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# Formation of exceptionally stable ketene during photo transformations of Bicyclo[2.2.2]oct-5-en-2-ones having mixed chromophores

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## Abstract

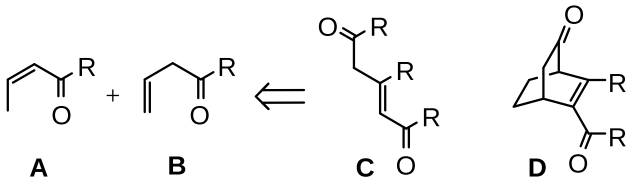
Photoreaction of Bicyclo[2.2.2]oct-5-en-2-ones having mixed chromophores like 5,6 dibenzoyl moiety and phenyl or isopropenyl like electron withdrawing groups at the bridgehead position have been checked in different solvent and different wavelength. In all cases regioselective 1,5-photophenyl migration leading to vinyl ketenes from more congested site of the molecule to the less one have been observed. The ketenes were exceptionally stable both in air and in solution. Its stability studies in acetonitrile through time dependent UV absorbance spectra revealed that it remained almost unchanged at least for couple of weeks.

## Keywords

Bridgehead position; enones; ketene; mixed chromophores

# Introduction

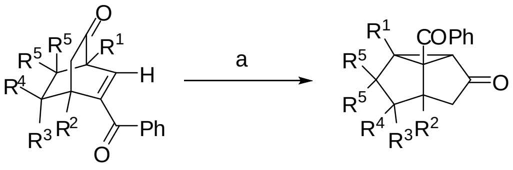
Enones exhibit a rich and diverse photochemistry. The deep-seated photochemical rearrangements found in these systems have attracted numerous mechanistic studies. In this context, the photochemistry of α,β- enone (**A**) and β,γ-enone (**B**) has become an actively researched area for more than two decades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



For several years our laboratory (S. Lahiri et al.) is primarily engaged in synthesizing various types of such multichromophoric systems to compare their photochemistry in detail [9a-f]. Since in acyclic enones like (**C**), E-Z photoisomerization becomes one of the major energy dissipation pathways, we selected rigid bicyclic multichromophoric enones like (**D**) to minimize this route. Although such rigid systems may be considered as α,β- or β,γ-enone with δ-keto conjugation, in one of our recent work [10], we have established that the system should be considered as α,β-enone with δ-keto homoconjugation.

Simple β,γ-enone systems show absorption band at about 210-250 nm characterized for ($\pi,\pi^*$) and at around 280-300 nm characterized for ($n,\pi^*$) transition. However, enone (**D**) shows enhanced intensity of $(n,\pi^*)$ absorption band near 300 nm (logε ~3.5), along with an additional weak $(n,\pi^*)$ absorption band near 350 nm (logε ~2.0), probably due to interactions of these two chromophores[11]. In many cases probable unselective populations of the excited states owing to the presence of these two individual chromophores are expected to give rise to different photoproduct(s) and in some cases distribution of these photoproducts may be wavelength dependent [11].

In order to check photoreaction of such enones, we observed complete 1,2-acyl shift photoproduct (1,2-AS) formation when **1a-i** have been irradiated (Scheme1)[9f, 10]. We also observed that such rearrangement took place very efficiently via triplet mediated pathway without use of any external sensitizer. Similar to bicyclic system, some of the tricyclic system like **1h** also yielded 1,2-AS product under similar reaction condition. Regarding the mechanism, initially there was a delama between the oxa-di-π-methane path (ODPM, characteristic of β,γ-enone moiety) and Type-B path (characteristic of α,β-enone moiety). However, with the help of PET reaction and photoreaction of partially olefinated product of the same, we have recognized that in a mixed α,β- and β,γ-enone system, the photorearrangement route is selectively from the α,β-enone part and we confirmed that the irradiation follows Type B rearrangement [10].

