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Total Synthesis of Enantiomers of (3Z,6Z)-*cis*-9,10-epoxy 1,3,6-Henicosatriene - the Pheromonal Component of *Diacrisia obliqua*

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Abstract : Synthesis of enantiomers of (3Z,6Z)-*cis*-9,10-epoxy 1,3,6-henicosatriene, the pheromonal component of *Diacrisia obliqua* was achieved through alkylative epoxide rearrangement and stereoselective Wittig olefination reactions as the key steps.
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Key words : *Pheromones; Epoxidation; Wittig reaction; Asymmetric synthesis.*

Diacrisia obliqua is a polyphagous insect attacking many crops, particularly oil seed crops in India and Bangladesh.[1] Earlier, our group has shown that the pheromone of Diacrisia obliqua is constituted with five components[2] viz. (3Z,6Z)-*cis*-9,10-epoxy-1,3,6-henicosatriene **I**, (3Z,6Z)-*cis*-9,10-epoxy-3,6-henicosadiene **II**, (9Z,12Z)-Octadecadienal **III**, (9Z,12Z,15Z)-octadecatrienal **IV** and (3Z,6Z,9Z)-henicosatriene **V**. As the 9S,10R isomer of **I** is showing high electroantennogram (EAG) activity, it is believed to be the active isomer present in the natural pheromone of the insect. But this has yet to be confirmed with wind-tunnel and field trial experiments. In order to evaluate the active isomer and also to determine the actual blend we have recently synthesised both the enantiomers of (3Z,6Z)-*cis*-9,10-epoxy-1,3,6-henocosatriene **I** in a new synthetic route as given in Figure 1.

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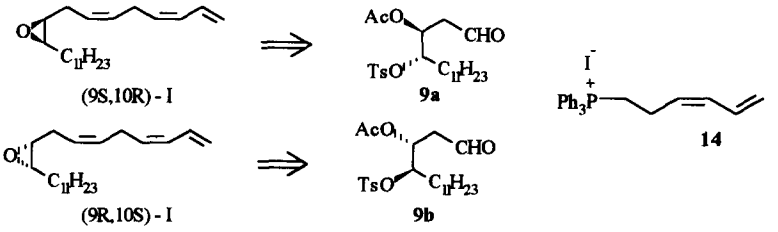
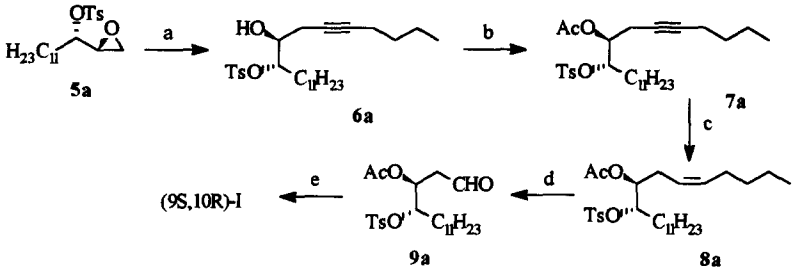


Figure 1

An earlier synthesis of the pheromonal component **I** has been reported by using Sharpless asymmetric epoxidation of Z-allylic alcohol as key step.[3] In our present approach we have employed an alkylative epoxide rearrangement[4] which allowed us to obtain the target molecule directly in enantiopure form, Scheme-I.

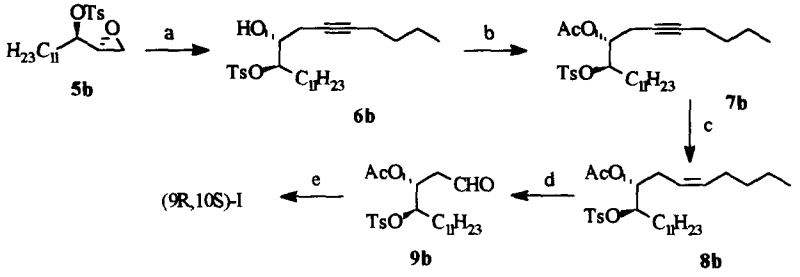


Reagents : 1) 1-hexyne, BuLi, $BF_3.OEt_2$, THF, -78°C; b) Ac_2O, pyridine, DMAP, DCM; c) Lindlar's catalyst-H_2; d) ozonolysis; e) (3Z)-hexa-1,3-dienyl triphenylphosphonium iodide, $NaN(SiMe_3)_2$, THF, -78°C.

