Photocyclization of 2,4,6,2′,4′,6′-Hexaalkylbenzils

Peter J. Wagner,*,† Bong-Ser Park,† Martin Sobczak,† Joseph Frey,‡ and Zvi Rappoport‡

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48824, and Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

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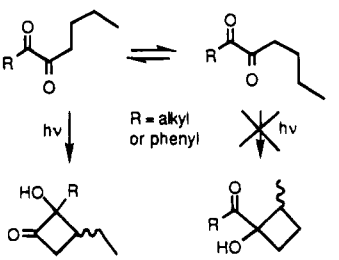
Abstract: Three of the title compounds—the hexamethyl-, hexaethyl-, and hexaisopropylbenzils—all photocyclize both in solution and as solids to 5,7-dialkyl-2-(2′,4′,6′-trialkylphenyl)-2-hydroxy-1-indanones. At wavelengths <370 nm these primary photoproducts undergo secondary photocleavage to ketoaldehydes. The hexaethylbenzil produces only the (*Z*)-hydroxyindanone in the solid but a 2/1 *Z*/*E* ratio at low conversion in solution. The solid-state reactivity and the preference for formation of the (*Z*)-hydroxyindanone from the hexaethylbenzil suggest that much of the reaction involves δ-hydrogen abstraction followed by coupling of the 1,5-biradical. The formation of (*E*)-hydroxyindanones from *o*-ethylphenyl diketones had been attributed to stereospecific rearrangement of a photodienol formed by γ-hydrogen abstraction. However, none of the H/D exchange of benzylic hydrogens expected of a photodienol occurs in methanol-d_4. Moreover, AM1-level semiempirical calculations suggest that a simple exothermic hydrogen transfer can convert the 1,4-biradical triplet dienol to the same 1,5-biradical formed by δ-hydrogen abstraction. The 1,5-biradical has two major conformations, one leading to *Z* product and an internally OH--O=C hydrogen bonded one leading to *E* product. The AM1 computations suggest that the two conformations are of comparable energy and thus implicate 1,5-biradicals as the major precursors to hydroxyindanone products. Stern–Volmer quenching studies indicate a triplet decay rate of 5×10^6 s^{-1} for the hexaisopropylbenzil. The known behavior of structurally similar monoketones predicts such a rate for δ-hydrogen abstraction but a much slower rate for γ-hydrogen abstraction. However, relative quantum efficiencies parallel those for benzocyclobutenol formation from 2,4,6-trialkylbenzophenones (iPr and Et ~0.3, Me ~0.03). The hexa-*tert*-butylbenzil undergoes very low quantum yield formation of 3,3-dimethyl-5,7-di-*tert*-butyl-1-indanone and 2,4,6-tri-*tert*-butylbenzaldehyde, presumably by δ-hydrogen abstraction and highly efficient radical cleavage of the resulting 1-aroyl-1-indanol.

Introduction

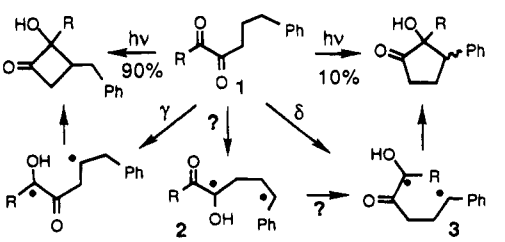
Hydrogen abstraction by the triplet states of α-diketones has received considerable attention over the past two decades; key aspects such as absolute reactivity[1–3] differ strongly from those observed for monoketones.[4,5] Intramolecular hydrogen abstraction shows fascinating regioselectivity in that one carbonyl typically reacts only *via* a cyclic 6-atom transition state that contains the other carbonyl; the resulting 2-keto-1,4-biradical cyclizes in high quantum efficiency to a 2-hydroxycyclobutanone.[6–8] As shown in Scheme 1, no acylcyclobutanols are formed, at least not as stable products, from either dialkyl or phenyl alkyl diketones.[6–9]

In the case of diketone **1**, the "wrong" mode of γ-hydrogen abstraction was proposed to explain a minor hydroxycyclopentanone product.[8] An internal 1,4 hydrogen atom transfer in 1,4-biradical **2** to produce 1,5-biradical **3** was suggested. Based on later work demonstrating competitive δ-hydrogen abstraction

Scheme 1



in some δ-substituted monoketones,[9] triplet **1** would now be predicted to produce 10% of **3** directly. Thus there is no need in this particular case to invoke the two-step mechanism with its atypical mode of triplet reactivity, although hydrogen transfer from OH to carbonyl is a well-known reaction of α-hydroxy radicals.[10] The photochemistry of o-alkylphenyl diketones is



particularly intriguing in this regard, since they form only

† Michigan State University.
‡ The Hebrew Uniersity.
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(1) Turro, N. J.; Lee, T. *J. Am. Chem. Soc.* **1969**, *91*, 5651.
(2) Wagner, P. J.; Zepp, R. G.; Liu, K.-C.; Thomas, M.; Lee, T.-J.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 8125.
(3) Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Photochem. Photobiol.* **1989**, *50*, 707.
(4) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.
(5) Wagner, P.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227.
(6) Urry, W. H.; Trecker, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 713. Urry, W. H.; Trecker, D. J.; Winey, D. A. *Tetrahedron Lett.* **1962**, 609.
(7) Bishop, R.; Hamer, N. K. *J. Chem. Soc. C* **1970**, 1197.
(8) Burkoth, T.; Ullman, E. J. *Tetrahedron Lett.* **1970**, 145.
(9) Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4958. Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500.
(10) Naguib, Y. M. A.; Steel, C.; Cohen, S. G. *J. Phys. Chem.* **1988**, *92*, 6574; Demeter, A.; Bérces, T. *J. Phys. Chem.* **1991**, *95*, 1228. Wagner, P. J.; Zhang, Y.; Puchalski, A. E. *J. Phys. Chem.* **1993**, *97*, 13368.

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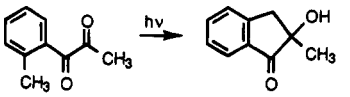
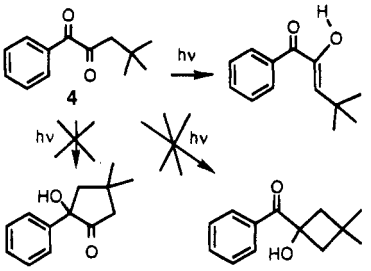
2-hydroxy-1-indanones.[8,11] When this photocyclization was first



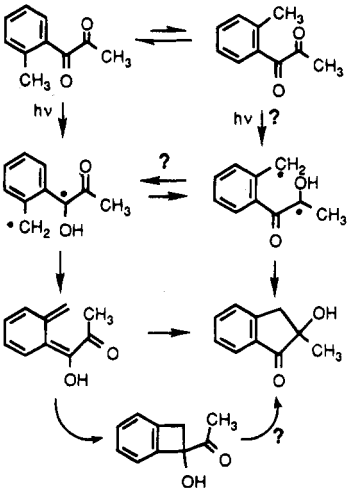
discovered, it was widely believed that intramolecular hydrogen abstractions occurred only at γ-carbons; so, as in the case of **1**, the only mechanisms suggested involved initial γ-hydrogen abstraction (opposite from the normal regiospecificity), followed by rearrangement either of the photodienol[8,12] or of a benzocyclobutenol.[11,13] Evidence both for and against a dienol reaction has been published, but no clear consensus ever emerged. Four groups have shown that properly substituted, *in situ* generated *o*-quinodimethanes rearrange to 2-hydroxy-1-indanones,[8,12-14] by what has been pictured as an internally catalyzed Aldol addition or a pericyclic rearrangement. Thus a dienol mechanism is feasible, although the initial γ-hydrogen abstraction and the lack of benzylic H/D exchange,[11] which normally accompanies such photoenolizations, both represent unexplained exceptions to standard behavior. Given the fact that phenyl alkyl diketones are unsymmetric and that only the benzoyl carbonyl undergoes γ-hydrogen abstraction,[2] it is conceivable that there is an electronic bias favoring reaction by the benzoyl group, which would favor photodienol formation from *o*-tolyl alkyl diketones. The behavior of 4,4-dimethyl-1-phenyl-1,2-pentanedione (**4**), which enolizes rather than abstract a γ-hydrogen by its 2-keto group, supports this possibility.[2,15]



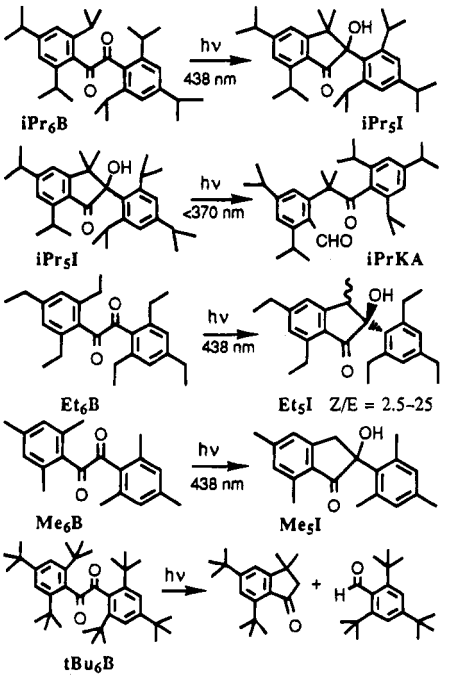
There is a similar class of monoketones that undergo facile triplet state δ-hydrogen abstraction: the α-(*o*-tolyl)- and α-(2,4,6-trialkylphenyl)acetophenones, most of which photocyclize to indanols in the solid state and in solution.[16,17] In the past decade we have established the wide scope of this process;[18] so there is no longer any plausible reason to ignore the possibility of δ-hydrogen abstraction as a mechanism to explain the hydroxyindanone photoproducts from *o*-tolyl diketones. Scheme 2 includes all of the mechanistic possibilities that have been suggested for the photocyclization of *o*-tolyl diketones, including δ-hydrogen abstraction.

Our independent interests in the effects of steric congestion on the photoreactivity[17] and the structure[19] of aryl ketones led us to study the highly congested 2,4,6,2′,4′,6′-hexaalkylbenzils, the photochemistry of which we report in this paper. Since these benzils are structurally symmetric, their two carbonyls

Scheme 2



Scheme 3



should be equally reactive and there can be no electronic bias favoring γ-hydrogen relative to δ-hydrogen abstraction such as may obtain for the *o*-tolyl alkyl diketones. A comparison of their solution and solid state reactions indicates that photocyclization of *o*-alkylbenzils can proceed by δ-hydrogen abstraction and allows a reappraisal of several possibilities included in Scheme 2, especially in light of advances in our understanding of photoenolization. The only previous study of such polyalkylbenzil photochemistry was reported by Maruyama and coworkers.[20] Some of our findings differ; the reasons provide insight into the geometric requirements for intramolecular hydrogen transfer.

