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Photochemical Reactions in Organic Synthesis: A Novel and Efficient Route to Angular and Linear Tetraquinanes

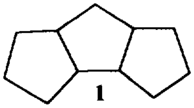
Vishwakarma Singh* and Prathap .S

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076 (India)

Abstract: Synthesis of angularly and linearly fused tetraquinanes **13** and **15** *via* triplet sensitized photoreaction of appropriately appended tricyclo[5.2.2.$0^{2,6}$]undecane systems such as **10a** and **10d**, followed by aldol condensation, is reported. In addition, synthesis of tricyclic systems **10a, d** from readily available aromatic precursors such as **8a, b** has also been described.

There has been an exceptional interest in the chemistry of polyquinanes in the past two decades which is continuing unabated.[1,2] While the presence of fused five membered rings in natural products has provided the stimuli for the synthetic activity in triquinanes,[3] the interest in tetraquinanes has been due to their synthetic potential towards higher polyhedra of fundamental significance such as dodecahedrane, hexaquinane and peristylane. Recently tetraquinanes have also provided the carbocyclic network of some unusual natural products. For example, functionalised tetraquinanes having framework **2** have served as precursors to fusicoccins, ophibolines[2f] and peristylane.[2g] Though a large number of synthetic methods have been developed[1] for triquinane framework of type **1**, only a few routes are known[2a-i] for synthesis of tetraquinanes of type **2**, and the synthesis of angularly fused tetraquinanes bearing the framework **3** has been reported only recently.[2j,k]

In continuation with our studies[3b,c] on polyquinanes, we desired to develop efficient routes to angularly and linearly fused tetraquinanes from readily available precursors. In this context it was envisaged that both the angularly and linearly fused tetraquinanes of type **4** and **5** could be obtained *via* aldol condensation of triquinanes **6a** and **6b** respectively having an acetonyl chain at appropriate centres (Scheme-1). It was further considered that the triquinanes **6a, b** should be amenable by triplet sensitised photoreaction[3] of strategically designed tricyclic chromophoric systems of type **7a, b**.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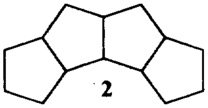
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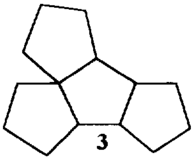
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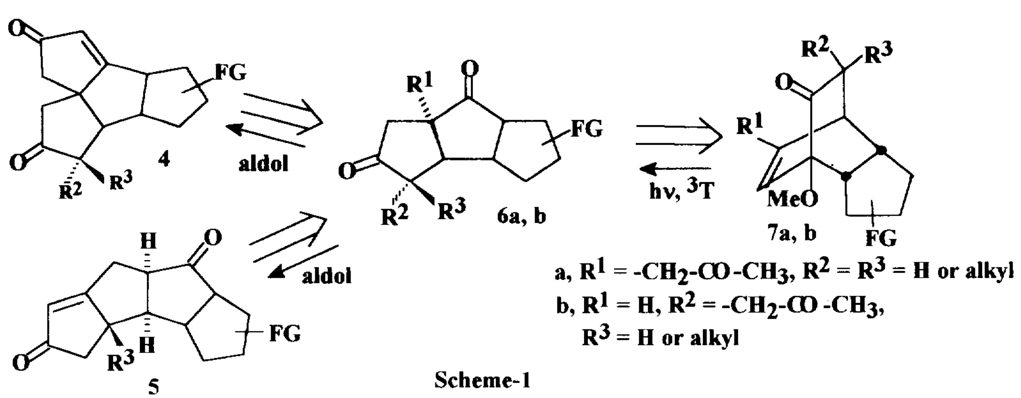


a, $R^1 = -CH_2-CO-CH_3$, $R^2 = R^3$ = H or alkyl
b, R^1 = H, $R^2 = -CH_2-CO-CH_3$,
R^3 = H or alkyl

