Efficient Photocyclization of *o*-Alkylbenzaldehydes in the Solid State: Direct Observation of *E*-Xylylenols en Route to Benzocyclobutenols

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The photocyclization to benzocyclobutenols of *o*-alkyl aromatic aldehydes that are predestined for γ-hydrogen abstraction is found to occur efficiently in the solid state; in contrast, solution-phase photolysis is known to afford a mixture of several products. It is shown that mesitaldehyde, which is a liquid, also undergoes efficient cyclization when subjected to photolysis as a solid inclusion complex. The marginal energy differences in the relative energies of the *E*-enols and the corresponding cyclobutenols in the case of cyano-substituted mesitaldehydes has permitted direct observation, for the first time, of the *E*-enols en route to benzocyclobutenols. The AM1 calculations suggest that the cyano-substitution causes intrinsic stabilization of the *E*-enols relative to the corresponding cyclobutenols, while the bromo groups do the opposite. The lack of observation of the red color in bromo- and formyl-substituted aldehydes is attributed to rapid cyclization of the *E*-enols to the their respective cyclobutenols even at low temperatures.

Introduction

The solution as well as solid-state photochemistry of *o*-alkylphenyl ketones has been well established;[1−9] cyclization to synthetically important benzocyclobutenols[10−15] is, in general, the major pathway of photolysis. In a striking contrast, the solution-state photochemistry of *o*-alkylaryl aldehydes is frustrated by the formation of myriad of products. For example, photolysis of *o*-methylbenzaldehyde has been reported to afford as many as seven photoproducts (Scheme 1) depending on the conditions of photolysis.[16,17] It should be noted that the synthetically useful benzocyclobutenol (CB) is only a minor product (10%). Surprisingly, the solid-state photoreactivity of *o*-alkylaromatic aldehydes has been explored only little if any.[18−20] The limited study has nonetheless revealed fascinating photochromism based on enolization. The photoinduced color change has been attributed to the formation of *o*-xylylenol, which has been shown by Wagner and co-workers to be the precursor of the cyclobutenol.[4] The latter, according to Ito and co-workers,[2,3] is obtained directly from the triplet-excited biradical (= triplet enol).[21] Be this mechanistic dichotomy as it may, the formation of cyclobutenol has been found to occur in a poor yield (ca. 10%) in a thoroughly examined case of solid-state photolysis of an *o*-alkylaromatic aldehyde.[19] Our recent observation of facile formation of cyclobutenol in the solid-state photolysis of *p*-anisaldehydes[20] prompted us to explore the solid-state photobehavior of *o*-alkylaromatic aldehydes that are predestined for γ-hydrogen abstraction. Furthermore, a detailed study deemed worthwhile in view of the formation of a complex mixture of products in the solution-state photolysis and intriguing photochromism in the solid state. Herein we report the efficient photocyclization of crystal-

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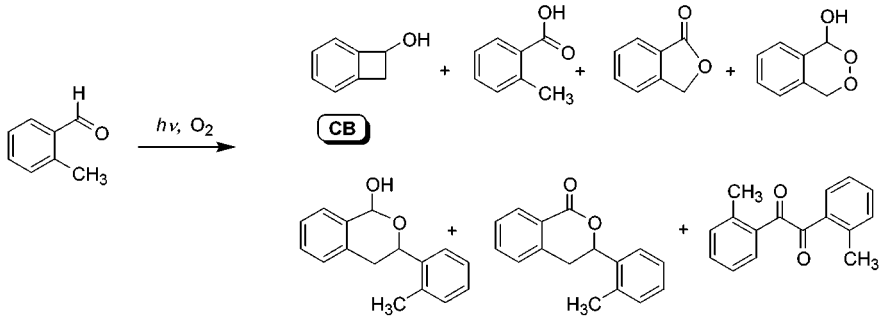
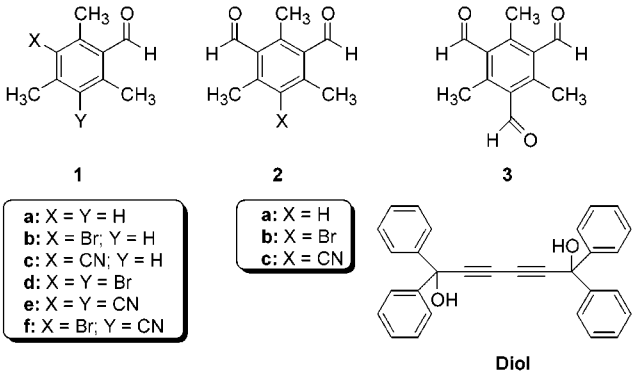
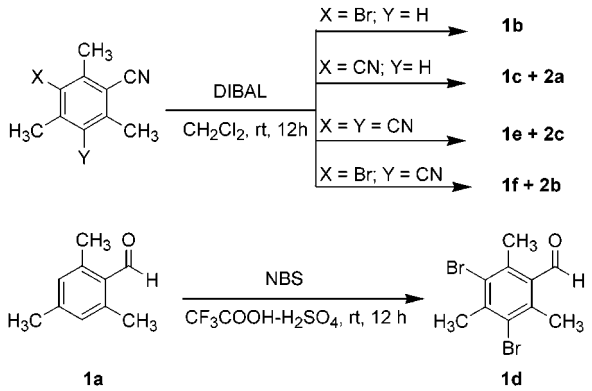
Scheme 1





line mesitaldehydes **1**−**3** and present evidence for direct observation of (E)-*o*-xylylenol on the way to cyclobutenol formation.

