Pergamon

Tetrahedron 55 (1999) 3209–3218

TETRAHEDRON

Stereo- and Regioselectivity of Intramolecular 1,2-Arene-Alkene Photocycloaddition in 2-Alkenyl-4-Chromanones[¶]

Govind P. Kalena, Padmanava Pradhan and Asoke Banerji*
Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai (Bombay)-400 085, India

Received 26 May 1998; revised 29 June 1998; accepted 30 June 1998

Abstract: Intramolecular 1,2-arene-alkene photocycloaddition of 2-alkenyl-4-chromanones gave complex multicyclic oxatetracyclotetradecanediones which on internal photo- and microwave induced thermal rearrangements provided a diverse array of compounds with [3.3.0]bicyclooctane carbon frame work. The stereo- and regiochemical aspects as well as desymmetrization of alkenyl chromanones due to intramolecular 1,2-arene-alkene photocycloaddition have also been discussed.

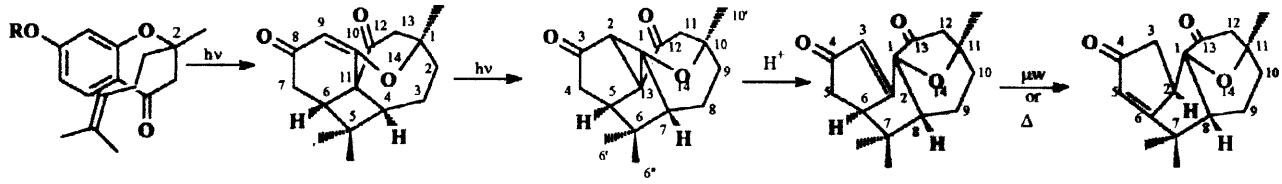
INTRODUCTION

Arene-alkene photocycloadditions, leading to non-aromatics from aromatics, provide elegant routes to a plethora of natural and synthetic compounds with multicyclic structures of exotic molecular architecture.[1] Compared to the intermolecular reactions, intramolecular arene-alkene photocyclisation with suitably selected alkene tethers not only enhances their scope but also improves the efficiency of the reaction. They are generally attended with high stereo- and regioselectivity. The internal strain of many of the photoadducts offer opportunity for further rational transformations through extensive bond rearrangements. We felt that easily accessible 2-alkenyl-4-chromanones[2,3] could provide interesting possibilities for intramolecular photocycloadditions. The participation of the alkenyl side chains with variable lengths could result in the formation of additional functionalised carbocyclic rings. The steric constraints of the heterocyclic ring are expected to contribute towards stereo- and regioselectivities. An account on the stereo- and regioselectivity in the formation of 1,2-arene-alkene photocycloadduct, its photochemical and microwave induced thermal secondary transformations and desymmetrization of judiciously modified prochiral substrate, are presented in this paper.

RESULTS AND DISCUSSION

I. Intramolecular Rearrangements of 2-Alkenyl-4-Chromanones

Photolysis of 2-methyl-2-(4'-methyl-3'-pentenyl)-7-hydroxy-4-chromanone (**1**) in different solvents furnished **4** (in C_6H_6) and **5** (in CH_3OH). Compound **5** being a highly strained molecule, undergoes acid catalysed rearrangement to **6** which thermally (or with microwave irradiation) rearranged to **7**. Thus, complex multicyclic compounds **4-7** could be generated from the easily accessible chromanones as described below.



1. R= H
2. R = CH_3
3. R = C_2H_5

4 **5** **6** **7**

Scheme- 1

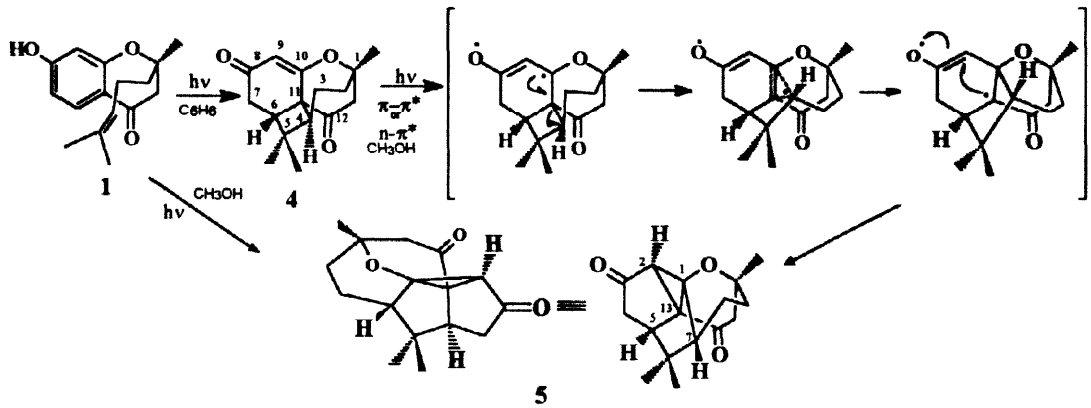
PII: S0040-4020(98)01134-X

I.1. *Phototransformation of 1 to (1R*,4S*,6R*,11R*)-1,5,5-trimethyl-14-oxatetracyclo[8.3.1.0^{4,11}.0^{6,11}]tetradeca-9-ene-8,12-dione (4).*

In a preliminary communication we reported[2] the photolysis of **1** in C_6H_6 with near UV irradiation (>300 nm) or sunlight, when a crystalline product ($C_{16}H_{20}O_3$, M^+ 260) **4** was obtained in 25% yield. From the IR, UV, ^1H and ^{13}C NMR spectra an intramolecular arene-alkene photocycloaddition was inferred. The intricate pattern in the ^1H NMR spectrum of **4** was resolved by elaborate 2D NMR studies. The assignments of the proton bearing carbons and the attached protons were made from the DEPT and ^1H-^{13}C HETCOR spectra. These data along with deuterium exchange experiment and the COLOC spectra established the structure as 1,2-arene-alkene photocycloadduct, (1*R**,4*S**,6*R**,11*R**)-1,5,5-trimethyl-14-oxatetracyclo [8.3.1.0.^{4,11}.0^{6,11}]tetradeca-9-ene-8,12-dione(**4**). The stereochemistry of H-6 and H-4 in **4** were derived from the NOESY spectra. X-ray crystallography[4] also confirmed the structure **4** (**Fig. 1**). It was interesting to note that photolysis of both **2** and **3** in C_6H_6 containing *p*-toluene sulphonic acid (PTS) yielded the same photoproduct **4** in 25% and 30% yields respectively. An enol ether intermediate was postulated for the phototransformation. This was supported by deuterium labelling experiment.[5]

I.2 *Photorearrangement of 1 to (1S*,2R*,5S*,7S*,10S*,13R*)6,6,10-trimethyl-14-oxapentacyclo [8.3.1.0^{1,7}.0^{2,13}.0^{5,13}]tetradeca-3,12-dione (5).*