Scheme-1

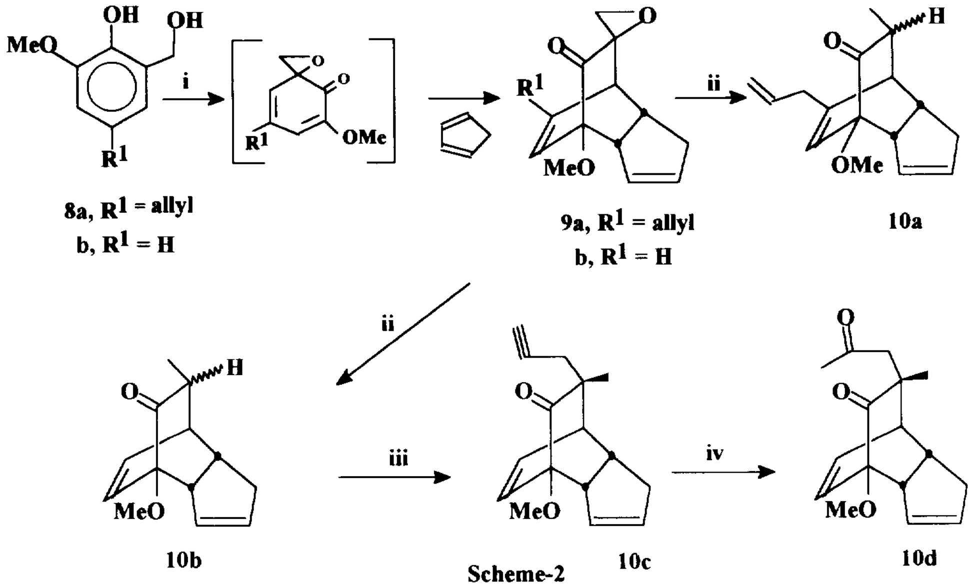
We wish to report herein a novel route to angularly and linearly fused tetraquinanes **13** and **15** (Scheme-3) along the above lines and also describe a facile synthesis of the tricyclic chromophoric systems **10a, d** from readily available starting materials such as phenol **8a** and **8b** (Scheme-2).

Towards the synthesis of the tricyclic chromophoric system **10a**, 2-methoxy-4-allyl-6-hydroxymethyl phenol **8a** was oxidised with sodium metaperiodate in acetonitrile-water and the spiroepoxycyclohexa-2,4-dienone generated *in situ* was intercepted by cyclopentadiene to give the adduct **9a** in reasonably good yield (45%), following a procedure developed in our laboratory.[3b,c] The structure of the adduct **9a** was thoroughly established by high field (300 MHz) ^{1}H NMR, ^{13}C NMR spectra and other analytical data.

The reductive deoxygenation of the epoxide group in the adduct **9a** with zinc in dry dioxane containing ammonium chloride[6] gave the desired compound **10a** (72%) as mixture of *syn:anti* isomers [1:4, ^{1}H NMR 500 MHz] whose stucture was clearly revealed from its spectral data. Similarly, the adduct **9b** was prepared from o-vanillyl alcohol, and was reduced with zinc to give the compound **10b**.[3c] Alkylation[7] of **10b** with propargyl bromide in the presence of NaH-THF at room temperature (~ 30^{0}C) furnished the propargylated ketone **10c** having the propargyl group *syn* to the double bond of the bicyclo[2.2.2]octane framework as a major product. Such type of stereoselective alkylation has also been observed by Stork and Paquette.[8] Hydration of the propargylated compound **10c** with mercuric oxide and sulphuric acid[9] finally gave the desired chromophoric system **10d** in good yield (80%) (Scheme-2).

