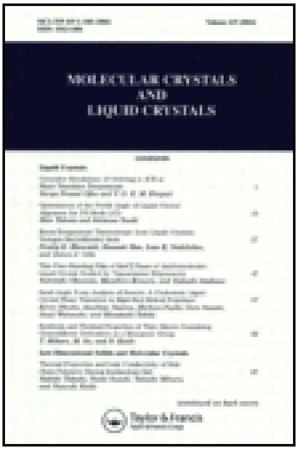

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Chemical Reactivity in Solution, in Crystalline Solids and in Polymer Films: A Comparative Study

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CHEMICAL REACTIVITY IN SOLUTION, IN CRYSTALLINE SOLIDS AND IN POLYMER FILMS: A COMPARATIVE STUDY

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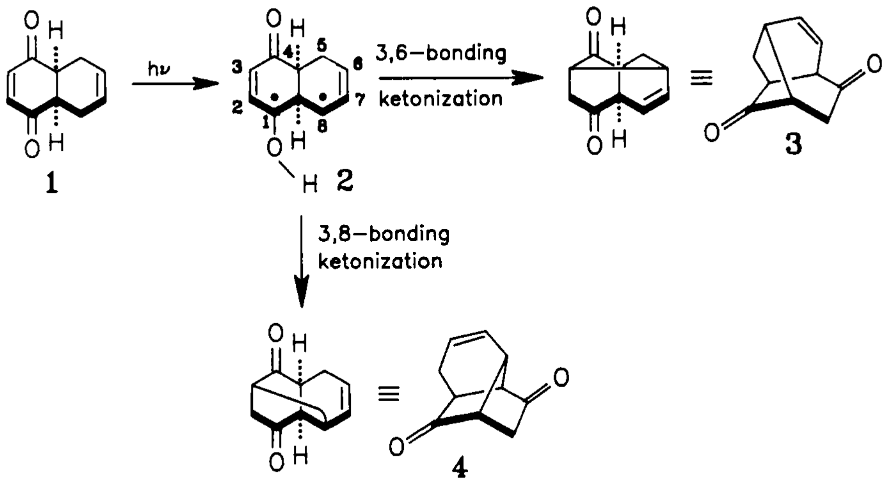
Abstract The photochemistry of ene-dione 1 has been studied in each of three different media: ethyl acetate solution, the pure crystalline phase and poly(methyl methacrylate) films. Topochemical [2+2] photodimerization is followed in the solid state owing to a favorable orientation of adjacent molecules in the crystal lattice. In the other media, an ill-defined photooligomerization process predominates accompanied by lesser amounts of hydrogen abstraction-initiated photorearrangement. The biradicals produced by hydrogen abstraction can collapse to various stable products depending on their conformation. The rate of interconversion of biradical conformers is viscosity-dependent, thus giving rise to different photoproducts in solution and in the polymer films.

INTRODUCTION

The research described in this paper arose from the simple idea that organic molecules dissolved in polymer films find themselves in environments that, while solid state-like in terms of their high viscosity, are also solution-like from the point of view that the molecular periodicity characteristic of the crystalline lattice is lost. As a result, compounds that exhibit different chemical behavior in the solid state and solution may be expected to display intermediate, and in some cases unique, behavior in a polymer film matrix. Two recent publications from our laboratory have documented exactly such an effect.[1,2] In the present paper we report a third example of such behavior.

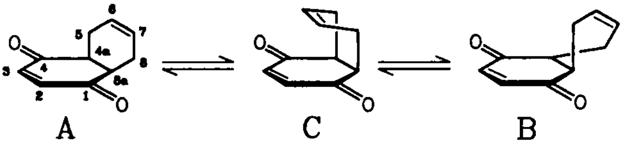
The compound chosen for study was the well-known adduct 1 (Scheme I) formed through Diels-Alder addition of butadiene to p-benzoquinone.[3] Some time ago[4] we showed that solution phase photolysis of this material gives rise to the interesting tricyclic diketones 3 and

4. The combined yield of these two products is around 10%, the remainder of the starting material having been transformed into an unidentified, high molecular weight solid. Based on deuterium labeling studies on closely related compounds, the mechanism by which photoproducts 3 and 4 are formed was suggested[4,5] to involve an initial five-membered transition state transfer of one of the allylic hydrogen atoms in the cyclohexene ring to a neighboring carbonyl oxygen atom. This generates the bis-allylic biradical 2, and internal coupling of this species followed by ketonization as indicated in Scheme I affords the observed photoproducts.



