Crystal Lattice Control of Unimolecular Photorearrangements. Medium-Dependent Photochemistry of Cyclohexenones[1]

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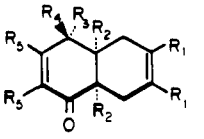
Abstract: The solid-state and solution photochemistry of seven compounds possessing the basic 1-oxy-*cis*-4a,5,8,8a-tetrahydronaphthoquin-4-ol structure has been investigated. In solution all seven substrates afford high yields of the corresponding [2 + 2] cage photoproducts when irradiated. On the other hand, for five of the substrates, photolysis in the solid state yields only traces of the cage compounds; instead, photoproducts are formed which are the result of intramolecular allylic hydrogen atom abstraction by the enone β-carbon atom followed by biradical collapse. The nature of the hydrogen-abstraction process (five-membered or six-membered transition state) was found to depend on the type of substituents at C(4) and on the relative configuration at this center. With the aid of X-ray crystallography, it was shown that the C(4) substituents control the adoption of one of two possible conformations (A or B) in the solid state through a preference for the bulkier substituent at this center to lie in the pseudo-equatorial position. The conformation adopted in turn determines the photochemistry, conformer A giving rise to five-membered transition-state hydrogen abstraction and conformer B leading to the six-membered transition-state process. The crystallographic distance and geometric parameters for these hydrogen-abstraction reactions are tabulated, discussed, and compared with previous results from our laboratory. Irradiation of the remaining two substrates in the solid state leads to somewhat different results. One is essentially unreactive owing, we believe, to an unusually long distance (2.92 Å) between the enone β-carbon atom and the intended allylic hydrogen atom. The second gives predominantly the cage-type photoproduct normally formed only in solution, perhaps as the result of crystal melting during photolysis. Finally, possible reasons for the solution/solid-state reactivity differences are discussed. It is concluded that in solution, conformational equilibrium is established during the lifetime of the excited state and that one of the minor conformers present (conformer C), in which the two carbon–carbon double bonds are adjacent and parallel, is responsible for rapid, intramolecular [2 + 2] photocycloaddition.

Many organic photorearrangements are known which occur from nonminimum energy reactant conformations. This situation arises in mobile phases when a minor conformer has available to it a particularly facile reaction pathway by virtue of certain favorable stereoelectronic features which are unique to that conformation. If the relative rate of reaction of the minor conformer is sufficiently great, no photoproducts will be observed from the more abundant, lower energy conformers which are present even though these conformers may be capable of alternative, slower photorearrangements.[2]

The situation is different in the solid state because, with very few exceptions, organic molecules crystallize exclusively in their lowest energy conformations. In this medium, irradiation cannot lead to the solution photoproduct, and one has the opportunity of unmasking the slow photoprocesses characteristic of the most stable conformer. In order to fully realize medium-dependent photorearrangement differences of this type, two further conditions must be met. (1) The slow, solid-state photorearrangement must be compatible with the lattice restraints present in the molecular crystal, i.e., be "topochemically allowed,"[3] and (2) the crystal-packing arrangement must be such that bimolecular processes between lattice neighbors do not predominate.[4]

This paper describes our investigation into the solution and solid-state photochemistry of the cyclohexenone system possessing the general structure shown below. Altogether, seven substrates were studied. In all seven cases, the crystal structure of the reactant was determined by X-ray diffraction methods, and the



data derived therefrom were used to more fully elucidate the solid-state photorearrangement mechanisms. The results correspond to the situation described above in which the solid-state medium limits reaction to one stable conformational isomer of a given substrate in contrast to the liquid phase where a minor, higher energy conformational isomer is the reacting species.

Results

Substrate Preparation. Table I shows the seven substrates studied. With the exception of compound **2c**, they were prepared by sodium borohydride reduction of the corresponding, readily available cyclohexenediones; substrate **2c** was synthesized by treatment of ene-dione **1** with methyllithium. Reduction of ene-diones bearing hydrogen atoms at the ring junctions (compounds **7** and **10**) gave nearly exclusively the 4aα,8aα-4β-ols, whereas sodium borohydride treatment of ene-diones **1** and **4** bearing methyl groups at ring junction carbon atoms 4a and 8a afforded both C(4) epimers with the relative 4aα, 8aα-4α-ol stereochemistry predominating. These stereochemical results are in accord with Baldwin's "approach vector analysis" concept for α,β-unsaturated ketone reduction.[5]

Solution Photolyses. Table I also shows the major products obtained when each of the seven cyclohexenone substrates was photolyzed in the liquid phase. These irradiations were generally carried out in benzene using a uranium glass filter (transmitting $\lambda > 330$ nm). In the case of **2a**, **2c**, **8**, and **11** it was demonstrated that identical results could be obtained using benzophenone as a photosensitizer. In five of the seven solution irradiations, a single photoproduct was obtained which could be isolated in essentially quantitative yield. However, for substrates **5a** and **5b**, small amounts of a second photoproduct could be isolated. In the case

(1) For preliminary communications on portions of this work, see: (a) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J.; Walsh, L. *J. Am. Chem. Soc.* **1980**, *102*, 1158–1160, 1160–1161, (b) Jiang, Z. Q.; Scheffer, J. R.; Secco, A. S.; Trotter, J. *Tetrahedron Lett.* **1981**, 891–894.

(2) For a general discussion of ground-state conformational control of photochemical behavior, see: Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6090–6099.

(3) (a) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1996–2000, (b) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386–393.

(4) For examples of competing bimolecular and unimolecular photoreactions in the solid state, see: Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163–2173. See also: Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283–290.

(5) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 738–741.

