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Intramolecular Diels-Alder Reaction of Cyclohexa-2,4-dienones: Synthesis and Photochemical Reactions of Oxa-Homobrendanes

Vishwakarma Singh,* S.Q.Alam and Mini Porinchu
Department of Chemistry, Indian Institute of Technology,
Powai, Bombay 400076, INDIA.

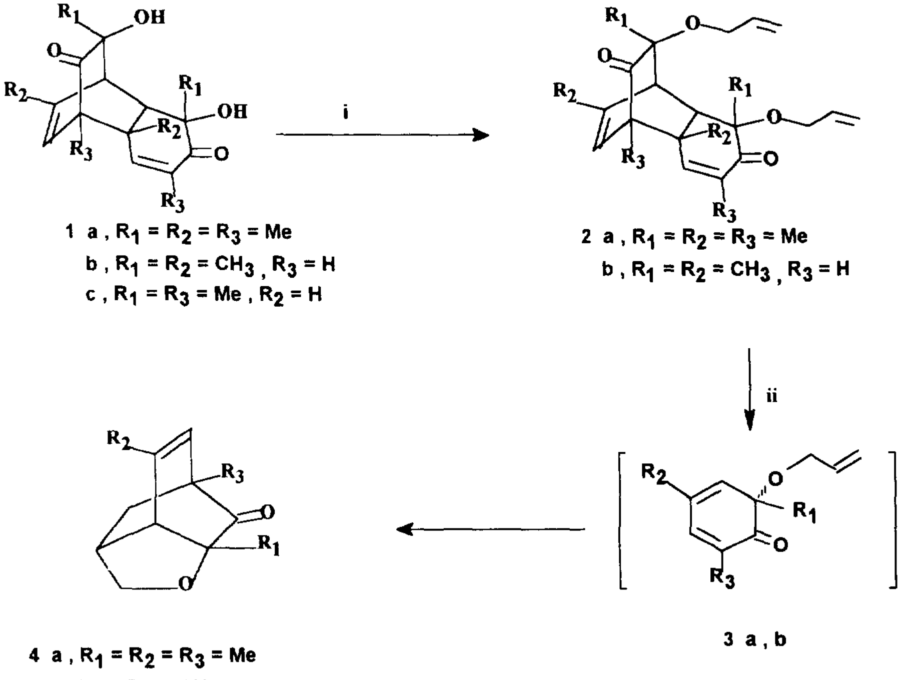
Abstract: Synthesis of Oxa-homobrendanes having β,γ-unsaturated carbonyl chromophore and their photoreactions in singlet (^{1}S) and triplet (^{3}T) excited states leading to novel bowl shaped molecules have been reported.

There has been a great deal of interest in the photochemical reactions of β,γ-enones in the past[1,2] which is further enhanced recently because of their synthetic potential and versatility.[3-5] While β,γ-unsaturated ketones may undergo photoreactions characteristic of olefinic and carbonyl chromophores, they generally undergo two unique reactions *i.e.* oxa-di-π-methane rearrangement(1,2-acyl shift) and 1,3-acyl shift upon triplet(^{3}T) and singlet(^{1}S) excitation respectively, as a result of extensive interaction between the alkene and carbonyl chromophore.[1] Though the scope of oxa-di-π-methane rearrangement and 1,3-acyl shift appears to be wide, they are sensitive to the structure of the chromophoric system, nature of functional groups and substituents.[6,7]

In continuation with our studies[3] in this area we desired to explore the photochemical behaviour of oxa-homobrendanes of type **4** (Scheme-1) in order to extend the scope of photoreactions of β,γ-enones, and develop a route to novel bowl shaped molecules. We wish to report herein an efficient synthesis of oxa-homobrendanes **4a,b** via intramolecular $\pi^4s+\pi^2s$ cycloaddition of cyclohexa-2,4-dienones **3a,b** and their photochemical reactions leading to novel tetracyclic systems **5a,b** having oxa-triquinacane framework and tricyclic systems **6a,b** and **7a,b** upon triplet(^{3}T) and singlet(^{1}S) excitations(Schemes 1 and 2).

Towards the synthesis of chromophoric systems it was envisaged that the desired oxa-homobrendanes having β,γ-enone chromophore could be readily obtained through intramolecular Diels-Alder reaction of cyclohexa-2,4-dienones of type **3**. We further thought that the dienones **3** should be readily generated *insitu* via pyrolysis of the dimer **2** which itself could be obtained via O-allylation of the readily available[8] diol dimers **1**.

