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Ring strain release as a strategy to enable the singlet state photodecarbonylation of crystalline 1,4-cyclobutanediones

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Challenging most chemists' intuition, highly reactive dialkyl biradicals can be reliably generated in the solid state by taking advantage of the photodecarbonylation of cyclic ketones. However, it has been shown that radical stabilizing groups with resonance-delocalizing abilities at the α -carbons of the precursor are required to facilitate the α -cleavage reaction, and that triplet state reactivity is essential to slow down the combination of the intermediate acyl-alkyl biradical back to the starting ketone. Relatively long triplet acyl-alkyl biradical lifetimes give a chance for the loss of CO to occur. Looking for additional strategies to generate transient biradicals in solids, we studied the solid state photochemistry of four aliphatic, dispiro-substituted 1,4-cyclobutandiones (1a–d) that were expected to react from the singlet state. We hypothesized that the release of ring strain from the small ring carbonyl would make the reverse acyl-alkyl combination disfavored, allowing for the loss of CO to occur efficiently and irreversibly. We report here the results of studies carried out in solution, bulk (powder) crystals, and nanocrystalline photochemistry. We have recently shown that excitation of dispirocyclohexyl-1,3-cyclobutanedione 1c led to the trapping of the intermediate oxyallyl with a half life of about 42 min. Our studies with the three other crystalline derivatives revealed that, while all react efficiently, the remarkably long lifetime of oxyallyl is unique to crystals of 1c. Copyright © 2011 John Wiley & Sons, Ltd.

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Keywords: crystalline photochemistry; nanocrystals; oxyallyl; photochemistry; photodecarbonylation

INTRODUCTION

The emergence of robust models of chemical reactivity in rigid media^[1-9] have led to new developments in solid state photochemistry.^[10–13] Although the topochemical postulate^[14–16] suggests that preorganization in the crystal lattice controls the outcome of photochemical reactions in crystals, it is the intrinsic properties of the chromophore that ultimately determine the feasibility of a given photoreaction.^[4,6,17] We have previously suggested that Norrish Type I decarbonylation of crystalline ketones to give radical intermediates is a stepwise process contingent on: (1) α substituents that lower the bond dissociation energy of the two α -bonds to be cleaved and (2) excited state reactivity occurring in the triplet manifold to slow down reversible bond formation long enough for the loss of CO to occur before the first acyl-alkyl radical pair returns back to the starting material.^[18] Recently, we extended the scope of reactivity with examples that involve singlet state photodecarbonylations in the crystalline solid state.^[19,20] As opposed to slowing down reversible bond formation by taking advantage of a spin-forbidden recombination, a promising route is to take advantage of ring strain. If the first α -cleavage reaction occurs with commitment release of ring strain, bond formation back to the starting ketone is unlikely to occur, even in the singlet manifold. Furthermore, it is well known that strained cyclic ketones generally undergo decarbonylation from the singlet excited state $\overline{[21,22]}$ and we have recently reported the photochemistry of crystalline diphenylcyclopropenone^[19,20] and dispiro[5.1.5.1]tetradecane-8,16-dione,^[23] both of which undergo an efficient singlet state decarbonylation despite lacking the radical-stabilizing substituents that would be needed for noncyclic aliphatic ketones. In order to confirm the generality of the cyclobutanedione reaction and to explore the effects of spiro ring substitution on the singlet state photodecarbonylation, we synthesized four 1,3-spirocyclobutanediones (**1a-d**, Scheme 1).

