

The Photochemistry of *o*-Benzylbenzophenone: a Pericyclic Cornucopia

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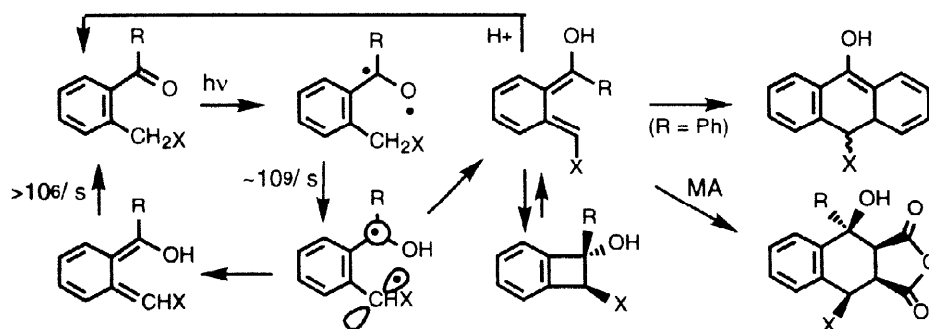
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Received 21 November 1997; revised 6 February 1998; accepted 8 February 1998

Abstract: UV irradiation of the title compound produces *cis*-1,2-diphenylbenzocyclobutenol quantitatively. While stable at temperatures below 0°, at room temperature it establishes a high enough equilibrium population of its *EE* *o*-xylylenol precursor to undergo slow reversion to ketone and rapid reaction with maleic anhydride or oxygen, as well as photoinduced cyclization to the *trans* cyclobutenol. © 1998 Elsevier Science Ltd. All rights reserved.

This paper describes some overlooked photoreactivity that reveals a previously unrecognized connection between two papers published in the 1960's. Yang and coworkers reported that *o*-benzylbenzophenone **oBnBP** undergoes reversible photoenolization to an *o*-xylylene intermediate.^{1,2} Ortho-alkylphenyl ketones have received widespread synthetic and mechanistic attention as photochemical sources of *o*-xylylenes ever since.^{3,4} Meanwhile, Huisgen and Seidl showed that the puzzling Diels-Alder cycloaddition of 1,2-diphenylbenzocyclobutene (**Ph₂CB**) to dienophiles⁵ involves reaction by trace amounts of an *o*-xylylene in equilibrium with **Ph₂CB**.⁶ Since then all sorts of benzocyclobutenes have been utilized as *in situ* thermal sources of *o*-xylylenes.⁷ The Yang and Huisgen work had the common feature of establishing that low concentrations of *o*-xylylenes, however produced, react very rapidly with dienophiles. We now find that the primary stable photoproduct from **oBnBP** is *cis*-1,2-diphenylbenzocyclobutenol (**c-CB**), a fact that had been overlooked for 36 years because **c-CB** rapidly establishes equilibrium with its highly reactive *o*-xylylenol⁸ precursor at room temperature. Thus understanding of **oBnBP** photochemistry depends on Huisgen's nonphotochemical work as well as on photochemical studies.

Scheme 1

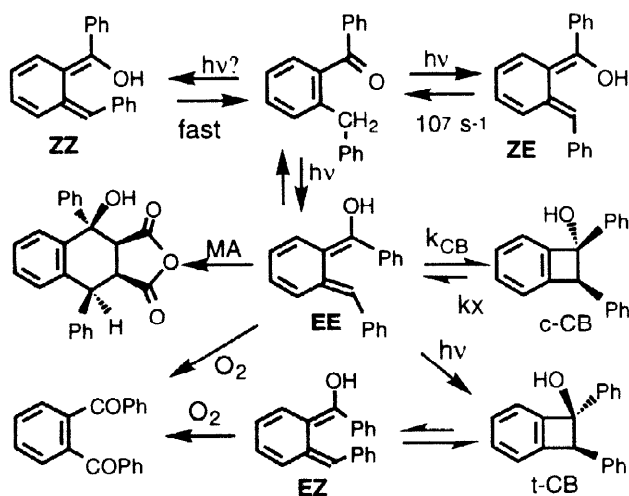


Scheme 1 depicts the current consensus⁴ as to the structure and chronology of the transient intermediates formed from triplet *o*-alkylphenyl ketones, as well as the major kinds of stable products formed. γ -Hydrogen abstraction produces a biradical triplet *o*-xylylenol;⁹ it decays to isomeric ground state *o*-xylylenols with both *E* and *Z* configurations of the OH group.¹⁰ The latter is very short-lived, reverting to starting ketone by a rapid 1,5-sigmatropic H-shift.⁷ Thus the former is responsible for all product formation. It undergoes acid/base catalyzed reketonization^{11,12} with benzylic H/D exchange¹ but usually lives long enough to undergo Diels-Alder cycloadditions,^{1,3,13} dihydroanthrol formation,¹⁴ benzocyclobutenol formation,^{15,16} and even dimerization.³

