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A NEW SYNTHESIS OF ANGULARLY SUBSTITUTED BICYCLIC SYSTEMS VIA AN ANIONIC OXY-COPE REARRANGEMENT

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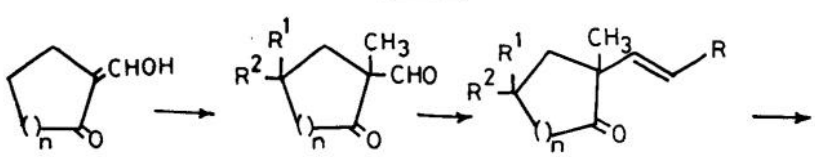
Abstract - A general synthesis of trans bicyclic carbinols with an angular methyl substituent using the anionic oxy-Cope rearrangement is reported. The carbinols 13a, 13b, 14a, 14b and 15 furnish the bicyclic carbinols 16a, 16b, 17a, 17b and 18 when treated with potassium hydride in 1,2-dimethoxyethane.

Anionic oxy-Cope rearrangements of 1,2-divinylcycloalkan-1-ols have been reported[1] to result in ring expansions. In a preliminary communication[2] we reported the synthesis of angularly substituted octalins - a ring system present in vetivene type sesquiterpenes via an anionic oxy-Cope rearrangement. We report herein full details of these studies and their extension to the synthesis of angularly methyl substituted trans hydrindane and trans bicyclo(5.4.0) undecane systems. The synthesis of trans hydrindane system with an angular methyl group has been a continuing challenge to organic chemists over the years because of its presence in steroids. Several approaches to this ring system have appeared in the literature[3,4,5]. The trans bicyclo(5.4.0) undecane ring system is present[6,7] in marine products like Dolastriol and Amijiol etc. Though a limited number of derivatives are known[8,9a,b] the parent bicyclic trans(5.4.0) undecane system itself has not been reported. Scheme 1 outlines the general reaction sequence for the synthesis of the bicyclic systems mentioned :

Scheme-1



n=1, n=2, n=3

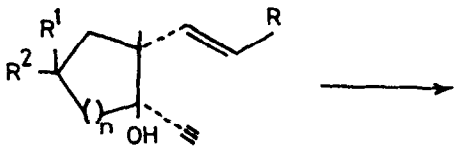
n=1 4a $R^1=R^2=CH_3$, 4b $R^1=R^2=H$

n=2 5 $R^1=R^2=H$, n=3 6 $R^1=R^2=H$

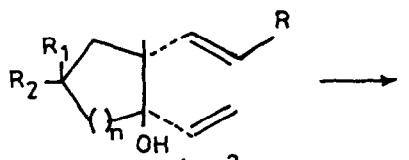
n=1 7a $R^1=R^2=CH_3$; R=COOEt, 7b $R^1=R^2=H$; R=COOEt

n=2 8a $R^1=R^2=H$; $R=COCH_3$, 8b $R^1=R^2=H$; R=COOEt

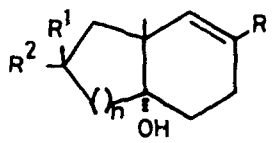
n=3 9 $R^1=R^2=H$, R=COOEt



n = 1 10a $R^1 = R^2 = CH_3$; R = COOEt
10b $R^1 = R^2 = H$; R = COOEt
n = 2 11a $R^1 = R^2 = H$; $R = COCH_3$
11b $R^1 = R^2 = H$; R = COOEt
n = 3 12 $R^1 = R^2 = H$; R = COOEt



n = 1 13a $R^1 = R^2 = CH_3$; R = COOEt
13b $R^1 = R^2 = H$; R = COOEt
n = 2 14a $R^1 = R^2 = H$; $R = COCH_3$
14b $R^1 = R^2 = H$; R = COOEt
n = 3 15 $R^1 = R^2 = H$; R = COOEt