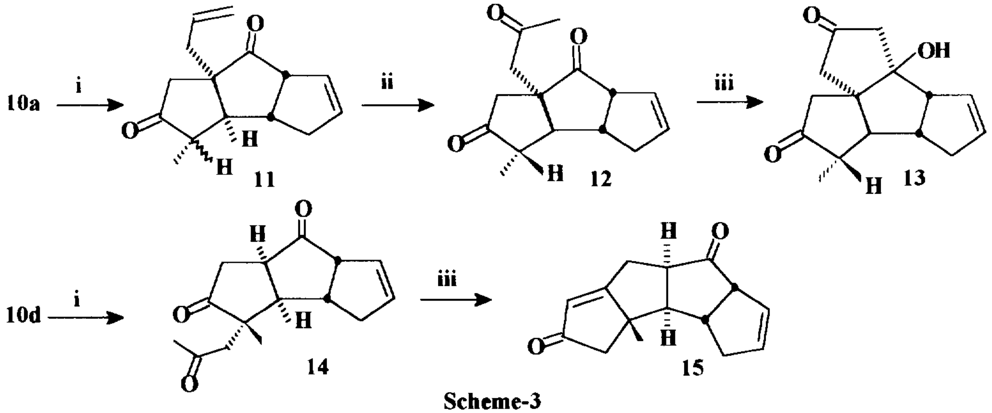
Towards the synthesis of angularly fused tetraquinane, first a solution of **10a** was irradiated (400 W, Hg vapour lamp, Applied Photophysics) in acetone (both as solvent and sensitizer) for 1.5h which gave the dione **11** as a major product whose structure was revealed through spectral and analytical data. Wacker type oxidation[10] of **11** followed by a careful chromatography of the product mixture furnished the trione **12** in good yield (62%) [Scheme-3] as a pure stereoisomer [^{1}H NMR, (300 MHz), ^{13}C NMR].

A brief treatment of the trione **12** with KO^{t}Bu in tertiary butanol[11] at room temperature (~30 °C) for 15



Scheme-2

Reagents/Conditions : i, $NaIO_4$, CH_3CN-H_2O, 0-10°C, ii, Zn, NH_4Cl, dioxane, Δ, iii, NaH, THF, $CH{\equiv}C$-CH_2-Br, iv, MeOH, HgO, H_2SO_4 (3%), r.t.



Scheme-3

Reagents/Conditions : i, hν, acetone, 400W Hg vapour lamp, ~1.5h, ii, $PdCl_2$, CuCl, O_2, DMF, 2h, iii, KO^{t}Bu-^{t}BuOH, r.t., ~15 min.

minutes followed by usual workup and chromatography furnished the tetraquinane **13** in 74% yield [mp 116°C] (Scheme-3), whose structure is fully consistent with its spectral data.

Towards the synthesis of linearly fused tetraquinane, the dione **10d** was irradiated in acetone for ~1.5h with mercury vapour lamp (400W, Applied Photophysics). Removal of solvent followed by chromatography gave directly the trione **14** as a solid (mp 62°C) in good yield (78%). The trione **14** was then subjected to intramolecular aldol condensation with KO^{t}Bu which gave the tetraquinane **15** (65%) whose structure was clearly revealed from its spectral data

EXPERIMENTAL:

General remarks: IR spectra were recorded on a Perkin-Elmer 681 and Nicolet FT-IR instrument Impact 400. UV spectra were recorded on Schimadzu 260 instrument. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on Varian VXR 300S instrument. Some ^{13}C NMR (125 MHz) were also taken on a GE NMR Omega instrument. All the samples were dilute solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Melting points were taken on a Buchi type melting point apparatus and are uncorrected. Elemental analysis were performed on a CEST 1106 instrument. All the organic extracts were dried over anhydrous sodium sulphate. Reactions were monitored with tlc and spots visualized with iodine vapour. Chromatographic separations were done on silica gel.

