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# Regioselectivity in Ketyl Radical Promoted Ring Cleavage of Configurationally Restricted α,α'-Diketocyclopropanes Under SET and PET Conditions

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***Abstract:*** Regioselective bond scission of cyclopropyl ketones **1a-d** in single electron transfer (SET) reductive process with tributytin hydride has been found to be controlled by radical stabilizing effect. In the case of **1e** and **11** stereoelectronic effect was also operative. Under photoinduced electron transfer (PET) condition similar regioselectivity was also observed. A ring expansion product **16** via intramolecular ketone-cyclopropane interaction was obtained from **1b** in this case. © 1998 Elsevier Science Ltd. All rights reserved.

Regioselective cleavage of the carbonyl conjugated cyclopropyl ring in tricyclo[3.3.0.0$^{2,8}$] octanone derivatives of type **I** provides a versatile starting point towards the syntheses of various cylcopentanoid natural products.[1-7] The regioselectivity of such ring cleavage of cyclopropyl ketones in simple system is controlled by steric and electronic factors.[8] However, in fused systems, the selectivity has been attributed to geometrical factors and the bond that cleaves is the one which has maximum overlap with the p-orbital of the carbonyl group.[9] From the bonding properties of cyclopropane it is known that, its interaction energy with the neighbouring group is at a maximum when the p-orbital axis of the neighbouring group and the plane of the cyclopropane ring are parallel to each other.[9b]

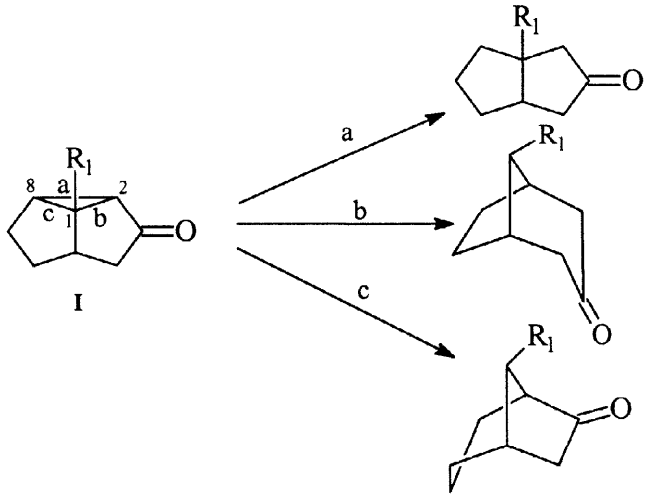


Fig.I Modes of cyclopropyl ring cleavage in system **I**


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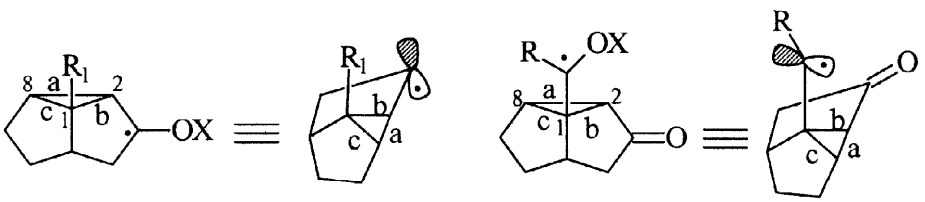
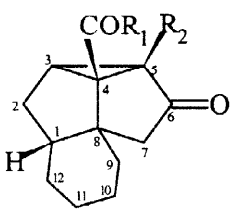
In the rigid tricyclic octanone system represented by **I**, cleavage of the cyclopropyl ring may follow any one or more of the three different routes (Fig. I). However, the major pathway has been the cleavage of the C2-C8 bond (path a)[1-7,10-13] arising from better overlapping of this bond with the neighbouring carbonyl p-orbital. There has also been cases of cleavage of the C1-C2 bond (path b).[2,4,5,7,11,13-15] We have recently disclosed that the selectivity in such systems can be completely altered by introduction of a second carbonyl group at C1 leading to exclusive cleavage of the C1-C8 bond (path c).[16]

A carbonyl group at C1 in **I** will have free rotation of the carbonyl group. Under radical scission condition of **I**, the ketyl radical from the cyclopentanone ketone is expected to have a better overlap with the C2-C8 bond (**A**)[13] whereas, the ketyl radical from the side chain may have a comparable overlap with both C1-C2 and C1-C8 bonds (**B**) leading to a lack of selectivity. However, radical stabilization consideration can be expected to




**A** **B**

induce a selective cleavage of the C1-C2 bond. In view of the current continued interest in the radical induced cleavage of rigid systems of type **I** for generating advanced intermediates to natural products, we have investigated the selectivity in the radical induced cleavage of the conformationally rigid tetracyclic cyclopropyl ketones **1a-e** and here we report the results.