As described above, photolysis of **1** in C_6H_6 yields **4**. However, using CH_3OH as a solvent, a different compound **5** was obtained as the major product (38%) while **4** was a minor component (around 5%). Photoproduct **5** was isomeric to **4** as revealed by GC-MS. The structure of **5** was derived by extensive use of multidimensional NMR spectroscopy.[6] The NOESY spectrum of **5** recorded in C_6D_6 showed nOe between H-5 and α- methyl protons at δ 0.71 whereas H-7 showed nOe with the β-methyl group at δ 0.40 of the *gem*-dimethyl moiety at C-6. This indicated that inversion had taken place during the rearrangement. The resonances of the protonated carbons were assigned by ^1H-^{13}C HETCOR and DEPT experiments. The information on long range couplings derived from COLOC spectra was very useful in the characterisation of **5**. The structure was confirmed as (*1S**,*2R**,*5S**,*7S**,*10S**,*13R**)-6,6,10-trimethyl-14-oxapentacyclo [8.3.1.0^{1,7}.0^{2,13}.0^{5,13}]tetradeca-3,12-dione[7] (**5**) based on NMR data and X-ray crystallography.[8] The perspective view of the molecular plot of **5** is shown in **Fig. 2**. Thus, it appears that *meta* cycloaddition is preferred in CH_3OH while in C_6H_6 *ortho* addition took place. This unusual observation required a closer investigation. A careful monitoring of photolysis of **1** in CH_3OH showed that **5** was the secondary photolytic rearrangement of **4** and not formed directly by a *meta* cycloaddition. This was further supported by the phototransformation of **4** in CH_3OH to **5** (63%) in an independent experiment. This transformation proceeded in a highly stereoselective manner with inversion at C-7. The reaction is initiated by the excitation of α,β-enone chromophore followed by di-π methane rearrangement related 1,2-shift as proposed by Zimmerman[9] for α,β-enones (**Scheme- 2**).



Scheme- 2

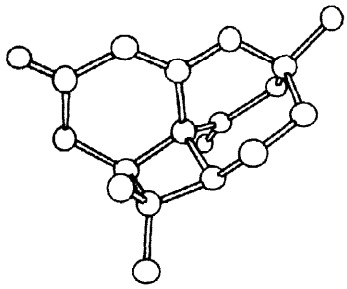


Fig. 1 X-ray crystal structure of 4

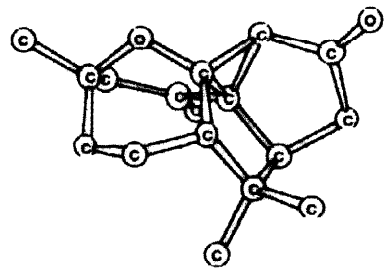
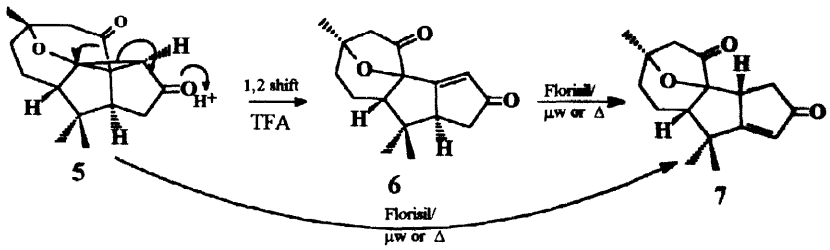


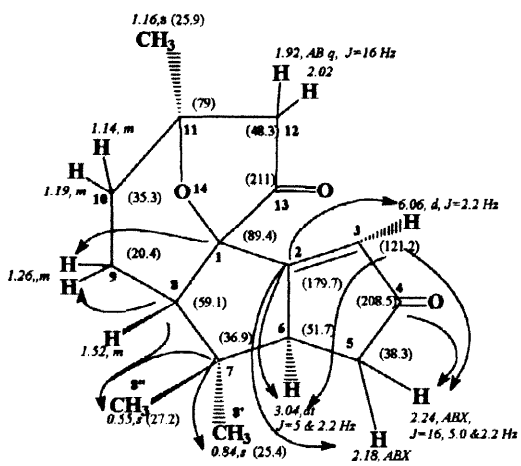
Fig. 2 X-ray crystal structure of 5

I.3 ***Acid catalysed rearrangement of 5 to (1S*,6R*,8S*,11R*)-7,7,11-trimethyl-14-oxatetracyclo [9.2.1.0^{1,8}.0^{2,6}]tetradeca-2-ene-4,13-dione (6).***

Compound **5** is a pentacyclic molecule with a cyclopropane ring. Therefore, it was not surprising that **5** underwent acid catalysed rearrangement. A highly crystalline product **6** was obtained in quantitative yield when **5** was refluxed with trifluoroacetic acid (TFA) or PTS in C_6H_6 (**Scheme- 3**). The molecular formula, $C_{16}H_{20}O_3$ (M^+ 260), remained unchanged. A comparative analysis of ^{13}C NMR and ^{13}C DEPT spectra revealed that both **5** and **6** had the same number of carbonyl, quaternary, methine, methylene and methyl carbons. However, one of the sp^3 methine carbon (δ 55.5 in **5**) was absent and a new olefinic carbon (δ 121) appeared in **6**. Based on long range heteronuclear correlation ($^3J_{CH}$ and $^2J_{CH}$) COLOC, HETCOR, COSY, DEPT, ^{13}C- and ^1H NMR spectra (**Fig. 3**) as well as IR data, the structure **6** was assigned to the rearranged product. It was confirmed as (1*S**,6*R**,8*S**,11*R**)-7,7,11-trimethyl-14-oxatetracyclo[9.2.1.0^{1,8}.0^{2,6}]tetradeca-2-ene-4,13-dione by X-ray crystallography[8] (**Fig. 5**). Mechanistically, the formation of the intermediate bridgehead carbonium ion at C-1 (in **5**) could be postulated by the acid catalysed enolisation of the carbonyl group at C-12 with synchronous 1,2-acyl shift.

