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NOVEL DIFFERENCES BETWEEN THE SOLID STATE AND SOLUTION PHASE PHOTOCHEMISTRY OF 1,2-CYCLODECANEDIONE

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Abstract. 1,2-Cyclodecanedione (**1**) undergoes a novel photorearrangement in the crystalline state that is different from the Norrish/Yang type II photocyclization process observed in solution. A possible mechanism is presented and discussed. © 1997 Elsevier Science Ltd.

Medium sized ring and macrocyclic diketones in which the carbonyl groups are separated by an equal number of methylene groups on either side (so-called diametric diketones) display a rich Norrish/Yang type II photochemistry that is strongly dependent upon the medium in which the photolyses are carried out.[1] In the present communication, we report our initial work with the corresponding 1,2-diketones—specifically 1,2-cyclodecanedione (**1**). The solution phase photochemistry of this compound was first investigated over 30 years ago by Urry, Trecker and Winey,[2] who reported that it undergoes type II cyclobutanol formation (Yang photocyclization) when irradiated through Pyrex in benzene. The stereochemistry of the cyclobutanol photoproduct was not elucidated, however, and one of the goals of our work was to establish this feature. Additional goals were (i) to investigate the *solid state photoreactivity* of 1,2-cyclodecanedione, (ii) to establish the *conformational preferences* for 1,2-cyclodecanedione and correlate this information with its reactivity, and (iii) to determine the C=O...H$_\gamma$ *abstraction geometry* for comparison with analogous data from the diametric diketones.

1,2-Cyclodecanedione (λ_{max} 395 nm) was prepared according to the literature procedure[3] and photolyzed in deoxygenated benzene through a uranium glass filter ($\lambda > 340$ nm). At these wavelengths, the cyclobutanol photoproducts 2 ($\lambda_{max} \sim 313$ nm) do not absorb, thus preventing the secondary photochemical reactions of these compounds reported by Urry *et. al.*[2] Under the conditions specified above, two photoproducts were detected by GC in a ratio of 7:1 and in a combined chemical yield of > 97%. These compounds were separated by silica gel column chromatography and identified by spectroscopic analysis as well as by X-ray crystallography.[4] The major photoproduct proved to be *cis*-cyclobutanol 2a (1785 cm^{-1} (C=O), mp 51-52 °C) and the minor isomer was the corresponding *trans*-cyclobutanol 2b (1789 cm^{-1} (C=O), mp 51-52 °C). The quantum yield for disappearance of diketone **1** in benzene was determined to be 0.11 ± 0.01 (benzophenone/benzhydrol actinometry[5]), and quenching studies employing 1,3-cyclohexadiene as quencher showed the photoreaction to be a triplet state process.
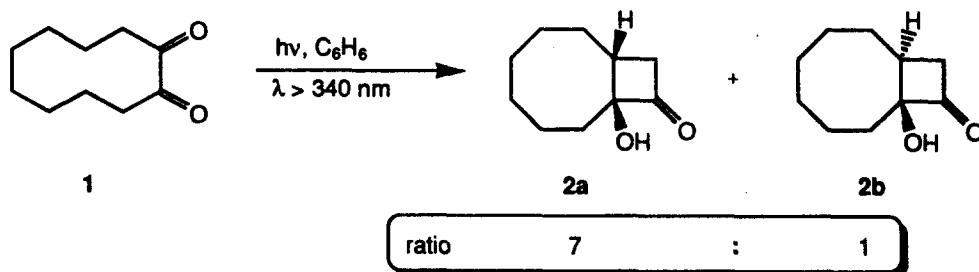
Samples for solid state photolysis were prepared by crushing crystals of diketone **1** between two Pyrex microscope slides and sealing the resulting "sandwiches" in a polyethylene bag under argon. Because 1,2-cyclodecanedione is relatively low melting (mp 41-42 °C), we sought to minimize the problem of melting during photolysis by carrying out the irradiations at -20 °C and limiting conversions to 10% or less. Under these conditions, GC showed that two products were formed in a ratio of 3:2. On the basis of a comparison with an authentic sample prepared independently by a non-photochemical route,[6] the major photoproduct was identified as keto-aldehyde **3**. The minor photoproduct of the solid state photolysis proved to be *cis*-cyclobutanol **2a**.
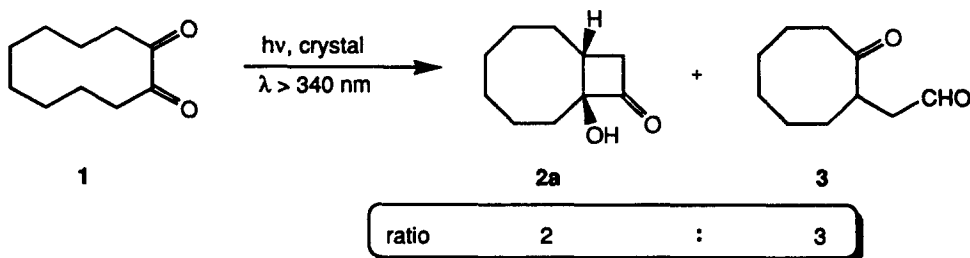

