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Aromatics to triquinanes: Studies on synthesis and photo reaction of *endo*-tricyclo[5.2.2.0^{2,6}]undecanes†

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Abstract

Synthesis of *endo*-tricyclo[5.2.2.0^{2,6}]undecanes having a β,γ-enone chromophore and their photochemical reaction upon triplet excitation is described. The key reaction for the synthesis of tricycloundecanes (**9–13**) involves generation and interception of spiroepoxycyclohexa-2,4-dienone (**5**) with cyclopentadiene and transformation on the resulting adduct (**6**). Photoreaction of **11** gave a mixture of products due to 1,2-acyl shift and $\pi^{2s} + \pi^{2s}$ cycloaddition. Irradiation of the hydroxyketone (**10**) furnished the triquinane (**17**) selectively, which was oxidized to give the embellished triquinane (**15**).

Keywords: Cycloaddition, spiroepoxycyclohexa-2,4-dienones, photochemical reaction.

1. Introduction

Efficient creation of structural complexity from simple precursors is an important aspect of development of new methods and synthesis design.[1,2] In view of the intense interest in the synthesis of triquinanes,[3,4] we have developed a method of generation of complex molecular structures from simple aromatic precursors featuring cycloaddition of spiroepoxycyclohexa-2,4-dienones and chemical reactions in excited states.[5] In continuation of our interest in this area, we wish to describe[6] a novel route to *endo*-tricyclo[5.2.2.0^{2,6}]undecanes of type **2** containing α-methoxy-β,γ-enone chromophore from the aromatic precursor (**1**) and the photoreactions of the chromophoric systems of type **2** leading to linearly fused *cis:anti:cis* tricyclopentanoids of type **3** (Fig. 1).

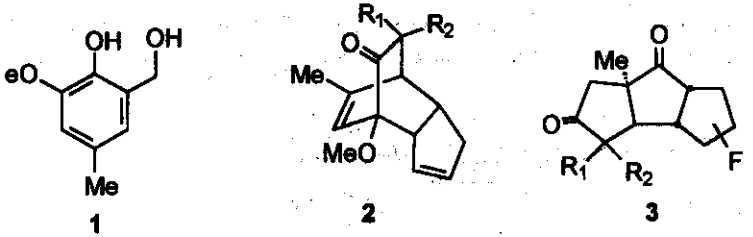

FIG. 1.

†Dedicated to Prof. S. C. Bhattacharyya.
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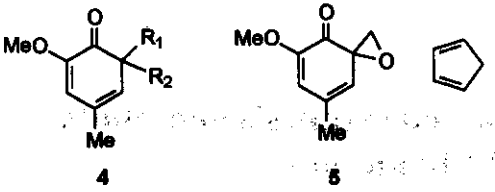


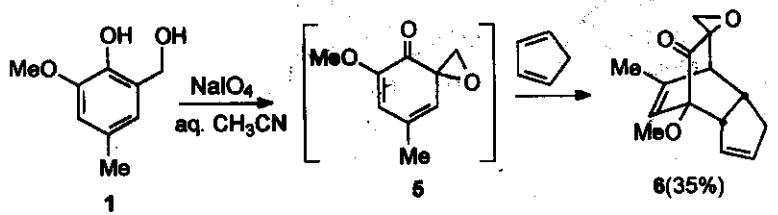
FIG. 2.

2. Synthesis of the chromophoric systems of type 2

Conceptually, the tricyclic systems of type **2** may be obtained by the cycloaddition of cyclohexa-2,4-dienones (**4**) and cyclopentadiene. However, there are no methods for the preparation of cyclohexadienones of type **4**. Therefore, we designed an indirect route to the chromophoric systems involving *in situ* generation of spiroepoxycyclohexa-2,4-dienone (**5**) and its cycloaddition with cyclopentadiene followed by manipulation of the resulting adduct, as presented below.

The aromatic precursor (**1**) was readily prepared from vanillin via Wolf–Kishner reduction[7] followed by hydroxymethylation.[8] Slow oxidation of **1** with sodium meta periodate in aqueous acetonitrile containing cyclopentadiene, following a procedure developed in our laboratory,[6] furnished the adduct (**6**), as a result of *in situ* generation of **5** and cycloaddition with cyclopentadiene (Scheme 1).

