

CONFORMATION-SPECIFIC PHOTOCHEMISTRY IN THE SOLID STATE

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Abstract. The unsymmetrical ene-dione $1b$ exists in solution as a mixture of two conformational isomers, A and B, in rapid equilibrium. Irradiation of $1b$ in this medium leads to four products, two from each conformer. In the solid state, however, compound $1b$ adopts a single conformation (A), and photolysis of crystals of $1b$ leads to a single product. The formation of one rather than two photoproducts in this instance is attributed to a unique solid state steric effect, termed steric compression.

Many organic molecules of moderate complexity consist of several rapidly equilibrating conformational isomers of similar energy in solution. For this reason, it is very difficult to restrict chemical reaction to a single one of these conformers in this medium. The situation in the crystalline state is different, however. In this medium, normally only one conformational isomer is present, and this is usually the most stable conformer. As a result, the solid state offers excellent prospects for "conformation-specific" chemistry. In this communication we report the conformation-specific solid state photochemistry of ene-dione $1b$ and demonstrate that the results are consistent with both its X-ray crystal structure and its solid state CPMAS C-13 NMR spectrum.^{1,2}

Based on our experience with ene-dione $1a$ ^{3,4} it seemed likely that ene-dione $1b$ would exist in solution as a nearly 1:1 mixture of conformers A and B. Enantiomeric in the case of $1a$, conformers A and B differ in the case of $1b$ in that the ring junction ethyl group (R_2) is pseudo-equatorial with respect to the cyclohexene ring in A and pseudo-axial in B; similarly, the methyl group (R_1) is pseudo-axial in A and pseudo-equatorial in B. Since methyl and ethyl groups are generally considered to have the same size,⁵ it was of considerable interest to determine whether ene-dione $1b$ would adopt a single conformation (either A or B) in the solid state or would consist of a mixture of the two.

The first indication that ene-dione $1b$ exists in a single conformation in the solid state and that this conformation is conformation A came from its solid state magic angle spinning C-13 NMR spectrum. First of all, the spectrum showed a doubling of the ring carbon resonances rather than the quadrupling which might be expected if two non-equivalent conformers were present.⁶ Secondly, the signal due to the carbon atom of the ring junction methyl group could

be identified by its very short relaxation time; its chemical shift is 11.2 ppm relative to TMS. This high field chemical shift is characteristic of pseudo-axial methyl groups in ene-diones analogous to $\underline{1b}$ (e.g., $\underline{1a}$) and has been attributed to the steric compression this methyl group experiences in its gauche-butane interaction with the cyclohexene methylene group.⁴ The presence of a pseudo-axial methyl group indicates, of course, that ene-dione $\underline{1b}$ exists in conformation A. Final confirmation that compound $\underline{1b}$ exists exclusively in conformation A in the solid state came from a direct method, single crystal X-ray diffraction study ($R = 0.039$) the details of which will be published elsewhere.

