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Photochemical reactions of 1-methoxymethylbicyclo[4.3.0]non-6-en-8-one and 5-methoxymethylbicyclo[3.3.0]oct-1-en-3-one

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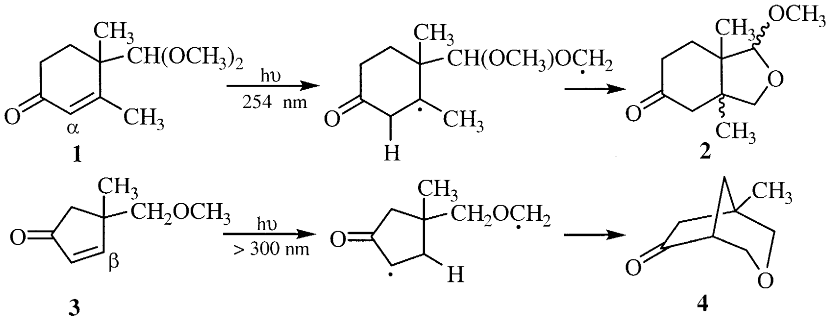
Abstract

Irradiation of the title compounds **5** and **6** with light of wavelengths 350 and 254 nm afforded products in different ratios. Abstractions of hydrogen atoms of the methoxyl groups by both C_α and C_β are the primary photochemical reactions leading to various products, but the total yield of the products derived from C_β H-abstraction increased when light of wavelength 350 nm was used. Plausible mechanisms for the formation of the products are proposed. © 2000 Elsevier Science Ltd. All rights reserved.

The photochemical intramolecular hydrogen abstraction of cyclic α,β-unsaturated ketones has attracted considerable attention.[1] Cyclohexenone **1**, for instance, underwent C_α H-abstraction upon $\pi\rightarrow\pi^*$ excitation (254 nm) to give inter alia cyclic ether **2**.[2] In contrast, cyclopentenone **3** underwent C_β H-abstraction upon $n\rightarrow\pi^*$ excitation (>300 nm) to generate **4**.[3] Our interest in the effect of ring size on the photochemical behavior of bicyclic enones[4] led to the investigation of the photochemistry of **5** and **6**.[5] The results reveal that their photochemical reactions depend on the wavelength of incident light.



Compounds **5** and **6** exhibit UV absorption maxima at 223 (ε 1.3×10^4), 325 (ε 47) nm and 222 (ε 1.7×10^4), 320 (ε 33) nm, respectively. The deoxygenated solutions (purged with argon for 45 min) of **5** and **6** in isooctane (0.01 M) were irradiated either in Pyrex tubes with light of wavelength centered

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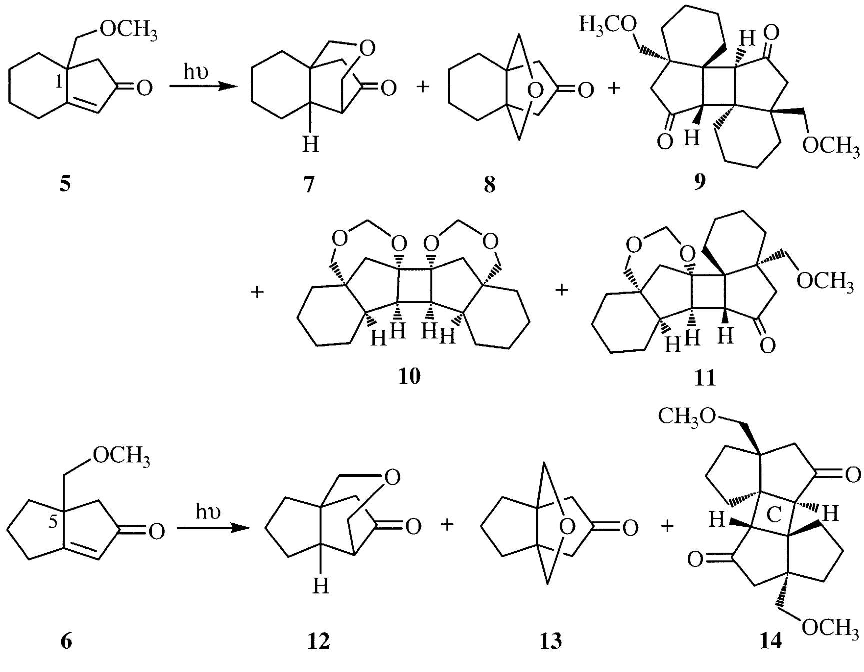
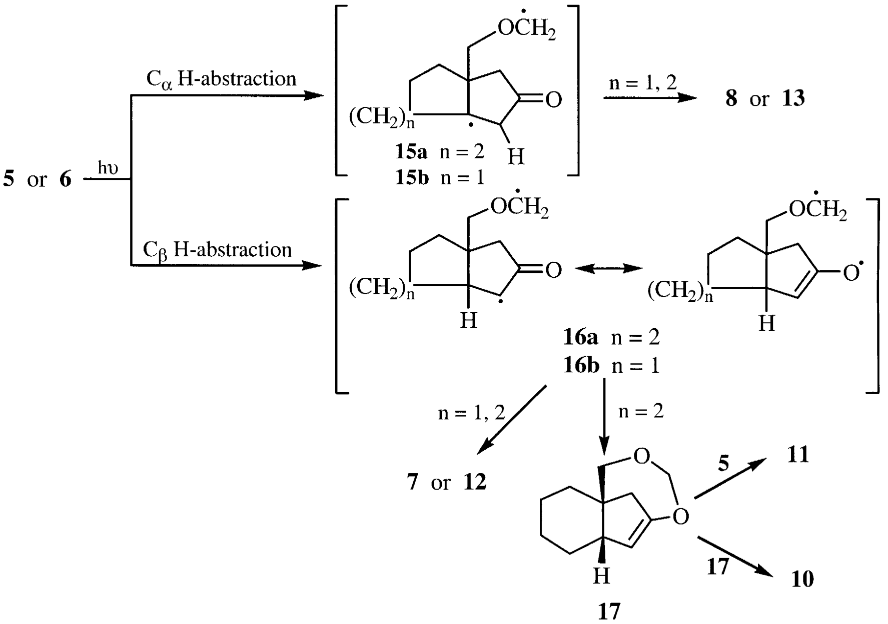
at 350 nm or in quartz tubes with light of wavelength at 254 nm with a Rayonet reactor. TLC analysis indicated that a complex mixture was produced in each case. Products were isolated and purified by means of flash chromatography, vacuum distillation (bulb-to-bulb) and recrystallization; the yields appear in Table 1. The structures of photoproducts **7**–**14** were assigned based on their IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. The assignments of **9**, **10**, **11** and **14** were further confirmed by an X-ray diffraction method.[6] Compounds **9** and **14** are shown to be the *cis,anti,cis* head-to-tail dimers of **5** and **6**, respectively. 2-Cyclopentenone is known to give head-to-tail dimer as the major product, especially in dilute hydrocarbon solvent.[7]