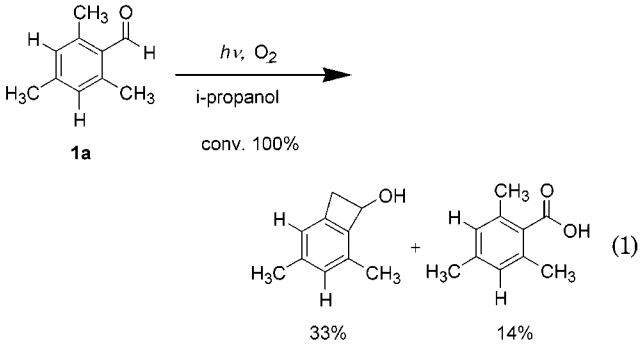
Scheme 2



Results

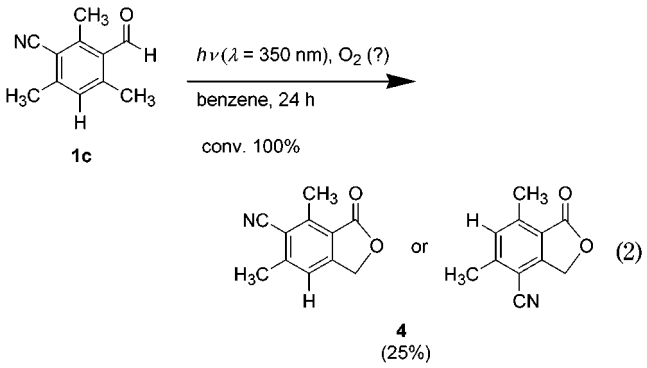
Synthesis of the Aldehydes 1−3. The mesitaldehyde **1b** was synthesized by the reduction of 4-bromo-2-cyanomesitylene using DIBAL (Scheme 2). The mesitaldehydes **1c** and **2a** were available together from the reduction of 2,4-dicyanomesitylene in the ratio of 1:1.08 (77% yield), respectively. The dibromomesitaldehyde **1d** was prepared by bromination of mesitaldehyde **1a** using NBS in TFA−H_2SO_4, a recently reported procedure.[22] The reduction of tricyanomesitylene using DIBAL afforded the aldehydes **1e** and **2c** (86%) in a ratio of 1:1.25. Similarly, the reduction of 2,4-dicyano-6-bromomesitylene yielded the aldehydes **1f** and **2b** (78%, 1:1.48). The trimethyltrimesaldehyde **3** was prepared by reducing tricyanomesitylene using large excess of DIBAL. The lattice inclusion host diol, viz., 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol, was synthesized following the reported procedure.[23]

Solution-State Photolysis. The solution-state photochemistry of the parent mesitaldehyde **1a** has been known for a long time;[24] accordingly, the photolysis of ca. 0.03 M solution of **1a** in 2-propanol yields the cyclobutenol and the mesitoic acid in 33 and 14% yields, respectively (eq 1). We have similarly tried to establish



(1)

the solution-state photochemistry of the aldehydes **1**−**3**. As representative cases, the benzene solutions (ca. 5 mM) of the aldehydes **1c**, **1d**, **2a**−**c**, and **3** were subjected to irradiation in a Rayonet reactor (λ = 350 nm) under oxygen-excluded conditions. After irradiation for 24 h, the only isolable product in the case of **1c** was found to be the phthalide **4** in 25% yield (eq 2);[25] the



(2)

remainder was a polar polymeric material. The TLC analysis of the photolysate from **1d** indicated the formation of several products and the cyclobutenol could not be readily identified. A similar scenario was found with

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Table 1. Results of Solid-State Photocyclization of Aldehydes 1−3[a]

entry	substrate	temp (°C)	conv (%)[b]	yield (%)[c]
1	**1a**	30	40	100[d]
2	**1b**	0[e]	33	92
		30[e]	40	82
3	**1c**	30	91	68
4	**1d**	30	100	90
5		30[e]	86	100[d]
6		−80[e]	42	100[d]
7	**1e**	30	100	90
8		30[e]	75	100[d]
9		−80[e]	18	100[d]
10	**1f**	30	72	89
11	**2a**	30	92	56[f]
12	**2b**	30	66	21[f]
13	**2c**	30	74	25[f]
14	**3**	30	79	24[f]

[a] Unless otherwise mentioned, all the photolyses were conducted in a Rayonet reactor (λ = 350 nm) for 24 h by dispersing the powdered samples in sealed test tubes purged with a stream of nitrogen gas. The samples were stirred periodically to ensure uniform exposure. [b] Based on recovered starting material. [c] Isolated yields based on conversion, unless otherwise mentioned. [d] From ^{1}H NMR analysis, error ± 10%. [e] High-pressure Hg-lamp ($\lambda \geq$ 300 nm), duration = 2 h. [f] The remainder was an intractable polymeric material.

the photolysis of **2a** and **3**. When **2b** was photolyzed until its disappearance (TLC analysis), a highly intractable polymeric material was obtained. However, the cyclobutenol (**2b-CB**) was isolated in 53% yield at 30% conversion. Similarly, **2c** afforded the cyclobutenol **2c-CB** in 21% yield at 80% conversion. Clearly, the solution-state photochemistry of *o*-alkylbenzaldehydes leads to a complex mixture of several products.

Solid State Photochemistry of the Inclusion Complex between Mesitaldehyde 1a and the Host Diol. As the parent mesiatldehyde **1a** is a liquid, we formed its crystalline inclusion complex with the well-known host diol.[26] The stoichiometry of the complex was established to be 1:2 (host:guest) from ^{1}H NMR analysis and unequivocally from X-ray crystal structure determination (vide infra). The photolysis of the gently ground crystals of the inclusion complex, dispersed in a Pyrex container purged with N_2 gas for 15 min, was conducted in a Rayonet reactor (λ = 350 nm). From ^{1}H NMR analysis of the irradiated crystals, the cyclobutenol was established to be the sole product at 40% conversion (entry 1, Table 1).