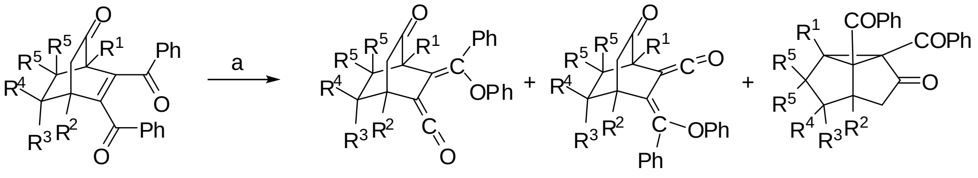


**1a-h** **2a-h**

where,
a: $R^1=R^2=R^3=R^4=R^5=H$
b: $R^1=CH_3$, $R^2=R^3=R^4=R^5=H$
c: $R^1=R^3=R^4=R^5=H$, $R^2=CH_3$
d: $R^1=R^2=CH_3$, $R^3=R^4=R^5=H$
e: $R^1=R^2=R^5=H$, $R^3=R^4=CH_3$
f: $R^1=R^2=R^3=R^4=H$, $R^5= CH_3$
g: $R^1=R^3=R^4=H$, $R^2=R^5=CH_3$
h: $R^1=R^3=R^5=H$, $R^2\text{-}R^4=(CH_2)_4$

**Scheme 1:** Reagent and condition: a) hv, solution

Another interesting sets of competitive 1,5-(C-O) acyl shift rearrangement with that of 1,2-acyl shift were observed when photoreaction of bridged bicyclic systems like **2a-g** were carried out [9a-e]. Such molecules contain δ-keto-α,β-enone system juxtaposed with *cis*-dibenzoylalkene moiety. Interestingly, photoreaction of **2a-f** were found to follow regioselective 1,5-photo-phenyl migration from more congested site of the molecule to the less one leading to formation of vinyl ketenes **3c-f** and **4b,d,f** along with the formation of 1,2-acyl shift **5a-d,g** (Scheme **2**). Some of the vinyl ketenes were stable enough to be kept at room temperature upto 24 hours together as verified by time dependent absorption spectra. Since for the conversion of these molecules, no external sensitization was needed it indicates the involvement of an efficient ISC in such systems to reach to the triplet state. Further fascinating aspects is that the two competitive pathways *viz*. 1,2-acyl shift and 1,5–photo-phenyl migration has been found to be subtly dependent on the substitution pattern. For instances, the rate of 1,2-acyl migration route in **2b** has been found to be much faster than **2e** probably due to the extra interferences of gem-dimethyl substitutions at C-7 position in the latter one. Moreover when **2g** was irradiated, we got only ODPM rearranged product [9b].

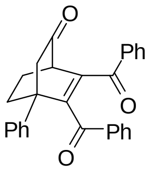


**2a-f** **3c-f** **4b,d,f** **5a-d,g**

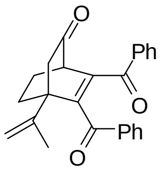
where,
a: $R^1=R^2=R^3=R^4=R^5=H$
b: $R^1=CH_3$, $R^2=R^3=R^4=R^5=H$
c: $R^1=R^3=R^4=R^5=H$, $R^2=CH_3$
d: $R^1=R^2=CH_3$, $R^3=R^4=R^5=H$
e: $R^1=R^3=R^4=H$, $R^2=R^5=CH_3$
f: $R^1=R^3=R^4=R^5=H$, $R^2=OCH_3$
g: $R^1=R^3=R^5=H$, $R^2\text{-}R^4=(CH_2)_4$

**Scheme 2:** Reagent and condition: a) hν, solution

In all of the molecules the bridgehead positions contain only electron donor groups (like OMe, Me or H), but same type of rigid enones having electron acceptor group at the bridgehead positions have not been checked so far. To bridge this gap we carried out the photoreactions of 5,6-dibenzoyl-4-phenylbicyclo[2.2.2]oct-5-en-2-one (**6**) and 5,6-dibenzoyl-4-isopropenylbicyclo-[2.2.2]oct-5-en-2-one (**7**) in detail. Both of the molecules at its bridgehead position (C-4) contain electron acceptor groups like phenyl & vinyl and these groups were bulkier than the earlier reported one.



