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Tetrahedron
Tetrahedron 63 (2007) 10979–10990

Synthesis of bicyclo[3.2.1]octanones via ketyl radical promoted rearrangements under reductive PET conditions

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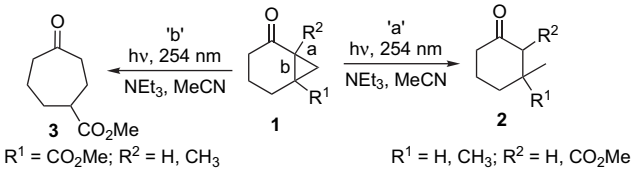
Received 9 June 2007; revised 30 July 2007; accepted 16 August 2007
Available online 22 August 2007

Abstract—Photoinduced electron transfer (PET) reactions from triethylamine (TEA) to ketones have been utilized for a clean and efficient route to bicyclo[3.2.1]octanones. A one-pot conversion of bicyclo[2.2.2]octenones to such molecules has been described. MeOH as well as acetonitrile/$LiClO_4$ combinations have been found to be the most effective solvents for these reactions.

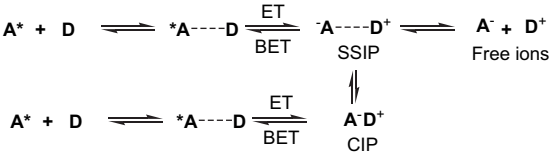
1. Introduction

In terms of synthetic applications, photoinduced electron transfer (PET) processes are becoming increasingly important for constructing complex molecules because of their chemo-, regio-, and diastereoselectivity.[1] In one of the first examples of the uses of PET for C–C bond cleavage reactions Mattay and Bischof[2] and Cossy et al.[3] independently reported the ring opening of fused α-keto small ring systems using a carbonyl group as an acceptor (A) and an amine as a donor (D). This process has also been successfully applied for cyclopropyl bond cleavage of α-ketocyclopropanes (Scheme 1).[4,5]



Scheme 1.

The process (Eq. 1) involves a fast electron transfer from the ground state of the amine (D) to the excited ketone (A), which in solvent may then lead to a solvent separated ion pair (SSIP). A contact radical ion pair (CIP) may also be formed at this stage inside a solvent cage and both processes may be in equilibrium. The overall process is a reversible one and back electron transfer (BET) may lead to the initial neutral states resulting in low conversion to products. To minimize BET, polar solvents are used for efficient solvation of the ion pair at this stage leading to free radical ions, which may then undergo ring cleavage in such strained rings (1).[4]



(1)

Depending on the better overlap of the cyclopropyl bond ('a') with the ketyl radical anion, regioselective bond cleavage of **1** (R=H or CH_3) followed by hydrogen abstraction from the solvent or from the amine then could give the final product **2**.[5d] The preferred regioselectivity of ring cleavage (*exo* 'a' vs *endo* 'b') is also dependent on the substitution pattern. Substitution of an electron-withdrawing group at the C(β) position preferentially led to 'b'-cleavage (*endo*) because of better radical stabilizing effects.[5a,6] Thus, under PET conditions **1** (R^1=CO_2Me) underwent 'b'-cleavage giving the ring-expanded product **3** (Scheme 1).[6] In the case of tricyclo[3.3.0.$0^{2,8}$]octanone system **4** (R=H), although the stereoelectronic factor of maximum overlap governed the regioselective cleavage of 'a' bond under PET conditions,[7] the corresponding diester derivative **4** (R=CO_2Me) yielded a mixture (5:1) of the kinetically favored 'a'-bond cleaved product **5** (R=CO_2Me) and the thermodynamically favored 'b'-bond cleaved product **6** (Scheme 2).[8] Interestingly, such reactions with α,α′-diketocyclopropanes-like ring-fused tricyclo[3.3.0.$0^{2,8}$]octanones gave only 'b' bond cleaved products in moderate yields.[8] Since bicyclo[3.2.1]octanes like **6** are very useful intermediates for the constructions of different bioactive natural molecules[9] and for their possible use as

Keywords: Bicyclo[3.2.1]octanones; Cyclopropyl ring cleavage; Photoinduced electron transfer (PET).
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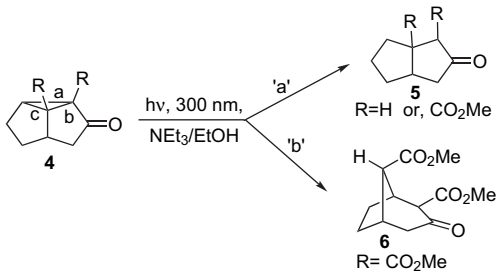
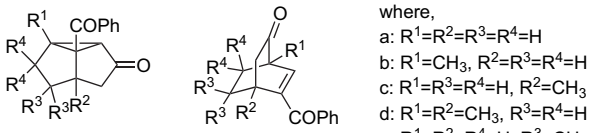
0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.08.054

phototriggers for liquid crystal-based optical switches,[10] we decided to explore this environment friendly PET method with 1-aroyl substituted tricyclo[3.3.0.0^{2,8}]-octanones (**7a–g**) for a convenient route to bicyclo[3.2.1]-octanone systems.



Scheme 2.

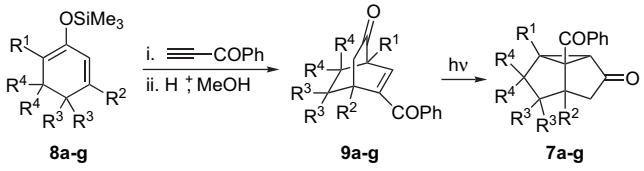


Secondly, oxanorbornanones under PET conditions are known to undergo cleavage of the oxa-bridge.[1b] Similar observations are not reported for analogous carbo-bicyclic compounds. We wished to extend this PET method to aroyl substituted bicyclo[2.2.2]octenone systems (**9a–g**) to explore their possible bond cleavage–bond migration reactions.

2. Results and discussion

2.1. Syntheses of bicyclo[2.2.2]oct-5-en-2-ones (9a–g)

5-Benzoyl-bicyclo[2.2.2]oct-5-en-2-ones (**9a–g**) were prepared by the Diels–Alder reactions of suitably substituted 2-trimethylsilyloxycylohexa-1,3-dienes (**8a–g**) and 1-phenylprop-2-yn-1-one (monobenzoylacetylene, MBA) following a reported procedure (Scheme 3, Table 1).[11,12,13] As reported earlier,[14] here also these additions of MBA were found to be highly regioselective and the ^{1}H NMR spectroscopic data of **9a–g** confirmed the exclusive regioselectivity of cycloadditions.



Scheme 3.

Table 1. Chemical yields of formation of **7a–g** in MeOH and benzene at 300 nm and quantum yields at 350 nm

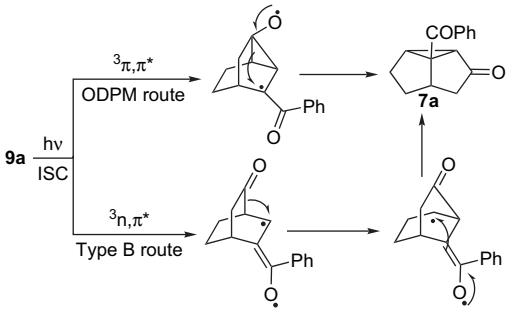
Diene	Adduct[a] (%)	Photoproducts			
		Compd.	Solvent, time (h)	Yield[a] (%)	(ϕ)[b]
8a	**9a** (75)	**7a**	MeOH, 1.5	91	0.16
8b	**9b** (43)	**7b**	MeOH, 1.5	90	0.17
8c	**9c** (66)	**7c**	MeOH, 1.5	91	0.13[c]
			Benzene, 2	92	
8d	**9d** (76)	**7d**	MeOH, 1.5	92	0.27[d]
8e	**9e** (26)	**7e**	MeOH, 1.5	90	
			Benzene, 1	90	
8f	**9f** (72)	**7f**	MeOH, 1.5	95	0.37
			Benzene, 1	90	
8g	**9g** (80)	**7g**	MeOH, 1.5	90	0.26
			Benzene, 1	90	

[a] Isolated yields.
[b] In benzene.
[c] For **7c** ϕ_{MeOH}: 0.20 and ϕ_{254}: 0.13.
[d] ϕ_{254}: 0.12.

2.2. Syntheses of tricyclo[3.3.0.0^{2,8}]octan-3-ones (7a–g)

Tricyclo[3.3.0.0^{2,8}]octanones (**7a–g**) were readily obtained from the photoisomerization of the corresponding bicyclo[2.2.2]octenones (**9a–g**). Photorearrangements of **9a–g** to **7a–g** took place quantitatively (90–95%) within 2 h in all types of solvents.

Better results were obtained using 300 and 350 nm lamps compared to using 254 nm lamps. As we have observed earlier for analogous cases,[8,12] no sensitizer was needed for the reaction to occur. A rapid inter-system crossing (ISC) was assumed to have taken place in the excited state of compound **9**, which may be considered as either a δ-keto-α,β-enone or a δ-keto-β,γ-enone and its transformation to **7** may occur either via Type B rearrangement (α,β-enone) or, via oxa-di-π-methane rearrangement (ODPM, β,γ-enone) (Scheme 4). At this stage it is difficult to differentiate between the two routes. However, unlike other β,γ-enones, **9** never gave 1,3-acyl-shift products and progressed without sensitizer supporting the Type B route operating in the present transformations. Further work toward this mechanistic aspect is presently under progress. Confirmation that the reactions involved triplet states was obtained by quenching with a triplet quencher like anthracene.

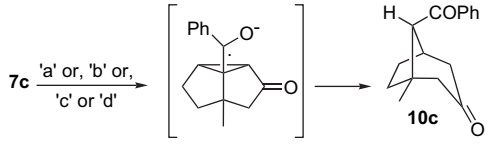


Scheme 4.

