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A NOVEL STEREOCONTROLLED SYNTHESIS OF (Z,Z)-3,13-OCTADECADIEN-1-YL ACETATE, THE SEX PHEROMONE OF SYNANTHEDON SPECIES

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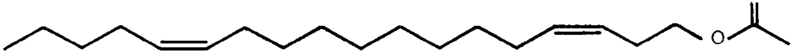
Abstract: Starting from 10-undecenoic acid, a stereocontrolled synthesis of (Z,Z)-3,13-octadecadien-1-yl acetate with high stereochemical purity was achieved by the use of Wittig-olefinations for the introductions of (Z)-double bonds.

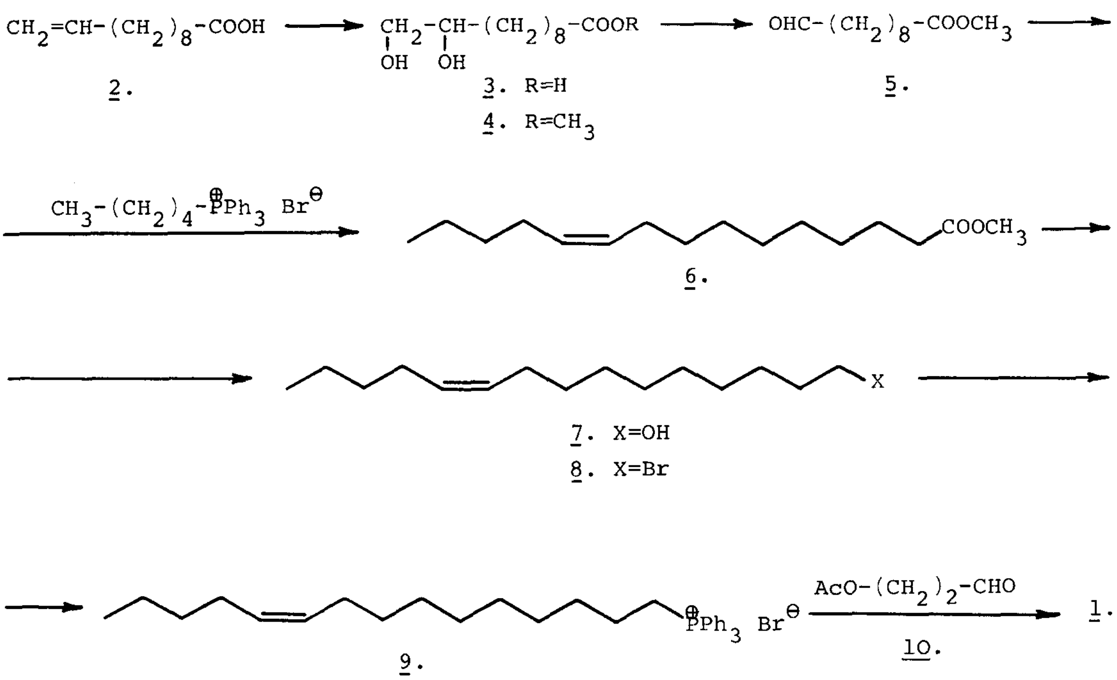
The Synanthedon species are frequent and occasionally serious pests of orchards in Eurasia. Tumlinson and co-workers have identified and synthesized the major components of the pheromone extract of the female lesser peachtree borer (*Synanthedon pictipes*, Grote, Robinson) as (Z,Z)-3,13-octadecadien-1-yl acetate[1] (1). Compound 1 and its (E,Z)-isomer are also the sex pheromones of *Synanthedon myopaeformis* Brkh., *Synanthedon tripuliformis*, Clerk and *Synanthedon hector*, Butler[2]. Several syntheses of this sex pheromone (1) have recently been published, making use of rather complicated reactions and expensive starting materials[3].



1.

We have now explored a more efficient synthesis which starts from the available 10-undecenoic acid (2), and gives high yield of title compound (1), as outlined in Scheme 1.

Scheme 1.