10-Allyl-1-methoxytricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-8-spirooxiran-9-one (9a):

To a solution of the compound **8a** (2g, 10.3 mmol) in acetonitrile (30ml) was added freshly cracked cyclopentadiene (8ml, excess) and the reaction mixture was cooled in ice bath (0-5°C). A solution of $NaIO_4$ (5g, 23.37 mmol) in water (50ml) was then added dropwise to the reaction mixture with stirring. After stirring for 5h, the reaction mixture was filtered and extracted with with ether (4x20ml). The organic layer was washed with brine (10ml) and dried over anhydrous sodium sulphate. Removal of solvent followed by chromatography [petroleum ether-ethyl acetate, (93:7)] of the crude product on silica gel yielded the adduct **9a** (1.25g, 45%), mp 70°C. IR (KBr) ν_{max}: 1730 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (m of d, J=6 Hz, 1H, olefinic H), 5.76-5.64 (complex m, 2H, olefinic H), 5.57 (m of d , J=6 Hz, 1H, olefinic H), 5.15 (br s, 1H, olefinic H), 5.10 (m of d, J=~6 Hz, 1H, olefinic H), 3.60 (s, 3H, OCH_3), 3.44 (m of d, J=9 Hz, 1H, proton at allylic ring junction), 3.12 (d of part of an AB system, J=~7 Hz, 1H, OCH_2), 3.08-3.02 (complex m, 1H, methine H), 2.97 (d with structure J=~7 Hz, 1H, doubly allylic H), 2.88 (d with structure, J=~7 Hz, 1H, doubly allylic H), 2.84 (d of part of an AB system, J=~7 Hz, 1H, OCH_2), 2.64 (m of dd, J_1=18 Hz, J_2=10 Hz, 1H, proton of the allylic methylene present in the five membered ring), 2.38 (superimposed dd, J_1=J_2=~3 Hz, 1H, methine H), 2.02 (m of d, J=18 Hz, 1H, proton of the allylic methylene present in the five membered ring). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.52 (s, CO), 141.62 (s), 134.13 (d), 133 75 (d), 127.59 (d), 122.39 (d) and 117.75 (t), (six olefinic carbons), 87.54 and 57.56 (s, quaternary carbons), 53.37 (q), 52.33 (d), 52.11 (t), 46.22 (d), 40.64 (t), 38.00 (t) and 36.71 (d). Analysis: Found C, 77.89; H, 6.83%. Calcd. for $C_{16}H_{18}O_3$ C, 77.42; H, 6.98%. Mass (m/z): 258 (M^+).

Preparation of 1-Methoxytricyclo[5.2.2.$0^{2,6}$]undeca-3,10-dien-8-spirooxiran-9-one (9b):

To a solution of the compound **8b** (2g, 12.9 mmol) in acetonitrile (30ml) was added freshly cracked cyclopentadiene (10ml, excess) and the reaction mixture was cooled to 0-5°C. A saturated solution of $NaIO_4$ (6g, 28.05 mmol) was then added dropwise to the reaction mixture with stirring. After stirring for 5h, the reaction mixture was filtered and extracted with ether (3x30ml). The organic layer was washed with brine (10ml) and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the residue was chromatographed. Elution with petroleum ether-ethyl acetate (94:6) furnished the compound **9b** (1.97g, 70%) as a solid, mp 86-88^{0}C. IR (KBr) ν_{max} : 1736 cm^{-1}. UV λ_{max} : 217, 317 nm. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 6.36 (dd, J_1=8.5 Hz, J_2=7 Hz, 1H, olefinic H), 6.18 (d with str., J=8.5 Hz, 1H, olefinic H), 5.8 (m of d, J=6 Hz, 1H, olefinic H), 5.62 (m of d, J=6 Hz, 1H, olefinic H), 3.59 (s, 3H, OCH_3), 3.44 (m of d, J=9 Hz, 1H, methine H), 3.15 (part of an AB system, J_{AB}=7 Hz, 1H, OCH_2), 3.12-3.06 (m, 1H, methine H), 2.86 (part of an AB system, J_{AB}=7 Hz, 1H), 2.7-2.61 (m of dd, J_1=15 Hz, J_2=8Hz, 1H, allylic methylene H), 2.59 (m, partly overlapped, 1H, methine H), 2.2 (m of d, J=5 Hz, 1H, allylic methylene H). The melting point and spectral features were identical to the adduct prepared by phase-transfer method.[3b] Mass (m/z): 218 (M^+).