In view of the above, the dimer **1a** was treated with sodium hydride in tetrahydrofuran and alkylated with allyl bromide which readily furnished the di-O-allylated compound **2a** in excellent yield(81.5%) (Scheme-1). Similarly allylation of **1b** also gave **2b** in good yield. However, similar alkylation of the diol dimer **1c** did not occur cleanly, it gave a complex mixture of products presumably due to the presence of the acidic proton at the allylic ring junction(C_7). The structures of the



1 a, $R_1 = R_2 = R_3 = Me$
b, $R_1 = R_2 = CH_3$, $R_3 = H$
c, $R_1 = R_3 = Me$, $R_2 = H$

2 a, $R_1 = R_2 = R_3 = Me$
b, $R_1 = R_2 = CH_3$, $R_3 = H$

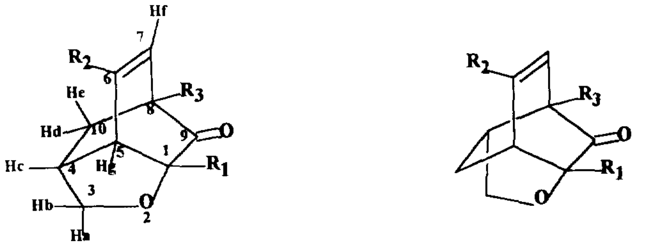
3 a, b

4 a, $R_1 = R_2 = R_3 = Me$
b, $R_1 = R_2 = CH_3$, $R_3 = H$

SCHEME 1

Reagents and conditions, i, NaH - THF, allyl bromide ; ii, 160°C o-dichlorobenzene/ 200°C diphenyl ether

allylated compounds **2a** and **2b** were deduced from ^{1}H NMR(300 MHz), ^{13}C NMR and other analytical data. Towards intramolecular Diels-Alder reaction, the di-O-allylated dimer **2a** was pyrolysed in *o*-dichlorobenzene at 160°C. Chromatography of the reaction mixture over silica gel furnished a single crystalline compound **4a** in very good yield(88%). The structure of the adduct was deduced from its spectral data as follows. The IR spectrum of **4a** showed a carbonyl absorption band at 1735 cm^{-1}. Its UV spectrum displayed a strong absorption band at 213 nm and a weak absorption at 310 nm, characteristic of a β,γ-unsaturated ketone in a bicyclo[2.2.2]octane framework.[1] ^{1}H NMR(300 MHz) of the adduct **4a** gave signals at δ 5.56(br m, J=2Hz) corresponding to β-proton(H_f) of β,γ-enone moiety.[3,9,10] It further showed signals at δ 3.99(dd, J_1=8Hz, J_2=4Hz, 1H), 3.73(d, J=8Hz, 1H) for *exo* and *endo* protons(H_a, H_b) of OCH_2 group. It also displayed resonances at δ 2.79(dd, J_1=4Hz, J_2=2Hz, 1H) and a complex multiplet at δ 2.52 for bridgehead proton at C_5(H_g) and the methine proton(H_c). Olefinic methyl was observed at δ 1.88(d, J=1.2Hz, 3H) while the other methylene protons(H_d, H_e) were shown at δ 1.73(dd, J_1=12Hz, J_2=10Hz, 1H) and 1.5(d, J=12Hz, 1H). The quaternary methyls gave signals at δ 1.28 and 1.21 respectively. Similarly the ^{13}C NMR of the adduct **4a** showed resonances at δ 207.55, 138.80 and 128.08 for carbonyl carbon and two olefinic carbons respectively.[11] It also gave resonances at δ 78.68(s) and 75.71(t) for quaternary O-C and carbon of OCH_2 group. Other resonances were observed at δ 53.30(d), 45.52(s), 40.18(t), 36.85(d), 21.45(q), 17.60(q) and 17.09(q) for other quaternary, methine, methylene and methyl carbons. These spectral features clearly suggested the structure **4a** for the above adduct and ruled out the alternate possibility such as **8**(Fig-1). The structure **8** was also discounted because of the strain involved in the transition state during its formation. Moreover the spectral characteristics of **4a** were found similar to analogous carbocyclic systems.[4]



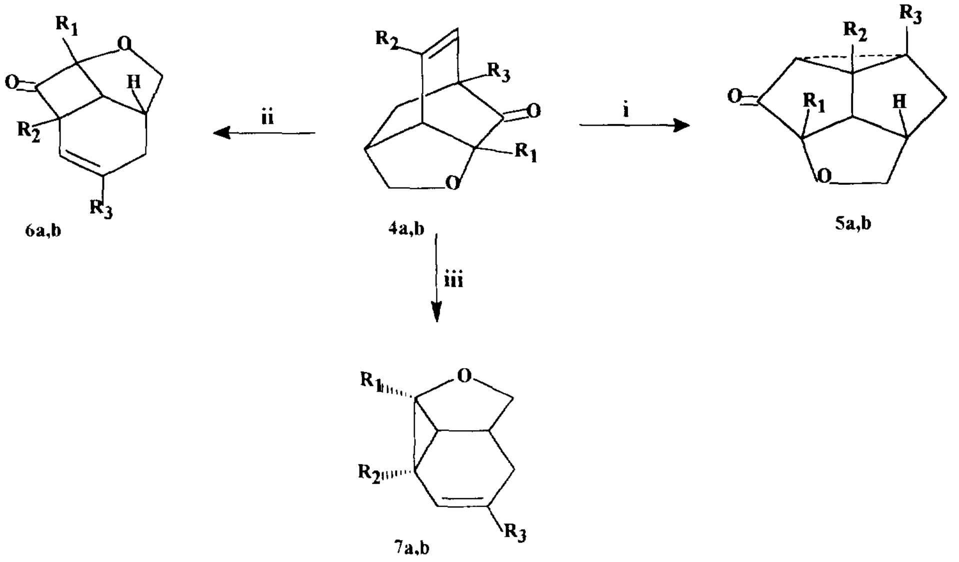
4 **8**

Fig.1

Similar pyrolysis of the dimer **2b** also gave a single adduct **4b** in excellent yield(92%) whose structure was clearly revealed from its spectral and analytical data.