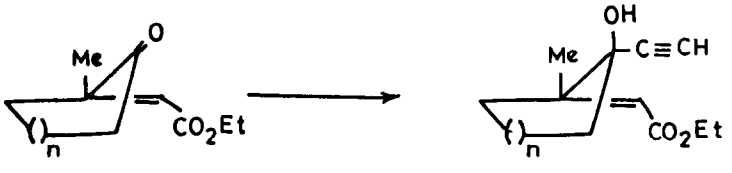


n = 1 16a $R^1 = R^2 = CH_3$; R = COOEt
16b $R^1 = R^2 = H$; R = COOEt
n = 2 17a $R^1 = R^2 = H$; $R = COCH_3$
17b $R^1 = R^2 = H$; R = COOEt
n = 3 18 $R^1 = R^2 = H$, R = COOEt

Some 2-methyl-2-(2'-substituted vinyl)cyclohexanones of the type 8a have been obtained[10,11,12] by Michael addition of 2-methylcyclohexanone to 1-chloropent-1-en-3-one and methyl 3-chloroacrylate. Woodward and Singh have reported[10] the Michael addition of 2-methylcyclohexanone to methyl ethynyl ketone in which a compound of the type 8a has been implicated but not isolated. The yields are unsatisfactory in the above methods and a new synthetic route for this class of compounds was worked out with 2-formyl-2-methylcyclohexanone 5 as the starting material. The preparation of this ketoaldehydes (as well as 4b & 6) was very much improved by methylation of 2-hydroxymethylenecycloalkanones with methyl iodide in dry t-butyl alcohol containing potassium t-butoxide at room temperature to give 50-70% of the

products in contrast to a published method[13]. The formyl cyclopentanone 4a was however obtained by the published[14] method. Wittig-Horner reaction of the 2-methyl-2-formylcycloalkanones 4b, 5 and 6 with triethylphosphonoacetate using sodium hydride in 1,2-dimethoxyethane gave the unsaturated ester 7b, 8b and 9 in 50-60% yields. The synthesis of compounds 7a, 8a and 8b has been already reported from this laboratory in connection with related studies[15]. The use of phosphoranes led to similar yields of products in this reaction. The formyl cyclohexanone 5 furnished the unsaturated dione 8a also in ca 50% yield upon treatment with 2-oxypropylidenetriphenylphosphorane in benzene. All these products had a coupling constant of 18 Hz for the olefinic protons thereby indicating the E stereochemistry of the olefinic double bond.

Regioselective ethynylation of cyclohexanone 8a & 8b occurred in 80% yield with lithium acetylide in THF or liquid ammonia at -78°C while the remaining ketones (7a, 7b, 9) afforded the corresponding ethynyl carbinols in 45-50% in THF only. Partial reduction of these ethynyl carbinols in pyridine ($Pd/CaCO_3$) gave excellent yields (ca 80%) of the vinyl carbinols 13a, 13b, 14a, 14b and 15 respectively. Though the stereochemistry of the above vinyl and ethynyl alcohols has not been determined unequivocally, it is presumed that the unsaturated moieties in these alcohols are cis to each other, in view of the fact that the vinyl alcohols rearrange readily; the cis geometry of the oledinic moieties is known to[1,16,17,18] favour concerted 3,3 shifts. Also the ethynylations of cycloalkanones 7b, 8b and 9 may be expected to occur from the less hindered side to give the carbinols 10b, 11b and 12 in which the ethynyl and olefinic groups are cis to each other.



