.: M^+ 100 (3), *m/e* 82 (41), 67 (100), 55 (34), 41 (67), 29 (20). – NMR. ($CDCl_3$): 1.3-1.9/5H($=C-CH_3$, $-CH_2-$), 1.9-2.5/3H(2H–C(3), –OH), 3.66/*t*, $J = 6.5$/2H($-CH_2-O-$), 5.1-5.9/2H($-CH=CH-$).

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