Solid-State Photolysis of the Aldehydes 1b−f, 2, and 3. The solid-state photolysis of all of these aldehydes was carried out in the same manner as described above. In preparative photolyses, ca. 100 mg of the solid sample was irradiated and subjected to column chromatography. The results of solid-state photolyses are given in Table 1. The aldehydes **1b−f** clearly afforded the cyclobutenols in good yields (entries 2−10). A notable difference in the photobehavior was observed when isophthalaldehydes **2** and trimesaldehyde **3** were subjected to solid-state photolysis. In all these cases, in addition to the cyclobutenol, a highly polar polymeric material was invariably formed in significant amounts. As may be seen from the results in Table 1, the yields of cyclobutenols from **2b**, **2c**, and **3** (entries 12−14) are significantly low, suggesting that the formation of intractable material increases with formyl substitution.

(26) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.

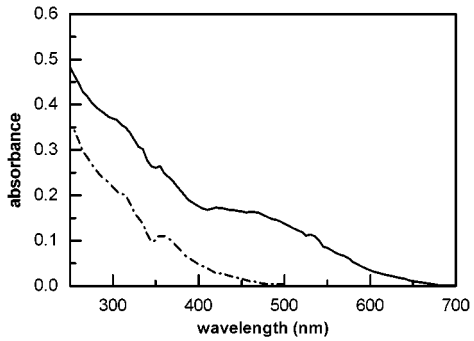
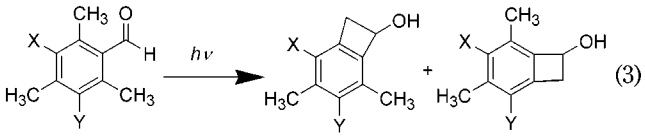


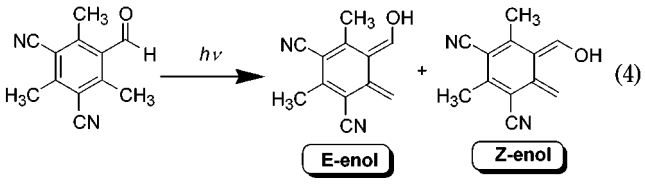
Figure 1. UV-vis absorption spectra of **1e** before (dotted line) and after (solid line) irradiation ($\lambda \geq$ 300 nm).

Two regioisomeric cyclobutenols are in principle possible for the aldehydes **1b**, **1c**, **1f,** and **2a−c** depending on the orientation of the formyl group in the crystal lattice (eq 3). In all of these cases, mixtures of the two possible regioisomeric cyclobutenols were isolated. No effort was made to separate the isomers and quantify their relative ratios.



(3)

All the cyano-substituted aldehydes **1c**, **1e**, and **1f** turned orange-red color upon exposure to UV-irradiation. The color persisted as long as the samples were exposed, but disappeared immediately (ca. 2 min at 25−30 °C) when protected from light at room temperature. A similar behavior was exhibited by the isophthaldehydes **2a** and **2c.** No color was observed in the case of **1a**−diol complex, **1b**, **1d**, and **2b**. The trimesaldehyde **3** gave rise to yellow color. Figure 1 shows the absorption spectra typically recorded for the case of **1e** before and after exposure to UV-radiation from a high-pressure Hg-lamp. On the basis of the documented kinetic behavior of *Z*- and *E*-enols,[1,27,28] we attribute the absorption in the visible region between 400 and 600 nm to the *E*-enol (eq 4);[29] the *Z*-enols are known to be considerably unstable and undergo rapid reversion to the aldehyde.[1,27]



(4)

The two aldehydes **1d** and **1e**, differing only in terms of their substituents, viz., bromo and cyano, exhibit quite contrasting behavior in that the latter turns red, while the former remains colorless upon irradiation. We have simultaneously irradiated these two aldehydes at low (−80 °C) and at room (30 °C) temperatures for 2 h using the high-pressure Hg source (λ > 300 nm). Both **1d** and **1e** were found to exhibit notable temperature depend-

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(28) Gebicki, J.; Krantz, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1623.

(29) For UV−vis absorption spectrum of the *E*-enol of *o*-methylbenzaldehydes, see: refs 20 and 28.

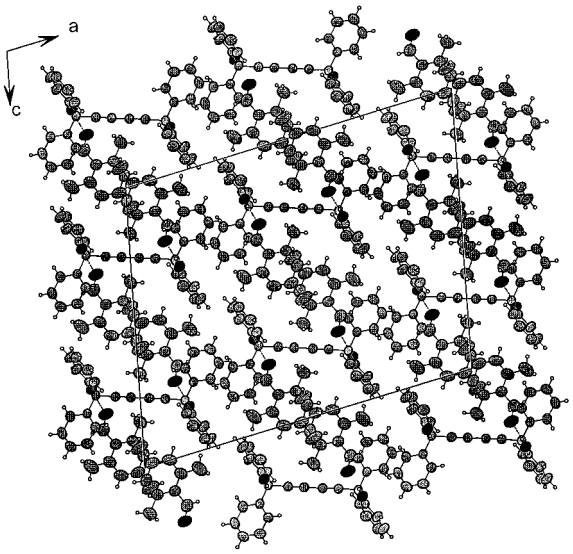


Figure 2. The crystal packing diagram of the complex of mesitaldehyde **1a** with the host diol. The hydrogen bonding between the guest carbonyl oxygen and the host diol are shown with a broken line.

ence; while the yield of cyclobutenol was higher (entries 5 and 8) at room temperature (ca. 30 °C), it considerably reduced at low temperature (entries 6 and 9).[30] Noticeably, the temperature effect is more pronounced in the case of **1e**.