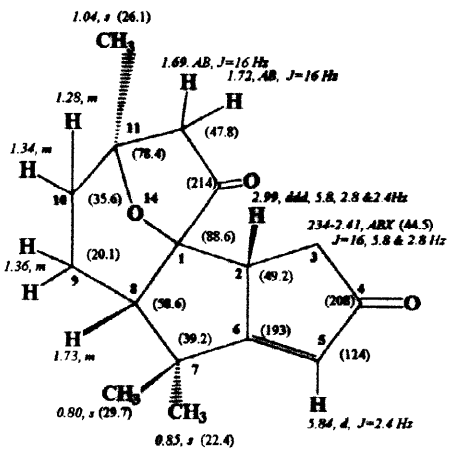


Scheme- 3



6

Fig. 3 Important COLOC interactions in 6



7

Fig. 4 ^1H and ^{13}C NMR of 7

I.4 *Microwave irradiation induced thermal rearrangement of 5 to (1R*,2R*,8S*,11R*)-7,7,11-trimethyl-14-oxatetracyclo[9.2.1.$0^{1,8}$.$0^{2,6}$]tetradeca-5-ene-4,13-dione (7).*

Compound **5** remained unchanged on heating up to 100 ^{0}C for 4 h. However, when it was supported on Florisil and heated to 100 ^{0}C for five h, in addition to **6** (60%), another compound **7** (40%) was also obtained. This suggested that **6** could be an intermediate in the transformation of **5** to **7**. In fact, **6** supported on Florisil, could be transformed to **7** by heating for 3 h. It is well known that many thermal transformations are accelerated by the microwave irradiation.[10] Indeed, the transformation of **5** to **7** could be affected in nearly quantitative yield on exposure to microwave for 10 min. Compound **7** has the unchanged molecular weight (M^+ 260). The UV data of **7** (232 nm) were considerably different than those of **6** (241 nm). The NMR data are depicted in **Fig. 4**. These data along with X-ray crystallography[8] (**Fig. 6**) confirmed the structure (1*S**,2*R**,8*S**,11*R**)-7,7,11-trimethyl-14-oxatetracyclo[9.2.1.$0^{1,8}$.$0^{2,6}$]tetradeca-5-ene-4,13-dione (**7**) (**Scheme-3**). The mechanism of this rearrangement is under investigation.

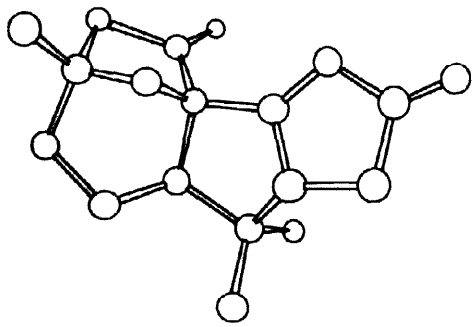


Fig. 5 X-ray crystal structure of 6

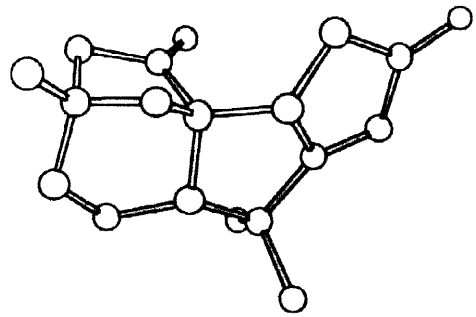


Fig. 6 X-ray crystal structure of 7

II. Intramolecular 1,2-Arene-alkene Photocycloaddition with *E* and *Z* Olefinic Tethers

Appropriately substituted 2-alkenyl-4-chromanones offer excellent substrates for the studies related to mechanism and stereospecificity of intramolecular 1,2-arene-alkene photocycloadditions. Elegant studies by Becker *et al.*[11] have established the involvement of 1,4-diradical intermediates in the 2+2 alkene cycloaddition in enones. Similar type of mechanism could be operative for the transformation of 2-alkenyl chromanones. To study the regiospecificity, *E*- (**10**) and *Z*- (**11**) isomers with double bonds at 3' and 7' positions were chosen as model substrates. Directed aldol condensation of 4-*O*-methylresacetophenone with a mixture of *trans*-6,10-dimethyl-5,9-undecadien-2-one (geranylacetone, **8**, 65%) and *cis*-6,10-dimethyl-5,9-undecadien-2-one (nerylacetone, **9**, 35%) gave condensation products in 70% yield (**Scheme- 4**). Cyclodehydration of the aldol products with HMPT yielded a mixture of two chromanones *viz.* 2-[(3'*E*)- 4',8'-dimethyl-nona-3',7'-dienyl]-7-methoxy-2-methyl-4-chromanone (**10**, 55%) and 2-[(3'*Z*)- 4',8'-dimethyl-nona-3',7'-dienyl]-7-methoxy-2-methyl-4-chromanone (**11**, 45%) in 65 % overall yield.[3] The *E*- and *Z*-isomers were conveniently separated by $AgNO_3$ impregnated SiO_2 preparative TLC. Compound **11** could be identified as the *Z* isomer on the basis of the nOe between the olefinic proton (H-3') and the adjacent methyl group (Me-4'). The ^{13}C chemical shifts of C-2' and C-5' also provided information on the geometry of the double bond. In case of the *E* isomer, carbons C-2' and C-5' appeared at δ 39.4 and 39.6 whereas in the *Z* isomer, the methylene carbon at C-5' shifted upfield to δ 31.8 due to Z-shielding[12] (**Fig. 7**). Photolysis of **10** gave a mixture of two epimers **12** (28%) and **13** (72%) (estimated by GLC and NMR). Similar results (20/80 mixture of **12** and **13**) were also obtained on the photolysis of **11** (**Scheme- 4**). The spectral characteristics of **12** and **13** showed close resemblance with **4** except that **12** and **13** had additional resonances at δ 1.58 and 1.66 (two singlets), a triplet at δ 5.09 for the 4'-methyl-3'-pentenyl moiety and a singlet for methyl at C-5. The ^{13}C NMR and MS (M^+ 328) were also in agreement with the structures **12** and **13.** The stereochemistry of the photoproducts was investigated by NOESY as was done for **4**.[2] The methyl group at C-5 in **12** appeared at δ 1.14 while **13** had the same at δ

1.05. The overlapping proton signal for H-6 could be resolved when the spectrum was recorded in the solvent mixture of CD_3OD and $CDCl_3$ (1:3). In compound **12**, methyl at δ 1.14 had the nOe interactions with the protons H-6 and H-4 while in the isomer **13** methyl group at δ 1.05 did not show nOe with H-4 and H-6. Therefore, the methyl (δ 1.14) had α-configuration in **12** and the methyl (δ 1.05) had β-configuration in the epimer **13**. Thus, the photoproduct was characterised as (1*R**,4*S**,5*RS*,6*R**,11*R**)-1,5-dimethyl-5-(4'-methyl-3'-pentenyl)-14-oxatetracyclo[8.3.1.$0^{4,11}$.$0^{6,11}$]tetradeca-9-ene -8,12-dione (an epimeric mixture of **12** and **13**). Thus it was established that the photocycloaddition occurred regioselectively at C-3' double bond and the diastereoselectivity was not much influenced by the geometry of the reactive alkene double bond. Steric factors were mainly responsible for the observed stereoselection. It was important to note that the recovered substrates after both the photoreaction were found to be a 1:1 mixture of **10** and **11** as revealed by GLC and NMR. This suggested that $E \rightarrow Z$ and $Z \rightarrow E$ isomerisation around the 3'-double bond occurred during the photoreactions. It was concluded from the above observations that the triplet ketone initiated 1,2-arene-alkene photocycloaddition of the 2-alkenyl chromanones (**10** and **11**) proceeded in a regioselective manner *via* common 1,4-diradical intermediates (**Scheme - 5**).

