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Aromatics to bis-triquinane: a tandem oxidative dearomatization of bis-phenol, cycloaddition, photorearrangement and a rapid entry into carbocyclic framework of Xeromphalinone E

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ABSTRACT

A novel approach for the synthesis of a bird-shaped bis-triquinane **3**, a fascinating carbocyclic framework closely related to the skeleton of Xeromphalinone E **1** from readily available 2,6-dimethyl phenol **8** has been reported. The synthesis of bis-cyclohexadienones **6**, **22a**–**e** by oxidative acetylation of tetramethyl bisphenols **7**, **20a**–**e** has been investigated using two different reagents under varying reaction conditions. The cycloaddition of bis-cyclohexadienone **6** gives two carbocycles, bis-adduct **4b** and mono-adduct **5d** in a stereocontrolled manner. The photochemical sigmatropic 1,2-acyl shift in **4b** furnished **3** and monotriquinane **9** linked with a 9-acetoxy-9-methyl-*endo*-tricyclo[5,2,2,$0^{2,6}$]undeca-4,10-diene-8-one system. Two different pentasubstituted phenols **13** and **14** were also isolated during an attempted oxa-di-π-methane (ODPM) rearrangement of mono-adduct **5d** via aromatisation of the cyclohexadienone ring. The photochemical behaviour of bis-cyclohexadienones **6**, **22a**–**e** has also been investigated under UV irradiation and two different aromatized products were isolated for each bis-cyclohexadienone by migration and elimination of acetate groups.

1. Introduction

Cyclopentanoid moiety is present as a core structure in a wide variety of synthetic intermediates and in vast number of natural products that show diverse biological and pharmaceutical activities.[1] Amongst them, the polyquinane sesquiterpenoids isolated from various plant, marine and living organisms have attracted enormous interest not only due to their promising activities but also due to their role as building blocks in the creation of exotic molecular architectures.[2] Organic chemists found impressive arena to develop new route towards their synthesis due to the presence of complex carbocyclic framework with sporadic occurrence of functionality.[2] As a result number of creative approaches have been developed for assembly of triquinane skeleton since its discovery in 1966.[3]

Continued research in the area of triquinane natural products on both extraction and synthesis, Opatz et al. encountered six new triquinane sesquiterpenoids from *Xeromphalina* sp., named Xeromphalinone (A–F) recently in 2010.[4] Four members of Xeromphalinone A–D belong to the linearly fused *cis-anti-cis* triquinane family while two Xeromphalinone E **1** and Xeromphalinone F **2** have a different type of molecular architecture composed with two triquinane skeleta connected with each other by an ethylene or an ester linkage that may be recognized as bis-triquinanes (Fig. 1). The two tricyclic frameworks possessing different functionalities coupled with stereochemical complexity has further enhanced the interest of chemists in this family of compounds.

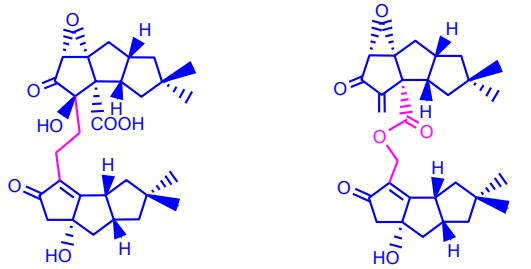

Fig. 1. Structures of bis-triquinane natural products extracted from *Xeromphalina* sp.

Taking inspiration from the above discovery, we recently developed a novel route to assemble the molecular architecture containing bis-triquinane framework **3** ($C_{31}H_{36}O_6$) by cycloaddition of bis-cyclohexadienone **6** with cyclopentadiene and subsequent ODPM (oxa-di-π-methane) rearrangement in bis-adduct **4**.[5] A detailed account of this work is presented herein. The photochemical

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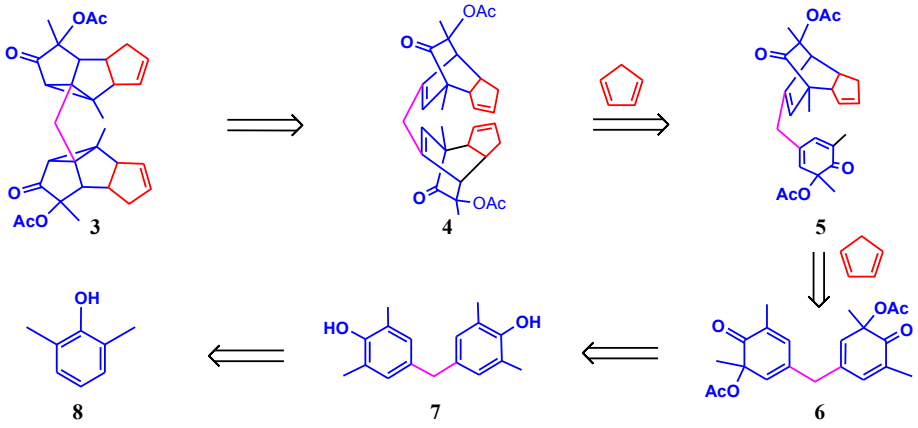
aromatization of highly substituted cyclohexadienone moiety of mono-adduct **5** is investigated during this transformation. We also report a novel method for the bisphenols **7**, **20a**–**e** and the synthesis of bis-cyclohexadienones **6**, **22a**–**e** under varying reaction conditions. The photochemical behaviour of **6**, **22a**–**e** has also been studied under UV irradiation, that is, not known in the literature to the best of our knowledge. Our strategy towards synthesis of bis-triquinane framework **3** is shown in Scheme 1. The key feature of our strategy is to create a stereocontrolled *cis-anti-cis* tricyclopentanoidal framework in a single step via 1,2-acyl shift simultaneously in both tricyclo[5.2.2.0^{2,6}]undecadienone moieties of the bis-adduct **4**.[6]

exo **5c** or *endo* **5d** stereoisomers. A single *endo* stereoisomer **5d** was isolated in accordance with our earlier report[6] (Fig. 2).

Similarly the bis-adduct **4** may also have *endo*–*exo* **4a** or *endo*–*endo* **4b** stereochemistry subsequent to second cycloaddition on **5d**. However, only a single stereoisomer **4b** was isolated (Fig. 2). The structure of **5d** was established through its X-ray single crystal analysis while that of **4b** was confirmed using ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC NMR.[7]

The photochemical reactions are one of the most employed protocol in synthetic organic chemistry for creation of various functionalities and simplification of multistep reactions in target oriented synthesis.[8,9] The synthetic potential of photochemical



Scheme 1. Retrosynthetic plan towards assembling the bis-triquinane skeleton **3**.

2. Results and discussion

Towards the synthesis of bis-triquinane skeleton **3**, it was necessary to have quick access to the precursors **4** and **5**. Precursor **4** was quickly assembled in three steps from **8**. An inverse electron demand Diels–Alder cycloaddition of **6** with cyclopentadiene gave adducts **4** and **5** (Scheme 1). While only product **5b** was isolated from the reaction, in principle the adduct **5** may have two different regio isomers **5a** and **5b** depending on the mode of approach of **6** to cyclopentadiene in the transition state. Further **5b** may also exist as

reaction of β,γ-enone chromophoric systems continues to capture attention of chemists since long time.[9] Compounds containing β,γ-enone functionality undergo two unique reactions, namely 1,2-acyl shift or ODPM rearrangement and 1,3-acyl shift. The photoreaction of rigid β,γ-unsaturated carbonyl systems is characteristic of their excited states. The lowest triplet (T_1) sensitized irradiation leads to 1,2-acyl shift while 1,3-acyl shift occurs from singlet (S_1) or higher triplet (T_2).[9] It was envisaged that bis-adduct **4b** on photolysis would give rise to different products **10**, **11** by 1,3-acyl shift and/or **3**, **9** by 1,2-acyl shift (Fig. 2, Scheme 2).