7b, 8b, 9 10b, 11b, 12

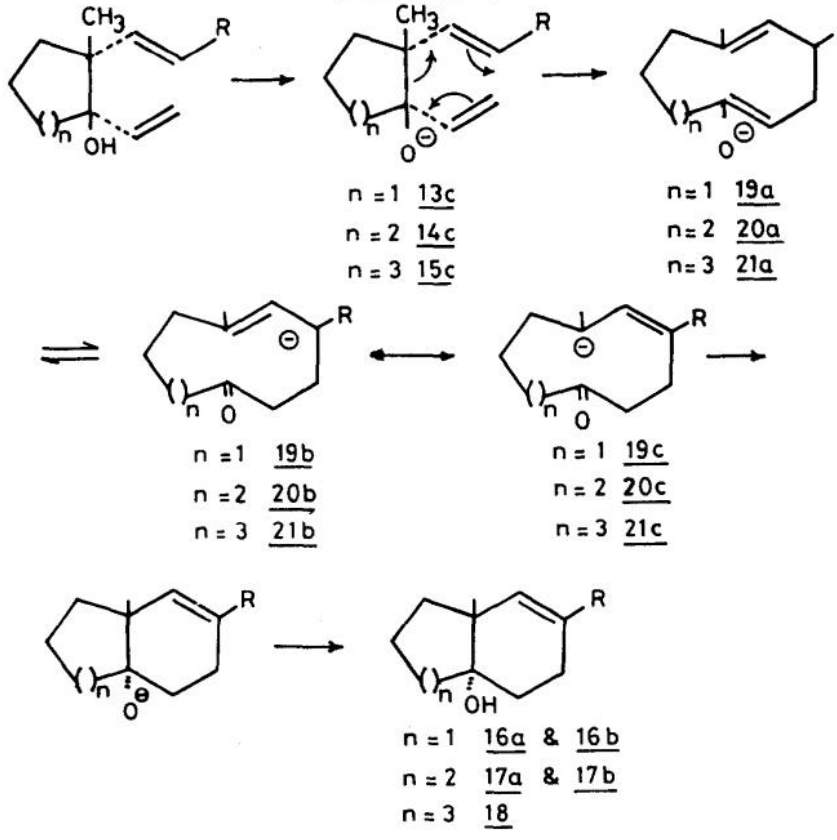
Treatment of the vinyl carbinols with potassium hydride in 1,2-dimethoxyethane at 0°C followed by workup and chromatography afforded the bicyclic carbinols (16a, 16b, 17a, 17b and 18) as major products in 40-50%

yield. The structures of these products were consistent with their ir & pmr data.

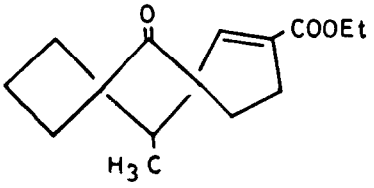
Stereochemical and mechanistic considerations :

The trans stereochemistry for the hydrindanols 16a & 16b is assigned on the basis of a) the appearance of their angular methyls at δ 0.95 and δ 1.00 respectively and b) mechanistic considerations. An angular methyl group in trans hydrindane derivatives is reported[4,19,20] to appear around δ 0.7-0.95 whereas in the corresponding cis isomers, it appears above δ 1.1. By analogy, the carbinols 17a, 17b and 18 are assigned a trans stereochemistry. Mechanistic considerations also favour a similar assignment. The transformation of the vinyl carbinols 13a, 14a and 15 (also 13b & 14b) involves the rearrangement of their enolates 13c, 14c and 15c to species 19a, 20a and 21a which may equilibrate with species 19b, 20b and 21b respectively.

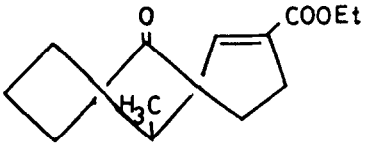
Scheme II



The formation of trans hydrindanol could involve transition state A or B. The medium ring geometry and steric factors will favour A more than B as the oxygen and the methyl group are away from each other in the former resulting in the trans orientation of the hydroxy and angular methyl groups in the products as the transannular bond formation takes place. A similar transition state for a related reaction has been proposed[21] by Stork et al. The overall transformation is essentially a latent anionic oxy-Cope rearrangement as the net result of the reaction is the formation of a sigma bond between the terminal olefinic carbon atoms without any apparent skeletol rearrangement. Mechanistically, the stereochemistry of the products is not

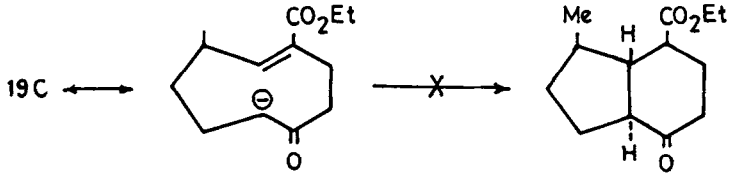


A



B

dependent on the stereochemistry of the starting materials. The conversion of the species 19c to the bicyclic carbinol 16b and the other similar conversions reported here are essentially vinylogous aldol condensations. An alternative internal Michael addition of the type indicated below can be envisaged but no products corresponding to such a reaction have been isolated.



