

## Generation and Reactivity of a Triplet 1,4-Biradical Conformationally Trapped in a Crystalline Cyclopentanone

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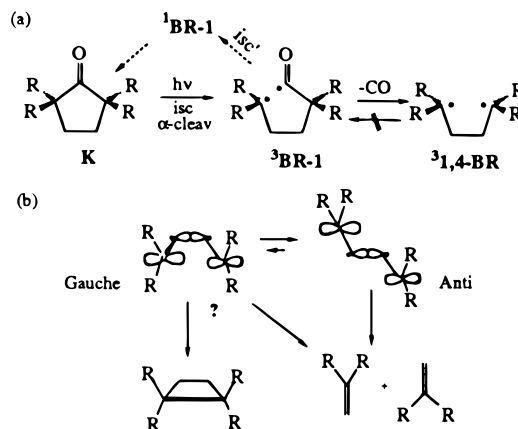
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Received January 12, 1998

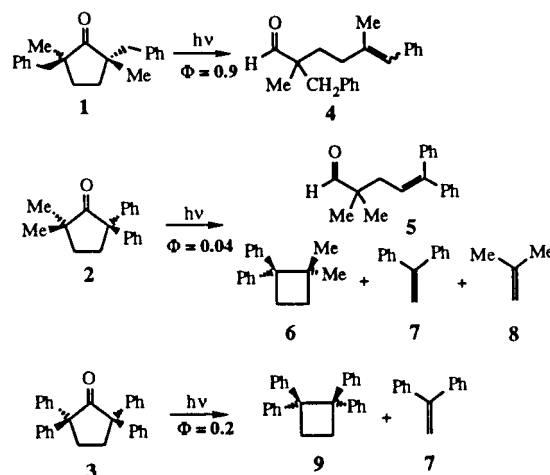
We have recently shown that the crystalline solid state offers a promising vehicle for controlling highly reactive intermediates. Carbenes, biradicals, and excited states may be confined to well-defined reaction trajectories,<sup>1–4</sup> and their selectivity can be analyzed in terms of molecular and environmental parameters determined by X-ray diffraction.<sup>5–8</sup> We report here our initial studies on the photochemical generation and reactivity of 1,4-biradicals (1,4-BR) in crystals of their cyclopentanone precursors (Scheme 1a).<sup>9</sup> Our interest in 1,4-BR is motivated by their chemical dichotomy in competing cyclization and cleavage reactions (Scheme 1b) and their intermediacy in  $2\pi + 2\pi$  dimerizations<sup>10–12</sup> and Norrish type-II reactions.<sup>13,14</sup> Although recent work on 1,4-BR has centered on the use of increasingly faster techniques,<sup>13,15,16</sup> controlling their reactivity in crystalline media is also of great interest. We analyze three model cyclopentanones to determine their suitability as precursors for 1,4-BR in crystals. Their photochemistry is characterized in terms of disproportionation vs decarbonylation and/or cyclization vs cleavage reactions. We also investigate whether the solid-state reaction may be carried out with high yields and maintained selectivity.

The strategy devised for the generation of 1,4-biradicals in crystals comes from our investigations on substituted cyclohexanones.<sup>2</sup> The proposed mechanism involves electronic excitation of the ketone followed by intersystem crossing (isc) and an  $\alpha$ -cleavage reaction in the triplet state (Scheme 1a). It is expected that triplet acyl-alkyl biradicals (<sup>3</sup>BR-1) formed in this manner may live long enough to undergo a spin-conserving decarbonylation ( $-\text{CO}$ ) to yield a triplet 1,4-BR in competition with intersystem crossing (isc') to <sup>1</sup>BR-1 and formation of the ground-state ketone (dotted lines, Scheme 1a). The role of the  $\alpha$ -substituents is to facilitate  $\alpha$ -cleavage and decarbonylation, which must compete with excited-state deactivation and intersystem

### Scheme 1

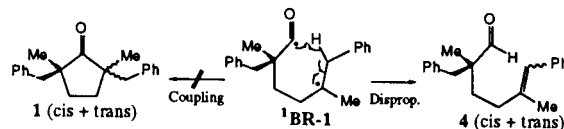


### Scheme 2



crossing (isc'), respectively. We have suggested that product formation from <sup>1</sup>BR-1 in crystals is unlikely due to rapid regeneration of the ground-state ketone.<sup>2</sup> In contrast, we expect that 1,4-BR should not revert back to BR-1 and ketone, but give cyclobutanes and/or olefins from their singlet manifold.