Results

All four of the simple 2,4,6,2′,4′,6′-hexaalkylbenzils shown in Scheme 3 were prepared in Jerusalem by known methods. They were subjected to various forms of Michigan irradiation,

(11) (a) Bishop, R.; Hamer, N. K. *J. Chem. Soc. C* **1970**, 1193. (b) Hamer, N. K.; Samuel, C. J. *J. Chem. Soc., Perkin Trans 2* **1973**, 1316.
(12) Ogata, Y.; Takagi, K. *J. Org. Chem.* **1974**, *39*, 1385.
(13) Hamer, N. K. *J. Chem. Soc., Perkin Trans. 1* **1979**, 508.
(14) Padwa, A.; Au, A. *J. Am. Chem. Soc.* **1976**, *98*, 5581.
(15) We have performed MM2 computations on this diketone that indicate a strong preference for the geometry shown, which would be ideal for the unobserved hydrogen abstraction.
(16) Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 9630.
(17) Wagner, P. J.; Zhou, B.; Hasegawa, T.; Ward, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 9640.
(18) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.
(19) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1005. Nadler, B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112. Hart, H.; Rappoport, Z.; Biali, S. E. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; pp 481–590.
(20) Maruyama, K.; Ono, K.; Osugi, J. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 847.

with the finding that the orange **Me$_6$B**, **Et$_6$B**, and **iPr$_6$B** all photocyclize to colorless 2-(2′,4′,6′-trialkylphenyl)-2-hydroxy-1-indanones both in solution and as solids. The initial photoproducts all undergo secondary photocleavage to keto benzaldehydes at wavelengths <370 nm in solution but not in the solid. In contrast, **tBu$_6$B** appears to undergo a different, very inefficient δ-hydrogen abstraction to produce a 2-aroyl-1-indanol photoproduct, which reacts so much more efficiently than **tBu$_6$B** itself that only secondary photocleavage products can be isolated.

A 0.01 M solution of **iPr$_6$B** in benzene under argon was irradiated with a Pyrex-filtered mercury arc. Two major products were isolated by column chromatography and preparative TLC: **iPr$_5$I** and **iPrKA**. However, irradiation of **iPr$_6$B** with ~438-nm light, where **iPr$_5$I** does not absorb, produces **iPr$_5$I** quantitatively. Irradiation of isolated **iPr$_5$I** in the UV converted it quantitatively to **iPrKA**. This photolability of such hydroxyindanone photoproducts was noted in the first reports of the photocyclization of *o*-tolyl diketones.[7,21] That **iPr$_5$I** might be a 1-aroylbenzocyclobutenol is ruled out by the fact that it forms **iPrKA**. Moreover, the 1704-cm^{-1} IR carbonyl stretching frequency and the 205-ppm ^{13}C-NMR carbonyl chemical shift are consistent with a 1-indanone but inconsistent with a free triisopropylbenzoyl group, which would be expected to have values of 1685 cm^{-1} and ~215 ppm,[22] as in **iPrKA**. It is noteworthy that rotation of the triisopropylphenyl group in **iPr$_5$I** is frozen; all 12 aromatic carbons and all 5 isopropyl groups have unique NMR resonances.

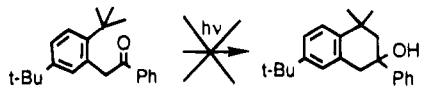
In methanol-d_4 the photoreaction of **iPr$_6$B** proceeded only with UV irradiation, was exceedingly slow, and did not produce any measurable disappearance of the *o*-isopropyl methine NMR resonances of starting material. Suspecting a possible acid impurity in the methanol, we irradiated two benzene samples in parallel, one of which contained a few crystals of *p*-toluenesulfonic acid. However, there was no difference between the two samples in rate of formation of **iPr$_5$I**; so it does not appear to be acid impurities in methanol that quench the reaction.

A sample of solid **iPr$_6$B** that had been left standing in room light for some time turned pale yellow because of the large amount of **iPr$_5$I** diluent. Some recrystallized **iPr$_6$B** was packed in capillary tubes held inside of a normal Pyrex test tubes, which were then degassed, sealed, and irradiated at either 313 or 365 nm. In both cases iPr$_5$I was the major product detectable by NMR, with only a trace of iPrKA.

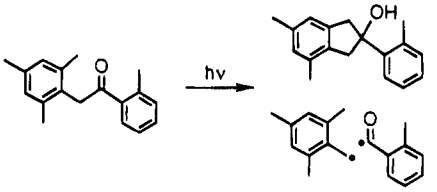
Several samples of 0.01 M **Me$_6$B** in benzene-d_6 were irradiated in deaerated NMR tubes. With UV irradiation, several products were formed in very low quantum efficiency; but at 438 nm or in the solid state **Me$_5$I** was the predominant product, as revealed by the AB quartet at δ 3.36 and 3.57 for the methylene group and by four distinct benzylic methyl and three distinct aromatic proton resonances. The 18-Hz coupling of the AB quartet is characteristic of 2-aryl-2-indanols produced by photocyclization of α-mesitylacetophenones[16,17] and distinguishes the product from the isomeric mesitoylbenzocyclobutenol, since the *J* coupling of the methylene protons in several 1-arylbenzocyclobutenols is only 14 Hz.[23]

Diketone **Et$_6$B** behaved similarly to **iPr$_6$B**, except that two diastereomers of the indanol product were formed; they were separated by TLC. The stereochemistries of these isomers were assigned by the chemical shifts of the doublets corresponding to the 3-methyl substituent: δ 0.98 for the *E* isomer, in which the methyl is cis to the shielding 2-aryl group, and δ 1.51 for the *Z* isomer. The two isomers differ in the rate of rotation of the triethylphenyl ring; resonances for the two *o*-ethyl methylene protons of the *Z* isomer are nearly coalesced at room temperature, whereas those of the more hindered *E* isomer are all clean doublets of quartets. Isomer ratios were determined by integration of the two methyl doublets and of the two corresponding methine quartets at δ 3.47 and 3.67. At low conversion, measured *Z*/*E* ratios were 2/1 in solution and >25/1 in the solid. In the solid a 6/1 *Z*/*E* ratio was obtained at 100% conversion, but by then the solid had turned into a liquid. In solution NMR signals for a ketoaldehyde appeared only with UV irradiation.

When irradiated through Pyrex, **tBu$_6$B** reacted sluggishly in both benzene and methanol to give a mixture of products. The two major products were 2,4,6-tri-*tert*-butylbenzaldehyde and 5,7-di-*tert*-butyl-3,3-dimethyl-1-indanone; some 2,4,6-tri-*tert*-butylbenzoic acid was also isolated. All were identified by their NMR spectra. No reaction occurred after 3 days irradiation at 438 nm. A simple monoketone analog of **tBu$_6$B**, which could undergo only ϵ-hydrogen abstraction, formed no photocyclization product after 3 days of irradiation.



We reinvestigated the photochemistry of α-mesityl-2′-methylacetophenone, which shares with ortho-substituted benzils the key feature of having hydrogens available for abstraction at both the γ- and δ-positions. When the compound was irradiated in benzene-d_6, the reaction products were derived only from δ-hydrogen abstraction and type I cleavage, as previously found by Zhou.[17] No trace of benzocyclobutenol could be found. From this result, it appears either that triplet δ-hydrogen abstraction is preferred over γ-hydrogen abstraction in this compound or that γ-abstraction is totally revertible.



Kinetics. The photokinetics of **iPr$_6$B** was studied as representative of this group of benzils. A quenching study was performed; 0.01 M benzene solutions containing 0.001−0.005 M pyrene were irradiated at 365 nm. A Stern−Volmer plot, corrected for 5−20% competitive absorption by the pyrene, provided a $k_q\tau$ value of 400 M^{-1}.

Spectroscopy. The phosphorescence spectra of all four benzils in methanol−ethanol were measured at 77 K; room temperature UV/vis spectra were recorded in benzene. Table 1 lists λ_{max} values and 0−0 phosphorescence band energies for the n,π^* transitions of all four diketones and compares them to those of some other diketones.

X-ray Crystallography. The structure of **iPr$_6$B** was determined by an X-ray diffraction study which is being reported separately.[24] Scheme 4 reproduces the structure; the diketone substructure is anti coplanar, with each aryl ring twisted 76.5° from that plane, so as to maintain an overall center of inversion in the molecule. There is some disorder with regard to the two *p*-isopropyl groups, which apparently exist in both of two geometries with their methine hydrogens parallel to the benzene ring. The *o*-isopropyl groups are fixed, however, and the positions of their methine hydrogens are well-defined. The tilt of the benzene rings places the two ortho-benzylic hydrogens

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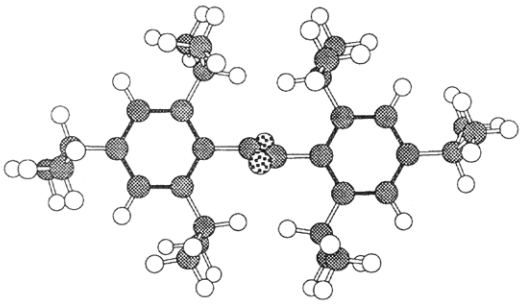
(22) Chen, A. C.-P. Ph.D. Thesis, Michigan State University, 1977.
(23) Wagner, P. J.; Subrahmanyam, D.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 709.
(24) Frey, J.; Faraggi, E.; Rappoport, Z.; Kaftory, M. *J. Chem. Soc., Perkin Trans 2*, in press.

