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STEREOSELECTIVE PREPARATION OF 1-CHLORO-(E,E)-1,3-DIENES. APPLICATION TO THE SYNTHESIS OF METHYL ELEOSTEARATE.

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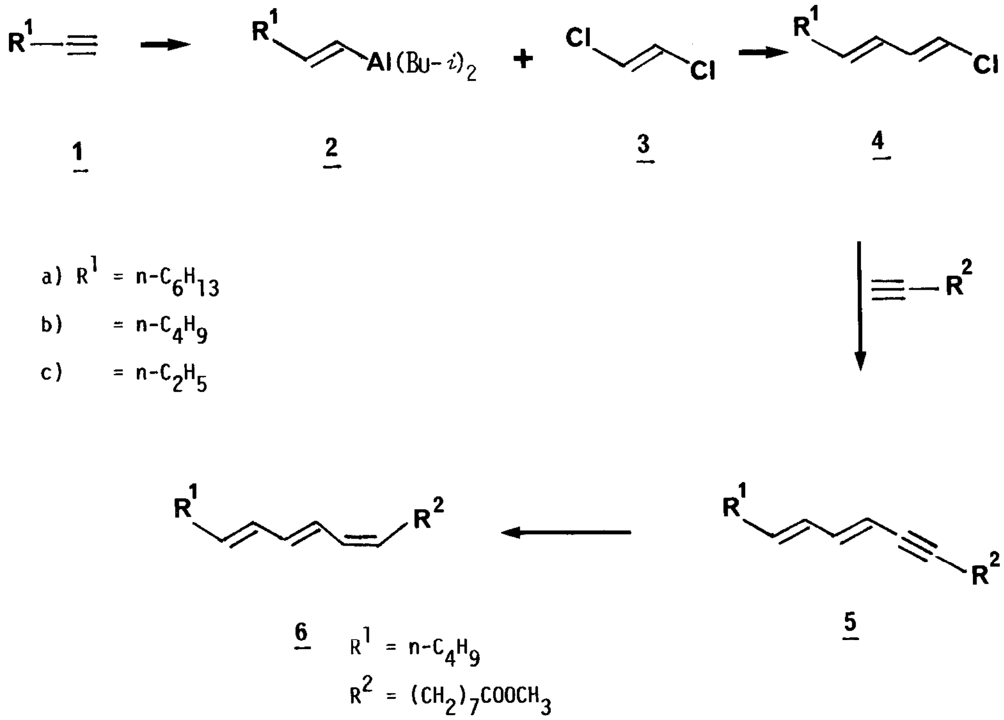
SUMMARY : *The nickel (or palladium) catalyzed reaction of alkenylalanes with (E)-dichloroethylene affords 1-chloro-(E,E)-1,3-dienes under mild conditions. The syntheses of methyl α-eleostearate which is reported to be a feeding deterrent for the boll weevil on cotton, and one of its isomers,methyl punicate, are described.*

Alkenyl halides are valuable precursors for the stereoselective synthesis of olefins and various methods for their preparation have been described 1).

We would like to report a simple synthesis of (E,E)-chlorodienes by reaction of (E)-alkenylalanes with (E)-dichloroethylene. Thus, when treated with the alkenylalane 2a (readily obtainable via hydroalumination of 1-octyne 2,3) and 0.01 equivalent of nickel tetrakis (triphenylphosphine) 4) - or 0.05 equiv. of palladium tetrakis (triphenylphosphine) 5,6 - in hexane-benzene at 20° for 6 h, (E)-1,2-dichloroethylene 3 (5 equiv.) gave 1-chloro-(E,E)-deca-1,3-diene 4a 7,8) (⩾99 % isomeric purity) in 80 % yield 9).

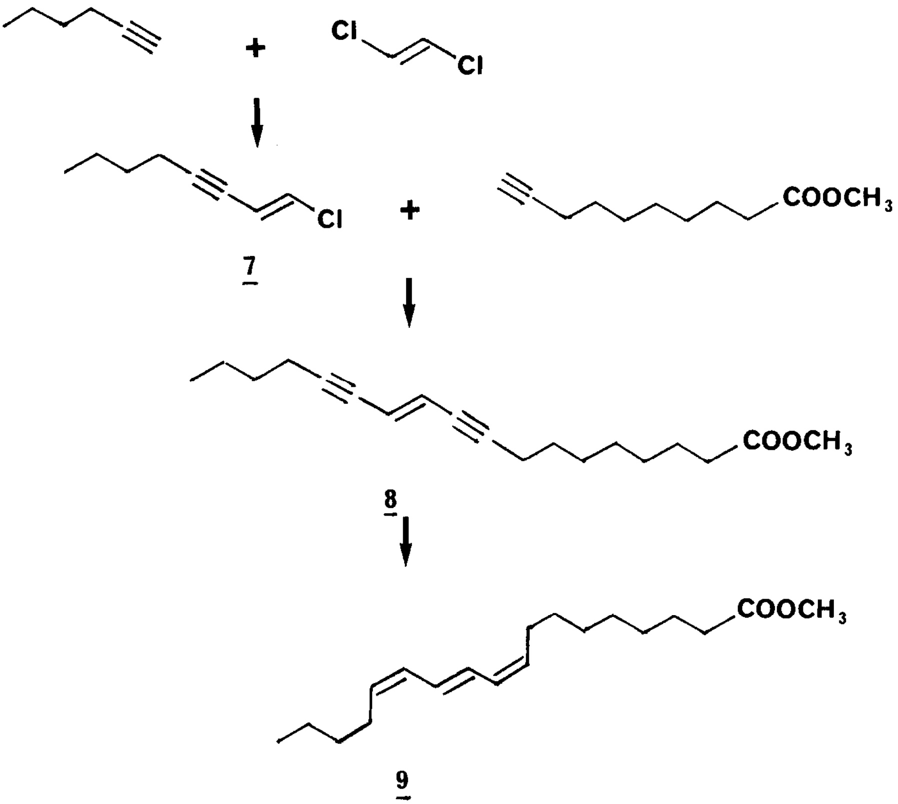
The chlorodienes 4 are efficient precursors of various unsaturated units 10). Thus, when treated with terminal acetylenes (1 equiv.) in the presence of palladium (tetrakis triphenylphosphine)(0.05 equiv.) and copper iodide (0.15 equiv.) in benzene containing n-butylamine (10 equiv.) at 20° for 10 h 11), they lead to dienynes 5 in 80-90 % yield.