2.3. Cyclopropyl ring cleavage under PET conditions

Following reported methods,[2–6] when we had attempted cyclopropyl ring cleavage of **7c** at 300 nm using a solution of 20% triethylamine (TEA) in acetonitrile, no significant

product formation was observed. Instead, use of a 40% solution of TEA in acetonitrile using 300 nm light for 1 h led to exclusive formation of **10c** in 62% yield along with 25% of unreacted starting material (Scheme 5). The structure and stereochemical assignment to **10c** were based on detailed spectroscopic analysis. In the IR spectrum there was a strong peak at 1711 cm^{-1} characteristic of a six-membered ketone, which confirmed the cleavage of the 'b' bond in **7c**. The proton at C8 appeared as a doublet ($J_{5,8}$ 4 Hz) at δ 3.49 in the ^1H NMR spectrum, which confirmed its stereochemistry to be *anti* to the ring carbonyl group.[8,11,15] The ^{13}C NMR spectrum showed signals due to one CH_3, four CH_2, two CH, two C=O and one quaternary carbon in addition to the aromatic signals.



a: hv, 300nm, 40% TEA-ACN; (62%, Recovered 7c:25%)
b: hv, 300nm, 40% TEA-ACN, $LiClO_4$(1eq.); (80%)
c: hv, 300nm, 40% TEA-MeOH; (86%)
d: n-Bu_3SnH, AIBN, Bz, 80 °C; (60%)

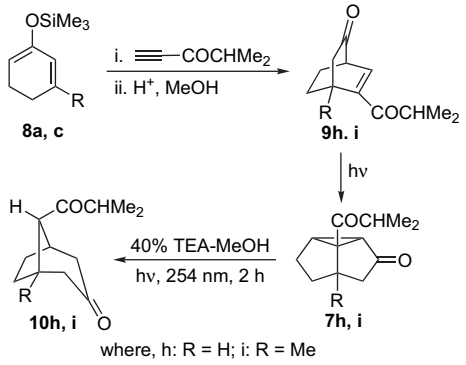
Scheme 5.

In such carbinyl radical mediated cyclopropyl ring opening reactions, use of $LiClO_4$ as an additive has been reported to accelerate an efficient formation of reductive ring-cleavage products.[5b,d] On addition of $LiClO_4$ the radical cation $Et_3N^{+\bullet}$ is exchanged by Li^+, which forms a tight ion pair with the ketyl radical anion. Such an exchange process dissociates the ketyl–amine radical ion pair and the bond migration can take place since proton transfer is delayed. Thus, the above reaction when was carried out in the presence of 1 equiv $LiClO_4$, the reaction was completed within 1 h and **10c** was isolated in 80% yield.

Since PET reactions are known to be preferred in polar solvents to avoid back electron transfer by stabilization of the radical ions, the reaction was attempted using methanol. Irradiation of **7c** in 40% TEA–methanol for 1 h gave **10c** in 86% isolated yield. Methanol is more polar than acetonitrile and has been reported to give higher yields in electron-transfer induced photo-allylation reactions.[16] However, to our knowledge, such preference for a polar protic solvent like methanol over aprotic polar solvent like acetonitrile has not been reported earlier for cyclopropyl ring cleavage under PET conditions.

The quantum yield of this reaction was found to be 0.16 in MeOH and involvement of a triplet state was confirmed by its quenching in the presence of oxygen and anthracene. Addition of TEA quenched the phosphorescence of **7c** (428 nm), which confirmed the electron transfer to occur between the triplet of **7c** and TEA.

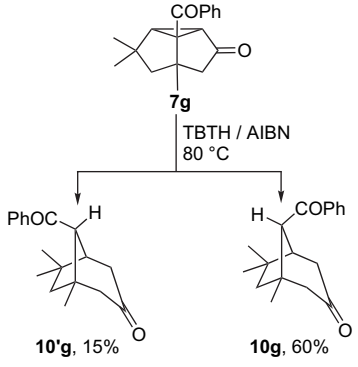
The reaction worked well with acyl ketone substituted compounds also. The diene **8a**,**c** and 4-methylpent-1-yn-3-one gave **9h**,**i**, which on irradiation gave the tricyclic compounds **7h**,**i** in quantitative yields. Under PET conditions **7h**,**i** underwent regioselective ring cleavage to give **10h**,**i** and irradiation with 254 nm yielded better results in these cases (Scheme 6). The peak around 1705 cm^{-1} in the IR spectrum confirmed the presence of a six-membered ring in both the cases.



Scheme 6.

2.4. Cyclopropyl ring cleavage using TBTH

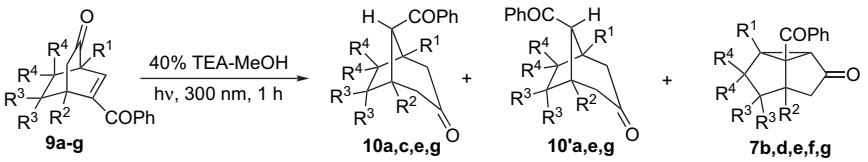
Use of tin hydride has been mostly a reagent of choice to generate carbon centered radicals.[17a,b] Enholm and coworkers employed tributyltin hydride (TBTH) to generate *O*-stannyl ketyl radicals by single electron transfer (SET) to promote the cleavage of cyclopropyl rings.[18] Application of this method to a tetracyclic ketone like **11** resulted in regioselective 'b' bond cleavage of the cyclopropyl ring.[8] Tricyclic ketones like **7c**,**i** when treated with *n*-Bu_3SnH (TBTH) and AIBN at 80 °C for 3 h yielded the corresponding bicyclo[3.2.1]octanones **10c**,**i** in 60% yields. Compound **7g** under the same reaction conditions generated an epimeric mixture (4:1) of **10g** and **10′g** (Scheme 7). An IR signal at 1709 cm^{-1} confirmed the cleavage of the 'b' bond, which gave a six-membered ketone. The stereochemistry of **10′g** was confirmed from its ^1H NMR spectrum where, like reported similar systems,[8,11,15] H-8 appeared as a singlet. Although use of TBTH is one of the preferred methods for generating radical centers, the toxicity of tin compounds as well as difficulty to remove the residual tin derivatives are the major drawbacks associated with this method.



Scheme 7.

2.5. One-pot conversion of bicyclo[2.2.2]octenones to bicyclo[3.2.1]octanones

PET reactions between ketones and amines can generate ketyl radical anions, which may lead to reductive bond



where, a: $R^1=R^2=R^3=R^4=H$; b: $R^1=CH_3$, $R^2=R^3=R^4=H$; c: $R^1=R^3=R^4=H$, $R^2=CH_3$; d: $R^1=R^2=CH_3$, $R^3=R^4=H$; e: $R^1=R^2=R^4=H$, $R^3=CH_3$; f: $R^1=R^2=R^3=H$, $R^4=CH_3$; g: $R^1=R^3=H$, $R^2=R^4=CH_3$

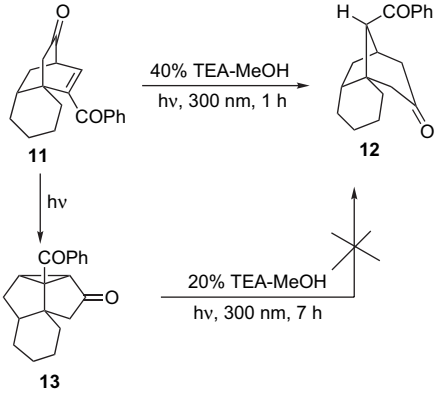
Scheme 8.

cleavage. This led us to explore the possibility of one-pot reductive bond cleavage–bond formation reactions of **9c** to give **10c** using such a method. Irradiation of **9c** in 40% TEA–methanol went very smoothly within 1 h to give **10c** in 86% yield (Scheme 8).

Similar results were obtained with the other bicyclo[2.2.2]octenones **9a**,**e**–**g** leading to their quantitative conversion to C-8 epimeric mixtures of bicyclo[3.2.1]octanones **10** and **10′** along with small quantities of **7e**–**g** (Scheme 8, Table 2). The six-membered ketone in **10a** was confirmed by the ν_{max} at 1711 cm^{-1}. Because of long range couplings in the ^1H NMR spectrum, the H-8 around δ 3.57 appeared as a multiplet, which coalesced to a triplet on irradiating one of the acyl protons confirming *syn*-stereochemistry of the benzoyl group to the larger ring. As expected, in the epimer **10′a** the H-8 at δ 3.77 appeared as a singlet confirming its *syn*-stereochemistry to the ring carbonyl group. The C-8 epimeric relationship between **10a** and **10′a** was confirmed by sodium hydroxide catalyzed epimerization of the major isomer **10a**, which was then 80% converted to **10′a**. The products obtained from **9e**–**f** were identical and were identified as **10e** and **10′e**. In **10e** the *syn*-stereochemistry of the multiplet for H-8 around δ 3.94 was confirmed by decoupling experiments and the *anti* stereochemistry in **10′e** was confirmed from the singlet at δ 3.61. The *anti*-isomer **10′e** was found to be the major product in this case. From **9g** the major compound was the *syn* isomer **10g** whose stereochemistry was again confirmed by decoupling experiments where the broad doublet of H-8 around δ 3.83 coalesced to a doublet on irradiating one of the acyl protons. In **10′g**, H-8 appeared as a singlet at δ 3.59.

The reaction yielded 12-benzoyltricyclo[6.3.1.$0^{1,6}$]dodecan-10-one (**12**) from 11-benzoyltricyclo[6.2.2.$0^{1,6}$]dodec-11-en-9-one (**11**) in 78% yield within 1 h (Scheme 9) while even the 4-benzoyltetracyclo[6.4.$0^{3,5}$.$0^{4,8}$]dodecan-6-one (**13**) has been reported to yield no definite product even after a short irradiation of 30 min in presence of 20% TEA–MeOH mixture.[8]

The reaction did not work for 1-methyl substituted compounds such as **9b** and **9d**. In the case of **9b**, the reaction gave a tarry mass from which no definite product could be isolated. The reaction failed to give any isolable product even from the corresponding cyclopropyl derivative **7b**. Although a short irradiation of 10 min of **7b**, gave non-isolable material, irradiation for a period of 5 min led to isolation of 2% of **10c** (Table 2). In the case of **9d**, the only product isolated after 1 h was 43% of **7d** along with 55% of unreacted **9d**. The reactions of **9d** as well as of **7d** were also unsuccessful with donors like dimethylaniline and DABCO.



