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INTRAMOLECULAR PHOTOCHEMICAL CYCLIZATION OF α,α'-DIMETHYLENE DIESTERS

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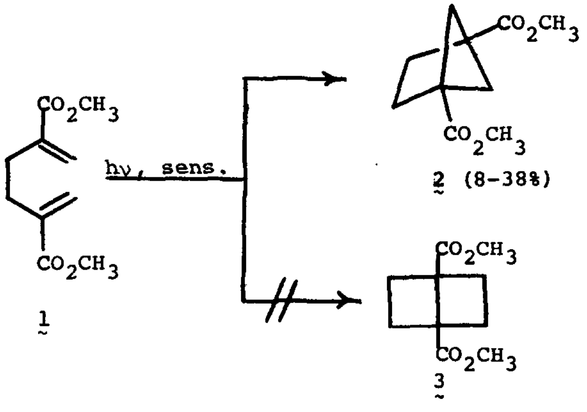
With few exceptions,[1] the intramolecular photochemical cyclization of either cyclic or acyclic 1,5-dienes leads to bicyclo[2.1.1]hexane derivatives[2,3] while 1,6-dienes produce bicyclo[3.2.0]heptane derivatives.[2b,3c,4] As part of our continuing studies on the preparation of bridgehead disubstituted bicyclic compounds as key intermediates in the synthesis of propellanes[5] and paddlanes,[6] the intramolecular photochemical cyclization of α,α'-dimethylene diesters seemed to be a ready entreé into some of the desired systems. We wish to report the results of the photosensitized irradiation of two of these esters which produces the two types of bicyclic products, one for the first time.

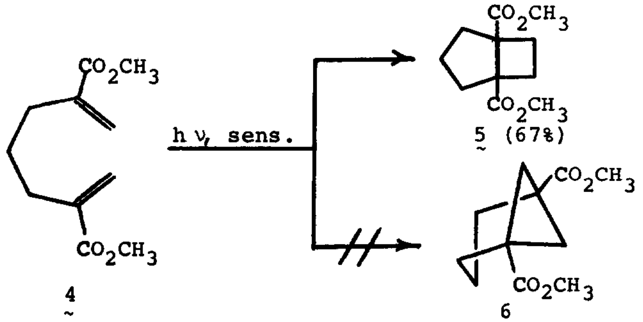
Irradiation [7] of dimethyl-α,α'-dimethylene adipate, 1,[8a] (0.1 - 1% solutions in acetonitrile) with benzophenone photosensitizer at 10° to 63° gave the product of a "crossed" intramolecular cyclization, dimethyl bicyclo[2.1.1]hexane-1,4-dicarboxylate, 2, in yields which varied from 8 to 38% (eq 1). The



(1)

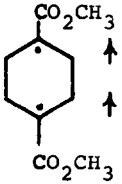
structure of 2 was consistent with its ir, nmr and mass spectra.[9] The product of a "straight" cycloaddition, dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate, 3,[8a] was not observed under conditions in which it could be isolated.

On the other hand, when dimethyl-α,α'-dimethylene pimelate, 4,[11] (0.2% solution in acetonitrile) was irradiated in the presence of benzophenone, it gave the product of a "straight" cycloaddition, dimethyl bicyclo[3.2.0]heptane-1,5-dicarboxylate, 5, in 67% yield (eq 2).[12] The structure and *cis*-stereochemistry of 5 were confirmed by comparison with an authentic sample.[8] No evidence was found for a "crossed" cycloaddition product, dimethyl bicyclo[3.1.1]-heptane-1,5-dicarboxylate, 6, or a *trans* isomer of 5.

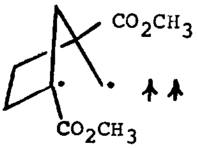


(2)

While our results confirm the propensity of 1,5- and 1,6-dienes to photochemically cyclize to bicyclo[2.1.1]hexanes and bicyclo[3.2.0]heptanes, respectively, the results which we have obtained with 1 cannot be completely rationalized in terms of radical stability. Thus, the most stable diradical formed from triplet 1 would be 7 and not 8. Spin inversion and closure of 7 would



7



8

yield 3, which we do not observe. The proclivity of diradicals such as 7 to fragment to 1,5-hexadienes is well documented,[13] however. Therefore if 7 is formed, it must reopen to triplet 1 and finally close to 8, giving 2 after spin inversion and closure.

References and Footnotes

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(7) In a typical experiment, 12.5 g of **1** and 3.0 g of benzophenone in 2800 ml of acetonitrile were irradiated for 35 h under nitrogen at 63° using a 450 watt Hanovia medium pressure mercury arc and Pyrex filter in the variable temperature photochemical reactor previously described.[8b] A yield of 2.7 g of **2**, bp 65-8°/1 mm and mp 36-8°, was obtained. *Anal*: Calc'd for $C_{10}H_{14}O_4$: C: 60.59; H: 7.12. Found: C: 60.27; H: 6.97.

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(9) Ir: 1735 cm^{-1}; molecular weight (mass spectrum): 198 (Calc'd 198). Nmr: (CCl_4), ppm downfield from TMS: 1.64 (dd-2H); 1.97 (sharp m) and ca. 2.05 (broad m- total 6H) and 3.67 (s-6H). Addition of 50 mg of $Eu(fod)_3$[10] to 50 mg of 2 in 0.5 ml CCl_4 gave: 2.48 (dd-2H); 2.70 (sharp m-4H); 3.21 (broad m-2H) and 4.55 (s-6H).

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(12) A solution of 10.6 g of **4** and 5.0 g of benzophenone in 5-1 of acetonitrile in a 5-1, 3-necked flask fitted with quartz immersion well was irradiated for 10 h under nitrogen at 10° with a 450 watt Hanovia medium pressure mercury arc through a Pyrex filter. A yield of 7.2 g of **5**, bp 75-76°/0.2 mm was obtained. Nmr: (CCl_4), ppm downfield from TMS: 1.6 (m-6H); 2.57 (m-4H) and 3.58 (s-6H). The reported nmr spectrum of **5** had the integrals incorrectly assigned due to a typographical error.[8]

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