To test the above expectations, we analyzed the solution and crystal photochemistry of compounds 1–3 (Scheme 2).<sup>17</sup> These were chosen to determine whether alkyl or aryl substituents may satisfy the requirements of the solid-state reaction. In benzene, compound 1 yields a 2:1 mixture of 2-benzyl-2,5-dimethyl-6-phenyl-5-hexenals 4 with a combined quantum yield of 0.9. The lack of cyclobutanes and/or alkenes indicates that decarbonylation is slower than intersystem crossing. The lack of ketone isomerization suggests that radical coupling is disfavored relative to disproportionation in <sup>1</sup>BR-1.



(17) Cyclopentanone 1 was prepared by hydrogenation of 2,6-benzylidene-cyclopentanone followed by reaction with tBuOK and MeI. Compounds 2 and 3 were prepared from 2,2-diphenylcyclopentanone (Easton, N. R.; Nelson, S. J. *J. Am. Chem. Soc.* 1953, 75, 640) by reaction with MeI and tBuOK, and by reaction with pentaphenyl bismuth (Barton, D. H. R.; Charpiot, B.; Pan, E. T. H.; Motherwell, W. B.; Pascard, C.; Pichon, C. *Helv. Chim. Acta* 1984, 67, 586), respectively.

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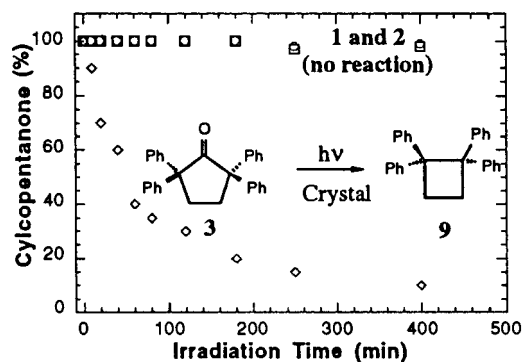
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**Figure 1.** Time course of the solid-state irradiation of cyclopentanones **1** (squares), **2** (circles), and **3** (diamonds).

The quantum yield of reaction from **2** in benzene is only one twentieth of that of **1** ( $\Phi = 0.04$ ). Low conversions (10–20%) yield pentenal **5**, cyclobutane **6**, and 1,1-diphenylethene **7** in a 5:2:3 ratio as determined by  $^1\text{H NMR}$ . The formation of aldehyde **5** indicates that  $\alpha$ -cleavage occurs at the side of the phenyl substituents.

The solution photochemistry of ketones **1** and **2** is characterized by low yields of decarbonylation and different tendencies for cyclization and disproportionation. In contrast, the solution photochemistry of tetraphenyl cyclopentanone **3** is dominated by decarbonylation with  $\Phi = 0.2$ . As reported by Barton et al.,<sup>18</sup> 1,1-diphenylethene **7** and tetraphenylcyclobutane **9** were obtained in a 3:1 ratio.<sup>18</sup>

Solid-state irradiations of **1**, **2**, and **3** were carried out at 20 °C with polycrystalline samples. Excitation wavelengths were chosen near the tail<sup>19</sup> of the  $n,\pi^*$  absorption ( $\lambda > 300 \text{ nm}$ ).<sup>20,21</sup> In contrast to solution photolysis where moderate to high reactivity was observed in all cases, only tetraphenyl cyclopentanone **3** reacted in the crystalline solid state (Figure 1). The efficient disproportionation of **1** in solution was fully suppressed and crystals of **1** and **2** (both have mp = 80–82 °C) remained unreacted. We assign their stability to slow decarbonylation rates which are unable to compete with  $\text{isc}'$  and reaction of  $^1\text{BR-1}$  back to the starting ketone (Scheme 1).