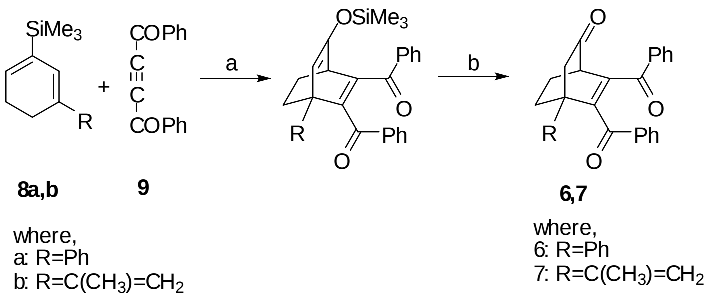
**6**



**7**

# Results and Discussion

5,6-dibenzoyl-4-phenylbicyclo[2.2.2]oct-5-en-2-one (**6**) and 5,6-dibenzoyl-4-isopropenylbicyclo[2.2.2]oct-5-en-2-one (**7**) have been prepared through [4+2] Diels Alder cycloaddition reaction between substituted silyoxy cyclohexa-1,3-dienes (**8a-b**) [12, 13] and dibenzoyl acetylene (**9**) followed by hydrolysis of the silyoxy adduct (Scheme **3**).

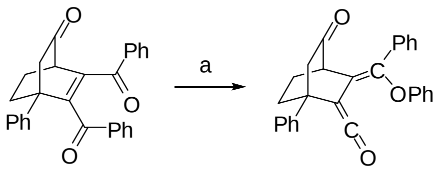


**Scheme 3:** Reagent and condition: a) dry benzene, overnight stirring under argon, b) 5% methanolic–HCl (5 mL), 20 min

Like UV spectrum of all types of δ-keto-α,β-enone, both of the **6** and **7** showed enhanced (n,π*) absorption band near 300 nm (log ε~3.5) along with an additional weak band near 343 nm (log ε~2.5) in their UV spectrum.

### Photoreaction of 6

In benzene: Irradiation of degassed solution of **6** in benzene at 254 nm for 3h yielded only a yellow solid of vinyl ketene (Z)-5-formyl-6-(phenoxy(phenyl)methylene)-4-phenyl-bicyclo[2.2.2] octan-2-one (**10**, 38%) (Scheme **4**) and we didn't get any 1,2-AS photoproduct.



**6** **10**

**Scheme 4:** Reagent and condition: a) hν, benzene

The structure of the ketene **10** was arrived at from its analytical and spectral data. The ketene band $\gamma_{C=C=O}$ was detected in IR spectrum at 2087 cm$^{-1}$ and the ring ketone appeared at 1730 cm$^{-1}$. The ketene **10** was exceptionally stable both in air and in solution. Its stability studies in acetonitrile through time dependent absorbance spectra (Fig.**1**) revealed that it remained almost unchanged at least for eight weeks.

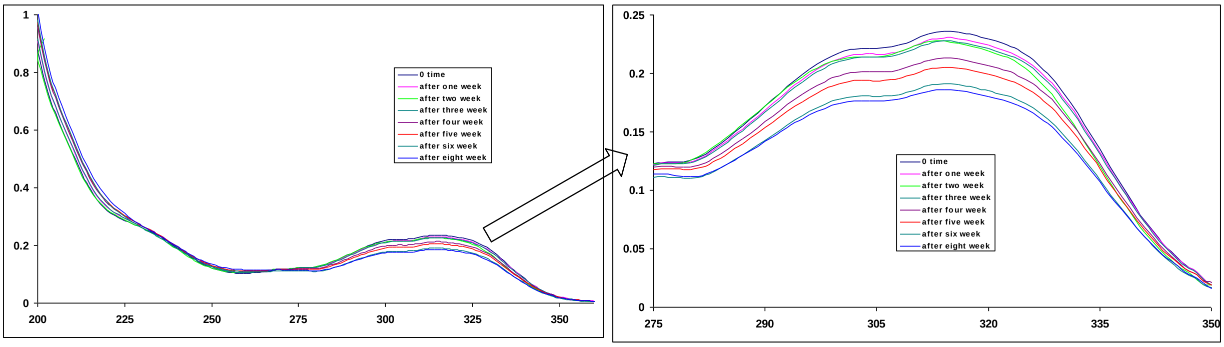
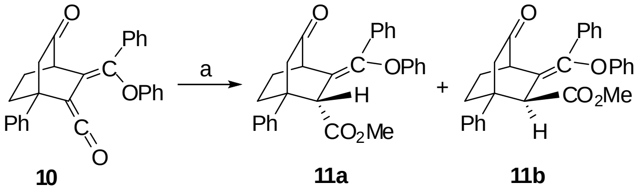