In context with photoreactions of **4a** and **4b**, the sensitized irradiation of the compound **4a** in acetone(both as a sensitizer and solvent) was attempted. However, it did not undergo oxa-di-π-methane rearrangement to give **5a**, instead the product **6a** was obtained as a result of 1,3-acyl shift(Scheme-2). It appeared that acetone(E_T=79 Kcal/mol)[12] is not a suitable sensitizer for the generation of triplet excited state of the compound **4a** and that the product **6a** must have been obtained via singlet excited state(^1S) apparently populated through direct absorption of light. This observation was indeed surprising since acetone is known to sensitize a variety of β,γ-enones.[1,2]

In view of the UV spectrum of **4a**, which showed absorption at little longer wavelengths(λ_{max}: 213, 310 nm) compared to UV absorption of other related β,γ-enones,it was suggested that acetophenone(E_T=74 Kcal/mol) might prove to be a good sensitizer for **4a**. Hence a solution of the compound **4a** in acetone(100ml) containing acetophenone(1ml) was irradiated with a mercury vapour lamp(125 W, Applied Photophysics) for 2h under nitrogen. Removal of the solvent and chromatography of the photolysate gave the oxa-di-π-methane product **5a** in good yield(85%)(Scheme-2). The structure of **5a** was deduced from its spectral data. The IR spectrum of **5a** showed absorption band at 1735 cm^{-1} characteristic of a carbonyl group in the cyclopentane ring. Its ^1H NMR(300MHz) did not show any signal for olefinic proton. However it gave following resonances at δ 3.86(dd, J_1=8.5 Hz, J_2=5Hz, 1H), 3.73(d with stucture, J=8.5Hz, 1H), 3.1(complex m, 1H) for O-CH_2 protons(H_a, H_b) and $H_c(C_4)$ respectively. The photoproduct **5a** further gave resonances at δ 2.71(d, J=7Hz, 1H), for the proton at $C_{10}(H_g)$ and 2.28(dd, J_1=15Hz, J_2=11.4Hz, 1H), 1.9(dd, J_1=15Hz, J_2=6Hz, 1H) for methylene protons(H_d, H_e) respectively. The signals for other methine and methyl protons were observed at δ 1.6(s, 1H), 1.4(s, 3H), 1.32(s, 3H) and 1.2(s, 3H) respectively. A comparison of the above spectral features with that of its progenitor clearly revealed the structure **5a** for the product. It is remarkable to note that the proton H_g at the bridgehead(C_5) in the compound **4a** which appeared as a dd(J_1=4.5Hz, J_2=2Hz) at δ 2.78 due to small coupling with H_c and H_f becomes a doublet(J=7Hz) in **5a** at δ 2.71. This is clearly due to reorganization of the chromophore to a new molecular structure wherein the long range coupling disappears but the coupling of H_g with the proton H_c in 5a increased due to reduced dihedral angle(H_c-C_4-C_{10}-H_g). The ^{13}C NMR of **5a** also supported its structure since it exhibited the following characteristics. It displayed a resonance at



Scheme-2

Reagents/Conditions : i, hv, acetophenone- acetone
ii, hv (125W),benzene or acetone, 1.5h, for 4a; hv (16W), 7h for 4b
iii, hv(125W), 3h for 4a;hv, 2h for 4b.

δ 214.06 for cyclopentanone carbonyl and 89.82(s), 74.78(t) for quaternary O-C and O-CH_2 carbons respectively, in addition to signals at 61.81, 48.97, 47.81, 41.12, 29.50, 20.70, 19.02 and 13.78 for other carbons.