Scheme-I

The (2S,3S)-*threo*-epoxytosylate **5a** on alkylation with 1-lithiohexyne in presence of $BF_3.OEt_2$ gave **6a** which on acetylation followed by partial hydrogenation using Lindlar's catalyst afforded **8a**. The intermediate **8a** on ozonolysis gave the aldehyde **9a** which is used as such without further purification. Accordingly stereoselective Wittig olefination[5] of **9a** with (3Z)-hexa-1,3-dienyl triphenylphosphonium iodide afforded directly (9S,10R) isomer of target molecule. The spectral data obtained for this target compound is identical with the literature.[3]

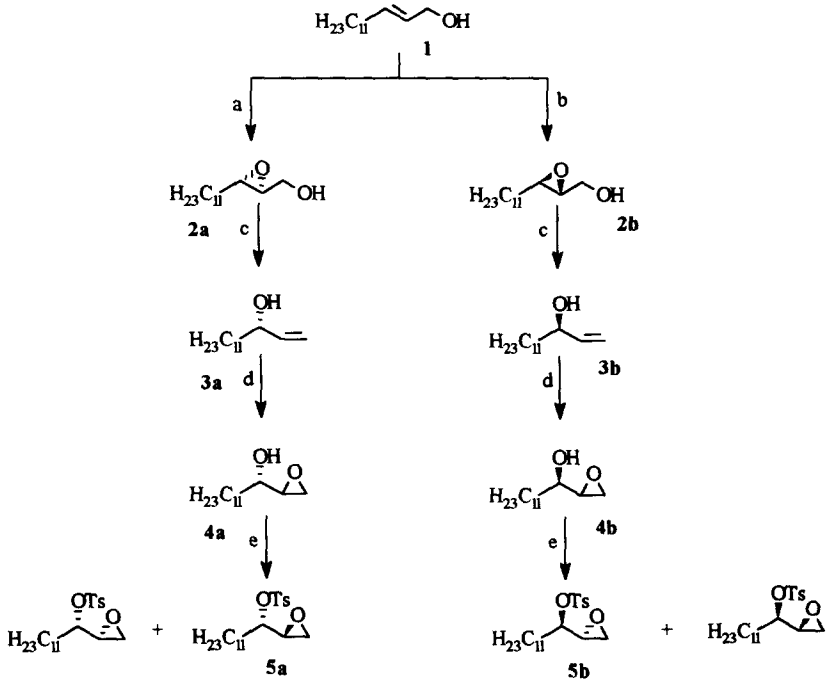
We have also synthesized the (9R,10S) isomer of **I** from (2R,3R) *threo* epoxytosylate **5b** employing the same sequence of reactions, Scheme-II.



Reagents : 1) 1-hexyne, BuLi, $BF_3.OEt_2$, THF, -78°C; b) Ac_2O, pyridine, DMAP, DCM; c) Lindlar's catalyst-H_2; d) ozonolysis; e) (3Z)-hexa-1,3-dienyl triphenylphosphonium iodide, $NaN(SiMe_3)_2$, THF, -78°C.

Scheme-II

The epoxy tosylates **5a** and **5b** are vital intermediates in the syntheses of several epoxy pheromones with an eleven carbon atom containing side chain and there are only two methods available in literature[4,6] for their synthesis. Here we report an efficient and simple method for the synthesis of these epoxytosylates using stereospecific opening of the epoxides with titanocene, a methodology developed earlier in our group,[7] Scheme-III.



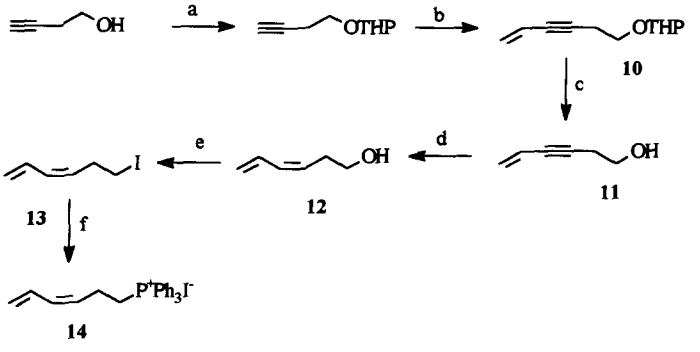
Reagents : a) 4Å molecular sieves, (+)-DIPT, TIP, TBHP, DCM, -25°C; b) 4Å molecular sieves, (-)-DIPT, TIP, TBHP, DCM, -25°C; c) Cp_2TiCl_2, Zn, $ZnCl_2$, THF, r.t. d) mCPBA, DCM; e) TsCl, TEA, DCM, 0°C.