**1a-e**

a) $R_1$= $CH_3$; $R_2$= H
b) $R_1$= $CH(CH_3)_2$; $R_2$= H
c) $R_1$= $C_6H_5$; $R_2$= H
d) $R_1$= $C_6H_5$; $R_2$= $COC_6H_5$
e) $R_1$= OMe; $R_2$= $CO_2Me$

## Results and Discussion

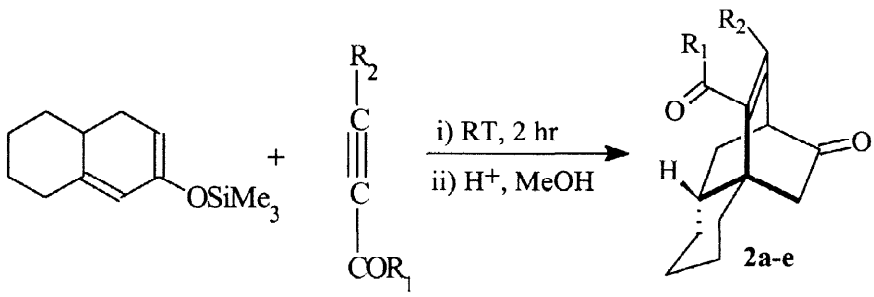
The tetracyclo[6.4.0.$0^{3,5}$.$0^{4,8}$]dodecan-6-ones **1a-e** were readily obtained from the oxa-di-pi-methane (ODPM) photoisomerizations of the corresponding tricyclo[6.2.2.$0^{1,6}$]dodec-11-en-9-ones (**2a-e**) (**Scheme-1**).[16-17]

The radical scissions of the cyclopropyl ketones **1a-e** were carried out using the one electron reduction process with tributyltin hydride. Although this reagent is commonly used to generate carbon centered

radicals,[18] the much less studied O-stannyl ketyl radical has recently been employed by Enholm and coworkers to promote the cleavage of cyclopropyl rings.[13,14]

The tetracyclic ketone **1a** was treated with n-$Bu_3SnH$ and AIBN at 80°C for 8h and afforded the

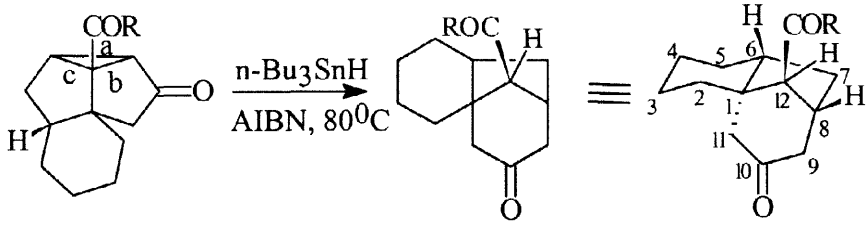
**Scheme I**




where,
a) $R_1 = CH_3$; $R_2 = H$
b) $R_1 = CH(CH_3)_2$; $R_2 = H$
c) $R_1 = C_6H_5$; $R_2 = H$
d) $R_1 = C_6H_5$; $R_2 = COC_6H_5$
e) $R_1 = OMe$; $R_2 = CO_2Me$

tricyclo[6.3.1.$0^{1,6}$]dodecanedione **3a** as the only isolated product in 85% yields (**Scheme-2**). The structure was established from a detailed spectral analysis. In the IR it showed a strong peak at 1710 $cm^{-1}$ suggesting the presence of a six member ketone. In $^1$H-nmr, the proton at C-12 appeared as a doublet ($J_{8,12}$ *5.23 Hz*) which confirmed its stereochemistry. The $^{13}$C-nmr spectra showed signals for one $CH_3$, seven $CH_2$, three CH, two C=O and one quaternary carbon.

**Scheme 2**



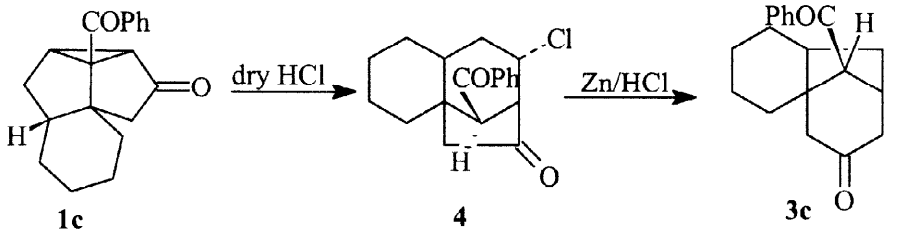

**1a-c** **3a-c**

where, (a) R = $CH_3$ ; (b) R = $CH(CH_3)_2$ ; (c) R = $C_6H_5$

In a similar fashion cleavage of **1b** and **1c** afforded the tricyclic ketones **3b** and **3c** respectively in good yields. Compound **3c** was found to be identical to the compound obtained by dehalogenation of 12-benzoyl-8-chlorotricyclo[7.2.1.$0^{1,6}$]dodecan-10-one (**4**) which was obtained from HCl-promoted cleavage of **1c**

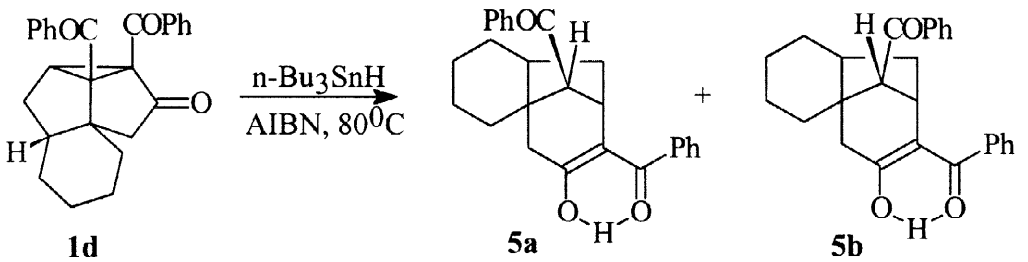
**(Scheme-3)**[16]. The selective cleavage of the 'b' bond in **1a-c** thus underscores the importance of radical stabilizing factors.

