Synthesis of bicyclo[2.2.2] System having α,β or β,γ-enone with δ-Keto Conjugation and Sterically Hindered Group at the Bridgehead Position

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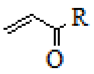
Abstract: ***Bicyclo[2.2.2] system having α,β or β,γ-enone with δ-Keto Conjugation is an important class of compound in terms of synthetic organic chemistry due to their versatile role as building blocks of many natural products and their interesting photochemical behaviors. Herein we have reported the synthesis of such bicyclo compounds having bulky group at the bridgehead position through Diels Alder reaction between 3-trimethylsilioxycyclohexa-1,3-diene and acetylenic ketones, followed by hydrolysis of the silyloxy adduct. It was observed that unlike previously reported diene, these dienes are highly susceptible towards even trace amount of moisture. Modifying the reaction condition including filtration under argon atmosphere gave the desired Bicyclo[2.2.2] system having sterically hindered group like phenyl and isopropenyl group at the bridgehead position.***

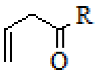
Keywords: Bicyclo[2.2.2] octenone, Diels Alder, steric hinderence, bridgehead and inert atmosphere.

1. Introduction

Enones exhibit a rich and diverse photochemistry. The deep-seated photochemical rearrangements found in these systems have attracted numerous mechanistic studies. In this context, the photochemistry of α,β (A) and β,γ-enone (B) has become an actively researched area for more than two decades,[1-6] particularly because of their fascinating photochemical rearrangements.

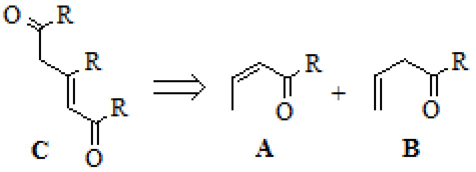


A

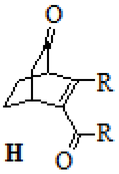


B

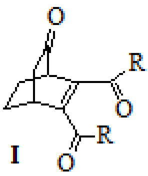
In view of the rich photochemistry exhibited by both α,β and β,γ-unsatuarated enones, it might be expected that incorporation of both enone into the same molecule (C) would lead to a variety of more interesting reactions. Indeed this type of mixed enone photochemistry is also an attractive field[7-8] for chemists because the photochemistry of such substrates could feature intramolecular competition of different photochemical rearrangements.



It is therefore of utmost importance to synthesize mixed chromophoric systems with molecular framework **C** to explore their competitive photochemical behavior in details. Since in acyclic enone of type (**C**), E-Z photoisomerization becomes one of the major energy dissipation pathways, we selected our enones with rigid geometry to minimize this route. Our selected system (**H and I**) is the rigid analogue of types **C** which can be considered as α,β- or β,γ-enone with δ-keto conjugation.



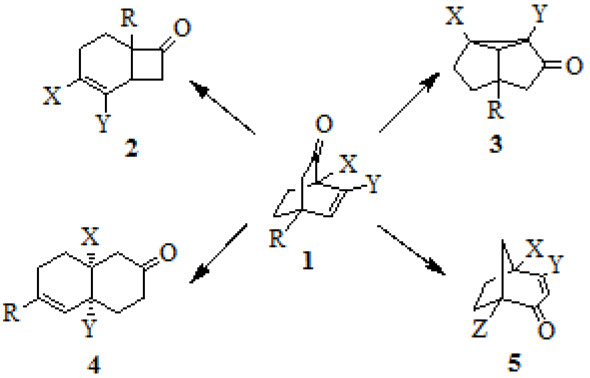
H



I

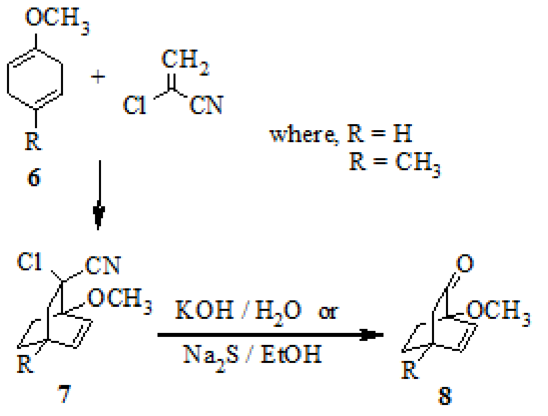
Now, most of the studies are mainly focused on the synthesis of functionalized β,γ-enone having bicyclo-[2.2.2]oct-5-en-2-ones skeletone (**1**). This is because of their versatile role as building blocks for the synthesis of bicyclo[4.2.0]oct-2-en-7-ones (**2**), tricyclo[3.3.0.0^{2,8}]-octane-3-ones (**3**),[9] [6,6] fused ring systems (**4**),[10] and bicyclo[3.2.1]octenone systems (**5**) (Scheme **1**).[11]