X-ray Crystal Structure Analyses and Structure−Reactivity Correlations. To establish (i) the complex formation between the lattice inclusion host diol and mesitaldehyde **1a** and (ii) to correlate the solid-state photoreactivity of mesitaldehydes with their crystal structures, we sought to examine the X-ray crystal structures of the complex of **1a** with the diol, **1d**, and **1e**. The aldehydes **1d** and **1e** were considered in particular, since both these aldehydes undergo efficient cyclization with only **1e** undergoing color change to red during irradiation. We surmised that the apparent differences in their photobehavior could be rationalized from the crystal packing analyses. While the crystals of **1a**−diol complex and **1e** could be grown readily, our efforts to obtain crystals of **1d** suitable for X-ray studies were not successful.

Figure 2 shows the perspective view of molecular packing diagram of the complex between **1a** and the diol. It can be readily discerned that the hydroxy groups at the termini of the linear chain of the diol act as anchors to bind the two guest mesitaldehyde molecules through strong O−H···O hydrogen bonds ($d_{O\cdots H} = 1.96$ Å, $\theta_{O-H\cdots O} = 169.7°$). Figure 3 shows the molecular packing diagram of **1e**. One observes that the weaker C−H···O and C−H···N intermolecular interactions operate in concert in controlling the crystal packing. The carbonyl oxygen participates in C−H···O intermolecular hydrogen bonding with two hydrogens of the methyl groups of different neighbors. Interestingly, both nitrogen atoms of the C≡N groups hydrogen bond to two different hydrogens of the neighboring molecules.

(30) Although the photolyses were carried out at identical conditions, a comparison of the temperature-dependent conversions of solid-state reactions is subject to a variety of factors such as homogeneous dispersion of the sample, uniform light intensity, etc. Since a similar trend in the yields was observed in three independent experiments, we believe that the reaction is indeed temperature-dependent.

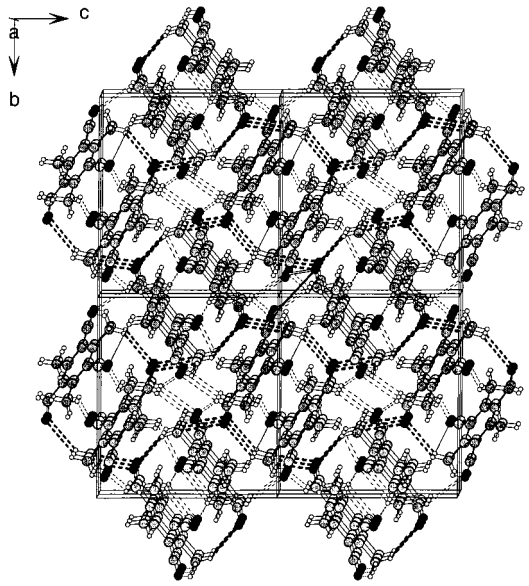


Figure 3. The molecular packing diagram of **1e**. The C−H···O bonds are shown with a bold broken line and those of C−H···N with a light broken line.

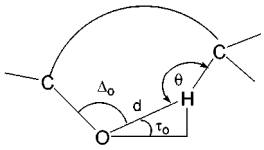


Figure 4. Geometrical parameters for γ-hydrogen abstraction.

Table 2. Scheffer's Geometrical Parameters for γ-Hydrogen Abstraction

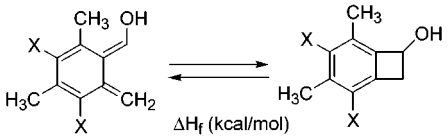
compound	d (Å)	θ (deg)	Δ_0 (deg)	τ_o (deg)
1a−diol	2.55	94.4	97.8	11.6
1e	2.43	112.6	94.8	10.3

From their extensive studies on photochemical γ-hydrogen abstraction of ketones in solid state, Scheffer and co-workers have set forth certain geometrical parameters, viz., d, Δ_o, θ, and τ_o, which quantitatively describe the feasibility of H-abstraction.[31] The abstraction is said to be at its best when $d = 2.3-3.0$ Å, $\Delta_o = 90-120°$, $\theta = 180°$, and $\tau_o = 0°$ (Figure 4). The values calculated from X-ray structural parameters for abstraction of closest methyl hydrogens for **1a**−diol complex and for **1e** are shown in Table 2. These values deviate significantly from the ideal ones, which are seldom realized. Nonetheless, they fall in the range generally observed for a variety of substrates that undergo Norrish Type II reaction in the solid-state.[31] Thus, the γ-hydrogen abstraction, the primary event, is facile in both cases to yield the triplet-excited 1,4-biradical/enol.

AM1 Calculations. Semiempirical AM1 calculations have been shown to yield results in good agreement with the experiment for the *o*-xylylenol to benzocyclobutenol transformation.[32] We have carried out these calculations (QCMP 137, MOPAC/PC)[33] for the aldehydes **1a**, **1d**, **1e**, and **3** to assess the relative stabilities of cyclobutenol and *E*-enol in these cases. In Scheme 3 are shown the

(31) Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885.
(32) Coll, G.; Costa, A.; Deya, P. M.; Flexas, F.; Rotger, C.; Saa, J. M. *J. Org. Chem.* **1992**, *57*, 6222.
(33) Dewar, M. J. S.; Zeobish, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3092.

Scheme 3. Enthalpies of Reaction



1a: X = H 1.99
1d: X = Br 3.79
1e: X = CN 1.16
3: X = CHO 2.79

enthalpies of reaction. The AM1 results predict that the dicyano-substitution (**1e**) stabilizes the *E*-enol relative to the cyclobutenol (ΔH_f = 1.16 kcal/mol vs 1.99 kcal/mol for mesitaldehyde **1a**), while the dibromo-substitution (**1d**) causes the opposite effect (ΔH_f = 3.79 kcal/mol). The latter is true even with diformyl substitution (**3**, ΔH_f = 2.79 kcal/mol).