The direct irradiation(125 W, Hg vapour lamp, Applied Photophysics) of the compound **4a** for 1.5h in benzene in a pyrex immersion well gave 1,3-acyl shift product which was identical to the compound **6a** obtained during its irradiation in acetone. The 1,3-acyl shift product **6a**(mp 56-57°C) showed a characteristic absorption band at 1785 cm^{-1} for a cyclobutanone carbonyl in its IR spectrum. Its ^1H NMR(300MHz) displayed resonance signals at δ 5.28(br s, 1H), 4.12(superimposed dd, J=8Hz, 1H), 3.35(dd, J_1=10Hz, J_2=8Hz, 1H) for olefinic and OCH_2 protons respectively. It is interesting to record that *endo* proton of OCH_2 group appears downfield compared to the *exo* proton because of anisotropy of carbon carbon double bond. Its ^1H NMR further showed signals at δ 2.7(complex m, 1H), 2.31(d, J=9Hz, 1H), 2.28(m, 1H, methine H flanked by two methylene groups) and 1.75(d, superimposed with another signal, J=16Hz, 1H, *endo* proton of allylic methylene group). The three methyl groups were observed at δ 1.72 (d, J= 1Hz, 3H, CH_3), 1.55(s, 3H, CH_3) and 1.30(s, 3H, CH_3). ^{13}C NMR of **6a** showed resonances at δ 218.03(CO), 132.91, 118.92 and 98.57 for carbonyl carbon, olefinic carbons and quaternary carbon(O-C) respectively. Other resonances were observed at δ 73.22, 55.69, 45.34, 36.04, 26.72, 24.18, 22.74 and 18.47 for quaternary, methine and methyl carbons. These spectral features clearly revealed the structure **6a** for the observed product. It was further observed that irradiation of **4a** in benzene for a long period of time 3h gave the product **7a** as a result of photodecarbonylation. The high volatility of **7a** deterred the determination of yield of the above transformation and also made the purification of **7a** difficult especially the exclusion of solvents from the sample after chromatography. Nevertheless the compound **7a** could be characterised through ^1H NMR(300MHz) spectra. Thus the compound **7a** did not show any absorption band for carbonyl group in its IR spectrum. Its ^1H NMR spectrum exhibited a signal at δ 5.39(br s, 1H), 4.36(d of dd, J_1=7.5Hz, J_2=5Hz, J_3= 1.5Hz, 1H) and 3.45(dd, J_1=7.5Hz, J_2= 1.5Hz, 1H) for olefinic proton and protons of OCH_2 group. It also displayed resonances at δ 2.84(m, 1H), 2.24(m of d, J_{gem}=17Hz, 1H), 1.86(d, J_{gem}=17Hz, 1H) for methine proton flanked by two methylene groups, *exo* and *endo* protons of allylic methylene group. The other methine proton appeared at δ 1.24(d, J=9Hz, 1H) and methyl groups were observed at δ 1.73(br m, 3H, CH_3), 1.5(s, 3H) and 1.08(s, 3H) respectively.

Similarly the acetophenone sensitized irradiation of **4b** furnished oxa-di-π-methane product **5b** in good yield(50%). However, the direct irradiation of **4b** in benzene with a 125 W mercury vapour lamp for just 2h gave mainly the photodecarbonylated product **7b**(62%) and the 1,3-acyl shift product **6b** as a minor product. Therefore the compound **4b** was irradiated with a 16W low pressure mercury vapour lamp(Applied Photophysics). Though the conversion was low(20%), we could obtain 1,3-acyl shift product **6b** in good yield(78%). The structures of both the photoproducts **6b** and **7b** were determined from their spectral data, though volatility of **7b** hampered its isolation and purification.

The detailed mechanism of formation of decarbonylated products is difficult to suggest at the moment. It appears that the decarbonylated products **7a,b** arise from further photoreaction of initially formed 1,3-acyl shift products.This contention is based on the observation that further irradiation of the 1,3-acyl shift product **6b** was found to give the decarbonylated product **7b**. In addition, it has been observed that the

1,3-acyl shift product **6b** is initially formed(^{1}H nmr, tlc) during the irradiation of **4b** and the decarbonylated product **7b** appears at later stages of the irradiation(^{1}H nmr, tlc).

In this context it may be mentioned that photodecarbonylation is only rarely observed[13] during photoreaction of β,γ-enones, although other reactions such as ketene formations and fragmentation are known.[14]

In summary, we have described a facile synthesis of oxa-homobrendanes and explored their photochemical reactions for the first time, leading to novel bowl shaped molecules which have generated significant interest recently.[15]

Experimental:

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

Preparation of 3,10-Di-O-allyl-3,5,7,8,10,11-hexamethyltricyclo [6.2.2.0^{2,7}]dodeca-5,11-dien-4,9-dione(2a):