**Scheme 3**



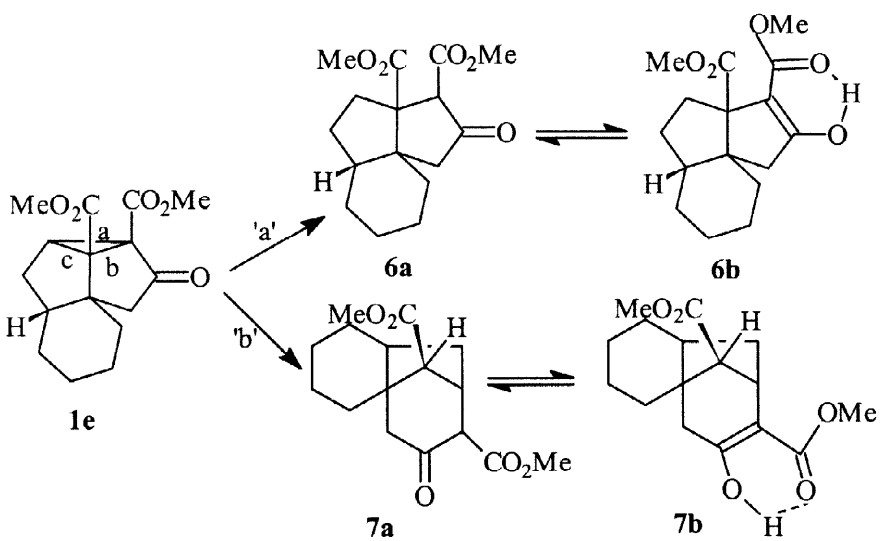

The reductive cleavage of **1d** afforded an epimeric mixture (4:1) of **5a** and **5b** (**Scheme-4**), in accordance with the expectation that the steric effect of an additional α-substituent does not affect the mode of

**Scheme 4**




bond cleavage in this type of systems. The reaction mixture showed two enolic protons at δ 15.62 and at δ 15.78 presumably for **5a** and **5b** respectively. The major epimer **5a** could be obtained in a pure form by fractional crystallization. The doublet at δ 3.24 (*J 5.7Hz*) confirmed its stereochemistry at C-12. The $^{13}$C-nmr spectral data for **5a** are recorded in **Table-I**. On treatment with base **5a** epimerized to **5b** confirming the structural assignments.

**Scheme 5**



In contrast to the above when the ketodiester **1e** was subjected to the reductive cleavage, it afforded a mixture (4:1) of **6** and **7** (**Scheme-5**) in very good yields arising from cleavage of 'a' and 'b' bonds respectively. The major product **6** could be obtained in a pure form by repeated fractional crystallization and was found to exist as a keto-enol tautomeric mixture (1:2), the ratio of which could be determined from their pmr signals for the respective methoxy groups.

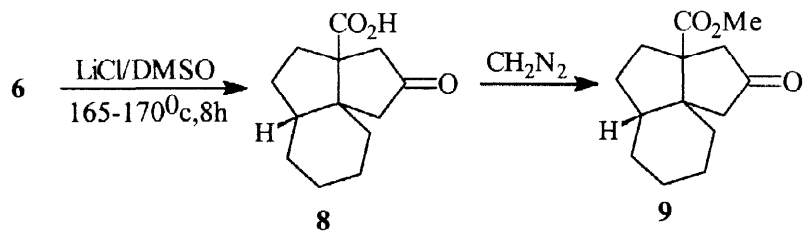
**Table-I** $^{13}$C-nmr data and characteristic pmr data for **5-6, 8-9, 13-14, 16**