Discussion

As noted at the outset, the solution-state photolysis of *o*-alkylaryl aldehydes leads to a complex mixture of products with a highly intractable polymeric material often formed in significant yields.[16,17,24,32] The reported results of photolysis for **1a**[24] and those for **1c** and **1d** (present study) in benzene solutions (5 mM, λ = 350 nm) further emphasize the complexity with solution phase photolysis. In contrast, the results of solid-state photolysis of aldehydes **1** are remarkable as can be seen from results given in Table 1. While the yields of benzocyclobutenols are good to excellent for aldehydes **1**, one begins to observe a complex mixture of products with considerable material loss leading to low yields of cyclobutenols in the case of aldehydes **2** and **3**. Nonetheless, the results for aldehydes **1** suggest that the solid-state photolysis is a viable alternative to access benzocyclobutenols.

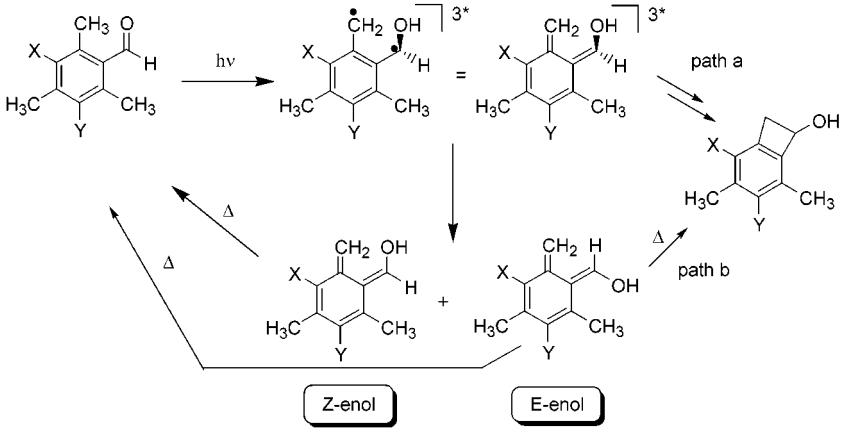
The results of photolysis of inclusion complex of **1a** with the host diol are significant in that the utility of lattice inclusion compounds for isolating the liquid samples as crystalline materials and regulating the photochemistry of included guest molecules is further demonstrated. Indeed, the inclusion complex formation with a chiral host is an excellent strategy for asymmetric synthesis and optical resolution.[26]

We shall now consider the mechanism with which the benzocyclobutenols may be formed in the crystal lattice. Scheme 4 is an exemplary of events that occur following photoexcitation of the aldehydes. The mechanism involves abstraction of a γ-hydrogen by the triplet-excited carbonyl to afford 1,4-radical, which is considered equivalent to the triplet-excited enol.[21] This species may decay either to the *E*-enol or *Z*-enol. The latter is known to be short-lived due to a faster reverse hydrogen transfer process (thermal 1,5-sigmatropic shift) that regenerates the precursor aldehyde.[1,27] On the other hand, the *E*-enols are longer-lived and all the bimolecular trapping chemistry is in agreement with its stereochemsitry.[1] Wagner and co-workers have convincingly shown that the benzocyclobutenols indeed derive from thermal conrotatory closure of the *E*-enols.[4] In contrary, Ito and co-workers believe that the cyclobutenols need not necessarily obtain from *E*-enols, but can derive from direct collapse of the 1,4-triplet biradical/enol.[2,3] Indeed, Coll et al. have also found no evidence for involvement of enols in the formation of cyclobutenols from methoxy-substituted benzaldehydes.[32] Thus, the mechanistic dichotomy with regard to the formation of cyclobutenols continues to be intriguing.

The Scheffer's geometrical parameters for **1a**−diol complex and for **1e** suggest that the primary γ-hydrogen abstraction in their crystal lattices is facile to afford the respective triplet 1,4-biradicals, whose structures have been shown from theoretical calculations to be twisted at one end.[34] The observation of red-color, attributed to *E*-enols, in all the cyano-substituted aldehydes **1c, 1e, 1f**, and **2c**, and efficient formation of cyclobutenols clearly suggest that pathway b (Scheme 4) is operative in the cyclizations. Indeed, the temperature dependence of the cyclization is clearly borne out from the comparison of the results of photolysis for **1d** and **1e** at low and high temperatures under otherwise identical conditions of irradiation. The yield of cyclobutenol is considerably low for **1e** at low temperature (entry 9, Table 1), but significantly high at room temperature (entry 8). A similar but less pronounced effect is observed for **1d** (entries 5 and 6). Therefore, the lack of observation of *E*-enol (red color) cannot be taken to imply that path b (Scheme 4) is not operative in this aldehyde, i.e., **1d**, and other aldehydes **1a**,**b**, **2a**,**b**, and **3** that do not turn red upon irradiation. After all, why the similar class of compounds differing only in terms of substituents should follow two different pathways cannot be easily reconciled.