The structure of the adduct **6** was deduced from the following spectral features and comparison. Thus, ^{1}H NMR spectrum of **6** exhibited signals at δ 5.8 (dd of d, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H) and 5.58(dd, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H) corresponding to olefinic protons of cyclopentene ring (H_f and H_e), respectively. The β-hydrogen (H_a) of the β,γ-enone moiety gave a signal at δ 5.72(dd, $J_1 = 3$ Hz, $J_2 = 2$ Hz, 1H). Further signals were shown at δ 3.58 (s, 3H) and 3.42 (m of d, $J = 10$ Hz, 1H) due to OCH_3 and H_d, respectively. It was interesting to observe that the CH_2 protons of the oxirane ring appeared separately at δ 3.14 (part of an AB system, $J = 7$ Hz, 1H) and 2.9 (part of an AB system, $J = 7$ Hz, 1H). The allylic methylene protons also appeared separately at δ 2.65 (q of d, $J_1 = 14$ Hz, $J_2 = 8$ Hz, $J_3 = 3$ Hz, 1H) and 2.65 (m of d, $J = 14$ Hz, 1H). The protons H_c and H_b showed resonances at δ 3.06 (complex m, 1H) and 2.33 (m of d, $J = 2$ Hz, 1H). Methyl group exhibited a characteristic signal at δ 1.94 (d, $J = 2$ Hz, 3H). These assignments were made with the help of a COSY spectrum which showed the following correlation (Fig. 3). Thus, the β proton H_a of the β,γ-enone group (δ 5.72) showed cross peaks with the signals at δ 2.33 (assigned to the bridgehead proton H_b) and 1.94 (olefinic methyl group),



Scheme 1.

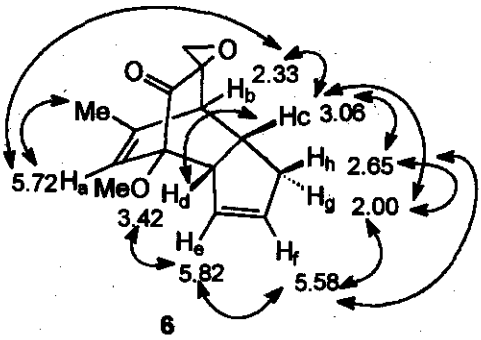


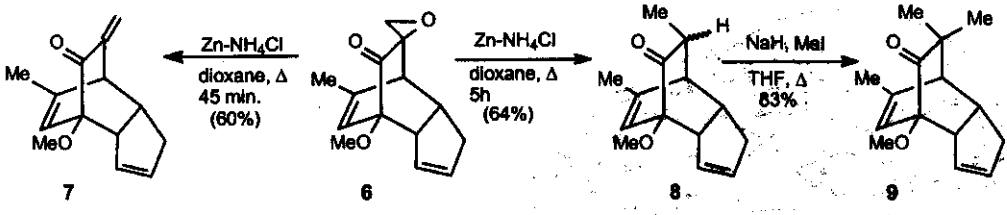
FIG. 3.

respectively. Similarly, the proton H_c (δ 3.06) showed correlation with the signals at δ 3.42 (H_d), 2.65 (allylic methylene H_h) and 2.00 (assigned to *endo* allylic methylene proton H_g) and the signal at δ 2.33 (H_b). Moreover, the signal at δ 3.42 (H_d) also showed correlation with olefinic protons at δ 5.80 and 5.58 (Fig. 3). The above relationship between protons, wherein H_b is coupled to the proton (H_c) which is further coupled to allylic methylenes, and H_d clearly suggested the formulation **6** for the adduct and ruled out alternative possibilities. The ^{13}C spectrum of the adduct also supported its formulation as it exhibited a characteristic resonance at δ 204.08 for the carbonyl carbon and signals at δ 139.75, 134.38, 127.85, 122.18 for the olefinic carbons. It also showed signals at δ 87.60, 57.64, 53.62, 52.25, 52.07, 48.13, 38.24, 36.98 and 22.82 for methine, methylene, methyl and quaternary carbons, respectively. The *anti* orientation of the oxygen atom of the oxirane ring was suggested on the basis of the known tendency[9,10] of α-functionalized cyclohexa-2,4-dienones during their cycloaddition and by comparison of the above spectral features with analogous compounds prepared in our laboratories.[6]

The presence of the keto-oxirane function at contiguous centres in **6** provided opportunity for elaboration of the oxirane ring into *gem* dimethyl group as presented below. Thus, the treatment of the adduct **6** with zinc-NH_4Cl in dry dioxane[11] gave the exocyclic enone **7** (scheme 2) as a major compound, whose structure was clearly revealed through spectral and analytical data.

Further treatment of the compound **7** with Zn-NH_4Cl in dry dioxane under reflux gave the monomethyl compound **8**. Alternatively, the compound **8** was directly prepared by reduction of the adduct **6** with Zn-NH_4Cl in refluxing dry dioxane for 5 h. The monomethyl ketone (**8**) was alkylated with methyl iodide in the presence of NaH-THF to give the desired dimethyl ketone (**9**) in good yield (83%) (Scheme 3).