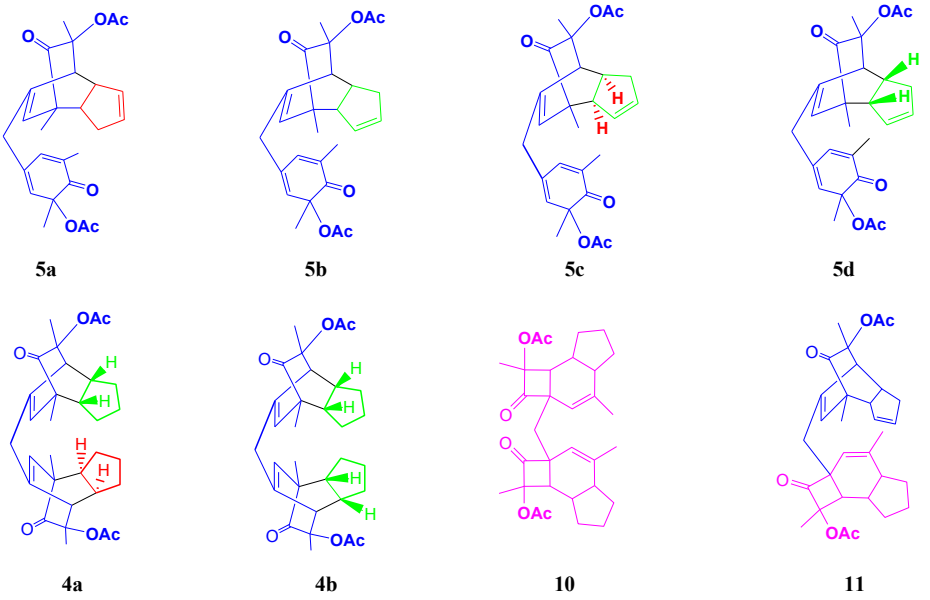
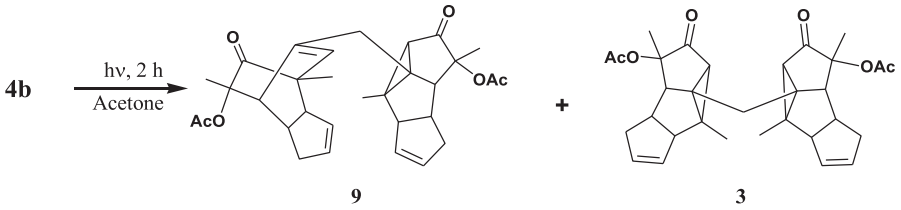


Fig. 2. Possible products during cycloaddition and photochemical rearrangements.



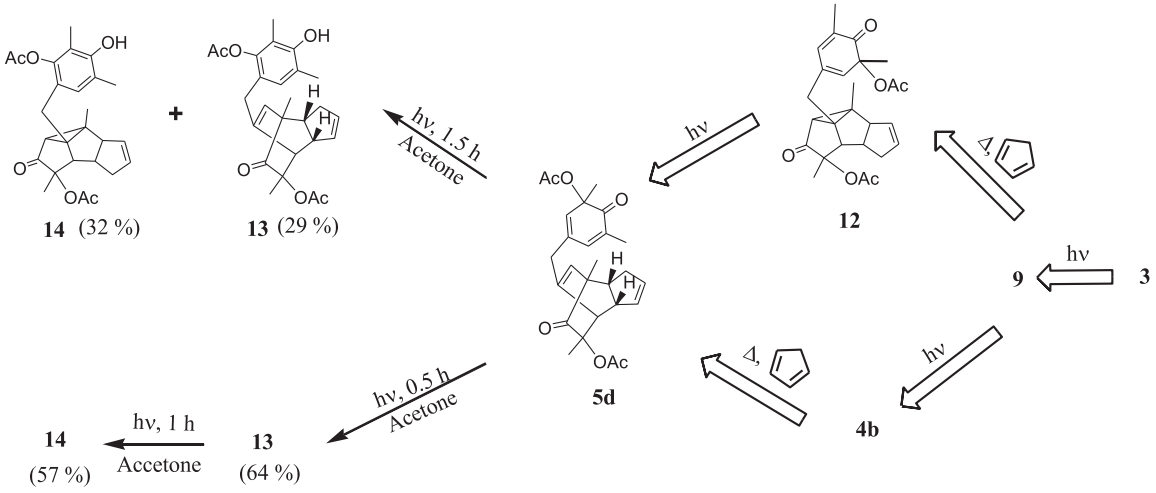
Scheme 2. Photochemical 1,2-acyl shift in bis-adduct **4b**.

Thus a solution of **4b** in acetone (both as solvent and as sensitizer) was irradiated using a mercury vapour lamp in a quartz immersion well for 2 h to furnish the products **3** and **9** whose structures were deduced by their FTIR, ^{1}H, ^{13}C, DEPT-90, DEPT-135 NMR and mass spectral analysis. It was interesting to observe half the number of signals in the NMR spectrum of **3** due to its highly symmetric structure.

Alternatively, it was also envisioned that the bis-triquinane **3** could also be accessed through a tandem photochemical–thermal–photochemical protocol from precursor **5d** (Scheme 3).

The photochemical reactions of cyclohexadienone systems have been reported in literature since very long time by different groups[11–13] but such an aromatization of cyclohexadienone moiety with migration of acetate group under these reaction conditions is not known. Hart et al. have reported photochemical transformation of 2,4-cyclohexadienone **15** in a reversible ring fission to give ketene **16**, which thermally rearranged to a bicyclo[3.1.0] hexenone **17**[12] (Scheme 4).

Baldwin et al. have also investigated the photochemical reaction of 6-acetoxycyclohexa-2,4-dienones **18a–c** and have proposed the formation of open chain products **19a–c**[13] (Scheme 5).



Scheme 3. Tandem photochemical–thermal–photochemical protocol for **3** and aromatization of cyclohexadienone.

However an attempted photochemical reaction of the precursor **5d** resulted in an unexpected formation of **13** as well as **14** by aromatization of the cyclohexadienone moiety and did not furnish any **12**. The photochemical reaction of **5d** in acetone for 0.5 h initially furnished **13**. Interestingly when the reaction was continued for 1.5 h, the aryl substituted tetracycle **14** was also isolated, which was also obtainable by further photo exposure of **13** for 1 h in acetone. The structure of **13** was discerned through its single crystal X-ray analysis.[10] The ORTEP diagram of **13** is shown in Fig. 3.

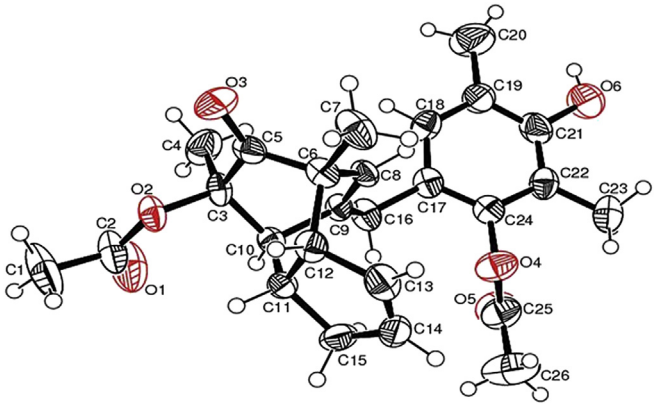
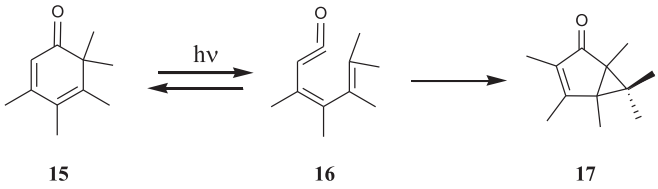


Fig. 3. ORTEP diagram of **13**.

This observation prompted us to study the effect of UV irradiation on bis-cyclohexadienone systems **6**, **22a–e**, that is, hitherto unknown in the literature.



Scheme 4. Photochemical reaction of cyclohexadienone **15**.