SCHEME I Formation of photoproducts 3 and 4.

A more detailed understanding of the reaction mechanism was developed through NMR and crystallographic studies on ene-dione 1 and some of its methylated derivatives. These studies showed that compounds of this type crystallize in so-called "twist" conformations in which there is a nearly perfectly staggered arrangement about the central C(4a)-C(8a) bond; the cyclohexene and cyclohexene-dione rings have half-chair and flattened half-chair geometries, respectively (Scheme II). Because of the cis ring junction stereochemistry, half-chair to half-chair ring inversion is possible in these compounds, and this converts conformer A into its enantiomer B. The equilibrium between conformers A and B passes through a higher energy eclipsed conformer C, which can be either endo (shown) or exo (not shown). This equilibrium is rapid on the NMR time scale in solution, even at temperatures as low as -90°C, giving rise to a time-averaged spectrum characteristic of a species possessing a plane of symmetry passing midway between C(2) and C(3), C(4a) and C(8a), and C(6) and C(7).[6] With the introduction of methyl substituents at C(4a) and C(8a), however, the equilibrium could be frozen out at -60 to -70°C ($\Delta G^{\ddagger}$=8.7-9.2 kcal/mole) . Below these temperatures the ^{13}C spectrum in solution resembles that obtained in the solid state and is characteristic of the individual conformers **A** and **B**. As we shall see, it is the equilibrium among these conformational isomers *following hydrogen atom abstraction* that controls the photoproduct ratios and leads to *new products* when the irradiations are carried out in polymer film matrices.

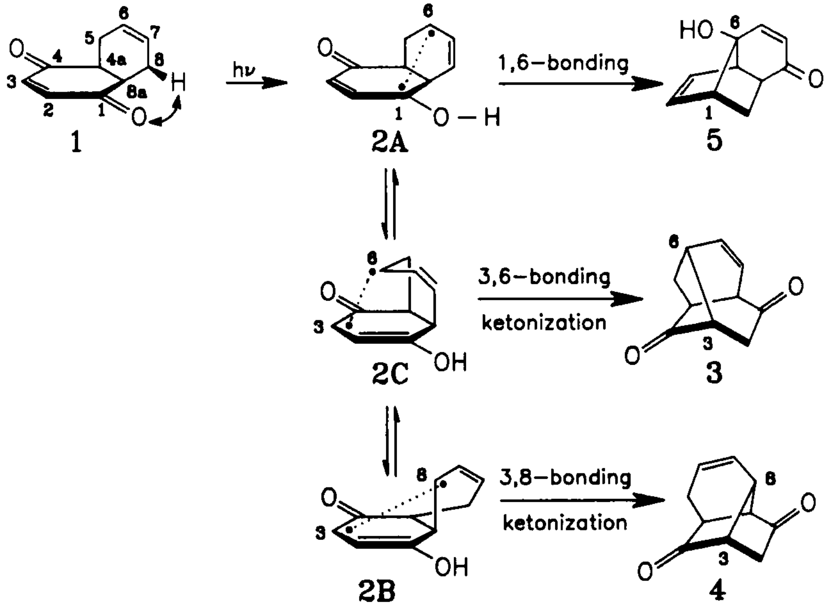


SCHEME II Ground state conformational equilibria.