Table 1. Electronic Spectroscopy of Various Diketones

diketone	λ_{max}, nm (ϵ) in benzene			E_T, kcal/mol
biacetyl	420 (80)[a]		450 (80)	56.2[b]
dipivaloyl[c]		365 (21)		51.6[d]
α-ketopropiophenone[d]		395		54.0
benzil		370 (79)[e]		53[d]
o-ethylbenzil[f]		402 (25)		~55[g]
2.4.6-trimethylbenzil[e]		400		
Me$_6$B	467[e]		493[e]	56.6 (506 nm)[h]
Et$_6$B[h]	467 (78)		493 (78)	56.6 (506 nm)
iPr$_6$B[h]	467 (45)		493 (45)	56.6 (506 nm)
tBu$_6$B[h]		407 (70)		54.0 (530 nm)

[a] Sandros, K. *Acta Chem. Scan.* **1964**, *18*, 2355. [b] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 171. [c] Leonard, N. J.; Mader, P. M. *J. Am. Chem. Soc.* **1950**, *72*, 5388. [d] Evans, T. R.; Leermakers, P. A. *J. Am. Chem. Soc.* **1967**, *89*, 4380. [e] Reference 25. [f] In pentane, reference 7. [g] Reference 47. [h] This work.

Scheme 4. Crystal Structure of iPr$_6$B



on a given triisopropylbenzoyl group at different distances from the carbonyl oxygen, 2.68 and 2.99 Å, and 2.86 and >3.1 Å from the other carbonyl oxygen. The reported crystal structure of **Me$_3$B** is nearly identical in major respects, with an anti coplanar diketone unit and mesityl rings twisted 76−78° out of conjugation with the carbonyls.[25]

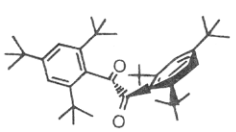
Discussion

Three of these highly crowded benzils undergo the same photocyclization to 2-hydroxy-1-indanones as do the simple *o*-tolyl diketones studied earlier. Both γ- and δ-hydrogen abstraction appear to be feasible reactions in all of them. We shall concentrate first on developing mechanistic understanding for these hexaalkylbenzils and shall then consider whether their behavior provides any clarification of the mechanistic possibilities for the same reaction in the simpler *o*-alkylphenyl diketones. The observed solid state reactivity and the diastereoselectivity of cyclization indicate that much of the photocyclization of these hexaalkylbenzils involves simple δ-hydrogen abstraction followed by 1,5-biradical cyclization. The kinetics are less easy to interpret but do suggest that γ-hydrogen abstraction could lead to hydroxyindanone products *via* a 1,4- to 1,5-biradical conversion.

Geometry. In order to understand the mechanism of this or any other intramolecular reaction, it is necessary to first understand the geometries accessible to the reactants. Fortunately X-ray crystallographic determinations of the crystal structures of three of these benzils have been performed. Since **iPr$_6$B**[24] and **Me$_6$B**[25] have very similar crystal structures, we feel safe in interpolating the same basic geometry for **Et$_6$B**, with both trialkylphenyl groups nearly perpendicular to the anti coplanar carbonyls.

Several pieces of evidence indicate that the molecular geometries of these benzils in solution are similar to those in the crystal lattice. Ever since the pioneering spectroscopic work of Leonard,[26] it has been recognized that the absorption energies of diketones depend strongly on the degree of coplanarity of their dicarbonyl units and that the conformations of aryl diketones vary significantly with substitution. The more each aryl group is conjugated with its substituent carbonyl group, the more it interferes sterically with the other carbonyl and the less coplanar the two carbonyls become. Since the lowest energy electronic transitions are n,π* in character and thus heavily localized on the diketone unit, increased conjugation of the benzoyl units reduces conjugation of the diketone and lowers λ_{max} values.[27] Table 1 compares the spectroscopic behavior of various aliphatic and aryl diketones of varying steric congestion. It is revealing that three of these sterically congested hexaalkylbenzils emit and absorb at energies even lower than those for both the unhindered biacetyl and glyoxal (λ_{max} = 450 nm),[28] which are known to have anti coplanar carbonyls. In contrast, benzil, with two nearly planar benzoyl groups twisted 72° out of conjugation with each other,[29] absorbs at much higher energy, like the twisted dipivaloyl. We conclude that **Me$_6$B**, **Et$_6$B**, and **iPr$_6$B** have anti coplanar diketone units in solution as well as in the solid. Molecular mechanics and semiempirical (AM1) computations predict the same geometry.

When the ortho positions of benzil are substituted, the benzoyl units twist, allowing the diketone unit to become more coplanar—thus the decrease in n,π* excitation energy upon moving from benzil to *o*-ethylbenzil, 2,4,6-trimethylbenzil, and our smallest three hexaalkylbenzils. It is quite interesting that the absorption and emission spectra of **tBu$_6$B**, the most hindered of our benzils, have λ_{max} and 0−0 bands intermediate between those of benzil and the other three hexaalkylbenzils, indicative of a partially twisted diketone unit. Its NMR spectra demand such a geometry. There are two sets of *o-tert*-butyl proton signals, the broadness of which indicates slow exchange even at ambient temperature, as first reported by Lauer and Staab.[30] Likewise there are two sets of *tert*-butyl and carbonyl carbon signals. Its X-ray structure[31] confirms that its somewhat bent benzene rings are twisted 74° out of conjugation with their substituent carbonyls and its two carbonyls are twisted 54° out of anti conjugation with each other, making the two *o-tert*-butyls and the meta protons on each ring nonequivalent. Apparently the extra methyl groups on the benzylic carbons of **tBu$_6$B** (compared to **iPr$_6$B**) interfere sufficiently with the distal carbonyl to force the two carbonyls out of coplanarity. The similar λ_{max} values for **tBu$_6$B** and benzils with intermediate substitution, such as 2,4,6-trimethylbenzil, suggest that the latter also have angles ~45−55° between their two carbonyls. It is noteworthy that the ^{13}C carbonyl resonances of these benzils reflect primarily steric effects within a singlet aroyl group, whereas the ^{17}O carbonyl resonances reflect the same order of O=C−C=O twisting as deduced from UV/vis spectra and X-ray studies (**Me$_6$B** = **iPr$_6$B** > **tBu$_6$B** > benzil).[32]



(25) (a) Biswac, S. C.; Sen, R. K. *Chem. Phys. Lett.* **1983**, *94*, 415. *Z. Kristollogr.* **1985**, *171*, 235. (b) Kaftory, M.; Rubin, M. B. *J. Chem. Soc., Perkin Trans. 2* **1983**, 149.

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(30) Lauer, D.; Staab, H. *Chem. Ber.* **1969**, *102*, 163.

(31) Gabe, E. J.; Le Page, Y.; Lee, F. L.; Barclay, L. R. C. *Acta Crystallogr.* **1981**, *B37*, 197.

(32) Cerioni, G.; Plumitallo, A.; Frey, J.; Rappoport, Z. *Magn. Reson. Chem.*, in press.

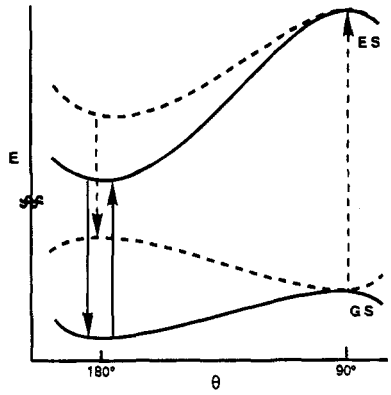


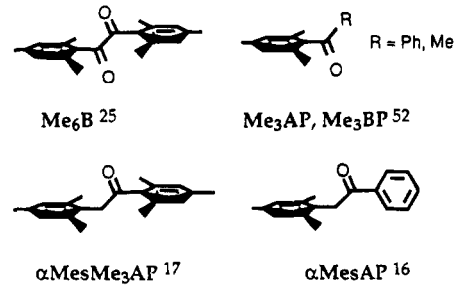
Figure 1. Potential energy diagrams for absorption and emission of diketones as a function of the dihedral angle θ for rotation around the OC−CO bond: (—) anti coplanar ground state; (— — —) twisted ground state. A common energy for the 90° geometry, with zero conjugative stabilization and zero steric destabilization, is assumed.

However much the ground state geometries of acyclic diketones may vary, their n,π^* excited states are known to prefer an anti-coplanar arrangement of the carbonyls.[33] The combination of such a common excited state geometry with a variable ground state geometry is known to be responsible for spectroscopic variations such as those observed for diketones. Figure 1 portrays the usual potential energy diagrams that explain increased absorption and reduced emission energies with increasing differences between ground and excited state geometries.[34] Thus, although the n,π^* absorption energies of **iPr$_6$B** and benzil differ by almost 20 kcal/mol, their phosphorescence 0−0 bands differ by only 3 kcal/mol. Since the ground states of our hexaalkylbenzils already have the preferred excited state geometry, we presume that their triplets retain their coplanar dicarbonyl ground state geometries, except for slight changes in O=C−C=O bond lengths. We assume that the aryl rings remain nearly perpendicular to the carbonyls, as in the ground state, since the low λ_{max} for benzil indicates little conjugative stabilization of the n,π^* states by the aryl rings.

In order to estimate the effects of twisting the trialkylphenyl−CO bond, we performed semiempirical calculations (AM1 level) on 1-(2,6-dimethylphenyl)-1,2-propanedione in both its ground and triplet states at various twist angles. In both cases the minimum energy geometry had a twist angle of 70−80°, although the potential surface was more shallow around this minimum in the triplet than in the ground state. As expected, in both states of the diketone the two carbonyls twist out of coplanarity as the dimethylbenzoyl group approaches coplanarity, causing a greater increase in overall energy for the triplet. These calculations support the premise that the benzils have much the same geometry in solution as in the crystal and that excitation does not greatly alter that geometry. The predicted low-energy wiggling of the aryl groups is in accord with the fact that the biradicals manage to cyclize.

Comparison of Monoketone and Diketone Geometries. The X-ray structures of the three hexaalkylbenzils that form hydroxyindanone photoproducts indicate that one γ and one δ benzylic hydrogen lie ≤2.9 Å from a carbonyl oxygen, well within the range known to allow triplet state hydrogen transfers in the solid.[35] In considering the mechanism for reaction of these benzils, we shall often refer to the behavior of some 2,4,6-trisubstituted monoketones of known structure that are models for either γ- or δ-hydrogen abstraction. Scheme 5 depicts the structure and provides a reference for each type of monoketone.