In agreement with experiments indicating that keto-aldehydes can be formed by photolysis of 2-hydroxycyclobutanones,[7] independent irradiation of **2a** through Pyrex (λ > 290 nm), both in the solid state and solution, led to approximately equimolar amounts of keto-aldehyde **3** and cyclooctanone. In their original paper,[2] Urry *et al.* had reported the formation from **2a** of cyclooctanone but not of compound **3**. We repeated the photolysis of compound **2a** using a uranium glass filter (λ > 340 nm) and found it to be completely inert, both in the solid state and solution.[8] Furthermore, there is no induction period for the formation of keto-aldehyde **3**, nor does the ratio of **2a** to **3** change with conversion as diketone **1** is photolyzed at λ > 340 nm in the solid state. These control experiments indicate that **2a** and **3** are both primary solid state photoproducts.

Application of molecular mechanics methods (MM3) to diketone **1** shows that its lowest energy conformation is of the "boat-chair-boat" type common to many 10-membered ring compounds. The next conformer located by MM3 was a relatively distant 8.13 kJ/mol higher in energy. As shown by the figure at the right, X-ray crystallography reveals that the boat-chair-boat conformation is also adopted by 1,2-cyclodecanedione in the solid state.[4]
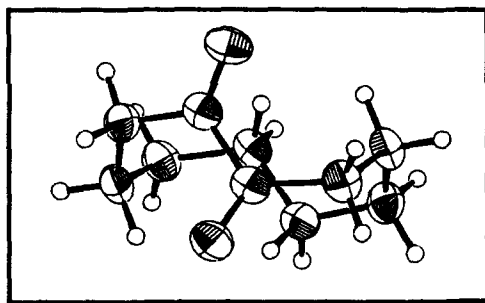
With this information, the hydrogen atom abstraction/cyclization process leading to cyclobutanol **2a** stands revealed. As depicted below, abstraction of either "bowsprit" γ-hydrogen atom leads to a 1,4-hydroxybiradical which is geometrically predisposed to cyclize to a *cis*-cyclobutanol; i.e., photoproduct **2a**. Because diketone **1** is not fully symmetrical in the solid state, the two γ-hydrogens have slightly different distances to their respective oxygen atoms—2.67 Å in one case and 2.69 Å in the other. These distances are slightly less than the sum of the van der Waals radii for hydrogen and oxygen (2.72 Å), thus accounting for the success of the abstraction, and both distances are also very close to the C=O...H_γ contacts found for the diametric diketones (2.74 ± 0.04 Å for nine separate compounds).[1,9]