Scheme-III

Tetradec-2-ene-1-ol **1** is prepared from propargylic alcohol THP ether through alkylation with undecylbromide followed by THP cleavage and LAH reduction of the resulting acetylenic alcohol. Compound **1** on Sharpless epoxidation with (+)-DIPT afforded (2S,3S)-epoxide **2a** which on stereospecific opening with titanocene afforded (3S)-alcohol **3a**. **3a** on epoxidation with mCPBA followed by tosylation gave (2S,3S)-epoxy tosylate **5a** as white needles after purification by normal column chromatography.

Application of (-)-DIPT in Sharpless epoxidation step allowed us to get (3R)- alcohol **3b** which afforded (2R,3R)-*threo*-epoxytosylate **5b**.

(3Z)-hexa-1,3-dienyltriphenylphosphonium iodide has been synthesised from homopropargylic alcohol as shown Scheme-IV.



Reagents : a) DHP, DCM, PTSA; b) vinylbromide, Pd, CuI, THF, TEA, 50-60^{0}C; c) MeOH, PTSA; d) Lindlar's catalyst-H_2; e) TPP, I_2, imidazole, benzene, r.t. f) TPP, benzene, reflux.

Scheme-IV

In summary, the present work describes a novel approach for the synthesis of epoxytriene component of sex pheromones of *Diacrisia obliqua* and *Hyphantia cunea*. In this method Wittig olefination and stereoselective epoxy ring closure have been achieved in one step.

Experimental Section

Melting points were recorded on Fisher-Johns hot-plate and are uncorrected. IR spectra were recorded on Perkin-Elmer infrared-683 spectrophotometer. All the samples were recorded as neat or as liquid films. The absorptions were measured in ν units. PMR spectra were recorded on Varian Gemini-200 MHz and Varian - 400 MHz spectrometers. The standard abbreviations s,d,t,q,m,dd,dt refer to singlet, doublet, triplet, quartet, multiplet, doublet of doublet, doublet of triplet respectively. Mass measurements were carried out on CEC-21-110 B double focussing mass spectrometer at 70 ev using direct inlet systems and are given in mass units (m/z). Only significant peaks are described for IR and Mass spectra. TLC were performed on precoated silicagel glass plates. Dry THF was made by distilling over sodium benzophenone ketyl. DCM, pyridine, TEA were distilled over CaH_2 and stored over molecular sieves. Silica gel used for column chromatography was 60-120 mesh silica gel.

2S,3S-Epoxy-tetradecanol, 2a : To a stirred and cooled (-20^{0}C) suspension of activated powered 4 Å molecular sieves (2.5 g) in dry DCM (50 ml) under nitrogen atmosphere were added (+)-DIPT (0.15 ml, 0.7 mmol) in dry DCM (2 ml) and titaniumisopropoxide (0.2 ml, 0.6 mmol) in dry DCM (2 ml) and stirred for fifteen minutes. After that compound **1** (2.5 g, 11.8 mmol) was added and stirred for further 30 minutes. Then TBHP (1.2 g, 4.75 ml, 3 M, 14.2 mmol) was added slowly and stirred at the same temperature for 4 hours. The reaction mixture was then poured into water(20 ml), containing $FeSO_4$ (6.5 g) and citric acid (2 g) and stirred for fifteen minutes. The organic layer was separated and aqueous layer was extracted with chloroform. Combined organic layer was concentrated, taken in ether (60 ml) and cooled to 0^{0}C and 30% NaOH (10 ml) was added and stirred for half an hour at that temperature. Diluted with ether (60 ml) and washed with water, 10% HCl, water, brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent at reduced pressure and purification by column chromatography (hexane : acetone, 10 : 1) afforded **2a** (1.88 g) in 70% yield. $[\alpha]_D$ = -15.1 (c = 1, $CHCl_3$). PMR ($CDCl_3$) : δ 0.89 (t, J = 6Hz, 3H, CH_3), 1.2-1.6 (m, 20H, $(CH_2)_{10}$), 2.8-2.95 (m, 2H,

Oxirane CH), 3.5-3.65 (m, 1H, CHH-OH), 3.8-3.95 (m, 1H, CHH-OH) IR (KBr) : 3550, 2980, 2950, 1460, 1080, 1010, 890 cm^{-1}. CIMS: m/z 229 (MH^+), 111, 97, 83, 69, 57, 55(bp).