10-Allyl-1-methoxy-8-methyltricyclo[5.2.2.$0^{2,6}$]undeca-3,10-dien-9-one (10a):

To a suspension of activated zinc[12] (4g, excess) and ammonium chloride (0.6g, excess) in dry dioxane (20 ml) was added a solution of the adduct **9a** (0.88g, 3.4mmol) in dioxane. The reaction mixture was then heated at 100^{0}C for 7h. It was then cooled and filtered to remove zinc. The dioxane was removed *in vacuo* and the residue was diluted with water (10ml) and extracted with ether (3 x 20ml). The combined ether layer was washed with water (10ml), brine (10ml) and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the residue was chromatographed. Elution with petroleum ether-ethyl acetate (95:5) gave the compound 10a (0.6g, 73%) as a *syn:anti* mixture (1:4). IR (Neat) ν_{max} : 1730 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.8-5.5 (merged multiplets, total 4H, olefinic H), 5.2-5.1 (m, 2H, olefinic H), 3.5 (s, 3H, OCH_3), 3.15-2.8 (complex multiplets, 4H), 2.5 (m, 2H), 2.15-2.0 (m, 2H),1.15 and 1.05 [two sets of d, J=6 Hz, total 3H, *anti* and *syn* methyl group, (4:1)]. Mass (m/z) : 244 (M^+).

1-Methoxy-8-methyltricyclo[5.2.2.$0^{2,6}$]undeca-3,10-dien-9-one (10b):

To a suspension of activated zinc (4g, excess) and NH_4Cl (5g, excess) in dry dioxane (20ml) was added a solution of the adduct **9b** (1g, 4.59 mmol) in dioxane (5ml). The reaction mixture was then heated at 100°C for ~7h. It was then filtered to remove zinc and the dioxane was removed *in vacuo*. The residue was diluted with water (10ml) and extracted with ether (3x20ml). The combined ether layer was washed with water (15ml), brine (10ml) and dried over anhydrous Na_2SO_4. The crude product obtained after removal of the solvent was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (95:5) yielded **10b** (0.61g, 65 %) as a liquid. IR (Neat) ν_{max}: 1728 cm^{-1}. UV λ_{max} : 302, 209 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ

6.41-6.36 (dd, J_1=9 Hz, J_2=6 Hz, 1H, γ-proton of β,γ-enone group), 6.13-6.10 (d with str., J=9 Hz, 1H, β-proton of β,γ-enone moiety), 5.76-5.72 (d with str. J=6 Hz, 1H, olefinic H), 5.62-5.58 (m, 1H, olefinic H), 3.55 (s, 3H, OCH_3), 3.11-3.06 (m of d, J=9 Hz, 1H, methine H), 2.96-2.88 (m, 1H, methine H), 2.85-2.75 (br m, 1H, methine), 2.64-2.54 (m, 1H, methylene H), 2.2-2.1 (q, J=9 Hz, 1H, CH_3-C-H), 2.04-1.94 (m of d, J=15 Hz, 1H, methylene H), 1.16 (d, J=9 Hz, 3H, CH_3). Mass (m/z) : 204 (M^+).

1-Methoxy-8-methyl-8-(1-propynyl)tricyclo[5.2.2.0^{2,6}]undec-3,10-dien-9-one (10c):