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Table I. Cyclohexenone Substrates Studied and Their Solution Photoproducts

Precursor Ene-dione	Cyclohexenone Substrate (mp)		Major Solution Photoproduct
	2o	(136.5–137.5°)	3o
1	2b	(170.5–171°)	3b
	2c	(156–157°)	3c
	5o	(115–116°)	6o[a]
4	5b	(118.5–119°)	6b[b]
7	8	(138–138.5°)	9
10	11	(109.5–110.5°)	12

[a] Photoproduct **18** also isolated in 6% yield. [b] Photoproduct **19** also isolated in 24% yield.

of **5a**, 5% of keto-alcohol **18** (cf. Table II) was formed along with major photoproduct **6a**, and for naphthoquinol **5b**, 24% of hemiacetal **19** could be isolated in addition to major photoproduct **6b**. Compounds **18** and **19** subsequently proved to be identical with the major products obtained when substrates **5a** and **5b** were photolyzed in the solid state (vide infra).

It was a relatively simple matter to demonstrate that the predominant product in each solution photolysis was the result of intramolecular [2 + 2] photocycloaddition. In the case of the 4α-ol systems **2b**, **2c**, and **5b**, this leads to a cage ketol which can spontaneously undergo hemiacetal formation as exemplified for **2b** in Scheme I.[6] Of course, the hydroxyl group stereochemistry of the cage photoproducts formed from the 4β-ol cyclohex-2-en-1-ones does not permit such a process, and they are isolated in the ketol form.

The cage photoproducts were characterized on the basis of their spectroscopic properties (see Experimental Section) plus, in some cases, by conversion to derivatives having a plane of symmetry. For example, pyridinium chlorochromate oxidation of **3a** and **6a** afforded the diketones **13a** and **13b**, respectively (Scheme I), whose planes of symmetry were indicated by proton and ^{13}C NMR spectroscopy. The hemiacetals **3b** and **6b** could also be oxidized to **13a** and **13b** with pyridinium chlorochromate, although the yields were considerably lower than for **3a** and **6a**.

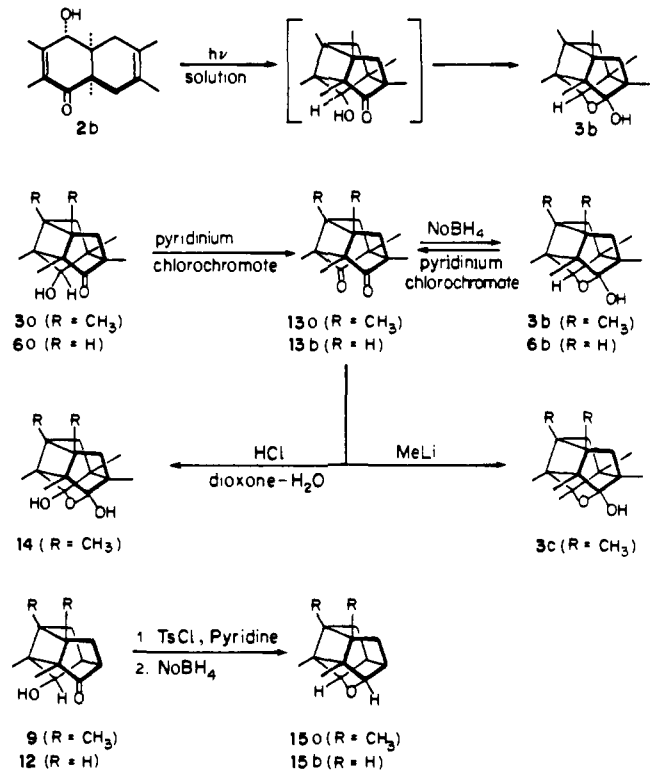
Further confirmation of the structural assignments was provided by the reactions of diketones **13a** and **13b**. Sodium borohydride

(6) In contrast, the ketol i does not undergo hemiacetal formation: Sasaki,

i

T.; Eguchi, S.; Kiriyama, T.; Hiroaki, O. *Tetrahedron* **1974**, *30*, 2707–2712. This can be explained as being due to an increase in the distance between the reacting centers of i which accompanies the introduction of the one-carbon-atom bridge.

Scheme I



reduction led to **3b** and **6b**, respectively, and treatment of **13a** with methyllithium gave material identical in every respect with photoproduct **3c**. The yields were >95% in each case. Oxidation of keto-alcohols **9** and **12** led in each case to material which appeared to be a mixture of the desired diketone and its bridged hydrate. These mixtures proved to be difficult to work with, and none of these diketones or their hydrates was fully characterized. It was later accidentally discovered that the hydrate **14** (Scheme I) of diketone **13a** was stable and could be formed in very high yield under mild Clemmenson reduction conditions (zinc amalgam, aqueous HCl, 25 °C).[7] Apparently, the increased methyl substitution next to the carbonyl groups in **13a** slows equilibration between the diketone and the hydrate sufficiently to allow each to be isolated.[8]

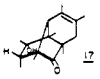
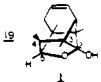
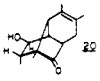
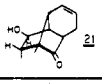
Solution photoproducts **9** and **12** were converted to mirror-symmetric derivatives of a different sort. Tosylation of **9** and **12** followed by sodium borohydride reduction afforded the interesting cyclic ethers **15a** and **15b**, respectively (Scheme I), whose proton and ^{13}C NMR spectra were once again indicative of a plane of symmetry. These ethers are highly crystalline, volatile solids with pronounced pine oil odors.

Solid-State Photolyses. Several different methods of solid-state photochemistry were investigated. For preparative runs, a useful technique was to coat, by slow evaporation, the inside of a photolysis vessel with a thin, polycrystalline film of the sample to be photolyzed and to irradiate from the inside using the standard immersion well configuration. This allowed an inert atmosphere to be maintained over the sample, and cooling could be carried out by immersing the entire apparatus in an appropriate cooling bath. A second method consisted of crushing the sample crystals between glass plates and encasing the resulting "sandwiches" in polyethylene bags using a heat sealing device. The sample bags could then be irradiated using an external light source and the temperature once again regulated by immersion in a cooling bath. Low-conversion analytical runs were carried out by irradiating

(7) Herbert, D. J.; Scheffer, J. R.; Secco, A. S.; Trotter, J. *Tetrahedron Lett.* **1981**, 2941–2944.