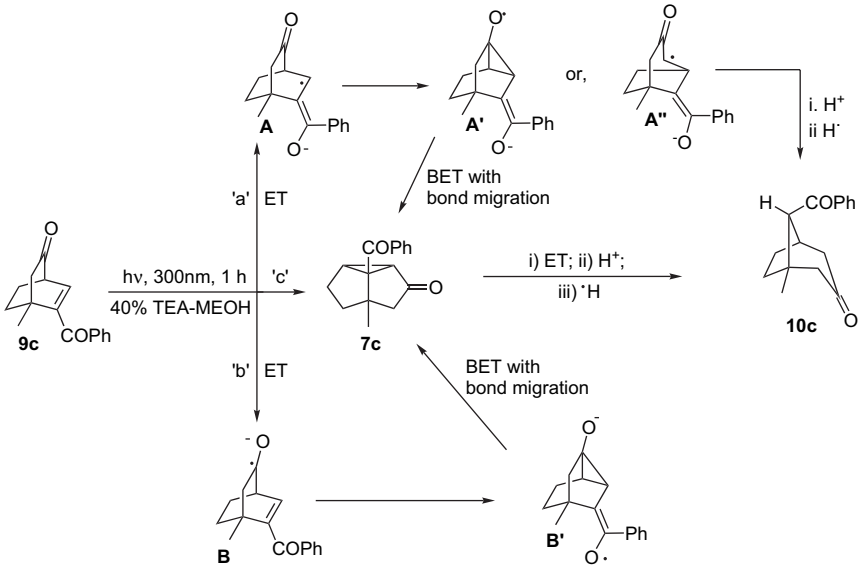
Scheme 9.

The conversion from **9c** to **10c** may take place via routes 'a' or, 'b' where the initially formed ketyl radicals **A** or **B** may undergo bond formation (**A′** or **B′**) or, bond migration (**A″**). Bond migration followed by back electron transfer (BET) from **A′** and **B′** may then lead to **7c**, which may then undergo PET mediated tandem bond migration to give **10c**. Similar oxa-di-π-methane rearrangement of ketyl radicals has also been propsed for β,γ-unsaturated aldehydes.[19] Another route via the rearranged product **7c** (route 'c') may also give **7c** (Scheme 10). Although a time dependent ^1H NMR spectroscopic analysis of the reaction clearly showed involvement of **7c** at least at the earlier stage of reaction (Fig. 1) suggesting 'c' as one of the routes, failure of the reaction with 1-methyl substituted derivatives like **9b**,**d** did not rule out path 'a'. Further, since a triplet state of the ketone is likely to be quenched by the TEA present in the system, direct conversion of **9c** to **7c** appeared to be less probable.

The one-pot conversion of 5-isobutyryl derivative **7h** needed irradiation at 254 nm for a longer time (3 h) and resulted in partial conversion to 8-isobutyrylbicyclo[3.2.1]octan-3-one (**10h**, 36%) and 40% of the tricyclo derivative **7h**.

Table 2. Yields of bicyclo[3.2.1]octanones by PET methods

Entry	Starting material	**10** (%)	**10′** (%)	**7** (%)
i	**9a**	**10a** (60)	**10′a** (33)	—
ii	**9b**	Tarry mass		
iii	**1b**	**5c** (2)	—	—
iv	**9c**	**10c** (86)	—	—
v	**7c**	**10c** (62)		
vi	**9d**	—	—	**7d** (43)
vii	**9e**	**10e** (17)	**10′e** (70)	**7e** (6)
viii	**9f**	**10e** (20)	**10′e** (69)	—
ix	**9g**	**10g** (69)	**10′g** (7)	**7g** (7)
x	**11**	**12** (78)	—	—



Scheme 10.

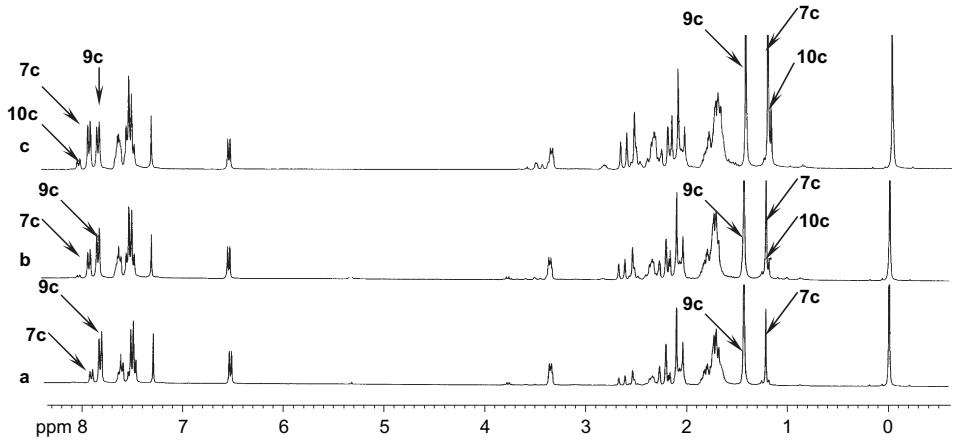


Fig. 1. ^{1}H NMR spectra of the crude reaction mixture from the photolysis of **9c** in 40% TEA–methanol after (a) 3 min (b) 6 min (c) 10 min.

Increase in irradiation time led to decreased yields via decomposition.

3. Conclusion

From our results we found the PET mediated ring opening of rigid cyclopropyl diketones are highly regioselective. Since the commonly used organotin reagents are toxic in nature and results in reduced yield because of difficulty in removing the residual tin derivatives, these methods can be used in its place for efficient generation of bicyclo[3.2.1]octanones.

4. Experimental

4.1. General

All melting points were measured in a Gallenkamp melting point apparatus. The IR spectra were recorded on an FTIR-8300 Shimadzu spectrometer. The NMR spectra were recorded in $CDCl_3$ solution at 300 MHz for ^{1}H and at 75 MHz for ^{13}C on a Brucker AC-300 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed with a Heraeus Combustion apparatus or on a 2400 series-II Perkin–Elmer CHN analyzer. High Resolution Mass Spectra were recorded on a Qtof Micro YA263 spectrometer. Flash Column Chromatography was performed using silica gel (230–400 mesh) under medium pressure and ordinary column chromatography was performed using silica gel (60–120 mesh). Triethylamine was distilled over KOH and solvents were purified, dried, and distilled using reported procedures.[20] Petroleum ether used was of the boiling range 60–80 °C. Ether refers to diethyl ether. Irradiation experiments were carried out in a Rayonet Photochemical Reactor using lamps of desired wavelength. MBA,[21] 4-methylpent-1-yn-3-one,[21] 11-benzoyltricyclo-[6.2.2.0^{1,6}]dodec-11-en-9-one[22] were prepared following reported procedures and the silyloxy-1,3-dienes were prepared following a general procedure.[23]

4.2. Syntheses of bicyclo[2.2.2]octenones (9a–g)

A mixture of suitable silyloxycyclohexa-1,3-diene and acetylenic dienophile was stirred under argon atmosphere for

desired time after which 5% methanolic–HCl (5 mL) was added to it and the mixture was stirred for 10 min. After removal of MeOH the mixture was extracted with ether (3×50 mL). The organic phases were combined, dried over Na_2SO_4, and evaporated in vacuo. The residue was chromatographed over a silica gel column.

4.2.1. 5-Benzoylbicyclo[2.2.2]oct-5-en-2-one (9a). Mixture of **8a** (2.5 g, 14.85 mmol) and MBA (1.00 g, 7.69 mmol) was stirred for 3 h. Elution of the column with 10% ethyl acetate (EA) in petroleum ether (PE) gave a solid of **6a** (1.31 g, 75%), mp 88–90 °C, as colorless crystals after recrystallization from ether–PE (1:7) mixture. UV (CH_3CN): 252 nm (log ε 4.20), 285 (3.48), 342 (2.20). IR: 1728, 1632 cm^{-1}. ^1H NMR: δ 1.62–2.25 (m, 6H), 3.39–3.41 (m, 1H), 3.80–3.81 (m, 1H), 6.87 (dd, *J* 7 and 1 Hz, 1H), 7.43–7.48 (m, 2H), 7.53–7.58 (m, 1H), 7.69–7.71 (m, 2H). ^{13}C NMR: δ 23.0 (CH_2), 24.2 (CH_2), 32.1 (CH), 39.8 (CH_2), 50.0 (CH), 128.3 (CH), 129.3 (CH), 132.3 (CH), 137.0 (C), 140.8 (CH), 147.1 (C), 193.0 (C═O), 211.0 (C═O). HRMS (ESI) calcd for $C_{15}H_{14}O_2Na$: 249.0891; found: $[M+Na]^+$ 249.0895.

4.2.2. 5-Benzoyl-1-methylbicyclo[2.2.2]oct-5-en-2-one (9b). Mixture of **8b** (4.46 g, 24.46 mmol) and MBA (1.77 g, 13.61 mmol) was stirred for 4 h. Elution of the column with 12% EA in PE gave a solid of **9b** (1.4 g, 43%), mp 94–96 °C, as colorless crystals after recrystallization from ether–PE (1:5) mixture. UV (CH_3CN): 253 nm (log ε 4.18), 293 (3.43), 338 (2.34). IR: 1724, 1639 cm^{-1}. ^1H NMR: δ 1.31 (s, 3H), 1.58–1.98 (m, 4H), 2.17 (dd, *J* 19 and 3 Hz), 2.25 (dd, *J* 19 and 2 Hz, 1H), 3.77–3.78 (m, 1H), 6.54 (d, *J* 2 Hz, 1H), 7.44–7.49 (m, 2H), 7.53–7.61 (m, 1H), 7.68–7.70 (m, 2H). ^{13}C NMR: δ 17.5 (CH_3), 25.9 (CH_2), 30.9 (CH_2), 32.0 (CH), 39.8 (CH_2), 51.1 (C), 128.4 (CH), 129.3 (CH), 132.3 (CH), 137.1 (C), 146.1 (CH), 146.9 (C), 193.0 (C═O), 211.7 (C═O). HRMS (ESI) calcd for $C_{16}H_{16}O_2Na$: 263.1048; found: $[M+Na]^+$ 263.1044.