During our investigation of the singlet state photodecarbonylation reaction of dispiro[5.1.5.1]tetradecane-8,16-dione **1c**, we discovered that bulk crystals exposed to UV light acquired a bright blue color with a half-life of about 42 min at 298K (Fig. 1). Using a combination of chemical trapping, spectroscopic techniques, and theoretical calculations, we were able to assign the species responsible for the blue color to the elusive reactive intermediate oxyallyl (Scheme 1). Although ubiquitous throughout the chemical literature,^[24-39] oxyallyl had eluded spectroscopic characterization and isolation,^[23] except for recent photoelectron spectroscopic studies in the gas phase.^[40] The spectroscopic and computational evidence obtained on the blue transient included matching femtosecond transient spectra measured in solution that matched calculations that helped assigned it as an open shell singlet.^[23,41,42] It is worth noting that crystals of **1c**

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Scheme 1. Photochemistry of 1,3-spirocyclobutanediones.

trapped the tetrasubstituted oxyallyl by extending its lifetime by about 10¹⁴ orders of magnitude relative to the solution. During the course of examining the singlet state photodecarbonylation of other 1,3-cyclobutanediones it was of interest to see whether the trapping and observation of oxyallyl would be possible, even though lifetimes greater than a few seconds would be needed. In this paper, we report the solution and solid state photochemistry of four spirocyclobutanediones. Experiments carried out in bulk crystals and in nanocrystalline suspensions showed that the solid state photoreaction is general, but only crystals of **1c** are able to extend the lifetime of oxyallyl to the extent that can be visible to the eye.

EXPERIMENTAL

Synthesis of dispirocyclobutanediones 1a-d

On the basis of a known procedure,^[43] the appropriate cycloalkylcarboxylchloride (about 7 mmol) was dissolved in 10 mL of dry benzene and cooled to 0°C in an oven-dried 50-mL three-neck round bottom flask fitted with a reflux condenser under Ar. After adding 15 mL of dry triethylamine over 10 min, the reaction



Figure 1. Photolysis of white **1c** at 312 nm resulted in a persistent blue color assigned to oxyallyl with a half-life of 42 min as determined by diffuse reflectance ultraviolet spectroscopy (DRUV).

mixture was then refluxed for 25 h to give crude **1a–d**. The latter was purified by column chromotagraphy, (1:5 Et₂O : Hex) and recrystallized from ethanol, cyclohexane, and then a second recrystallization from ethanol immediately prior to photochemical investigations, to give the final product in 45–71% yield after recrystallization. Compound 4,11-di-*t*-butyl-dispiro[5.1.5.1] tetradecane-8,16-dione **1d** formed two polymorphs, α and β , both from ethanol. A single crystal X-ray structure determination of the α -form was possible and the crystallographic information files were deposited in the Cambridge crystallographic data base. In contrast, after the initial characterization and photochemical experiments, the β polymorph could not be isolated again, despite numerous crystallizations under a wide variety of experimental conditions.

Quantum yield determination in the solid state

Relative quantum vield determinations were preformed with dicumyl ketone (Φ_{-CO} =0.18) as an internal standard in a Rayonet photochemical reactor using 312-nm lamps. Quantum yields were determined with equimolar, optically dense suspensions. Optically dense suspension of **1a-d** and dicumyl ketone (DCK) were prepared by the reprecipitation method.^[44] Typically, 16.7 µL of a saturated acetone solution of **1a-d** was injected into 3 mL of vortexing millipore purified water to give an optically dense, but nonscattering, suspension. Independently, 21.0 µL of a saturated acetone solution of DCK was injected into 3mL of vortexing millipore purified water. The suspensions were then combined immediately prior to irradiation in a 50mL quartz Erlenmeyer flask and irradiated. Every 150 s an aliquot was removed (approximately 1/20th of the suspension). The suspensions were extracted with ethyl ether (1mL), washed with brine $(2 \times 0.5 \text{ mL})$ and dried over magnesium sulfate. Samples were then subjected to gas chromatography-mass spectrometry to determine the extent of photoreaction and confirm product assignments. Quantum yields were determined in a minimum of three independent runs.

Quantum yield determination for solution

Using both optically matched (3 experiments), and equimolar (3 experiments) solutions of the cyclobutanediones **1a–d**, relative quantum yield determinations were performed with valerophenone (Φ =0.33) as an internal standard in a Rayonet photochemical reactor using 312nm lamps (BLE-8T312).^[45] Low conversions of less than 10% were used to minimize the possible formation of secondary photoproducts.