Scheme 5



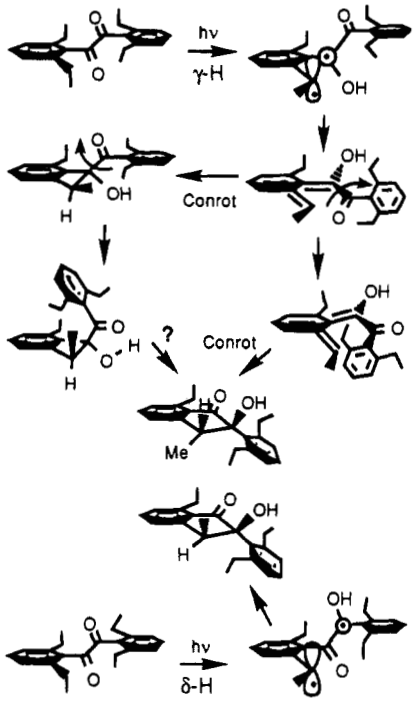
As in our benzils, the trialkylphenyl groups of the monoketones are nearly perpendicular to the carbonyls and those on an α-carbon eclipse the carbonyl group. It is important to note that 2,6-dimethyl substitution is sufficient to cause maximum twisting of these trialkylphenyl rings, so that the methyl-substituted compounds also depict the geometries of those with 2,6-diethyl and -diisopropyl substitution.

Mechanism of Hydroxyindanone formation: Solid-State Reactivity. It is well-known that the 1,4- and 1,5-biradicals generated by triplet state intramolecular hydrogen atom abstraction can revert to ground state ketone as well as cyclize.[5] That the three benzils cyclize in the solid indicates that both the initial hydrogen atom transfer and the motion necessary for subsequent cyclization of intermediates are allowed within the constraints of the crystal lattice. The corresponding α-(2,4,6−trialkylphenyl)acetophenones, which react by δ-hydrogen abstraction, also photocyclize to 2-indanols in the solid.[16,17,36] As Scheme 5 shows, the geometric relationship between their trialkylphenyl groups and carbonyls is similar to that in the benzils. Thus δ-hydrogen abstraction is geometrically feasible in both ketones and diketones and the intermediate 1,5-biradicals can cyclize efficiently in the solid state. 2,4,6-Triisopropylbenzophenone (**iPr$_3$BP**), which has the same skeletal structure as **Me$_3$BP**, also cyclizes efficiently in the solid state by γ-hydrogen abstraction.[37] The trialkylbenzoyl groups have identical geometries in both mono- and diketone; comparably efficient hydrogen abstraction should occur in both and cyclization of the photodienol to the benzocyclobutenol also can occur within the constraints of the crystal lattice. However, it is difficult to conceive of either photodienols or benzocyclobutenols being able to undergo the molecular contortions required for rearrangement to hydroxyindanones in the solid state.

Scheme 6 shows the geometric changes required of **Et$_6$B** (with *p*-ethyl groups removed for compactness' sake) by various proposed mechanisms. The arrows in the drawings of the initial geometries of dienol and cyclobutenol emphasize that ~180° rotations are required for the OH group to get into a position to transfer a proton to the carbonyl oxygen, the process thought to be the driving force for concerted rearrangement to the indanone.[11] Such a rotation would seem to sweep out too large a volume to be possible in the solid. In contrast, cyclization of the 1,5-biradical requires only a minimal geometry change, as just discussed. Unless these benzils have unusually flexible crystal lattices, we can conclude that the hexaalkylbenzils cyclize primarily by δ-hydrogen abstraction in the solid. That is not to say that γ-hydrogen abstraction does not occur. Inasmuch as it does, it is unlikely to form product *via* the earlier proposed rearrangements. Based on the example of **iPr$_3$BP**, γ-hydrogen abstraction by **iPr$_6$B** in the solid might be expected to form a 1-aroylbenzocyclobutenol. Our inability to detect such a product may be due to a low thermal stability relative to dienol, given

(33) Morantz, D. J.; Wright, J. C. *J. Chem. Phys.* **1970**, *53*, 1622; **1971**, *54*, 692.
(34) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820.
(35) Scheffer, J. R. *Org. Photochem.* **1987**, *8*, 249.
(36) Zand, A.; Wagner, P. J. Unpublished results.
(37) Ito, Y.; Matsuura, T.; Fukuyama, K. *Tetrahedron Lett.* **1988**, *29*, 3087.

Scheme 6



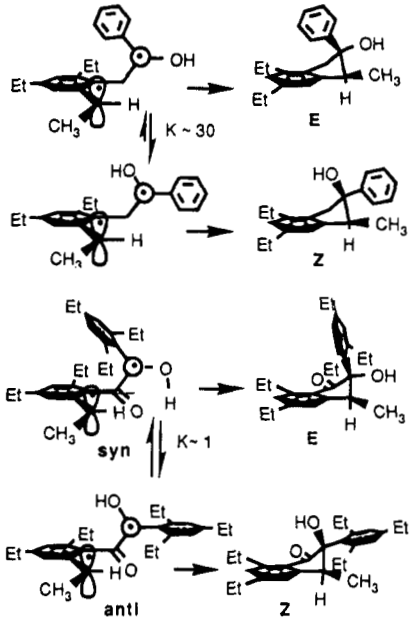
the strong donor and acceptor groups on one carbon.[38] Any dienols formed in the solid probably revert entirely to reactant.

Since δ-hydrogen abstraction appears to be the most likely mechanism in the solid state, it should also contribute at least partially in solution, given comparable molecular geometries in the two phases. We must now attempt to determine how much competing γ-hydrogen abstraction may contribute to product formation in solution, where rearrangements leading to hydroxyindanone are more likely than in the solid.

Mechanism of Hydroxyindanone Formation: Diastereoselectivity. In 1970 Bishop and Hamer reported that 1-(*o*-ethylphenyl)-1,2-propanedione photocyclizes to an isomeric mixture of two 2,3-dimethyl-2-hydroxy-1-indanones containing 65−75% of the *E* isomer.[11a] Although 25 years ago everyone dismissed δ-hydrogen abstraction as a possible mechanism, existing precedent for cyclization of 1,4-biradicals suggested that cyclization of a 1,5-biradical would have produced primarily the *Z* product, with the two methyls trans to each other. The predominance of the *E* product was interpreted in terms of stereospecific rearrangement of a photodienol to a benzocyclobutenol, which then rearranges with proton transfer to the (*E*)-hydroxyindanone.[11] We recently showed that photodienols indeed undergo conrotatory cyclizations to (*E*)-benzocyclobutenols;[23] and several labs have demonstrated that hydroxyindanones are formed when "photodienols" are produced from precursors other than *o*-tolyl diketones.[8,12−14] Regardless whether hydroxyindanones come directly from dienol or from cyclobutenol, *stereochemistry is set during formation of dienol.*[23] For the purpose of interpreting stereochemistry, it is important only to recognize that some stereospecific process *could* be required for the presumably less stable *E* product to be formed.

The diastereoselectivity shown by **Et$_6$B** contrasts with that found by Hamer for *o*-ethylphenyl alkyl diketones. *Z*-**Et$_5$I** is formed preferentially in solution and is essentially the only product in the solid, except at high conversion where melting allows more molecular motion. This preference for the *Z* product is what would be expected from a 1,5-biradical.[16]

Scheme 7



Scheme 7 compares the geometric situation for **Et$_6$B** to that for α-(2,4,6-triethylphenyl)acetophenone, which produces a 30/1 *Z/E* indanol ratio in benzene[39] and only the (*Z*)-indanol as a solid.[36] For both reactants δ-hydrogen abstraction produces 1,5-biradicals whose geometries differ only in the twist angle of the unreacted aryl ring. The product ratio from the monoketone has been ascribed to initial formation of the biradical conformation leading to (*Z*)-indanol and a rotational equilibrium favoring the same geometry by 1.8 kcal/mol with respect to its 180° twisted rotamer.[39] As depicted in the top half of Scheme 7, the small OH rather than the bulky aryl group lies preferentially over the trialkylphenyl ring.[39,40] Twisting of this trialkylphenyl ring in the diketone-derived biradical may cause a change in the equilibrium ratio of rotamers leading to the two diastereomeric products, but the one favoring (*Z*)-indanol should still be preferred in the absence of other factors. An AM1 geometry optimization and rotational map of the 1,5-biradical from **Et$_6$B** identified the anti geometry shown at the bottom left of Scheme 7 as the global minimum; the 180° rotated syn geometry that would form *E*-**Et$_5$I** is calculated to lie 3.2 kcal/mol higher in energy. Such a large energy difference would preclude formation of any *E*-**Et$_5$I** from the 1,5-biradical. However, the calculation did not consider possible stabilization of the syn rotamer by OH--O=C hydrogen bonding. When the syn geometry was reexamined with the OH proton pointed at the carbonyl oxygen instead of away from it, its calculated energy fell by 3 kcal/mol to 0.2 kcal/mol higher than that of the anti geometry. This change is attributed to hydrogen bonding, which apparently can stabilize the syn conformation of the diketone-derived 1,5-biradical sufficiently to allow comparable formation of both diastereomeric indanols. Thus it appears that the *Z/E* product ratios from these hexaalkyl benzils can be explained solely in terms of a 1,5-biradical, with no *need* to postulate stereospecific rearrangement of a dienol or a benzocyclobutenol formed by γ-hydrogen abstraction in order to explain *E* products.

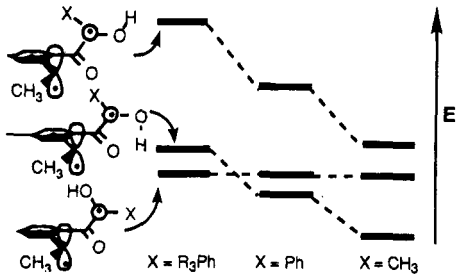
Given the ability of these AM1 calculations to estimate biradical conformational energies that agree with product ratios, we decided to calculate conformational energies of the less bulky biradicals formed from earlier studied diketones. Scheme 8 portrays the results. As the group X gets smaller, the energies

(38) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989. Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1157.

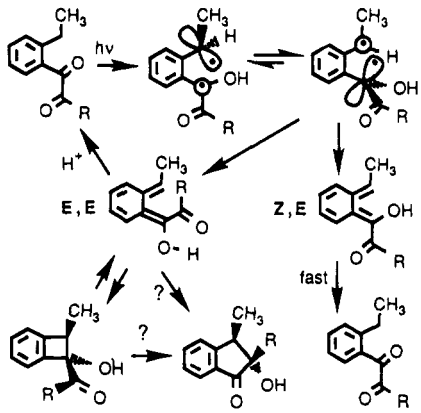
(39) Wagner, P. J.; Park, B.-S. *Tetrahedron Lett.* **1991**, *32*, 165.

(40) Kirmse, W.; Özkir, I. S.; Schnitzler, D. *J. Am. Chem. Soc.* **1993**, *115*, 792.