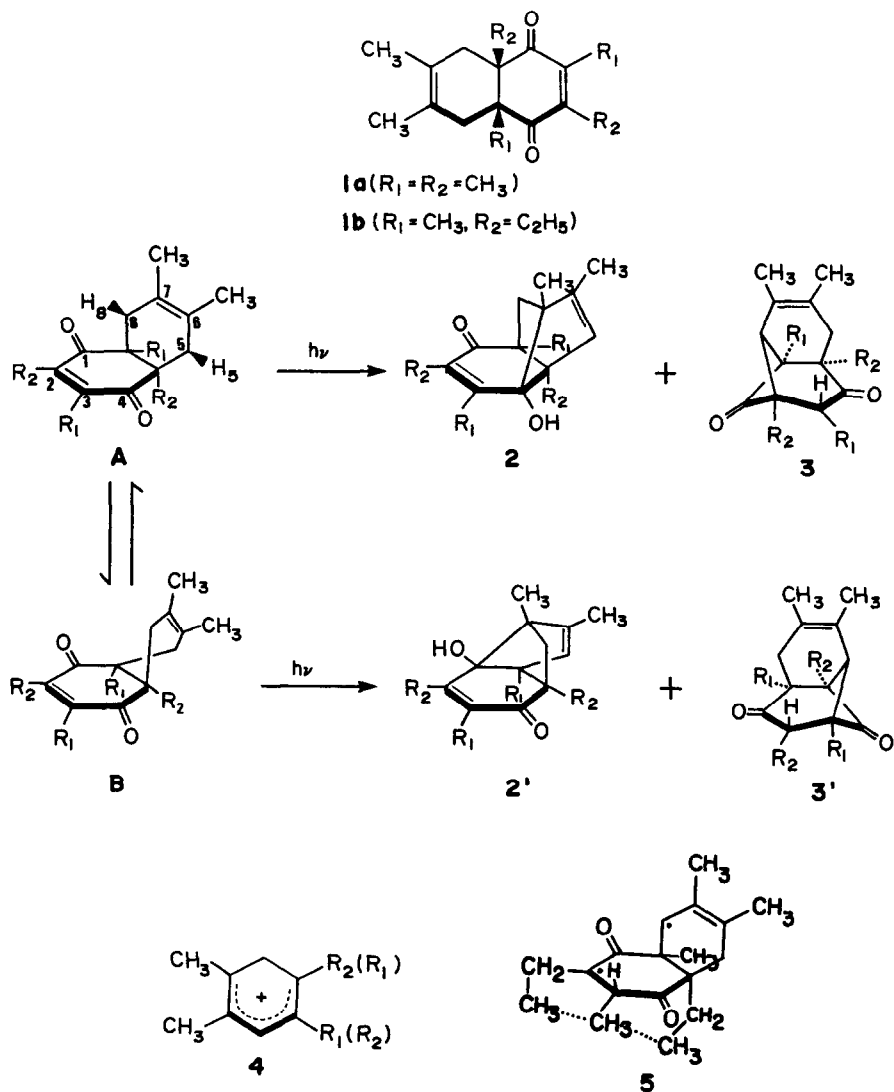
We have shown previously that irradiation of ene-dione $\underline{1a}$, both in solution and in the solid state, gives enone alcohol $\underline{2a} = \underline{2a'}$ and cyclobutanone $\underline{3a} = \underline{3a'}$.⁷ Production of the former involves H_5 hydrogen abstraction by O_4 followed by $C_4 - C_7$ bonding, and formation of the latter is brought about by transfer of H_8 to C_3 followed by $C_2 - C_8$ bonding; both processes are topochemically allowed. In the case of ene-dione $\underline{1b}$, however, $\underline{2b}$ and $\underline{2b'}$ are not identical nor are $\underline{3b}$ and $\underline{3b'}$. Thus in the solid state, photolysis of $\underline{1b}$ should give only $\underline{2b}$ and/or $\underline{3b}$ because only conformer A is present; irradiation in solution would be expected to provide a mixture of all four isomers.

This is exactly what is found experimentally. Irradiation of crystals of ene-dione $\underline{1b}$ with the output from a Molectron UV 22 nitrogen laser (337 nm) gives only enone-alcohol $\underline{2b}$, whereas laser photolysis of benzene or acetonitrile solutions of the same material affords mixtures of products $\underline{2b}$, $\underline{2b'}$, $\underline{3b}$ and $\underline{3b'}$ whose composition depends on the length of irradiation.⁸

The identity of the solid state photoproduct was established by a combination of deuterium labeling and gas chromatography-mass spectrometry. This followed from a mass spectral fragmentation pattern characteristic of enone alcohols [compound $\underline{2a}$: m/e 246 (M^+), 218, 203, 189 (base); compound $\underline{2b}$ (or $\underline{2b'}$): m/e 274 (M^+), 246, 231, 217 (base)]. When the mixture from the solid state photolysis of ene-dione $\underline{1b}$ was treated with NaOMe/DOMe followed by an aqueous workup, the photoproduct mass spectrum showed the incorporation of three rather than two deuterium atoms [m/e 277 (M^+), 249, 234, 220 (base)]. This conclusively establishes the structure of the photoproduct as $\underline{2b}$ rather than $\underline{2b'}$. In contrast, the cyclobutanone-containing photoproducts $\underline{3b}$ and $\underline{3b'}$, which were present after irradiation in solution,⁸ could not be distinguished by mass spectrometry. They did, however, show fragmentation patterns characteristic of this class of compound [base peak at m/e 135 ($R_1 = R_2 = CH_3$) and m/e 149 ($R_1 = CH_3$, $R_2 = C_2H_5$), attributable to ion $\underline{4}$].