To a suspension of sodium hydride (0.6g, 25mmol) (which was previously washed with dry light petroleum) in dry tetrahydrofuran (10ml) was added a solution of the ketone **10b** (1.5g, 7.01mmol) in tetrahydrofuran (5ml) and the reaction mixture was refluxed for 1h. It was then cooled to room temperature and propargyl bromide (80% solution in toluene, 3ml, excess) was added dropwise after 12h, the reaction mixture was quenched with water (10ml) and filtered. The filtrate was concentrated under vacuum. The residue was diluted with water (10ml) and extracted with ether (3 x 25ml). The combined extract was washed with water (5ml), brine (10ml) and dried over anhydrous sodium sulphate. Removal of solvent followed by chromatography [petroleum ether-ethyl acetate, (94:6)] of the residue on silica gel furnished the compound **10c** (1.1g, 62%) as a solid, which was recrystallized from petroleum ether-ethyl acetate mixture (90:10), mp 95°C. IR (KBr) ν_{max}: 1730 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.35 (superimposed dd, J_1=J_2=7 Hz, 1H, γ-proton of β,γ-enone moiety), 6.05 (d, J=7 Hz, 1H, β-proton of β,γ-enone group), 5.75 (d, J=~3 Hz, 1H, olefinic H), 5.60 (d, J=~3 Hz, 1H, olefinic H), 3.6 (s, 3H, OCH_3), 3.22 (br d, J=~8 Hz, 1H, methine H), 3.05 (merged m, 2H), 2.58 (dd, J_1=18 Hz, J_2=9 Hz, 1H, allylic methylene), 2.38 (part of an AB system, J_{AB}=15 Hz, 1H, propargylic methylene), 2.18 (part of an AB system, J_{AB}=15 Hz, 1H, propargylic methylene), 2.05 (s, 1H, acetylinic H), 2.0 (br d, J=18 Hz, 1H, allylic methylene H) and 1.25 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.97 (CO), 134.55, 133.76, 129.37, 128.67 (olefinic carbons), 87.51, 80.41, 71.67, 53.80, 52.03, 46.42, 44.47, 39.59, 36.59, 29.44, 21.04 (total sixteen carbons). Analysis : Found C, 79.68; H, 7.13% Calcd. for $C_{16}H_{18}O_2$ C, 79.34; H, 7.44%. Mass (m/z): 242 (M^+).

1-Methoxy-8-methyl-8- (acetonyl)tricyclo[5.2.2.0^{2,6}]undec-3,10-dien-9-one (10d):

A solution of the compound **10c** (0.14g, 0.58 mmol) in methanol (3ml) was added to a suspension of HgO (0.03g) in H_2SO_4 (3%, 1ml) at room temperature (~30°C). After stirring the reaction mixture for 15h it was poured into water (7ml) and extracted with ethyl acetate (3 x 10ml). The organic layer was washed with brine (10ml) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the residue was chromatographed. Elution with petroleum ether-ethyl acetate (88:12) gave the compound **10d** (0.12g, 80%) as a liquid. IR (Neat) ν_{max}: 1720 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.15 (superimposed dd, J_1=J_2=7.5 Hz, 1H, γ-proton of β,γ-enone moiety), 5.95 (d, J=7.5 Hz, 1H, β-proton of β,γ-enone group), 5.65 (m,1H, olefinic H), 5.45 (m, 1H, olefinic H), 3.45 (s, 3H, OCH_3), 3.2 (m, 1H, methine H), 3.05 (m, 1H, methine H), 2.90 (br m, 1H, methine H), 2.60 (part of an AB system, J=15 Hz, 1H, methylene proton of acetonyl chain), 2.45 (dd, J_1=15 Hz, J_2=~10 Hz, 1H, allylic H), 2.35 (part of an AB system, J=15 Hz, 1H, methylene proton of acetonyl chain), 2.0 (s, 3H, CH_3), 1.85 (d with structure, J=15 Hz, 1H, allylic H), 1.15 (s, 3H, CH_3). ^{13}C NMR (125 MHz): δ 212.75, 206.34 (carbonyl carbons), 134.03, 133.48, 129.17, 128.06 (olefinic carbons), 86.82, 53.21, 51.33, 50.12, 45.92, 43.60, 39.17, 36.19, 31.66 and 20.38. Mass (m/z): 260 (M^+).