Sodium hydride(50% suspension in mineral oil, 2.0g, excess) was placed in a three neck flask fitted with a reflux condensor and dropping funnel. It was washed several times with dry petroleum ether and freshly distilled dry tetrahydrofuran was added to it. A solution of the diol dimer **1a**(1.0g, 3.29mmol) in tetrahydrofuran(5ml) was added into the flask and the reaction mixture was refluxed for an hour. After which allyl bromide(5ml, excess) was added dropwise to the reaction mixture and reflux was continued for 15 hours during which more allyl bromide was added at regular intervals. After the reaction was complete the tetrahydrofuran was removed under vacuum and cold water was carefully added to the residue. It was extracted with ether(3x50 ml) and the ether extract was washed with sodium thiosulfate(10%, 2x20ml), water(2x20ml), brine(2x20ml) and dried. Removal of solvent and column chromatography furnished the di-O-allyl dimer **2a**(1.03g, 81.5%), mp 117-119^{0}C. IR(nujol) ν_{max}: 1725, 1695 cm^{-1}. ^{1}H NMR(300 MHz): δ 6.1-5.83(complex m, 3H, olefinic H), 5.34(q of d, J_1=16Hz, J_2=2Hz, 1H), 5.26(q of d, J_1=16Hz, J_2=2Hz, 1H), 5.16(q of d, J_1=16Hz, J_2=2Hz, 1H), 5.11(q of d, J_1=12Hz, J_2=2Hz, 1H), 4.99(br m, 1H), 4.40(dd of a dd, J_1=12Hz, J_2=4.5Hz, J_3=1.5Hz, 1H, O-CH_2 proton), 4.21(dd of dd, J_1=12Hz, J_2=4.5Hz, J_3=1.5Hz, 1H, OCH_2 proton), 4.06(dd of dd, J_1=12Hz, J_2=4.5Hz, J_3=1.5Hz, 1H), 4.01(dd of dd, J_1=12Hz, J_2=4.5Hz, J_3=1.5Hz, 1H, OCH_2 proton), 3.19(br t, J= 2Hz, 1H, methine H), 2.79(d, J=2Hz, 1H, methine H), 1.78(d, J=1.5Hz, 3H, olefinic CH_3), 1.74(d, J=1.5Hz, 3H, olefinic CH_3), 1.46(s, 3H, CH_3), 1.26(s, 3H, CH_3), 1.24(s, 3H, CH_3) and 1.04(s, 3H, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ 209.95(CO), 200.94(CO), 145.61, 142.54, 135.89, 135.18, 134.63, 127.82, 115.45, 115.09(eight olefinic carbons), 78.32, 74.95, 64.74, 63.80, 58.17, 49.57, 47.58, 44.79, 26.20, 23.68, 21.43, 19.65, 16.23, 12.61(total 24 carbons). Analysis: Found C, 75.55; H, 8.66% Calcd for $C_{24}H_{32}O_4$ C, 75.00; H, 8.33%.

3,10-Di-O-allyl-3,7,10,11-tetramethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-dien-3,9-dione(2b):

This compound was prepared from diol dimer **1b**(2.0g, 5.5mmol) following the above procedure which gave **2b**(2.06g, 79.8%), mp 92^{0}C. IR(nujol) ν_{max}: 1720, 1690 cm^{-1}. ^{1}H NMR(200 MHz, $CDCl_3$): δ 6.03-5.56 (Cluster of multiplets, 4H, olefinic H), 5.45-5.05(Cluster of multiplets, 5H, olefinic H), 4.40(m of d, J=12Hz, 1H, OCH_2), 4.20(m of d, J=12HZ, 1H, OCH_2), 4.15-4.0(m, 2H, OCH_2 protons), 3.20(m with long range coupling, 1H, methine H), 2.85(d, J= 2Hz, 1H, methine H), 2.75 (d, J=7Hz, 1H, methine H), 1.8(d, J= 2Hz, 3H, olefinic CH_3), 1.50(s, 3H, CH_3), 1.40(s, 3H, CH_3), 1.25(s, 3H, CH_3). Analysis: Found C, 74.79; H, 7.75% Calcd. for $C_{22}H_{28}O_4$ C, 74.15; H, 7.86%.

2-Oxa-1,6,8-trimethyltricyclo[4.3.1.0^{4,5}]dec-6-en-9-one(4a):

The di-O-allyl dimer **2a**(0.63g, 1.64mmol) was heated in *o*-dichloro benzene(7ml) at 160^{0}C for 8 hours. After which the solvent was removed under vacuum and the residue was chromatographed to give the compound **4a**(0.36g, 88%). mp 52^{0}C, IR(nujol) ν_{max}: 1735 cm^{-1}. UV λ_{max}(MeOH): 213, 310 nm. ^{1}H NMR(300 MHz, $CDCl_3$): δ 5.56(br m, J=2Hz, 1H, β-proton of the β,γ-enone moiety), 3.99(dd, J_1=8Hz, J_2=4Hz, 1H, OCH_2 proton), 3.73(d, J=8Hz, 1H, OCH_2 proton), 2.79(dd, J_1=4Hz, J_2=2Hz, 1H, bridgehead proton), 2.52(complex m, 1H, methine proton flanked by two methylenes), 1.88(d, J=1.2Hz, 3H, olefinic CH_3), 1.73(dd, J_1=12 Hz, J_2=10Hz, 1H, CH_2 proton), 1.50(d, J=12Hz, 1H, CH_2 proton), 1.28(s, 3H, CH_3) and 1.21(s, 3H, CH_3). ^{13}C NMR(75MHz, $CDCl_3$): δ 207.55(CO), 138.80, 128.08(olefinic carbons), 78.68, 75.71, 53.30, 45.52, 40.18, 36.85, 21.45, 17.60, 17.09 for other quaternary, methine, methylene and methyl carbons. Mass(m/z): 192 (M+).