Scheme 8



Scheme 9

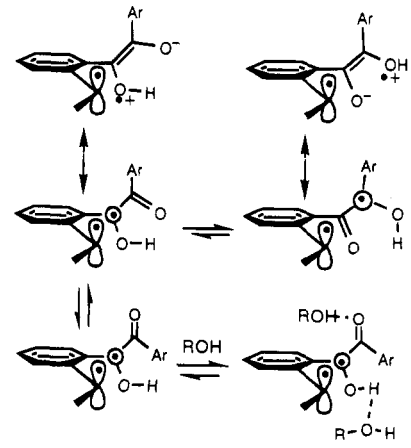


of both the H-bonded and non-H-bonded syn conformers drop relative to that of the anti conformer, with the H-bonded syn conformer becoming 0.3−1 kcal/mol lower in energy than the anti conformer.[41] Since (*E*)-indanol is formed from the syn biradical, its predominance would now be expected from a 1,5-biradical and does not necessitate the hypothesis of any concerted rearrangements.

Are Hydroxyindanones Formed from 1,4-Biradicals? Even though product formation could be attributed solely to 1,5-biradicals, we presume that both γ- and δ-hydrogen abstraction can occur in solution. Therefore we must consider the fate of the 1,4-biradicals (triplet dienols) originally considered to be the initial intermediates in this photoreaction. Scheme 9 extends the current picture[23] of photoenolization in monoketones to diketones, as incorporated in Scheme 6. The key stereochemical postulate is that decay of the preferred conformation of triplet dienol to ground state generates only *E,E* and *Z,E* dienols. The latter undergo rapid sigmatropic reversion to ground state ketone.[42] The former undergo acid-catalyzed reversion to ketone as well as competing electrocyclization to benzocyclobutenol and possibly to hydroxyindanone.

In support of his suggestion of a benzocyclobutenol precursor, Hamer emphasized that no H/D exchange takes place when *o*-tolyl diketones are irradiated in *O*-deuterated alcohol solvents. Such exchange is quite efficient for a large number of *o*-alkylphenyl monoketones, but we could detect none for our crowded benzils.[5] We already reported that added acid, even the small amount typically present in methanol, actually *prevents* benzocyclobutenol formation from monoketones by catalyzing dienol reversion to ketone and the accompanying H/D exchange.[23,43] Why then does acid (at least in low concentration)

Scheme 10



not quench hydroxyindanone formation? One possibility is that there is no significant formation of 1,4-biradical and dienol. Another was suggested by Ullman:[8] that rearrangement to hydroxyindanone may be sufficiently rapid to suppress the acid-catalyzed reversion of dienol to ketone. We now add the observation that the extra acyl group present on the dienol formed from diketones but not monoketones should lower the rate constant for protonation, which is in the 10^{4-6} M^{-1} s^{-1} range for monoketone-derived dienols.[43] Yet we wonder whether thermal rearrangement of dienol to hydroxyindanone could be fast enough to compete with such rapid protonation when closure to cyclobutenol is not. It is interesting also that methanol quenches hydroxyindanone formation, apparently not by acid catalysis, but does not quench benzocyclobutenol formation from 2,6-dialkylphenyl monoketones.[23]

There is a mechanism that explains these seeming anomalies. Ullman and Ogata[8,11] both suggested rearrangement of 1,4-biradicals to 1,5-biradicals by intramolecular H-transfer as a possible mechanism for hydroxyindanone formation. Hydrogen bonding of 1,4-biradicals to methanol could prevent this internal redox process, which starts with an internally hydrogen-bonded biradical. Such degenerate H-transfers are now known to have rate constants on the order of 10^4 M^{-1} s^{-1} when bimolecular.[10] The corresponding intramolecular process would be much faster, *provided it were exothermic*. Both the intramolecularity and the charge separated resonance (Scheme 10) expected in donor/acceptor substituted radicals[44] should work to speed up hydrogen transfer. In fact the concerted rearrangements of dienol or benzocyclobutenol suggested earlier were considered to be initiated by internal proton transfer. Thus all mechanisms involving 1,4-biradicals recognize this hydrogen transfer as the key step but differ in its timing.

We have extended our AM1-level semiempirical computations to the 1,4-biradicals formed from 2,6,2′,6′-tetraethylbenzil. Scheme 11 compares the calculated energies of the syn and anti 1,4- and 1,5-biradicals. The 1,4-biradical is 2−3 kcal/mol less stable than the 1,5-biradical, both with and without internal H-bonding. If these calculations are accurate,[45] most of the 1,4-biradicals formed in competition with 1,5-biradicals would rapidly convert to 1,5-biradicals, which tend to cyclize much faster than do triplet dienol 1,4-biradicals.[46] Thus product ratios would reflect primarily the conformational preferences of the 1,5-biradicals and product formation from dienol could be insignificant. Likewise added acid would not be expected to

(41) It is interesting that the anti conformer is calculated to be ~2 kcal/mol more stable when the hydroxyl proton is pointed toward rather than away from the benzene ring, in agreement with many observations of OH−π(Ar) hydrogen bonding: (a) Oki, M.; Iwamura, H. *Tetrahedron* **1968**, *24*, 1905 and references therein (b) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641 and references therein.

(42) (a) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595. (b) Das, P. K.; Scaiano, J. C. *J. Photochem.* **1980**, *12*, 85.

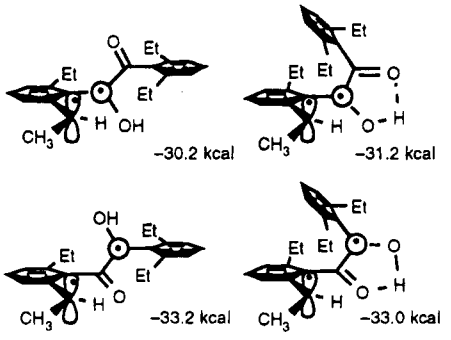
(43) Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Tetrahedron Lett.* **1992**, *33*, 5905.

(44) Baldock, R. W.; Hudson, P.; Katrizky, A. R.; Soti, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1422.

(45) The computational software knows enough to put the two unpaired electrons in perpendicular p-orbitals on the benzylic carbons.

(46) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.

Scheme 11



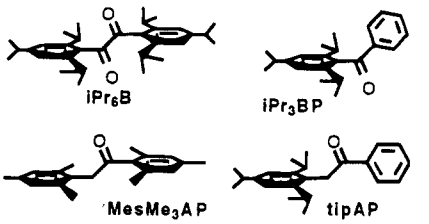
prevent 1,5-biradical formation or cyclization, The only unexplained fact is methanol's ability to totally quench hydroxyindanone formation. Normally alcohol solvents maximize quantum efficiencies for hydroxybiradical cyclization by suppressing disproportionation back to reactant.[5] In this case H-bonding of the 1,5-biradical to solvent would change the biradical's conformational distribution but should not prevent cyclization. Since the retarding effect of methanol is not due to acidic impurities, the default conclusion is that methanol must inhibit initial hydrogen abstraction. This conclusion agrees with the observation that laser flash excitation of 2,4,6-trimethylbenzil produces transients in benzene but not in methanol.[47] Further study is called for.

Kinetics. It has been observed more than once[46,48,49] that the triplet state kinetics of 2,6-disubstituted phenyl ketones do not succumb easily to human understanding. Nonetheless, in this section we compare the kinetics of monoketones and of these benzils to help distinguish between γ- and δ-hydrogen abstraction in the latter.

Triplet energy transfer to sterically congested ketones maintains rate constants near diffusion-controlled.[17,22,50] Such also appears to be true for at least one diketone, 2,4,6-trimethylbenzil; its triplet undergoes 3 kcal/mol *endothermic* energy transfer to dienes with a rate constant of 8×10^7 M^{-1} s^{-1}.[47] If we assume a k_q of 2×10^9 M^{-1} s^{-1} for pyrene quenching of these diketones, the value measured for exothermic quenching of several ortho- and 2,6-substituted ketones,[48,49,51] the observed quenching by pyrene indicates a rate of triplet decay of $\sim 5 \times 10^6$ s^{-1} for **iPr$_6$B**. Since this value represents mainly the rate constant for hydrogen atom abstraction, we may ask whether it corresponds more nearly to the anticipated value for either γ- or δ-abstraction. Rate constants for hydrogen abstraction by phenyl alkyl diketones average only 1/400 as large as those for the same reaction of the corresponding monoketones, the decrease reflecting low exothermicities of reaction and delocalization of the n orbital.[2] Multiplying our measured triplet decay rate by 400 provides a 2×10^9 s^{-1} rate constant for proper comparison to monoketone reactivity.

The measured rate constants for δ-hydrogen abstraction by α-mesityl and α-(2,4,6-triisopropylphenyl)acetophenone are in fact in the anticipated range of 10^9 s^{-1}.[16] These rates contain a component of charge transfer from aryl to carbonyl which dampens differences between C−H bond strengths.[16] In contrast, rate constants for γ-hydrogen abstraction by 2,4,6-trialkylbenzophenones are much lower, $3-5 \times 10^6$ s^{-1} for triisopropylbenzophenone (**iPr$_3$BP**) [48,51] and $<10^6$ s^{-1} for

Scheme 12



trimethylbenzophenone,[46] values comparable to those for decay of **iPr$_6$B** and **Me$_3$B**,[47] respectively. As Scheme 12 shows, the monoketones have geometries with the same nearly orthogonal orientation of the carbonyl and the triisopropylphenyl group as in **iPr$_6$B**, presumably in their triplets as well as their ground states. **Me$_3$B** may be an imperfect model for estimating the reactivity of **Me$_6$B**, since their geometries presumably differ somewhat. Nonetheless, the absolute rates for the benzils are >100 times larger than the models for γ-hydrogen abstraction predict. This comparison would suggest that our hexaalkylbenzil triplets react primarily by δ-hydrogen abstraction.

If we choose the 2,4,6-trialkylacetophenones as model monoketones for γ-hydrogen abstraction, we reach a different conclusion. The trimethyl ketone forms a long-lived triplet[46,48] that decays with $k \sim 10^7$ s^{-1} as well as a short-lived triplet[52] that forms cyclobutenol with $k \sim 5 \times 10^8$ s^{-1}; the triisopropyl ketone triplet reacts to form cyclobutenol with $k \sim 2 \times 10^9$ s^{-1}.[22] These high rates for monoketone γ-hydrogen abstraction extrapolate to the observed rates for the benzils and thus support our assumption based on geometry that both γ- and δ-hydrogen abstraction should occur competitively in these benzils.