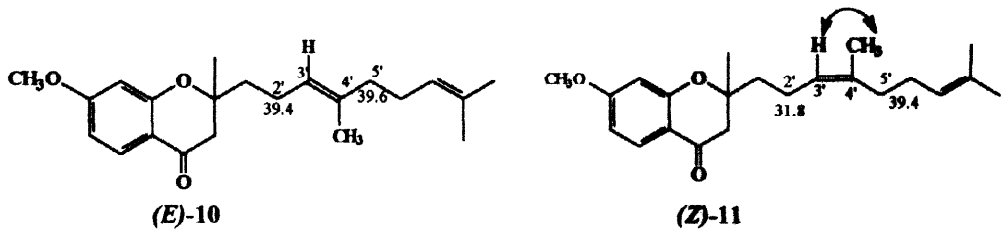
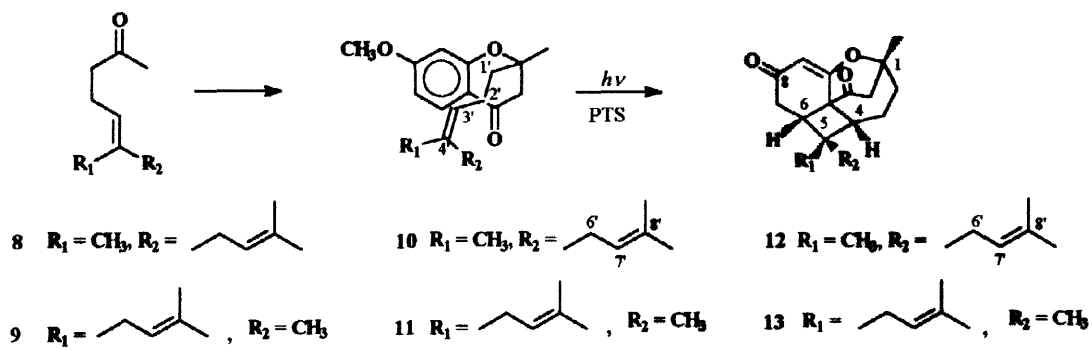
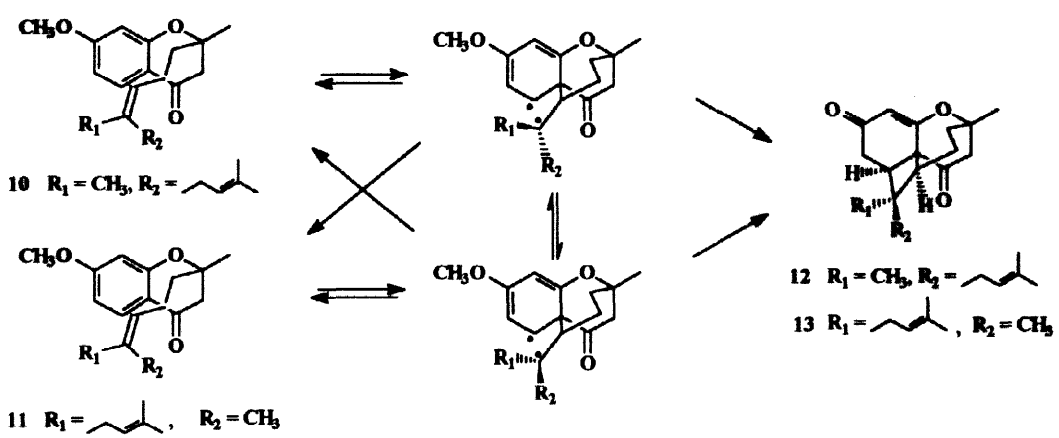


Fig. 7 *Z*-shielding in 11



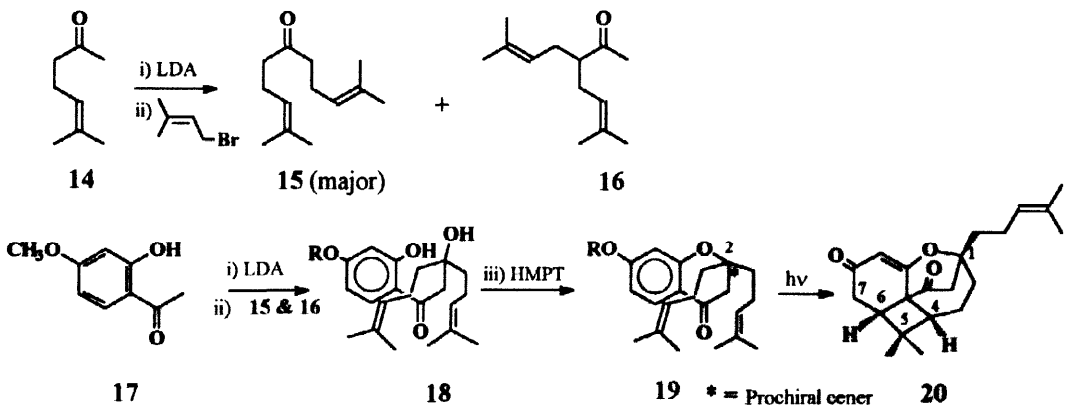
Scheme- 4



Scheme- 5

III. Intramolecular Desymmetrization *via* Arene-alkene Photocycloaddition

Desymmetrization of molecules with plane of symmetry provides a potentially powerful route for asymmetric synthesis.[13] As described above, during the stereo-tuned phototransformation of **1-3** to **4**, three new stereogenic centres are generated at the photo reactive sites in highly diastereoselective fashion. This prompted us to investigate the possible desymmetrization during 1,2-arene-alkene photocycloaddition of the 2,2-dialkenyl-4-chromanones, such as 7-methoxy-2,2-di(4'-methyl-3'-pentenyl)-4-chromanone (**19**) with prochiral centre at C-2 . The cycloaddition of one of the 4'-methyl-3'-pentenyl groups with the arene in **19** would generate three asymmetric centres by 2+2 cycloaddition, while the fourth is generated due to the desymmetrization at C-2. For the synthesis of **19**, the required ketone **15** was obtained by the alkylation of 6-methyl-5-hepten-2-one (**14**) with prenyl bromide using LDA under kinetically controlled conditions. This led to a mixture of two isomeric products, **15** being the major component[14] (65%, GLC) and **16** as a minor component (35%). Attempts to separate **15** in pure state were not successful. Therefore, the condensation of the lithioenolate of 4-O-methylresacetophenone (**17**) was carried out with the mixture of **15** and **16** at 0 to -5 ^{0}C. From the reaction mixture, the condensation product (**18**) was isolated in pure state in 55% yield by column chromatography. The cyclodehydration of **18** was affected by HMPT leading to the chromanone **19** in 73% yield.[3]



Scheme-6

III.1 ***Phototransformation of 19 to (1R*,4S*,6R*,11R*)-5,5-dimethyl-1-(4'-methyl-3'-pentenyl)-14-oxatetracyclo[8.3.1.0^{4,11}.0^{6,11}]tetradeca-9-ene-8,12-dione (20).***