RESULTS AND DISCUSSION

Spirocyclobutanediones 1a-d were chosen as photochemical precursors for singlet state Norrish Type I decarbonylation in crystals because it has been reported that most undergo decarbonylation upon irradiation at either 254 or 312nm in solution^[46] (Scheme 1), and all have relatively high melting points (> 75° C).^[47] Spirocyclobutanediones 1a-d differ by the size of the side rings (1a-1d), as well as by the substitution patterns (1c and 1d). For the remainder of the manuscript, compounds 1a-d will be referred by the size of the side ring (i.e., cyclobutyl 1a, cyclopentyl **1b**, cyclohexyl **1c**, and *t*-butylcyclohexyl **1d**). At the outset, it was assumed that these structural differences should not affect the photochemical properties of these molecules drastically, but that they may affect their packing in the crystal lattice. Spirocyclobutanediones **1a-d** were synthesized in one step from commercially available cycloalkylcarboxylic acid chlorides via ketene dimerization in good to moderate yields (71-45%).^[48] The diones **1a-d** all displayed highly symmetric ¹H-NMR and ¹³ C-NMR spectra, as well as the characteristic cyclobutanedione ¹³C-NMR carbonyl peak between 210–216ppm and infrared stretching frequencies from 1734–1736 cm⁻¹ (SI). Compounds 1a-d formed robust crystals from hexane or ethanol, which were characterized by powder X-ray diffraction, and for 1a, 1c, and α -1d, X-ray crystal structures were determined from suitable crystals grown from hexane. Two polymorphic phases of t-butyl **1d**, α and β , were obtained from ethanol and had different melting points, IR spectra, and X-ray powder diffraction patterns. A structure for the α form of spiro-(*t*-butylcyclohexyl)-dione **1d** was obtained by single crystal X-ray diffraction analysis (SI). Initially, the polymorphs crystallized into large single crystals, which could be manually separated. Individual crystals were then characterized by IR, powder X-ray diffraction patterns, and melting point to determine the polymorphic phase. The second polymorph, β , was metastable and converted entirely into the α form. Subsequent attempts to obtain *t*-butyl **1d** in the β form from a variety of solvents failed, rendering it one more case of a disappearing polymorph.^[49]

Previous work by Krapcho reported that photolysis of cyclobutanediones **1a-1c** in dichloromethane undergo either a formal reverse [2+2] cycloaddition to generate the ketenes 2a-c, or two sequential decarbonylations to form alkenes 4a-4c via the corresponding cyclopropanones 3a-3c.[47] In agreement with Krapcho's previous studies, diones **1a-c** undergo efficient photoreaction upon irradiation at 312nm in dichloromethane (DCM). The photochemical reactions were monitored by gas chromatography. The products were identified by comparison to the chromatographic properties of commercially available standards and analyzed by mass spectrometry.^[50] As shown in Scheme 1, all compounds underwent either reverse cycloaddition to give the corresponding ketenes 2a-c, which readily undergo hydrolysis to give the corresponding carboxylic acids, or sequential decarbonylations to give the corresponding alkenes 4a-4c. As in previous studies, the accumulation of cyclopropanones was not oberved, suggesting that they react faster than the cyclobutanediones under the reaction conditions. Although reports of oxacarbene formation and ring expansion during irradiation in methanol have been reported, no other primary photoproducts were detected during irradiation in DCM.^[51] The photochemistry of spiro-(4-t-butylcyclohexyl)-dione 1d in solution has not been described previously, but was similar to the unsubstituted analog 1c. Upon photolysis in DCM at 312nm, a mixture of cyclohexyl ketene 2d and cyclohexylidene alkenes 4d are formed in a ratio of approximately 1:19, by gas chromatography. The 4-t-butyl-cyclohexenyl ketene 2d is hydrolyzed to the carboxylic acid during analysis and its gas chromatographic retention time matches that of the commercially available carboxylic acid. Identification of bis-(4-t-butylcyclohexenyl) alkene 4d was accomplished by analysis of the gas chromatography-mass spectrometry fragmentation pattern.^[50] Although the photochemistry for spirodiones 1b-1d is similar, the photochemistry of cyclobutyl 1a is unique as only the starting material and carboxylic acid **7** are detected during analysis of the reaction mixture. Krapcho had previously reported that spirocyclobutanedione 1a reacts photochemically to form lactone 6, which is assumed to arise from a fragmentation of 1a followed by [2+2] heterocycloaddition of ketene 2a (Scheme 2). Lactone 6 was previously analyzed by strong IR stretches at 1870 and 1740 cm⁻¹. However, attempts to detect lactone 6 by IR measurements during photolysis in solution were negative. The only product detected was carboxylic acid 7, which can be formed by ring opening hydrolysis of 6 followed by ketonization. Quantum yields of reaction were also determined for **1a-d** using standard valerophenone actinometry (SI).^[52] Compounds 1a and 1b have relatively low quantum yields between 0.03-0.04. In agreement with previous reports, the cyclohexyl diones 1c,^[46,47] and 1d, undergo efficient photoreaction, with quantum yield of decarbonylations of 0.34 and 0.33, respectively (Table 1).