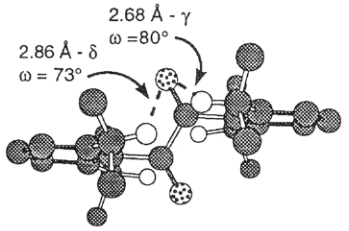
Which comparison is more appropriate? The trialkylacetophenones probably have more nearly planar benzoyl systems *in their triplets* than do the benzophenones and thus may attain orientations of C−H bonds and carbonyl orbitals more favorable for hydrogen transfer than are attainable in the more twisted geometries (see below). As discussed above, we are not sure of the situation for the triplet benzils but do know that the diketone unit is fully conjugated in all but **tBu$_6$B**. It does seem likely that the trialkylphenyl groups in the benzils mimic the benzophenones more nearly than the acetophenones in remaining twisted out of conjugation with the carbonyls even in their triplet states.

A comparison of quantum yields is worthwhile but does not provide any more insight into how much γ-hydrogen abstraction occurs. The relative quantum yields for photocyclization of these benzils, **iPr$_6$B** ~ **Et$_6$B** ≫ **Me$_6$B**, parallel those for benzocyclobutenol formation from the 2,4,6-trialkylbenzophenones.[51] Since the actual triplet lifetimes of both systems are in the microsecond range, this order probably reflects how well hydrogen abstraction competes with solvent quenching. The 2,4,6-trialkylacetophenones all cyclize in low quantum yield ~0.01;[48,53] and the α-(2,4,6-trialkylphenyl)acetophenones form products in high quantum efficiency independent of the alkyl group.[16] The lack of dependence on C−H bond strength reflects the high triplet reactivity in both systems. The very low quantum efficiencies for cyclization of the trialkylacetophenones are not related directly to triplet reactivity, since triplet yields are low[22] and the dienol photoproducts may cyclize to cyclobutenols inefficiently.[23]

There is one further set of comparisons to be made. As reported earlier, α-mesityl-2,4,6-trimethylacetophenone (**MesMe$_3$AP**) and α-mesityl-*o*-methylacetophenone display much different photoreactivity.[17] The former undergoes only radical cleavage, whereas the latter also forms indanols *via*

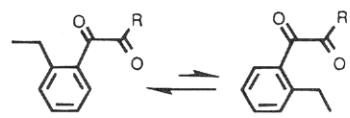
(47) Wintgens, V.; Netto-Ferreira, J. C.; Scaiano, J. C. Unpublished.
(48) Guerin, B.; Johnston, L. J. *Can. J. Chem.* **1989**, *67*, 473.
(49) Wagner, P. J.; Meador, M. A.; Park, B.-S. *J. Am. Chem. Soc.* **1990**, *112*, 5199.
(50) Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806.
(51) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsuura, T. *J. Am. Chem. Soc.*, **1983**, *105*, 1590.
(52) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259.
(53) Kitaura, Y.; Matsuura, T. *Tetrahedron*, **1971**, *27*, 1597.

Scheme 13



δ-hydrogen abstraction. The α-mesityl group totally suppresses the products that would be expected from γ-hydrogen abstraction. Given the structural similarity between these diketones and the monoketones, especially with regard to the position of the α-aryl ring relative to the carbonyl group, as depicted in Schemes 5 and 12, it is tempting to conclude that δ-hydrogen abstraction dominates in both sets of molecules. The lack of indanol formation from **MesMe$_3$AP** reflects a very rapid radical cleavage coupled with an apparent inhibition of δ-hydrogen abstraction. As mentioned above, triplet α-mesitylacetophenone (**MesAP**) abstracts a δ-hydrogen rapidly, $k = 5 \times 10^8$ s^{-1}. Since the α-mesityl groups of both **MesAP** and **MesMe$_3$AP** eclipse the remote carbonyl, why are they not equally reactive? The answer is found in the requirement that the α-mesityl group twist somewhat for a benzylic hydrogen to get within bonding distance of the carbonyl oxygen.[16] The twist angle and the bulk of the other aryl ring appear to strongly affect the energy requirement for the required conformational movement. In the diketones, radical cleavage of the OC−CO bond does not occur; δ-hydrogen abstraction certainly does; γ-hydrogen abstraction may but is not necessary to explain the products.

Dependence of Hydrogen Abstraction Rates on Geometry. Our conclusion that δ-hydrogen abstraction may dominate in these hexaalkylbenzils has important implications for understanding the behavior of α-diketones in general. Given the anti coplanar geometry of the dicarbonyl unit in the triplets, each oxygen has both a γ- and a δ-hydrogen within reaction distance. The dominant reaction now appears to involve the same regiospecific hydrogen abstraction by the distal rather than the proximate carbonyl that occurs in aliphatic and unsymmetric phenyl diketones. An obvious conclusion is that regiospecificity has a conformational rather than an electronic cause. In the case of *o*-tolyl alkyl diketones, the preferences for a *syn* geometry of *o*-toluyl groups[54] and for an anti coplanar diketone unit combine to minimize δ-hydrogen abstraction by the distal carbonyl. Inasmuch as dienol can rearrange directly to hydroxyindanone, the *E/Z* diastereoselectivity observed by Hamer may indeed measure competing formation of 1,4-biradical (triplet dienol) and 1,5-biradical. However, as shown above, internal hydrogen bonding in the 1,5-biradical should make the two conformations leading to *Z* and *E* products of comparable energy and even favor the latter. Since hydroxyindanones probably have 1,5-biradicals as their immediate precursors no matter what the competition between γ- and δ-hydrogen abstraction, there really is little evidence for the former.



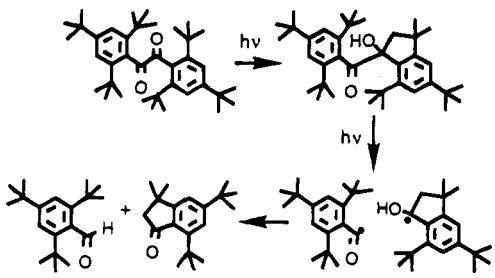
The question of orientational preferences for hydrogen atom abstraction by n,π* triplets has been of interest for some years.[35] Scheme 13 shows a 90° twisted skeleton of **iPr$_6$B** with the *p*-isopropyls and all but the four benzylic hydrogens deleted. The dicarbonyl unit lies in the plane of the paper so that the perspective shows that both γ- and δ-hydrogens lie close to the π-plane of the carbonyl, the angles ω indicating how much above the plane containing the long axis of the n orbitals each hydrogen lies. Neither hydrogen is well situated for reaction. However, small rotations around the OC−CO axis bring the δ-hydrogens to much smaller values of ω.[16] Such movement is probably more facile than rotation around OC−aryl bonds and would contribute strongly to the apparent preference for δ-hydrogen rather than γ-hydrogen abstraction.

Maruyama's group reported that 2,5,2′,5′-tetramethylbenzil cyclizes efficiently to hydroxyindanone but that **Me$_3$B**, 2,3,5,6-tetramethylbenzil, and **Me$_6$B** do not cyclize under the same conditions.[20] The nonreactivity of the first two has since been corroborated by Scaiano's group.[47] In fact, Maruyama's group reported that **Me$_6$B** undergoes only low quantum yield cleavage in THF solvent, trimethylbenzaldehyde being the only product that they isolated.[20] Since they irradiated the sample for 1 week, we suspect that photoreduction occurred, followed by secondary cleavage of the benzoin products. Any cyclization product probably would have undergone secondary cleavage also. Although we find that **Me$_6$B** does react sluggishly, the important point here is efficiency, which clearly is very low for all the 2,6-dimethylphenyl diketones. Maruyama *et al.* concluded from UV/vis and NMR spectra that 2,5,2′,5′-tetramethylbenzil has a geometry similar to that of benzil itself, while the others have their 2,6-methylated rings nearly orthogonal to the carbonyl, in agreement with our analysis above. This important geometric difference must be transferred in part to the excited triplets, and supports our suggestion above that the more nearly planar aroyl groups undergo γ-hydrogen abstraction faster. Ito, Matsuura, and co-workers have similarly concluded that the triplet reactivity of 2,4,6-trialkylphenyl ketones increases with increased coplanarity of the 2,4,6-trialkylbenzoyl unit.[51]

Hexa-*tert*-butylbenzil. This compound apparently forms the indanol **tBu$_5$I**, which is another sterically congested benzoin that cleaves to radicals readily. Disproportionation of the acyl and α-hydroxy radicals so formed would yield the observed products. The efficiency of this secondary photoreaction is understandable, but the inefficiency of the initial photocyclization to **tBu$_5$I** is puzzling. (The low extinction coefficient of **tBu$_6$B** at 438 nm is not sufficient to explain its nonreactivity.) The indanol probably is formed by δ-hydrogen abstraction such as occurs in *o*-*tert*-butylbenzophenone (**otBBP**).[55] Since this mode of reaction is atypical for diketones, as discussed in the Introduction, it must be slow. In the case of **otBBP** δ-hydrogen abstraction is very rapid; the 1,5-biradical cyclizes efficiently in methanol but inefficiently in hydrocarbon solvents. It is not clear why methanol does not enhance quantum efficiency for **tBu$_6$B** as it does for **otBBP**, unless the initial hydrogen abstraction is slowed as it seems to be for the other benzils. The benzene rings probably are highly twisted with respect to the carbonyls in triplet **tBu$_6$B** as they are in the ground state, but several hydrogen atoms are within abstracting distance at any twist angle. The 1,5-biradical leading to **tBu$_5$I** could be formed by an ε-hydrogen abstraction (which would follow the diketone regioselectivity "rule") followed by a 1,4 O-to-O hydrogen shift. However, such a hydrogen abstraction is too slow to occur in the model monoketone α-(*o*-*tert*-butylphenyl)-acetophenone. Therefore it seems an unlikely process in an intrinsically less reactive diketone.

(54) That the syn preference known for monoketones[56] also holds for diketones has been verified on both the ground states and the triplets by AM1-level computations.

(55) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.