Following the procedure of Swern[4], treatment of 10-undecenoic acid (2) with a mixture of formic acid and 30% hydrogen peroxide (*7:1, 40 °C, 2 h*) afforded 10,11-dihydroxy-undecanoic acid (3)[5] in a yield of 90%, which was esterified through its sodium salt with dimethyl sulfate in methanol (*reflux, 4 h*)[6]. The resulting ester (4)[5] [*95%;ir(neat)*ν_{max}*: 3350, 1740, 1200* cm^{-1}; ^{1}H*-nmr(DMSO-*d_6*)*δ*:1,35(14H,br.s,7* CH_2*),2,2(2H,m,*CH_2*), 3.60-3.50(5H,m,CH,OH), 3,65(3H,s,*OCH_3*);* ^{13}C*-nmr(DMSO-*d_6*)173,8(*C_1*), 29,8(*C_2*), 33,4(*C_9*),71,6(*C_{10}*), 66,1(*C_{11}*),51,5(*C_1'*)*][7], on lead(IV)-acetate oxidation[8,9](*in benzene,25°C,12 h*) produced methyl-9-formyl-nonanoate(5)[10][*90%,b.p.: 100-103/0,2mm;ir(neat)* ν_{max}*:2720,1740* cm^{-1}*;* ^{1}H*-nmr(*$CDCl_3$*)*δ*:1,35(12H,br.s,6*CH_2*),2,2(2H,m,*CH_2*),2,4 (2H,tt,J=7 and 2 Hz,*CH_2*), 3,65(3H,s,*OCH_3*),9,8(1H,t,J=2 Hz,CHO);* ^{13}C*-nmr(*$CDCl_3$*) 51,5(*C_1'*),174,1(*C_1*),202,6(*C_{10}*)*]. This aldehyde was then allowed to react with the ylide generated from pentyl-triphenyl-phosphonium bromide by sodium silazide-method[11](*ylid generation:NaHMDS in THF, 1 h reflux; coupling reaction:-78°C,1 h and then 25°C,20 h*). The resulting unsaturated ester

(6)[*50%;ir(neat)*ν_{max}*:1740,1650 cm*$^{-1}$*;*^{1}*H-nmr(CDCl*$_3$*)δ:0,85(3H,t,J=7 Hz,CH*$_3$*), 1,3 (16H,br.s,8CH*$_2$*),2,0(4H,m,2CH*$_2$*),2,2(2H,m,CH*$_2$*), 3,65(3H,s,OCH*$_3$*),5,35(2H,t,J=4Hz, CH=CH);* ^{13}*C-nmr(CDCl*$_3$*) 51,5(*C'_1*), 26,9 and 27,2(*C_9*,*C_{12}*),129,8 and 129,9(*C_{10}*,* C_{11}*),173,8(*C_1*)*][12] was reduced with LiAlH$_4$ in ether *(3 h,25*^{o}*C)* to yield the unsaturated alcohol (7)[3b], which was converted immediately to the corresponding bromo-derivate (8)*(PBr*$_3$*,85*^{o}*C,1 h, 80%)*. Reaction of the crude bromide with triphenylphosphine in acetonitrile at reflux *(24 h)* furnished quantitatively phosphonium salt (9)[^{1}*H-nmr(DMSO-d*$_6$*)δ:0,85(3H,t,J=8 Hz,CH*$_3$*), 1,3(18H, br.s,9CH*$_2$*),2,0(4H,m,2CH*$_2$*),2,7(2H,t,J=6 Hz,CH*$_2$*),5,34(2H,t,J=4 Hz,CH*$_2$*),7,8(15H, m,aromatic protons);*^{13}*C-nmr(DMSO-d*$_6$*)14,0(*C_{15}*), 19,5(*C_1*),117,7(*C'_1*),129,6 and 129,8(*C_{10}*,*C_{11}*),26,8 and 27,1(*C_9*,*C_{12}*),130,5(*C'_3*),133,5(*C'_2*),135,2(*C'_4*)*].

