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Supplementary Material Available: FAB mass spectra of **1** and **2**, NMR spectra (^1H, ^{13}C, and COSY) of **3**, and crystallographic information on **4** (10 pages). Ordering information is given on any current masthead page.

Mechanism for the Photocyclization of *o*-Alkyl Ketones to Cyclobutenols

Peter J. Wagner,* Duvvuri Subrahmanyam, and Bong-Ser Park

Chemistry Department, Michigan State University East Lansing, Michigan 48824

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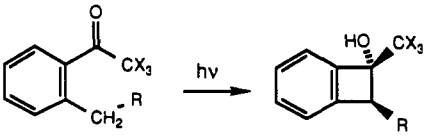
One of the unsolved puzzles of organic photochemistry has been the efficient formation of benzocyclobutenols from 2,6-dialkylphenyl ketones but not from simple *o*-alkylphenyl ketones.[1] It has been commonly assumed that *o*-alkyl ketones form only enols, which revert to ketone or can be trapped by various dienophiles,[1] although a couple of compounds were reported to provide benzocyclobutenols in low yield.[2,3] We report that a variety of *o*-alkyl ketones do in fact form cyclobutenols efficiently, quantitatively, and often stereoselectively and that the mechanism involves thermal electrocyclic closure of the initial dienol photoproducts.

Scheme I depicts several acetophenones that we have found to yield benzocyclobutenols as the major or only photoproducts upon irradiation of dilute ketone with wavelengths >290 nm.[4] In all cases a single diastereomer was produced.[5] NOE analysis of cyclobutenol **2a** indicated the *E* stereochemistry,[6] as did the concentration dependence of the OH signals in both IR and NMR spectra. (The *Z* isomers presumably would be internally hydrogen bonded.) Heating the alcohols at 80 °C or higher converts them quantitatively to the starting ketones, as has been observed for a wide variety of benzocyclobutenols.[3,7-9] This observation confirms Wilson's suggestion that dienol formation probably had been overlooked in the past because gas chromatographic analysis would thermally open the cyclobutenols.[3] It also confirms the *E* stereochemistry of **2a**, since the *Z* isomer would not open thermally at low temperatures.[7]

We have also studied several benzophenones. *o*-Methylbenzophenone forms cyclobutenol with no evidence for the other

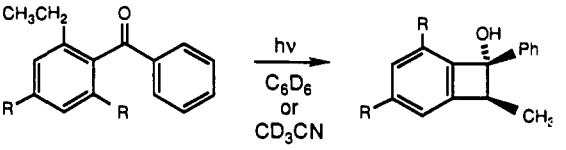
Scheme I



1a X = H, R = OCH_3
1b X = H, R = $OCH_2CH{=}CH_2$
1c X = H, R = $OCH_2CH_2CH{=}CH_2$
1d X = F, R = $CH_2CH_2CH{=}CH_2$
1e X = H, R = H

2

products reported by Wilson.[3] *o*-Ethylbenzophenone forms the (*E*)-cyclobutenol quantitatively with no trace of the *Z* isomer in a quantum yield estimated as 0.5.[10] The same single isomer was obtained in acetonitrile solvent. In CD_3OD used as received, no photoproduct was observed by NMR, but efficient benzylic H–D exchange[11,12] took place as evidenced by disappearance of the methylene quartet and collapse of the methyl triplet to a broad singlet with unresolved deuterium coupling. Adding methanol to solutions containing benzocyclobutenol caused no change, so this NMR solvent prevented formation of cyclobutenol. 2,4,6-Triethylbenzophenone also gives only the (*E*)-cyclobutenol in benzene, acetonitrile, and methanol-d_4.



R = H or Et

Early workers disagreed over whether dienol is formed from cyclobutenol[1] or cyclobutenol from dienol.[13] The former seems unlikely, since it is hard to imagine why a triplet biradical, known to be the first product in these reactions,[14,15] would directly cyclize only to the less stable cyclobutenol. Nonetheless, we sought firmer evidence. If cyclobutenols were formed before the dienols, irradiation of ketones in the presence of additives that react with the dienols would not quench cyclobutenol formation. However, benzene-d_6 solutions containing **1a**, *o*-ethylbenzophenone, or 2,4,6-trimethylbenzophenone and one crystal of *p*-toluenesulfonic acid (~0.005 M) produce *no* benzocyclobutenol after hours of irradiation. Valerophenone in benzene containing acid reacts completely after 15-min irradiation; so added acid does not destroy the ketones' intrinsic photoreactivity.[16] Addition of the same amount of acid to solutions containing only benzocyclobutenol causes very slow *E*/*Z* interconversion[17] with only trace reversion to ketone. (After several days the *Z*:*E* ratio stabilized at 7:3.) Since the cyclobutenols are stable to acid while the dienols are rapidly converted to ketone by acid, we conclude that *all* cyclobutenol formation must occur from the first-formed dienols.