Scheme 1



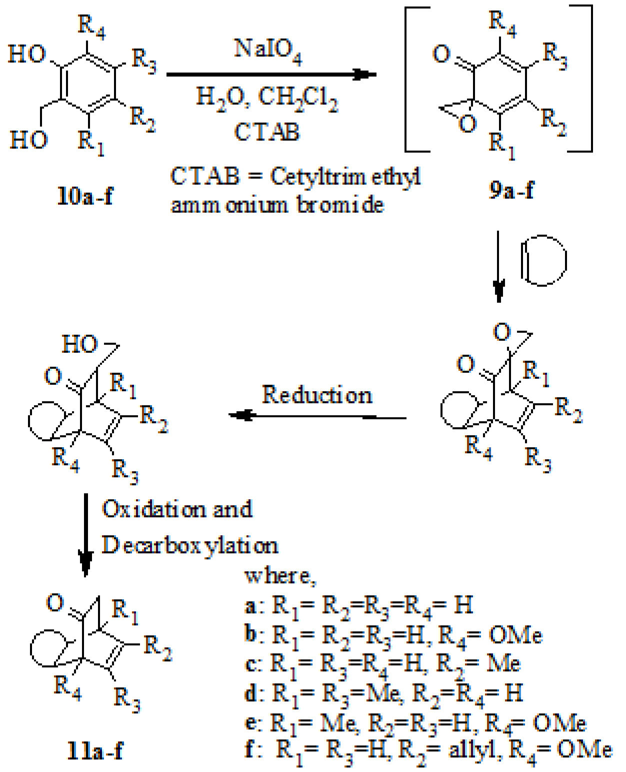
The most general method used for the synthesis of bicyclo[2.2.2]octenone (**8**) framework involves the Diels-Alder reaction of the substituted 1,3-cyclohexadienes (**6**) with ketene equivalent compounds like 2-chloroacrylonitrile or 2-acetoacrylonitrile (**7**), followed by hydrolysis (Scheme **2**)[12].

Scheme 2



Another convenient method involves the reaction of derivatives of cyclohexa-2,4-dienones (**9a-f**). Singh and coworker extensively used spiroepoxycyclohexa-2,4-dienones (**10a-f**) for preparing annulated bicyclo[2.2.2]octenones (**11a-f**) (Scheme **3**).[13]

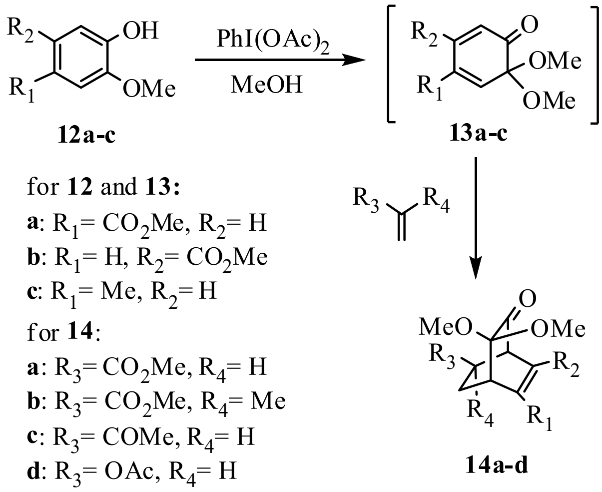
Scheme 3



where,
a: $R_1 = R_2 = R_3 = R_4 = H$
b: $R_1 = R_2 = R_3 = H$, $R_4 = OMe$
c: $R_1 = R_3 = R_4 = H$, $R_2 = Me$
d: $R_1 = R_3 = Me$, $R_2 = R_4 = H$
e: $R_1 = Me$, $R_2 = R_3 = H$, $R_4 = OMe$
f: $R_1 = R_3 = H$, $R_2 =$ allyl, $R_4 = OMe$

Liao and coworkers reported an efficient one pot synthesis of bicyclo[2.2.2]octenones (**14a-d**) starting from commercially available 2-methoxy phenols (**12a-c**).[14] Oxidation of 2-methoxyphenol (**12a-c**) with iodobenzene diacetate gave masked o-benzoquinones (**13a-c**) which then reacted in situ with suitable dienophiles to give the adduct **14a-d**. (Scheme **4**).