2R,3R-Epoxy-tetradecanol 2b : Sharpless epoxidation of 1 with (-)-DIPT afforded **2b**. The spectral data is identical with 2a. $[\alpha]_D$ = 14.9 (c = 1, $CHCl_3$).

(3S)-Tetradec-1-en-3-ol, 3a : To a red solution of titanocene (1.9 g, 7.5 mmol) in dry THF (20 ml) containing freshly fused zinc chloride (0.35 g, 2.5 mmol) was added zinc powder (0.5 g, 7.5 mmol) and stirred for one hour. To the resulting green colour solution was added to **2a** (0.575 g, 2.5 mmol) in dry THF (3 ml) through a canula. After five minutes the reaction mixture was treated with 5% HCl (5 ml) and extracted thoroughly with ether. The ether layer was washed successively with water, 10% aq. sodium bicarbonate, water, brine and dried (anhyd. Na_2SO_4). Concentration and subsequent purification by column chromatography (hexane : acetone, 20 : 1) afforded **3a** (0.48 g, 90%) as colourless liquid. $[\alpha]_D$ = 5.2 (c=1, $CHCl_3$). 98% ee as determined by relative intensities of methoxy signals which appeared as two singlets at 3.5 and 3.55 ppm in the ^1H NMR spectrum of the corresponding Mosher ester of **3a**. PMR ($CDCl_3$) : δ 0.89 (t, J = 7Hz, 3H, CH_3), 1.15-1.4 (br, s, 18H, $(CH_2)_9$), 1.5 (m, 2H, CH_2CHOH), 4.1 (d, J = 6.3Hz, 1H, CHOH), 5.0-5.3 (m, 2H, olefinic), 5.7-6.0 (m, 1H, olefinic). IR (neat) : 3350, 2900 cm^{-1}. MS : m/z 183 M^+ - C_2H_5), 183, 166, 85, 72, 57 (bp).

3R-Tetradec-1-ene-3-ol 3b : **2b** on reaction with titanocene gave **3b** spectral data identical with 3a. $[\alpha]_D$ = -5.1 (c=1, $CHCl_3$).

(3S)-1,2-Epoxy-3-hydroxy-tetradecane, 4a : A solution of **3a** (0.5 g, 2.36 mmol) in dry DCM (10 ml) was cooled to 0^0C under nitrogen atmosphere. 85% m-cpba (0.61 g, 3.54 mmol) was added slowly to this over 15 minutes. The resulting white mixture was brought to room temperature and stirred for half an hour. The solution was washed with aqueous $NaHCO_3$. The aqueous layer was extracted with DCM and the combined organic layer was washed with water, brine and dried over anhyd. Na_2SO_4. Concentration and purification by column chromatography (hexane : acetone, 10 : 1) afforded epoxy alcohol **4a** (0.43 g, 80%) as a colourless oil which

has solidified under vacuum. (0.1 mm.Hg). The ratio to *threo* and *erythro* epoxy alcohols was determined to be 3:2 by ^{1}H NMR integration of the carbinol methine proton resonances. PMR ($CDCl_3$) : δ 0.89 (t, J=7, 3H, CH_3), 1.1-1.4 (br, s, 18H, $(CH_2)_9$) 1.5 (m, 2H, CH_2CHOH), 2.7 (m, 1H, oxirane CH_2), 2.8 (m, 1H, oxirane CH_2), 2.95 (m, 1H, oxirane CH), 3.4 and 3.8 (2m, 1H, CHOH) (3:2). IR (neat) : 3300, 2900 cm^{-1}. MS: m/z 185 (M^+ - C_3H_7), 185, 111, 97, 83 (bp), 69, 57.

3R-1,2-Epoxy-3-hydroxy-tetradecane 4b **: 3b** on epoxidation with mCPBA afforded **4b.** The spectral data is identical with **4a**.