The ketone **9** was further transformed into other functionalized chromophoric systems **10**–**13** as follows. Allylic oxidation[12] of **9** with SeO_2 in refluxing dioxane containing KH_2PO_4 furnished a stereoisomeric mixture of allylic alcohol **10** which was further oxidized with PCC[13] to give the diene–dione (**11**). Reduction of **11** with sodium borohydride at ~10°C followed by Jones oxidation of the resulting alcohol gave the dione **12** whose structure is fully consistent with the spectral data. Thus, the IR spectrum of **12** showed absorption bands at 1730 and 1720 cm^{-1} corresponding to cyclopentanone carbonyl and the carbonyl group present in the



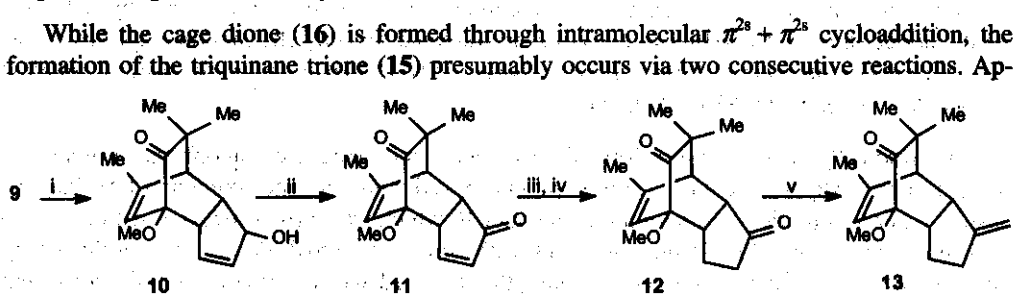
Scheme 2.

bicyclo[2.2.2]octane framework, respectively. ^{13}C NMR spectrum also supported its formulation since it displayed characteristic signals at δ 220 and 213.75 due to carbonyl groups present in the five-membered ring and at the ethano bridge, respectively.[14] Selective Wittig reaction[15] on the dione **12** gave the dienone **13** (Scheme 3) whose structure was easily deduced from its spectral data. The IR spectrum of **13** showed only one absorption band in the carbonyl region at 1728 cm^{-1} corresponding to CO group in the ethane bridge which clearly suggested that the cyclopentanone had reacted with triphenylphosphinemethylide. ^{13}C NMR spectrum of **13** also showed only one signal for carbonyl carbon at δ 214.93 for the CO group in the bridge. ^{1}H NMR (300 MHz) showed characteristic signals at δ 4.94 and 4.82 for the exocyclic olefinic protons, in addition to other signals.

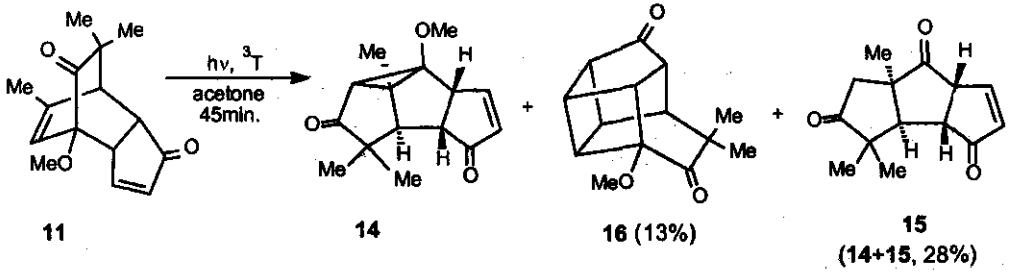
3. Photochemical reaction of 10, 11 and 13 upon triplet excitation

Photochemical reactions have proved to be versatile tools for the synthesis of polyquinanes, protoilludanes and marasmanes due to selective chemical pathway upon triplet and singlet excitation.[6] Though β,γ-enones may undergo reactions characteristic of both the olefinic and carbonyl chromophore,[16, 17] in general, rigid β,γ-enones undergo a 1,2-acyl shift upon triplet excitation.[6, 16–20] Singlet excitation of β,γ-enones, however, leads to a 1,3-acyl shift.[21, 22] Some times a mixture of products are obtained due to indiscriminate population of the excited states. In view of this, we first explored the photochemical reaction of the diene–dione (**11**) in triplet excited state. Thus, a solution of **11** in acetone (sensitizer and solvent) was irradiated under nitrogen. However, it furnished a mixture of three products, the 1,2-acyl shift product (**14**), the ene-trione (**15**) and the cage compound **16** resulting from intramolecular $\pi^{2s} + \pi^{2s}$ photocycloaddition (Scheme 4). The structures of all the photoproducts were established with the help of their spectral and analytical data.

While the cage dione (**16**) is formed through intramolecular $\pi^{2s} + \pi^{2s}$ cycloaddition, the formation of the triquinane trione (**15**) presumably occurs via two consecutive reactions. Ap-



Scheme 3. Reagents/conditions: (i) SeO_2, KH_2PO_4, dioxane–H_2O, Δ(91%); (ii) PCC, CH_2Cl_2 (81%); (iii) $NaBH_4$, MeOH (86%); (iv) Jones' reagent, acetone (77%); (v) $PPh_3CH_3^+I^-$, KO^{t}Bu (87%).