(8) For similar diketone hydrate formation, see ref 6 as well as: (a) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3062–3075, (b) Singh, P. *J. Org. Chem.* **1979**, *44*, 843–846.

Table II. Reactants, Products, and Hydrogen Abstraction Distances and Angles in Solid-State Photoreactions

Reactant	solid state conformation[a]	solid state photoproduct	hydrogen abstraction distance (Å)[b]	σ(Å)[c]	τ(°)[d]	Δ(°)[e]	Θ(°)[f]
2o	A	 16	2.72 (2)	3.30	53.2	78.5	107
2b	B	no reaction	2.92 (2)	3.23	49.5	75.2	108
2c	A	 17	2.81 (2)	3.35	50.0	78.3	104
5o	A	 g 18	2.78 (2)	3.30	51.9	77.5	105
5b	B	 19	2.85 (4)	3.17	50.6	71.6	107
8	A	 20	2.84 (5)	3.42	53.5	79	122
11	A	 21	2.84 (4)	3.42	54.1	79.7	101

[a] Refer to Figure 1. [b] Distance between enone β carbon, C(3), and abstracted hydrogen atom. [c] Distance between carbon atoms which become bonded to one another in photoproduct. [d] Degree by which abstracted hydrogen atom is out of coplanarity with mean plane of C(2)–C(3) double bond. Refer to Figure 3. [e] Angle formed between C(2), C(3), and the abstracted hydrogen atom. [f] Angle between the abstracting carbon, the abstracted hydrogen atom, and the carbon to which it is attached. [g] Minor product; major product in this case is 6a (cf. Table 1).

single crystals sealed in capillary tubes. The light source was the focused beam (approximately 5 mm in diameter) from a 100-W mercury lamp. The sample capillary tube plus a second capillary tube containing the thermocouple leads were placed in a windowed, Teflon cell and cooled by passing vaporized liquid nitrogen through the cell. The temperature could be maintained at the desired value by adjusting the liquid nitrogen boil-off rate.

The details of each photolysis in the solid state are given in the Experimental Section. In general, irradiations were carried out at temperatures below 0 °C in order to minimize sample melting. At temperatures below −60 °C, however, most reactions were extremely slow. The photolyses were generally faster when a Pyrex filter (transmitting $\lambda > 290$ nm) rather than a uranium glass filter (transmitting $\lambda > 330$ nm) was used. Each photolysis afforded a new product with the structure shown in Table II. These products were generally accompanied by varying small amounts of the corresponding solution photoproducts. An exception to this trend was found for substrate **5a**, however. In this case irradiation in the solid state, even at temperatures as low as −70 °C, afforded solution photoproduct **6a** as the major component accompanied by lesser amounts of ketol **18**. At present we can offer no explanation for this behavior except to note that in general the solid-state to solution product ratios were found to be greater for solid-state photolyses carried out at lower temperatures and smaller conversion percentages indicating that sample melting during irradiation may be the factor responsible for the solution-type photoproducts observed. Photochemical behavior in melts is known to parallel that observed in solution in one case where such a comparison has been made.[9]

The solid-state photoproduct structures were proved as follows. Compounds **16** and **20** were oxidized to the corresponding known[10] diketones **22a** and **22b**, respectively (Scheme II), and keto-alcohol **17** was prepared by treatment of **22a** with methyllithium. The structures of photoproducts **18** and **21** were assigned on the basis of the similarity of their spectra to compounds **16** and **20**, and

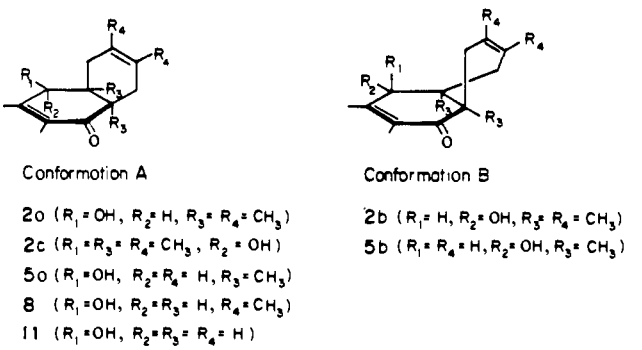
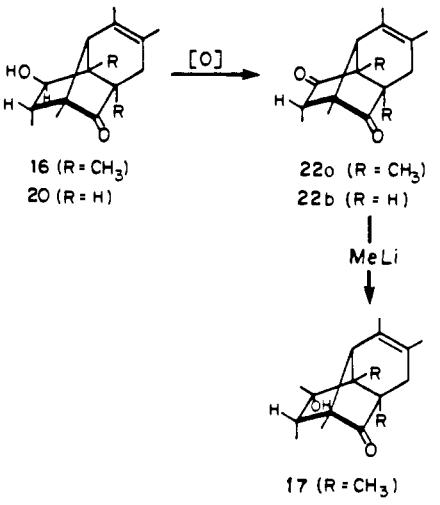


Figure 1. Solid-state conformations of substrates studied.

Scheme II



photoisomer **19** was identified by X-ray crystallography.[11]

Discussion

Two very fundamental questions are raised by the results just described. (1) Why are the products obtained by irradiation in the solid state different from those produced in solution? (2) What causes the variation in the solid-state photoproduct structures and why is substrate **2b** photochemically inert? In order to help answer these questions, the X-ray crystal structures of the starting cyclohexenones were obtained. The crystallography was carried out by Trotter, Greenhough, and Secco who have published the details separately.[12] The X-ray data used in this paper are taken from their work.

An important piece of information soon became apparent as the X-ray data were being accumulated: *The conformations of the starting cyclohex-2-en-1-ones in the solid state are determined by the nature of the substituents at C(4) and by the relative configuration at this center.* The data showed that the compounds studied (cf. Table II) crystallize in one of two conformations, A or B, as shown in Figure 1. Substrates **2b** and **5b** are found in conformation B whereas all the others adopt conformation A in the solid state. Both conformations may be described as consisting of a half-chair cyclohexene ring cis-fused to a half-chair-like cyclohexenone moiety. A half-chair to half-chair ring flip interconverts A and B which are rendered nonequivalent by virtue of the fact that C(1) and C(4) are unequally substituted. Stereodiagrams of compound **2a** (conformation A) and substrate **5b** (conformation B) are shown in Figure 2.