The photolysis of **19** in C_6H_6 in the presence of PTS gave a colourless crystalline photocycloadduct **20** in 25% yield. The structure of the photoproduct was determined by spectral analysis. The IR (1720, 1640, 1600 cm^{-1}) and UV (268.7 nm) spectra of **20** were similar to those of **4**. In its ^{1}H NMR spectra, the resonances at δ 2.35 (d, 2H) for 7-CH_2, δ 2.67 (s, 2H) for 3-CH_2 , δ 3.25 (t, 1H), δ 5.68 (s, 1H) due to olefinic protons and two singlets at δ 1.04 and 1.09 for *gem*-dimethyl group at C-5 were similar to those of **4**. In addition the presence of the 4'-methyl-3'-pentenyl group was inferred from the two singlets at δ 1.62 and 1.69 for *gem*-dimethyl on double bond and a triplet at δ 5.09 (1H, 6Hz) for olefinic proton. The singlet for methyl at C-1 (in **4**) was absent in **20**. The ^{13}C NMR and MS (M^{+} 328) of the product were also in agreement with the structure **20**. Thus, **20** was characterised as (1*R**,4*S**,6*R**,11*R**)-5,5-dimethyl-1-(4'-methyl-3'-pentenyl)-14-oxatetracyclo[8.3.1.0^{4,11}.0^{6,11}]tetradeca-9-ene-8,12-dione. It was obtained as a single isomer and thus, the desymmetrization of the prochiral chromanone **19** occurred with high diastereoselection (**Scheme-6**).

III.2 ***Stereoselectivity.***

The photoadduct **4** from the chromanones **1-3** and **20** from **19** were obtained exclusively as single isomers. This high diastereoselectivity can be rationalized from the molecular modelling of the 2-alkenyl-4-chromanones. Extensive overlap of the arene with the alkene double bond is possible only when the alkenyl tether has axial conformation. However, in the case of **19** both the alkenyl tethers at the prochiral centre at C-2

can overlap with the arene to the same extent but from the opposite stereofaces. This molecule provides an opportunity to study the photo induced asymmetric desymmetrization using chiral element like polarised light.

CONCLUSION

This triplet ketone initiated intramolecular 1,2-arene-alkene photocycloaddition in the 2-alkenyl chromanones proceeds *via* 1,4-diradical intermediates. The resulting photoadducts undergo further photolytic and microwave induced thermal rearrangements to furnish a variety of fused multicyclic bridged compounds such as oxatetracyclodecadiones and oxapentacyclodecadiones. The strategy has the flexibility and we anticipate that using appropriate substrates, these reactions will find use in the synthesis of many complex natural products such as tricyclo[9.3.1.$0^{3,8}$]pentadecane. Our efforts to extend this approach towards functionalised taxoids skeleton led to a rare intramolecular 1,4- arene-alkene photocycloaddition[15,16] which will be reported elsewhere.

EXPERIMENTAL

General. Melting points were recorded on Fisher-Jones melting point apparatus and are uncorrected. The IR spectra were measured as KBr pellets or thin films on NaCl plates using a Perkin-Elmer spectrophotometer Model 783. The UV spectra were recorded on a Shimadzu UV-240 spectrophotometer. Mass spectra were obtained using a Shimadzu GCMS-QP1000A spectrometer with 70eV. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.13 MHz and 50.33 MHz respectively with $SiMe_4$ as internal reference. The photochemical reactions were carried out in purified solvents. The solvents were degassed by passing O_2-free argon (IOLAR) prior to use. The Hanovia immersion well was used for the photochemical reactions. Mercury medium pressure lamp with Pyrex filter or sunlight was used as the radiation source. The GLC analysis was carried out with 3% OV-17 at 240 or 250 ^0C for isothermal monitoring or with appropriate temperature programming. Microwave irradiation was carried out in a domestic microwave oven (Batliboi EDDY) generating a microwave frequency of 2450 MHz (980 W) equipped with twin table and was used with full power. Photolyses using sunlight as a source, were carried out by the exposure of the reaction solutions in Corning® glass vessels between 10.00 to 16.00 Hr. in the months of Feb. to June with clear sky. Column chromatography was carried out on silica gel (Merck 70-230 mesh). Commercial sample of geranyl acetone containing 35% neryl acetone (Aldrich® Chemicals) was used after distilling from CaH_2.

Typical procedure for the photolysis of alkyl ethers of* 1 *and related compounds.

The solution of 7-methoxy alkenyl chromanones (0.100 g) in C_6H_6 (200 ml) containing PTS (7 mg) in a conical flask (500 ml) was exposed to sunlight (5 h). $NaHCO_3$ (25 mg) was added to the reaction mixture and stirred (5 min). The solution was filtered and evaporated under reduced pressure. The reaction products were isolated by preparative TLC (pet. ether/EtOAc, 8:2) as colourless solids.

Photolysis of 2-methyl-2-(4'-methyl-3'-pentenyl)-7-hydroxy-4-chromanone (1) in C_6H_6: The solution of 1 (0.100 g) in C_6H_6 (200 ml) was irradiated (3 h) in Hanovia immersion Well using mercury medium pressure lamp. The solvent was removed under reduced pressure and the product 4 was isolated by preparative TLC (pet. ether/EtOAc; 4:1) as a colourless solid, 0.038 g (38%); m.p. 215 ^0C (C_6H_6).[2]

Photolysis of 2-methyl-2-(4'-methyl-3'-pentenyl)-7-hydroxy-4-chromanone (1) in MeOH: The solution of 1 (0.100 g) in MeOH (200 ml) was irradiated (5 h) as described above. The solvent was removed under reduced pressure and the product 5 was isolated by preparative TLC (pet. ether/EtOAc; 4:1) as a colourless crystalline solid, 0.038 g (38%); m.p. 94 ^0C (hexane); IR (KBr): 1750, 1680 cm^{-1}; UV (MeOH): 236 nm; MS: (m/z) 260 [M^+]; ^1H NMR (C_6D_6): δ 0.40 (s, 3H, 6'-CH_3), 0.71 (s, 3H, 6"-CH_3), 0.90 (s, 3H, 10'-CH_3), 1.10 and 1.31 (AB, m, J_{AB} = 14.8 Hz, 2H, 9-CH_3), 1.46 and 1.56 (AB, m, J_{AB} = 15.7 Hz, 2H, 8-CH_2), 1.86 and 2.08 (AB quartet, 2H, J_{AB} = 14.4 Hz, 11-CH_2), 2.04 (t, J = 2.9 Hz, 1H, 7-CH), 1.98 and 2.13 (ABX, J_{AB} = 16.9, J_{AX} = 7.6 and J_{BX} = 1.4 Hz, 4-CH_2), 2.70 (dd, 1H, J = 7.6 and 1.4 Hz, 5-CH), 2.81 (s, 1H, 2-CH). (For ^{13}C NMR, ^1H-^{13}C HETCOR, COLOC data see table in reference 6).