In fact, the work cited[19] above refers to such a reaction.

Experimental

All melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 598 instrument. PMR & CMR spectra were recorded in a Varian EM-390 and Jeol FX 90Q instruments respectively. The chemical shifts are given in ppm downfield from the internal TMS. Mass spectra were recorded using Varian Mat CH-7 mass spectrometer. TLC was developed on glass plates coated with silica gel-G(ACME) of 0.25 mm thickness and visualised with iodine. Anhydrous sodium sulphate was used as the

drying agent.

The hydroxyformylation of cycloalkanones was done by an improved procedure[22].

Alkylation of 2-formylcycloalkanones (1,2,3) : General procedure

To a well stirred solution of potassium t-butoxide(33.6 g, 0.3 mole) in t-butyl alcohol (250 ml) was added 1 (33.6 g, 0.3 mole) slowly over a period of 45 min. To the resulting solution, methyl iodide was added dropwise (49 g, 0.35 mole) followed by stirring for 6 hr. The precipitated potassium iodide was filtered off. Removal of the solvent afforded the crude product which was distilled under reduced pressure to yield 4b (20 g, 52%). bp. 69-70°/0.5 mm. IR(CCl_4) ν max 1740, 1720 cm^{-1}; PMR(CCl_4/TMS) δ 1.1(S, 3H), 1.6-2.0 (m, 4H, alicyclic methylenes), 2.2-2.4(m, 2H, CH_2-C=O), 9.6 (s, 1H, H-C=O). Compound 5 was obtained in 70% yield and the yield of 6 was 52%. Compound 6 bp.69-72°/0.7 mm. IR(CCl_4) ν max 1730, 1705 cm^{-1}; PMR(CCl_4/TMS) δ 1.1(s, 3H), 1.6-2.0(m, 8H, alicyclic methylenes), 2.2-2.4(m, 2H, O=C-CH_2), 9.6(s, 1H, H-C=O).

Wittig reaction of 2-formyl-2-methylcycloalkanones 4a, 4b, 5 and 6 with triethylphosphonoacetate

General procedure : A solution of triethylphosphonoacetate (0.1 mole) in 1,2-dimethoxyethane (20 ml) was added dropwise to a well stirred suspension of sodium hydride (2.4 g, 0.1 mole) in the same solvent (100 ml). Then 4b (12.6 g, 0.1 mole) was added slowly keeping the temperature below 35°. The reaction mixture was further stirred for 4 hr at room temperature. The formation of a thick gelatinous semisolid indicated completion of the reaction. The mixture was poured into water (200 ml) and extracted with chloroform (3 x 100 ml). The extract was dried, concentrated and distilled at vacuum to yield 7b (10.2 g, 52%). b.p. 82-84°/0.1 mm. IR(CCl_4) ν max 1740, 1720, 1640 cm^{-1}; PMR(CCl_4/TMS) δ 1.1 (s, 3H), 1.2 (t, 3H), 1.5-1.9(m, 6H, alicyclic methylenes), 4.15(q, 2H), 5.8(d, 1H, O=C-CH=CH, J = 18Hz), 7.1(d, 1H, O=C-CH=CH- J = 18Hz). Analysis $C_{11}H_{16}O_3$ requires C=67.32, H=8.21; found C=67.44, H=8.25%. Compound 9 (58%) bp 120°/0.3 mm. IR(CCl_4) ν max 1705-15,1640 cm^{-1}; PMR(CCl_4/TMS) δ 1.1(s, 3H), 1.2(t, 3H), 1.5-2.2(m, 10H), 4.15 (q, 2H), 5.8(d, 1H, O=C-CH=CH, J = 18Hz), 7.0(d, 1H, O=C-CH=CH, J = 18Hz). Analysis $C_{13}H_{20}O_3$ requires C=69.61, H=8.98, Found C=69.74, H=8.92%.