(9) Slivinskas, J. A.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 3043–3056.
(10) Scheffer, J. R.; Bhandari, K. S.; Gayler, R. E.; Wostradowski, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 2178–2189.
(11) Greenhough, T. J.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *36*, 1835–1839.
(12) **2a** and **2b**: Greenhough, T. J.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *36*, 1831–1835, **2c**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, in press, **5a**: Greenhough, T. J.; Trotter, J. *Ibid.* **1980**, *36*, 2843–2846, **5b**: Greenhough, T. J.; Trotter, J. *Ibid.* **1980**, *36*, 1835–1839, **8**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, *38*, 1229–1232, **11**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, *38*, 1233–1237.

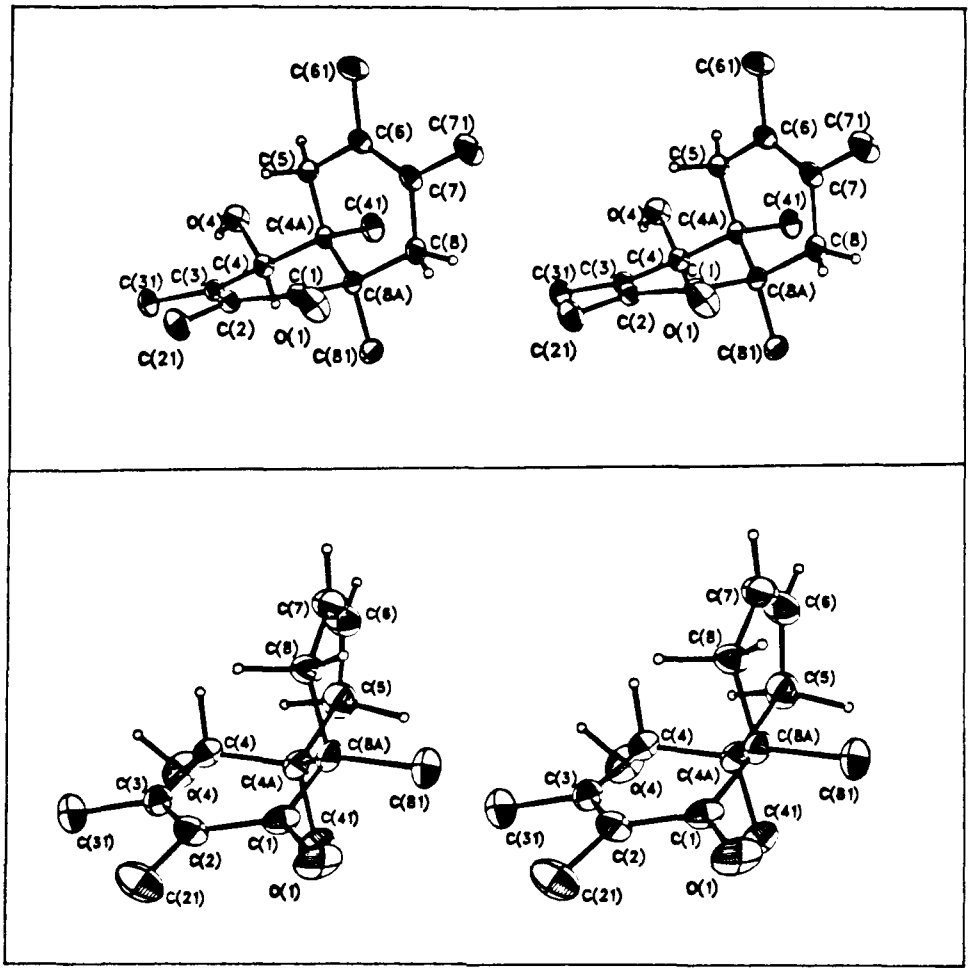


Figure 2. Stereodiagram of conformation A (compound **2a**, top) and conformation B (compound **5b**, bottom). The methyl hydrogen atoms are omitted for clarity.

With these results in hand, it is readily apparent that the factor which determines whether conformation A or B is adopted in the solid state is the preference for the bulkier substituent at C(4) to lie in the pseudo-equatorial position. In every case but one, the C(4) substituents are hydrogen and hydroxyl, the latter, of course, being the larger and therefore occupying the pseudo-equatorial position. In the case of substrate **2c**, the C(4) substituents are methyl and hydroxyl, and now the hydroxyl group is no longer the larger of the two with the result that compounds **2b** and **2c** adopt opposite conformations despite the fact that the hydroxyl group is α in both instances.[13]

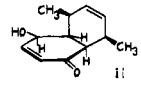
One additional point should be mentioned at this juncture, and that is that in each case the bulkier C(4) substituent adopts the pseudo-equatorial position in spite of an unfavorable $A^{(1,2)}$ strain interaction between itself and the adjacent C(3) methyl group.[14] This presumably reflects the fact that the $A^{(1,2)}$ strain interaction is less unfavorable than the pseudo-1,3-diaxial interaction which would result if the bulky group were to adopt the pseudo-axial position at C(4).

The results thus indicate that internal molecular energetics dictate the preferred solid-state conformations as opposed to intermolecular crystal lattice packing forces such as, for example, hydrogen bonding. Each of the substrates studied does, in fact, exhibit intermolecular hydrogen bonding in the solid state.[12] Two types of hydrogen bonds are observed. The first, found in naphthoquinols **2a**, **2b**, **2c**, **5a**, and **5b**, occurs between the hydroxyl proton and carbonyl oxygen of adjacent molecules. The second type, which is unique to substrate **11**, takes place between the hydroxyl proton of one molecule and the hydroxyl oxygen atom of its neighbor. In one instance (naphthoquinol **8**), both types of hydrogen bonding are present in the solid.

