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OBSERVATION OF A PHOTOREARRANGEMENT UNIQUE TO THE POLYMER MATRIX

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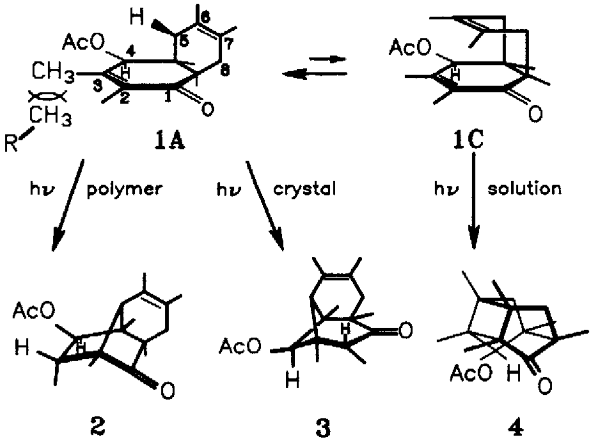
Abstract. As a result of differences in the local environment, the keto-acetate 1 displays unique and characteristic photoreactivity in each of three different media: isotropic liquid solutions, the pure crystalline phase and poly(methyl methacrylate) films.

There are many examples in the literature of organic molecules whose solution phase and solid state chemical behavior are very different owing to the anisotropic steric environment of the crystal lattice.[1] Termed the reaction cavity by Cohen,[2] the environment around a given molecule in the bulk of a crystal may sterically impede certain reaction pathways of that molecule and allow others in a manner that is completely dependent on the packing arrangement. Organic molecules dissolved in polymer films find themselves in environments that, while still restricting diffusion and major conformational change to a considerable degree, are less uniform and probably less resistant to deformation than those existing in the crystal.[3] In other words the polymer matrix provides a reaction cavity that is different from that in the crystal, and one may hope to observe chemical behavior in this medium that is different from that observed in both the liquid and crystalline phases. This communication reports the realization of this concept.

The compound chosen for study was the substituted cyclohexenone **1** (Scheme). Previous work from our laboratory had shown that photolysis of this material in benzene affords quantitative yields of the cage product 4, whereas irradiation of crystals of 1 slowly gives rise to 3 as the sole volatile product.[4] These photoproducts were suggested to arise from different conformational isomers of 1, conformer **1A** leading to 3 via transfer of H(5) to C(2) followed by C(3)···C(5) bonding, and conformer **1C** giving 4 through intramolecular [2+2] photocycloaddition. A remarkable difference was noted between these results and those obtained with a number of close analogues of compound 1.[5] This concerns the regioselectivity of the solid state hydrogen transfer step. The endo hydrogen atom at C(5) is virtually equidistant from C(2) and C(3), and in every case studied except that of 1 transfer occurs to C(3), presumably so as to form the more favorable resonance stabilized radical at C(2); biradical closure then leads to products analogous to **2**. X-ray crystallography revealed the probable cause of the unique photobehavior of enone 1 in the solid state: a particularly close contact between the methyl group at C(3) and a methyl group of a neighboring molecule located below it in the lattice (Scheme). This contact was suggested to raise the activation energy of the normally favored hydrogen transfer to C(3) through steric hindrance of the downward motion of the methyl group which accompanies pyramidalization at this center; there was no such contact involving the methyl group attached to C(2).

If this explanation is correct, then immobilizing enone 1 in conformation **1A** in a matrix that lacks the specific close contact to the C(3) methyl group and which slows the

Scheme



conformational isomerization to 1C might well lead to compound 2 upon photolysis. Such is indeed the case. Microscope slides coated with thin films of poly(methyl methacrylate) containing dissolved 1 (prepared as described in the preceding communication[6]) were irradiated through a uranium glass filter ($\lambda > 340$ nm) using a Hanovia 450 W lamp. At -50 °C the photoproduct mixture consisted of 65% 2, 8% 3, 20% 4 and 7% of an unknown compound; at 20 °C the corresponding ratios were 47:9:35:9. Keto-acetate 2, mp 53-55 °C, was isolated and its structure proved by comparison with an authentic sample prepared by acetylation of the corresponding known[5] keto-alcohol. The finding that some photoproduct 3 is obtained in the polymer matrix may indicate the presence of microcrystallites of 1 in this medium. It is more likely, however, that this simply reflects a close competition between the two hydrogen transfer pathways leading to 2 and 3.

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