Ethynylation of substituted cycloalkanones 7a, 7b, 8a, 8b and 9 : General procedure :

A stream of acetylene was bubbled through dry tetrahydrofuran (200 ml) for 2 hr at -78° under nitrogen. Then n-butyllithium (20 m moles) in

dry ether(100 ml) was added dropwise over a period of 20 min. The resulting solution of lithium acetylide was stirred for 10 min and a solution of 7b (3.92 g, 20 m moles) in dry tetrahydrofuran(25 ml) was added over a period of 10 min. It was stirred at -78° for 2.5 hr and then allowed to warm to room temperature. Water (20 ml) was added followed by potassium carbonate until the aqueous phase became pasty. The organic phase was decanted and the aqueous layer was washed with ether (2 x 50 ml). The combined organic phase was dried and the solvent was distilled off to give a crude product which was chromatographed over a column of silica gel. Elution with hexane: ethyl acetate (5:1) gave the starting material (1 g) which was identified by its ir and pmr spectra. Further elution with hexane:ethyl acetate (2:1) afforded 1-hydroxy-1-ethynyl-2-methyl-2(2'-carbethoxyvinyl)cyclopentane 10b as a light yellow liquid (2 g, 45%). IR($CHCl_3$) ν max 3600, 3300, 1720,1640 cm^{-1}; PMR($CDCl_3$/TMS) δ 1.1(s, 3H), 1.2(t,3H), 1.5-2.1(m,7H alicyclic methylenes and hydroxyl), 2.5(s, 1H, C≡CH), 4.1(q, 2H), 5.8(d, 1H, O=C-C<u>H</u>=CH- J = 18Hz), 7.2(d, 1H, O=C-CH=C<u>H</u> J = 18Hz). MS : m/e 222. Analysis $C_{13}H_{18}O_3$ requires C = 70.24, H = 8.16, Found C = 70.48, H = 8.21%. Compound 10a (45%) mp. 71-72° (CCl_4-hexane). IR(CCl_4) ν max 3600, 1720, 1640 cm^{-1}; PMR (CCl_4/TMS) δ 1.15(s, 3H), 1.2(s, 3H), 1.27(s, 3H), 1.3(t, 3H), 1.5-2.2 (m, 5H, alicyclic methylenes and hydroxyl), 2.5(s, 1H, C≡CH), 4.2(q, 2H), 5.8 (d, 1H, O=C-C<u>H</u>=CH-, J = 18Hz), 7.2(d, 1H, O=C-CH=C<u>H</u>, J = 18Hz). Analysis $C_{15}H_{22}O_3$ requires C = 71.97, H = 8.86, Found C = 72.18, H = 9.09%. Compound 11a (80%) mp 65-66° (CCl_4-hexane) IR(CCl_4) ν max 3600, 3300, 1670, 1620 cm^{-1}; PMR(CCl_4/TMS) δ 1.2(s, 3H), 1.5-1.8(m, 8H, alicyclic methylenes) 2.3(s, 3H) 2.55(s, 1H, C≡C<u>H</u>) 3.2(bs, 1H, -OH), 6.2(d, 1H, O=C-C<u>H</u>, J = 18Hz), 7.3(d, 1H, O=C-CH=C<u>H</u>, J = 18Hz). MS : m/e 206. Analysis $C_{13}H_{18}O_2$ requires C = 75.72, H = 8.73, Found C = 75.53 H = 8.68%. Compound 11b (80%) hexane : benzene (9:1). IR(CCl_4) ν max 3600, 3300, 1720, 1640 cm^{-1}; PMR(CCl_4/TMS) δ 1.2(s,3H) 1.3(t, 3H), 1.4-1.8(m, 8H), 2.5(s, 1H), 2.55(bs, 1H), 4.2(q, 2H), 5.8(d, 1H, O=C-C<u>H</u>=CH, J = 18Hz), 7.3(d, 1H, O=C-CH=C<u>H</u> J = 18Hz). Analysis $C_{14}H_{20}O_3$ requires C = 71.13, H = 8.53, Found C = 71.47, H = 8.58%. Compound 12 (50%) bp 128-129°/0.05. IR($CHCl_3$) ν max 3600, 3300, 1720, 1640 cm^{-1}; PMR($CDCl_3$/TMS) δ 1.1(s, 3H), 1.2(t, 3H), 1.5-2.1(m, 11H alicyclic methylene and hydroxyl), 2.5(s, 1H, C≡CH), 4.15(q, 2H), 5.8(d, 1H, O=C-C<u>H</u>=CH, J = 18Hz), 7.2(d, 1H, O=C-CH=C<u>H</u>, J = 18Hz). CMR($CDCl_3$/TMS) values in ppm[23]. 165.6(s, C_{11}), 151.63 (d,C_9), 119.94(d,C_{10}), 86.58(s,C_1), 74.43(d,C_{15}), 73.52(s,C_{14}), 60.61(t,C_{12}), 54.22(s,C_2), 21.58(q,C_{13}), 14.48(q,C_8) and other carbons at 43.08, 41.06, 36.94, 27.28, 25.02. Analysis $C_{15}H_{22}O_3$ requires C = 71.96, H = 8.85, Found C = 71.82, H = 8.81%.