Before our study, few products had been reported from irradiation of **oBnBP**. In the presence of maleic anhydride (**MA**), **oBnBP** produces a *single* endo Diels-Alder cycloadduct with stereochemistry (*cf.* Scheme 1 or 2) indicative of an *EE* *o*-xylylenol precursor.¹⁷ Yang reported that nothing but H/D exchange occurred upon irradiation of **oBnBP** in alcohol solvents without dienophiles present,¹ whereas irradiation in benzene produced a yellow, fluorescent solution and a possible dimer of unknown structure.² A recent paper¹⁸ reported the detection by GC/MS analysis of two major products in both benzene and trifluoroethanol; one was assigned as 10-phenylanthrone, the other as 10-phenyl-10-hydroxyanthrone, both oxidation products of a dihydroanthrol.

We have confirmed the stereoselective Diels-Alder reaction when **oBnBP** is irradiated with **MA**. Irradiation of dilute **oBnBP** at 77°K produces the bright yellow characteristic of *o*-xylylenols.¹⁹ Irradiation in argon-purged acetonitrile, methanol, or toluene at temperatures from -70 to 25°C produces a yellowish solution that fluoresces blue-green just as Yang reported.²⁰ However, NMR analysis revealed major products that had not been detected previously (*cf.* Scheme 2). Depending on conditions, two isomeric 1,2-diphenylbenzocyclobutenols²¹ are formed. Brief irradiation rapidly converts **oBnBP** quantitatively into *c*-**CB**. (The quantum yield at 24° and 13% conversion is 10%.) The only NMR-detectable indication of additional products appeared in heavily irradiated samples as small signals between 5.8-6.8 ppm. If these correspond to a dihydroanthrol byproduct, it represents a <5% yield. Upon extended irradiation at 24° *c*-**CB** gradually is partially converted into a mixture of its *trans* isomer *t*-**CB** and **oBnBP**. The *c*-**CB** is stable below 0°; but when left in the dark at room temperature, it slowly (with a half-life of *several hours*) reverts completely to **oBnBP**. A little yellow coloration is present immediately after complete conversion of **oBnBP** to *c*-**CB**, with a *uv*/*vis* spectrum matching that reported for *o*-xylylenols;¹⁸ but more grows in as *c*-**CB** reverts to ketone²² and then persists for months as long as air is excluded. In solutions containing mixtures of the two **CB**'s, only the *cis* isomer reketonizes, while *t*-**CB** remains unchanged, as does the green fluorescence. Heating the solution accelerates the reversion and *enhances* the fluorescence. Addition of

Scheme 2



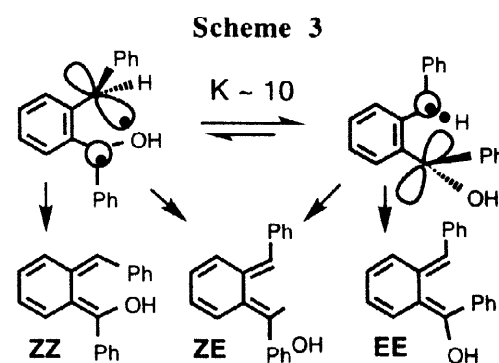
0.01 M **MA** converts, *in a few minutes*, only the *c*-**CB** to the same Diels-Alder adduct obtained by direct irradiation of **oBnBP** with **MA**. (This conversion confirms the stereochemistry of *c*-**CB**.) Addition of air rapidly converts both **CB** isomers to *o*-dibenzoylbenzene, and destroys the fluorescence. Irradiating **oBnBP** in oxygen-saturated solution also produces *o*-dibenzoylbenzene quantitatively. We conclude that the dihydroanthrol inferred in ref. 18 either was the only photoproduct that did not thermally revert to ketone or was formed from *c*-**CB** during GC analysis, not photochemically from **oBnBP**. Likewise, the mass 286 product in ref. 18 may have been *o*-dibenzoylbenzene rather than 10-phenyl-10-hydroxyanthrone.