The next phase of the synthesis, attachment of the C_1-C_3 moiety required 3-acetoxy-propanal (10). This was synthesized from 3-bromo-propanol by displacement of bromine with acetoxy group *(AgOAc in 2-butanone,48 h,reflux)*, followed by oxidation of the resultant 3-acetoxy-propanol[*ir(neat)*ν_{max}*:3350, 1760,1260,1040 cm*$^{-1}$*;*^{1}*H-nmr(CDCl*$_3$*)δ:2,05(3H,s,OCH*$_3$*), 2,10(2H,tt,J=6 and 8 Hz, CH*$_2$*), 2,95(1H,s,OH),3,45(2H,t,J=8 Hz,CH*$_2$*),3,8(2H,t,J=6 Hz, CH*$_2$*); b.p.: 70/13 mm*] with pyridinium chlorochromate on alumina[13] *(hexane, 25*^{o}*C,3 h)*[*80%; ir(neat)*ν_{max}*:2720,1760 cm*$^{-1}$*;*^{1}*H-nmr(CDCl*$_3$*)δ:2,05(3H,s,CH*$_3$*),2,4(2H,tt,J=7 and 2 Hz,CH*$_2$*), 3,4(2H,t,J=7 Hz,CH*$_2$*),9,7(1H,t,J=2 Hz,CHO)*][14].

To complete the synthesis acetoxy-aldehyde (10) was reacted with the ylide generated from the above phosphonium salt (9)*(NaHMDS in THF,-78*^{o}*C, 1 h and 20 h at 25* ^{o}*C)* affording the target sex pheromone (1) in 60% yield and of 98% isomer purity[15] [*ir(neat)*ν_{max}*: 3030,2650,1740,1210 cm*$^{-1}$*,*^{1}*H-nmr(CDCl*$_3$*) δ:0,85(3H,t,J=8 Hz,CH*$_3$*),1,3(16H,br.s,8CH*$_2$*), 2,05(3H,s,OCH*$_3$*), 1.95-2,10(8H,m, 4CH*$_2$*), 4,05(2H,t,J=6 Hz,CH*$_2$*),5,35(4H,t,J=6 Hz,CH=CH);* ^{13}*C-nmr(CDCl*$_3$*) 14,0 (*C_{18}*),20,9(*C'_2*),22,4(*C_{17}*),26,9(*C_{15}*),27,7(*C_{12}*),27,8(*C_5*),27,9(*C_2*),32,05(*C_{16}*), 63,1(*C_1*),129,8 and 129,9(*C_3*,*C_4*,*C_{13}*,*C_{14}*),170,4(*C'_1*)*][3a,c,f].

Our synthetic approach proved to be attractive economically and applicable to large-scale production of the title pheromone.

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6/ When the esterification of 3 was carried out in methanol in the presence of catalytic amount of sulfuric acid the formation of 4 was observed only with moderate yield due to previous lactonization.

7/ IR spectra were recorded on SPECORD IR 75 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a VARIAN XL-100-15 instrument. All signals are expressed by the ppm downfield from TMS used as an internal standard.

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9/ The known periodic acid procedure [See: KING,G.: J.Chem.Soc. 1938 1826; WITTCOFF,H.; MOE,O.A; IWEN,M.H.: J.Am.Chem.Soc. 1948 /70/ 742] gives lower yield /70 %/ and we noticed many side reactions. Using lead(IV)-acetate in glacial acetic acid the yield was around 40%. [See: SCANLAN,J.T; SWERN,D.: J.Am.Chem.Soc. 1940 /62/ 2305]. The tri- and tetramerisation of obtained aldehyde (5) was of very large scale.

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12/ GC analysis showed that 6 had chemical and stereoisomeric purity higher than 98%. PERKIN ELMER instrument, CP57CB capillary column /25m x 0,22 mm i.d./ and a FID detector/column at 170 °C, temp. of detector 290 °C /. R_t(Z-isomer) 7,27 min, R_t/E-isomer/ 7,14 min.

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15/ GC analysis showed that 1 had 99% chemical purity and 98% isomeric purity. R_t (Z,Z-isomer) 17,2 min.

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