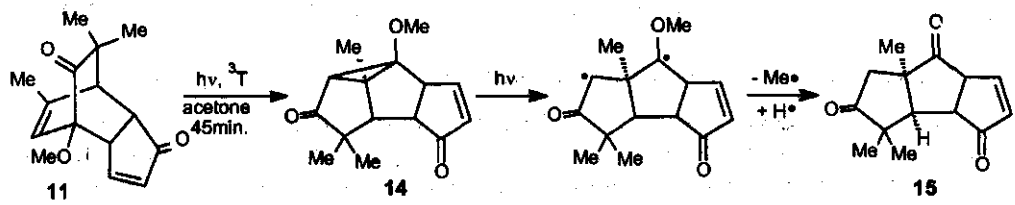
Scheme 4.

parently, triplet sensitization of the β,γ-enone moiety in **13** causes a 1,2-acyl shift to give the usual product (**14**) which subsequently undergoes cleavage of peripheral cyclopropane sigma bond followed by the loss of methyl radical and hydrogen abstraction[20] to give the ene-trione (**15**) (Scheme 5). This contention was supported from the observation that further irradiation of the mixture containing **14** and **15** with 6 W mercury vapour lamp was found to enrich the mixture with **15**.[6]

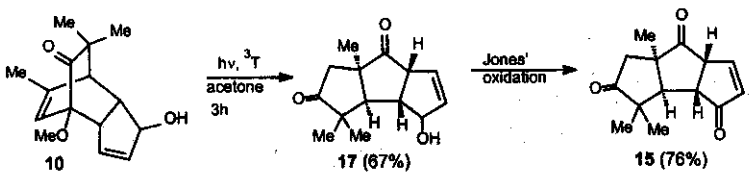
The formation of **16** during the above photoreaction is due to competitive sensitization of the α,β-enone moiety in addition to α,β-enone group. In order to avoid the complication due to excitation of α,β-enone group, we considered to prepare the functionalized triquinane (**15**) via irradiation of the keto-alcohol (**10**) and oxidation of the resulting product. Thus, a solution of the keto-alcohol (**10**) in acetone was irradiated (200 W Hg vapour lamp). Interestingly, it gave the triquinane (**17**) as a sole product in good yield (67%) whose structure was clearly revealed from its spectral data and comparison with the spectral features of its precursor. Oxidation of **17** with Jones[23] reagent readily gave the functionalized triquinane (**15**) in good yield (Scheme 6).

The photochemical reaction of the diene–dione (**13**) was also explored. However, it gave a mixture of products which were difficult to separate and purify.

In summary, we have described a novel route to variously functionalized *endo*-tricyclo[5.2.2.0^{2,6}]undecanes endowed with a β,γ-unsaturated carbonyl chromophore from a simple aromatic precursor. Photoreaction of some of the chromophoric systems was explored. It has been shown that the photoreaction also depends on the other functional groups present in the chromophore. Synthesis of linearly fused triquinane having functional groups in all the three five-membered rings has also been reported.



Scheme 5.



Scheme 6.

4. Experimental

IR spectra were recorded on Nicolet Impact 400 FT-IR Instrument. UV spectra were recorded on Schimadzu 260 instrument. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on Varian VXR 300 instrument. Most of the samples were dilute solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Mass spectra were recorded on HP GCD 1800A mass spectrometer. Melting points were determined on a veego apparatus of Buchi type and are uncorrected. All the organic extracts were dried over anhydrous sodium sulphate. Reactions were monitored with thin-layer chromatography and spots were visualized with iodine vapour. Column chromatography was performed using Acme/SRL silica gel (60–120 and 100–200 mesh). The elution was done with petroleum ether (60–80°C) and ethyl acetate mixtures. The fractions eluted from column were concentrated at reduced pressure on a Buchi-RE 111 rotary evaporator.

4.1. *1-Methoxy-10-methyl-endo-tricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-8-spirooxiran-9-one (6)*

To a solution of compound (**1**) (1.0 g, 5.95 mmol) in acetonitrile (20 ml) was added freshly cracked cyclopentadiene (4 ml, excess) and the reaction mixture was cooled in ice bath (0–5°C). A solution of $NaIO_4$ (3 g, 14.02 mmol) in water (25 ml) was then added dropwise to the reaction mixture with stirring. After stirring for 5 h, the reaction mixture was filtered and extracted with ether (4 × 20 ml). The organic layer was washed with brine (10 ml) and dried over anhydrous sulphate. Solvent was removed and the residue was chromatographed on silica gel. Elution with petroleum ether–ethyl acetate (90:10) gave the adduct (**6**) (0.48 g, 35%) as a solid which was recrystallized from petroleum ether–ethyl acetate (95:5), m. p. 110°C. IR (KBr) ν_{max}: 1730 cm^{-1}. UV (MeOH) λ_{max}: 224, 319 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.8 (ddd, J_1 = 6 Hz, $J_2 = J_3 = 2$ Hz, 1H), 5.72 (d with long range coupling, $J = 2$ Hz, 1H), 5.58 (dd with long range coupling, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H), 3.59 (s, 3H, OCH_3), 3.40 (m of d, $J = 10$ Hz, 1H), 3.14 (part of an AB system, $J_{AB} = 7$ Hz, 1H, OCH_2), 3.06 (complex m, 1H), 2.90 (part of an AB system, $J_{AB} = 7$ Hz, 1H, OCH_2), 2.65 (m of dd, $J_1 = 18$ Hz, $J_2 = 12$ Hz, 1H, CH_2), 2.34 (superimposed dd, $J_1 = J_2 = 3$ Hz, 1H), 2.0 (m of d, $J = 18$ Hz, 1H, CH_2), 1.94 (d, $J = 2$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.68 (C = O), 139.75, 134.38, 127.85, 122.18 (olefinic carbons), 87.60, 57.64, 53.62, 52.25, 52.07, 48.13, 38.24, 36.98, 22.82. Mass (*m/z*): 232 (M^+).