Photorearrangement of 4 to 5 : A solution of **4** (0.100 g) in MeOH (100 ml) was irradiated with medium pressure lamp in Hanovia immersion well. After the completion of the reaction (GLC), **5** was isolated by preparative TLC (pet. Ether/EtOAc; 4:1) as a colourless solid, 0.063 g (63%).

Acid catalysed rearrangement 5 to 6: Compound **5** (0.100 g) was dissolved in TFA (10 ml) and the mixture was refluxed till completion of the reaction (10 min). The solvent was evaporated under reduced pressure and **6** was isolated by TLC (pet. Ether/EtOAc; 4:1) as a colourless solid, 0.095 g (95%); m.p 146 ^{0}C (C_6H_6); IR (KBr): 2960, 1736, 1702, 1632, 1090, cm^{-1}; UV (MeOH): 241 nm; MS: (m/z) 260 [M$^+$]; ^{1}H NMR (C_6D_6), ^{13}C NMR ($CDCl_3$) and important ^{1}H-^{13}C COLOC interactions are given in the **Fig. 3.**

Microwave induced rearrangement 5 to 7: Florisil (1.0 g) was added to a solution of compound **5** (0.030 g) in $CHCl_3$ (1 ml). The solvent was removed under reduced pressure. The solid was dried in vacuum and exposed to microwave irradiation for 10 min in a microwave oven. The product was isolated by elution with $CHCl_3$ and purified by TLC (pet. Ether/EtOAc; 4:1) as a colourless solid, 0.028 g (93%); m.p. 152-153 ^{0}C (ether/hexane); IR (KBr): 2936, 1740, 1698, 1620, 1458, 1085, 867 cm^{-1}; UV(MeOH): 232 nm; MS: (m/z) 260 [M$^+$]; ^{1}H NMR (C_6D_6) and ^{13}C NMR ($CDCl_3$) are given in the **Fig. 4**

7-Methoxy-2-methyl-2-(4',8'-dimethyl-nona-3',7'-dienyl)-4-chromanones (10 and 11): Aldol condensation of 6,10-dimethyl-5,9-undecadien-2-one (*E*, **8** and *Z*, **9**; 65:35; 1.9 g, 10 mmol) with 4-*O*-methylresacetophenone (**17**, 1.6 g, 10 mmol) was carried out as described earlier[3]; 1.9 g (70%). The cyclodehydration[3] of this product (1.0 g) with HMPT gave a mixture of cyclised products (**10** and **11**; 45:55), 0.61 g (65%). **10** and **11** were separated by preparative TLC with $AgNO_3$ impregnated SiO_2 as thick pale yellow liquids. Attempts to obtain **10** and **11** in microanalytical purity were not successful.

(*E*)-7-Methoxy-2-methyl-2-(4',8'-dimethyl-nona-3',7'-dienyl)-4-chromanone (10): IR (film): 2930, 1695, 1625, 1590, 1450, 1270, 1165 cm^{-1}; UV (MeOH): 272, 312 nm; MS: (m/z) 342 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.64 (s, 6H, 2 x CH_3), 2.10 (m, 4H, 2 x CH_2), 1.60-1.85 (m, 4H, 2 x CH_2), 2.59 and 2.75 (AB quartet, 2H, J = 16.4, $COCH_2$), 3.82 (s, 3H, OCH_3), 5.08 (t, 2H, J = 6.4 Hz, 2 x CH=C), 6.38 (d, 1H, J = 2.2 Hz, 8-H), 6.53 (dd, 1H, J = 8.8 and 2.2 Hz, 6-H), 7.78 (d, 1H, J = 8.8 Hz, 5-H); ^{13}C NMR ($CDCl_3$): δ 15.9(s, 4'- CH_3), 17.7 (9'-CH_3), 25.7 (8"-CH_3), 26.6 (2-CH_3), 22.2 (1'-CH_2) and 23.1 (6'-CH_2), 39.4 (2'-CH_2) and 39.6 (5'-CH_2), 47.1 ($COCH_2$), 55.5 (OCH_3), 81.5 (>C<), 101.1, 109.2 and 123.1 (3 x ArC), 124.1(3'-CH=) and 128.2 (7'- CH=), 114.3 (ArC), 131.4 (C=), 135.9 (C=), 161.8 (ArC), 166.2 (ArC), 191.1 (CO).

(*Z*)-7-Methoxy-2-methyl-2-(4',8'-dimethyl-nona-3',7'-dienyl)-4-chromanone (11): IR (film): 2965, 1690, 1620, 1590, 1450, 1275, 1170 cm^{-1}; UV (MeOH): 264, 312 nm; MS: (m/z) 342 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.66 (s, 6H, 2 x CH_3), 2.09 (m, 4H, 2 x CH_2), 1.55-1.85 (m, 4H, 2 x CH_2), 2.58 and 2.73 (AB quartet, 2H, J = 16.4, $COCH_2$), 3.82 (s, 3H, OCH_3), 5.07 (t, 2H, J = 6.2 Hz, 2 x CH=C), 8.37 (d, 1H, J = 2.1 Hz, 8-H), 6.52 (dd, 1H, J = 8.8 and 2.1 Hz, 6-H), 7.78 (d, 1H, J = 8.8 Hz, 5-H); ^{13}C NMR ($CDCl_3$): δ 17.8 (s, 3H, 4'- CH_3), 18.9 (s, 3H, 9'-CH_3), 25.7 (s, 3H, 8"-CH_3), 26.6 (s, 3H, 2-CH_3), 22.0 (1'-CH_2) and 23.1 (6'-CH_2), 31.8 (2'-CH_2), 39.4(5'-CH_2), 47.1 (CO CH_2), 55.5 (OCH_3), 81.4 (>C<), 101.1, 109.2 and 123.2 (3 x ArC), 128.2 (3'- and 7'-CH=), 114.2 (ArC), 131.7 (C=), 135.9 (C=), 161.8 (ArC), 166.3 (ArC), 191.0 (CO).

Photolysis of 10: The photolysis of the pure **10** (0.100 g) in C_6H_6 as described in the typical procedure gave mixture of epimers **12** and **13** (28/72 by GLC analysis; isothermal 250 ^{0}C) (TLC, pet. ether/EtOAc, 9:1, multiple developments), 0.033 g (34%); m.p. 95 ^{o}C (hexane/ether); IR (KBr): 3120, 1718, 1645, 1600, cm^{-1}; UV (MeOH): 265 nm; MS: (m/z) 328 [M$^+$]; The recovered substrate (30%) was a 1:1 mixture of **10** and **11**.

Photolysis of 11: Similarly photolysis of the pure **11** (0.100 g) in C_6H_6 as above provided a mixture of epimers **12** and **13** (20/80; by GLC analysis; isothermal 250 ^{0}C) (TLC, pet. ether/EtOAc, 9:1, multiple developments), 0.033 g (34%); IR (KBr): 3120, 1718, 1645, 1600 cm^{-1}; UV (MeOH): 265.5 nm; MS: (m/z) 328 [M$^+$]. The recovered substrate (30%) was a 1:1 mixture of **10** and **11** by GLC.