4.2.3. 5-Benzoyl-4-methylbicyclo[2.2.2]oct-5-en-2-one (9c). Mixture of **8c** (2.5 g, 13.71 mmol) and MBA (0.9 g, 6.92 mmol) was stirred for 3 h. Elution of the column with 8% EA in PE gave a solid of **9c** (2.32 g, 66%), mp 45–47 °C, as colorless crystals after recrystallization from ether–PE (1:7) mixture. UV (CH_3CN): 249 nm (log ε 4.22), 283 (3.44), 338 (2.16). IR: 1732, 1682 cm^{-1}. ^1H NMR: δ 1.43 (s, 3H), 1.68–1.86 (m, 3H), 2.07 (d, *J* 18 Hz) mixed with 2.01–2.10 (m, total 2H), 2.23 (d, *J* 18 Hz, 1H), 3.32–3.35 (m, 1H), 6.50 (d, *J* 7 Hz, 1H), 7.43–7.48 (m, 2H), 7.56–7.61 (m, 1H), 7.78–7.80 (m, 2H). ^{13}C NMR: δ 22.1 (CH_3), 24.2 (CH_2), 33.0 (CH_2), 40.2 (C), 47.6 (CH_2), 49.5 (CH), 128.5 (CH), 129.9 (CH), 133.1 (CH), 135.1 (CH), 137.3 (C), 149.5 (C), 194.9 (C═O), 211.0 (C═O). HRMS (ESI) calcd for $C_{16}H_{16}O_2Na$: 263.1048; found: $[M+Na]^+$ 263.1049.

4.2.4. 5-Benzoyl-1,4-dimethylbicyclo[2.2.2]oct-5-en-2-one (9d). Mixture of **8d**, (1.65 g, 8.40 mmol) and MBA (0.55 g, 4.23 mmol) was stirred under argon atmosphere for 4 h. Elution of the column with 8% EA in PE gave a thick liquid of **9d** (0.82 g, 76%). UV (CH_3CN): 250 nm (log ε 4.40), 280 (3.68), 338 (2.46). IR: 1724, 1651 cm^{-1}. ^1H NMR: δ 1.29 (s, 3H), 1.42 (s, 3H), 1.62–1.94 (m, 4H), 2.10 (d, *J* 19 Hz, 1H), 2.27 (dd, *J* 19 and 2 Hz, 1H), 6.18 (s, 1H), 7.44–7.49 (m, 2H), 7.56–7.61 (m, 1H), 7.77–7.79 (m, 2H). ^{13}C NMR: δ 17.1 (CH_3), 21.7 (CH_3), 31.9 (CH_2), 34.5 (CH_2), 39.8 (C), 47.3 (CH_2), 50.3 (C), 128.2 (CH), 129.6 (CH), 132.9 (CH), 137.2 (C), 140.1 (CH), 149.0 (C), 194.5 (C═O), 211.2 (C═O). HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$: 277.1204; found: $[M+Na]^+$ 277.1216.

4.2.5. 5-Benzoyl-8,8-dimethylbicyclo[2.2.2]oct-5-en-2-one (9e). Mixture of **8e** (0.88 g, 4.48 mmol) and MBA (0.44 g, 3.38 mmol) was heated at 50–60 °C for 10 h. Elution of the column with 10% EA in PE gave a solid of **9e** (0.22 g, 26%), mp 76–78 °C, as colorless crystals after recrystallization from ether–PE (1:7) mixture. UV: (CH_3CN) 254 nm (log ε 4.39), 287 (3.69), 340 (2.58). IR: 1720, 1641 cm^{-1}. ^1H NMR: δ 1.03 (s, 3H), 1.22 (s, 3H), 1.60 (dd, *J* 13 and 3 Hz, 1H), 1.80 (dd, *J* 13 and 2 Hz, 1H), 2.01 (dd, *J* 19 and 3 Hz, 1H), 2.54 (dd, *J* 19 and 2 Hz, 1H), 3.27–3.31 (m, 1H), 3.33–3.34 (m, 1H), 6.86 (dd, *J* 6 and 1 Hz, 1H), 7.43–7.48 (m, 2H), 7.54–7.59 (m, 1H), 7.70–7.73 (m, 2H). ^{13}C NMR: δ 28.2 (CH_3), 31.2 (CH_3), 33.5 (C), 35.9 (CH_2), 38.6 (CH_2), 43.4 (CH), 51.2 (CH), 128.2 (CH), 129.0 (CH), 132.0 (CH), 137.0 (C), 139.5 (CH), 148.2 (C), 192.9 (C═O), 210.9 (C═O). HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$: 277.1204; found: $[M+Na]^+$ 277.1220.

4.2.6. 5-Benzoyl-7,7-dimethylbicyclo[2.2.2]oct-5-en-2-one (9f). Mixture of **8f** (3.5 g, 17.82 mmol) and MBA (1.2 g, 9.23 mmol) was heated at 40 °C for 10 h. Elution of the column with 8% EA in PE gave a solid of **9f** (1.69 g, 72%), mp 103–105 °C, as colorless crystals after recrystallization from ether–PE (1:6) mixture. UV (CH_3CN): 254 nm (log ε 4.20), 287 (3.48), 340 (2.41). IR: 1717, 1638 cm^{-1}. ^1H NMR: δ 1.00 (s, 3H), 1.12 (s, 3H), 1.52–1.58 (m, 1H), 1.70 (dd, *J* 13 and 3 Hz, 1H), 2.11–2.12 (m, 2H), 3.01 (d, *J* 7 Hz, 1H), 3.71–3.73 (m, 1H), 6.81 (dd, *J* 7 and 2 Hz, 1H), 7.42–7.46 (m, 2H), 7.52–7.57 (m, 1H), 7.67–7.70 (m, 2H). ^{13}C NMR: δ 30.2 (CH_3), 30.7 (CH_3), 32.5 (CH), 36.1 (C), 38.0 (CH_2), 40.1 (CH_2), 63.1 (CH), 128.2 (CH), 129.0 (CH), 132.2 (CH), 136.9 (C), 141.0 (CH), 146.0 (C), 192.7 (C═O), 210.7 (C═O). HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$: 277.1204; found: $[M+Na]^+$ 277.1206.

4.2.7. 5-Benzoyl-4,7,7-trimethylbicyclo[2.2.2]oct-5-en-2-one (9g). Mixture of **8g** (3 g, 14.26 mmol) and MBA (1.40 g, 10.76 mmol) was stirred for 4 h. Elution of the column with 8% EA in PE gave a solid of **9g** (2.32 g, 80%), mp 53–54 °C, as colorless crystals after recrystallization from ether–PE (1:7) mixture. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 81.15; H, 7.16. UV (CH_3CN): 251 nm (log ε 4.14), 288 (3.33), 344 (2.30). IR: 1730, 1666 cm^{-1}. ^1H NMR: δ 1.04 (s, 3H), 1.13 (s, 3H), 1.39 (s, 3H), 1.54 (d, *J* 13 Hz, 1H), 1.63 (dd, *J* 13 and 3 Hz, 1H), 2.01 (d, *J* 18 Hz, 1H), 2.20 (dd, *J* 18 and 3 Hz, 1H), 2.95 (d, *J* 7 Hz, 1H), 6.47 (d, *J* 7 Hz, 1H), 7.43–7.48 (m, 2H), 7.55–7.60 (m, 1H), 7.77–7.81 (m, 2H). ^{13}C NMR: δ 22.4 (CH_3), 30.5 (CH_3), 31.2 (CH_3), 37.4 (C), 41.0 (C), 46.3 (CH_2), 49.8 (CH_2), 62.9 (CH), 128.9 (CH), 130.2 (CH), 133.5 (CH), 136.0 (CH), 137.8 (C), 149.0 (C), 195.0 (C═O), 211.2 (C═O).

4.2.8. 5-Isobutyrylbicyclo[2.2.2]oct-5-en-2-one (9h). Mixture of **8a** (2.2 g, 13.06 mmol) and 4-methylpent-1-yn-3-one (0.94 g, 9.78 mmol) was stirred at 45 °C for 4 h. Elution of the column with 10% EA in PE gave a colorless liquid of **9h** (1.10 g, 58%). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.87; H, 8.37. UV (CH_3CN): 244 (log ε 3.59), 296 (2.78), 338 (2.10). IR: 1734, 1666 cm^{-1}. ^1H NMR: δ 1.11(d, *J* 7 Hz, 3H), 1.13 (d, *J* 7 Hz, 3H), 1.43–1.53 (m, 1H), 1.62–1.83 (m, 2H), 1.97 (ddd, *J* 19, 3 and 3 Hz) mixed with 1.92–2.03 (m, total 2H), 2.11 (dd, *J* 19 and 2 Hz, 1H), 3.23 (h, *J* 7 Hz, 1H), 3.35–3.39 (m, 1H), 3.72–3.75 (m, 1H), 7.12 (dd, *J* 7 and 2 Hz, 1H). ^{13}C NMR: δ 19.1 (CH_3), 19.2 (CH_3), 22.7 (CH_2), 23.8 (CH_2), 30.2 (CH), 33.9 (CH), 39.4 (CH_2), 49.7 (CH), 136.9 (CH), 146.8 (C), 201.1 (C═O), 211.2 (C═O).

4.2.9. 5-Isobutyryl-4-methylbicyclo[2.2.2]oct-5-en-2-one (9i). Mixture of **8c** (3.0 g, 16.46 mmol) and 4-methylpent-1-yn-3-one (1.10 g, 11.45 mmol) was stirred at 45 °C under argon atmosphere for 4 h. Elution of the column with 8% EA in PE gave a colorless liquid of **9i** (1.30 g, 55%). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.32; H, 8.57. UV (CH_3CN): 239 (log ε 3.70), 289 (2.04). IR: 1732, 1678 cm^{-1}. ^1H NMR: δ 1.07 (d, *J* 7 Hz, 3H), 1.09 (d, *J* 7 Hz, 3H), 1.40 (s, 3H), 1.54–1.75 (m, 3H), 1.95 (d, *J* 18 Hz, 1H), 2.06 (d, *J* 18 Hz) mixed with 1.92–2.10 (m, total 3H), 3.06 (h, *J* 7 Hz, 1H), 3.27–3.30 (m, 1H), 6.77 (d, *J* 7 Hz, 1H). ^{13}C NMR: δ 18.1 (CH_3), 18.5 (CH_3), 22.5 (CH_3), 23.9 (CH_2), 33.0 (CH_2), 37.5 (CH), 39.8 (C), 47.5 (CH_2), 49.3 (CH), 133.5 (CH), 150.5 (C), 204.9 (C═O), 211.0 (C═O).