6-Allyl-3-methyltricyclo[6.3.0.0^{2,6}]undec-9-en-4,7-dione (11):

The compound **10a** (0.3g, 1.23mmol) was irradiated in acetone (300ml) with a mercury vapour lamp (400W, APP) under nitrogen for 1.5h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with petroleum ether- ethyl acetate (95:5) first gave some unchanged starting material (0.11g) followed by triquinane **11** (0.11g, 62%, based on recovered starting material) as a liquid. IR (Neat) ν_{max}: 1730 cm^{-1}.The NMR spectrum of this compound was found to be complex since it is mixture of stereoisomers at the carbon bearing methyl group. Neverthless comparison of its spectral features with that of its precursor revealed the structure which was also confirmed through its subsequent transformation. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.9-5.6 (multiplets, 3H, olefinic H), 5.12-5.00 (complex m, 2H, olefinic H), 3.6 (m, 1H), 3.05-2.82 (two sets of multiplets, due to both stereoisomers, total 1H), 2.80-2.70 (m, 1H), 2.60-2.21 (m, 4H), 2.20-1.9 (m, 3H) and 1.18 (two doublets superimposed to each other, J=6 Hz, CH_3).^{13}C NMR (75 MHz, $CDCl_3$): ^{13}C NMR also gave signals due to both isomers, δ 216.60, 216.16 (CO's), 133.36, 133.25, 132.67, 131.96, 128.45, 126.86, 118.93, 118.57 (for eight olefinic carbons, four signals for each isomer), 60.11, 59.80, 55.02, 54.21, 51.34, 51.09, 45.91, 43.89, 43.59, 41.13, 40.95, 40.26, 38.29, 37.12, 13.25, 9.75 (for quaternary, methine, methyl carbons of both isomers). Mass (m/z): 230 (M^+), 66 ($C_5H_6^+$).

6-Acetonyl-3-methyltricyclo[6.3.0.0^{2,6}]undec-9-en-4,7-dione (12):

$PdCl_2$ (0.1g), cuprous chloride (0.4g) and water (0.2ml) were taken in DMF (5ml) and oxygen was bubbled into the reaction mixture for 20 minutes. A solution of the compound **11** (0.15g, 0.65mmol) in DMF (3ml) was added to the reaction mixture and the contents were stirred at room temperature in an oxygen atmosphere. After 2h the reaction mixture was quenched with 10% HCl and it was extracted with ether (4x10ml). The combined organic layer was washed with brine and dried over anhydrous sodium sulphate. The crude product obtained after removal of the solvent was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (75:25) yielded **12** as a major compound (0.10g, 63%). IR (Neat) ν_{max}: 1730 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.83 (complex m, 1H, olefinic H), 5.79 (m, 1H, olefinic H), 3.63 (complex m, 1H, methine H), 3.04 (part of an AB system, J=18 Hz, 1H, methylene H), 2.76 (complex m,1H), 2.72 (part of an AB system, J=18 Hz, 1H, methylene H), 2.60 (cluster of m, 2H), 2.40 (dd, J_1=18 Hz, 1H, allylic methylene), 2.28 (br d with str., J=18 Hz, 1H, allylic methylene H), 2.10 (s, 2H, CH_2 of the 3 carbon chain), 2.10 (s, 3H, CH_3) and 1.18 (d, J=~7 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 216.19, 215.84, 205.04 (carbonyl carbons), 130.54, 128.09 (olefinic carbons), 59.85, 52.31, 51.93, 46.88, 45.82, 43.50, 40.17, 37.47, 30.08 (CH_3) and 9.77 (CH_3) [total 15 carbons]. Mass (m/z): 246 (M^+).

1-Hydroxytetracyclo[6.6.$0^{1,11}$.$0^{2,6}$]tetradec-3-en-9,13-dione (13):