Mechanisms. We are now in a position to interpret the solid-state photochemical results. *A key feature of this interpretation is the recognition that conformers A and B react differently.* The suggested mechanisms are outlined in Scheme III using substrate **2c** to illustrate type A reactivity and compound **5b** to exemplify type B reactivity.

Type A photoreactivity involves initial transfer of the proximal allylic hydrogen atom on C(5) to the top lobe of the p orbital at C(3), the β carbon of the α,β-unsaturated ketone chromophore. This establishes the stereochemistry at this center in the final product **17**. The hydrogen transfer forms biradical **23** which can collapse directly to **17**. The photoreactivity of B also involves hydrogen atom abstraction by the β carbon of the enone moiety, but in this case it is the C(8) allylic hydrogen atom which is transferred. This produces biradical **24** which undergoes closure followed by internal hemiacetal formation to give final product **19**. It is noteworthy that the type A and type B hydrogen abstractions proceed through cyclic transition states having different ring sizes, five membered for A and six membered for B. While by no means common, there are a number of literature examples suggesting photochemical hydrogen abstraction by olefinic carbon atoms through six-membered transition states.[15] However, the

(13) An additional interesting molecule from the conformational analysis point of view is compound ii which adopts conformation A in the solid state

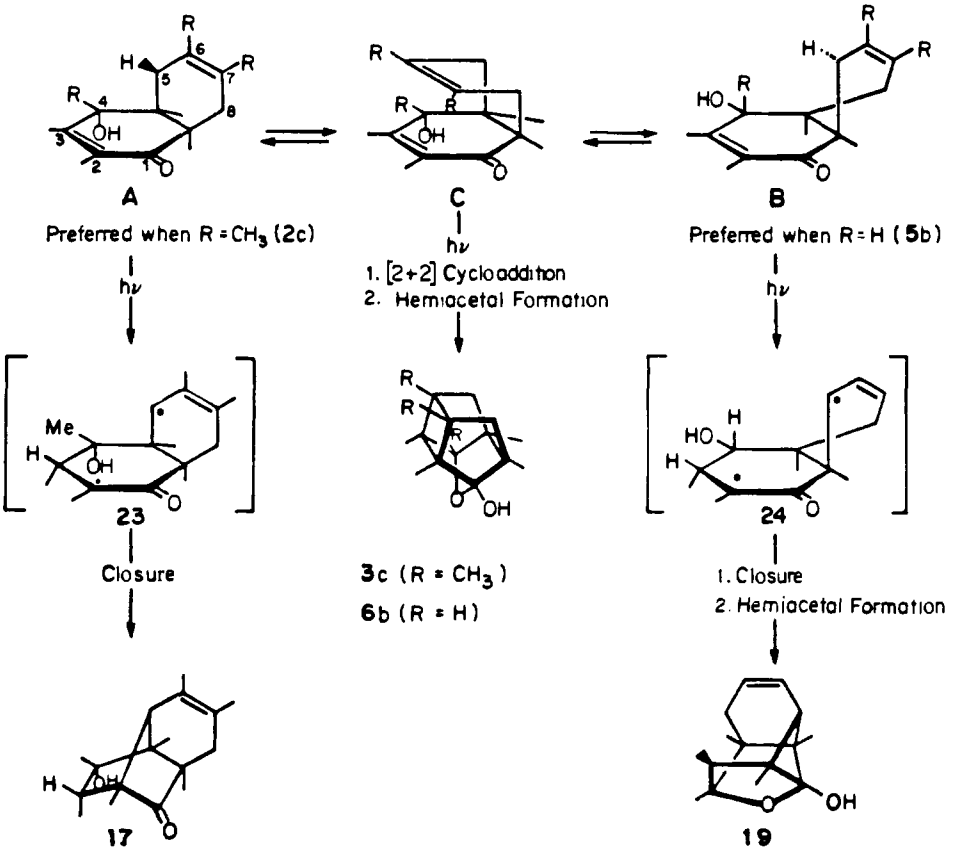


ii

owing to "offsetting" C(5) pseudo-axial and C(8) pseudo-equatorial methyl groups while retaining a pseudo-equatorial hydroxyl substituent at C(4): Greenhough, T. J.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *36*, 2091–2094.

(14) Johnson, F. *Chem. Rev.* **1968**, *68*, 375–413.

Scheme III



corresponding five-membered transition-state process is, to the best of our knowledge, unprecedented.

Crystal Structure–Reactivity Correlations. Are the suggested hydrogen atom transfers and subsequent carbon–carbon bond formations, in fact, geometrically feasible? An indication of this can be obtained by consideration of the internuclear abstraction and bonding distances and angles as determined by X-ray crystallography. In Table II we list five relevant parameters for each of the seven substrates. These are (1) the distance (Å) between the abstracting carbon and abstracted hydrogen atoms; (2) α, the distance between the carbon atoms which ultimately become bonded to one another in the final products; (3) τ, the angle subtended by the C(3) to H_{abs} vector and its projection on the mean plane of the C(2)–C(3) double bond (see Figure 3); (4) Δ, the C(2)–C(3)–H_{abs} angle; and (5) θ, the angle between the abstracting carbon, the abstracted hydrogen atom, and the carbon to which the latter is attached.

Several aspects of these structural data deserve comment. First, the distance over which hydrogen abstraction occurs is invariably less than 2.90 Å, the sum of the van der Waals radii of the atoms involved (carbon, 1.70 Å; hydrogen, 1.20 Å).[16] It is most interesting to note that the one unreactive substrate, **2b**, has a hydrogen abstraction distance of 2.92 Å, just outside this sum. At present we can offer no other explanation for the lack of reactivity of **2b**, although additional examples are clearly desirable. The crystal structure of **2b** exhibits no unusual features relative to the other members of the series, and the values of α, τ, Δ, and θ for **2b** do not differ significantly from the other values listed. The discovery that intramolecular photochemical hydrogen abstraction occurs when the abstraction distances in the ground state are less than or equal to the sum of the van der Waals radii of the atoms involved has been shown to be valid in other systems and applies equally well when carbonyl oxygen is the abstracting atom (van der Waals radii sum, 2.72 Å).[4] Including this work, we have demonstrated the validity of this correlation with 18 separate examples.