Similar to the results observed in solution, photolysis of bulk crystals at 254 or 312nm led to the formation of the corresponding ketene and alkene, as detected by gas chromatography. The use of nanocrystalline suspensions of organic crystals in water provides a simple method to measure steady state quantum yields in the solid state. Nanocrystalline suspensions of 2,4-spiro-1,3-cyclobutanediones **1a-d** were prepared by the reprecipitation method (SI).^[44] Nanocrystalline suspensions synthesized in this manner can reproducible form crystals with an average size of about 200nm. Powder X-ray diffraction patterns confirmed that suspensions prepared in this manner are crystalline, and are the same polymorph as the bulk material (SI). Dicumylketone $(\Phi_{Rxn}=0.18)^{[53]}$ was used to determine the quantum yield of reactions as both optically matched and optically dense suspensions (SI). As shown in Table 1, the quantum yield of reaction for spirocyclobutyl 1a and spirocyclopentyl 1b are similar. The cyclobutyl **1a** has a quantum yield of decarbonylation (Φ_4) of 0.08, and a quantum yield for fragmentation (Φ_2) of 0.18. The cyclopentyl-1,3-dione derivative **1b** has a similar quantum yield of decarbonylation, Φ_4 =0.09, but undergoes reverse cycloaddition less efficiently, Φ_2 =0.05. In contrast to **1a** and **1b**,



Scheme 2. Photochemistry of 1,3-spirocyclobutanedione 1a

Table 1.	Quantum yields of retro $[2+2]$ cyclization (Φ_2) and	k
decarbon	lation (Φ ₄)	

Compound	DCM			Nanocrystals		
	Φ_2	Φ_4	2:4	Φ2	Φ_4	2:4
1a	0.03	0.00	100:0	0.18	0.08	69:31
1b	0.00	0.04	0:100	0.05	0.09	36:64
1c	0.01	0.34	3:97	< 0.001	< 0.001	
α-1 d	0.01	0.33	3:97	\approx 0.002	0.01	17:83
β- 1d				0.03	0.10	23:77

spirocyclohexyldione **1c** has a very low quantum yield of reaction in the solid state ($\Phi_{2+4} < 0.001$). The α form of spiro-(4-*t*-butylcyclohexyl) derivative **1d** also had very low quantum yields of reaction as a nanocrystalline suspension, with $\Phi_4=0.01$, and $\Phi_2\approx 0.002$. However, the β form (4-*t*-butylcyclohexyl) derivative **1d** had a moderate quantum yield of $\Phi_4=0.10$, and $\Phi_2=0.03$.