To a solution of the compound **12** (0.043g, 0.175mmol) in tertiary butanol (2ml) was added potassium tertiary butoxide (0.25g) at room temperature (~30°C) under nitrogen for 25 minutes. The reaction mixture was then quenched by adding a saturated solution of ammonium chloride and the aqueous layer was extracted with ethyl acetate (3x10ml). The combined organic layer was washed with brine (5ml) and dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the crude product was subjected to column chromatography on silica gel. Elution with petroleum ether-ethyl acetate (50:50) furnished the tetraquinane **13** (0.03g, 74%). mp 116°C. IR (Neat) ν_{max}: 3409, 1733 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.81 (complex m, 1H, olefinic H), 5.55 (complex m, 1H), 3.68 (m, 1H, methine H), 2.84-2.64 (cluster of m, 4H), 2.48 (part of an AB system, J=18 Hz, 1H, methylene H), 2.28-2.02 (cluster of m, 5H), 1.9 (dd, J_1=12 Hz, J_2=2 Hz, 1H), 1.40 (superimposed dd with str., J=6 Hz, 1H), 1.3 (d, J=6 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 216.67, 206.80 (CO's), 132.79, 127.15 (olefinic carbons), 81.38 (quaternary carbon having hydroxyl group), 61.87, 59.04, 53.7, 53.35, 51.19, 48.19, 46.52, 45.97, 41.19 and 14.47 (total 15 carbons). Analysis: Found C, 73.46; H, 6.97%. Calcd. for $C_{15}H_{18}O_3$ C, 73.17; H, 7.32%. Mass (m/z): 246 (M^+).

3-Acetonyl-3-methyltricyclo[6.3.0.$0^{2,6}$]undec-9-en-4,7-dione (14):

A solution of the compound **10d** (0.41g, 1.58 mmol) in dry acetone (both as solvent and sensitizer) was irradiated by a mercury vapour lamp (400 W, Hanovia) in a pyrex immersion well under nitrogen. After 1.5h, the acetone was removed *in vacuo* to give the residue which was chromatographed on silica gel. Elution with ethyl acetate-light petroleum (60-80°C) [12:88] first gave some unchanged starting material. Further elution [ethyl acetate-light petroleum, (30:70)] gave the desired rearranged product **14** (0.23g, 78%) as a solid, mp 62°C. IR (KBr) ν_{max}: 1750, 1730 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.85 (br m, 1H, olefinic H), 5.55 (m, 1H, olefinic H), 3.35 (m, 1H, methine H), 3.0 (cluster of m, 2H), 2.90-2.80 (cluster of m, 4H), 2.6 (multiplets 2H), 2.35 (br d, J=15 Hz, 1H), 2.1(s, 3H, $COCH_3$) and 0.75 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 219.93, 217.83, 206.29 (CO's), 134.47, 127.75 (olefinic carbons), 61.44, 51.93, 51.13, 48.99, 44.28, 42.66, 37.12, 35.72, 30.41 and 19.45 (total 15 carbons). Mass (m/z) : 246 (M^+).

14-Methyltetracyclo[6.6.$0^{2,6}$.$0^{10,14}$]tetradeca-5, 10-dien-7,12-dione (15):

To a solution of the compound **14** (0.05g, 0.203mmol) in tertiary butanol (2ml) was added potassium tertiary butoxide (0.03g) at room temperature under nitrogen. After 15 minutes, the reaction mixture was quenched by a saturated solution of NH_4Cl and the aqueous layer was extracted with ethyl acetate (3x10ml).

The organic layer was washed with brine and dried over anhydrous sodium sulphate. Removal of solvent and chromatography [petroleum ether-ethyl acetate, (70:30)] furnished the tetraquinane **15** (0.03g, 65%) as a solid, mp 93°C. IR (KBr) ν_{max}: 1740, 1712, 1643 cm^{-1} . ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.88 (m, 1H, olefinic H), 5.80 (s, 1H, α-H of α,β-enone moiety), 5.58 (m, 1H, olefinic H), 3.45 (complex m, 1H, methine H), 3.1 (cluster of m, 3H), 2.9 (superimposed m, 2H), 2.35 (cluster of m, 3H), 2.25 (d, J=9 Hz, 1H) and 0.90 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 218.33, 209.64 (CO's), 192.27 (β-carbon of α,β-enone), 134.51, 127.68, 124.53 (other olefinic carbons), 61.90, 56.85, 51.26, 50.02, 43.06, 36.82, 29.92, 27.24, 21.49 (total 15 carbons). Mass (m/z) : 228 (M$^+$).

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