4.2. *1-Methoxy-10-methyl-8-methylene-endo-tricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (7)*

A solution of the compound (**6**) (0.9 g, 3.87 mmol) in dioxane (5 ml) was added to a suspension of activated zinc (5 g, excess) and ammonium chloride (0.6 g, excess) in dry dioxane (15 ml). The reaction mixture was refluxed for 45 min. It was then cooled and filtered to remove zinc. Dioxane was removed *in vacuo* and the residue was dissolved in water and extracted with ether (3 × 20 ml). The combined extract was washed with water (10 ml), brine

(10 ml) and dried over anhydrous sodium sulphate. Removal of solvent and chromatography of the residue [petroleum ether–ethyl acetate (93:7)] yielded the title compound (0.5 g, 60%), m.p. 61°C. IR (KBr) ν_{max}: 1710 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.82 (d, J = 2 Hz, 1H), 5.75 (m of dd, J_1 = 6 Hz, J_2 = 2 Hz, 1H), 5.66 (dd, J_1 = 3 Hz, J_2 = 2 Hz, 1H), 5.58 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1H), 5.18 (d, J = 2 Hz, 1H), 3.60 (s, 3H, OCH_3), 3.25 (m of d, J = 10 Hz, 1H), 3.22 (superimposed dd, J = 2 Hz, 1H), 2.74 (complex m, 1H), 2.56 (m of dd, J_1 = 15 Hz, J_2 = 10 Hz, 1H), 1.98 (m of d, J = 15 Hz, 1H), 1.89 (d, J = 2 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.23 (C = O), 141.73 (s), 140.73 (s), 133.91 (d), 128.54 (d), 121.65 (d), 114.65 (t), 87.38 (s), 53.64 (q), 51.30 (d), 49.87 (t), 40.78 (d), 38.26 (d), 22.21 (q). Mass (*m/z*): 216 (M^+).

4.3. *1-Methoxy-8,10-dimethyl-endo-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-9-one (8)*

To a suspension of activated zinc (5 g, excess) and ammonium chloride (0.6 g, excess) in dry dioxane (15 ml) was added a solution of the adduct (**6**) (1 g, 4.3 mmol) in dioxane (5 ml). The reaction mixture was then heated at 100°C for 5 h. It was then cooled and filtered to remove zinc. The dioxane was removed *in vacuo*, the residue diluted with water (1 × 10 ml) and extracted with ether. The combined ether layer was washed with water (1 × 10 ml), brine (1 × 10 ml) and dried over anhydrous sodium sulphate. Removal of the solvent followed by chromatography [petroleum ether–ethyl acetate (93:7)] of the crude product on silica gel yielded the compound (**8**) (0.6 g, 64.5% as a *syn:anti* mixture) m.p. 43°C. IR (KBr) ν_{max}: 1730 cm^{-1}. UV (MeOH) λ_{max}: 219.4, 305.8 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.75 (m, 1H, olefinic H), 5.65 (d with str, J = 2 Hz, 1H), 5.55 (m, 1H, olefinic H), 3.54 (s, 3H, OCH_3), 3.07 (m of d, J = 10 Hz, 1H, methine H), 2.9 (complex m, 1H, methine H), 2.62–2.50 (complex m, 2H, methylene H), 2.10 (m, 1H, methine H), 1.95 (m of d, J = 18 Hz, methine H), 1.89 (d, J = 1.5 Hz, 3H, olefinic CH_3) and 1.16 (d, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.45 (C = O), 143.30, 133.87, 128.52, 120.50 (olefinic carbons), 87.62, 53.54, 52.51, 47.75, 42.48, 38.40, 35.15, 22.6 and 14.21. Mass (*m/z*): 218 (M^+).

4.4. *1-Methoxy-8,8,10-trimethyl-endo-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-9-one (9)*

