

Photochemistry of bicyclo[2.2.2]octenones: an uncommon oxidative decarbonylation

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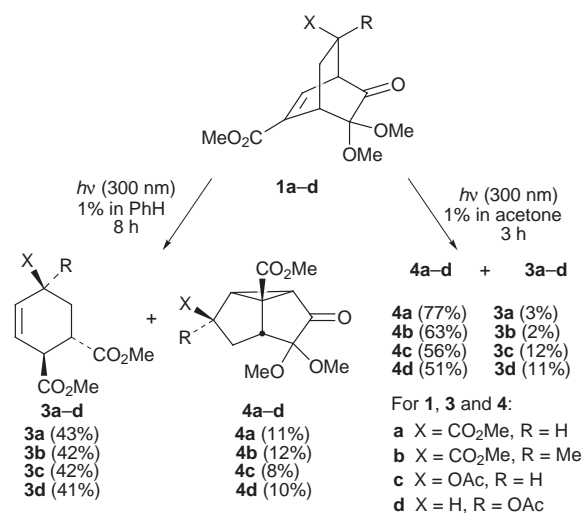
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Several substituted 3,3-dialkoxy-5-methoxycarbonylbicyclo[2.2.2]oct-5-en-2-ones underwent unusual oxidative decarbonylation to produce polysubstituted cyclohexenes upon direct irradiation and usual ODPM rearrangement under sensitized conditions. A plausible mechanism for the oxidative decarbonylation is also given.

Bicyclo[2.2.2]octenones, with an embedded β,γ -unsaturated carbonyl chromophore, are rich with photochemistry.¹ They are known to undergo a variety of photochemical reactions such as decarbonylation, ketene extrusion, 1,3-acyl shift and most importantly the 1,2-acyl shift, also known as oxa-di- π -methane (ODPM) rearrangement, depending on reaction conditions, substrate structure and the wavelength of the incident light.¹ Apart from the ODPM rearrangement, and the 1,3-acyl shift,²⁻⁴ other reactions of bicyclo[2.2.2]octenones or β,γ -unsaturated ketones in general have been considered as undesirable side reactions and received little attention.⁵ This may be due to the fact that these fragmentation reactions were observed only when the desired ODPM rearrangement or 1,3-acyl shift are inefficient processes for the given substrate or when the substrate undergoes reactions in indeterminate modes. Furthermore, these reactions appear to be more structure dependent and selectively affecting them may not always be possible. Apparently, the synthetic potential of decarbonylation has remained unexplored apart from a few cases.

We have been interested in this area of research for sometime and we have already employed the ODPM rearrangement reactions of bicyclo[2.2.2]octenones in the synthesis of iridoids and both angular and linear triquinanes.^{6,7} In continuation of our efforts towards exploitation of the synthetic potential of bicyclo[2.2.2]octenones,⁸ a study of the photochemical reactions of compounds **1** and **2** was contemplated. We now report that direct irradiation of bicyclo[2.2.2]octenones **1** and **2** in benzene results in the production of stereochemically pure polysubstituted cyclohexenes and under sensitized conditions **1** and **2** yield the usual ODPM rearrangement products in fair yields as one of the major isolable products (Schemes 1 and 2). To the best of our knowledge such formation of cyclohexenes *via* photochemical oxidative decarbonylation of bicyclo[2.2.2]octenones is unprecedented.

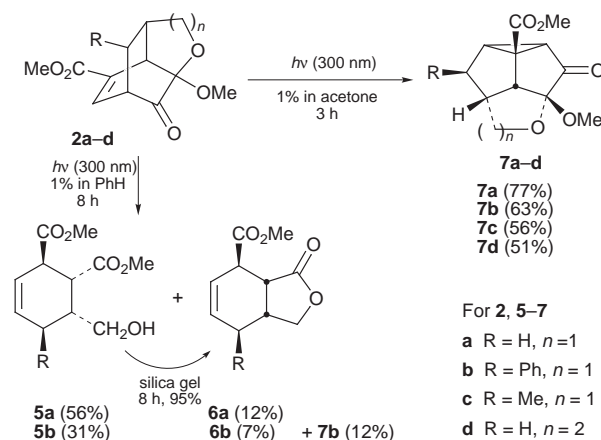
Accordingly the required bicyclo[2.2.2]octenones **1a-d** were prepared *via* intermolecular Diels-Alder reactions of methyl acrylate, methyl methacrylate and vinyl acetate with masked *o*-benzoquinone generated *in situ* by the oxidation of methyl vanillate using diacetoxyiodobenzene in MeOH. Compounds **2a-d** were prepared *via* intramolecular Diels-Alder reactions of masked *o*-benzoquinones generated by the oxidation of methyl vanillate in presence of allyl alcohol, crotyl alcohol, cinnamyl alcohol and homoallyl alcohol in CH₂Cl₂ using the procedure developed in our laboratory.⁹ Direct irradiation of compounds **1a-d** in benzene (1% w/v) using light of wavelength centered at 300 nm in a Rayonet reactor for about 8 h furnished cyclohexenes **3a-d** in 41–43% yield along with ODPM rearrangement products **4a-d** in about 8–12% yield. However, irradiation of **1a-d** in acetone for 3 h produced the expected ODPM rearrangement products **4a-d** in 51–77% yield along with 2–12% of **3a-d** (Scheme 1).