These methods offer a convenient access to natural products of the triene type of predictable stereochemistry.

Methyl α-eleostearate 6 which is a feeding deterrent for the boll weevil on cotton [12] was thus prepared by a three-step synthesis in a 48 % overall yield : Treatment of the chlorodiene 4b with methyl 9-decynoate under palladium-copper catalysis [11] at room temperature for 10 h gave the ester 5 (R^1=nC_4H_9,R^2=$(CH_2)_7CO_2CH_3$) in 79 % yield [13,14]. Reduction of the triple bond with diisoamylborane afforded (75 %) methyl (Z,E,E) octadeca-9,11,13 trienoate 6 (R^1= nC_4H_9, R^2= $(CH_2)_7CO_2CH_3$).

Saponification gave α-eleostearic acid mp 47° [15,16]. The stereochemistry of the double bonds has been ascertained by 400 MHz ^{1}H NMR analysis [13,17]



The (Z,E,Z) isomer, methyl punicate 9 [15], was prepared in a similar way : reaction of 1-hexyne with (E)-1,2-dichloroethylene gave the chloroenyne 7 in 98 % yield [1c]. Coupling with methyl 9-decynoate (1 equiv.) under palladium-copper catalysis [11] gave the ester 8 [13,18] in 80 % yield. Reduction of the two triple bonds with diisoamylborane led to (Z,E,Z) octadeca-9,11,13 trienoate 9 [19]. The overall yield of the three-step synthesis was 60 %.

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7) All new compounds exhibited satisfactory spectral and physical properties.

8) ^{1}H NMR (250 MHz, CDCl$_3$) δ = 5.73 (1H,dt, J=7Hz), J = 16Hz, H-4) ; 5.99 (1H,dd, J=11Hz), J=16Hz, H-3) ; 6.09 (1H,d, J=13.5Hz, H-1) ; 6.45 ppm (1H,dd, J=11Hz, J=13.5 Hz, H-2).

9) 4b was obtained in 80 % yield in the same way. 2c was prepared by hydroalumination of 1-butyne (2 equiv.) at 8° for 16 h. ; reaction with 3 gave 4c in 70 % yield.

10) By treatment with methyllithium (2 equiv.) and TMEDA (2 equiv.) in ether at -70° for 1.5h , and then warming up to room temperature within 1h, 4a gave (3E)-decen-1-yne in 95 % yield.

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13) We are grateful to Dr. E. Guittet (Institut de Chimie des Substances Naturelles, Gif-sur-Yvette) for 400 MHz NMR analysis of these products.

14) ^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.46 (1H, broad d, J=15.5 Hz, H-11) ; 5.73 (1H, dt, J=7 Hz, J=15 Hz, H-14) ; 6.05 (1H,dd, J=11 Hz, J=15Hz, H-13) ; 6.47 ppm (1H,dd, J=11 Hz, J=15.5 Hz, H-12).

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17) ^{1}H NMR (400 MHz, CDCl$_3$) δ = 5.37 (1H,dt, J=10.5 Hz, J=7.5 Hz, H-9) ; 5.68 (1H,dt, J=14 Hz, J=7Hz, H-14) ; 5.96 (1H,t, J=11 Hz, H-10) ; 6.08(dd, J=14 Hz, J=11 Hz, H-13) ; 6.14(dd, J=14 Hz, J=11 Hz, H-12) ; 6.36 ppm (1H,dd, J=14Hz, J=11 Hz, H-11).

18) 8 ^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.65 (3H,s,OCH$_3$) ; 5.86 ppm (2H,s, H-11 and H-12).

19) Saponification gave punicic acid in 95 % yield m.p. = 42 - 43° ; [15]. ^{1}H NMR(250 MHz,CDCl$_3$) δ=5.46 and 5.48(2H, two overlapping dt J=11Hz and J=7.5Hz, H-9 and H-14) ; 6.10(2H,m, H-13 and H-10) ; 6.50(2H,m, H-11 and H-12) ; double irradiation at 2.20 ppm of the allylic methylene protons H-8 and H-15 transformed the signals at 5.46 and 5.48 ppm assigned to H-9 and H-14 into two doublets (J=10Hz). The multiplet at 6.5 ppm assigned to H-11 and H-12 collapsed to a singlet by irradiation at 6.10 ppm (H-13 and H-10). The multiplet at 6.10 ppm collapsed to a doublet (J=10Hz) by irradiation at 6.50 ppm.

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