Does this correlation have any relevance for the situation in the *excited state*? We believe that is does because for the systems with which we have been concerned, it seems likely that the

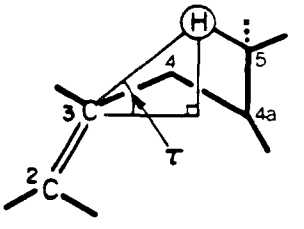


Figure 3. Definition of angle τ illustrated for conformation A.

(15) (a) Scharf, H. D. *Tetrahedron* **1967**, *23*, 3057–3065, (b) Scharf, H. D. *Fortschr. Chem. Forsch.* **1969**, *11*, 216–244, (c) Bellus, D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1969**, *52*, 971–1009, (d) Fund, T. M.; Williams, V. Z.; Osawa, E.; von R. Schleyer, P. *Tetrahedron Lett.* **1970**, 3877–3880, (e) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129–6140, (f) Wolff, S.; Schreiber, W. L.; Smith, A. B., III; Agosta, W. C. *Ibid.* **1972**, *94*, 7797–7806, (g) Scully, F.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1973**, 529–530, (h) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961–1968, (i) Smith, A. B., III; Agosta, W. C. *Ibid.* **1974**, *96*, 3289–3295, (j) Gloor, J.; Schaffner, K. *Helv. Chim. Acta* **1974**, *57*, 1815–1845, (k) Pratt, A. C. *J. Chem. Soc., Chem. Commun.* **1974**, 183–184, (l) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850–1853, (m) Inone, Y.; Moritsugu, K.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 569–574, (n) Hornback, J. M. *Tetrahedron Lett.* **1976**, 3389–3392, (o) Herz, W.; Iyer, V. S.; Nair, M.; Saltiel, J. *J. Am. Chem. Soc.* **1977**, *99*, 2704–2713, (p) Hasegawa, T.; Watabe, M.; Aoyama, H.; Omote, Y. *Tetrahedron* **1977**, *33*, 485–488, (q) Ayral-Kaloustian, S.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 5984–5992, (r) Nobs, F.; Burger, U.; Schaffner, K. *Helv. Chim. Acta* **1977**, *60*, 1607–1628, (s) Hornback, J. M.; Proehl, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 7367–7373, (t) Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *Ibid.* **1979**, *101*, 5743–5759, (u) Padwa, A.; Blacklock, T. J. *Ibid.* **1979**, *101*, 3390–3392, (v) Maruyama, K.; Ishitoku, T.; Kubo, Y. *Ibid.* **1979**, *101*, 3670–3671, (w) Padwa, A.; Chou, C. S. *Ibid.* **1980**, *102*, 3619–3620, (x) Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *Ibid.* **1981**, *103*, 3057–3068, (y) The corresponding seven-membered transition-state process has also been demonstrated.[15q] In addition, see: Hiyama, T.; Fugita, S.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3222.

(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451. See also: Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261–270.

abstraction distances will remain very similar in the ground and excited states.[4] With reference to the cyclohexenone systems studied in the present work, for example, the twisting about the carbon–carbon double bond which accompanies photoexcitation[17] should not greatly affect the β-carbon to allylic hydrogen-abstraction distances. In fact, such twisting, if present in the reactive excited state,[17] may actually facilitate abstraction by tilting the abstracting β-carbon p orbital more directly toward the hydrogen atom being abstracted. This would amount to increasing τ from its ground-state angle of approximately 50° (cf. Table II) more toward the ideal of 90° in the excited state. Twisting in the other direction would, of course, have the opposite effect. We note also that twisting about the C(2)–C(3) double bond in the excited state should not markedly affect the angles Δ or θ. The former, at approximately 75°, is quite close to the optimum value of 90° for hydrogen abstraction by a 2p atomic orbital on carbon.[4] With regard to the angle θ, a linear geometry (θ = 180°) appears to be favored in bimolecular hydrogen atom abstractions.[18] The present results (θ = 104 to 122°) provide quantitative evidence for what has been qualitatively obvious for some time, namely, that large deviations from the preferred linear approach may be tolerated in intramolecular photochemical hydrogen abstractions.

Finally we turn to a brief discussion of the parameter α, the ground-state distance between the carbon atoms which become bonded to one another in the final product. Strikingly, the values for α are once again very nearly equal to or less than the sum of the van der Waals radii for two carbon atoms, 3.40 Å. These values, coupled with the reasonable assumption that the biradical intermediates **23** and **24** (Scheme III) have the same basic conformations as their immediate precursors A and B, are clearly indicative, in a qualitative sense, of the "topochemical allowedness" of the final carbon–carbon bond formations. Thus, as we have seen in other multistep solid-state photoreactions,[4,19] all steps must be compatible with the restraints present in the crystal lattice and must proceed without a major change in conformation along the reaction coordinate.

Solution vs. Solid-State Reactivity. We turn now to the interesting question of why intramolecular [2 + 2] photocycloaddition occurs only in solution whereas internal hydrogen abstraction is the major photoprocess observed in the solid state. The answer to this question is twofold. First, the X-ray crystal structure data clearly indicate that [2 + 2] photocycloaddition should be topochemically forbidden in the solid state. The C(2)–C(3) and C(6)–C(7) double bonds are not only nonparallel but are too far apart to permit cycloaddition. This is true of both conformations A and B (Scheme III) which have nearly identical relative double-bond orientations. Specifically, the angle between the C(2)–C(3) and C(6)–C(7) vectors was found to be very close to 50° in each case, and the double-bond separations were all >4.4 Å. Thus cycloaddition in the solid state would have to be accompanied by a substantial conformational change and is not permitted.