(2S,3S)-1,2-Epoxy-3-(tosyloxy)-tetradecane, 5a : A solution of epoxy alcohol **4a** (1 g, 4.4 mmol) in dry DCM (20 ml) was stirred under nitrogen atmosphere at 0^{0}C. To this anhydrous TEA (1.34 g, 13.1 mmol) was added dropwise. Then tosylchloride (freshly recrystallised from pet. ether) (0.75 g, 6.6 mmol) was added slowly. The reaction mixture was kept at 5^{0}C (refrigerator) for 4 days. Diluted with water and extracted with DCM. The organic layer was washed with brine and dried over anhyd. Na_2SO_4. Concentration and purification by column chromatography (hexane : acetone, 50 : 1) yielded *threo*-epoxytosylate **5a** (0.9 g) as white solid and *erythro*-epoxytosylate (0.5 g) as colourless oil

***Threo*-(5a)** : M.P. 53-56^{0}C. $[\alpha]_D$ = 8.3 (c=1, $CHCl_3$). lit. $[\alpha]_D$ = 8.7 (c=1, CCl_4),[4] $[\alpha]_D$ = 4.3 (c=0.7)[6]. PMR ($CDCl_3$) : δ 0.89 (t, J = 6Hz, 3H, CH_3), 1.25 (br, s, 18H, $(CH_2)_9$), 1.65 (m, 2H, CH_2-$CHOSO_2$), 2.45 (S, 3H, $ArCH_3$), 2.6 (dd, J = 5Hz; J_2 = 2.5Hz, 1H, oxirane CH_2), 2.75 (t, J = 5Hz, 1H, oxirane CH_2), 3(m, 1H, oxirane CH), 4.35 (q, J_1 = 5Hz, J_2 = 15Hz, 1H, CH-OSO_2), 7.35 (d, J = 7.5Hz, 2H, 3,5 Ar), 7.8 (d, J = 7.5Hz, 2H, 2,6-Ar). IR (KBr) : 3050, 1595, 1350 cm^{-1}. MS : m/z 227 (M^+ - $C_{11}H_{23}$), 227, 197, 173, 155 (bp), 91.

(2R,3R)-1,2-Epoxy-3-(tosyloxy)-tetradecane 5b **: 4b** on Tosylation afforded **5b.** Spectral data identical with **5a**. $[\alpha]_D$ = -7.2 (c=1, $CHCl_3$). lit. $[\alpha]_D$ = 7.3 (c=1, CCl_4).[4]

(8S,9S)-8-Hydroxy-9-tosyloxy icos-5-yne, 6a : A solution of 1-hexyne (0.3 g, 3.6 mmol) in 5ml of anhydrous THF was stirred at -78^{0}C. A solution of n-BuLi (1.5 ml, 2.4 M, 3.6 mmol) in hexane was added dropwise. The resulting dark yellow solution was stirred for 20 minutes and then to

this borontrifluoride ethylethereate (0.45 ml, 0.511 mg, 3.6 mmol) was added with syringe. After another 20 minutes, a solution of (±)-*threo*-epoxytosylate **5a** (0.5 g, 1.3 mmol) in THF (5 ml) was added and stirred for 1h at -78^{0}C. After that, the reaction was quenched, washed with NH_4Cl solution and extracted with ether. Ether layer was washed with water, brine and dried (anhyd. Na_2SO_4). Concentration under reduced pressure and purification by column chromatography (hexane : acetone, 20 : 1) afforded **6a** (0.425 g, 70%) as a colourless liquid. $[\alpha]_D$ = 6.4 (c=1, $CHCl_3$). PMR ($CDCl_3$) : δ 0.9 (m, 6H, 2 x CH_3), 1.1-1.7 (m, 24H, 12 x CH_2, 2.1-2.25 (m, 2H, CH_2-C≡C), 2.3-2.4 (m, 2H, C≡C-CH_2-CH-OH), 2.45 (S,3H, $ArCH_3$), 3.8-3.9 (br, s, 1H, CHOH), 4.6-4.7 (m, 1H, CH-OTs), 7.3 (d, J = 8.5Hz, 2H, aromatic), 7.8 (d, J = 8.5Hz, 2H, aromatic). IR (neat) : 3400, 1170 cm^{-1}. CIMS : m/z 465 (MH^+), 155, 91 (bp).

(8R,9R)-8-hydroxy-9-tosyloxy-icos-5-yne 6b : **5b** on alkylation with 1-hexyne in presence of BuLi and $BF_3.OEt_2$ afforded **6b**. The spectral data were identical with those of **6a**. $[\alpha]_D$ = -6.2 (c=1, $CHCl_3$).