| Compound | δ (ppm) | | | | | |
|---|---|---|---|---|---|---|
| | $-CH_2$ | $\geq CH$, $-CH_3$ | $-\overset{\vert}{C}-$ | $\diagdown C{=}O$ | $-OH$ | $-OMe$ |
| **5a** | 20.6, 25.1, 26.3, 36,9 38.2, 39.7 | 37.9, 47.9, 59.6 127.3,127.7, 127.8 128.3, 128.5,129.6 132.6 | 42.4, 114.1, 134.5,137.4 177.1 | 200.4, 201.1 | 15.62 | |
| **6a** | 22.1, 25.5, 27.4, 27.8 29.7, 33.3, 42.7 | 44.9, 52.2, 52.3 61.1 | not identified | not identified | | 3.72, 3.73 |
| **6b** | 22.5, 25.6, 26.7, 29.6 34.9, 36.5, 38.7 | 48.5, 51.2, 51.7 | 61.1, 63.6 105.3, 169.4 | 174.4, 175.3 | 10.28 | 3.63, 3.69 |
| **7b** | | | | | 11.6 | 3.58, 3.70 |
| **9** | 22.6, 25.8, 28.1, 28.9 33.8, 34.5, 43.7, 48.6 | 46.4, 52.4 | 55.7, 59.2 | 175.7, 216.9 | | 3.71 |
| **10** | 20.3, 25.4, 26.1, 33.4 35.8, 42.6, 46.4 | 34.2, 48.2, 51.3, 55.2 | 44.5 | 172.9, 211.4 | 3.68 | |
| **14b** | 30.3, 34.8, 36.7 | 33.9, 34.7, 49.5 51.6, 51.9 | 103.2, 171.7 | 170.7, 172.4 | 11.91 | 3.69, 3.8 |
| **16** | 20.8, 26.1, 26.2, 26.4 36.4, 40.9 | 16.3, 19.9, 43.6 49.3, 53.9, 85.7 | 48.7, 102.7 147.7 | 206.3 | | |

The assigned structure was further confirmed by decarbomethoxylation of **6** by Krapcho procedure[19] using lithium chloride in hot aqueous dimethyl sulfoxide which also resulted in hydrolysis of the tertiary ester to furnish the ketoacid **8**. An absorption at 1745 cm$^{-1}$ in IR of **8** identified the cyclopentanone moiety and the

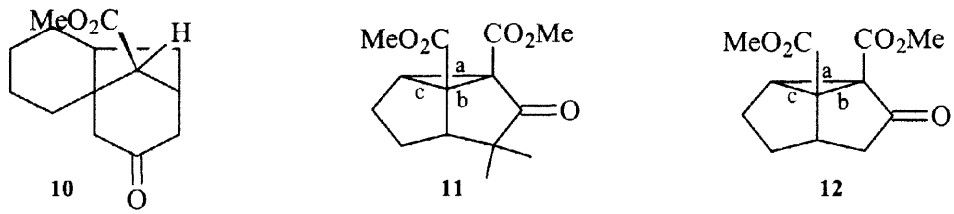
structure was further supported by the nmr spectral data. Esterification of **8** with diazomethane furnished the ketoester **9** (**Scheme-6**). The analytical as well as pmr and $^{13}$C-nmr data (**Table I**) of **9** confirmed its structure. The minor compound **7** could not be obtained in a pure form. Attempts at decarboxylation and esterification of the mixture **6** and **7** and separation of the resultant ketoesters **9** and **10** were also not fruitful. The structure of **10** was arrived at from the pmr spectrum of a partially pure (75% of **10**) mixture which showed a doublet at δ 2.53 ($J_{8,12}$ *5.4 Hz*) for 12-H, a multiplet around δ 2.7 for the bridgehead proton and the corresponding $^{13}$C-nmr spectrum (**Table-I**).

**Scheme 6**




**8** **9**

The isolation of **6** and **7** from the reductive cleavage of **1e** points to the operation of both steric and radical stabilisation factors in the cyclopropyl bond scission of this substrate. Although this was in conformance with an earlier observation relating to the cleavage of both 'a' and 'b' bonds in **11**,[11] this was in




**10** **11** **12**

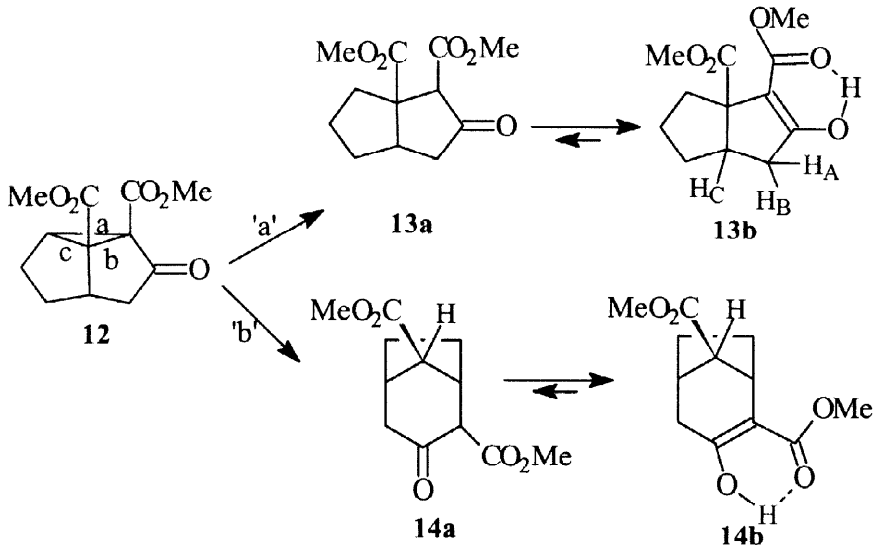
sharp contrast to the recently regioselective cleavage of the 'a' bond from O-stannyl ketyl promoted fragmentation of **12**.[13] The later in a configurationally restricted α-ketocyclo-propane has been explained on the basis of preferential cleavage of the bond with the maximum overlap with the ketyl radical even in the presence of radical-stabilizing groups. In view of such observed discrepancy we decided to reinvestigate the reaction of **12** with n-$Bu_3SnH$.