4.3. Photisomerization of 9a–g to tricyclo[3.3.0.0^{2,8}]-octan-3-ones (7a–g)

Unless otherwise stated, solutions of **9a–i** (100 mg) in MeOH (30 mL) were degassed with argon for 7 min and then irradiated at 300 nm for specified time. The solvents were removed in vacuo and the residues were chromatographed over columns of silica gel (60–120 mesh).

4.3.1. 1-Benzoyltricyclo[3.3.0.0^{2,8}]octan-3-one(7a). Time: 1.5 h. Elution of the column with 12.5% EA in PE gave **7a** (91 mg, 91%), mp 64–66 °C, as colorless crystals obtained by recrystallization from ether–PE (1:6) mixture. UV (CH_3CN): 241 nm (log ε 4.08), 277 (3.02), 307 (2.50). IR: 1719, 1670 cm^{-1}. ^1H NMR: δ 1.67–1.86 (m, 2H), 1.96 (d, *J* 18 Hz, 1H), 2.26–2.41 (m, 2H), 2.77–2.86 (m, 3H), 3.39–3.44 (m, 1H), 7.45–7.50 (m, 2H), 7.54–7.59 (m, 1H), 7.69–7.71 (m, 2H). ^{13}C NMR: δ 25.0 (CH_2), 40.1 (CH), 40.2 (CH), 41.0 (CH_2), 47.5 (CH_2), 49.4 (CH), 57.7 (C), 127.8 (CH), 128.7 (CH), 132.5 (CH), 137.9 (C), 199.9 (C═O), 212.2 (C═O). HRMS (ESI) calcd for $C_{15}H_{14}O_2Na$: 249.0892; found: $[M+Na]^+$ 249.0891.

4.3.2. 1-Benzoyl-8-methyltricyclo[3.3.0.0^{2,8}]octan-3-one (7b). Time: 1.5 h. Elution of the column with 10% EA in PE gave a thick liquid of **7b** (90 mg, 90%). UV (CH_3CN) 242 nm (log ε 4.08), 278 (3.08), 313 (2.36). IR: 1724, 1657 cm^{-1}. ^1H NMR: δ 1.31 (s, 3H), 1.65–1.71 (m, 1H), 1.92 (d, *J* 18 Hz, 1H), 2.09–2.23 (m, 2H), 2.59–2.70 (m, 2H), 2.74 (s, 1H), 3.22 (dd, *J* 9 and 6 Hz, 1H) 7.47–7.52 (m, 2H), 7.56–7.61 (m, 1H), 7.75–7.77 (m, 2H). ^{13}C NMR: δ 19.1 (CH_3), 32.6 (CH_2), 39.3 (CH_2), 42.1 (CH), 48.6 (CH_2), 50.9 (CH), 51.6 (C), 61.1 (C), 127.8 (CH), 128.7 (CH), 132.6 (CH), 138.4 (C), 199.2 (C═O), 212.4 (C═O). HRMS (ESI) calcd for $C_{16}H_{16}O_2Na$: 263.1048; found: $[M+Na]^+$ 263.1045.

4.3.3. 1-Benzoyl-5-methyltricyclo[3.3.0.0^{2,8}]octan-3-one (7c). Time: 1.5 h. Elution of the column with 10% EA in PE gave **7c** (91 mg, 91%), as thick liquid. UV (CH_3CN): 246 nm (log ε 4.20), 281 (3.24), 311 (2.55). IR: 1726, 1665 cm^{-1}. ^1H NMR: δ 1.21 (s, 3H), 1.70–1.86 (m, 3H), 2.13 (d, *J* 18 Hz, 1H), 2.28–2.40 (m, 2H), 2.47–2.56(m, 1H), 2.63 (d, *J* 18 Hz, 1H), 7.46–7.51 (m, 2H), 7.57–7.62 (m, 1H), 7.86–7.89 (m, 2H). ^{13}C NMR: δ 23.1(CH_3), 24.7 (CH_2), 36.5 (CH), 45.6 (CH), 48.4 (CH_2), 49.3 (C), 54.7 (CH_2), 55.9 (C), 128.7 (CH), 133.3 (CH), 137.6(C), 197.6 (C═O), 212.4 (C═O). HRMS (ESI) calcd for $C_{16}H_{16}O_2Na$: 263.1048; found: $[M+Na]^+$ 263.1046.

At 350 nm:

solvent: benzene; time: 1.5 h. Yield of **7c**: 91 mg, 91%,
solvent: MeOH; time: 1.5 h. Yield of **7c**: 96 mg, 96%,
solvent: CH_3CN; time: 1.5 h. Yield of **7c**: 92 mg, 92%.

At 300 nm:

solvent: benzene; time: 2 h. Yield of **7c**: 92 mg, 92%,
solvent: acetone; time: 1.5 h. Yield of **7c**: 92 mg, 92%,
solvent: CH_3CN; time: 1.5 h. Yield of **7c**: 94 mg, 94%.

At 254 nm:

solvent: benzene; time: 2 h. Yield of **7c**: 84 mg, 84%,
solvent: MeOH; time: 2 h. Yield of **7c**: 90 mg, 90%,
solvent: CH_3CN; time: 2 h. Yield of **7c**: 91 mg, 91%.

4.3.4. 1-Benzoyl-5,8-dimethyltricyclo[3.3.0.0^{2,8}]octan-3-one (7d). Time: 1.5 h. Elution of the column with 10% EA in PE gave a thick liquid of **7d** (92 mg, 92%). UV (EtOH): 249 nm (log ε 4.01), 320 (2.20). IR: 1720, 1663 cm^{-1}. ^1H NMR: δ 1.12 (s, 3H), 1.19 (s, 3H), 1.63 (dd, *J* 6 and 6 Hz, 1H), 1.90–2.13 (m, 3H), 2.32–2.40 (m, 2H), 2.53 (d, *J* 18 Hz, 1H) 7.45–7.49 (m, 2H), 7.54–7.57 (m, 1H), 7.81–7.84 (m, 2H). ^{13}C NMR: δ 20.8 (CH_3), 22.9 (CH_3), 31.9 (CH_2), 45.9 (C), 46.5 (CH_2), 50.3 (CH), 50.4 (C), 55.3 (CH_2), 60.2 (C), 128.59 (CH), 128.63 (CH), 133.1 (CH), 138.1 (C), 197.2 (C═O), 211.9 (C═O). HRMS (ESI) calcd for $C_{17}H_{19}O_2$: 255.1385; found: $[M+H]^+$ 255.1382.

4.3.5. 1-Benzoyl-6,6-dimethyltricyclo[3.3.0.0^{2,8}]octane-3-one (7e). Time: 1.5 h. Elution of the column with 10% EA in PE gave a white solid of **7e** (90 mg, 90%), mp 71–73 °C, which was recrystallized from a mixture of ether–PE (1:5). UV (CH_3CN): 242 nm (log ε 3.70), 278 (2.65), 307 (2.12). IR: 1730, 1663 cm^{-1}. ^1H NMR: δ 0.94 (s, 3H), 1.06 (s, 3H), 1.49 (dd, *J* 14 and 2 Hz, 1H), 1.85 (ddd, *J* 14, 7 and 2 Hz, 1H), 2.38 (d, *J* 18 Hz, 1H), 2.72 (d, *J* 18 Hz) mixed with 2.66–2.75 (m, total 2H), 2.80–2.87 (m, 1H), 7.43–7.48 (m, 2H), 7.52–7.55 (m, 1H), 7.63–7.66 (m, 2H). ^{13}C NMR: δ 23.1 (CH_3), 28.5 (CH_3), 35.1 (CH), 37.8 (CH_2), 42.2 (CH_2), 49.6 (CH), 49.7 (CH), 49.8 (C), 57.4 (C), 127.3 (CH), 128.4 (CH), 132.1 (CH), 137.8 (C), 200.1

(C═O), 212.0 (C═O). HRMS (ESI) calcd for $C_{17}H_{19}O_2$: 255.1385; found: $[M+H]^+$ 255.1354.

At 350 nm:

solvent: benzene; time: 1 h. Yield of **7e**: 22 mg, 84% from 26 mg of **9e**,
solvent: MeOH; time: 1 h. Yield of **7e**: 24 mg, 92% from 26 mg of **9e**,
solvent: CH_3CN; Time: 1 h. Yield of **7e**: 23 mg, 88% from 26 mg of **9e**.

At 300 nm:

solvent: benzene; time: 1 h. Yield of **7e**: 18 mg, 90% from 20 mg of **9e**,
solvent: acetone; time: 1 h. Yield of **7e**: 18 mg, 90% from 20 mg of **9e**.

4.3.6. 1-Benzoyl-7,7-dimethyltricyclo[3.3.0.0^{2,8}]octan-3-one (7f). Time: 1.5 h. Elution of the column with 7.5% EA in PE gave a thick liquid of **7f** (95 mg, 95%). UV (CH_3CN): 242 nm (log ε 4.16), 276 (3.15), 308 (2.56). IR: 1728, 1661 cm^{-1}. ^{1}H NMR: δ 1.20 (s, 3H), 1.34 (s, 3H), 1.61 (d, *J* 13 Hz, 1H), 2.22 (d, *J* 18 Hz, 1H), 2.42 (dd, *J* 13 and 7.5 Hz, 1H), 2.56 (d, *J* 10 Hz, 1H), 2.76 (d, *J* 10 Hz, 1H), 2.86 (dd, *J* 18 and 10 Hz, 1H), 3.44–3.49 (m, 1H), 7.46–7.51 (m, 2H), 7.55–7.60 (m, 1H), 7.70–7.73 (m, 2H). ^{13}C NMR: δ 27.9 (CH_3), 33.3 (CH_3), 41.0 (CH), 41.6 (C), 48.3 (CH), 49.5 (CH_2), 53.9 (CH_2), 54.0 (CH), 59.4 (C), 127.5 (CH), 128.6 (CH), 132.3 (CH), 137.6 (C), 199.7 (C═O), 212.6 (C═O). HRMS (ESI) calcd for $C_{17}H_{19}O_2$: 255.1385; found: $[M+H]^+$, 255.1382.