(8S,9S)-8-Acetoxy-9-tosyloxy-icos-5-yne, 7a : The alcohol **6a** (0.4 g, 0.86 mmol) was taken in dry DCM and cooled to 0^{0}C. To this pyridine (0.1 g, 1.29 mmol) and catalytic amount of DMAP were added. Acetic anhydride(0.11 g, 1.03 mmol) was added and the reaction mixture was allowed to attain room temperature. After half an hour, reaction was quenched with water and extracted with DCM. The organic layer was washed successively with saturated $CuSO_4$ solution, water, brine and dried over anhyd. Na_2SO_4. Concentration and purification by column chromatography (hexane : acetone, 50 : 1) afforded **7a** (0.395 g, 90%) as colourless liquid. $[\alpha]_D$ = 5.7 (c=1, $CHCl_3$). PMR ($CDCl_3$) : δ 0.8-1.0 (m, 6H, 2 x CH_3), 1.1-1.7 (m, 24H, 12 x CH_2, 2 (s, 3H, $COCH_3$), 2.1 (m, 2H, CH_2-C≡C), 2.3-2.4 (m, 2H, C≡C-CH_2-CHOAc), 2.45 (s, 3H, $ArCH_3$), 4.7-4.85 (m, 1H, CH-OTs), 4.85-50 (m, 1H, CH-OAc), 7.3 (d, J = 8.5Hz, 2H, aromatic), 7.75 (d, J = 8.5Hz, 2H, aromatic). IR (neat) : 3050, 2930, 2210, (weak), 1730, 1170 cm^{-1}. CIMS: m/z 507 (MH^+), 155, 91 (bp), 43.

(8R,9R)-8-Acetoxy-9-tosyloxy-icos-5-yne 7b : **6b** on acetylation afforded **7b**. spectral data identical with **7a**. $[\alpha]_D$ = -5.6 (c=1, $CHCl_3$)

(8S,9S)-8-Acetoxy-9-tosyloxy-icos-5-ene, 8a : Compound **7a** (0.3 g, 0.6 mmol) was subjected to partial hydrogenation under atmospheric pressure over Lindlar catalyst (20 mg) in dry THF (5 ml) containing a drop of TEA. After absorbing the required amount of hydrogen (13.5 ml) the reaction mixture was filtered and concentrated to get **8a** (0.29 g) in almost quantitative yield. $[\alpha]_D$ = 5.4 (c=1, $CHCl_3$). PMR ($CDCl_3$) : δ 0.9 (t, 6H, 2 x CH_3), 1.1-1.4 (br, s, 20H, (10 x CH_2, 1.5-1.7 (m, 2H, CH_2-CH-OTs), 1.95 - 2.0 (s, 3H, $COCH_3$; m, 2H, CH_2-C=C), 2.2-2.4 (m, 2H, C=C-CH_2-CH-OAc), 2.45 (s, 3H, $ArCH_3$), 4.6-4.7 (m, 1H, CH-OTs), 4.8-4.9 (m, 1H, CH-OAc), 5.15-5.3 (m, 1H, olefinic) 5.35 - 5.5 (m, 1H, olefinic), 7.3 (d, J = 8.5Hz, 2H, aromatic), 7.8 (d, J=8.5Hz, 2H, aromatic). IR (neat) : 3050, 2930, 2220, (weak), 1735, 1150 cm^{-1}. CIMS : m/z 509 (MH^+), 155, 91 (bp), 43.

(8R,9R)-8-acetoxy-9-tosyloxy-icos-5-ene, 8b : **7b** on acetylation afforded **8b**. The spectral data are identical with those of **8a**. $[\alpha]_D$ = -5.2 (c=1, $CHCl_3$).

(3S,4S)-3-Acetoxy-4-tosyloxy pentadecanal, 9a : Ozone gas was bubbled into solution of **8a** (0.3 g, 0.59 mmol) in dry DCM (10 ml) at -78^{0}C until the solution becomes saturated with ozone. The ozonide was quenched with DMS (41 ml) and stirred for 2h. Dried over anhyd. Na_2SO_4 filtered and concentrated at reduced pressure. The crude aldehyde was used as such in Wittig reaction.