2-Oxa-1,6-dimethyltricyclo[4.3.1.0^{4,5}]dec-6-en-9-one(4b):

Pyrolysis of the di-O-allylated dimer **2b**(1.60g, 5mmol) in diphenyl ether(35ml) at 200^{0}C for 6h, followed by chromatography of the crude product on silica gel gave the adduct **4b**(1.47g, 92%) as thick liquid. IR(neat) ν_{max}: 1730cm^{-1}. UV λ_{max}(MeOH): 217.2, 309.6 nm. ^{1}H NMR(200MHz, $CDCl_3$): δ 5.85(m of d, J=7.5Hz, 1H, β-H of β,γ-enone moiety), 4.0(dd, J_1=8Hz, J_2=4Hz, 1H, OCH_2 proton), 3.72(d, J=8Hz, 1H, OCH_2 proton), 3.0(m, 1H, methine H), 2.80(m, 1H, methine H), 2.45(complex m, 1H, methine H), 1.8(d, J= 3Hz, 3H, olefinic CH_3), 1.75(m, 2H, methylene H), 1.25(s, 3H, CH_3). ^{13}C NMR(125MHz, $CDCl_3$): δ 207.4(CO), 139.8, 123.3(olefinic carbons), 78.0, 76.1, 54.2, 45.2, 35.5, 33.0, 22.2 and 18.1(11 carbon atoms). Mass(m/z): 178(M$^+$).

Photoreaction of 4a, synthesis of 2-Oxa-1,6,7-trimethyl tetracyclo[5.2.1.0^{4,10}.0^{6,8}]decan-9-one(5a):

A solution of the compound **4a**(0.1g, 0.52mmol) was irradiated in acetone(100ml) containing acetophenone(1ml) for 2h under nitrogen in a pyrex immersion well with a 125 W mercury vapour lamp(Applied Photophysics). Removal of solvent in vacuo and chromatography of the photolysate on silica gel furnished the oxa-di-π-methane product **5a** as a liquid(0.06g, 60%). IR(neat) ν_{max}: 1735 cm^{-1}. ^{1}H NMR(300MHz, $CDCl_3$): δ 3.86(dd, J_1=8.5Hz, J_2=5Hz, 1H, OCH_2 proton), 3.73(d with st, J=8.5Hz, 1H, OCH_2 proton), 3.10(complex m, 1H, methine H), 2.71(d, J=7Hz, 1H, proton at C_{10}), 2.28(dd, J_1=15Hz, J_2=11.4Hz, 1H, CH_2 proton), 1.90(dd, J_1=15Hz, J_2=6Hz, 1H, CH_2 proton), 1.60(s, 1H, methine H at C_8), 1.4(s, 3H, CH_3), 1.32(s, 3H, CH_3) and 1.20(s, 3H, CH_3). ^{13}C NMR(75MHz, $CDCl_3$): δ 214.06(CO), 89.82, 74.78, 61.81, 48.97, 47.81, 41.12, 29.50, 20.70, 19.02, 13.78. Mass(m/z): 192(M$^+$).

2-Oxa-1,7-dimethyltetracyclo[5.2.1.0^{4,10}.0^{6,8}]decan-9-one(5b):

A solution of **4b**(0.17g, 1mmol) in acetone(100ml) containing acetophenone(2ml) as sensitizer was irradiated(125 W Hg vapour lamp, Applied Photophysics) in a pyrex immersion well for about 3 hours. Removal of solvent and chromatography gave the product **5b**(0.085g, 50%) as a liquid. IR(neat) ν_{max}: 1725 cm^{-1}. ^{1}H NMR(300 MHz, $CDCl_3$): 3.86(d of part of AB system, J_1=8Hz, J_2=5Hz, 1H, OCH_2), 3.78(d of part of AB system, J_1=8Hz, 1H, OCH_2), 3.22(complex m, 1H), 2.72(d, J=8Hz, 1H), 2.50(complex m, 1H), 1.9(merged multiplets, 2H), 1.68(dd, J_1=13Hz, J_2=6Hz, 1H, methylene H), 1.48(s, 3H, CH_3), 1.34(s, 3H, CH_3). ^{13}C NMR(125MHz, $CDCl_3$): δ 90.5, 75.8, 61.3, 51.9, 44.5, 42.0, 35.0, 21.4, 18.2(carbonyl carbon and one of the quaternary carbons were not observed). Mass(m/z): 178(M$^+$), 150(M^+-CO), 135(M^+-CO-CH_3), 109.

3-Oxa-4,6,8-trimethyltricyclo[4.3.1.$0^{4,10}$]dec-7-en-5-one(6a):

