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117. Synthesis of 'Pear Ester'
A novel synthesis of 2,4-diolefinic aldehydes and esters

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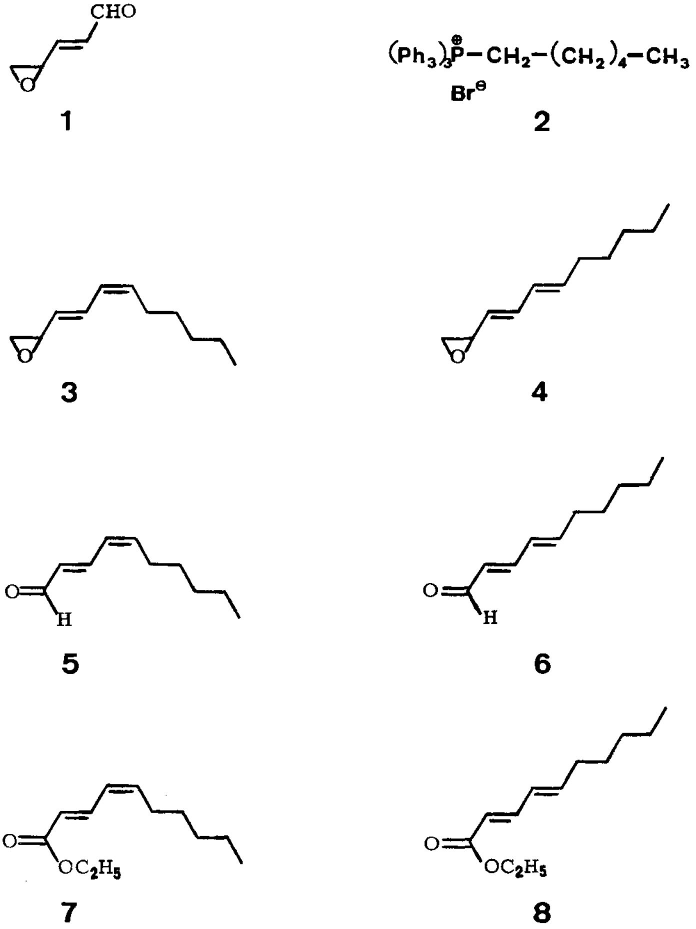
(21. II. 73)

Summary. Vinylogous epoxyaldehydes undergo stereospecific *Wittig* condensations in high yields. The resulting diolefinic epoxides are cleaved at the C(1)–C(2) single bond, when treated with periodic acid, to give the corresponding aldehydes. Direct transformation into the corresponding ethyl-ester leads to an efficient synthesis of the 'pear ester'.

Recently several new syntheses of olefinic carboxylates [1] [2] *via* organometallic intermediates have been developed. Ethyl-*trans*-2-*cis*-4-decadienoate, identified as a

Scheme 1



part of the odoriferous principle of *Bartlett* pears [4], was prepared by stereospecific addition of vinylcopperlithium complex to ethyl propiolate.

In the present communication we report a new approach to the synthesis of 'pear ester' and related compounds (see Scheme 1). Reaction of the readily available 4,5-epoxy-2-*trans*-pentenal (**1**)¹) [5], with the ylid prepared from *n*-hexyltriphenylphosphonium bromide (**2**) [6] gives a mixture of 1,2-epoxy-3,5-undecadiene isomers (**3**, **4** in ratio 85:15). This highly stereospecific [7] introduction of the *cis*-double bond in the 5-position was achieved in 87% yield. Treatment of the mixture of epoxides **3** and **4** with an ether solution of periodic acid [8] gave the 2,4-decadienals **5** and **6** in 96% yield. GLC.-analysis showed the ratio of isomers **5** and **6** to be the same that of **3** and **4**. A rapid work-up of the mixture is recommended to avoid isomerisation of the 4-*cis* double bond in **5**. Conversion of aldehydes **5** and **6** to the corresponding ethyl esters **7** and **8** was achieved in 92% yield, using the sodium cyanide/manganese

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¹) Commercially available from *Fluka* AG.

dioxide method of *Corey et al.* [9]. The total yield of pear ester is 70%. Depending upon the *Wittig* reagent **2** employed, compounds homologous to **3**–**8** can also be prepared by this general method.

Experimental part

All experiments were carried out under nitrogen. Boiling points and melting points are uncorrected. GLC.-analysis were performed on a *Varian* 1740 (analytical) or a *Varian* 700 (preparative) chromatograph, using silicon rubber gum SE-30 and Carbowax 20 M columns. NMR.-spectra were obtained with a *Varian* A-60 spectrometer. Chemical shifts are given in ppm downfield from TMS. IR.-spectra were recorded on a *Perkin-Elmer* A-21 spectrophotometer. Mass spectra were obtained using an *Atlas* CH-4 mass spectrometer, inlet temperature ca. 150°, electron energy 70 eV.