Hydrogenation of ethynyl carbinols 10a, 10b, 11a, 11b and 12 :

A solution of ethynyl carbinol 10b (2g) in dry pyridine (20 ml) was hydrogenated over 5% palladium on calcium carbonate (0.1 g) at 40 psi for 30 min. The catalyst was filtered and the solvent was removed by distillation under reduced pressure. The residue was dissolved in ether (100 ml) and washed with 1% ice-cold hydrochloric acid and water (2 x 20 ml). After drying the solvent was evaporated to give a crude product which was chromatographed over silica gel. Elution with hexane:ethyl acetate(2:1) yielded pure 13b as a light yellow liquid (1.6 g, 80%). IR($CHCl_3$) ν max 3600, 1720, 1640 cm^{-1}; PMR($CDCl_3$/TMS) δ 1.05(s, 3H), 1.2(t, 3H), 1.5-2.1(m, broad, 7H, alicyclic methylenes and hydroxyl), 4.15(q, 2H), 5.2(m, 2H, -CH=C<u>H</u>$_2$) 5.8(d, 1H, O=C-C<u>H</u>=CH, J = 18Hz), 5.9(m, 1H, -C<u>H</u>=CH_2), 7.2(d, 1H, O=C-CH=C<u>H</u>-, J = 18Hz). Analysis $C_{13}H_{20}O_3$ requires C = 69.61, H = 8.98, Found C = 69.52, H = 8.96%.

Compound 13a (80%) IR(CCl_4) ν max 3600, 1720, 1640 cm^{-1}; PMR(CCl_4/TMS) δ 1.15(s, 3H), 1.2(s, 3H), 1.27(s, 3H), 1.3 (t, 3H), 1.5-2.2(m, 5H, alicyclic methylenes and hydroxyl), 4.15(q, 2H), 5.2 (m, 2H, -CH=C<u>H</u>$_2$), 5.8(d, 1H, O=C-C<u>H</u>=CH J = 18Hz), 7.2(d, 1H, CO-CH=C<u>H</u>-, J = 18Hz).

Compound 14a (80%) IR(CCl_4) ν max 3600, 1670, 1620 cm^{-1}; PMR(CCl_4/TMS) δ 1.2(s, 3H), 1.4-1.8(m, 9H, alicyclic methylene and hydroxyl), 2.2(s, 3H), 5.3(m, 2H, -CH=C<u>H</u>$_2$), 6.0 (d, 1H, O=C-CH=C<u>H</u>-, J = 18Hz), 6.2(m, 1H, C<u>H</u>=CH_2), 7.2(d, 1H, O=C-CH=C<u>H</u>- J = 18Hz).

Compound 14b (80%) IR(CCl_4) ν max 3600, 1720, 1640 cm^{-1}; PMR(CCl_4/TMS) δ 1.1(s, 3H), 1.2(t, 3H), 1.4-1.8(m, 9H, alicyclic methylenes and hydroxyl), 4.2(q, 2H), 5.3(m, 2H, CH=C<u>H</u>$_2$), 5.7(d, 1H, O=C-C<u>H</u> J = 18Hz), 6.0(m, 1H, -C<u>H</u>=CH_2), 7.3(d, 1H, O=C-CH=C<u>H</u>- J = 18Hz).