The twist conformation of ene-dione 1 has a geometry that is ideal for the postulated five membered transition state hydrogen abstraction leading to photoproducts 3 and 4. The endo allylic hydrogen atom at C(8) lies almost exactly in the plane of the carbonyl group at C(1) (Scheme III). This is the plane that contains the oxygen atom non-bonding orbitals, the orbitals that are thought to be responsible for hydrogen atom abstraction through the carbonyl n,π^* excited state.[7] Photophysical studies on close relatives of ene-dione 1 implicate the $(n,\pi^*)^1$ excited state as the reactive species.[5] The C(1)=O···H(8) distance in 1, at 2.5 Å, is also very favorable for abstraction. Using van der Waals radii of 1.2 Å for hydrogen and 1.5 Å for oxygen,[8] it is apparent that the abstraction distance lies well below the sum of the radii for the atoms involved. This aspect of our research, that is the correlation of hydrogen atom abstraction reactivity with crystallographically determined geometric parameters, has been summarized in a recent review article.[9]

It is reasonable to assume that, following abstraction, biradical **2A** also possesses the basic twist conformation of its immediate precursor (Scheme III). Intramolecular coupling of this biradical between carbon atoms 1 and 6 is geometrically feasible owing to the proximity of these centers (3.4 Å in the ground state) and also to favorable orbital overlap. The product of this coupling reaction, enone-alcohol **5**, has never been observed in solution photolyses of ene-dione **1**, although, as we shall see, there is some evidence that it is involved in the formation of the oligomeric material that comprises the bulk of the reaction mixture. Enone-alcohols analogous to **5** are, however, ubiquitous in the photochemistry of substituted ene-diones, and in fact are often the major photoproducts.[4,5]

The conformation of biradical **2A** does not permit the modes of biradical collapse that lead to the observed solution photoproducts **3** [C(3)···C(6)] and **4** [C(3)···C(8)]; C(6) and C(8) have negligible orbital overlaps with, and are far removed from, C(3). In order to undergo C(3)···C(6) bonding, biradical **2A** must undergo a conformational

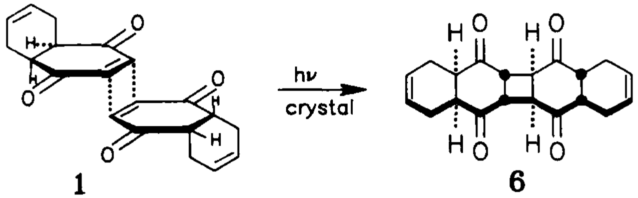


SCHEME III Biradical conformations and reaction pathways.

isomerization analogous to the **A** → **C** process discussed earlier. As shown in Scheme III, this brings C(3) and C(6) into bonding distance of one another and leads (after ketonization) to photoproduct **3**. Using a similar line of reasoning, it is apparent that C(3)···C(8) bonding to give **4** can occur only from biradical **2B**, which is produced by conformational isomerization of **2C**. Again, this has direct analogy in the ground state **C** → **B** interconversion discussed previously.

Evidence for the biradical structure-reactivity relationships outlined in Scheme III comes from two sources: first, photoproducts analogous to **3** and **4** are formed in vanishingly small amounts from ene-diones bearing bulky substituents at the ring junction carbon atoms C(4a) and C(8a).[4] This is attributable to the increased activation energy for the required conformational isomerizations brought about by these substituents. As a result, other processes, including closure to enone-alcohol type products, predominate. Secondly, analogues of **3** and **4** are absent in the *solid state* photochemistry of substituted ene-diones, again reflecting a restriction of the necessary conformational isomerizations relative to competing processes.

Rather than intramolecular hydrogen abstraction, some ene-diones undergo *bimolecular* photochemistry in the solid state, and the Diels-Alder adduct **1** is one of these. Irradiation of crystals of **1** leads to good yields of the dimer **6** (Scheme IV).[10] This reaction is an example of a topochemical (lattice-controlled) [2+2] photodimerization, of which many examples are known.[11] It follows the rules laid down for such processes by Schmidt and Cohen, namely a parallel orientation of the reacting double bonds with a center-to-center distance of around 4 Å or less.[12] The center-to-center distance in the case of crystals of ene-dione **1** is 3.8 Å.