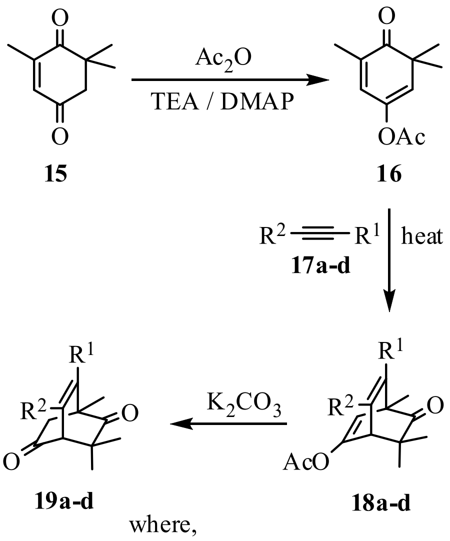
Scheme 4



for **12** and **13:**
a: $R_1 = CO_2Me$, $R_2 = H$
b: $R_1 = H$, $R_2 = CO_2Me$
c: $R_1 = Me$, $R_2 = H$
for **14**:
a: $R_3 = CO_2Me$, $R_4 = H$
b: $R_3 = CO_2Me$, $R_4 = Me$
c: $R_3 = COMe$, $R_4 = H$
d: $R_3 = OAc$, $R_4 = H$

The same group has recently developed an efficient procedure for multigram scale preparation of bicyclo[2.2.2]octane-2,5-diones (**19a-d**), which involves i) the conversion of hydroquinones (**15**) to (**16**), ii) the Diels-Alder reactions of **16** with acetylenic dienophiles (**17a-d**) to afford adducts (**18a-d**) and iii) the hydrolysis of the same by suitable reagent to give **19a-d** (Scheme **5**).[15]

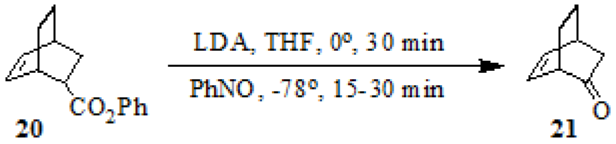
Scheme 5



where,
a: $R_1 = CO_2Et$, $R_2 = H$
b: $R_1 = R_2 = CO_2Me$
c: $R_1 = Ph$, $R_2 = H$
d: $R_1 = Ph$, $R_2 = Ph$

Another recently developed method by Yamamoto et al. for production of **21** involved a nitrosobenzene mediated oxidative decarboxylation of **20** (Scheme **6**).[16]

Scheme 6



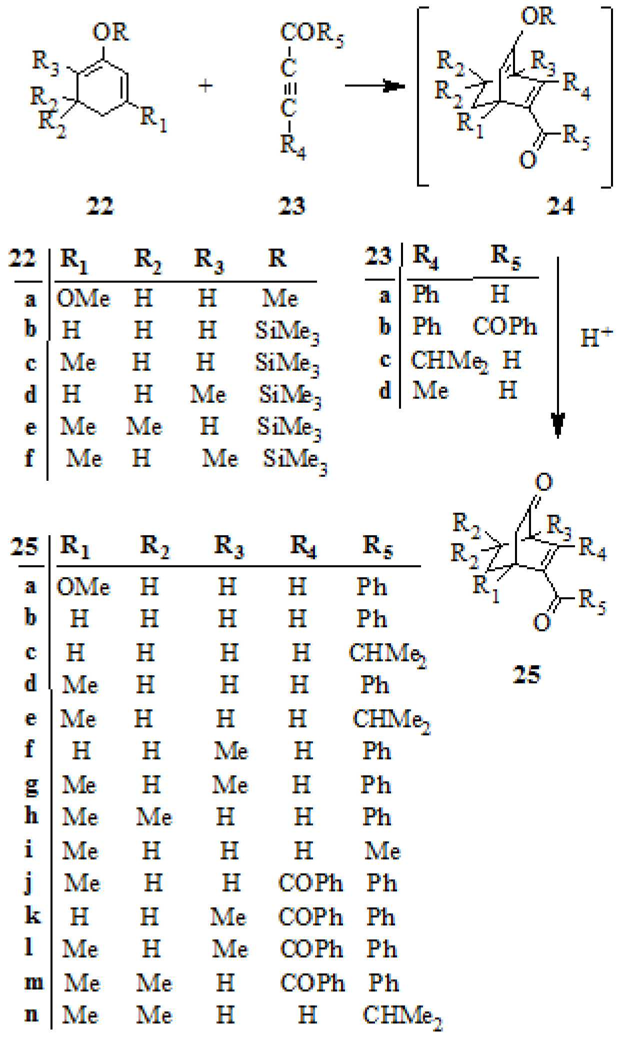
Thus, most of the methods are concentrated on the synthesis of β,γ–enones framework incorporated in bicyclo[2.2.2]-