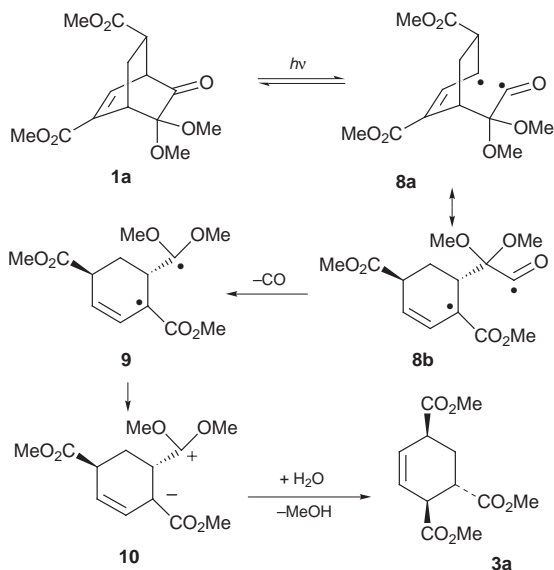
Scheme 1

On the other hand, irradiation of **2a** in benzene provided the expected cyclohexene **5a** and the corresponding lactone **6a** in a total yield of 68%. No ODPM rearrangement product could be observed. In contrast, **2b** provided both decarbonylated products **5b** and **6b** as well as ODPM rearrangement product **7b**. Both **5a** and **5b** could be transformed into **6a** and **6b** respectively by treatment with silica gel in EtOAc. The reaction mixtures obtained upon irradiation of **2c** and **2d** in benzene could not be separated into individual compounds. However, irradiation of **2a-d** in acetone furnished the expected ODPM rearrangement products **7a-d** in good yields (Scheme 2).

All the new compounds were thoroughly characterized *via* their IR, ¹H (400 MHz) and ¹³C NMR, DEPT, low and high resolution mass spectral analyses. The relative stereochemistry of compounds **3a**, **4b**, **6b** and **7c** was unambiguously established with the aid of ¹H-¹H COSY and NOESY spectra. The stereochemical assignments of their analogues were based on analogy and coupling constants.

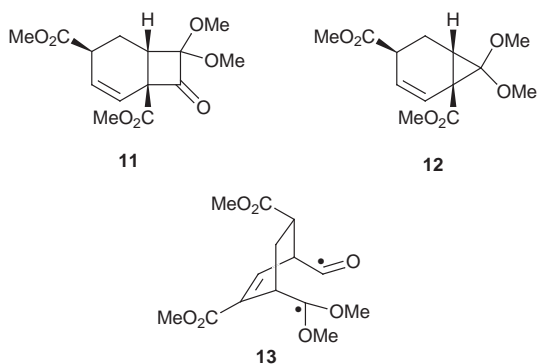


Scheme 2



Scheme 3

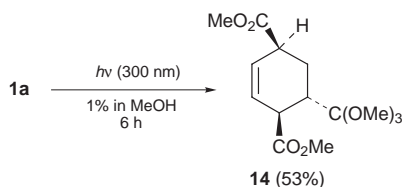
The following mechanism is believed to be responsible for the formation of cyclohexenes upon direct irradiation of compounds **1** and **2** (Scheme 3). The initial Norrish type I α -cleavage of the C₁-C₂ bond results in the diradical species **8**.¹⁰ The diradical **8**, instead of undergoing 1,3-acyl shift to provide the cyclobutanone derivative **11**, undergoes decarbonylation to