At 350 nm:

solvent: benzene; time: 1 h. Yield of **7f**: 17 mg, 85% from 20 mg of **9f**,
solvent: MeOH; time: 1 h. Yield of **7f**: 58 mg, 96% from 60 mg of **9f**,
solvent: CH_3CN; time: 1 h. Yield of **7f**: 18 mg, 90% from 20 mg of **9f**.

At 300 nm:

solvent: benzene; Time: 1 h. Yield of **7f**: 18 mg, 90% from 20 mg of **9f**,
solvent: acetone; time: 1 h. Yield of **7f**: 17 mg, 85% from 20 mg of **9f**.

At 254 nm:

solvent: benzene; time: 2 h. Yield of **7f**: 44 mg, 88% from 50 mg of **9f**,
solvent: MeOH; time: 2 h. Yield of **7f**: 45 mg, 90% from 50 mg of **9f**,
solvent: CH_3CN; time: 2 h. Yield of **7f**: 46 mg, 92% from 50 mg of **9f**.

4.3.7. 1-Benzoyl-5,7,7-trimethyltricyclo[3.3.0.0^{2,8}]octan-3-one (7g). Time: 1.5 h. Elution of the column with 10% EA in PE gave **7g** (95 mg, 95%), mp 60–61 °C, as colorless crystals after recrystallization from ether–PE (1:6) mixture. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.63; H, 7.32. UV (CH_3CN): 247 nm (log ε 4.09), 280 (3.10), 317 (2.18). IR: 1717, 1657 cm^{-1}. ^{1}H NMR: δ 1.17 (s, 3H), 1.19 (s, 3H), 1.39 (s, 3H), 1.68 (d, *J* 13 Hz, 1H), 2.22 (dd, *J* 13 and 2 Hz, 1H), 2.25 (dd, *J* 10 and 2 Hz, 1H), 2.41 (d, *J* 18 Hz, 1H), 2.46 (br d, *J* 10 Hz, 1H), 2.71 (ddd, *J* 18, 2 and 2 Hz, 1H), 7.44–7.49 (m, 2H), 7.55–7.61 (m, 1H), 7.83–7.86 (m, 2H). ^{13}C NMR: δ 25.0 (CH_3), 27.7 (CH_3), 33.7 (CH_3), 40.4 (C), 46.5 (CH), 49.9 (CH), 50.5 (C), 56.5 (CH_2), 58.7 (C), 62.4 (CH_2), 129.05 (CH), 129.07 (CH), 133.6(CH), 138.0 (C), 197.7 (C═O), 213.3 (C═O).

At 350 nm:

solvent: benzene; time: 1.5 h. Yield of **7g**: 91 mg, 91%,
solvent: MeOH; time: 1.5 h. Yield of **7g**: 96 mg, 96%,
solvent: CH_3CN; time: 1.5 h. Yield of **7g**: 93 mg, 93%.

At 300 nm:

solvent: benzene; time: 1.5 h. Yield of **7g**: 93 mg, 93%,
solvent: acetone; time: 2 h. Yield of **7g**: 96 mg, 96%,
solvent: CH_3CN; time: 1.5 h. Yield of **7c**: 93 mg, 93%.

At 254 nm:

solvent: benzene; time: 2 h. Yield of **7g**: 90 mg, 90%,
solvent: MeOH; time: 2 h. Yield of **7g**: 92 mg, 92%,
solvent: CH_3CN; time: 2 h. Yield of **7g**: 88 mg, 88%.

4.3.8. 1-Isobutyryltricyclo[3.3.0.0^{2,8}]octan-3-one (7h). Time: 2 h. Elution of the column with 10% EA in PE gave **7h** (95 mg, 95%), mp 58–60 °C, as colorless crystals on recrystallization from a mixture of ether–PE (1:6). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.99; H, 8.29. UV (CH_3CN): 203 nm (log ε 3.97), 284 (2.38). IR: 1724, 1678 cm^{-1}. ^{1}H NMR: δ 1.09 (d, *J* 6 Hz, 3H), 1.11 (d, *J* 6 Hz, 3H), 1.59–1.78 (m, 1H), 1.89 (d, *J* 18 Hz, 1H), 2.14–2.30 (m, 3H), 2.68 (d, *J* 18 Hz) mixed with 2.56–2.79 (m, total 4H), 3.46–3.51 (m, 1H). ^{13}C NMR: δ 18.68 (CH_3), 18.7 (CH_3), 24.7 (CH_2), 35.8 (CH), 37.2 (CH), 39.8 (CH), 40.6 (CH_2), 47.0 (CH_2), 48.8 (CH), 57.8 (C), 210.2 (C═O), 211.9 (C═O).

At 350 nm:

solvent: benzene; time: 1.75 h. Yield of **7h**: 90 mg, 90%,
solvent: MeOH; time: 1.75 h. Yield of **7h**: 95 mg, 95%,
solvent: CH_3CN; time: 1.75 h. Yield of **7h**: 93 mg, 93%.

At 300 nm:

solvent: benzene; time: 2 h. Yield of **7h**: 91 mg, 91%,
solvent: acetone; time: 2 h. Yield of **7h**: 93 mg, 93%,
solvent: CH_3CN; time: 1.5 h. Yield of **7c**: 95 mg, 95%.

At 254 nm:

solvent: benzene; time: 2 h. Yield of **7h**: 86 mg, 86%,
solvent: MeOH; time: 2 h. Yield of **7h**: 94 mg, 94%,
solvent: CH_3CN; time: 2 h. Yield of **7h**: 91 mg, 91%.

4.3.9. 1-Isobutyryl-5-methyltricyclo[3.3.0.0^{2,8}]octan-3-one (7i). Time: 2 h. Elution of the column with 10% EA in

PE gave **7i** (90 mg, 90%), mp 52–54 °C, as colorless crystals on recrystallization from ether–petroleum ether (1:8). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.49; H, 8.99. UV (EtOH): 290 nm (log ε 3.51). IR: 1732, 1688 cm^{-1}. ^1H NMR: δ 1.05 (d, *J* 7 Hz, 6H), 1.55 (s, 3H), 1.62–1.72 (m, 2H), 2.02 (d, *J* 18 Hz, 1H), 2.15–2.20 (m, 2H), 2.39 (h, *J* 7 Hz, 1H), 2.47 (d, *J* 18 Hz) mixed with 2.44–2.52 (m, total 2H), 2.62 (d, *J* 10 Hz, 1H). ^{13}C NMR: δ 18.1(CH_3), 18.5 (CH_3), 23.2 (CH_3), 24.0 (CH_2), 36.3 (CH), 38.0 (CH), 47.0 (CH), 48.2(C), 48.4 (CH_2), 54.8 (CH_2), 55.7 (C), 209.2 (C=O), 211.2 (C=O).

4.4. Quantum yields for the phototransformations of 9a,c,d,f,g to7a,c,d,f,g

Standard solutions (about 3×10^{-3} M) of **9a**,**c**,**d**,**f**,**g** were prepared in benzene or methanol and subjected to 4 cycles of freeze–pump–thaw. From these solutions, 10 mL aliquots were irradiated in the presence of argon and anthracene (about 1.5×10^{-2} M) in a Rayonet photoreactor at the desired wavelength using a merry-go-round. The time of irradiation for each set was so chosen so as to bring about 30–40% conversion of the starting material. Comparative phototransformations (%) were calculated from NMR spectra and quantum yields for product formations were determined using uranyl oxalate as actinometer ($\varphi_{C_2O_4}$ was 0.468 at 350 nm and 0.602 at 254 nm)[24] (Table 1).

4.5. PET mediated cyclopropyl ring cleavage of 7c to 8-benzoyl-1-methylbicyclo[3.2.1]octan-3-one (10c)

To a solution of 1-benzoyl-5-methyltricyclo[3.3.0.$0^{2,8}$]-octan-3-one (**7c**, 30 mg, 0.13 mmol) in dry solvent (6 mL) was added TEA (4 mL) and the resulting solution was degassed with argon for 7 min. This solution was then irradiated with 300 nm lamp in a pyrex tube for 1 h, after which the volatile components were removed by distillation over a water bath under reduced pressure. The resulting mixture was then flash chromatographed over a column of silica.

4.5.1. In acetonitrile. Elution of the column with 8% EA in PE gave a solid of **10c** (20 mg, 62%), mp 58–60 °C, as colorless crystals after recrystallization from ether–PE (1: 8) mixture. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found C, 79.74; H, 7.60. IR: 1711, 1670 cm^{-1}. ^1H NMR: δ 1.19 (s, 3H), 1.51–1.60 (m, 1H), 1.66–1.71 (m, 2H), 2.13 (br d, *J* 17 Hz), and 2.16 (br d, *J* 17 Hz), mixed with 2.06–2.19 (m, total 3H), 2.43 (br d, *J* 17 Hz, 1H), 2.82 (hextet, *J* 4 Hz, 1H), 3.40 (br d, *J* 17 Hz, 1H), 3.49 (d, *J* 4 Hz, 1H), 7.48–7.53 (m, 2H), 7.58–7.63 (m, 1H), 7.97–7.99 (m, 2H). ^{13}C NMR: δ 24.9 (CH_3), 28.8 (CH_2), 38.6 (CH_2), 39.5 (CH), 44.2 (C), 44.9 (CH_2), 52.0 (CH_2), 55.2 (CH), 128.0 (CH), 128.8 (CH), 133.3 (CH), 137.9 (C), 201.6 (C=O), 211.7 (C=O).

Further elution of the column with 8% EA in PE gave back unreacted starting material **7c** (8 mg, 25%, superimposed spectra).

4.5.2. In acetonitrile and $LiClO_4$. The above procedure was repeated in the presence of $LiClO_4$ (14 mg, 1 equiv). Chromatographic separation using 8% EA in PE gave a solid of **10c** (26 mg, 80%) mp 58–60 °C (mmp 58–60 °C).