octenone-models. However, none of these methods were suitable for preparing our bicyclo[2.2.2]-octenone-models with both δ-keto-α,β or β,γ–enones system like **H** and **I.**

2. Results and Discussion

Synthesis of some bicyclo[2.2.2]-octenone-models with δ-keto-α,β or β,γ–enones like system **H** have been reported only by Lahiri and co-worker. The method involves a [4+2] cycloaddition of the 3-trimethylsilioxycyclohexa-1,3-diene (**22a-f**) with acetylenic ketones (**23a-d**), followed by hydrolysis of the silyloxy adduct (**24a-m**) to get the desired bicyclo[2.2.2]octenone adducts (**25a-m**) (Scheme **7**).[17,18]

Scheme 7



22 **23** **24**

22	R_1	R_2	R_3	R
a	OMe	H	H	Me
b	H	H	H	$SiMe_3$
c	Me	H	H	$SiMe_3$
d	H	H	Me	$SiMe_3$
e	Me	Me	H	$SiMe_3$
f	Me	H	Me	$SiMe_3$

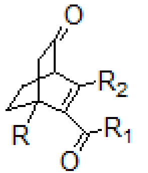
23	R_4	R_5
a	Ph	H
b	Ph	COPh
c	$CHMe_2$	H
d	Me	H

25	R_1	R_2	R_3	R_4	R_5
a	OMe	H	H	H	Ph
b	H	H	H	H	Ph
c	H	H	H	H	$CHMe_2$
d	Me	H	H	H	Ph
e	Me	H	H	H	$CHMe_2$
f	H	H	Me	H	Ph
g	Me	H	Me	H	Ph
h	Me	Me	H	H	Ph
i	Me	H	H	H	Me
j	Me	H	H	COPh	Ph
k	H	H	Me	COPh	Ph
l	Me	H	Me	COPh	Ph
m	Me	Me	H	COPh	Ph
n	Me	Me	H	H	$CHMe_2$

25

Now our target was to synthesize more rigid bicyclic compounds with additional keto group at 6 position and highly sterically hindered group at the bridge head position. For this we have chosen three compounds (Table 1)