Table 1
The conditions and yields of the photoproducts of **5** and **6** in isooctane

Entry	Enone	hυ/nm	Reaction Time/h	Conversion/%	Product (Yield/%)
1	**5**	350	10	91	**7**(44), **8**(2), **9**(9), **10**(3), **11**(7)
2	**5**	254	4	80	**7**(25), **8**(26), **9**(6)
3	**6**	350	10	86	**12**(51), **14**(4)
4	**6**	254	5	79	**12**(24), **13**(10), **14**(6)



Plausible mechanisms for the formation of other photoproducts are given in Scheme 1. Products **8** and **13** are derived from the abstraction of a hydrogen atom of the methoxyl groups by the C_α atoms of excited states of **5** and **6**, respectively, via seven-membered-ring transition structures followed by ring closure of the ensuing diradicals **15a** (n=2) and **15b** (n=1). An alternative route for the formation of these two compounds via H-abstraction by the oxygen atoms is less likely because of sterically unfavorable eight-membered-ring transition states. Compounds **7** and **12** are similarly produced through **16a** (*n*=2) and **16b** (*n*=1) from hydrogen abstraction by their C_β atoms via six-membered-ring transition states. Compounds **10** and **11** are generated from enol ether **17** which is obtained from the ring closure of **16a** with the formation of a C–O bond; the absence of parallel reactions for **16b** is mainly due to a greater strain of the corresponding tricyclic enol ether. Intermediate **17**, which is of a high strain, is expected to be very reactive because it possesses a bridgehead double bond[8] in a bicyclo[4.2.1]non-1(8)-ene system.[9] The dimerization of **17** gives **10** and the reaction of **17** with **5** yields **11**. It is interesting to note that **10** and **11** possess distinctive regio- and stereochemistry; **10** is a *cis,syn,cis* head-to-head dimer, whereas **11** is a *cis,anti,cis* head-to-tail adduct. The cycloaddition to form **11** may be stepwise;[9d] the head-to-tail manner may be mainly due to a dipole–dipole interaction between the twisted enol ether moiety in **17** and the enone moiety in **5**, whereas the *cis,anti,cis* arrangement may be attributed to a steric factor. The dimerization of **17** leading to **10** may also be stepwise;[9d] the head-to-head arrangement may be due to the ability of oxygen atoms to stabilize the diradical intermediate but an explanation for the preferential *syn* orientation is lacking.



Scheme 1.

That n→π* and π→π* excitations of **5** and **6** resulted in the formation of different types of products indicate that the reactions presumably proceed via distinctive excited states; however, further confirmation requires kinetic studies. The processes of C_α and C_β H-abstractions are competitive; their relative rates depend on the ring size and the nature of excited states of **5** and **6**. C_α H-abstraction is a less efficient process than C_β H-abstraction in the case of n→π* excitation as indicated by the absence of **13** and only 2% of **8**, but these two processes become compatible during π→π* excitation; the yields of **13** and **8** increase to 10 and 26%, respectively. It may be noted that neither product derived from C_α H-abstraction of **3**[3] nor product from C_β H-abstraction of **1**[2] was reported. No attempt was made to investigate the nature of the excited states involved in the photochemical reactions of **5** and **6**; however, an n,π* triplet and an upper (S_2) state (upper triplet states cannot be excluded) were suggested to be responsible for C_β H-abstraction of **3**[3] and C_α H-abstractions of **1**,[2] respectively.

The present study shows that the photochemistry of the title compounds depends on the wavelength of incident light. Both C_α and C_β H-abstractions occur upon n→π* and π→π* excitations, but the relative percentage of C_β H-abstraction increases during n→π* excitation. A strained intermediate **17** underwent dimerization and [2+2] cycloaddition with cyclopentenone **5** in a distinctive regio- and stereochemical manner.

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