Summary

All four hexaalkylbenzils appear to undergo δ-hydrogen abstraction with variable efficiency upon irradiation, the 1,5-biradicals so formed cyclizing to hydroxyindanones that themselves undergo highly efficient radical cleavage reactions under UV but not visible irradiation. The three benzils with benzylic hydrogens may also undergo γ-hydrogen abstractions. However, analysis of the solid state reactivity, the diastereoselectivity for product formation, and the kinetics strongly suggests that all 1-hydroxy-2-indanone products could arise from 1,5-biradicals. It is not clear to what extent γ-hydrogen abstraction also occurs; any 1,4-biradicals so formed may undergo a 1,4-hydrogen transfer to generate the 1,5-biradicals that form product. AM1 calculations suggest that the diastereoselectivity for cyclization of the simpler aryl diketones as well as of these hexaalkylbenzils can be explained entirely by the conformational populations of 1,5-biradicals. Triplet reactivity in these highly congested molecules appears to be controlled by conformational inflexibility. The regioselectivity of triplet hydrogen abstraction by simpler diketones also appears to be dominated by conformational factors, although it is difficult to deduce triplet regioselectivity from product ratios when so many intermediates can revert to ground state reactant. Methanol as solvent appears to greatly deactivate the triplets of all these benzils.

Experimental Section

General. Deuterated NMR solvents were used as obtained from Aldrich. Other solvents were cleaned and distilled before use. NMR spectra were obtained at 300 or 500 MHz (^{1}H) or 75 MHz (^{13}C) on Varian instruments. Chemical shifts are reported in ppm from $CHCl_3$ (7.24 ppm for ^{1}H, 77.0 ppm for ^{13}C) or C_6D_5H (7.10 ppm). Melting points are uncorrected. High-resolution mass spectra were obtained on a JEOL AX-505 or JEOL HX-110 double focusing mass spectrometer, with exact masses determined by peak matching in the FAB experiments. Phosphorescence spectra were measured on a Perkin-Elmer MPF-44A spectrometer. UV spectra were recorded on a Shimadzu UV-160 spectrometer. IR spectra were recorded in CCl_4.

Reactants. All of the substituted benzils were prepared in Jerusalem by known methods or modifications thereof.

2,4,6,2′,4′,6′-Hexamethylbenzil was prepared as described by Fuson *et al.*[56] as an orange powder: mp 118−9 °C; IR (CCl_4) 1698 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.04 (6H, s), 2.16 (12H, s), 6.61 (4H, s); ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 6 H), 2.23 (s, 12 H), 6.80 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.1, 21.2, 128.8, 133.6, 135.4, 140.1, 197.4.

2,4,6,2′,4′,6′-Hexaethylbenzil was prepared as a byproduct in a modification of Fuson's method to prepare the enediol[57] as an orange powder: mp 75−6 °C; IR (Nujol) 1700 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.12 (6H, t, J = 7.5 Hz), 1.14 (12H, t, J = 7.5 Hz), 2.46 (4H, quar, J = 7.5 Hz), 2.57 (8H, quar, J = 7.5 Hz), 6.83 (4H, s); ^{1}H NMR (CD_3OD) δ 1.11 (6H, t, J = 7.5 Hz), 1.25 (12H, t, J = 7.5 Hz), 2.43 (4H, quar, J = 7.5 Hz), 2.65 (8H, quar, J = 7.5 Hz), 7.0(4H, s); ^{1}H NMR ($CDCl_3$) δ 1.18 (t, J = 7.5 Hz, 12 H), 1.26 (t, J = 7.5 Hz, 6 H), 2.49 (quar, J = 7.5 Hz, 8 H), 2.65 (quar, J = 7.5 Hz, 4 H), 6.98 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.25, 15.84, 26.86, 28.78, 125.85, 132.96, 141.54, 146.54, 198.02.

2,4,6,2′,4′,6′-Hexaisopropylbenzil was obtained as a 50% byproduct in a modification of Fuson's method[58] to prepare the enediol. Triisopropylbenzoyl chloride was reduced with a magnesium/iodine mixture in a 30:40 ether/benzene solution. After acid quenching, extraction, washing with base and thiosulfate, and drying, a mixture of white and orange crystals was obtained. The enediol was removed by washing the mixture with cold petroleum ether (40−60 °C). The remaining orange-yellow powder was recrystallized from methanol: mp 155−6 °C; IR (CCl_4) 1698 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.16 (d, 24 H), 1.18 (d, 12 H), 2.74 (sept, 2 H), 2.97 (sept, 4 H), 7.08 (s, 4 H); ^{1}H NMR ($CDCl_3$) δ 1.13 (24 H, d, J = 6.8 Hz), 1.23 (12 H, d, J = 6.9 Hz), 2.59 (4 H, septet, J = 6.8 Hz), 2.88 (2 H, septet, J = 6.9 Hz), 7.01 (4 H, s); ^{13}C NMR ($CDCl_3$) δ 23.9, 24.0, 32.0, 34.4, 121.2, 132.2, 145.8, 150.9, 200.8.

2,4,6,2′,4′,6′-Hexa-*tert*-butylbenzil was prepared as described in the literature[30,59] as lemon yellow crystals: mp 204−5 °C (lit. mp 204−6 °C); IR (CCl_4) 1705 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.03 (18H, broad s), 1.28 (18H, s), 1.65 (18H, broad s), 7.33 (2H, broad s), 7.60 (2H, broad s); ^{1}H NMR ($CDCl_3$) δ 0.87 (18H, broad s), 1.30 (18H, s), 1.48 (18H, broad s), 7.20 (2H, broad s), 7.45 (2H, broad s); ^{13}C NMR ($CDCl_3$) δ 31.1, 32.1, 33.2, 121.6, 124.6, 128.5, 147.0, 150.3, 201.3, 203.3.

The 77 K phosphorescence spectra of the benzils were measured on 10^{-3} M glassy solutions in either 60:40 methanol/ethanol (**iPr$_6$B**) or 2-methyltetrahydrofuran (the rest). Three had nearly superimposable spectra, with a 0−0 band at 505.5 nm, a 4-fold more intense band at 567 nm, and weak bands on either side of the strongest band. The emission of **tBu$_6$B** was bright green with a broad band at 530 nm and a broader shoulder at ~585 nm.

α-(2,5-Di-*tert*-butylphenyl)acetophenone was prepared by reduction of 2,5-di-*tert*-butylbenzoic acid[60] to the alcohol with lithium aluminum hydride, conversion of the alcohol to the chloride with thionyl chloride, S_N2 displacement with sodium cyanide in DMSO, addition of phenyl magnesium bromide, and acid hydrolysis: ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9 H), 1.34 (s, 9 H), 4.60 (s, 2 H), 7.01 (d, J = 3.0 Hz, 1 H), 7.25 (dd, J = 7.5, 3.0 Hz, 1 H), 7.36 (d, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.4 Hz, 2 H), 7.56 (tt, J = 7.4, 1.8 Hz, 1 H), 8.02 (dt, J = 7.5, 1.8 Hz, 2 H); MS *m/z* 308, 293, 251, 203, 161, 105, 77, 57; Hi-Res *m/z* 308.2141 (calcd for $C_{22}H_{28}O$ 308.214).

Identification of Photoproducts. Irradiations were performed in several ways. For simple NMR analysis of product mixtures, solutions ~0.01 M in benzil were placed in NMR tubes fixed with rubber septa and then deaerated by argon bubbling. They were irradiated by fixing them to the outside of a Vycor filter jacket surrounding a standard Ace Glass water-cooled immersion well containing a 450-W Hanovia medium-pressure mercury arc. The arrangement provided a 1 cm path of filter solution in the outer Vycor vessel. Larger 0.01 M samples for product isolation were irradiated the same way, except in 100 mL test tubes. Large-volume samples were irradiated in 500-mL cylindrical vessels with the immersion well in the middle and with constant argon bubbling. Solid samples were packed into melting point capillary tubes, which were placed inside 13 × 100 culture tubes for irradiation.

Use of a Pyrex filter sleeve and no filter solution provided the full lamp output above 290 nm. Various mercury emission bands were isolated with the following filters: 313 nm, an aqueous solution of 0.002 M potassium chromate and 0.1 M potassium carbonate ; 365 nm, Corning #7-37 glass filter combinations; 438 nm, a uranium glass filter sleeve around the mercury arc plus 500 mL of water containing 20 g of cupric sulfate, 25 g of sodium nitrite, and 34 mL of concentrated ammonium hydroxide in the Vycor vessel.

2,4,6,2′,4′,6′-Hexaisopropylbenzil (0.03 g) in 80 mL of benzene was irradiated to 100% conversion with a Pyrex-filtered mercury arc. The crude product mixture was separated by column chromatography using 4% ethyl acetate in hexane and was further purified by preparative TLC using 3% ethyl acetate in hexane. Two major products were isolated as white solids:

2-Hydroxy-2-(2′,4′,6′-triisopropylphenyl)-3,3-dimethyl-5,7-diisopropyl-1-indanone: mp 150−1 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (3H, d, J = 6.8 Hz), 1.14 (3H, d, J = 6.8 Hz), 1.15 (3H, s), 1.21 (3H, d, J = 6.8 Hz), 1.22 (3H, d, J = 6.8 Hz), 1.23 (3H, d, J = 6.8 Hz), 1.25 (3H, d, J = 6.8 Hz), 1.27 (3H, d, J = 6.8 Hz), 1.30 (6H, d, J = 6.8 Hz),

(56) Fuson, R. C.; McKeever, C. H.; Corse, J. *J. Am. Chem. Soc.* **1940**, *62*, 600.
(57) Fuson, R. C.; Corse, J.; McKeever, C. H. *J. Am. Chem. Soc.* **1939**, *61*, 2010.
(58) Fuson, R. C.; Horning, E. C. *J. Am. Chem. Soc.* **1940**, *62*, 2962.
(59) Frey, J.; Nugiel, D. A.; Rappoport, Z. *J. Org. Chem.* **1991**, *56*, 446.
(60) Betts, E. E.; Barclay, L. R. *Can. J. Chem.* **1955**, *33*, 1768.

1.33 (3H, d, J = 6.8 Hz), 1.59 (3H, s), 2.69 (1H, s, OH), 2.19 (1H, sept, J = 6.8 Hz), 2.83 (1H, sept, J = 6.8 Hz), 2.99 (1H, sept, J = 6.8 Hz), 4.02 (1H, sept, J = 6.8 Hz), 4.21 (1H, sept, J = 6.8 Hz), 6.86 (1H, d, J = 2 Hz), 7.09 (1H, d, J = 2 Hz), 7.14 (1H, d, J = 1 Hz), 7.18 (1H, d, J = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 205.3, 162.47, 157.16, 150.80, 150.58, 146,98, 146.08, 135.76, 126.84, 124.06, 123.20, 122.20, 119.10, 86.2, 35.00, 33.60, 33.34, 30.46, 28.97, 27.18, 26.22, 25.96, 25.55, 25.42, 23.84, 23.78, 23.74, 23.43, 23.37; IR (CCl_4) 3551, 2966, 2870, 1704, 1604, 1461 cm^{-1}; UV (hexane) ϵ_{313} = 220 M^{-1} cm^{-1}; ϵ_{365} = 23 M^{-1} cm^{-1}; MS m/z 462.3521 (calcd for $C_{32}H_{46}O_2$, 462.3510). Assignment of each ^{1}H NMR peak was made based on the results from 2D COSY and NOE experiments.