(3R,4R)-3-Acetoxy-4-tosyloxy pentadecanal 9b : **8b** on ozonolysis afforded **9b.**

Tetrahydropyranyloxy hex-5-yne-3-ene, 10 : Diethylamine (50 ml), $Pd(PPh_3)_4$ (0.1 g), cuprous iodide(0.1 g) and homopropargylic alcohol THP ether (10 g, 63.9 mmol) are taken in a 100 ml R.B. flask. The contents were warmed to 60^{0}C and stirred for 1h. Then vinyl bromide(200 mmol) along with 30 ml of dry ether was added portionwise to it. Cold finger was provided inside the flask for 2-3 h and the mixture was stirred for 12 h at room temperature. During this period ether was added for effective stirring. The suspension was filtered with a sintered funnel and rinsed thoroughly with ether. The filtrate was concentrated and washed with aqueous ammonium chloride, water, brine, dried (anhyd. Na_2SO_4) and concentrated. Purification by column chromatography (hexane) afforded **10** (8.7 g, 75%) as dark red oil. PMR ($CDCl_3$) : δ

1.4-2.0 (m, 1H, $(CH_2)_3$), 2.55-2.8 (t, 2H, J = 6.7 Hz, CH_2-C≡C), 3.4-3.7 (m, 2H, CH_2-O), 3.7-4.0 (m, 2H, CH_2-O), 4.65 (S, 1H, O-CH-O), 5.35-5.85 (m, 3H, olefinic). IR (neat) : 2210 (weak), 1600, 1160, 1080, 1020 cm^{-1}. MS : m/z 180 (M^+), 86 (bp).

Hex-5-yn-3-en-1-ol, 11 : p-TSA (catalytic) was added to a solution of **10** (8.5 g, 4.7 mmol) in methanol (30 ml) and stirred for 18 h. Methanol was removed and the residue was dissolved in ether. The ether layer was washed with water, $NaHCO_3$ solution, brine and dried over anhyd. Na_2SO_4. Concentration at reduced pressure and purification by column chromatography (hexane : acetone, 10 : 1) afforded **11** (4 g, 90%) as light yellow oil. PMR ($CDCl_3$) : δ 2.6 (t, J = 6Hz, 2H, CH_2-C≡C), 3.6 (br, s, 2H, CH_2-OH), 5.35-5.85 (m, 3H, olefinic). I.R : 3350, 3075, 3010, 2220 (weak) cm^{-1}. MS : m/z 96 (M^+), 78 (M^+ - 18).

(3Z,5)-Hexadienol, 12 : To a solution of **11** (4 g, 41.7 mmol) in THF (50 mmol), one drop of TEA was added. Lindlar catalyst (50 mg) was added and stirred under hydrogen until required amount of hydrogen gas (41.7 mmol, 931 ml) is absorbed. The reaction mixture was filtered and concentrated under reduced pressure to afford **12** (4 g) in almost quantitative yield. PMR ($CDCl_3$) : δ 2.4 (t, J = 6Hz, 2H, CH_2-C=C), 3.65 (t, J = 6.7Hz, 2H, CH_2-OH), 4.9-5.85 (m, 3H, olefinic), 6.05 (deformed t, 1H, olefinic), 6.65 (m, 1H, olefinic). IR (neat) : 3350, 3095, 3020, 1650, 1600cm^{-1}. MS : m/z 98 (M^+), 80, 67 (bp).

1-Iodo-(3Z,5)-hexadiene, 13 : To the stirred solution of the compound **12** (3.5 g, 35.7 mmol) in dry benzene, TPP (13.1 g, 49.9 mmol), iodine (5.9 g, 46.4 mmol) and imidazole (7.3 g, 107 mmol) are added and stirred at room temperature for 40 minutes. TLC was monitored, when reaction was complete, mixture was decanted. The pasty mass (red brown) was washed with ether. Solvents were evaporated and the residue was purified by column chromatography (hexane) to give **13** (7.2 g, 90%) as colourless oil with caution to avoid exposure to strong light. PMR ($CDCl_3$) : δ 2.4 (t, J = 7Hz, 2H, CH_2-C=C), 3.25 (t, J = 7.75Hz, 2H, CH_2-I), 4.9-5.85 (m, 3H, olefinic), 6.05 (deformed t, 1H, olefinic), 6.65 (m, 1H, olefinic). IR (neat) : 3075, 3020, 1650, 1600, 500 cm^{-1} MS : m/z 208 (M^+), 81 (bp).