Towards this photochemical study, we required bis-cyclohexadienones as they are not readily available. We have previously reported the use of compilation of reagents $NaIO_4$ in Ac_2O for the synthesis of various types of acetoxycyclohexadienones by oxidative acetylation of structurally different phenols.[14] In the present work, we planned to explore the use of this reagent for the synthesis of **22a–e** by oxidative acetylation of bisphenols. However the reaction of bisphenol **20a** with $NaIO_4$ in Ac_2O at 75 °C for 3 h, furnished the novel di-acetate **21a** rather than the expected bis-acetoxy cyclohexadienone **22a**.[15] (Scheme 6) Other bisphenols **20b–e** were treated similarly to obtain only acetylated products in all the cases and no product from oxidative acetylation was isolated (Scheme 6, Table 1).

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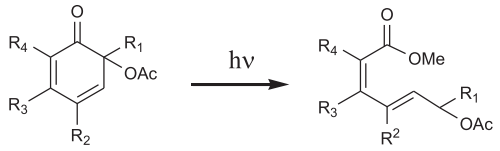
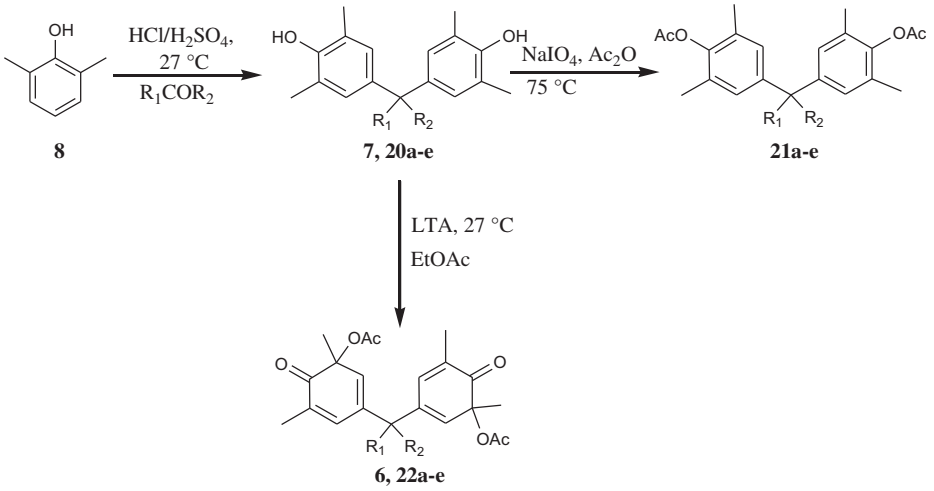


18(a-c) **19(a-c)**

a) R_1= R_2 = CH_3, R_3=R_4=H; **b**) R_1=R_2=R_4=CH_3, R_3=H; **c**) R_1=R_3=CH_3, R_2=R_4=H

Scheme 5. Photochemical reaction of acetoxycyclohexadienones **18a**–**c**.



8 **7, 20a-e** **21a-e** **6, 22a-e**

Scheme 6. Preparation of bisphenols **7**, **20a**–**e**, their oxidative acetylation using LTA and acetylation using $NaIO_4$ in Ac_2O.

Table 1
Synthesis of bis-phenols (**7**, **20a**–**e**), diacetates (**21a**–**e**) and bis-cyclohexadienones (**6**, **22a**–**e**)

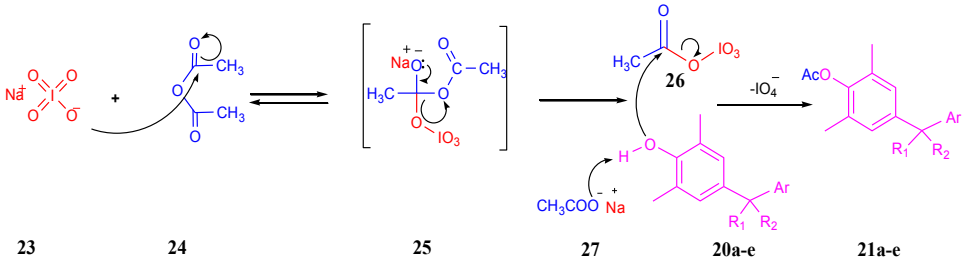
Entry	R_1	R_2	Time (min)	Yield of bisphenols (**7**, **20a**–**e**) (%)	Time (min)	Yield of diacetates (**21a**–**e**) (%)	Time (min)	Yield of bis-cyclohexadienones (**6**, **22a**–**e**) (%)
1	H	H	150	93 (**7**)	—	—	45	82 (**6**)
2	Me	H	210	92 (**20a**)	180	88 (**21a**)	45	76 (**22a**)
3	Et	H	240	94 (**20b**)	210	87 (**21b**)	40	84 (**22b**)
4	*n*-Pr	H	180	94 (**20c**)	210	87 (**21c**)	50	84 (**22c**)
5	Me	Me	210	94 (**20d**)	240	84 (**21d**)	47	78 (**22d**)
6	$-(CH_2)_4-$		240	91 (**20e**)	270	88 (**21e**)	40	64 (**22e**)

It was thought that the acetylation of phenol might be taking place due to nucleophilic attack of phenolic OH on a carbonyl of acetic anhydride without involvement of $NaIO_4$. To test this hypothesis, **20a** was heated under reflux in Ac_2O without $NaIO_4$, however the formation of acetylated product was not observed. This clearly indicated some role of $NaIO_4$ in the acetylation of bisphenol.

We have proposed a plausible mechanism for the formation of the acetylated products of bisphenols (Scheme 7). Periodate **23** perhaps attacks first on the carbonyl carbon of the anhydride **24** to generate sodium acetate **27** and ethanoylperiodate **26** via intermediate **25**. Sodium acetate thus formed is a conjugate base, which initiates the nucleophilic substitution of bis-phenols **20a**–**e** on ethanoylperiodate **26** to give the acetylated products **21a**–**e**. Acetylation of two hydroxyls in the bisphenol molecule may be synchronous or stepwise.

To support above mechanism we have also studied the acetylation of bisphenol **20a** in Ac_2O with KIO_4, CH_3COONa and CH_3COOH (Table 2).

It was found that the use of KIO_4 shortens the reaction time as compared to $NaIO_4$. This may be due to the formation of conjugate base CH_3COOK that releases the acetate ion more easily than CH_3COONa (Table 2). The reaction of **20a** in Ac_2O with CH_3COONa



23 **24** **25** **27** **20a-e** **21a-e**

Scheme 7. Acetylation of bisphenols using $NaIO_4$ in Ac_2O.

Table 2
The acetylation of bisphenol **20a** in Ac_2O using different reagents

Entry	Reagent	Temp (°C)	Time (min)	Yield %
1	$NaIO_4$	75	180	88
2	KIO_4	75	90	90
3	CH_3COONa	120	210	82
4	CH_3COOH	118	360	80[a]

[a] The reaction did not reach completion, yield is based on the recovery of starting material.

requires higher temperature and longer reaction time than $NaIO_4$. This indicates the involvement of species **26** in acetylation during the reaction of bisphenols with $NaIO_4$ or KIO_4 in Ac_2O. We have also attempted the acetylation of **20a** in Ac_2O in the presence of CH_3COOH. The reaction with acetic acid not only required high temperature and longer time but also did not reach completion even under reflux (Table 2).

We have also improvised the method for the preparation of bisphenols in light petroleum by using HCl/H_2SO_4 instead of base, which gives better yields of the products and offers simplicity in work up.[16]

We then thought of exploring the Wessely oxidation of bisphenols **7**, **20a**–**e** using LTA to access bis-cyclohexadienones **6**, **22a**–**e**. During the course of this study we found that **6** can also be obtained from **7** using LTA by replacing benzene (carcinogenic!) with toluene (52%) and with ethyl acetate (82%) with an improved yield in a shorter reaction time at room temperature (~27 °C). For the generality of the procedure, we have investigated the oxidative acetylation of bisphenols **20a**–**e** using LTA in ethyl acetate. Usual workup followed by column chromatography furnished **22a**–**e** in good yields (Table 1).