To a suspension of sodium hydride (0.5 g, 20.8 mmol, which was previously washed with dry light petroleum) in dry THF (10 ml), was added a solution of the ketone (**8**) (0.4 g, 1.8 mmol) in THF (3 ml) and the reaction mixture refluxed for 1 h. After this, methyl iodide (3 ml, excess) in THF (3 ml) was added dropwise to the reaction mixture and further refluxed for 6 h. The reaction mixture was then quenched with water (5 ml) and the THF was removed in vacuum, and water (5 ml) was added to the residue and extracted with ether (3 × 20 ml). The combined extract was washed with water (10 ml), brine (10 ml) and dried over anhydrous sodium sulphate. The solvent was removed and the residue was chromatographed. Elution with petroleum ether–ethyl acetate (95 : 5) furnished the compound **9** (0.35 g, 83.3%) m. p.: 65°C. IR (KBr) ν_{max}: 1725 cm^{-1}. UV (MeOH) λ_{max}: 221.6, 305.8 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.75 (m, 1H, olefinic H), 5.59 (m, 1H, β-proton of β, γ-enone moiety), 5.56 (complex m, 1H, olefinic H), 3.54 (s, 3H, OCH_3), 3.16 (m of d, J = ~9 Hz, 1H, allylic H), 3.0 (complex m, 1H, methine H), 2.54 (m of dd, J_1 = 15 Hz, J_2 = 9 Hz, 1H, allylic methylene H), 2.36 (superimposed dd, J = 3 Hz, 1H, methine H), 1.94 (m of d merged with another signal, J = 15 Hz, 1H, methylene H), 1.90 (d, J = ~1.5 Hz, 3H, olefinic CH_3), 1.12 (s, 3H, CH_3), 1.07 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.76 (C = O), 142.78 (s), 133.87 (d), 128.47 (d), 119.62 (d),

(olefinic carbons), 87.24 (s), 53.31 (d), 53.10 (q), 50.86 (d), 43.83 (s), 38.22 (d), 36.32 (t), 25.85 (q), 24.13 (q) and 23.76 (q). Mass (*m/z*): 232 (M^+).

4.5. *5-Hydroxy-1-methoxy-8,8,10-trimethyl-endo-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-9-one (10)*

A solution of the compound **9** (0.7 g, 3 mmol) in dioxane (5 ml) was added dropwise to a suspension of SeO_2 (0.6 g, 5.4 mmol) in dioxane (10 ml), water (1 ml) and potassium dihydrogen orthophosphate (0.3 g) at 90°C. The reaction mixture was heated for 7 h. It was filtered through a celite pad and washed with ether (2 × 10 ml). The solvent was removed under vacuum and diluted with water (10 ml) and extracted with ether (3 × 20 ml). The combined organic extract was washed with water (15 ml), brine (10 ml) and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue was chromatographed [petroleum ether–ethyl acetate, 60:40] over silica gel to give the hydroxy ketone (**10**) (0.68 g, 90.91%) as a stereoisomeric mixture. IR (Neat) ν_{max}: 3400, 1720 cm^{-1}. UV (MeOH) λ_{max}: 209.6, 304.6 nm. ^1H NMR (300 MHz, $CDCl_3$): δ 5.88 (m, 1H, olefinic H), 5.8 (m, 1H, olefinic H), 5.54 (d with str, $J = 2$ Hz, 1H, β-proton of β,γ-enone moiety), 4.36 (m, 1H, H-C-OH), 3.52 (s, 3H, OCH_3), 3.31 (m, 1H, methine H), 2.80 (br, 1H, OH), 2.68–2.6 (merged m, 2H, methine H), 1.9 (d, $J = 1.5$ Hz, 3H, olefinic CH_3), 1.12 (s, 3H, CH_3) and 1.08 (s, 3H, CH_3). These signals correspond to the major stereoisomer. ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.52 (C = O), 142.76, 136.60, 133.18, 119.33, (olefinic carbons), 87.22, 81.62, 53.52, 51.87, 51.31, 50.31, 43.34, 25.68, 23.69, and 22.80 for quaternary, methine, methylene and methyl carbons of the major isomer. Mass (*m/z*): 248 (M^+).

4.6. *1-Methoxy-8,8,10-trimethyl-endo-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-5,9-dione (11)*

A solution of the compound (**10**) (0.3 g, 1.2 mmol) in CH_2Cl_2 (5 ml) was added to a suspension of PCC (0.25 g, excess), and sodium acetate (0.1g) in CH_2Cl_2 (5 ml) at room temperature (~25°C). After stirring for 2 h, ether (30 ml) was added to the reaction mixture and decanted. The insoluble residue was washed thoroughly with ether (3 × 20 ml), and the combined organic layer was passed through a short silica gel column. The solvent was removed and the residue chromatographed (petroleum ether–ethyl acetate, 80:20) on silica gel to give the diene–dione (**11**) (0.24 g, 80.5%), m. p. 95°C. IR (KBr) ν_{max}: 1730, 1700 cm^{-1}. UV (MeOH) λ_{max}: 220.6 nm. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (dd, $J_1 = 6$ Hz, $J_2 = 3$ Hz, 1H, β-proton of α,β enone), 6.33 (dd, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H, α-proton of α,β-enone), 5.45 (d with str, $J = 2$ Hz, 1H, olefinic H), 3.6 (s, 3H, OCH_3), 3.35 (m of d, $J = 12$ Hz, 1H, ring junction proton), 2.85 (dd, $J_1 = 12$ Hz, $J_2 = 6$ Hz, 1H, ring junction proton), 2.77 (dd, $J_1 = 6$ Hz, $J_2 = 3$Hz, 1H, bridge head proton). 1.79 (d, $J = 2$Hz, 3H, olefinic CH_3), 1.17 (s, 3H, CH_3). 1.13 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.26 (C = O), 208.84 (C = O), 162.0 (d), 143.22 (s), 138.05 (d), 117.48 (d) (olefinic carbons), 87.27 (s), 53.92 (d), 49.47 (d), 46.31 (d), 45.90 (q), 42.69 (s), 25.49 (q), 23.47 (q), 22.49 (q). Mass (*m/z*): 246 (M^+).