We previously reported that irradiation of white crystals of cyclohexyl dione **1c** take on a persistent deep blue color. This blue color is immediately quenched by dissolving the crystals but it decays slowly under argon or oxygen atmospheres with a half-life of about 42min in the crystal lattice.^[23] The intermediate responsible for this blue color was trapped with furan in an interfacial liquid–solid reaction to quantitatively form the tetracyclic ketoether **5** (at about 6% corv.). The trapped product was presumed to arise via a [3+4] cycloaddition between furan and oxyallyl.^[54,55] Extended irradiations (>24h) resulted in a photobleaching of the intermediate and the only product detected is cyclohexylidene alkene **4c**. In combination with computational results, the experimental results led us to conclude that oxyallyl was efficiently trapped in the crystal lattice.^[23]

The following experiments were preformed to determine whether oxyallyl could be trapped on timescales of a few seconds in the crystal lattice of the photochemical precursors. Attempts to detect oxyallyl upon irradiation of bulk crystals of **1a**, **1b**, or α -**1d** met with no success. In all cases, irradiation of the bulk crystals resulted in efficient singlet state decarbonylation but there was no detectable blue coloration, either visible to the eye or by diffuse reflectance UV–Vis. To test the possibility that colorless oxyallyl could be forming and accumulating in crystals of **1a**, **1b**, and α -**1d** with an absorption $\lambda_{max} < 400$ nm,^[23] crystals were irradiated at 298K and immediately dissolved in neat furan. Noting that no trapped products analogous to the tetracyclic ketoether **5** were detected, one may conclude that crystals of spirocyclobutanediones **1a**, **1b**, and α -**1d** are

not able to extend the lifetime of oxyallyl as much as crystals of the cyclohexyl derivative **1c**. To determine if oxyallyl was formed, but was rapidly undergoing ring closure at room temperature, irradiation of crystals of all spirocyclobutanediones **1a–d** was performed at 77K. After confirming that crystals of cyclohexyl **1c** acquired a pale blue coloration at 77K, we found that crystals of **1a**, **1b**, and α -**1d** remained unchanged.

Given the structural and photochemical similarities of the spirocyclohexyl derivatives 1c and 1d, it was of interest to explore whether substantial differences in the crystalline environment may be responsible for the different kinetic behavior of oxyallyl. The single crystal structure of 1c, grown from hexane and solved in a Cmca orthorhombic space group,^[56] has been previously reported.^[23] A single crystal of the α polymorph of spiro-(4-tbutylcylcohexyl) 1d was grown from hexane and solved in the orthorhombic space group Pmna.[57] A single crystal structure of the disappearing β polymorph could not be acquired. As shown in Figures 2(A) and (B), the packing arrangements of 1c and α -1d are similar with both compounds packing in alternating layers with different lateral displacements. Each dione has a different symmetry operation relating the two cyclohexyl rings. Whereas cyclohexyl 1c has a C2 axis perpendicular to the cyclobutane ring, t-butylcyclohexyl 1d has a mirror plane through the 1,3-butadione moiety. As a result of the C₂ axis of symmetry relating the spirocyclohexyl rings in 1c, to form the cyclopropanone 3c, one of the cyclohexyl rings seems to undergo approximately a 60° angular displacement, so that the corresponding 4-carbon atom must be displaced by about 0.137 nm (Fig. 3). To accomplish the ring closure, the cyclohexyl moiety would either have to move through space occupied by an adjacent carbonyl moiety, or wait for the neighboring molecules to unergo larger local displacements. In contrast, both cyclohexyl rings are oriented in the same direction in crystals of α -(4-t-butylcyclohexyl) **1d** as a result of the orientation of the two cyclohexyl moieties. We speculate that two rings may partake in less motion to undergo ring closure so that the resulting cyclopropane may fit better within the original cavity of the reactant. This suggestion is supported in part by comparing the packing coefficient of spirocyclohexyl **1c** and α -(t-butylcyclohexyl) 1d, which are 0.71 and 0.67, respectively.^[58] The lower packing density of α -(t-butylcyclohexyl) **1d** indicates that there is more void space present in the crystal lattice that might accommodate more local displacements. We tentatively conclude that there is enough void space and flexibility in the lattice to allow for ring closure. A single crystal of cyclobutyl 1a was grown from hexane and solved in the monoclinic space group P2₁/c.^[59] One can see that the crystalline environment of cyclobutyl 1a is highly congested. The crystal lattice forms alternating rows of