It is well-known that both *E* and *Z* enols are formed from the triplet ketones.[14,15] The latter undergo a very rapid 1,5-sigmatropic H shift to regenerate ketone,[16] while the former live for as long

(1) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.
(2) Arnold, B. J.; Mellows, S. M.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 401.
(3) Wilson, R. M.; Hannemann, K. *J. Am. Chem. Soc.* **1987**, *109*, 4741.
(4) Acetonitrile solutions (450 mL) 0.02 M in ketone were irradiated with a Pyrex-filtered 450-W Hanovia mercury arc. Products were isolated by silica gel chromatography with 5% ethyl acetate in petroleum ether eluent. At 75% conversion, yields were quantitative. For **1d**, 3-h irradiation was sufficient; the other ketones required 20 h.
(5) For **2a**: mp 73 °C; ^1H NMR ($CDCl_3$) δ 1.62 (s, 3 H), 3.20 (br s, 1 H, D_2O exchanged), 3.56 (s, 3 H), 4.70 (s, 1 H), 7.25–7.38 (m, 4 H). For **2b**: IR (CCl_4) 3560, 3400, 3050, 1620, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (s, 3 H), 3.20 (br s, 1 H, OH), 4.18–4.33 (qdt, *J* = 13, 5.7, 1.6 Hz, 2 H), 4.84 (s, 1 H), 5.21–5.62 (m, 2 H), 5.93–6.08 (m, 1 H), 7.25–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 23.76, 71.16, 80.27, 85.05, 117.87, 121.82, 126.5, 129.66, 130.26, 136.51, 142.69, 151.96.
(6) For **2a**, irradiation at 4.70 ppm (methine proton) produced a much larger NOE enhancement of the methoxy proton resonance than of the methyl resonance.
(7) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 409, 415.
(8) (a) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. (b) Jensen, F. R.; Coleman, W. E.; Berlin, A. J. *Tetrahedron Lett.* **1962**, 15. (c) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. (d) Oppolzer, W.; Keller, K. *J. Am. Chem. Soc.* **1971**, *93*, 3836.
(9) Carre, M. C.; Viriot-Vilaume, M.-L.; Caubere, P. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1395, 2542.
(10) A 1-mL sample of 0.02 M ketone in benzene-d_6 in a deaerated NMR tube was irradiated at >290 nm for 20 m, at which point no starting ketone remained. Only one compound remained: ^1H NMR ($CDCl_3$) δ 0.90 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 3.77 (quar, *J* = 7 Hz, 1 H, $CHCH_3$), 7.2–7.4 (m, 4 H).
(11) Yang, N. C.; Rivas, C. *J. Am. Chem. Soc.* **1961**, *83*, 2213.
(12) Huffman, K. R.; Loy, M.; Ullman, E. F. *J. Am. Chem. Soc.* **1965**, *87*, 5417.
(13) Kitaura, Y.; Matsuura, T. *Tetrahedron* **1971**, *27*, 1597.
(14) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.
(15) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.
(16) These conditions obviously are not acidic enough to alter reactivity; butyrophenone is photoinert in phosphoric acid but not in ethanol containing 5% HCl: Rauh, R. D.; Leermakers, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 2246.
(17) The more stabe *Z* isomer is characterized by a 0.40 ppm higher chemical shift for the methyl group than in the *E* isomer. For a summary of previous such observations, see: Wagner, P. J.; Meador, M. A.; Park, B.-S. *J. Am. Chem. Soc.* **1990**, *112*, 5199.

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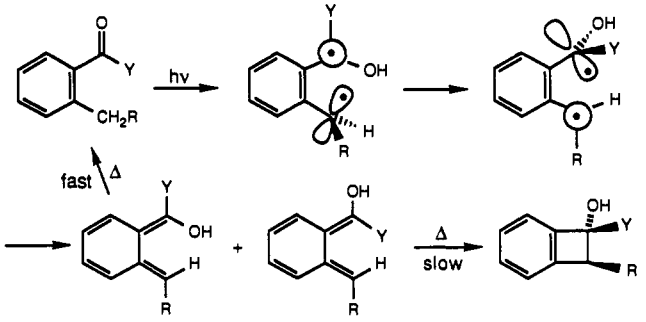
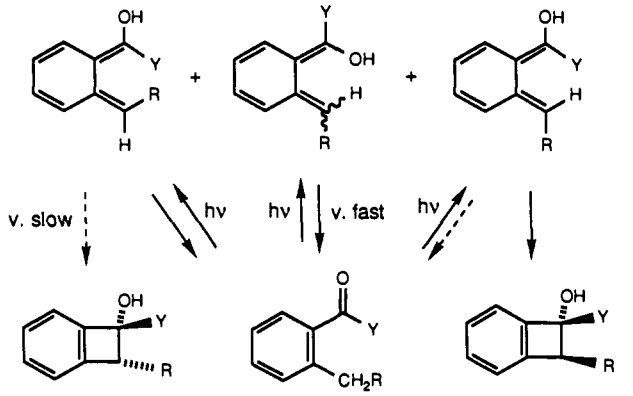
as a few seconds unless trapped with dienophiles or acid.[14,15,18] Since only the *E* enols are trapped by dienophiles,[1] we assume that they also are the ones that rearrange to cyclobutenol.