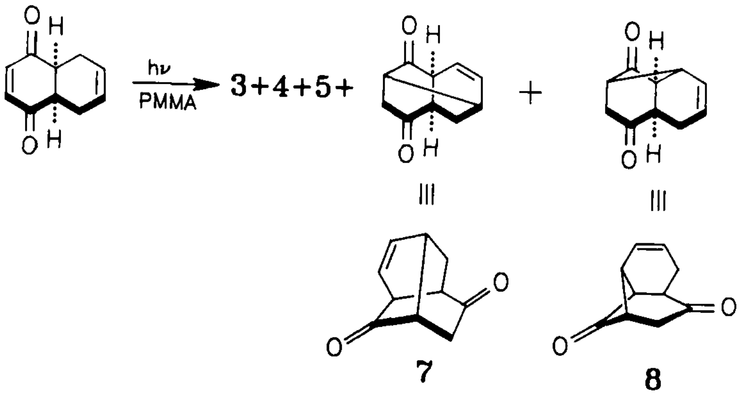
SCHEME IV Solid state photodimerization of ene-dione 1.

RESULTS AND DISCUSSION

With the solution phase and crystalline state photochemistry of ene-dione 1 reasonably well understood, we turned our attention to its photochemical behavior in polymer matrices. The expectation was that photodimerization would not occur in this medium owing to the loss of solute crystallinity under these conditions. As a result we hoped to observe unimolecular photoreactivity in the polymer, and because of the high viscosity of such matrices, it was hoped that conformational isomerization of the biradicals **2A**-**2C** might be restricted, thus leading to new products in the films. Such indeed proved to be the case. Before proceeding to a description of the photochemical results, a brief outline of the experimental procedure followed in the polymer film irradiations is in order.

Low molecular weight poly(methyl methacrylate) as supplied by Aldrich Chemical Company was used as the matrix material. Before use the polymer was freed of stabilizers and other low molecular weight impurities by dissolution in chloroform, precipitation by addition of methanol, suction filtration and vacuum drying. This process was repeated three times. The films were prepared by applying ca. 0.5 ml of a solution containing polymer (0.6 g) and compound 1 (0.1 g) in 20 ml of chloroform to the top of a microscope slide and distributing it evenly over the surface using a second slide as a straightedge. After coating the films were air dried for 24 hours and then dried in vacuo for 48 hours at room temperature. The films so prepared had thicknesses of 5-10 microns. Irradiations were conducted using a Hanovia medium pressure mercury lamp fitted with a uranium glass filter (transmitting $\lambda \geq 330$ nm). After photolysis, the films were dissolved in chloroform and the PMMA reprecipitated using methanol. Filtration followed by removal of the solvent in vacuo afforded the photoproducts. Preparative scale photolyses were carried out using thicker, more concentrated films and larger glass plates.

The results of the photolysis of ene-dione 1 in PMMA films are shown in Scheme V. As can be seen, three new monomeric products, 5, 7 and 8, are formed in addition to the previously observed solution products 3 and 4; no photodimerization was observed. Interestingly, the combined yield of all five photoproducts rose to ca. 40% in the matrix. At -20°C, the product ratios as determined by gas chrom-



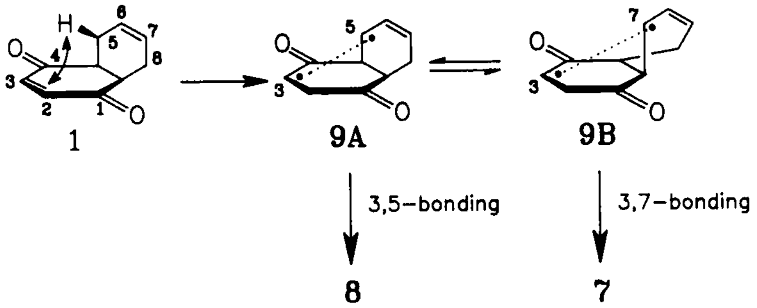
SCHEME V Photolysis of ene-dione 1 in PMMA films.

atography were 6% 3, 47% 4, 42% 5, 2% 7 and 2% 8. At room temperature, the ratios were 17% 3, 39% 4, 31% 5, 6% 7 and 7% 8.