To answer the question as to why some aldehydes exhibit red color due to *E*-enols and some others not, we undertook AM1 theoretical calculations. The AM1 enthalpies of the reaction in Scheme 3 for the aldehydes

Scheme 4



1a,**d**,**e** and **3** show that cyano-substitution causes intrinsic stabilization of the *E*-enols relative to the corresponding cyclobutenols, while the bromo and formyl groups do the opposite. Whether or not these gas-phase results are applicable to the condensed phase is questionable. Nonetheless, it is reasonable to assume that a similar trend in the relative energies of the enols and cyclobutenols operates in the solid-state such that the exothermicity associated with cyclization is higher for all aldehydes without cyano substituents.[35] The rapid cyclization thus may preclude the *E*-enols from being observed even at low temperatures. The observation of red color in all the cyano-substituted aldehydes can similarly be reasoned based on a marginal difference in the energies of *E*-enols and the corresponding cyclobutenols in the crystal lattice. A closer inspection of the molecular packing diagram for **1e** reveals that the hydroxyl group of the *E*-enol (formed in the crystal lattice) can find itself in the close proximity of cyano groups, such that that the *E*-enol may be stabilized through O−H···N intermolecular hydrogen bonds involving the nitrogen atoms of the cyano group. Presumably, a composite of the effects due to crystal lattice stabilization and cyano-substitution (of enols) cause the energy difference between the cyclobutenols and the corresponding enols marginal. Otherwise, the red color due to *E*-enols would not be observed.

In conclusion, it is shown that the synthetically important benzocyclobutenols are efficiently formed in the solid-state photolysis of mesitaldehydes that are predestined for γ-hydrogen abstraction. Thus, the solid-state photolysis is a convenient way to access benzocyclobutenols in contrast to the solution-phase photolysis of *o*-alkylbenzaldehydes, which leads to notoriously complex mixtures. The strategy based on the formation of inclusion complex for photolysis in the solid state of liquid samples is further demonstrated using the diol host. The marginal energy differences in the relative energies of the *E*-enols and the respective cyclobutenols in the case of cyano-substituted mesitaldehydes has permitted direct observation, for the first time, of the *E*-enols en route to benzocyclobutenols. The AM1 calculations suggest that the cyano-substitution causes intrinsic stabilization of the *E*-enols relative to the corresponding cyclobutenols, while the bromo groups do the opposite. The lack of observation of the red color in bromo- and formyl-substituted aldehydes is attributed to rapid cyclization of the *E*-enols to their respective cyclobutenols even at low temperatures.

Experimental Section

General Aspects. UV−vis absorption spectra were run on Shimadzu spectrophotometer (UV 160 A) and Infrared spectra on Bruker Vector 22 FT-IR spectrophotometer. NMR spectra were run on JEOL 400 MHz NMR Spectrophotometer with deuterated solvents as internal standards. The elemental analyses were performed on Thermoquest CE (EA 1110) instrument. The melting points were determined with Perfit Melting Point Apparatus (Perfit India) and are uncorrected. The solvents were used as received and purified by standard procedures where necessary. The commercial chemicals from Lancaster (UK), S.D. Fine Chemicals (India), DIBAL (Lancaster) were used as purchased. Column chromatography was conducted on silica gel (particle size: 60−120 μm; Acme Synthetic Chemicals, India).

Syntheses. 2-Bromomesitylene, 2,4-dibromomesitylene, 2,4,6-tribromomesitylene were prepared according to the reported procedures.[36] The cyanomesitylenes, viz., 2-cyano-4-bromomesitylene, 6-bromo-2,4-dicyanomesitylene, 2,4-dicyanomesitylene, and 2,4,6-tricyanomesitylene were synthesized from the corresponding bromomesitylenes following the reported procedure using CuCN in DMF.[37] The host diol was available from the known literature procedure.[23]

The aldehyde **1b** was synthesized by reducing 4-bromo-2-cyanomesitylene using DIBAL in CH_2Cl_2. The mesitaldehydes **1c** and **2a** were available together in 1:1.08 ratio from the reduction of 2,4-dicyanomesitylene using DIBAL in 77% total yield. The aldehydes **1e** and **2c** were obtained from the reduction of tricyanomesitylene (86%, **1e**:**2c** = 1:1.25). Similarly, the reduction of 6-bromo-2,4-dicyanomesitylene with DIBAL yielded **1f** and **2b** (1:1.48) in an overall yield of 78%. The aldehyde **1d** was prepared by bromination of mesitaldehyde according to the recently reported procedure using NBS in TFA−H_2SO_4.[22] The trimethyltrimesaldehyde **3** was prepared from reduction of 2,4,6-tricyanomesitylene using DIBAL.

Synthesis of 1d. To a solution of mesitaldehyde **1a** (0.74 g, 6 mmol) in trifluoroacetic acid (2.6 mL) was added 5.4 mL of concd H_2SO_4. To this reaction mixture was added 1.5 g of *N*-bromosuccinimide, and the reaction mixture was stirred at room temperature for 18 h. After this period, the contents were poured crushed ice and the solution was made alkaline with 2 N NaOH. The organic matter was extracted with dichloromethane (30 mL × 2). The combined extracts were washed with water, dried over anhyd Na_2SO_4, filtered, and removed in vacuo. The residue was subjected to silica gel column chromatography (10% EtOAc−petroleum ether) to obtain 1.35 g (88%) of **1d** as colorless crystals,[38] mp 160 °C (dec); IR (KBr) cm^{-1} 2923, 1698, 1444, 1378, 1557, 1156, 1104; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 6H), 2.67 (s, 3H), 10.40 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 26.8, 125.0, 127.6, 137.0, 137.6, 194.0.

General Procedure for the Reduction of Cyano-Substituted Mesitadehydes. A 20 mL solution of dicyanomesitaldehyde (2.5 mmol) in dichloromethane was taken in a two-necked round-bottom flask under a nitrogen gas atmosphere and cooled to 0 °C in an ice bath. After 10 min, 6.0 mL (6.0 mmol) of DIBAL in toluene was slowly introduced into the reaction flask. The reaction mixture was gradually allowed to attain the room temperature. After stirring for 12 h, it was quenched with dil HCl, and the contents were heated at reflux for 30 min. Subsequently, the reaction mixture was extracted with dichloromethane (25 mL × 3), dried over anhyd Na_2SO_4, and filtered and solvent removed in vacuo. The crude product was submitted to silica gel column chromatography.