It is known that the cyclohexadienone **28** of phenol **8** is very reactive and easily undergoes self-cycloaddition to give its dimer **29**[17] (Fig. 4). Similar oxidative acetylation of bisphenols to bis-cyclohexadienones could in principle lead to the formation of several oxidation products, such as **30**, **31** by inter- and intra molecular modes of cycloaddition. But the reaction only furnished a single product for each substrate (Table 1).

a mercury vapour lamp in a quartz immersion well for 1 h to furnish two aromatized products **32** and **33**.

The compound **32** was formed by migration of both the acetate groups and aromatization of the cyclohexadienone ring, while **33** resulted by migration of an acetate group in one of the cyclohexadienone unit and deacetylation of the other unit in either synchronized or stepwise fashion (Scheme 8).

The structures of the products **32** and **33** were easily discernible through their spectral and analytical data.

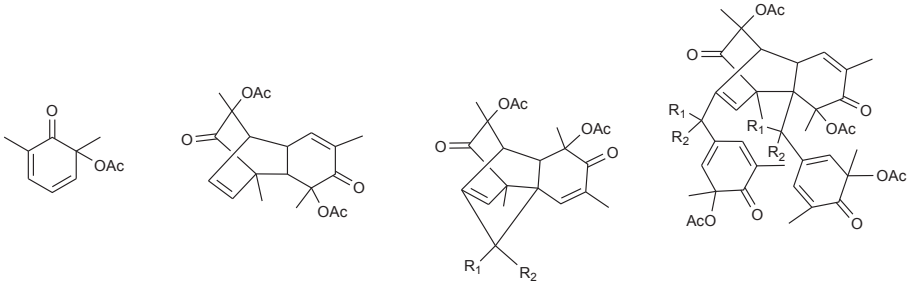
In view of above results, other bis-cyclohexadienones **22**(**a**–**e**) were also treated similarly for different time intervals. In all the cases the reaction furnished two different aromatized products for each substrate (Table 3). The structures of all the products were deduced from their IR, ^1H and ^{13}C NMR and mass spectral analysis.

Table 3
Photochemical reaction of **6**, **22**(**a**–**e**)

Entry	R_1	R_2	Biscyclohexadienones (**6**, **22a**–**e**)	Time (min)	Yield of **32**, **34**(**a**–**e**) (%)	Yield of **33**, **35**(**a**–**e**) (%)
1	H	H	**6**	60	64 (**32**)	8 (**33**)
2	Me	H	**22a**	85	58 (**34a**)	6 (**35a**)
3	Et	H	**22b**	150	62 (**34b**)	4 (**35b**)
4	*n*-Pr	H	**22c**	180	66 (**34c**)	6 (**35c**)
5	Me	Me	**22d**	165	66 (**34d**)	8 (**35d**)
6	$-(CH_2)_4-$		**22e**	180	68 (**34e**)	4 (**35e**)

3. Conclusions

The photochemical 1,2-acyl shift of both the chromophoric systems **4b** and **5d** was exploited under UV irradiation towards the synthesis of *cis-anti-cis* bis-triquinane skeleton **3**. The photochemical reaction in **4b** led to the formation of mono-triquinane connected with tricyclo[5.2.2.$0^{2,6}$]undecenones **9** and bis-triquinane **3**. On the other hand, UV irradiation of **5d** resulted in the formation of two different products, a pentasubstituted phenol connected with tricyclo[5.2.2.$0^{2,6}$]undecadienone **13** and a pentasubstituted phenol linked with a triquinane skeleton **14**. We have

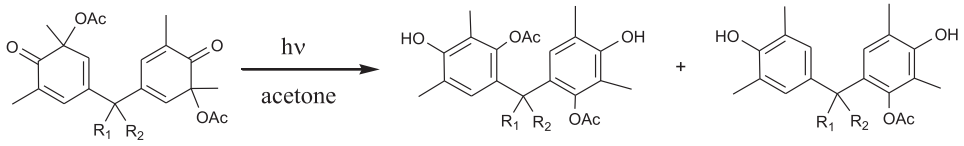


28 29 30 31

Fig. 4. Possible products of oxidative acetylation and dimerization of **7** and **8**.

Taking a clue from our observation on unexpected aromatization of cyclohexadienone moiety of **5d** (vide supra) we investigated the photochemical behaviour of **6**, **22a**–**e** under UV irradiation. Thus initially a solution of **6** in acetone was irradiated with

also reported a novel method for the preparation of bisphenols **7**, **20a**–**e** and their oxidative acetylation for obtaining the corresponding bis-cyclohexadienones **6**, **22a**–**e** by modifying Wessely oxidation. The photochemical reaction of these dienones under UV



6, 22a-e 32, 34a-e 33, 35a-e

Scheme 8. Photochemical reaction of bis-cyclohexadienone **6**, **22a**–**e**.

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irradiation resulted in the formation of two different bis-phenols via migration of both the acetate groups and aromatization while other by migration of an acetate group in one cyclohexadienone unit and deacetylation of the other unit in either synchronized or stepwise fashion.

4. Experimental section

4.1. General remarks

2,6-Dimethyl phenol, various aldehydes and ketones were purchased from Sigma Aldrich and were used without further purification. All solvents were purchased as commercial grade and were distilled prior to use. Melting points were recorded in open capillary tubes and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer PC-16 FT IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300/400 MHz NMR spectrometer (75/100 MHz for ^{13}C, respectively) using $CDCl_3$ (TMS as an internal standard). Elemental analyses were recorded on Thermo Scientific flash 2000 organic elemental analyzer at Pharmacy Department, The M.S. University of Baroda. High resolution mass (HR-ESI-MS) spectra was recorded on an Agilent Q-Tof B.05.00 (B5042.0) Higher resolution MSMS spectrometer using electrospray ionization.

Purification of the reaction products was carried out by column chromatography on a column of silica gel (60–120 mesh size), using a mixture of hexane and ethyl acetate as eluents. Thin layer chromatography was performed using Acme's Silica gel for TLC and the spots were visualized in iodine vapour.

4.2. Experimental procedures

*4.2.1. Mono-triquinane (**9**) and bis-triquinane (**3**).* A solution of precursor (**4**) (500 mg, 0.9 mmol) in acetone (600 ml) was irradiated for 2 h with a mercury vapour lamp 125 W in a quartz photochemical reactor. After completion of the reaction solvent was evaporated under vacuo to furnish a yellow solid, which was purified by flash chromatography. Elution of column with 10% EtOAc/hexane afforded compound (**3**) (146 mg, 20%) as colourless solid, R_f (20% EtOAc/hexane) 0.48.

Mp=252 °C. IR (KBr) ν_{max}: 1234, 1728, 2931, 3039 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (6H, s, $2CH_3$), 1.53 (6H, s, $2CH_3$), 1.90 (2H, s, CH_2), 2.07 (6H, s, $2CH_3$), 2.54 (4H, m, $2CH_2$), 2.77 (2H, m, 2CH), 2.91(2H, super-imposed dd, J=7.6 Hz, 2CH), 3.04 (2H, s, 2CH-α to carbonyl), 3.36 (2H, t, J=2.4 Hz, 2CH), 5.54 (2H, dd, J_1=5.5 Hz, J_2=2.0 Hz, olefinic), 5.69 (2H, m, olefinic).

^{13}C NMR (100 MHz $CDCl_3$): δ 15.72, 20.43, 21.98 (6C, CH_3), 47.30 (2C, CH), 38.40, 43.61 (2C, CH_2), 51.20 (2C, CH), 51.73 (2C, Cq), 53.46, 58.58 (4C, CH), 64.26 (2C, Cq), 80.47 (2C, attached to $OCOCH_3$), 127.55, 128.77 (4C, olefinic), 170.22, 206.78 (4C, CO). HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{31}H_{36}O_6$: 527.2401; found 527.2403.

Further elution of the column with 15% EtOAc/hexane furnished the compound (**9**) (164 mg, 32%) R_f (20% EtOAc/hexane) 0.43.