(1*R,4*S**,5*RS*,6*R**,11*R**)-1,5-Dimethyl-5-(4'-methyl-3'-pentenyl)-14-oxatetracyclo[8.3.1.0.^{4,11}0^{6,11}]tetradeca-9-ene-8,12-dione (12 and 13):** ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 0.6H, 5-CH_3), 1.14 (s, 2.4H, 5-CH_3), 1.35-1.55 (2H, m, CH_2), 1.51 (s, 0.6H, 1-CH_3), 1.54 (s, 2.4H, 1-CH_3), 1.58 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.65-2.1 (8H, m, 4 x CH_2 and a CH), 1.92 and 2.18 (2H, AB multiplet, CH_2), 2.15 (1H, m, CH), 2.35 (2H, d, J = 3.3 Hz, CH_2), 2.75 and 2.63 (AB quartet, J_{AB} = 19.2 Hz), 3.26 (1H, t, J = 3.3 Hz, CH), 4.97 (0.8H, t, J =5.5 Hz, CH=), 5.00 (0.2H, t, J = 5.5 Hz, CH=C<), 5.68 (s, 1H, -COCH=); ^{13}C NMR ($CDCl_3$): δ 15.80 (=C-CH_3), 17.67 (=C-CH_3), 21.98 (CH_2), 22.67 (CH_2), 24.11 (CH_2), 25.66 (=C-CH_3), 28.69 (CH_3), 31.05 (CH_3), 32.37 (CH_2), 33.17 (CH_2), 34.75 (CH), 36.42 (CH), 37.86 (CH_2), 38.07 (CH_2), 45.76 ($COCH_2$), 49.97 ($COCH_2$), 52.43 (CH), 52.99 (>C<), 53.4 (>C<), 79.16 (>C<), 107.12 (CH=), 123.78 (CH=), 124.15 (CH=), 131.92 (C=), 171.4 (-C), 197.8 (CO), 200.4 (CO); 200.7 (CO). (Microanalysis of the mixture of epimers Found: C, 76.55; H, 8.47; $C_{21}H_{28}O_3$: requires C,76.78; H,8.60).

Alkylation of 6-methyl-5-hepten-2-one (14): To a stirred solution of LDA (30 mmol) in THF (50 ml) was added a solution of 6-methyl-5-hepten-2-one (**14**, 30 mmol, 3.78 g) in THF (50 ml) at -78 ^{0}C. After 30 min, a solution of 2-methyl-4-bromo-2-butene (32 mmol, 4.47 g) in THF was added to it and stirring continued for an additional 3 h. The reaction was worked up by adding saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with ether. The ethereal extract was dried over anhydrous Na_2SO_4. On removal of solvent at room temperature under reduced pressure, an orange liquid (5.0 g) was obtained which was distilled under reduced pressure to give a pale yellow liquid; 1.2 g (21%); b.p. 100-110 ^{0}C/10 mm, containing a mixture of **15** and **16** in the ratio of 65:30 [GLC (OV-17; temp. program; 4 ^{0}C/min, 100-150 ^{0}C)]. Attempts to separate **15** and **16** from the mixture were not successful and therefore, the mixture was used as such for the next step of condensation with **17**.

Preparation of 7-methoxy-2,2-di(4'-methyl-3'-pentenyl)-4-chromanone (19): To a stirred solution of LDA (10 mmol) in THF (30 ml), was added a solution of **17** (5 mmol, 0.830 g) in THF (50 ml) at -25 ^{0}C. After 30 min, a mixture of **15** and **16** (5 mmol, 1.0 g) in THF (20 ml) was added and stirring continued for an additional 3 h at -5 ^{0}C. The reaction was worked up as above and the condensation product **18** was isolated from the mixture as a pale yellow thick liquid by column chromatography (SiO_2, pet. ether/EtOAc, 98:2), 1 g (55%); IR (film): 3480, 1645 cm^{-1}; UV (MeOH): 276, 319 nm; MS: (m/z) 360 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 6H, 2 x CH_3), 1.59 (s, 6H, 2 x CH_3), 1.62 (m, 4H, 2 x - CH_2), 2.02 (m, 4H, 2 x CH_2), 3.05 (s, 2H, $COCH_2$), 3.84 (s, 3H, OCH_3), 5.07 (t, 2H, J = 7 Hz, 2 x -CH=C), 6.42 (d, 1H, J = 2 Hz, ArH), 6.44 (dd, 1H, J = 8.6 and 2 Hz, ArH), 7.64 (d, 1H, J = 8.6 Hz, ArH), 12.7 (s, 1H, ArOH). A mixture of the condensation product (**18**, 2 mmol, 0.72 g) and HMPT (2.8 mmol, 0.50 g) was heated at 155 ^{0}C for 4 h. The reaction was monitored by TLC. The product **19** was isolated by preparative TLC (pet. ether/ EtOAc; 80/20) as a colourless liquid, 0.50 g (73%); IR (film): 2920, 2980, 1680, 1620 cm^{-1}; UV (MeOH): 272, 312 nm; MS: (m/z) 342 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ 1.66 (s, 6H, 2 x CH_3), 1.57 (s, 6H, 2 x CH_3), 1.78 (m, 4H, 2 x - CH_2), 2.05 (m, 4H, 2 x - CH_2), 2.63 (s, 2H, -$COCH_2$), 3.63 (s, 3H, -OCH_3), 5.05 (t, 2H, J = 6.4 Hz, 2 x -CH=C), 6.38 (d, 1H, J = 1.8 Hz, 8-H), 6.52 (dd, 1H, J = 8.6 and 1.8 Hz, 6-H), 7.78 (d, 1H, J = 8.6 Hz, 5-H); ^{13}C NMR ($CDCl_3$): δ 17.6, 25.6 (4 x CH_3), 22.1, 36.2 (4 x CH_2), 45.2 ($COCH_2$), 55.5 (OCH_3), 83.3 (>C<), 101.1, 109.1 and 123.3 (3 x ArC), 107.6 (ArC), 128.1 (2 x CH), 132.2 (2 x C), 161.7 and 166.2 (2 x ArC), 191.1 (CO). Attempts to purify **18** and **19** to microanalytical purity were not successful.