α-(2-Formyl-3,5-diisopropylphenyl)-2′,4′,6′-triisopropylisobutyrophenone: mp 150−1 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (6H, d, J = 6.8 Hz), 1.02 (6H, d, J = 6.8 Hz), 1.19 (6H, d, J = 6.8 Hz), 1.198 (6H, d, J = 6.8 Hz), 1.20 (6H, d, J = 6.8 Hz), 1.63 (6H, s), 2.21 (2H, sept, J = 6.8 Hz), 2.82 (1H, sept, J = 6.8 Hz), 2.84 (1H, sept, J = 6.8 Hz), 3.13 (1H, sept, J = 6.8 Hz), 6.88 (2H, s), 7.12 (1H, d, J = 1 Hz), 7.13 (1H, d, J = 1 Hz), 10.71 (1H, s); ^{13}C NMR ($CDCl_3$) 22.30, 23.80, 23.92, 24.11, 25.95, 29.49, 29.86, 31.89, 34.11, 34.48, 53.77, 120.75, 122.74, 123.78, 136.09, 136.50, 141.33, 144.00, 147.71, 149.15, 150.19, 199.81, 215.54; IR (CCl_4) 2985, 2930, 2870, 1701, 1688, 1605, 1462 cm^{-1}.

Some crystals of the benzil were packed into melting point capillary tubes which were placed inside standard Pyrex test tubes, which were then degassed and sealed. The samples were irradiated at 438 or 366 nm, after which the tubes were opened and the samples dissolved in $CDCl_3$. NMR analysis indicated only the hydroxyindanone product together with starting benzil. Irradiation in methanol-d_4 at 438 or 366 nm led to no reaction and no H/D exchange of the o-methine protons. Several hours of irradiation with Pyrex-filtered light destroyed all the benzil and left unidentified products.

Irradiation of ~0.01 M hydroxyindanone in benzene-d_6 at 365 or 313 nm, but not at 438 nm, converted it completely to the ketoaldehyde, as judged by NMR analysis.

2,4,6,2′,4′,6′-Hexamethylbenzil (0.0035 g) in 0.75 mL of benzene-d_6 in a deaerated NMR tube was irradiated through a 435-nm filter solution. One major product (>90%) appeared in the ^{1}H NMR spectrum. A solid sample was packed into a 1-cm length of melting point capillary tube. After the sample was irradiated, the capillary tube was broken into pieces inside a small round-bottomed flask and the residue was extracted with $CDCl_3$ for NMR analysis. Again, only one major product was formed:

2-Hydroxy-2-(2′,4′,6′-trimethylphenyl)-5,7-dimethyl-1-indanone: ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3H), 2.26 (broad s, 6H), 2.41 (s, 3H), 2.66 (s, 3H), 3.36 and 3.57 (AB quartet, J = 18 Hz, 2H), 6.90 (s, 2H), 7.0 (s, 1H), 7.06 (s, 1H).

2,4,6,2′,4′,6′-Hexaethylbenzil (0.0040 g) in 0.75 mL of benzene-d_6 in a deaerated NMR tube was irradiated through a 435-nm filter solution. Two isomeric products were formed in a 2:1 ratio, as judged from integration of methyl doublets in the ^{1}H NMR spectrum. The two products were separated by TLC, with benzene as the eluent.

(*Z*)-2-Hydroxy-2-(2′,4′,6′-triethylphenyl)-3-methyl-5,7-diethyl-1-indanone: ^{1}H NMR (C_6D_6) δ 1.03 (t, J = 7.5 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H), 1.19 (br t, J = 7.5 Hz, 6H), 1.36 (t, J = 7.5 Hz, 3H), 1.51 (3H, d, J = 7.2 Hz), 2.39 (quartet, J = 7.5 Hz, 2 H), 2.49 (quartet, J = 7.5 Hz, 2H), 2.45−2.63 (br m, 2H), 2.8−3.0 (br s, 2H), 2.73 (s, OH), 3.22, 3.32 (AB quartet of quartet, J = 14.1, 7.5 Hz, 2H), 3.47 (quartet, J = 7.2 Hz, 1H), 6.86 (1H, s), 6.87 (1H, s), 6.91 (2H, s); ^{13}C NMR ($CDCl_3$) δ 13.94, 14.83, 15.13, 15.18, 16.96 (br, 2), 25.0, 27.93 (2), 28.14, 29.48, 46.66, 84.54, 121.76, 128.04, 128.12 (br), 128.49, 135.68, 142.68, 146.10, 152.33, 156.66, 204.64; IR ($CDCl_3$) 3570, 2970, 2936, 2876, 1707, 1604, 1460, 1210, 875 cm^{-1}.

(*E*)-2-Hydroxy-2- (2′,4′,6′-triethylphenyl)-3-methyl5,7-diethyl-1-indanone: ^{1}H NMR (C_6D_6) δ 0.98 (d, J = 7.5 Hz, 3H), 1.05 (t, J = 7.5 Hz, 3H), 1.18 (t, J = 7.5 Hz, 3H), 1.25 (t, J = 7.5 Hz, 3H), 1.34 (t, J = 7.5 Hz, 3H), 1.36 (t, J = 7.5 Hz, 3H), 2.14, 2.29 (AB quartet of quartet, J = 15, 7.5 Hz, 2H), 2.40 (quartet, J = 7.5 Hz, 2H), 2.52 (quartet, J = 7.5 Hz, 2H), 2.76 (s, OH), 2.79 (d of quartet, J = 15, 7.5 Hz, 1H), 3.17 (d of quar, J = 15, 7.5 Hz, 1H), 3.27 (d of quartet, J = 15, 7.5 Hz, 1H), 3.40 (d of quartet, J = 15, 7.5 Hz, 1H), 3.67 (quartet, J = 7.5 Hz, 1 H), 6.84 (br s, 1H), 6.876 (br s, 1H), 6.879 (d, J = 1.5 Hz, 1 H), 7.047 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.84, 15.12, 15.19, 15.28, 17.30, 18.71, 24.96, 28.25, 28.54, 29.46, 29.70, 45.27, 85.07, 122.68, 126.13, 128.10, 128.43, 128.45, 135.07, 141.02, 142.68, 145.80, 146.26, 152.58, 157.79, 204.58; IR ($CDCl_3$) 3560, 2970, 2936, 2876, 1707, 1605, 1460, 1210, 876 cm^{-1}.

When the diketone was irradiated through $CuSO_4$ solution (>320 nm) to high conversion, a secondary photoproduct was also observed and assigned as the ketoaldehyde from the NMR spectrum of the reaction mixture. The ratio of ketoaldehyde:(*Z*)-indanol:(*E*)-indanol was 26:67:7. A small sample vial containing 0.004 g of the solid diketone was exposed to sunlight from a south-facing window for 3 weeks. C_6D_6 was added to the resulting liquid and its ^{1}H NMR spectrum was taken. The sample had undergone complete reaction to the two isomeric indanol photoproducts, formed in a 6:1 *Z/E* ratio. A crystalline sample was irradiated in a sealed capillary tube. After irradiation, it was dissolved in $CDCl_3$ and analyzed by NMR, which indicated a mixture of starting material and **Z-Et$_6$I**. When the diketone (0.0040 g) was irradiated in 0.75 mL of methanol-d_4, the *Z/E* ratio was 3−4 to 1 at low conversion. No loss of ortho-benzylic signal intensity was observed. Conversion was only a few percent after 2 days of irradiation at 435 nm whereas it was more than 70% in benzene under the same irradiation conditions. Moreover, the reaction mixture in methanol contained several unidentified products.

2,4,6,2′,4′,6′-Hexa-*tert*-butylbenzil (0.02 g) in 80 mL of benzene was irradiated with a Pyrex filtered mercury arc for 3 days. The crude product mixture was separated by preparative TLC, with hexane eluent, into three major products. One, which did not move on the TLC plate, was identified as 2,4,6-tri-*tert*-butylbenzoic acid after the NMR spectrum was compared with one reported by Neckers.[61] The other two were identified based on their ^{1}H NMR spectra:

2,4,6-Tri-*tert*-butylbenzoic acid: ^{1}H NMR ($CDCl_3$) δ 1.31 (9H, s), 1.49 (18H, s), 7.45 (2H, s). No carboxylic acid −OH peak was found. (This peak was also missing from ref 61; D_2O in the solvent may be responsible.)

2,4,6-Tri-*tert*-butylbenzaldehyde: ^{1}H NMR ($CDCl_3$) δ 1.36 (9H, s), 1.40 (18H, s), 7.40 (2H, s), 11.15 (1H, s, −CHO).

5,7-Di-*tert*-butyl-3,3-dimethyl-1-indanone: ^{1}H NMR ($CDCl_3$) δ 1.38 (9H, s), 1.40 (6H, s), 1.48 (9H, s), 2.59 (2H, s), 7.32 (1H, s), 7.41 (1H, s); ^{13}C NMR ($CDCl_3$) δ 29.8, 30.4, 31.2, 31.4, 36.0, 37.2, 54.3, 117.7, 122.4, 150.9, 157.0, 158.0, 167.2, 205.0.

Quantitative irradiations were performed on benzene solutions containing 0.01 M **iPr$_6$B**, 0.0023 M eicosane, and 0 to 0.005 M pyrene. Equal volumes (2.8 mL) of each solution were placed in 13 × 100 Pyrex culture tubes that were degassed, sealed, and irradiated in a standard merry-go-round apparatus[62] with 365-nm filters. Yields of hydroxyindanone were determined by gas chromatography on a DB210 Megabore column.

Computations were performed with the Tektronix Cache MOPAC implementation. AM1-level biradical and triplet energies were minimized with TRIPLET/UHF, PRECISE, and NOANCI keywords. Occasionally GEO-OK was necessary to allow dihedral drives to explore high energy, sterically crowded conformations. Geometries identified as energy minima from dihedral drives were then further minimized with no constraints.

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