4.7. *1-Methoxy-8,8,10-trimethyl-endo-tricyclo[5.2.2.0^{2,6}]undeca-10-ene-5,9-dione (12)*

Sodium borohydride (0.145 g, 3.84 mmol) was added in small portions to a solution of the enone (**11**) (0.8 g, 3.25 mmol) in methanol (15 ml) at 0°C (30 min). The reaction mixture was

concentrated *in vacuo*, diluted with water (10 ml), and extracted with CH_2Cl_2 (3 × 10 ml). The combined organic extract was washed with water (15 ml), brine (10 ml) and dried over anhydrous sodium sulphate. Removal of the solvent followed by chromatography (petroleum ether–ethyl acetate, 75:25) gave hydroxy ketone (0.68 g, 83.6%), which was subjected to further oxidation with Jones' reagent as follows. To an acetone (15 ml) solution of the above hydroxy ketone (0.68 g, 2.72 mmol) thus obtained, a freshly prepared Jones' reagent was added dropwise until the reaction was complete (TLC). Usual work-up and chromatography yielded the diketone (**12**) (0.52 g, 77%). IR (Neat) ν_{max}: 1730, 1720 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.61 (brs, 1H, β proton of β,γ-enone), 3.46 (s, 3H, OCH_3), 2.9 (m, 1H, methine H), 2.83 (superimposed dd, J = 6 Hz, 1H, methine H), 2.66 (brd, J = 1.5 Hz, 1H, methine H), 2.2 (complex m, 1H, methylene H), 2.07–1.9 (overlapped m, 3H, methylene H), 1.72 (brs, 3H, olefinic CH_3), 1.02 (s, 3H, CH_3) and 0.97 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 220 (C = O), 213.75 (C = O), 146.25, 120.0 (olefinic carbons), 86.25, 53.75, 50.75, 49.50, 53.25, 38.75, 38.20, 25.0, 24.0, 22.5 and 21.0. Mass (*m/z*): 248 (M^+).

4.8. *1-Methoxy-8,8,10-trimethyl-5-methylene-endo-tricyclo[5.2.2.0^{2,6}]undeca-10-en-9-one (13)*

To a suspension of methyltriphenylphosphonium iodide (0.2 g, 0.496 mmol) in dry toluene (5 ml) was added potassium *t*-butoxide (0.08 g, excess) followed by a solution of the compound (**12**) (0.05 g, 0.202 mmol) in toluene (3 ml).The reaction mixture was then heated at 70°C for 1 h. It was brought to room temperature and quenched with a saturated solution of ammonium chloride. It was further diluted with water and extracted with ether (3 × 25 ml). The combined organic extract was washed with brine (10 ml) and dried. Removal of solvent followed by chromatography (petroleum ether–ethyl acetate, 97:3) of the residue gave the titled compound (**13**) (0.041 g, 82.6%). IR (neat) ν_{max}: 1728, 1654 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 4.94 (d, J = 2 Hz, 1H, exocyclic methylene proton), 4.82 (d, J = 2 Hz, 1H, exocyclic methylene proton), 3.51(s, 3H, OCH_3), 3.25 (m of d, J = 12 Hz, 1H, methine proton), 2.68 (m, 1H, methine proton), 2.48 (dd, J_1 = 5.5 Hz, J_2 = 2 Hz, 1H, methine proton), 2.26 (m of t, J = 9 Hz, 2H, methylene H), 1.84 (d, J = 1.5 Hz, 3H, CH_3), 1.74 (m, 2H, methylene proton), 1.13 (s, 3H, CH_3), 1.06 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.93 (C = O), 155.25, 146.13, 119.47, 104.98 (olefinic carbons), 86.89, 53.29, 53.06, 45.25, 43.72, 42.87, 34.95, 26.72, 26.08, 24.25 (two carbons). Mass (*m/z*): 246 (M^+).

4.9. *Photochemical reaction of dien-dione 11: Formation of the compounds 14, 15 and 16*

A solution of the compound (**11**) (0.15 g, 0.61 mmol) in dry acetone (both as a solvent and sensitizer) was irradiated by a mercury vapour lamp (125W, APP) in a Pyrex immersion well under nitrogen for 3 h. Acetone was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with ethyl acetate–light petroleum ether (60–80°C)[20:80] first gave some unchanged starting material followed by the cage compound (**16**) (0.02 g, 13.3%). Further elution with ethyl acetate–petroleum ether (25:75) gave a mixture of **14** and **15** (0.04 g, 28%) which was again chromatographed. Elution with ethyl acetate–petroleum ether (25:75) furnished the 1,2-acyl shift product (**15**) as pure compound. Continued elution with the same solvent gave the compound (**14**).