1,2-Epoxy-undeca-3,5-diene **3** *and* **4** (*mixture of isomers*). 65 g of 22% butyl lithium in hexane was added under nitrogen at room temperature to a suspension of *n*-hexyltriphenylphosphonium bromide (80,4 g) **2** in 1000 ml anhydrous diethyl ether and the resulting red solution was stirred 30 min. A solution of *trans*-4,5-epoxy-2-pentenal (15,6 g) **1** [5] in 120 ml of ether was added dropwise at 10° and the mixture allowed to stand at room temperature for 1 h. After the addition of cold water, the organic layer was separated, washed with water, dried (Na_2SO_4) and evaporated. The partly crystallized residue was extracted several times with hexane. Evaporation and distillation of the residue afforded 22.6 g (85%) of a mixture, b.p. 62°/0.05 Torr; $d_4^{20} = 0.8816$; $n_D^{30} = 1.4939$. GLC.-analysis indicated a mixture of isomeric dienes **3** and **4** in the ratio 85:15.

3 *and* **4**. NMR.-spectrum: 0.93 (3H, *t*, $J = 5$ Hz, $-CH_3$); 1.98–2.55 (4H, *m*, ${}^{H}_{H}\!>\!C\underset{O}{\diagdown\!\diagup}C\!<$, $>\!C{=}\overset{|}{C}{-}CH_2{-}$); 3.22 (1H, *d*, $J = 8$ Hz, $>\!C\underset{O}{\diagdown\!\diagup}C\!<^{}_{H}$); 5.32–7.11 (4H, *m*, $-CH{=}CH{-}CH{=}CH{-}$) ppm. – IR.-spectrum (neat): 3005 ($>\!C{=}CH{-}$), 1655, 1615 ($>\!C{=}\overset{|}{C}{-}\overset{|}{C}{=}C\!<$), 1240 ($>\!C\underset{O}{\diagdown\!\diagup}C\!<$), 984 (CH=CH, *trans*), 735 (CH=CH, *cis*) cm^{-1}. – MS.: M^+ 166 (19); *m/e*: 137 (9), 123 (4), 109 (8), 95 (41), 81 (100), 67 (83), 55 (32).

trans-*2*-cis-*4-Decadienal* **5** *and* trans-*2*-trans-*4-decadienal* **6**. A mixture of periodic acid (7.5 g) and 500 ml of anhydrous ether was stirred for 1 h at room temperature [8], and the resulting suspension filtered. To the filtrate a solution of epoxydienes (5.0 g) **3** and **4** in 50 ml of anhydrous ether was added rapidly with vigorous stirring. Precipitation of iodic acid occurred instantly. Stirring was continued for 5 min., followed by filtration. The filtrate was washed with a 10% solution of sodium thiosulfate and with water, dried (Na_2SO_4) and evaporated. Distillation of the residue afforded 4.4 g (96%) of a mixture, b.p. 58–61°/0.05 Torr; $d_4^{20} = 0.8999$; $n_D^{20} = 1.5142$. GLC.-analysis indicated a mixture of aldehydes **5** and **6** in the ratio of 77:23. Samples of each isomer were collected for analysis.

5. NMR.-spectrum: 0.92 (3H, *t*, $J = 5$ Hz, $-CH_3$); 1.93–2.60 (2H, *m*, $>\!C{=}\overset{|}{C}{-}CH_2{-}$); 5.62–6.50 (3H, *m*, $-CH{=}\overset{|}{C}{-}CH{=}CH{-}$); 6.82–7.7 (1H, *m*, $>\!C{=}CH{-}\overset{|}{C}{=}C\!<$); 9.60 (1H, *d*, $J = 8$ Hz, $-CHO$) ppm. – IR.-spectrum (neat): 3010 ($>\!C{=}CH{-}$), 2710 ($-CHO$), 1680 ($>\!C{=}O$), 1630, 1590 ($>\!C{=}\overset{|}{C}{-}C{=}C\!<$), 985 ($-CH{=}CH{-}$, *trans*), 725 ($-CH{=}CH{-}$, *cis*) cm^{-1}. MS.: M^+ 152 (8); *m/e*: 123 (3), 109 (2), 95 (12), 81 (100), 67 (21), 55 (21).