Reductive cleavage of **12** furnished essentially a mixture of two products in 75% combined yield. Although a complete separation was not possible, pure forms of both could be obtained by flash chromatography. The less polar fraction corresponded to **13**, arising from bond 'a' cleavage and was confirmed from its pmr spectral identity with reported values[20] (**Scheme 7**). The more polar component was identified as the bridged compound **14** from detailed analysis of its analytical and spectral data (**Table I**). These two products were obtained in a ratio of 1.2 : 1.

From the above results it appeared that although cleavage of bond 'a' may be a kinetically favored route in system **I**, in the presence of a radical stabilizing substituent, 'b'-cleaved product becomes

thermodynamically more preferred. Such thermodynamic preference has been supported by MMX energy calculation also. This has also been reflected in the case of a derivative of **I** ($R_1$ = $CO_2Me$) where only the 'b'-bond cleaved product is reported to be formed.[13]

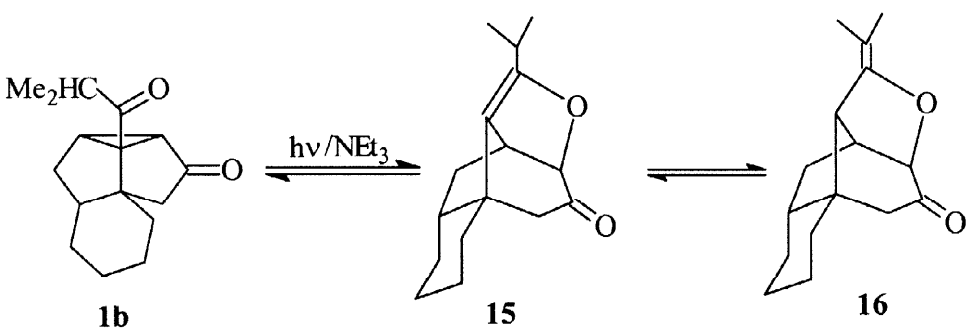
**Scheme 7**




The radical cleavage of strained 3- and 4- member ring systems under photoinduced electron transfer (PET) condition has been reported to proceed via radical anion.[21] A regioselective 'a'-cleavage of the cyclopropyl ring has been reported in the case of **I** ($R_1$ = H) under PET condition.[12] We explored such reductive cyclopropyl ring scission of **1a-e** under PET condition also.

When an acetonitrile solution of **1a** was irradiated for 8 hr in the presence of triethylamine (TEA), 15% of **3a** was found to be formed along with 80% of the unreacted starting material. Total conversion of the starting material was not obtained even after irradiation of 38 h when the reaction mixture gave 40% of **3a** along with 50% of **1a**.

**Scheme 8**




When an ethanol solution of **1b** was irradiated for 16 hr in the presence of triethylamine (TEA), the reaction mixture was found to be a mixture (2:1, 75%) of **1b** and the ring opened product **3b**. An interesting intramolecular PET induced ketone-cyclopropane reaction was also observed in this reaction where a small

amount (10%) of **16** was obtained from this reaction (**Scheme-8**). Although PET initiated ketone-olefin reaction as well as vinylcyclopropane ring expansion is known in the literature,[22] ketone-cyclopropane reaction is not a common reaction. The structure of **16** has been assigned on the basis of its analytical and spectral data. In the IR it showed a carbonyl absorption at 1725 $cm^{-1}$ characteristic of a six-member ketone. The $^{13}$C-nmr spectrum was particularly informative and it showed signals due to two $CH_3$, six $CH_2$, four CH, one quaternary carbon, two C=C and one C=O. In $^1$H-nmr spectrum a singlet for the methyl protons at δ 1.69 and a doublet at δ 4.22 (*J 6.3Hz*) for the acyl proton supported the assignment.

In the case of **1c** no definite product could be obtained even after a short irradiation of 30 mins. On the other hand the triketone **1d**, under similar reaction condition gave 71% of the expected ring-opened product **14a** in a mixture (5 :1) with its epimer **14b**.

The dicarbomethoxy derivative **1e** gave 37% of a mixture of **5** and **6** (5:1) and 50% of the starting compound. Increase in irradiation time led to destruction of the product as well as the starting material.

**Experimental:**

All melting points are uncorrected and were determined in a Gallenkamp apparatus. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. Electronic spectra were recorded on a Hitachi 200-20 UV spectrophotometer using ethanol as solvent. $^1$H-NMR spectra were recorded on Bruker-300, Bruker AC-200 or Varian EM 360 spectrometer in $CDCl_3$ using tetramethylsilane as internal standard. $^{13}$C-NMR spectra were recorded at 75 or 50 MHz on Bruker-300 and Bruker AC-200 instruments. Elemental analyses were performed with the Heraeus combustion apparatus or 2400 series-II. Perkin Elmer CHN analyzer. Column chromatography was performed using dry-packed silica gel (60-120 mesh) column under normal pressure. Solvents for photolysis experiments were purified, dried and distilled before use. Petroleum ether used was the fraction of b.p. 60-80°C. Ether refers to diethyl ether.