Scheme 2 suggests how the various products arise from irradiation of **oBnBP**. The relatively long-lived *EE* *o*-xylylenol, if not trapped by **MA** or oxygen, cyclizes to *c*-**CB**. Bolstered, compared to other diphenylbenzocyclobutenes,⁵⁻⁷ by the large acceleration of electrocyclic cyclobutene ring opening afforded by oxy groups,^{3,23,24} *c*-**CB** rapidly establishes equilibrium at 24° with the *EE* *o*-xylylenol, which then gets a second chance to partition

itself among all its reactions in Scheme 2. In the absence of additives, slow irreversible reversion to ketone, catalyzed by trace acid or base, predominates. Addition of **MA** or air regenerates little ketone, so the rates of Diels-Alder and O_2 addition are faster than the rate of reversion. Upon continued irradiation, the **EE** *o*-xylylenol absorbs enough light to undergo disrotatory cyclization to **t-CB** in competition with its thermal reactions. **t-CB** should establish its own thermal equilibrium with an *o*-xylylenol; since conrotatory ring opening strongly favors twisting the **OH** out rather than in,^{3,23} the elusive, sterically congested **EZ** xylylenol presumably is formed. The apparent low reactivity of **t-CB** may reflect slow opening to the **EZ** *o*-xylylenol, and/or steric hindrance to bimolecular attack at the diene termini of the **EZ** *o*-xylylenol.^{5-7,13} The reaction of **t-CB** with oxygen but not with **MA** supports the latter effect.

With four *o*-xylylenols possible from **oBnBP**, the Diels-Alder stereoselectivity originally was explained on the basis of the **EZ** xylylenol being so much more congested than its **EE** isomer that it either was not formed or reacted too slowly.¹⁷ Any **EZ** xylylenol that might form certainly should be able to cyclize to **t-CB**; the fact that **t-CB** is formed only as a secondary photoproduct strongly suggests that little, if any, **EZ** xylylenol is formed directly from triplet ketone. However, we do not think that the lack of **EZ** xylylenol formation is due to its steric congestion. We have recently summarized a variety of experimental and theoretical evidence²⁵ to support our earlier contention¹⁶ that *o*-xylylenol isomer distributions and thus product geometries are set when the biradical triplet xylylenol decays to the ground state. We have suggested that the relative energies of the biradical conformers are determined by the relative radical stabilizing abilities of the substituents on the two ends of the *o*-xylylenol. The end with the "better" substitution is twisted, since it has less need for conjugation with the central ring. Upon decaying to ground state xylylenol, the twisted end rotates to both **E** and **Z** configurations about the exocyclic double bond; the configuration about the other end is established in the biradical before its decay. Two low energy triplet xylylenol conformers are expected from **oBnBP**; they are calculated (3-21G*) to differ by only 1.4 kcal/mole and should both be populated, such that decay to ground state would form the **EE**, **ZE**, and **ZZ** xylylenols, but not the **EZ**.

Ref. 18 updated the early^{2,11} flash kinetic studies of **oBnBP** by reassigning transient absorption peaks: two with lifetimes of ~ 30 ns and $470 \mu\text{s}$ were assigned as the **ZE** and **EE** ground state xylylenols, respectively. A ~ 10 sec yellow transient had been detected in both earlier studies and assigned as the **EE**-enol.⁸ It thus seems possible that the three "expected" *o*-xylylenols have been detected directly. Since our study provides a thermal source of the **EE**-xylylenol, analysis of the kinetics of **c-CB** reactions could help determine which of the two longer-lived flash transients is the **EE**-xylylenol responsible for products. A full analysis will be provided in a full paper. In short, the initial absorption intensity at 420 nm of 10^{-2} M **c-CB**, presumed to be equilibrated xylylenol,²² indicates that $k_X/k_{CB} \leq 10^{-4}$. The rapidity with which **c-CB** reacts with **MA**, via **c-CB** \rightleftharpoons **EE**-xylylenol equilibrium, then requires that $k_X \sim 10^{-2} \text{ s}^{-1}$ and $k_{CB} = 10^2\text{--}10^3 \text{ s}^{-1}$. Our results appear to corroborate ref. 18's assignment of the $470 \mu\text{s}$ transient as the **EE** xylylenol. The 10 sec transient's identity remains undetermined; it seems to behave like a sluggish xylylenol. If it were a minor product like a dihydroanthrol, it could react with dienophiles; but its short lifetime would require explanation. The fluorescent species probably is a xylylenol; which one also remains to be determined, but the sterically congested and thus relatively unreactive **EZ** isomer is an intriguing possibility.