Table 1

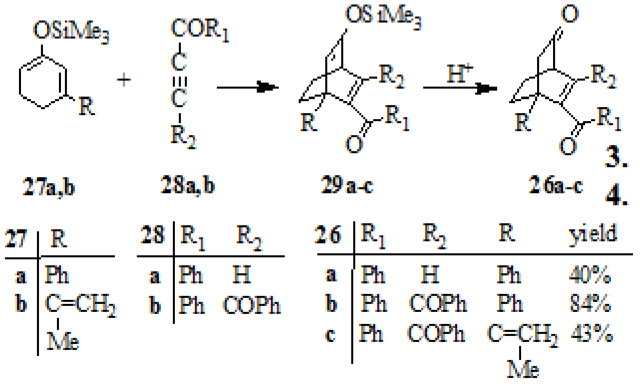


26a-c

26	R_1	R_2	R
a	Ph	H	Ph
b	Ph	COPh	Ph
c	Ph	COPh	$\underset{\text{Me}}{\underset{\vert}{C}}=CH_2$

Now in order to prepare 5-benzoyl-4-phenylbicyclo[2.2.2]oct-5-en-2-one (**26a**), several attempts were made to prepare the desired diene - trimethyl(3-phenylcyclohex-2-enyloxy)silane (**27a**) from 3-phenylcyclohexenone following the usual procedure as mentioned in the literature.[17] However, it was observed that the *O*-silyloxydiene was highly unstable and during work up it decomposed to the starting enone, probably due to presence of sterically hindered group like phenyl. Hence all of the steps of the reaction, even the work up procedure were performed in presence of inert (argon) atmosphere while preparing the diene. Thus modification of the usual reaction procedure followed by Diels Alder cycloaddition reaction between the substituted O-silyloxycyclohexa-1,3-dienes (**27a**) and acetylenic ketone (**28a**) in presence of inert atmosphere resulted desired **26a** in 40% yield (Scheme **8**). Similarly 5,6-dibenzoyl-4-phenylbicyclo[2.2.2]oct-5-en-2-one (**26b**) was prepared in 84% yield using O-silyloxycyclohexa-1,3-dienes (**27a**) and acetylenic keto **28b**. 5,6-dibenzoyl-4-isopropenylbicyclo[2.2.2]oct-5-en-2-one (**26c**) was also prepared in 43% yield following the same modified procedure from diene **27b** and acetylenic keto **28b** (Scheme **8**).

Scheme 8



27a,b **28a,b** **29a-c** **26a-c**

27	R
a	Ph
b	$\underset{\text{Me}}{\underset{\vert}{C}}=CH_2$

28	R_1	R_2
a	Ph	H
b	Ph	COPh

26	R_1	R_2	R	yield
a	Ph	H	Ph	40%
b	Ph	COPh	Ph	84%
c	Ph	COPh	$\underset{\text{Me}}{\underset{\vert}{C}}=CH_2$	43%

3. Conclusion

From the above result, it is evident that we can prepare our desired rigid bicyclic compound having α,β- or β,γ-enone with δ-keto conjugation as well as bulky group at the bridgehead position carrying out the normal Diels Alder reaction including work up in inert atmosphere.

4. Experimental

All melting points were measured in a Gallenkamp melting point apparatus and were uncorrected. UV absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. The IR spectra were recorded on an FTIR-8300 Shimadzu spectrometer. Gas chromatography was carried out on a Shimadzu gas chromatograph GC-9A using SE-30 column. The NMR spectra were recorded in $CDCl_3$ solution at 300 MHz for ^1H 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). Petroleum ether used was of the boiling range 60–80^{0} and is referred as PE. EA refers to ethyl acetate. Ether refers to diethyl ether. Analytical grade acetonitrile was used for recording UV spectra. Solvents were purified and dried using reported procedure.[19]

Monobenzoyl acetylene, **28a** (MBA),[20] dibenzoyl acetylene, **28b** (DBA),[21] were prepared according to literature procedures. the silyloxy-1,3-dienes[22] were prepared following general procedure.

6(a) Synthesis of 5-Benzoyl-4-phenyl-bicyclo[2.2.2]oct-5-en-2-one (26a)