6. NMR.-spectrum: 0.92 (3H, *t*, $J = 5$ Hz, $-CH_3$); 1.92–2.50 (2H, *m*, $>\!C{=}\overset{|}{C}{-}CH_2{-}$); 5.70–6.50 (3H, *m*, $-CH{=}\overset{|}{C}{-}CH{=}CH{-}$); 6.80–7.30 (1H, *m*, $>\!C{=}CH{-}\overset{|}{C}{=}C\!<$); 9.53 (1H, *d*, $J = 8$ Hz, $-CHO$) ppm. – IR.-spectrum (neat): 3015 ($>\!C{=}CH{-}$), 1685 ($>\!C{=}O$), 1640, 1600 ($>\!C{=}\overset{|}{C}{-}\overset{|}{C}{=}C\!<$), 985 ($-CH{=}CH{-}$, *trans*) cm^{-1}. – MS.: M^+ 152 (7); *m/e*: 123 (2), 95 (10), 81 (100), 67 (17), 55 (16).

Ethyl-trans-*2*-cis-*4-decadienoate* **7** *and ethyl*-trans-*2*-trans-*4-decadienoate* **8** [3]. 2,4-Decadienals (100 g) **5** and **6**, sodium cyanide (16.0 g), acetic acid (6.0 g), 115 g of activated manganese dioxide [9] and 1000 ml of ethyl alcohol were stirred at room temperature for 12 h. The mixture was filtered and cold water added. The esters were extracted several times into ether. The combined extracts were dried (Na_2SO_4) and evaporated. Distillation of the residue gave 12.0 g (92%) of isomeric esters **7** and **8** in the ratio 75:25, b.p. 84–86°/0.05 Torr; $d_4^{20} = 0.9208$; $n_D^{20} = 1.4863$. Separation was achieved by fractional distillation.

7. NMR.-spectrum 2): 0.92 (3H, *t*, $J = 5$ Hz, $-CH_3$); 1.30 (3H, *t*, $J = 7$ Hz, $-CH_3$); 2.0–2.5 (2H, *m*, $>C{=}\overset{|}{C}{-}CH_2{-}$); 4.13 (2H, *q*, $J = 7$ Hz, $-O{-}CH_2{-}$); 5.75 (1H, *d*, $J = 15$ Hz, $>C{=}CH_a{-}$); 5.5–6.3 (2H, *m*, $>C{=}CH_b{-}$, $>C{=}CH_c{-}$); 7.48 (1H, *d* of *d*, $J = 15$ Hz, $>C{=}CH_d{-}$) ppm. – IR.-spectrum: 1710 ($>C{=}O$), 1640, 1600 ($>C{=}\overset{|}{C}{-}\overset{|}{C}{=}C<$), 992 ($-CH{=}CH-$, *trans*), 705 ($-CH{=}CH-$, *cis*) cm^{-1}. – MS.: M^+ 196 (44); *m/e*: 167 (4), 151 (43), 139 (3), 125 (77), 108 (19), 97 (71), 81 (100), 67 (81), 55 (42).

8. NMR.-spectrum 1): 0.89 (3H, *t*, $J = 5$ Hz, $-CH_3$); 1.28 (3H, *t*, $J = 7$ Hz, $-CH_3$); 1.9–2.3 (2H, *m*, $>C{=}\overset{|}{C}{-}CH_2{-}$); 4.13 (2H, *q*, $J = 7$ Hz, $-O{-}CH_2{-}$); 5.72 (1H, *d*, $J = 15$ Hz, $>C{=}CH_a{-}$); 6.0–6.25 (2H, *m*, $>C{=}CH_b$, $>C{=}CH_c$); 6.95–7.50 (1H, *m*, $>C{=}CH_d{-}$) ppm. – IR.-spectrum: 1710 ($>C{=}O$), 1640, 1620 ($>C{=}\overset{|}{C}{-}\overset{|}{C}{=}C<$), 998 ($-CH{=}CH-$, *trans*) cm^{-1}. – MS.: M^+ 196 (47); *m/e*: 181 (3), 151 (40), 139 (4), 125 (100), 111 (13), 97 (76), 81 (84), 67 (61), 55 (8), 41 (36).

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2) Designation of olefinic protons: $CH_3(CH_2)_4CH_e = CH_b{-}CH_d{=}CH_a{-}CO_2Et$.

Erratum

Helv. *56*, 442, (1973), Abhandlung Nr. 33 von *Th. Wagner-Jauregg, Q. Ahmed* und *E. Pretsch*: Die Fussnote 4) soll richtig lauten: Die Chemical Abstracts Bezeichnung für **9** ist *N*,2-Dialkyl-1,2,3,3a,4,5-hexahydro-1,3-dioxo-9b*H*-pyrrolo[3,4-*f*]quinoline-9b-succinimide

oder

N-Alkyl-5-(1-alkyl-2,5-dioxo-3-pyrrolidinyl)-5,6,7,8-tetrahydro-5,6-quinolinedicarboximide

oder

2-Alkyl-9b-(1-alkyl-2,5-dioxo-3-pyrrolidinyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*f*]quinoline-1,3-(2*H*)-dione.