1b: Colorless crystalline powder; mp 81−83 °C; IR (KBr) cm^{-1} 2924, 1743, 1584, 1455, 1376; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.35 (s, 3H), 2.42 (s, 3H), 2.61 (s, 3H), 6.91 (s, 1H), 10.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 20.1, 24.7, 127.2, 129.9, 132.2, 139.2, 140.3, 143.7, 193.2. Anal. Calcd for $C_{10}H_{11}$-BrO (mol wt 227.10) C, 51.78; H, 4.34. Found: C, 51.31; H, 4.97.

1c: 86%, colorless powder, mp 102−104 °C; IR (KBr) cm^{-1} 2963, 2924, 2218, 1688, 1592, 1552, 1434, 1379, 1281, 1070; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H), 2.54 (s, 3H), 2.74 (s, 3H), 7.00 (s, 1H), 10.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.3, 20.8, 21.2, 113.7, 116.5, 131.1, 144.8, 145.4, 146.8, 191.8.

1e: Colorless powder, mp 124−126 °C; IR (KBr) cm^{-1} 2923, 1697, 1560, 1446, 1383, 1261; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.75 (s, 3H), 2.78 (s, 6H), 10.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 29.7, 115.0, 148.0, 190.7.

1f: Colorless solid, mp 165 °C (dec); IR (KBr pellet) cm^{-1} 2924, 2222, 1697, 1559, 1210, 1022; ^{1}H NMR ($CDCl_3$, 400 MHz)

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(35) It is relevant to note that 2,6-dialkyl substitution is known to enhance photocyclization of phenyl alkyl ketones, see: Kitaura, Y.; Matsuura, T. *Tetrahedron* **1971**, *27*, 1597.

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δ 2.63 (s, 3H), 2.64 (s, 3H), 2.66 (s, 3H), 10.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2, 20.6, 24.0, 114.8, 116.2, 128.0, 133.6, 142.0, 144.3, 146.2, 192.2.

2a: Colorless solid, mp 81−82 °C; IR (KBr) cm^{-1} 2922, 1697, 1680, 1581, 1377, 1091; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.50 (s, 6H), 2.72 (s, 3H), 6.93 (s, 1H), 10.55 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 20.9, 15.3, 132.5, 133.1, 143.0, 145.1, 193.4. Anal. Calcd for $C_{11}H_{12}O_2$ (mol wt 176.22) C, 74.98; H, 6.86. Found: C, 74.63; H, 6.71.

2b: Colorless powder, mp 150 °C (dec); IR (KBr) cm^{-1} 2924, 2853,1695, 1555, 1442, 1261, 1204, 1067; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.56 (s, 6H), 2.49 (s, 3H), 10.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.5, 20.9, 128.8, 129.6, 135.1, 138.1, 142.7, 194.0. Anal. Calcd for $C_{11}H_{11}BrO_2$ (mol wt 255.11) C, 51.79; H, 4.34. Found: C, 52.22; H, 4.55.

2c: Colorless powder, mp 155−160 °C (dec); IR (KBr) cm^{-1} 2923, 2853, 2223, 1695, 1557, 1382, 1072; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.68 (s, 3H), 2.72 (s, 6H), 10.52 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.0, 18.9, 118.0, 133.9, 145.0, 147.0, 192.4.

3: Colorless solid, mp 170 °C (dec); IR (KBr) cm^{-1} 2885, 1689, 1557, 1418, 1387, 1069; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.58 (s, 9H), 10.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.2, 134.9, 143.1, 194.2. Anal. Calcd for $C_{12}H_{12}O_3$ (mol wt 204.23) C, 70.57; H, 5.92. Found: C, 70.94; H, 5.73.

Inclusion Complex Formation between Mesitaldehyde 1a and the Host Diol. The crystals of the inclusion complex between **1a** and diol were easily grown by slow evaporation of their solution (2.5:1 equiv) in $CH_2Cl_2-C_6H_6$ (1:1) at room temperature. The stoichiometry of the complex was established to be 1:2 (host:guest) from integrations of the characterstic signals of the host and guest in the ^{1}H NMR spectrum.

Solution-State Photolysis. The benzene solutions (100 mL, ca. 5 mM) of aldehydes **1c**,**d**, **2a**−**c**, and **3** were purged with a stream of N_2 gas for 15 min and irradiated in the Rayonet reactor (λ = 350 nm) for 24 h. The photolysates were periodically monitored by TLC. In all the cases, excepting **1c**, the TLC analysis indicated the formation of several products and the cyclobutenols were not readily identifiable. In the case of **1c**, the formation of a single product was clearly observed. Silica gel chromatography (10% EtOAc/petroleum ether) of the photolysate afforded a colorless crystalline product in 25% yield, which was subsequently characterized from ^{1}H and ^{13}C NMR analyses as the phthalide **4**.[25] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (s, 3H), 2.70 (s, 3H), 5.33 (s, 2H), 7.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.6, 20.7, 16.8, 104.6, 114.5, 122.5, 132.9, 144.8, 148.3, 150.9, 169.2.

Preparative Solid-State Photolysis. In a typical reaction, ca. 100 mg of the gently ground aldehyde was dispersed in a Pyrex container and purged with a stream of nitrogen gas for 15−10 min. The solid sample was subsequently irradiated, under a nitrogen gas atmosphere, in a Rayonet reactor fitted with 350 nm lamps for 24 h. After this period, the irradiated mixture was subjected to silica gel column chromatography. The combined fractions from the chromatography corresponding to the cyclobutenol were stripped off the solvent in vacuo at room temperature and characterized.