The structure of enone-alcohol 5, mp 95-97°C, follows from its infrared spectrum (OH absorption at 3421 cm^{-1} and C=O at 1679 cm^{-1}) and from its NMR spectrum. Particularly revealing in the latter was the presence of four vinyl hydrogen resonances, two at 6.08 and 6.45 ppm due to the hydrogen atoms on the non-conjugated double bond, and two at 5.97 and 6.91 ppm due to the enone double bond hydrogens. Photoproduct 5 is the product of immediate reaction of biradical **2A** without prior conformational isomerization (Scheme III). Thus, as anticipated, the polymer matrix has slowed the isomerization of **2A** to 2C to such an extent that C(1)···C(6) coupling is competitive.

The structures of photoproducts 7 (mp 167-168°C) and 8 (oil) follow from their spectral properties[13] plus, in the case of the twistane derivative 7, from an X-ray crystal structure determination.[14] Compound 7 (but not 8) is also formed in small amounts when ene-dione 1 is irradiated in solution. For example, at room temperature in ethyl acetate solution, diketone 7 comprises approximately 15% of the photoproducts detectable by gas chromatography. This product was missed in our initial work on the solution photochemistry of ene-dione 1.[4,5]

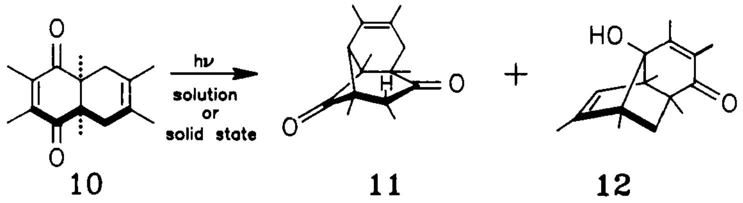
Photoproducts 7 and 8 have structures that cannot be formed by collapse of the bis-allylic biradical **2A** or any of its conformational isomers. We suggest, therefore, that they originate from a different initial hydrogen abstraction process of conformer **A**, namely transfer of an allylic hydrogen atom from C(5) to C(2), a six-membered transition state process. The endo hydrogen atom on C(5) lies above the C(2)–C(3) double bond and is within 2.9 Å (the sum of the van der Waals radii for C and H)[8] of C(2). As outlined in Scheme VI, this abstraction process generates biradical **9A**, which has the same basic conformation as its precursor, and direct closure of this species by C(3)····C(5) bonding leads to the cyclobutanone-containing photoproduct **8**. Alternatively, **9A** can undergo the now-familiar **A→B** conformational isomerization to give biradical **9B**, and C(3)···C(7) coupling of this intermediate (a process that is sterically impossible for **9A**) affords twistane derivative **7**. In direct analogy to the



SCHEME VI Mechanism of formation of photoproducts **7** and **8**.

scenario postulated for biradical **2A**, conformational isomerization of **9A** is evidently faster in solution than closure, so that compound **7** is the exclusive photoproduct in this medium. In PMMA films, however, isomerization of **9A** to **9B** is restricted by the viscous matrix, with the result that **9A** has a lifetime sufficient for closure to photoproduct **8**.

In previous studies on methylated derivatives of ene-dione **1**,[4,5] photoproducts analogous to cyclobutanone **8** have been commonly observed and suggested to arise through $(\pi,\pi^*)^3$ excited states. For example, irradiation of hexamethyl ene-dione 10 (Scheme VII) in solution or the solid state gave high yields of an approximately 2:1 ratio of compounds 11 and 12. The former is the methylated analogue of 8 and the latter is the hexamethyl derivative of enone-alcohol 5. It is noteworthy that photolysis of 10 does not lead to products analogous to twistane derivative 7, either in the solid state or solution. This result is once again readily explicable in terms of the mechanism outlined in Scheme VI: initial hydrogen abstraction in the case of 10 gives a biradical analogous to 9A that is incapable of the requisite 3,7-bonding, and owing to the presence of methyl groups at the ring junction carbon atoms, the isomerization of 9A-Me$_6$ to 9B-Me$_6$ is slow relative to 3,5-bonding to give 11. Thus, as we saw in the case of biradicals 2A-2C, the polymer matrix exerts the same effect as ring junction methyl substitution, namely retardation of biradical conformational isomerization and a change in the pattern of the photoproducts formed.