4.5.3. In methanol. Elution of the column with 8% EA in PE gave a solid of **10c** (28 mg, 86%) mp 58–60 °C (mmp 58–60 °C).

4.6. Quantum yield for PET reaction of 7c to 10c

A standard solution (about 3×10^{-3} M) of **7c** was prepared in 40% TEA–methanol solution and subjected to 4 cycles of freeze–pump–thaw process. From this, 10 mL aliquots were irradiated in the presence of argon, oxygen, and anthracene (about 1.5×10^{-2} M) in a Rayonet photoreactor at the desired wavelength using a merry-go-round. The time of irradiation for each set was so chosen so as to bring about 30–40% conversion of the starting material. The comparative phototransformation (%) was calculated from NMR spectra and quantum yields for product formations were determined using uranyl oxalate as actinometer[24] ($\varphi_{C_2O_4}$ was 0.570 at 302 nm).

4.7. PET mediated cyclopropyl ring cleavage of 7h to 8-isobutyrylbicyclo[3.2.1]octan-3-one (10h)

The above procedure was carried out with 1-isobutyryltricyclo[3.3.0.$0^{2,8}$]octan-3-one (**7h**, 100 mg, 0.52 mmol) in dry methanol (24 mL) and TEA (16 mL) using 254 nm lamps in a pyrex tube for 3 h. Elution of the column with 5% EA in PE gave a thick liquid of **10h** (40 mg, 40%). IR: 1703 cm^{-1}. ^1H NMR: δ 1.15 (d, J 7 Hz, 6H), 1.59 (dd, *J* 16 and 7 Hz, 2H), 1.89–1.93 (m, 2H), 2.22 (d, *J* 16 Hz, 2H), 2.72–2.85 (m, 4H), 2.87 (h, *J* 7 Hz) 2.92–2.94 (m, 1H), 2.73–2.94 (m, total 6H). ^{13}C NMR: δ 18.6 (CH_3), 29.5 (CH_2), 37.1 (CH), 40.4 (CH), 46.2 (CH_2), 54.2 (CH), 211.6 (C=O), 215.7 (C=O). HRMS (ESI) calcd for $C_{12}H_{18}O_2Na$: 217.1205; found $[M+Na]^+$ 217.1245.

Further elution of the column with 7.5% EA in PE gave a solid of unreacted **7h** (35 mg, 35%) mp 58–60 °C (mmp 59 °C).

4.8. PET mediated cyclopropyl ring cleavage of 7i to 8-isobutyryl-5-methylbicyclo[3.2.1]octan-3-one (10i)

The above procedure was carried out with 1-isobutyryl-5-methyltricyclo[3.3.0.$0^{2,8}$]octan-3-one (**7i**, 46 mg, 0.22 mmol) in dry methanol (9 mL) and TEA (6 mL) using 254 nm lamps in a pyrex tube for 2.5 h. Elution of the column with 5% EA in PE gave a thick liquid of **10i** (35 mg, 77%). IR: 1707 cm^{-1}. ^1H NMR: δ 1.11 (s, 3H), 1.12 (d, *J* 7 Hz, 3H), 1.14 (d, *J* 7 Hz, 3H), 1.46–1.62 (m, 3H), 2.01 (ddd, *J* 17, 2 and 2 Hz) mixed with 1.94–2.03 (m, total 2H), 2.20 (br d, *J* 16 Hz, 1H), 2.47 (ddd, *J* 16, 3 and 3 Hz, 1H), 2.76 (h, *J* 7 Hz) mixed with 2.68–2.73 (m, total 2H), 2.81–2.83 (m, 1H), 3.17 (dd, *J* 17 and 2 Hz, 1H). ^{13}C NMR: δ 18.1 (CH_3), 18.8 (CH_3), 25.3 (CH_3), 29.4 (CH_2), 38.5 (CH_2), 39.0 (CH), 42.4 (CH), 44.6 (C), 45.3 (CH_2), 52.2 (CH_2), 58.4 (CH), 211.9 (C=O), 216.7 (C=O). HRMS (ESI) calcd for $C_{13}H_{20}O_2Na$: 231.1361; found $[M+Na]^+$ 231.1360.

Further elution of the column with 7.5% EA in PE gave a solid of unreacted **7i** (10 mg, 22%) mp 52–54 °C (mmp 52–54 °C).

4.9. TBTH mediated cyclopropyl ring cleavages of 7c,g,i to 10c,g,i

To the solutions of the tricyclic compounds (100 mg) and AIBN (catalytic) in 15 mL benzene at 80 °C, TBTH (2 equiv) was slowly added dropwise via a syringe. The resulting mixture was refluxed at 80 °C for further 3 h after which the mixture was cooled and the solvent was removed at reduced pressure. The residue was hydrolyzed by stirring overnight with dilute HCl (5 mL), after which the mixture was worked up with ether and dried over anhydrous Na_2SO_4. The solvent was then removed and the residue was chromatographed over a column of silica gel.

4.9.1. 8-Benzoyl-1-methylbicyclo[3.2.1]octan-3-one (10c) from 7c. Elution of the column with 8% EA in PE gave colorless crystals of **10c** (60 mg, 60%) mp 58–60 °C (mmp 58–60 °C).

4.9.2. 8-Benzoyl-1,6,6-trimethylbicyclo[3.2.1]octan-3-ones (10g,10′g) from 7g. Elution of the column with 10% ethyl acetate in petroleum ether gave **10g** (60 mg, 60%), mp 64–66 °C, as colorless crystals after recrystallization from ether–petroleum ether (1:4) mixture. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found C, 80.18; H, 8.03. IR: 1709, 1670 cm^{-1}. ^1H NMR: δ 1.01 (s, 3H), 1.18 (s, 3H), 1.31 (s, 3H), 1.50 (d, *J* 13 Hz, 1H), 1.60 (dd, *J* 13 and 3 Hz, 1H), 2.16 (br d, *J* 18 Hz, 1H), 2.18 (dd, *J* 18 and 4 Hz, 1H), 2.33 (q, *J* 4 Hz, 1H), 2.42 (br d, *J* 18 Hz, 1H), 3.45 (dd, *J* 18 and 3 Hz, 1H), 3.83 (br d, *J* 4 Hz, 1H), 7.47–7.52 (m, 2H), 7.57–7.62 (m, 1H), 7.94–7.97 (m, 2H). ^{13}C NMR: δ 27.7 (CH_3), 28.3 (CH_3), 35.8 (CH_3), 41.4 (C), 42.9 (CH_2), 46.4 (C), 52.3 (CH), 54.4 (CH_2), 56.5 (CH), 57.5 (CH_2), 130.2 (CH), 130.9 (CH), 135.4 (CH), 139.9 (C), 203.4 (C=O), 214.1 (C=O). HRMS (ESI) calcd for $C_{18}H_{23}O_2$: 271.1698; found $[M+H]^+$ 271.1661.

Further elution of the column with 10% ethyl acetate in petroleum ether gave the other 8-epimer (**10′g**, 15 mg, 15%), mp 67–69 °C, as colorless crystals after recrystallization from ether–petroleum ether (1: 8) mixture. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found C, 79.91; H, 8.24. IR: 1713, 1682 cm^{-1}. ^1H NMR: δ 0.94 (s, 3H), 0.97 (s, 3H), 1.33 (s, 3H), 1.55 (dd, *J* 13 and 1 Hz, 1H), 2.30 (d, *J* 13 Hz, 1H), 2.36 (dd, *J* 4 and 3 Hz, 1H), 2.42 (s, 2H), 2.65 (dd, *J* 17 and 4 Hz, 1H), 2.81 (dd, *J* 17 and 3 Hz, 1H), 3.59 (s, 1H), 7.47–7.52 (m, 2H), 7.56–7.62 (m, 1H), 7.94–7.97 (m, 2H). ^{13}C NMR: δ 23.0 (CH_3), 28.8 (CH_3), 32.5 (CH_3), 41.0 (C), 44.1 (C), 47.9 (CH_2), 50.7 (CH), 52.3 (CH_2), 59.0 (CH_2), 61.6 (CH), 128.1 (CH), 128.7 (CH), 133.0 (CH), 137.0 (C), 201.0 (C=O), 211.3 (C=O). HRMS (ESI) calcd for $C_{18}H_{23}O_2$: 271.1698; found: $[M+H]^+$ 271.1695.

4.9.3. 8-Isobutyryl-1-methylbicyclo[3.2.1]octan-3-one (10i) from 7i. Elution of the column with 7% ethyl acetate in petroleum ether gave a thick liquid of **10i** (60 mg, 60%). IR: 1707 cm^{-1}. ^1H NMR: δ 1.11 (s, 3H), 1.12 (d, *J* 7 Hz, 3H), 1.14 (d, *J* 7 Hz, 3H), 1.46–1.62 (m, 3H), 2.01 (ddd, *J* 17, 2 and 2 Hz) mixed with 1.94–2.03 (m, total 2H), 2.17 (br d, *J* 16 Hz, 1H), 2.47 (ddd, *J* 16, 3 and 3 Hz, 1H), 2.76 (h, *J* 7 Hz) mixed with 2.68–2.73 (m, total 2H), 2.81–2.83 (m, 1H), 3.17 (dd, *J* 17 and 2 Hz, 1H). ^{13}C NMR: δ 18.1 (CH_3), 18.8 (CH_3), 25.3 (CH_3), 29.4 (CH_2), 38.5 (CH_2), 39.0 (CH), 42.4 (CH), 44.6 (C), 45.3 (CH_2), 52.2 (CH_2), 58.4 (CH), 211.9 (C=O), 216.7 (C=O). HRMS (ESI) calcd for $C_{13}H_{20}O_2Na$: 231.1361; found: $[M+Na]^+$ 231.1360.

Further elution of the column with 10% ethyl acetate in petroleum ether gave back unreacted starting material **7i** (15 mg, 15%) mp 52–54 °C (mmp 52–54 °C).