The benzocyclobutenol from the solid-state photolysis of the complex of mesitaldehydes **1a** and diol host was established by comparison of its spectral data with those documented in the literature.[24] All of the cyclobutenols exhibited similar spectral characteristics.

1b-CB: IR (KBr) cm^{-1} 3301, 2920, 1462, 1202, 1169; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 3H), 2.26 (s, 3H), 2.81 (d, J = 14 Hz, 1H), 3.41 (dd, J_1 =14 Hz, J_2 = 4.4 Hz, 1H), 5.10 (d, J = 4.4 Hz, 1H), 6.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.0, 22.5, 42.0, 68.5, 115.7, 123.5, 131.3, 138.7, 142.5, 144.4.

1c-CB: IR (KBr) cm^{-1} 3434, 2924, 2224, 1610, 1457, 1401, 1296, 1219; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.38 (s, 3H), 2.45 (s, 3H), 2.94 (d, J = 15.2 Hz, 1H), 3.51 (dd, 1H, J_1 =15.2 Hz, J_2 = 4.7 Hz), 5.23 (d, 1H, 4.4 Hz), 6.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.5, 21.5, 42.2, 69.9, 111.8, 117.4, 122.7, 130.1, 137.1, 144.2, 146.9.

1d-CB: IR (KBr) cm^{-1} 3286, 2923, 1439, 1140; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23 (s, 3H), 2.51 (s, 3H), 2.81 (d, 1H, J_1 = 14.4 Hz), 3.40 (dd, 1H, J_1 = 14.7 Hz, J_2 = 4.4 Hz), 5.16 (d, 1H, J = 3.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.2, 24.1, 41.9, 68.7, 116.5, 127.0, 133.2, 138.2, 141.2, 144.6.

1e-CB: IR (KBr) cm^{-1} 3469, 2924, 2228, 1604, 1382, 1131; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.46 (s, 3H), 2.67 (s, 3H), 3.12 (dd, 1H, J_1= 15.9 Hz, J_2 = 1.9 Hz), 3.67 (dd, 1H, J_1 = 15.9 Hz, J_2 = 4.4 Hz), 5.29 (d, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.2, 20.3, 42.1, 69.4, 107.3, 114.1, 114.5, 115.6, 142.3, 145.2, 147.7, 150.4.

1f-CB: IR (KBr) cm^{-1} 3415, 2923, 2223, 1597, 1418, 1380; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.54 (s, 3H), 3.48 (dd, 1H, J_1 = 15.9 Hz, J_2 = 4.4 Hz), 2.93 (dd, 1H, J_1 = 15.9 Hz, J_2 = 2.0 Hz), 5.22 (d, 1H, d = 22.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.5, 21.6, 42.5, 68.2, 114.0, 116.8, 127.1, 136.5, 143.0, 144.8, 147.8.

2a-CB: IR (neat film) cm^{-1} 3400, 2925, 1690, 1614, 1265, 1127; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H), 2.54 (s, 3H), 3.08 (d, 1H, J = 15.4 Hz), 3.72 (dd, 1H, J_1 = 15.4 Hz, J_2 = 3.2 Hz), 5.26 (d, 1H), 10.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.0, 18.1, 41.9, 70.7, 116.3, 127.8, 131.9, 139.8, 144.5, 146.0, 190.2.

2b-CB: IR (KBr) cm^{-1} 3376, 1680, 1601, 1375, 1262, 1217, 1173, 1123; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.67 (s, 3H), 3.06 (dd, 1H, J_1= 15.5 Hz, J_2 = 2.0 Hz), 3.68 (dd, 1H, J_1 = 15.6 Hz, J_2 = 4.4 Hz), 5.29 (d, 1H), 10.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.1, 19.5, 42.1, 71.2, 118.6, 129.6, 128.8, 140.6, 141.3, 145.2, 190.1.

2c-CB: IR (KBr) cm^{-1} 3450, 2924, 2222, 1686, 1603, 1379, 1261, 1131; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3H), 2.79 (s, 3H), 3.19 (dd, 1H, J_1= 16.1 Hz, J_2 = 4.4 Hz), 3.78 (dd, 1H, J_1 = 16.2 Hz, J_2 = 4.4 Hz), 5.31 (d, 1H), 10.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.4, 17.9, 42.7, 70.5, 113.4, 116.3, 128.5, 143.2, 145.3, 145.9, 150.1, 188.9.

3-CB: IR (KBr) cm^{-1} 3406, 2924, 1672, 1377, 1261, 1098; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H), 2.81 (s, 3H), 3.15 (dd, 1H, J_1 = 16.1 Hz, J_2 = 2.0 Hz), 3.75 (dd, 1H, J_1= 16.1 Hz, J_2 = 2.7 Hz), 5.33 (d, 1H, J = 2.7 Hz), 10.31 (s, 1H), 10.55 (s, 1H).

Temperature-Dependent Solid-State Photolysis. For examining the temperature dependence on the yields of the photoreactions, two portions of the same sample (**1d** or **1e**) were dispersed in NMR tubes and purged with a N_2 gas for 15 min. The irradiation of each at a particular temperature was conducted by focusing the Pyrex-filtered radiation from high-pressure Hg-lamp on to the sample held in a quartz Dewar Vessel equipped with a window (Applied Photophysics Limited). The bath temperature in the Dewar was externally controlled. During low temperature photolysis, the condensate that formed on the window of the Dewar flask was constantly removed by blowing hot air from a dryer. The whole setup was maintained undisturbed during the photolysis at two different temperatures, except for changing the NMR tubes containing the samples. In three independent experiments, a similar trend in the yields, i.e., the yield at low temperature (−80 °C) was significantly lower than that at room temperature (30 °C), was observed.

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Supporting Information Available: The crystallographic data for **1a**−diol complex and **1e**, and summary output files of AM1 calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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