Figure 2. Space-filling views from the crystal structures of **1c** (A) and α -**1d** (B) showing similar packing and packing coefficients, 0.71 and 0.67, respectively. The similarity of their packing motifs is highlighted by the molecules within the blue boxes (which do not correspond to the unit cells). (C) The highly congested crystal lattice of **1a** with alternating rows of 2,4-spirocyclobutyl-1,3 cyclobutadiones



Figure 3. Hypothetical structures of oxyally derived from the X-ray crystal structures of diones **1c** (A) and α -**1d** (B) obtained by removing one of the carbonyl groups. The energy minimized structures of the corresponding cyclopropanone products are shown on the right. While it appears that one of the two rings in **1c** must undergo a much greater displacement than the other, as shown by the arrows, smaller displacements in a lower density crystals may be shared by the two cyclohexyl groups in the case of α -**1d**

two crystallographically independent molecules (Fig. 2(C)). Cyclobutyl **1a** is unique among the cyclobutadiones in that it has a strong preference for retro [2+2] cycloaddition over decarbonylation in both solution and the crystalline environment. Comparison of the ratio of retro [2+2] cycloaddition (2a) and decarbonylation (4a) in DCM and the crystalline environment indicates that the decarbonylation reaction is favored in the solid state (Table 1). Inspection of the crystal structure indicates that retro [2+2] cycloaddition may be difficult. Numerous close contacts are within the crystal lattice, which may impede the motions needed for the ring opening process in the crystal lattice. This may be the reason why spirocyclobutyl **1a** has a much greater quantum yield of decarbonylation as a nanocrystalline suspension than in solution. A single crystal for cyclopentyl **1b** could be grown from hexane, but the crystals were of poor quality.

It is notable that only the crystal lattice of cyclohexyl 1c stabilized oxyallyl for the accumulation of a steady state concentration that is visible to the eye. Hoping to confirm that the crystal lattice of **1c** was the stabilizing force behind the trapping of oxyallyl, we searched for polymorphs of cyclohexyl 1c to confirm that the long lifetime is due to crystal packing effects. Unfortunately, no new polymorphs could be grown from a variety of organic solvents or from the melt. In addition, the photolysis of cyclohexyl 1c was attempted in other rigid media. Samples of 1c were dissolved independently in methylcyclohexane, methyltetrahydrofurn, and toluene. The solutions of about 0.01M were cooled down to 77K to form transparent glasses and irradiated at λ =312nm. No color was present in any of the glassy matrixes during irradiation times as long as 4 h.^[52] Subsequent gas chromatographic analysis confirmed that the reaction in the matrixes had taken place (about 40% conversion). Dione 1c was also embedded in a rigid sucrose matrix^[60,61] and irradiated both at 77 and 298K (SI). There was no detectable discoloration of the sucrose glass during irradiation at either temperature. Finally, mixed crystals of about 1% of cyclohexyl 1c embedded within the crystal lattice of cyclopentyl 1b and t-butylcyclohexyl 1d were irradiated at 312nm. No purple coloration could be

observed by diffuse reflectance UV–Vis upon irradiation of the mixed $\mbox{crystals}.^{\rm [62]}$

CONCLUSIONS

We have gathered strong photochemical evidence suggesting that the release of ring strain in cyclobutanediones is a viable strategy to facilitate the formation of biradicals from crystalline ketones that are known to react primarily from the singlet excited state. Using bulk dry powders and nanocrystalline suspensions, we found that all five aliphatic diones studied in this work undergo decarbonylation ($\Phi_{-CO} \approx 0.01-0.2$) despite lacking radical stabilizing groups. We had recently reported that oxyallyl is efficiently trapped in the crystal lattice of dispiro[5.1.5.1] tetradecane-8,16-dione 1c, but all attempts to generate and trap oxyallyl in the crystal lattices of the other precursors or in other rigid matrixes failed. We conclude that the crystal lattice of 1c is unique in its ability to stabilize and trap oxyallyl for a time scale of several minutes and we plan to analyze the formation of oxyallyl as a short-lived intermediate in nanocrystals of the other precursors.

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