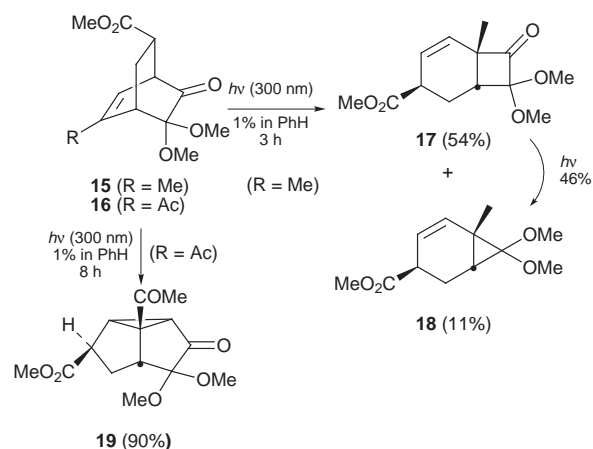
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result in the relatively more stable diradical **9**. The diradical **9** fails to cyclize to provide the cyclopropane derivative **12**, and instead results in the zwitterion **10**, which upon stereoselective abstraction of a proton from the traces of water present in benzene followed by hydrolysis provides **3a**. An alternative pathway for the formation of **11** via the diradical **13**, which in turn could result from C₂-C₃ bond cleavage, cannot be ruled out. The intermediacy of the zwitterion gained support from the formation of the orthoester **14** as the sole isolable product when compound **1a** was irradiated in MeOH at 300 nm (Scheme 4).

The fact that both **11** and **12** were not observed indicates that the recyclization, prior to decarbonylation (1,3-shift) or fol-



Scheme 4



Scheme 5

lowed by decarbonylation, is constrained probably by electronic factors. The stability of the zwitterion **10** appears to be the driving force for the preferential decarbonylation against formation of strained cyclobutanone **11** or cyclopropane **12**. In order to verify this hypothesis, compound **15** (R = Me) was irradiated under identical conditions to obtain both 1,3-acyl shift product **17** and cyclopropane **18**. On the other hand, irradiation of **16** in benzene at 300 nm furnished ODPM rearrangement product **19** in 90% yield (Scheme 5). Obviously, the C-5 ester group is responsible for prevention of 1,3-acyl shift and formation of cyclopropane.

Nevertheless, these reactions provide an easy access to stereochemically defined polysubstituted cyclohexenes and tricyclo[3.3.0.0^{2,8}]octanones of established synthetic potential. Furthermore the starting materials are obtained from inexpensive aromatic compounds in excellent yields. In conclusion the present study has unravelled previously unknown photochemical behavior of a type of bicyclo[2.2.2]octenones.

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Notes and references

- 1 K. N. Houk, *Chem. Rev.*, 1976, **76**, 1; D. I. Schuster, in *Rearrangements in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980, vol. 3, p. 167.
- 2 H. E. Zimmerman and D. Armesto, *Chem. Rev.*, 1996, **96**, 3065 and references cited therein.
- 3 M. Demuth and K. Schaffner, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 820.
- 4 V. Singh and M. Porinchu, *J. Chem. Soc., Chem. Commun.*, 1993, 134.
- 5 S. Katayama, H. Hiramatsu, K. Aoe and M. Yamauchi, *J. Chem. Soc., Perkin Trans. 1*, 1997, 561.
- 6 C.-C. Liao and C.-P. Wei, *Tetrahedron Lett.*, 1989, **30**, 2255.
- 7 J.-T. Hwang and C.-C. Liao, *Tetrahedron Lett.*, 1991, **32**, 6583; D.-S. Hsu, P. D. Rao and C.-C. Liao, *Chem. Commun.*, 1998, 1795.
- 8 C.-S. Chu, C.-C. Liao and P. D. Rao, *Chem. Commun.*, 1996, 1537; T.-H. Lee, C.-C. Liao and W.-C. Liu, *Tetrahedron Lett.*, 1996, **37**, 5897; T.-H. Lee and C.-C. Liao, *Tetrahedron Lett.*, 1996, **37**, 6869; P.-Y. Hsiu, Y.-C. Lee and C.-C. Liao, *Tetrahedron Lett.*, 1998, **39**, 659; W.-C. Liu and C.-C. Liao, *Chem. Commun.*, 1999, 117.
- 9 C.-S. Chu, T.-H. Lee and C.-C. Liao, *Synlett*, 1994, 635.
- 10 C. Bohne, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool and P.-S. Song, CRC Press, New York, 1995, p. 416.

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