(3Z)-Hexaa1,3-dienyl triphenylphosphonium iodide, 14 : Compound **13** (6.5 g, 31.1 mmol) was taken in dry benzene and to this TPP (9 g, 34.2 mmol) was added. The reaction mixture was refluxed for 24h under nitrogen atmosphere. Reaction mixture was cooled back to room temperature. Benzene was evaporated and to this dry hexane was added upon which white solid separated out. This was filtered, washed with dry hexane and air dried. PMR ($CDCl_3$) : δ 2.4 (m, 2H, C=C-CH_2), 3.95 (m, 2H, CH_2-P) 4.9-5.85 (m, 3H, olefinic), 6.05 (deformed t, 1H, olefinic), 6.65 (m, 1H, olefinic), 7.8 (m, 15H, Ar).

(3Z,6Z)-cis-9S,10R-Epoxy-1,3,6-henicosatriene : To a suspension of (3Z)-hexa-1,3-dienyltriphenylphosphonium iodide (0.4 g, 0.85 mmol) in dry THF (5 ml) under nitrogen atmosphere at -78^{0}C, a solution of NaHMDS (0.68 mmol, 1 M, 0.68 ml) in hexane was added. The reaction mixture was allowed to attain room temperature and stirred for half an hour. The resulting dark ylide solution was slowly added to a precooled (-78^{0}C) solution of aldehyde **9a** (0.25 g, 0.57 mmol) in dry THF (5 ml) under nitrogen atmosphere. The reaction mixture was stirred at -78^{0}C for 1 h and slowly allowed to attain 0°C. After 1 h, reaction mixture was quenched with saturated ammonium chloride solution. The ether layer was washed with water, brine and dried (anhyd. Na_2SO_4). Concentration at reduced pressure and purification by column chromatography (hexane : acetone, 50 : 1) afforded (9S,10R)-**I** (70mg, 40%) as low melting solid (m.p. = 14-15^{0}C). $[\alpha]_D$ = -0.45 (c=1.97, $CHCl_3$), lit. $[\alpha]_D$ = -0.41 (c=1, $CHCl_3$)[3] PMR ($CDCl_3$, 400 MHz) : δ 0.88 (t, J = 6.8Hz, 3H), 1.1-1.7 (m, 20H), 2.2-2.3 (m, 1H), 2.3-2.4 (dd, J = 6.0, 14.4Hz, 1H), 2.8-3.0 (m, 4H), 5.13 (dd, J = 7.0 17Hz, 1H), 5.22 (dd, J = 2.0, 17.0Hz, 1H), 5.41 (dd, J = 8.0, 18.0Hz, 1H), 5.45-5.57 (m, 2H), 6.05 (deformed t, 1H, olefinic), 6.65 (dddd, J = 1.1, 10.0, 11.0, 17.0Hz, 1H, olefinic). IR (film) : 3090, 3020, 2930, 2860, 1640, 1590, 1460, 1380, 1260, 995, 900, 720 cm^{-1}. HRMS : calcd. for $C_{21}H_{36}O$: 304.2766, found : 304.2742

(3Z,6Z)-cis-9R,10S-epoxy-1,3,6-henicosatriene : **9b** on Wittig olefination with **14** afforded (9R,10S)-isomer of **I**. Its spectral data were identical with those of (9S,10R)-isomer. $[\alpha]_D$ = 0.43 (c=1, $CHCl_3$), lit. $[\alpha]_D$ = 0.43 (c=2.39, $CHCl_3$).[3] HRMS : calcd for $C_{21}H_{36}O$: 304.2766, found 304.2746.

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References :

1. Mathur AC. *Ind. J. Ent.*, **1962**; 24:286-287.
2. Persoons CJ, Yadav JS, Prasad AR, Subhashini S, Prasoona AL, Jyothi KN, *IOBC/WPRS Bulletin*, **1993**; 16: 136-140.
3. Mori K, Tadashi Takeuchi. *Liebigs Ann. Chem.*, **1989**; 453-457.
4. Thomas WB, James AC. *J. Org. Chem.*, **1993**; 58:5153-5162.
5. Bestmann WS, Olto V, *Chem. Ber.*, **1976**; 109:1694-1700.
6. Soulie J, Boyer T, Lallemand JY. Tett. Assym., 1995; 625-636.
7. Yadav JS, Sekhram T, Gadgil VR. JCS. Chem. Commun., 1990; 843-844.