It is a well-established concept that intermolecular [2 + 2] photocycloaddition in the solid state requires a parallel double-bond orientation with a separation of approximately 4.1 Å.[4,20] Surprisingly, little is known about the geometric and distance requirements for the intramolecular process, however.[21] We have very briefly investigated this by obtaining the X-ray crystal structure of the 1,3-cyclohexadiene–*p*-benzoquinone Diels–Alder adduct **25**.[22] Some time ago, Cookson et al.[8a] showed that **25** undergoes very efficient intramolecular [2 + 2] photocycloaddition in the solid state to afford diketone **26**. The X-ray crystal

25 **26**

structure data for **25** shows that its carbon–carbon double bonds are, in fact, parallel. The ene-dione ring is very nearly planar, and the double-bond center-to-center distance is 3.53 Å. We conclude that the inter- and intramolecular reactions have similar orientation and separation requirements.

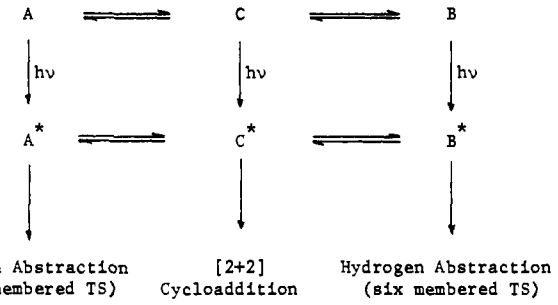
Thus with [2 + 2] photocycloaddition forbidden for both conformers A and B in the solid state, intramolecular hydrogen abstraction is observed instead. These processes are, as we have seen in the previous section, compatible with the restraints imposed by the solid-state environment. They are, of course, "topochemically allowed" in solution as well, yet only [2 + 2] photocycloaddition is observed in this medium. Why? The answer must be that cycloaddition is occurring from a different conformation in solution. Furthermore, it must be a minor conformational isomer since conformers A and B will be preferred in solution as well as in the solid state. The obvious candidate for the reactive conformer in solution is C (Scheme III). This conformation would be expected to be of higher energy than conformers A and B owing to eclipsing about the ring-junction carbon atoms.

Lewis, Johnson, and Johnson[2] have pointed out that two limiting conditions are possible when conformational isomers can react photochemically in solution to yield different products. The activation energies for conformational isomerization in the excited state can be either less than (case I) or greater than (case II) the activation energies of the primary photochemical steps. In case II, the ratio of the final products will depend on the excited-state conformer population (A*, B*, and C*) and hence (since excitation is much faster than molecular motion) also on the ground-state conformer distribution and extinction coefficients.[2] Since it is certain that C is the minor conformer in solution and is unlikely to have an extinction coefficient greatly different from A and B, it appears that case I is followed in the present instance. Thus in the case I situation, conformational equilibrium is established during the lifetime of the excited state, and the photoproduct composition depends only upon the relative photochemical activation energies (Curtin–Hammett principle).

At present we have no direct evidence regarding the excited-state conformational barriers nor the relative or absolute activation energies for the various photochemical processes involved.[23] What is clear, however, is that if our analysis is correct, intramolecular [2 + 2] photocycloaddition in the systems studied must have a substantially lower activation energy than either of the two competing hydrogen-abstraction reactions. In addition we can conclude that the difference between the conformational and reaction activation energies must be small, particularly when the substrate bears methyl groups at the C(4a) and C(8a) bridgehead positions which would be expected to raise the conformational barriers involved. This factor can reasonably be concluded to be responsible, at least in part, for the hydrogen-abstraction-derived photoproducts observed in the solution photochemistry of naphthoquinols **5a** and **5b**.[24] Experiments designed to test this idea are in progress.

(17) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816–3822.
(18) Lewis, E. S. *Top. Curr. Chem.* **1978**, *74*, 31–44.
(19) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1979**, *101*, 213–215.
(20) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647–678.
(21) Irngartinger, H.; Acker, R-D.; Rebafka, W.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 674–675, have reported the X-ray crystal structure and intramolecular [2 + 2] solid-state photocycloaddition reaction of a conformationally rigid system involving close (ca. 3 Å) parallel approach of the reacting double bonds.
(22) Greenhough, T. J.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *36*, 2840–2843.
(23) Recent temperature-dependent ^{13}C NMR measurements on ene-dione **1** indicate a $\Delta G^{\ddagger}$ of approximately 9 kcal/mol for interconversion of (equivalent) conformers of the A and B type in the ground state: Scheffer, J. R.; Wong, H., unpublished results.
(24) It is also possible, as pointed out by a referee, that the solution photoproduct ratios could be influenced by reverse hydrogen abstraction (biradical disproportionation) which, in the extreme, might even obscure the conformational effects. It is unlikely that such is the case in the present instance, however, as evidenced by the insensitivity of the photoproduct ratios to added Lewis base (*tert*-butyl alcohol). It is well established that Lewis bases strongly retard the disproportionation of Norrish type II 1,4-biradicals, particularly those derived from aralkyl ketones. See: Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.*, **1981**, *103*, 7329–7335. Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *Ibid.*, **1972**, *94*, 7489–7494.

Scheme IV



Finally, with respect to the excited-state lifetimes, in the one case where it was measured (substrate **5b**, vide infra), the excited-state lifetime at 77 K in a glassy matrix was found to be sufficiently long (ca. 10^{-2} s) to be qualitatively consistent with the case I mechanism.