Mp=236 °C. IR (KBr) ν_{max}: 1586, 1754, 2950, 3126 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.43 (1H, s, α-CH), 1.51 (3H, s, CH_3), 1.58 (3H, s, CH_3), 1.71–1.83 (2H, m, CH_2), 2.07 (s, 6H, CH_3), 2.12–2.47 (2H, m, CH_2), 2.76–2.39 (cluster of multiplets, 3H, CH), 2.99 (1H, m, CH superimposed with signal of CH_2), 2.93 (2H, m, CH_2), 3.26 (1H, d, J=8 Hz, CH), 3.52 (1H, s, CH bridgehead), 5.48 (2H, m), 5.70 (1H, s, β-H of enone group), 5.71 (2H, m).

^{13}C NMR (75 MHz $CDCl_3$): δ 15.04, 17.11, 20.39, 21.57, 21.97, 22.17 (6C, CH_3), 47.31 (1C, CH), 37.95, 38.23, 40.48 (3C, CH_2), 41.97, 42.16 (2C, CH), 45.08, 48.62 (2C, Cq), 50.26 (1C, CH), 51.42 (1C, CH), 53.59, 57.58, 58.06 (3C, CH), 80.50, 88.87 (2C, attached to $OCOCH_3$), 124.76, 128.49, 131.06, 132.93, 145.76, 141.92 (6C, olefinic), 169.42, 170.20, 206.57, 207.86 (4C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{31}H_{36}O_6$: 527.2401; found 527.2403.

*4.2.2. Photoaromatized phenol (**13**).* A solution of precursor (**5**) (500 mg 1.1 mmol) in acetone (600 ml) was irradiated for 0.5 h with a mercury vapour lamp in a quartz photochemical reactor. The solvent was evaporated under vacuo to give the crude product, which was purified by column chromatography (10% EtOAc/hexane) furnished compound (**13**) (320 mg, 64%) colourless solid, R_f (25% EtOAc/hexane) 0.48.

Mp=194 °C. IR (KBr) ν_{max}: 1486, 1757, 2944, 3572 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.78 (2H, superimposed dd, J=3.9 Hz, 2CH), 2.00 (3H, s, CH_3), 2.05 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.47 (1H, m, CH), 2.73 (1H, m, CH_2), 2.86 (1H, m, CH_2), 3.20 (2H, s, CH_2), 3.71 (1H, s, CH bridgehead), 4.93 (1H, s, olefinic), 5.19 (1H, br s, phenolic OH), 5.46 (1H, m, olefinic), 5.70 (1H, m, olefinic), 6.70 (1H, s, CH).

^{13}C NMR (75 MHz $CDCl_3$): δ 9.76, 15.55, 15.74, 19.88, 20.47, 21.88 (6C, CH_3), 37.84, 47.71 (2C, CH_2), 38.27, 48.67, 51.34 (3C, CH), 53.61 (1C, Cq), 116.65, 120.49, 121.24, 125.45 (4C, olefinic), 80.78 (1C, attach to $OCOCH_3$), 128.27, 141.78, 145.82, 144.97, 146.40, 151.61 (6C, aromatic), 168.98, 170.21, 207.12 (3C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{26}H_{30}O_6$: 461.1934; found 461.1930.

ORTEP diagram of single crystal analysis of aromatised product (**13**) is shown in Fig. 3.

*4.2.3. Photoaromatized phenols (**13**) and (**14**).* A solution of compound (**5**) (0.5 g 1.1 mmol) in acetone (600 ml) was irradiated in a quartz photochemical reactor for 1.5 h. The solvent was evaporated under vacuo to furnish a yellow solid, which was purified by flash chromatography over a column of silica gel. Elution of column with 10% EtOAc/hexane afforded compound (**13**) (146 mg, 20%) as crystalline solid, R_f 0.56 (30% EtOAc/hexane). Its identity was confirmed by completely matched mp, IR, ^{1}H and ^{13}C NMR data with the compound (**13**) mentioned above. Further elution of column with 15% EtOAc/hexane afforded compound (**14**) (164 mg, 32%) colourless solid R_f 0.45 (30% EtOAc/hexane).

Mp=186 °C. IR (KBr) ν_{max}: 1444, 1481, 1716, 1751, 2976, 3282 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (6H, s, $2CH_3$), 1.63 (1H, d, J=4.8 Hz, CH), 1.72 (2H, s, CH_2), 2.06 (6H, s, $2CH_3$), 2.19 (3H, s, CH_3), 2.31 (2H, m, CH_2), 2.36 (3H, s, CH_3), 3.04 (2H, m, CH), 3.14 (1H, s, CH), 4.84 (1H, s, phenolic OH), 5.68 (2H, m, olefinic), 6.81 (1H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.88, 15.74, 17.53, 18.41, 20.69, 21.67 (6C, CH_3), 28.67, 38.02 (2C, CH_2), 42.54, 45.91, 47.82, 49.90 (4×C, CH), 54.82, 55.15 (2C, Cq), 88.06 (1C, attach to $OCOCH_3$), 116.70, 121.47 (2C, olefinic), 122.48, 141.36, 130.83, 132.59, 146.26, 151.67 (6C, aromatic), 169.10, 169.90, 209.48 (3C, carbonyl).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{26}H_{30}O_6$: 461.1934; found 461.1934.

*4.2.4. Typical experimental procedure for bis-phenols (**7**, **20a**–**e**).*[12,18] To a stirred mixture of 2,6-dimethyl phenol **8** (5.0 g, 41.0 mmol) and aldehyde/ketone (94.0 mmol) in light petroleum (40 ml) hydrochloric acid (5 ml, 36% w/v) was added in the case of aldehydes or H_2SO_4 (1.5 ml, 98%) in the case of ketones over a period of 15 min at room temperature (27 °C) and was further stirred for an appropriate time (Table 1). The reaction mixture was then diluted 10 times of its volume with water and was further stirred for 15 min. The solid thus obtained was filtered on a Buchner funnel, washed thoroughly with water and dried at 85–90 °C under vacuum to give the crude product, which was purified by flash chromatography. Elution of the column

with EtOAc/hexane afforded bisphenol as a white crystalline solid. The structures of the products **7**, **20**(**a**–**e**) were confirmed by completely matched mp, IR, ^{1}H and ^{13}C NMR and mass data reported in literature.[12,18]

*4.2.5. Typical experimental procedure for diacetates of bisphenol (**21a**–**e**).* To a stirred solution of bisphenol (4.0 mmol) in acetic anhydride (10 ml) was added sodium metaperiodate (1.28 g, 6.0 mmol) in portions over a period of 15 min. Stirring was further continued for appropriate time period (Table 1) while maintaining the reaction temperature 75 °C. The reaction mixture was allowed to cool down to room temperature and then poured into a saturated solution of sodium bicarbonate (75 ml). The aqueous layer was then extracted with ethyl acetate (25 ml×3) and organic extracts were washed with water (20 ml), brine (20 ml) and dried over anhydrous sodium sulfate. The solvent was evaporated under vacuo to give the crude product, which was purified by flash chromatography over a column of silica gel using a mixture of EtOAc/hexane furnished white solid as acylated product (Scheme 6, Table 1). The structures of the products were confirmed by their analytical and spectral data are given below.

*4.2.6. 4-[1-(4-Acetoxy-3,5-dimethyl-phenyl)-ethyl]-2,6-dimethyl-phenyl ester (**21a**).* R_f (20% EtOAc/hexane) 0.62. Mp 112 °C. IR (KBr) ν_{max}: 1253, 1408, 1762, 3049 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (3H, d, J=7.2 Hz, CH_3), 2.12 (12H, s, 4CH_3), 2.31 (6H, s, 2CH_3), 3.96 (1H, q, J=2.6 Hz, CH), 6.88 (4H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 16.45 (C, CH_3), 20.53 (2C, CH_3), 22.00 (2C, CH_3), 43.61 (1C, CH), 127.74, 129.72, 143.60, 146.38 (12C, aromatic), 169.03 (2C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{22}H_{26}O_4$: 377.1729; found 377.1728.