***Starting Compounds:*** Compounds **1a-e** and **2a-e** were prepared following previously reported procedures.[16,17] n-$Bu_3SnH$ and AIBN were purchased from Aldrich Chemical Company Inc.

**(A) Reductive cyclopropyl ring opening of 1a-e by $nBu_3SnH$:** *General Procedure*: The tetracyclic ketones (0.1M) were dissolved in dry benzene, catalytic amount of AIBN and $nBu_3SnH$ (two equivalents) were added and the reaction mixture was stirred at 80°C for 3h under argon atmosphere. Solvent was removed in vacuum and water (5ml) and hydrochloric acid (1-2 drops)were added and stirring was continued for further 1h. reaction mixture was extracted with ether and dried over anhydrous $Na_2SO_4$. After removal of the solvent the crude material was purified by column chromatography.

**4-acetyltetracyclo[6.4.0$^{3,5}$.0$^{4,8}$]dodecan-6-one (1a):** The above procedure was repeated with a solution of **1a** (100mg, 0.45mmol) in dry benzene (5ml) and catalytic amount of AIBN and n-$Bu_3SnH$ (200mg, 0.72mmol). Elution of the column with 10% ethyl acetate in petroleum ether gave 12-acetyltricyclo-

[6.3.1.$0^{1,6}$]dodecan-10-one (**3a,** 85mg, 85%) as a liquid; Anal Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; Found: C, 75.87; H, 9.08; IR (neat) $\nu_{max}$: 1705 $cm^{-1}$. $^1$H-NMR (200MHz) δ (ppm): 0.78-0.91 (m, 1H); 1.02-1.73 (m, 10H); 1.85-1.97 (m, 1H); 2.17 (s) superimposed with 2.19-2.35 (m, total 5H); 2.53 (d, *J 5.23Hz*, 1H), 2.69 (d, *J 6.8Hz*,1H), 2.71-2.77 (m, 1H). $^{13}$C-NMR (50MHz) δ(ppm): 20.22, 25.09, 26.12, 33.78, 35.78, 42.45, 46.08, ($CH_2$), 30.47, 34.31, 48.19, 62.92, (CH, $CH_3$), 209.42, 210.80

**4-isobutyryltetracyclo[6.4.$0^{3,5}$.$0^{4,8}$]dodecan-6-one (1b)**: The above mentioned procedure was repeated with a solution of **1b** (200mg, 0.81mmol) in dry benzene (8ml) and catalytic amount of AIBN and $nBu_3SnH$ (400mg, 1.44mmol). Elution of the column with 10% ethyl acetate in petroleum ether gave 12-isobutyryl-tricyclo[6.3.1.$0^{1,6}$]dodecan-10-one (**3b,** 165mg, 82%) as a liquid. Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74; Found: C, 77.07; H, 9.58. IR (neat) $\nu_{max}$: 1710 $cm^{-1}$. $^1$H-NMR (200MHz) δ(ppm): 0.81-0.92 (m, 1H); 1.04 (d, *J 6.8Hz*) and 1.06 (d, *J 6.8Hz*) superimposed with 1.15-1.23 (m, total 8H); 1.29-1.61 (m, 6H); 1.65-1.82 (m, 2H); 2.08-2.32 (m, 3H); 2.55 (d, *J 18.3Hz*), 2.67 (d, *J 5.7Hz*) and 2.76 (d, *J 18.3Hz*) superimposed with 2.62-2.76 (m, total 4H). $^{13}$C-NMR (50mhz) δ(ppm): 17.52, 18.71; 20.32, 25.15, 26.19, 34.58, 35.87 42.56, 46.18; 45.22; 34.68, 41.35, 48.08, 59.93, 211.34, 216.26.

**4-Benzoyltetracyclo[6.4.$0^{3,5}$.$0^{4,8}$]dodecan-6-one (1c):** The above mentioned procedure was repeated with a solution of **1c** (100mg, 0.35mmol) in dry benzene (4ml), catalytic amount of AIBN and n-$Bu_3SnH$ (200mg, 0.72mmol). Elution of the column with 10% ethyl acetate in petroleum ether gave a solid (70mg, 70%), which on crystallization from ether and petroleum ether gave white crystals of 12-benzoyltricyclo[6.3.1.$0^{1,6}$]dodecan-10-one ( **3c)** m.p. 124$^0$C (mmp[13] 124$^0$C).