Compound 15 (80%) IR($CHCl_3$) ν max 3600, 1720, 1640 cm^{-1}; PMR($CDCl_3$/TMS) δ 1.05(s, 3H), 1.2(t, 3H), 1.5-2.0(m, broad, 11H, alicyclic methylenes and hydroxyl), 4.15(q, 2H), 5.2(m, 2H, -CH=C<u>H</u>$_2$), 5.8(d, 1H, O=C-C<u>H</u>=CH-, J = 18Hz), 5.9(m, 1H, C<u>H</u>=CH_2), 7.2(d, 1H, -CO-CH=C<u>H</u>- J = 18Hz). Analysis $C_{15}H_{24}O_3$ requires C = 71.39, H = 9.58, Found C = 71.52, H = 9.48%.

Rearrangement of vinyl carbinols 13a, 13b, 14a, 14b and 15 :

To a stirred suspension of potassium hydride (0.4 g, 10 m mole) in dry 1,2-dimethoxyethane(20 ml) was added slowly a solution of vinyl carbinol 13b (1.12 g, 5 m moles) in the same solvent (5 ml) at 0° under nitrogen. The reaction mixture was maintained at 0° for 1 hr, then it was decomposed by the addition of saturated ammonium chloride solution and extracted with

chloroform(2 x 25 ml). The dried extract was concentrated to give a viscous liquid which was chromatographed over a column of silica gel to afford pure 16b (0.4 g, 40%). IR($CHCl_3$) ν max 3600, 1720, 1640 cm^{-1}; PMR($CDCl_3$/TMS) δ 1.00(s, 3H), 1.2(t,3H), 1.5-2.1(m, 11H), alicyclic methylenes and hydroxyl) 4.15(q, 2H), 6.6(s, 1H, CO-C=C<u>H</u>) MS : m/e 224 Analysis $C_{13}H_{20}O_3$ requires C = 69.61, H = 8.98; Found C = 69.74, H = 8.92%.

Compound 16a (40%) IR(CCl_4) ν max 3600, 1720, 1650 cm^{-1}; PMR(CCl_4/TMS) δ 0.95(s, 3H), 1.05(s, 3H), 1.2(s, 3H), 1.3(t, 3H), 1.5-2.4(m, 9H, alicyclic methylene and hydroxyl), 4.15(q, 2H), 6.55(s, 1H, O=C-C=C<u>H</u>). Analysis $C_{15}H_{24}O_3$ requires C = 71.39, H = 9.59, Found C = 71.05, H = 9.50%.

Compound 17a (50%) IR(CCl_4) ν max 3600, 1670, 1640 cm^{-1}; PMR(CCl_4/TMS) δ 1.2(s, 3H), 1.4-1.8(m, 11H, alicyclic methylenes and hydroxyl), 2.2(s, 3H), 2.4(m, 2H, -C<u>H</u>$_2$-C=CH-), 6.4(s, 1H, -CO-C=C<u>H</u>-). Analysis $C_{13}H_{20}O_2$ requires C = 75.00, H = 9.61, Found C = 74.83, H = 9.58%.

Compound 17b (50%) IR(CCl_4) ν max 3600, 1720, 1650 cm^{-1}; PMR(CCl_4/TMS) δ 1.1(s, 3H), 1.2(t, 3H), 1.4-1.8(m, 11H, alicyclic methylenes and hydroxyl), 2.4(m, 2H, -C<u>H</u>$_2$-C=CH), 4.2(q, 2H), 6.5(s, 1H, -CO-C=C<u>H</u>-). Analysis - $C_{14}H_{22}O_3$ requires C = 70.59, H = 9.24, Found C = 70.55, H = 9.28%.