Fig.**1**: Time dependent absorbance spectra of **10** in acetonitrile

Such photoinduced intramolecular 1,5-phenyl migration from carbon to proximate oxygen is a general reaction route for cis-dibenzoylalkene chromophore [14] and in unsymmetrical derivatives such migrations have been found to take place from the benzoyl group attached to the more crowded olefinic carbon atom to the less one. Similar behavior has been noticed in our laboratory in such bicyclo[2.2.2]octenone systems [9e]. Thus, selective formation of **10** from **6** appeared to be an expected process with only exception that the ketene **10** was unusually stable.

The regio-selective formation of **10** was further confirmed by converting it quantitatively to the corresponding methyl esters: (2R,Z)-methyl 5-oxo-3-(phenoxy(phenyl)methylene)-1-phenylbicyclo[2.2.2] octane-2-carboxylate (**11a**) and (2S,Z)-methyl 5-oxo-3-(phenoxy(phenyl)methylene)-1-phenylbicyclo[2.2.2]-octane-2-carboxylate (**11b**) by its overnight refluxing with methanol (Scheme **5**). NMR spectrum of the crude reaction mixture indicated the presence of **11a** and **11b** in a (1:6) ratio. Since the polarity of the two methyl esters are very close, we could not isolate it through column chromatography. However, through repeated preparative TLC, we could separate **11a** only in a trace amount.



**Scheme 5:** Reagent and condition: a) methanol, reflux, overnight

In methanol: When a degassed solution of **6** in methanol was irradiated under similar reaction condition, a mixture of methyl esters **11a** and **11b** was obtained in same 1:6 ratios with a moderate yield (60%).

Carrying out the reaction of **6** in other solvents like acetone and acetonitrile at different wavelength did not bring about any change in the reaction and only the yellow solid of vinyl ketene **10** was isolated in moderate yields in all the cases (Table **1**).

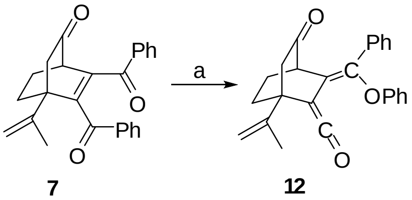
**Table 1:** Result of photo reaction of **6** at various wavelengths in different solvents

| Wavelength (nm) | Solvent | Time (h) | Product 10 (%)a | Recovered 6 (%) |
|---|---|---|---|---|
| 254 | Benzene | 3 | 38 | 49 |
| | Acetonitrile | 3 | 54 | 35 |
| | Acetone | 3 | 44 | 42 |
| 300 | Benzene | 5 | 46 | 34 |
| | Acetonitrile | 5 | 41 | 42 |
| | Acetone | 5 | 49 | 40 |
| 350 | Benzene | 5 | 43 | 46 |
| | Acetonitrile | 5 | 49 | 39 |