**4,5-Dibenzoyltetracyclo[6.4.0.$0^{3,5}$.$0^{4,8}$]dodecan-10-one (1d) :** The above mentioned procedure was repeated with a solution of **1d** (140mg, 0.36mmol) in dry benzene (4ml) and $nBu_3SnH$ in presence of catalytic amount of AIBN for 3h and then hydrolysis of the reaction mixture by water gave a mixture (120mg, 86%) of **5a** and **5b** (4:1). Fractional crystallization of the mixture gave pure crystals of 9-*syn*-12-dibenzoyl-tricyclo[6.31.$0^{1,6}$]dodecan-9-en-10-one (**5a,** 75mg, 54%) m.p. 181°C. Anal Calcd for $C_{26}H_{26}O_3$ : C, 80.80; H, 6.78; Found: C, 80.42; H, 6.58 ; IR (KBr) $\nu_{max}$: 1675, 1610 $cm^{-1}$. UV (EtOH) $\lambda_{max}$: 312.8nm (logε, 4.04); 245.6 (4.15) $^1$H-NMR (300MHz) δ(ppm): 0.84-1.71 (m, 9H); 2.23 (d, *J 12.3Hz*, 1H); 2.39-2.49 (m, 1H); 2.8 (d, *J 19.8Hz*, 1H); 2.95 (d, *J 19.8Hz*, 1H); 3.24 (d, *J 5.7Hz*, 1H); 3.29-3.33 (m, 1H); 6.8-7.72 (m, 10H); 15.62 (s, 1H, enolic -OH).

*Epimerization of* **5a :** To a solution of **5a** (50mg, 0.13mmol) in dry methanol, NaOMe (50mg, 2mmol) was added and the reaction mixture was stirred overnight at room temperature. Solvent was removed and the reaction mixture was extracted with ether. Removal of solvent gave a mixture (45mg, 90%) with enolic protons at δ 15.62 and at δ 15.78 for **5a** and **5b** (6:1) respectively.

**4,5-Dicarbomethoxytetracyclo[6.4.0.$0^{3,5}$.$0^{4,8}$]dodecan-6-one (1e):** The same procedure was repeated with a solution of **1e** (100mg, 0.35mmol) in dry benzene (4ml) catalytic amount AIBN and n-$Bu_3SnH$

(200mg, 0.72mmol). Elution of the column with 10% ethyl acetate in petroleum ether gave a solid mixture (4:1) of **6** and **7** (85mg, 85%). Repeated fractional crystallization of the mixture gave white crystals of the major product 9,10-dicarbomethoxytricyclo[7.3.0.$0^{1,9}$]dodec-10-en-11-one (**6**, 45mg, 45%) m.p. 116°C. Anal Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.24; H, 7.68; IR (KBr)$\nu_{max}$: 1725, 1680, 1630 $cm^{-1}$ ; UV (EtOH) $\lambda_{max}$: 251nm (log$\varepsilon$, 3.86); $^1$H-NMR (200MHz) $\delta$(ppm): 0.88-2.08 (m, 16H); 2.1-2.9 (m, 6H); 3.63 (s, 3H); 3.69 (s, 3H), 3.72 (s, 1.5H) 3.73 (s, 1.5H); 10.28 (bs, 1H) for the keto-enol mixture.

*Decarbomethoxylation of* **6**: To a solution of **6** (200mg, 0.68mmol) in DMSO (5ml) two drops of water and LiCl (50mg, 1.3mmol) were added and the reaction mixture was heated at 165-170°C for 8h. The reaction mixture was extracted with ether. Removal of solvent gave a solid, which on crystallization gave crystals of **8** (100mg, 67%) m.p. 152°C which was used for esterification without further purification; IR (KBr) 1745, 1690$cm^{-1}$; $^1$H-NMR (300MHz) $\delta$(ppm): 0.96-1.08 (m, 1H); 1.13-1.51 (m, 5H); 1.62-2.05 (m, 6H); 2.11 (d, *J 19.3Hz*, 1H); 2.30 (d, *J 19.3Hz*, 1H); 2.43 (d, *J 18.3Hz*, 1H); 2.52-2.67 (m, 1H); 3.16 (d, *J 18.3Hz*, 1H); $^{13}$C-NMR (75MHz) $\delta$(ppm): 22.65, 25.78, 28.88, 33.64, 34.42, 43.68, 48.43, 46.42, 57.20, 59.04, 181.54, 216.68.

*Esterification of* **8**: To the solution of acid (**8**, 50mg, 0.23mmol) in ether (15ml) diazomethane prepared from nitrosomethylurea (1.4gm) and 70% KOH in 15 ml ether was passed slowly in ice cold condition and the reaction mixture was stirred for further 15min and then was decomposed with acetic acid. The reaction mixture was extracted with ether and the ether layer was washed with $NaHCO_3$ and brine solution. After removal of the solvent, the crude reaction mixture was purified by column chromatography. Elution of the column with 5% EtOAc in PE gave **9** as a liquid (45mg, 85%). Anal. Cald for $C_{14}H_{20}O_3$; C, 71.16, H, 8.53; Found, C, 70.87, H, 8.73. IR (Neat) 1745, 1725$cm^{-1}$, $^1$H-NMR (300MHz) $\delta$(ppm): 0.92-1.42 (m, 6H); 1.63-1.92 (m, 6H); 2.05 (d, *J 19Hz*, 1H); 2.24 (d, *J 19Hz*, 1H); 2.37 (d, *J 18Hz*, 1H); 2.47-2.58 (m, 1H); 3.17 (d, *J 18Hz*, 1H); 3.71 (s, 3H).