*4.2.7. 4-[1-(4-Acetoxy-3,5-dimethyl-phenyl)-propyl]-2,6-dimethyl-phenyl ester (**21b**).* R_f (30% EtOAc/hexane) 0.62. Mp 96 °C. IR (KBr) ν_{max}: 1190, 1774, 2985, 3140 cm^{-1}.

^{1}H (400 MHz, $CDCl_3$): δ 0.82 (3H, t, J=7.2 Hz, CH_3), 1.976 (2H, m, CH_2), 2.105 (12H, s, 4CH_3), 2.30 (6H, s, 2CH_3), 3.50 (1H, t, J=7.6 Hz, CH), 6.88 (4H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 11.49 (1C, CH_3), 12.92 (4C, CH_3), 16.49 (2C, CH_3), 28.66 (1C, CH_2), 52.10 (1C, CH), 127.97, 129.70, 142.42, 146.41 (12C, aromatic), 168.96 (2C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{23}H_{28}O_4$: 391.1880; found 391.1979.

*4.2.8. 4-[1-(4-Acetoxy-3,5-dimethyl-phenyl)-butyl]-2,6-dimethyl-phenyl ester (**21c**).* R_f (20% EtOAc/hexane) 0.64. Mp 118 °C. IR (KBr) ν_{max}: 1240, 1762, 2852, 3045 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, J=7.4 Hz, CH_3), 1.25 (2H, m, CH_2), 1.92 (2H, m, CH_2), 2.10 (12H, s, 4CH_3), 2.29 (6H, s, 2CH_3), 3.71 (1H, t, J=7.8 Hz, CH), 6.89 (4H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 14.11 (1C, CH_3), 16.50 (4C, CH_3), 20.53 (1C, CH_2), 21.18 (1C, CH_3), 37.99 (1C, CH_2), 49.91 (1C, CH), 127.93, 129.70, 142.60, 146.39 (12C, aromatic), 168.96 (2C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{24}H_{30}O_4$: 405.2036; found 405.2036.

*4.2.9. 4-[1-(4-Acetoxy-3,5-dimethyl-phenyl)-1-methyl-ethyl]-2,6-dimethyl-phenyl ester (**21d**).* R_f (20% EtOAc/hexane) 0.65. Mp 138 °C. IR (KBr) ν_{max}: 1402, 1480, 1764, 3028 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (6H, s, 2CH_3), 2.09 (12H, s, 4CH_3), 2.31 (6H, s, 2CH_3), 6.89 (4H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 16.58 (4C, CH_3), 20.55 (2C, CH_3), 30.09 (2C, CH_3), 42.09 (1C, Cq), 127.06, 129.16, 146.08, 147.77 (12C, aromatic), 169.01 (2C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{23}H_{28}O_4$: 391.1880; found 391.1876.

*4.2.10. 4-[1-(4-Acetoxy-3,5-dimethyl-phenyl)-1-cyclopentyl]-2,6-dimethyl-phenyl ester (**21e**).* R_f (20% EtOAc/hexane) 0.63. Mp 160 °C. IR: (KBr): 1428, 1760, 3028 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71 (4H, m, 2CH_2), 1.94 (4H, m, 2CH_2), 2.14 (12H, s, 4CH_3), 2.34 (6H, s, 2CH_3), 6.49 (4H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 15.48 (4C, CH_3), 20.69 (2C, CH_3), 22.91 (2C, CH_2), 36.51 (2C, CH_2), 54.51 (1C, Cq), 127.27, 131.93, 142.92, 146.60 (12C, aromatic), 169.01 (2C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{25}H_{30}O_4$: 417.2036; found 417.2034.

*4.2.11. Typical experimental procedure for bis-acetoxycyclohexadienones (**6**, **22a**–**e**).* A mixture of bisphenol (4.0 mmol) and lead tetra acetate (5.32 g, 12.0 mmol) in ethyl acetate (30 ml) was stirred at room temperature (~27 °C) for appropriate time (Table 1). After completion of the reaction it was diluted with ethyl acetate (150 ml) and stirred further for 15 min. The reaction mixture was then filtered through Celite and the solvent was evaporated in vacuo to give the crude product, which was purified by flash chromatography. Elution of the column with 20% EtOAc/hexane gave pure product in good yield. Structure of the product was confirmed by its spectral and analytical analysis.

*4.2.12. 3-[1-(3-Acetoxy-3,5-dimethyl-4-oxo-cyclohexa-1,5-dienyl)-ethyl]-1,5-dimethyl-6-oxo-cyclohexa-2,4-dienyl ester (**22a**).* R_f (30% EtOAc/hexane) 0.50. Mp 149 °C. IR (KBr) ν_{max}: 1267, 1672, 1734, 3024 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (3H, d, J=6.3 Hz, CH_3), 1.37 (6H, s, 2CH_3), 1.90 (6H, s, 2CH_3), 2.08 (6H, s, 2CH_3), 3.11 (1H, q, J=6.2 Hz, CH), 5.91 (2H, s, olefinic), 6.60 (2H, s, olefinic).

^{13}C NMR (75 MHz $CDCl_3$): δ 13.91 (1C, CH_3), 15.19, 20.32, 28.83 (6C, CH_3), 42.30 (1C, CH), 78.32 (2C, carbon attached to $OCOCH_3$), 134.26, 134.97, 138.05, 138.72 (8C, olefinic), 168.99, 198.70 (4C, CO).

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{22}H_{26}O_6$: 409.1622; found 409.1621 (M$^+$).

*4.2.13. 3-[1-(3-Acetoxy-3,5-dimethyl-4-oxo-cyclohexa-1,5-dienyl)-propyl]-1,5-dimethyl-6-oxo-cyclohexa-2,4-dienyl ester (**22b**).* *Rf* (30% EtOAc/hexane) 0.52. IR (KBr) ν_{max}: 1220, 1681, 1740, 3028 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, t, J=7.2 Hz, CH_3), 1.61 (2H, m, CH_2), 1.85 (6H, s, 2CH_3), 2.14 (6H, s, 2CH_3), 2.32 (6H, s, 2CH_3), 3.56 (1H, t, J=7.2 Hz, CH), 6.04 (2H, s, olefinic), 6.98 (2H, s, olefinic).

^{13}C NMR (100 MHz $CDCl_3$): δ 13.98 (1C, CH_3), 15.38 (1C, CH_2), 20.52, 24.14, 32.60 (6C, CH_3), 48.14 (1C, CH), 78.55 (2C, carbon attached to $OCOCH_3$), 145.73, 147.34, 138.27, 139.36 (8C, olefinic), 169.30, 199.07 (4C, CO).

Anal. Calcd for $C_{23}H_{28}O_6$: C, 69.98; H, 7.05; found: 69.92; H, 7.12.

*4.2.14. 3-[1-(3-Acetoxy-3,5-dimethyl-4-oxo-cyclohexa-1,5-dienyl)-butyl]-1,5-dimethyl-6-oxo-cyclohexa-2,4-dienyl ester (**22c**).* R_f (30% EtOAc/hexane) 0.52. IR (KBr) ν_{max}: 1242, 1680, 1760, 3042 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, t, J=7.5 Hz, CH_3), 1.24 (2H, m, CH_2), 1.44 (6H, s, 2CH_3), 1.62 (2H, m, CH_2), 1.91 (6H, s, 2CH_3), 2.09 (6H, s, 2CH_3), 2.93 (1H, t, J=7.0 Hz, CH), 5.91 (2H, s, olefinic), 6.55 (2H, s, olefinic).

^{13}C NMR (100 MHz $CDCl_3$): δ 14.12 (1C, CH_3), 15.47 (2C, CH_3), 20.27 (2C, CH_3), 24.05 (2C, CH_3), 31.93, 32.59 (2C, CH_2), 78.44 (2C, carbon attached to $OCOCH_3$), 145.70, 147.34, 138.24, 139.98 (8C, olefinic), 169.34, 199.03 (4C, CO).