A final point concerns the interesting observation of a single photoproduct, enone alcohol $\underline{2b}$, in the solid state irradiation of ene-dione $\underline{1b}$. This was unexpected because in our previous work on the solid state photochemistry of ene-dione $\underline{1a}$,⁷ enone alcohol $\underline{2a}$ was found to be the minor photoproduct, with cyclobutanone $\underline{3a}$ predominating. We attribute this to an unfavorable solid state steric effect accompanying attempted cyclobutanone formation in the case of $\underline{1b}$ but not $\underline{1a}$. Recently we have shown that such steric effects, termed "steric compression control," can exert a profound influence on solid state chemical processes.⁹ Specifically, we suggest that steric compression retards the rate of the first step of cyclobutanone formation (transfer of H_8 to C_3) in the case of $\underline{1b}$ but not $\underline{1a}$. The steric compression which develops in $\underline{1b}$ is shown by the dotted lines in structure $\underline{5}$ and involves two unfavorable intramolecular methyl-methyl interactions between the downward-moving C_3 methyl group and its neighboring

ethyl groups; when the neighboring groups are methyl (i.e., ene-dione **1a**), no such interactions exist. Similarly, in solution, where ethyl group rotation is less restricted than in the solid state, steric compression in **1b** can be avoided, and cyclobutanone formation is permitted (as observed). Computer simulation⁹ of the hydrogen-hydrogen contacts developed during the pyramidalization of **C₃** in the solid state support this interpretation. The calculated distances at full pyramidalization are 1.58 and 1.75 Å which correspond to a total non-bonded repulsion energy of approximately 35 kcal/mole.¹⁰



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1. For previous examples of conformation specific solid state photochemistry, see W.K. Appel, Z.Q. Jiang, J.R. Scheffer and L. Walsh, J. Am. Chem. Soc., 105, 5354 (1983).
2. Ene-dione 1b, mp 70-71 °C, was prepared by the Diels-Alder addition of 2,5-dimethyl-3,6-diethyl-p-benzoquinone [B. Eistert, H. Fink, J. Riedinger, H.G. Hahn and H. Durr, Chem. Ber., 102, 3111 (1969)] to 2,3-dimethylbutadiene.
3. X-ray crystal structure: S.E.V. Phillips and J. Trotter, Acta Cryst., Sect. B, 32, 3088 (1976).
4. CPMAS C-13 solid state NMR: C.A. McDowell, A. Naito, J.R. Scheffer and Y-F. Wong, Tet. Lett., 22, 4779 (1981).
5. N.L. Allinger and L.A. Freiberg, J. Org. Chem., 31, 894 (1966).
6. S. Ariel, J.R. Scheffer, J. Trotter and Y-F. Wong, Tet. Lett., 24, 4555 (1983).
7. J.R. Scheffer and A.A. Dzakpasu, J. Am. Chem. Soc., 100, 2163 (1978).
8. For example, after a seven minute irradiation in acetonitrile, the product composition (assuming identical gas chromatographic detector responses) was 1b, 5%; 2b, 63%; 2b', 9%; 3b, 8%; 3b', 6%; unidentified, 9%. Photoproducts 3b and 3b' increase with time due to the fact that the formation of enone alcohols 2b and 2b' is photoreversible.
9. S. Ariel, S. Askari, J.R. Scheffer, J. Trotter and L. Walsh, J. Am. Chem. Soc., 106, 5726 (1984).
10. Calculated using the Lennard-Jones "6-12" potential function which relates interatomic hydrogen-hydrogen distance and non-bonded repulsion energy. A. Warshel and S. Lifson, J. Chem. Phys., 53, 582 (1970).

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