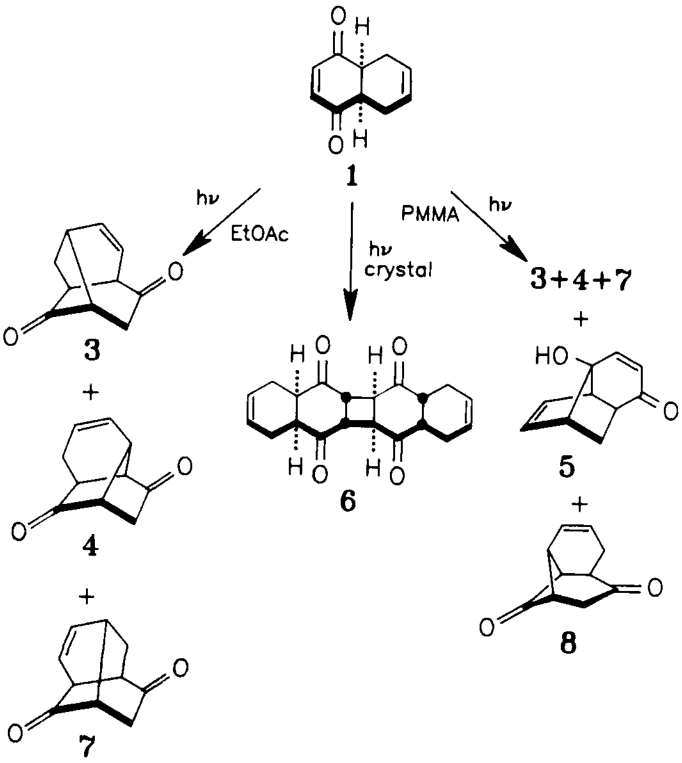


SCHEME VII Photolysis of hexamethyl ene-dione 10.

A final point concerns the higher yields of monomeric photoproducts obtained in PMMA films (40%) as compared to solution (10%). This is related to the source of the oligomeric material that predominates in both media. Isolated as a sparingly soluble white powder, this material shows peaks in the mass spectrum corresponding to 2X, 3X and 4X the mass of ene-dione 1. The infrared spectrum shows strong OH and saturated C=O absorptions, and the NMR spectrum, while generally featureless, exhibits weak signals in the vinyl hydrogen region. These data suggest that oligomerization occurs through [2+2] photocycloaddition in which one of the components is the enone double bond of photoproduct 5. This would account for the OH and C=O peaks observed in the infrared spectrum. It is not clear what the other π-component of the cycloaddition is, but it is probably not a second enone double bond, as this would tend to halt oligomerization at the dimer stage. Perhaps the other component is the non-conjugated double bond of a second molecule of 5; in agreement with these ideas, solution phase irradiation of 5 does lead to rapid and virtually complete oligomerization. Overall, therefore, we ascribe the lower yield of oligomer and the higher yield of monomeric products in polymer films to a restriction of the diffusion necessary for the intermolecular process.

SUMMARY

Scheme VIII summarizes the results of photolysis of ene-dione 1 in each of three different media: ethyl acetate solution, the pure crystalline phase and a PMMA matrix. Regio- and stereoselective photodimerization is favored by proximity and orientation effects in the crystal lattice. In the other media, an ill-defined photooligomerization process predominates accompanied by formation of lesser amounts of photorearrangement products. These latter products arise *via* intramolecular hydrogen abstraction reactions of photoexcited 1. The biradicals produced by hydrogen abstraction can collapse to various stable products depending on the biradical conformations. Conformational isomerization of the initially formed biradicals in solution tends to be *faster* than direct closure, thus leading to products that are different from those formed in the polymer films, where conformational isomerization of the initially formed biradicals is restricted by the viscous matrix and is therefore *slower* than direct radical coupling.



SCHEME VIII Summary of photochemical results.

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