A solution of the compound **4a**(0.1g, 0.52mmol) in benzene was irradiated(125 W Hg vapour lamp, Applied Photophysics) in a pyrex immersion well for 1.5 hours. The solvent was removed in vacuo and the photolysate was chromatographed on silica gel. Elution with petroleum ether(60-80^{0}C)-ethylacetate(95:5) furnished the 1,3-acyl shift product **6a**(0.05g, 76%) as a solid , mp 56-57^{0}C. IR(nujol) ν_{max}: 1785 cm^{-1}. UV λ_{max}(MeOH): 211, 339 nm. ^{1}H NMR(300MHz, $CDCl_3$): δ 5.28(br s, 1H, olefinic H), 4.12(superimposed dd, J=8Hz, 1H, proton of OCH_2 group), 3.35(dd, J_1=10Hz, J_2=8Hz, 1H, OCH_2 proton), 2.7(complex m, 1H, methine proton flanked by two methylenes), 2.31(d, J=9Hz, 1H, methine proton at cyclobutanone ring junction), 2.28(m, 1H, CH_2), 1.75(d, J=10Hz, 1H, CH_2), 1.72(d, J= 1Hz, 3H, olefinic CH_3), 1.55(s, 3H, CH_3), 1.30(s, 3H, CH_3). ^{13}C NMR(75MHz, $CDCl_3$): δ 218.03(CO), 132.91, 118.92(olefinic carbons), 73.22, 55.69, 45.34, 36.04, 26.72, 24.18, 22.74 and 18.47 for methine, methylene and methyl carbons. Mass(m/z): 202(M^+). Continued elution with the same solvent gave some unchanged starting material(0.025g).

3-Oxa-4,6-dimethyltricyclo[4.3.1.$0^{4,10}$]dec-7-en-5-one(6b):

Irradiation of a solution of **4b**(0.34g, 2mmol) in benzene with a mercury vapour lamp(16W, Applied Photophysics) in a pyrex immersion well for 7h and chromatography gave the compound **6b**(0.054g, 78%) as a neat liquid. IR(neat) ν_{max} : 1778 cm^{-1}. ^{1}H NMR(300MHz, $CDCl_3$): δ 5.78(d of dd, J_1=10Hz, J_2=6Hz, J_3= 1.5Hz, 1H, olefinic H), 5.57(dd with structure, J_1=10Hz, J_2= 2Hz, 1H, olefinic H), 4.14(dd, J_1=11Hz, J_2=8.5Hz, 1H, *endo* proton of OCH_2 group), 3.44(dd, J_1=11Hz, J_2=9Hz, 1H, *exo* proton of OCH_2 group), 2.66(complex m, 1H, methine H flanked by methylene groups), 2.36(d, J=9Hz, 1H, methine H at cyclobutanone ring junction), 2.30(m of d, J=16Hz, 1H, *endo* proton, allylic methylene group), 1.82(dd, J_1=16Hz, J_2=6.5Hz, 1H, *exo* proton of allylic methylene group), 1.58(s, 3H, CH_3) and 1.33(s, 3H, CH_3). Mass(m/z): 178(M^+).

2,7,9-Trimethyl-3-oxa-tricyclo[4.3.0.$0^{2,9}$]non-7-ene(7a):

A solution of **4a**(0.130g, 0.677mmol) in benzene(100ml) was irradiated with 125 W mercury vapour lamp(Applied Photophysics) in a pyrex immersion well for about 3h. Careful removal of solvent under vacuum at 40^{0}C followed by chromatography gave the decarbonylated product **7a**(0.058g, 52%). IR (neat) ν_{max}: no band for CO group, ^{1}H NMR(300MHz, $CDCl_3$): δ 5.39(br s, 1H, olefinic H), 4.36(d of dd, J_1=7.5 Hz, J_2=5Hz, J_3= 1.5Hz, 1H,

OCH_2), 3.45(dd, J_1=7.5Hz, J_2= 1.5Hz, 1H, OCH_2), 2.84(m, 1H, methine H), 2.24(m of d, J=17Hz, 1H, CH_2), 1.73(br m, 3H, CH_3), 1.6(m of d, J_1=17Hz, 1H, CH_2), 1.5(s, 3H, CH_3), 1.24(d, J=9Hz, 1H, methine H) and 1.08(s, 3H, CH_3). Mass(m/z): 164(M^+).

2,9-Dimethyl-3-oxatricyclo[4.3.0.$0^{2,9}$]non-7-ene(7b):

A solution of the ketone **4b**(0.155g, 0.8mmol) in dry benzene(110ml) was irradiated under nitrogen with 125 W mercury vapour lamp(Applied Photophysics) in a pyrex immersion well for 2.5 hours. Benzene was removed under vacuum at 40^{0}C and the residue was chromatographed on silica gel. Elution with petroleum ether(bp 60-80^{0}C) furnished the decarbonylated product **7b**(0.082g, 62%) as a major product. Continued elution with the same solvent gave some 1,3-acyl shift product **6b**(0.02g, 15%). Data of **7b**: IR(neat) ν_{max}: no band for CO group. ^{1}H NMR(300MHz, $CDCl_3$): δ 5.8(d of dd, J_1=9Hz, J_2=5Hz, 1H, olefinic H), 5.7(dd ,J_1=9Hz, J_2= 2Hz, 1H, olefinic H), 4.40(superimposed dd, J_1=J_2=7.5Hz, 1H, OCH_2), 3.55(dd, J_1=7.5Hz, J_2= 1Hz, OCH_2), 2.8(br m, 1H, methine H), 2.25(m of d, J=17Hz, 1H, CH_2), 1.77(m of dd, J_1=17Hz, J_2=4Hz, 1H, CH_2), 1.51(s, 3H, CH_3), 1.3(d, J=7.5Hz, 1H, methine H), 1.1(s, 3H, CH_3). ^{13}C NMR(125MHz, $CDCl_3$): δ 129.8, 125.5(olefinic carbons), 83.1, 37.8, 30.6, 28.6, 20.4 and 16.4(Total eight carbons, one of the quaternary carbons not shown). Mass(m/z): 150(M^+), 135(M^+-CH_3), 109, 91.