Compound 18 (45%) IR($CHCl_3$) ν max 3600, 1720, 1640 cm^{-1}; PMR($CDCl_3$/TMS) δ 1.05(s, 3H), 1.2(t, 3H), 1.5-2.4(m, 15H, alicyclic methylene and hydroxyl), 4.15(q, 2H), 6.5(s, 1H, O=C-C=C<u>H</u>). CMR[23] ($CDCl_3$/TMS), 165.48 (s, C_{11}), 151.52(d, C_1), 119.42(s, C_2), 73.85(s, C_{4a}), 60.85(t, C_{12}), 54.87(s, C_{9a}), 21.42(q, C_{13}), 14.28(q, C_{10}) and other carbons at 43.82, 41.29, 36.42, 35.52, 33.78, 27.28, 25.02 MS : m/e 252. Analysis $C_{15}H_{24}O_3$ requires C = 71.39, H = 9.58, Found C = 71.52, H = 9.51%. TLC analysis of the crude products in all the above rearrangements showed other minor sports in addition to the rearrangement products isolated above; no useful products corresponding to the minor spots could be obtained by preparative TLC.

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References

1) Gadwood, R.C.; Lett, R.M. J. Org. Chem. 1982, 47, 2268 and references cited therein.

2) Thangaraj, K.; Srinivasan, P.C.; Swaminathan, S. Tet. Lett. 1982, 23,4983

3) Stork, G.; Atwal, K.S. Tet. Lett. 1983, 24, 3819.

4) Narula, A.S.; Paul Sethi, S. ibid 1984, 25, 685.

5) Corey E.J.; Engler, T.A. ibid, 1984, 25, 149 and references cited therein.

6) Petit, C.R. J. Am. Chem. Soc. 1976, 98, 4677.

7) Crews, P.; Klein, T.E.; Hogue, E.R.; Myers, B.L. J. Org. Chem. 1982, 47, 811.

8) Selvarajan, R.; John, J.P.; Narayanan, K.V.; Swaminathan, S. Tetrahedron 1966, 22, 949.

9) a) Ireland, R.E.; Thompson, W.J.; Srouji, G.J.; Rolf Etter, J. Org.Chem. 1981, 46, 4863.

b) Ireland, Robert, E.; Aristoff, Paul A.; Hoyng, Charles, F.; J. Org. Chem. 1979, 44, 4318.

10) Woodward, R.B.; Singh, T. J. Am. Chem. Soc. 1950, 72, 494.

11) Hills, P.R.; Mcquillen, F.J. J. Chem. Soc. 1953, 4060.

12) House, H.O.; Roelofs, W.L.; Trost, B.M. J. Org. Chem. 1966, 31, 646.

13) Sen, H.K.; Mondal, K. J. Ind. Chem. Soc. 1928, 5, 609.

14) Ryerson, G.D.; Wasson, R.L.; House, H.O. Org. Syntheses Coll. Vol.IV, 1963, 957.

15) Thangaraj, K.; Srinivasan, P.C.; Swaminathan, S. Synthesis 1982, 855.

16) Berson, J.A.; Jones Jr, M. J. Am. Chem. Soc. 1964, 86, 5017, 5019.

17) Evans, D.A.; Golob, A.M. J. Am. Chem. Soc. 1975, 97, 4765.

18) Miyashi, T.; Hazato, A.; Mukai, T. J. Am. Chem. Soc. 1978, 100, 1008.

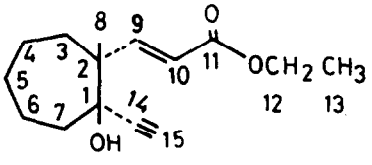
19) Stork, G.; Shiner, C.S.; Winkler, J.D. J. Am. Chem. Soc. 1982, 104,3767

20) Hajos, Z.G.; Parrish, D.R. J. Org. Chem. 1974, 39, 1615.

21) Stork, G.; Winkler, J.D.; Saccomano, W.A. Tet. Lett. 1983, 24, 465.

22) Ravikumar, V.T.; Sathyamoorthi, G.; Rajagopalan, K.; Swaminathan, S. Ind. J. Chem. 1987, 26B, 255.

23) The CMR values refer to the carbons as numbered in structures 12 & 18.



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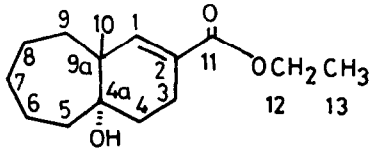

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