Acknowledgment: This work was supported by NSF grants No. CHE91-20931 and CHE95-08308. The NMR spectrometers used were partially funded by NSF grant CHE88-00770 and NIH grant RR047550.

References:

- (1) Yang, N. C.; Rivas, C. *J. Am. Chem. Soc.* **1961**, *83*, 2213.
- (2) Zwicker, E. F.; Grossweiner, L. I.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2671.
- (3) Sammes, P. G. *Tetrahedron*, **1976**, *32*, 405-422.
- (4) Wagner, P.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227.
- (5) Jensen, F. R.; Coleman, W. E. *J. Am. Chem. Soc.* **1958**, *80*, 6149.
- (6) Huisgen, R.; Seidl, H. *Tetrahedron Lett.* **1964**, 3381.
- (7) e.g., Quinkert, G.; Opitz, K.; Wiersdorff, W. W.; Finke, M. *Tetrahedron Lett.* **1965**, 3009; Paul, T.; Hassan, M. A.; Korth, H.-G.; Sustmann, R.; Avila, D. V. *J. Org. Chem.* **1996**, *61*, 6835.
- (8) We describe the hydroxy-xylylene intermediates with the term "o-xylylenol" instead of the commonly used "photoenol", because the former is specific to this particular form of photoenolization.
- (9) Das, P. K.; Scaiano, J. C. *J. Photochem.* **1980**, *12*, 85.
- (10) (a) Haag, R.; Wirz, J.; Wagner, P. *J. Helv. Chim. Acta* **1977**, *60*, 2595; (b) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.
- (11) Porter, G.; Tchir, M. *J. Chem. Soc. A* **1971**, 3772.
- (12) Scaiano, J. C.; Wintgens, V.; Netto-Ferreria, J. C. *Tetrahedron Lett.* **1992**, *33*, 5905.
- (13) Pfau, M.; Sarver, E. W.; Heindel, N. D. *Bull. Soc. chim. France* **1973**, 183.
- (14) Ullman, E. F.; Huffman, K. R.; Loy, M. *J. Am. Chem. Soc.* **1965**, *87*, 5417.
- (15) Kitaura, Y.; Matsuura, T. *Tetrahedron* **1971**, *27*, 1597.
- (16) Wagner, P. J.; Subrahmanyam, D.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 709.
- (17) Pfau, M.; Combrisson, S.; Rowe, J. E.; Heindel, N. D. *Tetrahedron* **1978**, *34*, 3459.
- (18) Netto-Ferreira, J. C.; Wintgens, V.; Scaiano, J. C. *Can. J. Chem.* **1994**, *72*, 1565.
- (19) Garcia-Garibay, M. A.; Gamarnik, A.; Bise, R.; Pang, L.; Jenks, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 10264
- (20) 10^{-2} M samples in deuterated solvents were irradiated in Pyrex NMR tubes sealed with Teflon-wrapped septa. Light sources were either a Pyrex filtered 450-W mercury arc or a Rayonet reactor with 300 nm lamps.
- (21) $^1\text{H-NMR}$ (C_6D_6): c-CB, δ 2.20 (s, OH), 4.74 (s, CHPh) 6.8-7.3 (14 H); t-CB δ 2.06 (s, OH), 4.83 (s); $^{13}\text{C-NMR}$ (C_6D_6) c-CB, δ 67.0, 87.3, 123.2, 125.0, 126.5, 127.2, 127.5, 127.6, 128.5, 128.6, 130.0, 130.1, 138.8, 141.0, 144.4, 148.9; t-CB, δ 66.1, 92.1, 123.3, 124.7, 125.9, 127.0, 127.5, 127.9, 128.0, 128.5, 129.0, 129.1, 139.5, 140.8, 144.8, 150.2.
- (22) An initial OD of 0.01 at 420 nm was attained from 0.01 M oBnBP, which would represent 10^{-6} M of a substance with an ϵ of 10^4 , as expected for xylylenes; the final OD, after the 0.01 M c-CB had reverted to oBnBP, was 0.1.
- (23) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1985**, *107*, 2099; Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1157.
- (24) Rickborn, B.; Moss, R. J.; White, R. O. *J. Org. Chem.* **1985**, *50*, 5132.
- (25) Wagner, P. J.; Sobczak, M.; Park, B.-S. *J. Am. Chem. Soc.*, in press.