4.10. *Data of 2-methoxy-3,6,6-trimethyltetracyclo[6.3.0.0.^{2,4}0^{3,7}]undeca-10-en-5,9-dione (14)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (dd, $J_1 = 6.5$ Hz, $J_2 = 3$ Hz, 1H, proton at the β-carbon of β,γ-enone). 6.37 (d, $J = 3$ Hz, 1H, proton attached to the α-carbon of β,γ-enone), 3.64 (m, 1H, methine H), 3.50 (s, 3H, OCH_3), 2.53 (s, 1H, methine H), 2.42 (d, $J = 6$ Hz, 1H, methine H), 1.9 (s, 1H, methine H), 1.35 (s, 3H, CH_3), 1.2 (s, 3H, CH_3), 0.9(s, 3H, CH_3). Mass (*m/z*); 246 (M^+).

4.11. *Data of 3,3,6-trimethyltricyclo[6.3.0.0^{2,6}]undeca-9-en-4,7,11-trione (15)*

m. p. 158°C. IR (KBr) ν_{max}: 1750, 1730,1708 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (dd, $J_1 = 7$ Hz, $J_2 = 4$ Hz, 1H, proton at the β-carbon of α,β-enone). 6.35 (dd, $J_1 = 7$ Hz, $J_2 = 2.5$ Hz, proton attached to the α-carbon of α,β-enone), 3.7 (m, 1H, methine H), 2.95 (d, $J_{gem} = 18$ Hz, 1H, CH_2), 2.90 (m, 1H, methine H), 2.56 (s, 1H, methine H), 2.10 (d, $J_{gem} = 18$ Hz, 1H, CH_2), 1.22(s, 1H, methine H),1.15 (s, 3H, CH_3), 0.87(s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 218.1, 215.5, 210.3 (three C = O groups), 160.9, 135.3, 57.2, 56.3, 52.0, 50.3, 46.4, 45.4, 27.4, 23.4, 21.6. Mass (*m/z*): 232 (M^+).

4.12. *Data of the cage compound 16*

m. p. 64°C. IR (KBr) ν_{max}: 1760,1720 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.49 (m, 1H, methine H), 3.45 (s, 3H, OCH_3), 3.10 (ddd, $J_1 = 12$ Hz, $J_2 = 6$ Hz, $J_3 = 2$ Hz, 1H, methine H), 3.02 (dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, 1H, methine H), 2.66 (m of d, $J = 6$ Hz, 1H, methine H), 2.43 (dd, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H methine H), 2.1 (brs, 1H, methine H), 1.45 (s, 3H, CH_3), 1.2 (s, 3H, CH_3), 1.18 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.8, 211.6 (two C = O groups), 84.0, 53.7, 52.9, 51.5, 46.9, 44.93, 44.6, 43.0, 40.5, 31.99, 24.8, 24.6, 24.4. Mass (*m/z*): 246 (M^+).

4.13. *11-Hydroxy-3,3,6-trimethyltetracyclo[6.3.0.0^{2,6}]undeca-9-en-4,7-dione (17)*

A solution of the hydroxy ketone (**10**) (0.12 g, 0.48 mmol) in acetone was irradiated with a mercury vapour lamp (200 W, Hanovia) under nitrogen for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with petroleum ether–ethyl acetate (60:40) furnished the triquinane (**17**) (0.07 g, 62%). IR (KBr) ν_{max}: 3450, 1730 cm^{-1}. UV (MeOH) λ_{max}: 207.8, 296.6 nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 (m, 2H, olefinic H), 5.39 (s, 1H, OH), 4.8 (s, 1H, H-C-OH), 3.7 (m, 1H, methine H), 2.7 (d, $J_{gem} = 18$ Hz, 1H, methylene H), 2.64 (m, 1H, methine H), 2.19 (d, $J = 6$ Hz, 1H, methine H), 2.14 (d, $J_{gem} = 18$ Hz, 1H, methylene H), 1.24 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.05 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 219.12, 216.67 (C = O), 134.69 (d), 133.42 (d), 85.26 (d), 59.63 (d), 59.13 (d), 50.86 (s), 49.87 (s), 48.45 (d), 45.09 (t), 25.63 (q), 24.82 (q), 20.84 (q). Mass (*m/z*): 234 (M^+).

4.14. *Jones' oxidation of 17: Synthesis of 3,3,6-trimethyltetracyclo[6.3.0.0^{2,6}]undeca-9-en-4,7,11-trione (15)*

To a solution of the keto-alcohol (**17**) (0.6 g, 2.56 mmol) in acetone was added a freshly prepared Jones' reagent dropwise at ~5°C. After the oxidation was complete (TLC) acetone was removed under vacuum and the residue was diluted with water and extracted with ether

(4 × 15 ml). The combined extract was washed with sodium bicarbonate (2 × 10 ml), water (15 ml) and brine (10 ml), and dried. Removal of the solvent followed by chromatography (petroleum ether–ethyl acetate, 75:25) of the residue on silica gel furnished the trione (**15**) (0.45g, 76%) which was found to be identical to the trione (**15**) obtained during the irradiation of **11**.

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