*Decarbomethoxylation of* **7**: The above procedure of decarbomethoxylation followed by esterification of the acid was carried out with a mixture of **6** and **7** (100mg, 0.34 mmol). A pure sample of 12-carbomethoxytricyclo[6.3.1.$0^{1,6}$]dodecan-9-en-10-one (**10**) could not be separated from the mixture of **9** and **10**. The nmr spectra were recorded with a 75% pure sample of **10**. $^1$H-nmr (300MHz) $\delta$(ppm): 0.87-0.95 (m), 1.13-1.39 (m), 1.42-1.55 (m), 1.74-1.79 (m). 2.01(d, *J 12Hz*), 2.11-2.27 (m), 2.36-2.47 (m), 2.53 (d, *J 5.4Hz*), 2.66 (m, *J 1.8Hz*), 2.71-2.77 (m).

**1,2-Bis(methoxycarbonyl)tricyclo[3.3.0. $0^{2,8}$]octan-3-one (12) :** The above mentioned procedure was repeated with a solution of **12** (640mg, 2.67mmol) in benzene (25ml) with tributyl tin hydride (2.1gm, 7.2 mmol) and catalytic amount of AIBN. Elution of the column with 10% EtOAc in PE gave a clear thick oil of **13** and **14** (1.2:1) (470mg, 74%) which were separated by flash column chromatography. Elution of the column with 10% EtOAc in PE firstly gave a clear thick liquid of **13a/13b** having identical pmr spectral data

as reported[20]; followed by mixtures of **13** and **14** and lastly a thick liquid of **14a/14b**. Anal Calcd for $C_{12}H_{16}O_5$; C, 59.97; H, 6.71; Found C, 59.44; H, 7.0. IR (Neat) $\nu_{max}$ 3450 (broad), 1735, 1650, 1610 $cm^{-1}$; $^1$H-NMR (300 MHz) δ(ppm): 0.95 (m, 1.2H); 1.30-1.47 (m, 2H); 1.51-1.74 (m, 2.5H); 1.78-2.02 (m, 2.3H); 2.05-2.12 (m, 2H); 2.70-2.76 (m, 1.8H); 2.92-2.99 (m, 1.3H); 3.34-3.37 (m, 1H); 3.69 (s, 3H); 3.82 (s, 3H); 11.91 (s, 0.7H).

**(B) Reductive cyclopropyl ring opening of 1a-e under PET condition:** *General Procedure :* The substrate (0.02M) was dissolved in 20% triethylamine (TEA) in ethanol or acetonitrile (by volume). The solution was purged with slow stream of argon gas for 10-15 mins and then irradiated in Rayonet photoreactor at 300nm. The progress of reaction was monitored by GC/TLC. The solvent was evaporated under reduced pressure and the crude product so obtained was purified on a silica gel column using petroleum ether and EtOAc mixture as eluent.

**Irradiation of 1a :** A solution of **1a** (170mg, 0.078mmol) in acetonitrile was irradiated for 8h in the presence of TEA. Elution of the residue with 5% EtOAc in PE gave **3a** (25mg, 15%). Further elution of the column with 10% EtOAc in PE gave **1a** (135mg, 80%) m.p. 48°C (mmp 48°C). Irradiation of **1a** under the same condition for 38h gave **3a** (40%) and **1a** (50%) m.p. 48°C (mmp 48°C ) from the reaction mixture.

**Irradiation of 1b :** Solution of **1b** (300mg, 1.25mmol) in TEA /acetonitrile was irradiated at 300nm for 16h. Elution of the column with 5% EtOAc in PE gave **16** (30mg, 10%) as a liquid. Anal. Cald for $C_{16}H_{22}O_2$: 77.99, H, 9.01; Found: 77.83, H, 8.72. IR (Neat) $\nu_{max}$ 1725 $cm^{-1}$; $^1$H-NMR (200MHz) δ(ppm): 0.95-1.06 (m, 1H); 1.20-1.37 (m, 4H); 1.69 (s) superimposed with 1.52-1.78 (m, total 10H); 1.80-1.97 (m, 2H); 2.10 (d, *J 16.5Hz*, 1H); 2.60 (d, *J 16.5Hz*, 1H); 2.86-2.92 (m, 2H), 4.22 (d, *J 6.3Hz*, 1H).

Further elution of the column gave a mixture (250mg, 75%) of **1b** and **3b** (1:2 from GC) which was not purified further.

**Irradiation of 1d :** A solution of **1d** (140mg, 0.36mmol) in TEA-ethanol was irradiated for 8h. Elution of the residue with 20% EtOAc in PE gave a mixture (100mg, 71%) of **5a** and **5b** (5:1). Fractional crystallization of the compound gave pure crystals of **5a** (50mg, 35%) m.p. 181°C (mmp 181°C).

**Irradiation of 1e :** A solution of **1e** (320mg, 1.09mmol) in TEA-ethanol was irradiated for 6h. Elution of the residue with 5% EtOAc in PE gave white solid (120mg, 37%) of **6** and **7** (5:1), which on fractional crystallization gave pure white crystals of **6** (65mg, 20%) m.p. 116°C (mmp 116°C).Further elution of the column with 20% EtOAc in PE gave **1e** (160mg, 50%) m.p. 66°C (mmp 66°C).

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