Irradiations of polycrystalline **3** (mp = 180–182 °C) proceeded in a smooth solid-to-solid reaction with maintained chemoselectivity to give cyclobutane **9** as the only solid-state product. The influence of the crystalline solid state on the selectivity of cyclization vs cleavage pathways is unprecedented for analogous 1,4-biradicals.<sup>22</sup> Cyclization requires gauche conformations that allow for bonding interactions between the two radical termini, and cleavage may in principle occur from syn, gauche, or anti conformers as long as overlap between the singly occupied p-orbitals and the biradical 2,3-bond is allowed (Scheme 1b). The yields of cyclization and cleavage in solution reflect a complex interplay among conformational equilibrium, conformational-dependent triplet to singlet  $\text{isc}$  rates, and the elementary rates of cyclization and cleavage from singlet biradicals.<sup>11,16,23,24</sup> In

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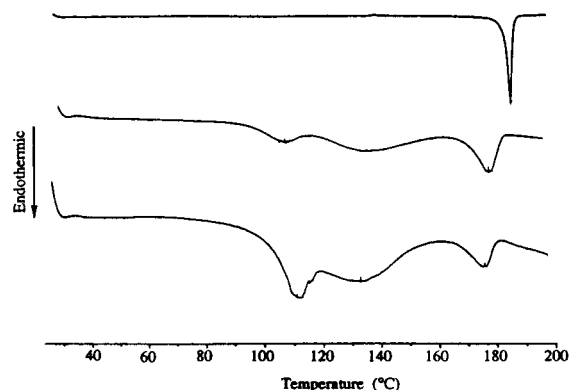
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**Figure 2.** DSC traces of partially reacted samples of compound **3** (conversion: top 0%, middle 40%, and bottom 65%).

contrast, since conformational relaxation in crystals of **3** is unlikely, 1,4-BR produced by decarbonylation should remain trapped in high energy syn or gauche conformations to give products with a selectivity that reflects the rate constants for product formation in this medium.

Interestingly, while both reactions may in principle occur from syn (or gauche) conformers, only cyclization was observed. Although this preference may come from intrinsically faster cyclization rates, it may also come from environmental restrictions associated with differences in reaction and activation volumes. While cyclization has negative reaction and activation volumes, cleavage of the 1,4-biradical to yield two molecules of 1,1-diphenylethene has activation and reaction volumes that are large and positive.<sup>25</sup> McBride et al.<sup>26</sup> have shown that internal pressure in crystals may reach extremely high values, which may control the chemoselectivity observed.

An interesting aspect of the crystal photochemistry of **3** comes from the high yields of **9** attainable. Solid-to-solid reactions are postulated to occur through solid solutions of the product in the crystal phase of the reactant.<sup>21,27</sup> Exceptionally, reactions may continue along a given crystal phase in single crystal-to-single crystal, or topotactic transformations. More commonly, product phases separate at concentrations where their solubility is exceeded.<sup>4,20,21</sup> Differential scanning calorimetry (DSC) analysis of partially reacted samples of **3** suggests a phase separation mechanism. While melting of the pure reactant and product phases occur at 183 and 121 °C, respectively, partially reacted samples showed a eutectic transition at 108 °C (Figure 2). A broad endotherm between melting of the reactant and the eutectic suggests either a three phase system or a spatially heterogeneous sample.<sup>28</sup> Although intermediate phases between those of the reactants and products may be possible, photochemical reactions in crystals proceed along an irradiation front and we favor the second explanation. That the chemoselectivity of the reaction is maintained as the composition changes strongly suggests the potential of solid-state photochemistry for preparative purposes. Work in progress is aimed at the detection of the biradical intermediates and at a more detailed characterization of their solid-state chemistry.

**Acknowledgment.** Support by the National Science Foundation (CHE-9320619 and CHE-9624950), and by the donors of the Petroleum Research Fund, is gratefully acknowledged.

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