1 "pre-*cis*" biradical **2a**
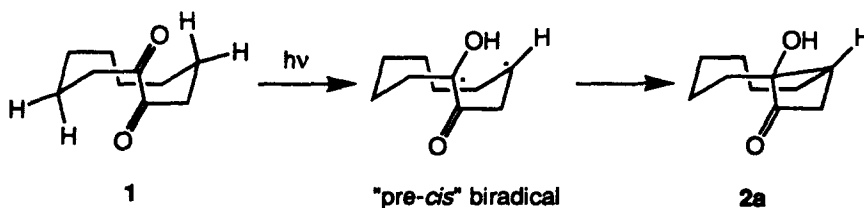
The question remains as to the origin of keto-aldehyde **3** in the solid state photolyses. We speculate that this may occur *via* initial α-cleavage between the two carbonyl groups of diketone **1**.[10] As shown in the mechanism on the next page, this would produce a diacyl biradical, one resonance contributor of which has carbenic character on the acyl carbon. Insertion of this carbene into the close-lying C-H_γ bond[11] would afford the alkoxy-acyl biradical shown at the lower right (two possible isomers), and hydrogen transfer in this latter species would then complete the rearrangement. This mechanism raises a number of interesting questions, not the least of which is why such a process should be unique to the crystalline state. Again we can only speculate that this may stem from the conformationally restrictive nature of the solid state medium which, unlike fluid media, maintains the C-H bond in position for insertion following α-cleavage. Preliminary studies indicate that a keto-aldehyde analogous to **3** is not formed in the solid state photochemistry of 1,2-cyclododecanedione.
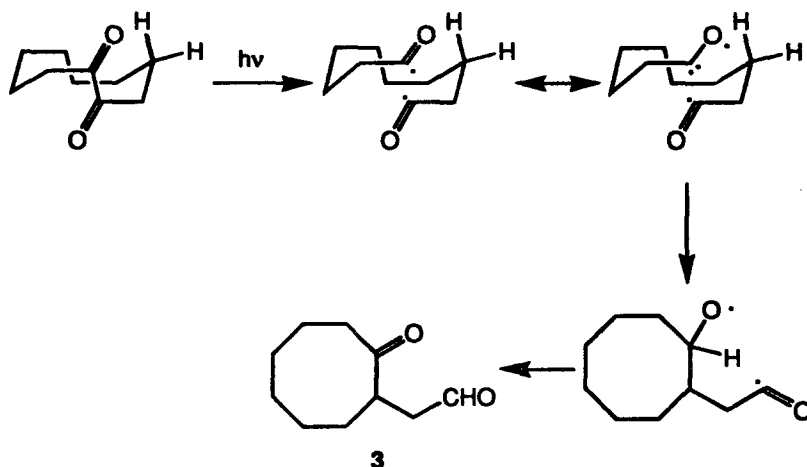
3

References and Footnotes

1. Gudmundsdottir, A.D.; Lewis, T.J.; Randall, L.H.; Scheffer, J.R.; Rettig, S.J.; Trotter, J.; Wu, C-H. *J. Am. Chem. Soc.* **1996**, *118*, 6167.
2. Urry, W.H.; Trecker, D.J.; Winey, D.A. *Tetrahedron Lett.* **1962**, 609.
3. (a) Allinger, N.L. *Org. Syntheses* **1964**, *4*, 840; (b) Gream, G.E.; Worthley, M.S. *Tetrahedron Lett.* **1968**, 3319
4. Diketone **1**: P$\bar{1}$; a = 7.978(1), b = 9.181(1), c = 6.9712(8) Å; α = 100.32(1), β = 109.290(9), γ = 92.71(1)°; Z = 2; R = 3.7%. Cyclobutanol **2a**: P2$_1$/a; a = 13.411(2), b = 5.6041(5), c = 13.761(2) Å; β = 113.818(8)°; Z = 4; R = 3.5%. Cyclobutanol **2b**: P2$_1$/a; a = 13.670(3), b = 5.232(1), c = 14.521(3) Å; β = 114.82(2)°; Z = 4; R = 6.6%.
5. Wagner, P.J.; Zepp, R.G.; Liu, K-C.; Thomas, M.; Lee, T-J.; Turro, N.J. *J. Am. Chem. Soc.* **1976**, *98*, 8125.
6. Compound **3** was synthesized by converting cyclooctanone into 2-allylcyclooctanone (Crandall, J.K.; Magaha, H.S.; Henderson, M.A.; Widener, R.K.; Tharp, G.A. *J. Org. Chem.* **1982**, *47*, 5372) followed by ozonolysis and reductive workup.
7. Wagner, P.J.; Park, B-S.; Sobczak, M.; Frey, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1995**, *117*, 7619.
8. Keto-aldehyde **3** also does not absorb at λ > 340 nm, thus ruling out its conversion to **2a** and/or **2b**.
9. The crystallographic values of the parameters ω (the γ-hydrogen out of plane angle), Δ (the C=O...H$_γ$ angle) and θ (the C-H$_γ$...O angle) for diketone **1** were (two values of each): 53.4°/54.8°, 84.4°/84.1°, and 118°/116°, respectively. These values also compare favorably with those found for the diametric diketones.[1]
10. Precedent for this type of process can be found in Rubin, M.B. *Top. Curr. Chem.* **1985**, *129*, 1.
11. The crystallographic γ-H to acyl carbon distances in **1** are 2.82 and 2.83 Å. These distances are below the sum of the van der Waals radii for carbon and hydrogen (2.90 Å). Carbenic insertions of this type are, to the best of our knowledge, unprecedented.