To a solution of freshly distilled di-isopropylamine (2.3 mL, 16.5 mmol) in dry THF (20 mL) n-butyllithium (8.8 mL of 1.5 M solution in hexane, 13.2 mmol) was added dropwise under argon atmosphere at -78 ^{o}C. Temperature of the reaction bath was then slowly raised to -10 ^{o}C and then again cooled to -78 ^{o}C after 30 min. A solution of 3-phenylcyclohexenone (1.9 g, 11.0 mmol) in dry THF (5 mL) was added in drops to the reaction mixture for a period of 2-3 min via syringe when the color of the solution turned deep orange. Stirring was continued for additional 5 min at -78 ^{o}C, and then the reaction mixture was quenched rapidly with freshly distilled chlorotrimethylsilane (2.1 mL, 16.5 mmol). The stirred solution was brought to room temperature during next 2 h. The solvent was removed under reduced pressure followed by immediate flushing of the reaction vessel with argon. The residue was stirred three times with dry n-pentane (3x15 mL) under inert atmosphere and the supernatant liquid was transferred very carefully via a cannula to an oven dried thoroughly argon flushed flask. The total solvent (~45 mL) was then removed in vacuo to get the yellow liquid of trimethyl(5-phenylcyclohexa-1,5-dienyloxy)silane (**27a**).[23] Dry benzene (5 mL) and a solution of MBA, **28a** (1.3 gm, 10 mmol) in dry benzene (5 mL) were immediately added to the diene and the mixture was stirred for 6 h under inert atmosphere. A solution of 5% methanol-HCl (5 mL) was added to it and the mixture was stirred for additional 20 min. After removal of MeOH the mixture was extracted with ether (3x25 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was chromatographed over a silica gel column. Elution of the column with 10% EA in PE gave a solid of 5-Benzoyl-4-phenylbicyclo[2.2.2]oct-5-en-2-one (**26a**, 1.20 g, 40%), mp 97-98 ^{o}C, as colorless crystals after recrystallization from ether-PE (1:7) mixture. Anal. calcd. for $C_{21}H_{18}O_2$**:** C, 83.42; H, 6.00; found C, 83.31; H, 6.15. HRMS Calcd. for $C_{21}H_{18}O_2$**:** $[M+Na]^+$ 325.1205, found**:** 325.1208; Ir (KBr) ν_{max} (cm^{-1})**:** 2918 (C-H), 1724 (C=O), 1660 (C=O), 1596 (C=C), UV(MeCN) λ_{max}(nm)**:** 259 (logε 4.01), 283 (3.6), 345 (2.4); ^{1}H-NMR δ (ppm)**:**1.95-2.04 (m, 1H), 2.12-2.32 (m, 3H), 2.48 (d, *J* 18.4, 1H), 2.77 (dd, *J* 18.4 and 3 Hz, 1H), 3.49 (br m, 1H), 6.66 (d, *J* 6.6 Hz, 1H), 7.17-7.30 (m, 5H), 7.41-7.59 (m, 3H), 7.76-7.78 (m, 2H); ^{13}C NMR δ(ppm) **:** 2.9 (CH_2), 31.4 (CH_2), 46.5 (CH_2), 47.7 (C), 49.4 (CH), 125.9 (C), 126.1 (CH), 126.6 (CH) 128.28 (CH), 128.31 (CH), 129.5 (CH), 132.9 (CH), 134.8 (CH), 136.7(C), 142.4 (C), 150.9 (C) 193.7 (CO), 209.5 (CO).

6 (b)Synthesis of 5,6-Dibenzoyl-4-phenyl-bicyclo[2.2.2]oct-5-en-2-one (26b)

The trimethyl-(5-phenyl-cyclohexa-1,5-dienyloxy)-silane (**27a**, 3.66 gm, 15 mmol) was prepared from the 3-Phenylcyclohexenone by the same procedure as mentioned in the preparation of **26a**. Dry benzene (3 mL) and a solution of DBA (**28b**, 2.34 gm, 10 mmol) in dry benzene (10 mL) were immediately added to the diene and the mixture was stirred for overnight under inert atmosphere. After that 5% methanolic–HCl (5 mL) was added to it and the mixture was stirred for additional 20 min. After removal of MeOH, the mixture was extracted with ether (3x25 mL). The organic phases were combined, dried over Na_2SO_4, and evaporated in *vacuo*. The residue was filtered through a small column with 10% EA in PE which gave a solid of 5,6-Dibenzoyl-4-phenyl-bicyclo[2.2.2]oct-5-en-2-one (**26b**, 3.41 g, 84%), mp 224-226 ^{0}C, as colorless crystals after recrystallization from DCM–PE (1:10) mixture. Anal. Calcd. for $C_{28}H_{22}O_3$**:** C, 2.74; H, 5.46; Found**:** C, 82.91; H, 5.38; HRMS Calcd for $C_{28}H_{22}O_3$**:** $[M+Na]^+$ 429.1467; Found**:** 429.1462; *IR (neat)* ν_{max} (cm^{-1})**:** 3060, 2979, 2935, 2860(C-H), 1726 (C=O), 1666 (C=O), 1647 (C=O), 1595(C=C); UV (MeCN) λ_{max} (nm)**:** 255 (log ε 4.01), 283 (3.6), 343 (2.4); ^{1}H-NMR δ (ppm)**:** 2.15-2.32 (m, 3H), 2.55 (d, J 18.5 Hz) superimposed with 2.50-2.59 (m) total 2H, 3.04 (dd, J 18.5 and 3.3 Hz, 1H), 3.82 (t, J 2.5 Hz, 1H), 7.12-7.49 (m, 15H); ^{13}C NMR δ (ppm)**:** 23.9 (CH_2), 31.3 (CH_2), 45.5 (CH_2), 49.1(C), 51.1 (CH), 126.6 (CH), 127.2 (CH), 128.25 (CH), 128.29 (CH), 128.34 (CH), 129.1 (CH), 133.0 (CH), 133.15 (CH), 136.1 (C), 137.1 (C), 138.4 (C), 140.3 (C), 154.8 (C), 193.3 (CO), 195.4 (CO), 208.4 (CO).