Matsuura studied the cyclization of 2,4,6-triethylacetophenone and -benzophenone.[13] The former gave only the *E* product, as we have observed for all ketones studied. The latter gave different amounts of *E* and *Z* products depending on solvent, in contrast to our findings. Matsuura suggested that cyclobutenols are formed by stereospecific conrotatory cyclization of the dienols, with product distribution reflecting the distribution of the possible enols. Our results appear to corroborate this mechanistic picture for both *o*-alkyl and 2,6-dialkyl ketones, except that only one of the two possible *E* enol products is formed. Since Matsuura analyzed the cyclobutenols *after* workup, we strongly suspect that some acid-catalyzed $E \rightarrow Z$ isomerization took place. We presume that the reaction quenching that we observed in unpurified methanol is caused by typical acid impurities[19] trapping dienols before they can rearrange.

Why is only one *E* enol apparently formed? The overall reaction is known to occur by triplet-state γ-hydrogen abstraction[20] that yields a triplet 1,4-biradical, which coincidentally happens to be the triplet of the enol product.[14,15] We invoke the common assumption that the biradical triplet enol resembles a triplet diene[21] in having one conjugated benzylic radical site and one twisted 90° out of conjugation. The biradicals are quite long-lived[14,15] and apparently can undergo facile coupled rotation about both ring–benzylic carbon bonds; otherwise *Z* and *E* enols could not both be formed.[14,15] The *E* enol that thermally produces the observed cyclobutenols clearly is the less congested *E* enol. We conclude that the biradical assumes a conformation with the α-methyl site conjugated and the hydroxy site twisted before intersystem crossing to ground-state enol occurs. In the benzophenone-derived systems, the second benzene ring can stabilize the hydroxy radical site, as has been observed in other biradicals.[22] In the acetophenone-derived systems, conjugation of the hydroxy radical with the oxygen lone pair may be sufficient to fix the twisting preference. Whatever the exact cause, the observed stereoselectivity of cyclization indicates that the methyl radical site has time to assume its more stable geometry before biradical decay.



An alternative possibility is that the other *E* enol also is formed but closes to cyclobutenol much more slowly, so that it is completely trapped by trace acid. It is well-known that there is a much larger barrier to the interconversion of cyclobutenes and dienes that have terminal alkyl or alkoxy groups pointed in.[23] Therefore the possibility that the observed diastereoselectivity of cyclobutenol formation represents vastly different rates of closure of isomeric *E* enols cannot be dismissed. We are conducting additional experiments to define the generality and mechanistic causes of the diastereoselectivity already observed.



This picture of dienol behavior is in accord with the general belief that steric congestion favors cyclobutenol formation.[1,13] The rate at which the first-formed dienol closes to cyclobutenol presumably is greatly increased by additional buttressing *o*-alkyl groups, since the two benzylic centers cannot both lie coplanar with the benzene ring. The fact that such cyclobutenols are much more stable thermally than those from monoalkyl ketones also demonstrates the effect of steric congestion of dienol energy. The difficulty in detecting transient intermediates in these congested systems[15] also may be due to unusually short-lived enols. The fact that 2,4,6-triethylbenzophenone cyclizes in the same methanol that totally quenches the cyclization of *o*-ethylbenzophenone is further evidence for sterically enhanced reactions of the intermediate dienols.

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(18) Porter, G.; Tchir, M. F. *J. Chem. Soc. A* **1973**, 3772. Findley, D. M.; Tchir, M. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1096.
(19) Bartlett, P. D.; Baumstark, A. L.; Landis, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 5557.
(20) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239.
(21) (a) Hoffman, R. *Tetrahedron* **1966**, *22*, 521. (b) Saltiel, J.; Townsend, D. E.; Sykes, A. *J. Am. Chem. Soc.* **1973**, *95*, 5968. (c) Caldwell, R. A.; Singh, M. *J. Am. Chem. Soc.* **1982**, *104*, 6121–2.
(22) Wagner, P. J.; Meador, M. A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7988. Wagner, P. J.; Giri, B. P.; Pabon, R.; Singh, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 8104.
(23) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

Novel Transition-Metal–Main-Group Hybrid Cages: Synthesis and Characterization of $[MoAs_2Se_{10}]^{2-}$ and $[W_2As_2Se_{13}]^{2-}$

Samuel C. O'Neal, William T. Pennington, and Joseph W. Kolis*

Department of Chemistry, Clemson University Clemson, South Carolina 29634

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Group 16 elements have a very rich coordination chemistry with transition metals.[1] They form an enormous number of metal complexes of both theoretical and practical interest. Though sulfur has been the most heavily investigated member of the group,[2] we[3] and others[4] have recently extended this work to selenium and

(1) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (c) Fenske, D.; Ohmer, J.; Hachgenie, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277.
(2) (a) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613. (b) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. (c) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840. (d) Harmer, M. E.; Halbert, T. R.; Pan, W.-H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986**, *5*, 341. (e) Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349. (f) Müller, A. *Polyhedron* **1986**, *5*, 323.
(3) (a) Flomer, W. A.; O'Neal, S. C.; Pennington, W. T.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1702. (b) Flomer; W. F.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 3682.

0002-7863/91/1513-710$02.50/0