**a**: isolated yield

**Photoreaction of 7:**

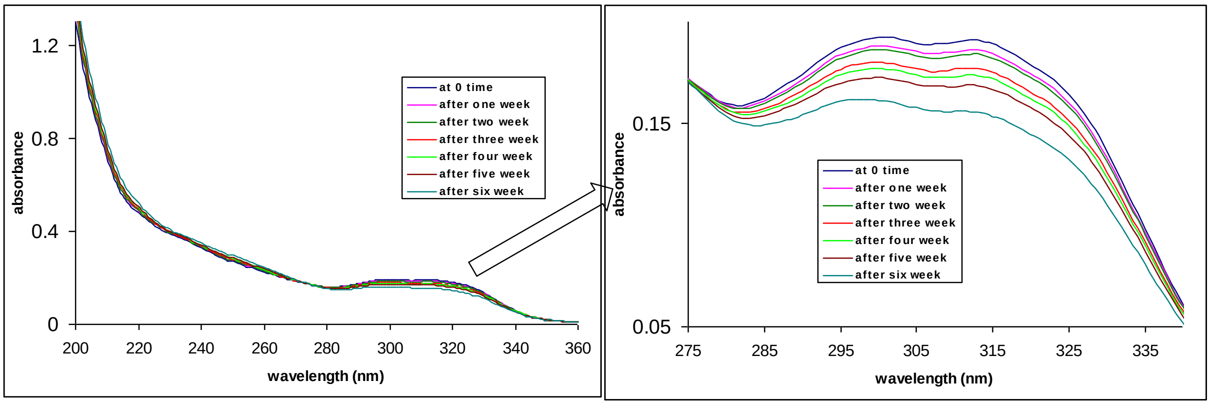
In benzene: Irradiation of degassed solution of **7** in benzene at 254 nm for 4h also yielded only a yellow solid of vinyl ketene (Z)-5-formyl-6-(phenoxy(phenyl)methylene)-4-(prop-1-en-2-yl)bicyclo [2.2.2]octan-2-one (**12,** 32%) (Scheme **6**).



**Scheme 6:** Reagent and condition: a) hv, benzene

The structure of the ketene **12** was also established from its analytical and spectral data. Like **10**, the vinyl ketene **12** was also found to be exceptionally stable in solution. The UV absorbance spectrum of **12** in acetonitrile has been recorded at different time intervals which showed only a minute change in its absorption spectra even after six weeks (Fig.**2**).

Fig.**2**: Time dependent absorbance spectra of **12** in acetonitrile



Irradiation under similar reaction condition yielded the same photoproduct **12** both in acetonitrile and acetone. However, in no cases we found alternative 1,2-AS photoproduct. Even changing in wavelength had no effect on reactivity and similar results were also obtained at 300 nm. The results are summarized in (Table **2**).

**Table 2** Result of photo reaction of **16** at various wavelengths in different solvents

| Wavelength(nm) | Solvent | Time (h) | Product 12 (%)a | Recovered 7 (%) |
|---|---|---|---|---|
| 254 | Benzene | 4 | 32 | 54 |
| | Acetonitrile | 4 | 38 | 51 |
| | Acetone | 4 | 33 | 47 |
| 300 | Benzene | 5.5 | 41 | 51 |
| | Acetonitrile | 5.5 | 40 | 47 |

**a**: isolated yield

# Conclusion

Thus it may be concluded that the presence of electron withdrawing bulky group at the bridgehead position of bicyclo[2.2.2]oct-5-en-2-ones juxtaposed with *cis*-

dibenzoylalkene moiety facilitates the regioselective 1,5-photophenyl migration from more congested site of the molecule to the less one leading to the formation of exceptionally stable vinyl ketenes and the process is faster than any other rearrangement route. Since no sensitization is required throughout the process, we may conclude that the reaction moves via triplet mediated pathway. Since in no instances we get 1,2-acyl shift product, we may also conclude that β,γ-enone part is inactive while *cis*-dibenzoylalkene like α,β-enone part of such multichromophoric bicyclic system is only active part for such photorearrangement.

# Experimental

Full details of the synthesis, photochemical studies and spectra of all new compounds can be found in Supporting Information File 1.

# Acknowledgements

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