(1*R,4*S**,6*R**,11*R**)-5,5-Dimethyl-1-(4'-methyl-3'-pentenyl)-14-oxatetracyclo[8.3.1.0.^{4,11}0^{6,11}]tetradeca-9-ene-8,12-dione (20) by Photoreaction of 19:** Photolysis of **19** (0.100 g) in C_6H_6 (200 ml) and PTS (7 mg) was carried out in sunlight as described in the typical procedure. The photoproduct **20** was isolated by preparative TLC (pet. ether/EtOAc, 9:1, multiple developments), 0.024 g (25%); colourless solid, m.p. 93-94 ^{0}C (hexane/ether); IR (KBr): 1720, 1640, 1600 cm^{-1}; UV (MeOH): 268.7 nm; MS: (m/z) 328 [M$^+$]; ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.69 and 1.62 (2s, 6H, C=(CH_3)$_2$), 2.05-1.6 (m, 9H, 6-H and 4 x CH_2), 2.67 (s, 2H, $COCH_2$), 2.35 (d, 2H, J = 4.9 Hz , 7-CH_2), 3.25 (t, 1H, J = 4.9 Hz, 6-H), 5.09 (t, 1H, J = 6 Hz, CH=C(CH_3)$_2$), 5.68 (s, 1H, =CHCO-); ^{13}C NMR ($CDCl_3$): δ 17.4 and 25.4 [C=C(CH_3)$_2$], 18.6 and 31.5 [>C(CH_3)$_2$], 21.1 and 21.5 (3- CH_2 and 2'-CH_2), 32.3 (7-CH_2), 34.9 (6-CH), 36.0 (2-CH_2), 37.3

(5-C), 43.3 (1'-CH_2), 47.7 (13-CH_2), 52.9 (4-CH and 11-C), 80.7 (1-C), 106.8 (9-CH), 122.5 (3'-CH), 132.5 (4'-C=), 171.0 (10-C), 197.4 (8-CO), 200.4 (12-CO); (Found: C, 76.61; H, 8.32; $C_{21}H_{28}O_3$; requires C,76.78; H,8.60).

REFERENCES AND NOTES

1. Wender, P. A.; Siggel, L.; Nuss, K. *Org. Photochem.* **1989**, *10*, 357; Wender, P. A.; von Geldern, T. W. Aromatic compounds: Isomerisation and Cycloaddition. In *Photochemistry in Organic Synthesis*; Coyle, T. W., Ed.; RSC, Cambridge, **1989**, pp. 232.
2. Kalena, G. P.; Pradhan, P.; Banerji, A. *Tetrahedron Lett.* **1992**, *33*, 7775.
3. Banerji, A.; Kalena, G. P. *Synth. Commun.* **1989**,*19*, 159.
4. Kabaleswaran, V.; Rajan, S. S.; Kalena, G. P.; Pradhan P.; Banerji, A. *Acta Cryst.* **1995**, *C52*, 1981.
5. Deuterium labelling: Photolysis of **2** (0.050 g) in CH_2Cl_2 solution(25 ml containing D_2O, 0.05 ml) was carried out in sunlight (2 h). The deuterated product **4** was isolated by preparative TLC; UV (MeOH): 273 nm; MS: *m/z* 262 [M^+]; ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 3H, 5-CH_3), 1.10 (s, 3H, 5-CH_3), 1.51 (s, 3H, 1-CH_3), 1.72 (m, 2H, 3-CH_2), 1.92 and 2.17 (m, 2H, 2-CH_2), 2.24 (m, 1H, 4-H), 2.62 and 2.75 (AB q, 2H, J_{AB} = 19.2 Hz, 13-CH_2), 3.27 (s, 1H, 6-CH), 5.68 (s, 1H, 9-CH).
6. Kalena, G. P.; Pradhan, P.; Swaranlatha, Y.; Singh, T. P.; Banerji, A. *Tetrahedron Lett.* **1997**, *38*, 5551.
7. The IUPAC name of **3** was generated with the courtesy of ACD Labs™ through internet.
8. **The crystal data and molecular structure of 5:** $C_{16}H_{20}O_3$ has been determined from single crystal X-ray diffraction. The compound crystallizes in monoclinic centrosymmetric space group $P2_1/c$ from *n*-hexane. The cell parameters are *a* =7.237(2) Å, *b* = 19.977(1) Å, *c* = 9.850(2) Å, β = 107.92 (1)°, *V* = 1354.9 (5) Å^3, *Z* = 4, *D* = 1.276 Mg/m^3, *F*(000) = 560, μ = 0.811 cm^{-1}, T = 295 °K, *R* = 6.55 and R_W = 7.38. **The crystal data and molecular structure of 6**: $C_{16}H_{20}O_3$ has been determined from single crystal X-ray diffraction. The compound crystallizes in triclinic space group P_1 Bar from C_6H_6. The cell parameters are *a* =7.499 (1) Å, *b* = 10.030 (3) Å, *c* = 10.445 (2) Å, α = 70.17 (2)^0, β = 88.68 (1)°, γ = 69.69 (2)^0, *V* = 689.1 Å^3, *Z* = 2, *Dc* = 1.2547 Mg/m^3, *F*(000) = 280, μ = 0.853 cm^{-1}, *R* = 5.34% and R_W = 5.66%. **The crystal data and molecular structure of 7:** $C_{16}H_{20}O_3$ has been determined from single crystal X-ray diffraction. The compound crystallizes in triclinic, space group P_1 Bar from ether/*n*-hexane. The cell parameters are *a* =6.680(5) Å, *b* = 10.471(1) Å, *c* = 11.272(4) Å, α = 113.82 (2)^0, β = 101.61 (5)°, γ = 91.18 (3)^0, *V* = 701.9 (6)Å^3, *Z* = 2, *Dc* = 1.23 Mg/m^3, *F*(000) = 280, μ = 0.811 cm^{-1}, T = 295 °K, *R* = 6.55 and R_W = 7.38. The detailed X-ray structure will be discussed elsewhere. The simulation of the molecular plot was carried out by *CS Chem3D Pro(tm)*, Molecular Modelling and Analysis, Cambridge Soft Corporation, Cambridge, Massachusetts, USA.
9. Schuster, D. I., Photochemical Rearrangements of Enones. In *Rearrangements in Ground and Excited State*; de Mayo, P., Ed.; Academic Press, New York, **1980**, *Vol. 3*, pp. 167 and references cited therein.
10. Caddick, S. *Tetrahedron*, **1995**, *51*, 10403; Srikrishna, A.; Kumar, P. P. *Tetrahedron Lett.*, **1995**, *36*, 6331.
11. Becker, D.; Nagler, M.; Harish, S.; Ramun, J. *J. Chem. Soc., Chem. Commun.*, **1983**, 371.
12. Hope, K.D.; Robinson, C.Y.; Vaezi, M. F.; Brouillette, W. J.; Mucio, D.D. *Mag. Reson. Chem.* **1987**, *25*, 1040 and Rossi, R.; Carpita, A.; Cuirici, M. G.; Veracini, C. A. *Tetrahedron*, **1982**, *38*, 639.
13. Mikami, K.; Terada, M.; Narisawa, S.; Nakai, T. *Synlett* **1992**, 255.
14. Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.*, **1978**, *43*, 2907.
15. Preliminary communication, Pradhan, P.; Kalena, G. P.; Banerji, A. Novel Multicyclic Compounds *via* Intramolecular Arene-Alkene Photocycloadditions. In *New Horizons in Organic Synthesis*, Nair, V. and Kumar, S., Ed.; New Age International (P) Ltd, Mumbai, **1997**. pp. 222.
16. Kalena, G. P.; Pradhan, P.; Banerji, A., unpublished work.

[1] Dedicated to the memory of the Late Sir Derek Barton.