4.10. PET mediated conversion of bicyclo[2.2.2]octenones to bicylo[3.2.1]octanones

A solution of the bicyclo-compounds (150 mg) in methanol (30 mL) containing (20 mL) TEA, was degassed by purging with argon for 7 min. The solution was then irradiated in a pyrex tube at 300 nm for 1 h under argon after which the volatile materials were removed under reduced pressure. The residue was then purified by flash chromatography over a column of silica gel (230–400 mesh) to yield the products.

4.10.1. Conversion of 5-benzoylbicyclo[2.2.2]oct-5-en-2-one (9a). Elution of the column with 7.5% EA in PE gave 8-benzoylbicyclo[3.2.1]octan-3-one (**10a**, 90 mg, 60%) as a white solid after recrystallization from ether–PE (1:4) mixture, mp 95–97 °C. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.38; H, 7.06. IR: 1711, 1668 cm^{-1}. ^1H NMR: δ 1.66 (dd, *J* 15 and 7 Hz, 2H), 2.02–2.06 (m, 2H), 2.22 (br d, *J* 16 Hz, 2H), 2.89 (br d, *J* 16 Hz) mixed with 2.86 (br m, total 4H), 3.56–3.59 (m, 1H), 7.47–7.52 (m, 2H), 7.57–7.62 (m, 1H), 7.95–7.97 (m, 2H). ^{13}C NMR: δ 29.4 (CH_2), 37.5 (CH), 45.9 (CH_2), 51.8 (CH), 127.9 (CH), 128.6 (CH), 133.0 (CH), 137.2 (C), 201.3 (C=O), 211.6 (C=O). HRMS (ESI) calcd for $C_{15}H_{17}O_2$: 229.1229; found: $[M+H]^+$ 229.1235.

Further elution of the column with 7.5% EA in PE gave a white solid of the other 8-epimer **10′a** (50 mg, 33%), which was recrystallized from ether–PE (1:4) mixture, mp 67–69 °C. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.65; H, 7.15. IR: 1713, 1674 cm^{-1}. ^1H NMR: δ 1.53–1.60 (m, 2H), 2.00–2.03 (m, 2H), 2.47 (dd, *J* 18 and 2 Hz, 2H), 2.65 (br d, *J* 18 Hz, 2H), 2.86 (br m, 2H), 3.77 (s, 1H), 7.48–7.53 (m, 2H), 7.58–7.62 (m, 1H), 7.99–8.02 (m, 2H). ^{13}C NMR: δ 28.3 (CH_2), 38.3 (CH), 50.4 (CH_2), 57.1 (CH), 128.3 (CH), 128.7 (CH), 133.1 (CH), 135.6 (C), 200.0 (C=O), 211.0 (C=O). HRMS (ESI) calcd for $C_{15}H_{17}O_2$ 229.1229; found $[M+H]^+$ 229.1245.

4.10.2. Conversion of 5-benzoyl-4-methylbicyclo[2.2.2]-oct-5-en-2-one (9c). Elution of the column with 7.5% EA in PE gave 8-benzoyl-1-methylbicyclo[3.2.1]octan-3-one (**10c**, 130 mg, 86%) as a white solid, which was recrystallized from ether–PE (1:4) mixture, mp 58–60 °C (mmp 58–60 °C).

4.10.3. Conversion of 5-benzoyl-1,4-dimethylbicyclo[2.2.2]oct-5-en-2-one (9d). Elution of the column with 7.5% EA in PE gave **9d** (82 mg, 55%, superimposed spectra). Further elution of the column with 7.5% EA in PE gave 1-benzoyl-5,8-dimethyltricyclo[3.3.0.$0^{2,8}$]octan-3-one (**7d**, 64 mg, 43%, superimposed spectra).

4.10.4. Conversion of 5-benzoyl-8,8-dimethylbicyclo[2.2.2]oct-5-en-2-one (9e). Elution of the column with 7.5% EA in PE gave 8-benzoyl-6,6-dimethylbicyclo[3.2.1]-octan-3-one (**10e**, 30 mg, 17%) as a white solid, which was recrystallized from ether–PE (1:4) mixture, mp 59–61 °C. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.51; H, 7.92. IR: 1707, 1668 cm^{-1}. ^1H NMR: δ 1.06 (s, 3H), 1.26 (s, 3H), 1.41 (d, *J* 14 Hz, 1H), 1.92 (ddd, *J* 14, 7 and 3 Hz, 1H), 2.23 (br d, *J* 18 Hz, 1H), 2.35–2.38 (m, 1H), 2.46 (br d, *J* 18 Hz, 1H), 2.61 (dd, *J* 18 and 4 Hz, 1H), 2.83–2.85 (m, 1H), 3.03 (ddd, *J* 18, 3 and 3 Hz, 1H), 3.92–3.95 (m, 1H), 7.46–7.52 (m, 2H), 7.56–7.59 (m, 1H), 7.92–7.95 (m, 2H). ^{13}C NMR: δ 26.2 (CH_3), 32.8 (CH_3), 37.6 (CH), 39.8 (C), 41.8 (CH_2), 46.0 (CH_2), 46.1 (CH_2), 48.3 (CH), 50.8 (CH), 127.8 (CH), 128.6 (CH), 133.0 (CH), 137.2 (C), 201.5 (C═O), 211.7 (C═O). HRMS (ESI) calcd for $C_{17}H_{21}O_2$: 257.1542; found $[M+H]^+$ 257.1538.

Further elution of the column with 7.5% EA in PE gave a white solid of 1-benzoyl-6,6-dimethyltricyclo[3.3.0.0^{2,8}]-octan-3-one (**7e**, 10 mg, 6%), which was recrystallized from ether–PE (1:5) mixture, mp 71–73 °C (superimposed spectra).

Further elution of the column with 7.5% EA in PE gave a white solid of the other 8-epimer **10′e** (120 mg, 70%), which was recrystallized from ether–PE (1:5) mixture, mp 69–71 °C. IR: 1705, 1682 cm^{-1}. ^1H NMR: δ 0.78 (s, 3H), 0.97 (s, 3H), 1.43 (d, *J* 14 Hz, 1H), 2.19 (dd, *J* 14 and 7 Hz, 1H), 2.53–2.54 (m, 3H), 2.66 (dd, *J* 17 and 4 Hz, 1H), 2.77 (dd, *J* 17 and 3 Hz, 1H), 3.09–3.10 (m, 1H), 3.61 (s, 1H), 7.48–7.52 (m, 2H), 7.57–7.62 (m, 1H), 7.95–7.97 (m, 2H). ^{13}C NMR: δ 28.0 (CH_3), 32.3 (CH_3), 35.8 (CH), 40.6 (C), 44.7 (CH_2), 47.6 (CH_2), 50.4 (CH_2), 50.8 (CH), 59.1 (CH), 128.2 (CH), 128.6 (CH), 132.9 (CH), 135.9 (C), 201.1 (C═O), 211.6 (C═O). HRMS (ESI) calcd for $C_{17}H_{20}O_2Na$: 279.1361; found $[M+Na]^+$ 279.1349.

4.10.5. Conversion of 5-benzoyl-7,7-dimethylbicyclo[2.2.2]oct-5-en-2-one (9f). Elution of the column with 7.5% EA in PE gave 8-benzoyl-6,6-dimethylbicyclo[3.2.1]octan-3-one (**10e**, 40 mg, 20%) as a white solid, which was recrystallized from ether–PE (1:4), mp 59–61 °C (mmp 59–61 °C).

Further elution of the column with 7.5% EA in PE gave a thick liquid of 1-benzoyl-7,7-dimethyltricyclo[3.3.0.0^{2,8}]octan-3-one (**7f**, 10 mg, 5%, superimposed spectra).

Further elution of the column with 7.5% EA in PE gave a white solid of the other 8-epimer **10′e** (140 mg, 69%) mp 69–71 °C (mmp 69–71 °C).

4.10.6. Conversion of 5-benzoyl-4,7,7-trimethylbicyclo[2.2.2]oct-5-en-2-one (9g). Elution of the column with 7.5% EA in PE gave colorless crystals of 8-benzoyl-1,6,6-trimethylbicyclo[3.2.1]octan-3-one (**10g**, 120 mg, 79%) mp 64–66 °C (mmp 64–66 °C).

Further elution of the column with 7.5% EA in PE gave a white solid of 1-benzoyl-5,7,7-trimethyltricyclo[3.3.0.0^{2,8}]octan-3-one (**7g**, 10 mg, 7%) mp 60–61 °C (mmp 60–61 °C).

Further elution of the column with 7.5% EA in PE gave a white solid of the 8-epimer **10′g** (10 mg, 7%), mp 67–69 °C (mmp 67–69 °C).

4.10.7. Conversion of 5-isobutyrylbicyclo[2.2.2]oct-5-en-2-one (9h). Time: 4 h. Elution of the column with 5% EA in PE gave 8-isobutyrylbicyclo[3.2.1]octan-3-one (**10h**, 55 mg, 36%) as a thick liquid (superimposible spectra).

Further elution with 7.5% EA in PE gave a solid of 1-isobutyryltricyclo[3.3.0.0^{2,8}]octan-3-one (**7h**, 60 mg, 40%) mp 58–60 °C (mmp 58–60 °C).

4.10.8. Conversion of 11-benzoyltricyclo[6.2.2.0^{1,6}]dodec-11-en-9-one (11). The procedure was repeated with **11** (70 mg, 0.25 mmol) in dry MeOH (15 cc) and TEA (10 cc). Elution of the column with 7.5% EA in PE gave 12-benzoyltricyclo[6.3.1.0^{1,6}]dodecan-10-one (**12**, 55 mg, 78%) mp 122–124 °C (lit.[11] mp 124 °C) as a white solid, which was recrystallized from ether–PE (1:4) mixture.

4.11. Epimerisation of 8-benzoylbicyclo[3.2.1]octan-3-one (10a)

To a solution of (**10a**, 50 mg, 0.22 mmol) in 5 cc MeOH, methanolic NaOH solution (10%, 5 cc) was added and the mixture was stirred at room temperature for 12 h. After which the mixture was extracted with ether (3×15 cc). The combined extracts were washed with brine till neutral, dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure and the residue was column chromatographed. Elution with 10% EA in PE gave the epimeric 8-benzoylbicyclo[3.2.1]octan-3-one (**10′a**, 40 mg, 80%) mp 67–69 °C, mmp 67–69 °C.

References and notes

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