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REFERENCES

1. Schuster, D.I. in *Rearrangement in Ground and Excited States*, deMayo, P. (ed) Academic press, New York, **1980**, Vol.3, pp.232-279; Houk, K.N., *Chem.Rev.*, **1976**, 76, 1-74 and references cited therein; Hixon, S.S., Mariano, P.S.and Zimmerman, H.E., *Chem.Rev*, **1973**, **73**, 531-535; Dauben, W.G., Lodder, G. and Ipaktschi, J., *Top.Curr.Chem.*, **1974**, 54, 73-114.
2. Demuth, M., in *Organic Photochemistry*, Padwa, A. (Ed), Marcell Decker Inc. New York, **1991**, Vol.11, pp.37-97.; Demuth, M. in *Comprehensive Organic Chemistry*, Trost, B.M., Flemming, I. and Paquette, L.A.(eds) Pergamon press, Oxford, **1991**, Vol.5, pp.215-237.
3. Singh, V.K., Deota, P.T. and Bedekar, A.V., *J.Chem.Soc.*, *Perkin Trans.1*, **1992**, 903-912; Singh, V.K. and Thomas, B., *J.Chem.Soc.*,

Chem.Commun., **1992**, 1211-1213; Singh, V.K. and Porinchu, M., *J.Chem.Soc.*, *Chem.Commun.*, **1993**, 134-136.

4. Schultz, A.G., Lavieri, F.P., Shead, T.E., *J.Org.Chem.*, **1985**, 50, 3086-3091.
5. Parker, S.D. and Rogers, N.A.J., *Tetrahedron. Lett.*, **1976**, 4389-4392; Eckersley, T.J., and Rogers, N.A.J., *Tetrahedron.*, **1984**, 40, 3759-3768.
6. Demuth, M. and Schaffner, K., *Angew.Chem.*, *Int.Ed.(Engl)*, **1982**, **21**, 820-836; Givens, R.S., Chae, W.K. and Matuszewski, B., *J.Am.Chem.Soc.*, **1982**, 104, 2456-2466.
7. Uyehara, T., Kabasawa, Y., Kato, T., Furuta, T., *Tetrahedron.Lett.*, **1985**, 26, 2343-2346; Uyehara, T., Kabasawa, Y., Kato, T., Furuta, T., *Bull.Chem.Soc.*, *Jpn*, **1986**, 59, 539-543.
8. Adler, E. and Holmberg, K., *Acta.Chem.Scand. Ser B.*, **1974**, 28, 465-472; Adler, E., Junghahn, L., Lindberg, V., Berggren, B. and Westin, G., *Acta.Chem.Scand.*, **1960**, 14, 1261.
9. Labhat, H., Waghiere, G., *Helv.Chem.Acta*, **1959**, 42, 2219-2227.; Bays, D.E., Cookson, R.C., Mackenzie, S., *J.Chem.Soc.*, *B.*, **1967**, 215-226.
10. Jackman, L.M., Sternhell, S., *Application of NMR Spectroscopy in Organic Chemistry*, Pergamon Press, New York, **1969**; Marchand, A.P., *Stereochemical Applications of NMR Studies in Bicyclic Systems*, Verlag Chemie, International, Florida, **1982**.
11. Levy, G.C.and Nelson, G.L., *C-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley Interscience, New York, **1977**, Vol.**2.**
12. Carless, H.A.J. in *Synthetic Organic Photochemistry*, Horspool, W.M.,(Ed) Plenum press, New York and London, **1984**, pp. 425-487.
13. Singh, V.K., Thomas, B. and Sharma, U., *Tetrahedron.Lett*, **1995**, 36, 3421-24; Scharf,H.D., Kusters, W., *Chem.Ber.*, **1971**,104, 3016-3029.
14. EcKersley,T.J., Parker, S.D.and Rogers, N.A.J., *Tetrahedron* **1984**,40, 3749-3758.
15. Moyano, A., Serratosa, F., Almansa, C., *Tetrahedron*, **1992**, 48, 1497-1506.; Marchand, A.P., Annapurna, P., Taylor, R.W., Simmons, D.L., Watson,W.H., Nagl, A., Flippen-Anderson, J.L., Gilardi, R. and George, C., *Tetrahedron*, **1990**, 46, 5077-5084.; Thummel, R.P. and Hegde, V., *J.Org.Chem.*, **1989**, 54, 1720-1725.; Thummel, R.P. and Lim, J.L., *Tetrahedron Lett.*, **1987**, 28, 3319-3322.

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