6(c) Synthesis of 5,6-Dibenzoyl-4-isopropenyl-bicyclo[2.2.2]oct-5-en-2-one (26c):

To a solution of freshly distilled di-isopropylamine (2.1 mL, 15 mmol) in dry THF (20 mL) n-butyllithium (8 mL of 1.5 M solution in hexane, 12 mmol) was added dropwise under argon atmosphere at -78 ^{o}C. Temperature of the reaction bath was then slowly raised to -10 ^{o}C and then again cooled to -78 ^{o}C after 30 min. A solution of 3-Isopropenyl-cyclohex-2-enone (1.36 g, 10.0 mmol) in dry THF (5 mL) was added in drops to the reaction mixture for a period of 2-3 min via syringe when the color of the solution turned deep yellow. Stirring was continued for additional 5 min at -78 ^{o}C, and then the reaction mixture was quenched rapidly with freshly distilled chlorotrimethylsilane (2 mL, 15 mmol). Stir brought to room temperature during next 1 h. The solvent was removed under reduced pressure followed by immediate flushing of the reaction vessel with argon. The residue was stirred three times with dry n-pentane (3x15 mL) under inert atmosphere and the supernatant liquid was transferred very carefully via a cannula to an oven dried thoroughly argon flushed flask. The total solvent (~45 mL) was then removed in vacuo to get the pale yellow liquid of trimethyl(5-Isopropenylcyclohexa-1,5-dienyloxy)silane (**27b**).[23] Dry benzene (5 mL) and a solution of DBA (**28b**, 1.638 gm, 7 mmol) in dry benzene (5 mL) were immediately added to the diene and the mixture was stirred for 6 h under inert atmosphere. A solution of 5% methanol-HCl (5 mL) was added to it and the mixture was stirred for additional 20 min. After removal of MeOH the mixture was extracted with ether (3x25 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was chromatographed over a silica gel column. Elution of the column with 15% EA in PE gave a solid of 5,6-Dibenzoyl-4-isopropenyl-bicyclo[2.2.2]oct-5-en-2-one (**26c**,1.09 g, 43%), mp 144-146 °C, as colorless crystals after recrystallization from DCM–PE (1:10) mixture. Anal. Calcd. for $C_{25}H_{22}O_3$**:** C, 81.06; H, 5.99; Found**:** C, 80.95; H, 6.08; HRMS Calcd for $C_{25}H_{23}O_3$**:** $[M+H]^+$ 371.1321, found**:** 371.1327; IR (neat) ν_{max} (cm^{-1})**:** 2869 (C-H), 1722 (C=O), 1664 (C=O), 1595 (C=C); UV (MeCN) λ_{max} (nm)**:** 256 (log ε 3.7), 284 (3.4), 346 (2.3); ^{1}H NMR δ (ppm) **:** 1.64 (s, 3H), 1.91-1.99 (m, 1H), 2.06-2.22 (m, 2H), 2.29 (d, *J* 18.5 Hz) superimposed with 2.26-2.35 M total 2H, 2.79 (dd, *J* 18.5 and 2.9 Hz, 1H), 3.73 (t, *J* 2.7 Hz, 1H) 4.96 (s, 1H), 4.98 (s, 1H), 7.24-7.51(m, 10H); ^{13}C NMR δ (ppm)**:** 21.6 (CH_3), 24 (CH_2), 29.9(CH_2), 44.2(CH_2), 50.9(C), 51.1(CH), 114.5 (=CH_2), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.2 (CH), 133.3 (CH), 133.5 (CH), 136.5 (C), 137.1 (C), 139.2 (C), 44.1 (C), 152.7 (C), 194.8 (CO), 208.9 (CO).

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[23] This diene is highly susceptible towards even trace amount of moisture and maintaining the inert atmosphere throughout the process is very important.