Anal. Calcd for $C_{24}H_{30}O_6$: C, 69.54; H, 7.30; found: C, 69.49; H, 7.32.

4.2.15. 3-[1-(3-Acetoxy-3,5-dimethyl-4-oxo-cyclohexa-1,5-dienyl)-1-methyl-ethyl]-1,5-dimethyl-6-oxo-cyclohexa-2,4-dienylester

(**22d**). R_f (30% EtOAc/hexane) 0.58. Mp 140 °C. IR (KBr) ν_{max}: 1267, 1672, 1734, 3024 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.15 (3H, s, $2CH_3$), 1.45 (6H, s, $2CH_3$), 1.88 (6H, s, $2CH_3$), 2.09 (6H, s, $2CH_3$), 5.95 (2H, s, olefinic), 6.58 (2H, s, olefinic).

^{13}C NMR (75 MHz $CDCl_3$): δ 15.44 (2C, CH_3), 20.55 (2C, CH_3), 24.05 (2C, CH_3), 25.77 (2C, CH_3), 41.25 (1C, Cq), 78.43 (2C, carbon attached to $OCOCH_3$), 145.41, 145.65, 138.09, 138.75 (8C, olefinic), 169.19, 198.84 (4C, CO).

Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05; found: 68.89; H, 7.6.

*4.2.16. 3-[1-(3-Acetoxy-3,5-dimethyl-4-oxo-cyclohexa-1,5-dienyl)-cyclopentyl]-1,5-di methyl-6-oxo-cyclohexa-2,4-dienylester (**22e**).* R_f (30% EtOAc/hexane) 0.54. IR (KBr) ν_{max}: 1240, 1674, 1730, 3010 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (6H, s, $2CH_3$), 1.66 (4H, m, $2CH_2$), 1.81 (4H, m, $2CH_2$), 1.90 (6H, s, $2CH_3$), 2.10 (6H, s, $2CH_3$), 5.97 (2H, s, olefinic), 6.58 (2H, s, olefinic).

^{13}C NMR (75 MHz $CDCl_3$): δ 15.50 (2C, CH_3), 20.63 (2C, CH_3), 22.78, 24.21 (4C, CH_2), 34.01 (2C, CH_3), 54.21 (1C, Cq), 78.50 (2C, carbon attached to $OCOCH_3$), 145.68, 136.30, 138.56, 138.66 (8C, olefinic), 169.45, 198.97 (4C, CO).

Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09; found: 70.20; H, 7.16.

*4.2.17. Typical experimental procedure for photoreaction of bis-cyclohexadienones (**6**, **22a**–**e**).* A solution of bis-acetoxy cyclohexadienone (3.0 mmol) in acetone (600 ml) was irradiated with a mercury vapour lamp (125 W) in a quartz immersion well. After completion of the reaction solvent was evaporated under vacuo to give crude product, which was purified by flash chromatography over a column of silica gel. Elution of the column with EtOAc/hexane afforded two different products for each substrate (Scheme 8, Table 3). The structures of the products were then confirmed by their mp, FTIR, ^1H and ^{13}C NMR and HRMS spectral analysis.

*4.2.18. 3-Hydroxy-6-(4-hydroxy-3,5-dimethyl-benzyl)-2,4-dimethyl-phenyl ester (**32**).* R_f (30% EtOAc/hexane) 0.44. Mp 172 °C. IR (KBr) ν_{max}: 1432, 1482, 1740, 3410 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 2.04 (6H, s, $2CH_3$), 2.15 (6H, s, $2CH_3$), 2.28 (6H, s, $2CH_3$), 3.53 (2H, s, CH_2), 4.72 (2H, exchangeable OH), 6.67 (2H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.66 (2C, CH_3), 15.77 (2C, CH_3), 20.51 (2C, CH_3), 41.81 (1C, CH_2), 116.40, 120.79, 123.61, 141.14, 146.20, 151.07 (12C, aromatic), 169.41 (2C, CO).

HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{21}H_{24}O_6$: 395.1465; found 395.1462.

*4.2.19. 6-(2-Acetoxy-4-hydroxy-3,5-dimethyl-benzyl)-3-hydroxy-2,4-dimethyl-phenylester (**33**).* R_f (30% EtOAc/hexane) 0.65. Mp 167 °C. IR (KBr) ν_{max}: 1440, 1578, 1750, 3426 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 2.04 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.21 (6H, s, $2CH_3$), 2.28 (3H, s, CH_3), 3.63 (2H, s, CH_2), 4.84 (2H, s, exchangeable OH), 6.77 (3H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.70 (2C, CH_3), 15.80, 15.96 (2C, CH_3), 20.58 (1C, CH_3), 47.23 (1C, CH_2), 116.53, 120.84, 122.90, 125.13, 128.91, 141.23, 131.84, 146.17, 150.44, 151.01 (10C, aromatic), 169.28 (1C, CO).

Anal. Calcd for $C_{19}H_{24}O_4$: calculated C, 72.13; H, 7.65; found: 72.02; H, 7.61.

*4.2.20. 3-Hydroxy-6-[1-(4-hydroxy-3,5-dimethyl-phenyl)-ethyl]-2,4-dimethyl-phenyl ester (**34a**).* R_f (30% EtOAc/hexane) 0.44. Mp 184 °C. IR (KBr) ν_{max}: 1234, 1482, 1740, 3407 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (3H, d, J=7.2 Hz, CH_3), 2.00 (6H, s, $2CH_3$), 2.18–2.34 (12H, m, $4CH_3$), 4.15 (1H, q, J=7.2 Hz, CH), 4.70 (2H, s, exchangeable OH), 6.80 (2H, s, aromatic).

^{13}C NMR (50 MHz $CDCl_3$): δ 9.74 (1C, CH_3), 16.03 (2C, CH_3), 20.55 (2C, CH_3), 20.82 (2C, CH_3), 31.95 (1C, CH), 116.41, 120.73, 126.38, 141.20, 145.58, 150.86 (12C, aromatic), 171.28 (2C, CO).

HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{22}H_{26}O_6$: 409.1622; found 409.1617.

*4.2.21. 6-[1-(2-Acetoxy-4-hydroxy-3,5-dimethyl-phenyl)-ethyl]-3-hydroxy-2,4-dimethyl-phenyl ester (**35a**).* R_f (30% EtOAc/hexane) 0.65. IR (KBr) ν_{max}: 1190, 1480, 1760, 2860, 3542 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.45 (3H, d, J=7.2 Hz, CH_3), 1.86 (3H, s, CH_3), 2.02 (3H, s, CH_3), 2.21 (6H, s, $2CH_3$), 2.34 (3H, s, CH_3), 3.78 (1H, q, J=7.2 Hz, CH), 4.71 (2H, s, exchangeable OH), 6.78 (3H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.83 (1C, CH_3), 15.26 (2C, CH_3), 16.07, 20.60, 41.72 (3C, CH_3), 37.54 (1C, CH), 116.48, 122.73, 126.68, 127.55, 132.70, 145.43, 140.46, 146.11, 150.45, 151.47 (10C, aromatic), 169.41 (1C, CO).

Anal. Calcd for $C_{20}H_{24}O_4$: C, 72.15; H, 7.37; found: 72.02; H, 7.21.

*4.2.22. 6-[1-(2-Acetoxy-4-hydroxy-3,5-dimethyl-phenyl)-propyl]-3-hydroxy-2,4-dimethyl-phenyl ester (**34b**).* R_f (30% EtOAc/hexane) 0.44. Mp 190 °C. IR (KBr) ν_{max}: 1226, 1482, 1745, 3445 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 1.28 (3H, t, J=7.2 Hz, CH_3), 1.87 (2H, m, CH_2), 1.99 (6H, s, $2CH_3$), 2.20 (6H, s, 2 CH_3), 2.45 (6H, s, $2CH_3$), 4.13 (1H, t, J=7.2 Hz, CH), 4.65 (2H, s, exchangeable OH), 6.82 (2H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.87 (1C, CH_3), 13.08 (2C, CH_3), 14.17 (2C, CH_3), 16.10 (2C, CH_3), 20.58 (1C, CH_2), 31.62 (1C, CH), 116.48, 120.59, 124.69, 126.83, 146.26, 150.79 (12C, aromatic), 169.56 (2C, CO).

HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{23}H_{28}O_6$: 423.1778; found 423.1776.

*4.2.23. 3-Hydroxy-6-[1-(4-hydroxy-3,5-dimethyl-phenyl)-propyl]-2,4-dimethyl-phenyl ester (**35b**).* R_f (30% EtOAc/hexane) 0.62. IR (KBr) ν_{max}: 1200, 1750, 2870, 4740 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, J=7.2 Hz, CH_3), 1.27 (2H, m, CH_2), 2.00 (3H, s, CH_3), 2.22 (9H, superimposed s, $3CH_3$), 2.45 (3H, s, CH_3), 3.54 (1H, t, J=7.2 Hz, CH), 4.50 (2H, s, exchangeable OH), 6.81 (1H, s, aromatic), 6.83 (2H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.28 (1C, CH), 12.98 (2C, CH_3), 15.10, 16.11, 20.83 (3C, CH_3), 28.92 (1C, CH_2), 41.72 (1C, CH), 113.67, 120.64, 122.69, 127.78, 127.83, 128.09, 136.10, 137.42, 147.12, 150.24 (10C, aromatic), 170.44 (1C, CO).

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65; found: 72.58; H, 7.61.

*4.2.24. 6-[1-(2-Acetoxy-4-hydroxy-3,5-dimethyl-phenyl)-butyl]-3-hydroxy-2,4-dimethyl-phenyl ester (**34c**).* R_f (30% EtOAc/hexane) 0.44. Mp 142 °C. IR (KBr) ν_{max}: 1205, 1483, 1747, 4176, 3440 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, t, J=7.2 Hz, CH_3), 1.27 (2H, m, CH_2), 1.83 (2H, m, CH_2), 1.99 (6H, s, $2CH_3$), 2.19 (6H, s, $2CH_3$), 2.45 (6H, s, $2CH_3$), 3.97 (1H, t, J=7.2 Hz, CH), 4.72 (2H, s, phenolic OH), 6.82 (2H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 9.87 (1C, CH_3), 17.45, 18.00, 19.46 (6C, CH_3), 41.07, 31.67 (2C, CH_2), 36.72 (1C, CH), 116.49, 120.65, 126.90, 145.98, 146.62, 150.79 (12C, aromatic), 169.16 (1C, CO).

HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{24}H_{30}O_6$: 437.1935; found 437.1931.

*4.2.25. 3-Hydroxy-6-[1-(4-hydroxy-3,5-dimethyl-phenyl)-butyl]-2,4-dimethyl-phenyl ester (**35c**).* R_f (30% EtOAc/hexane) 0.65. IR (KBr) ν_{max}: 1204, 1480, 1760, 2880, 3432 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, J=7.2 Hz, CH_3), 1.26 (2H, m, CH_2), 1.96 (2H, m, CH_2), 2.11 (3H, s, CH_3), 2.25 (9H, s, CH_3), 2.45 (3H, s, CH_3), 3.66 (1H, t, J=7.2 Hz, CH), 4.61 (2H, s, phenolic OH), 6.81 (2H, s, aromatic), 6.83 (1H, s, aromatic).

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^{13}C NMR (100 MHz $CDCl_3$): δ 14.12 (1C, CH_3), 16.12 (2C, CH_3), 20.27, 21.30, 26.32 (3C, CH_3), 41.72, 32.69 (2C, CH_2), 39.73 (1C, CH), 112.77, 118.83, 122.69, 127.73, 130.57, 134.51, 138.01, 140.86, 146.52, 149.65 (10C, aromatic), 172.45 (1C, CO).

HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{22}H_{28}O_4$: 379.1880; found 379.1881.

*4.2.26. 6-[1-(2-Acetoxy-4-hydroxy-3,5-dimethyl-phenyl)-methyl-ethyl]-3-hydroxy-2,4-dimethyl-phenyl ester (**34d**).* R_f (30% EtOAc/hexane) 0.46. Mp 202 °C. IR (KBr) ν_{max}: 1205, 1483, 1747, 3440 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67 (6H, s, $2CH_3$), 1.88 (12H, s, $4CH_3$), 2.26 (6H, s, $2CH_3$), 4.70 (2H, s, exchangeable OH), 7.08 (2H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 16.19, 28.48, 30.98, 31.25 (8C, CH_3), 41.37 (1C, Cq), 122.16, 126.96, 132.18, 136.47, 142.73, 149.89 (12C, aromatic), 170.16 (2C, CO).

HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{23}H_{28}O_6$: 423.1778; found 423.1776.

*4.2.27. 3-Hydroxy-6-[1-(4-hydroxy-3,5-dimethyl-phenyl)-1-methyl-ethyl]-2,4-dimethyl-phenyl ester (**35d**).* R_f (30% EtOAc/hexane) 0.62. Mp 186 °C. IR (KBr) ν_{max}: 1204, 1480, 1580, 1760, 3540 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (6H, s, $2CH_3$), 2.20 (3H, CH_3), 2.22 (12H, s, $4CH_3$), 4.54 (2H, s, exchangeable OH), 6.85 (3H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 10.02 (2C, CH_3), 14.21, 16.06, 20.55, 41.79, 31.61 (5C, CH_3), 39.44 (1C, Cq), 117.58, 119.96, 125.24, 128.28, 132.57, 134.71, 143.54, 145.79, 150.65, 152.57 (10C, aromatic), 168.49 (2C, CO).

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65; found: 72.68; H, 7.62.

*4.2.28. 6-[1-(2-Acetoxy-4-hydroxy-3,5-dimehyl-phenyl)-cyclo-pentyl]-3-hydroxy-2,4-dimethyl-phenylester (**34e**).* R_f (30% EtOAc/hexane) 0.42. Mp 212 °C. IR (KBr) ν_{max}: 1226, 1482, 1603, 1741, 3493 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (4H, m, $2CH_2$), 1.93 (4H, s, $2CH_2$), 2.12 (6H, s, $2CH_3$), 2.14 (6H, s, $2CH_3$), 2.34 (3H, s, CH_3), 5.32 (2H, s, OH), 6.49 (2H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 15.00, 20.14, 30.99 (6C, CH_3), 38.04, 55.22 (4C, CH_2), 58.77 (1C, Cq), 126.08, 141.24, 130.45, 132.74, 142.74, 147.46 (12C, aromatic), 165.44 (1C, CO). Anal. Calcd for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53; found: 70.28; H, 7.60.

*4.2.29. 3-Hydroxy-6-[1-(4-hydroxy-3,5-dimethyl-phenyl)-cyclo-pentyl]-2,4-dimethyl-phenylester (**35e**).* R_f (30% EtOAc/hexane) 0.64. IR (KBr) ν_{max}: 1234, 1482, 1731, 3407 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (4H, m, CH_2), 1.56 (4H, m, CH_2), 1.61 (6H, s, $2CH_3$), 2.08 (6H, s, $2CH_3$), 2.10 (6H, s, $2CH_3$), 4.45 (2H, s, exchangeable OH), 5.83 (2H, s, aromatic), 5.94 (1H, s, aromatic).

^{13}C NMR (100 MHz $CDCl_3$): δ 14.97 (2C, CH_3), 18.24, 22.82, 28.16 (2C, CH_3), 30.99, 38.01 (4C, CH_2), 50.22 (1C, Cq), 120.88, 125.62, 126.55, 127.70, 141.37, 130.04, 134.40, 136.73, 137.59, 143.90 (10C, aromatic), 175.43 (1C, CO).

Anal. Calcd for $C_{23}H_{28}O_6$: C, 74.97; H, 7.66; found: 74.98; H, 7.59.

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Supplementary data

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