A second potential source of solid-state/solution reactivity differences arises from the possibility that different reactive excited states may be involved in the two media. To test this we investigated the luminescence properties of a typical substrate, compound **5b**, in a glassy solvent matrix (2 MTHF) and in the crystalline state, both at 77 K. The results were identical in both media and consisted of weak, slightly structured phosphorescence ($\tau \sim 0.01$ s) consistent with a $(\pi,\pi^*)^3$ excited state. Insofar as the solvent matrix can be equated with the liquid state, this experiment indicates that excited-state differences are probably not responsible for the solid-state/solution reactivity differences. In addition, since it is likely that the emitting excited state is also the reactive excited state, we further conclude that intramolecular hydrogen abstraction by enone β carbon proceeds from the $(\pi,\pi^*)^3$ state. Other investigators, working on other systems in solution, have come to the same conclusion.[15c,f,o] Recently, Schuster and co-workers have convincingly demonstrated the involvement of $(\pi,\pi^*)^3$ states for *inter*molecular hydrogen abstractions by the β-carbon atoms of enones in solution.[25]

Summary

We have demonstrated that tetrahydronaphthoquinols possess three distinct conformational isomers and that each of these conformers displays a unique photochemical reactivity. This may be represented as shown in Scheme IV. We may select whichever of the three processes we desire by first of all choosing a reaction medium. In solution, equilibration among A*, B*, and C* is rapid and [2 + 2] cycloaddition is observed exclusively because of its high relative rate even though conformers A and B are undoubtedly present in excess. In the solid state, however, hydrogen abstraction predominates owing to the fact that conformer C is not present. We may choose between reactions A and B by selecting substituents which will favor either conformation A or conformation B according to the principles of conformational analysis. We have thus realized the concept of "crystal engineering" for this system; that is, we have developed a theoretical framework which allows for the design and synthesis of new analogs of the naphthoquinol system whose solid-state (and solution) photoreactions can be predicted with a high degree of certainty. Such predictability, regardless of reaction medium, is the ultimate goal of all investigations into chemical reactivity.

Experimental Section

General. Melting points were determined on a Fisher-Johns hot stage or Gallenkamp (sealed tube samples) melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 701B, 257, and 137 spectrophotometers using potassium bromide disks for solid samples and a thin film pressed between two sodium chloride plates for pure liquids. Proton nuclear magnetic resonance spectra were recorded with Varian HA-100, Nicolet-Oxford H-270, or Bruker WH-400 spectrometers. ^{13}C NMR spectra were recorded with Varian CFT-20 and Bruker WP-80 spectrometers. The signal positions are reported using tetramethylsilane as internal standard. Mass spectra were obtained on a Varian/MAT Atlas CH-4B mass spectrometer which was operated at an ionizing potential of 70 eV. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda. For gas chromatography, a Hewlett-Packard 5380A flame ionization model was used; K grade nitrogen was the carrier gas. Columns used were 6 ft × $^1/_8$ in. stainless steel packed with either 5% OV-101, 5% OV-17, or 10% OV-210 on Chromosorb WHP 60/80 and operated at a flow rate of approximately 30 mL/min. For silica gel column chromatography, the columns were slurry packed in the eluting solvent with Silica Gel 60 (from E. Merck), 230–400 mesh ASTM.

2,3,4aα,6,7,8aα-Hexamethyl-1-oxy-4a,5,8,8a-tetrahydronaphthoquin-4β-ol (2a) and -4α-ol (2b). To a solution of 1.52 g (6.2 mmol) of ene-dione **1**[26] in 60 mL of 95% ethanol was added a solution of 0.18 g (4.7 mmol) of sodium borohydride in 20 mL of 95% ethanol during 10 min at room temperature. After stirring for 24 h at room temperature, the solution was acidified by the dropwise addition of glacial acetic acid, diluted with cyclohexane, and evaporated to dryness. The residue was dissolved in chloroform and successively extracted with saturated, aqueous solutions of sodium chloride, sodium carbonate, and sodium chloride once again. Removal of chloroform in vacuo afforded 1.41 g (92%) of a white solid which was shown by GC (OV 210, 180 °C) to consist of a mixture of the 4α- and 4β-ols **2b** and **2a**, respectively. These were separated by careful column chromatography on silica gel using chloroform as the eluting solvent to give 0.77 g (35%) of **2a** and 0.54 g (50%) of **2b**.

Substrate **2a** was obtained as colorless flakes, mp 136.5–137.5 °C, from petroleum ether: IR (KBr) 3425 (OH) and 1645 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H, C(4a) or C(8a) CH_3), 1.12 (s, 3 H, C(4a) or C(8a) CH_3), 1.54 (br s, 3 H, C(6) or C(7) CH_3), 1.62 (br s, 3 H, C(6) or C(7) CH_3), 1.68 (s, 1 H, exchangeable, OH), 1.78 (br s, 3 H, C(2) CH_3), 1.97 (br s, 3 H, C(3) CH_3), 2.43–2.75 (m, 1 H), 4.30 (br s, 1 H, C(4) CH), 1.45–2.30 (multiplicity unknown, 3 H, signals buried underneath methyl resonances); mass spectrum parent *m/e* 248.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.14; H, 9.69.

Cyclohexenone **2b** afforded colorless needles, mp 170.5–171 °C, from ethanol–petroleum ether: IR (KBr) 3450 (OH) and 1635 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.88 (s, 3 H, C(4a) or C(8a) CH_3), 1.10 (s, 3 H, C(4a) or C(8a) CH_3), 1.60 (s, 6 H, C(6) and C(7) CH_3), 1.70 (s, 1 H, exchangeable, OH), 1.78 (br s, 3 H, C(2) CH_3), 1.98 (br s, 3 H, C(3) CH_3), 4.33 (br s, 1 H, C(4) CH), 1.38–2.48 (m, 4 H, partially submerged beneath methyl resonances); mass spectrum parent *m/e* 248.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.64; H, 9.92.

2,3,4β,4aα,6,7,8aα-Heptamethyl-1-oxy-4a,5,8,8a-tetrahydronaphthoquin-4α-ol (2c). A solution of 1.67 g (6.8 mmol) of ene-dione **1** in 30 mL of freshly distilled, anhydrous THF was cooled to −78 °C and 7 mL of 1.1 M methyllithium in ether added via syringe during 2 min with stirring. After stirring for 1 h at −78 °C, the solution was treated with 1 mL of saturated aqueous ammonium chloride solution and extracted with ether. The ethereal extract was dried over magnesium sulfate and concentrated in vacuo; the solid residue was recrystallized from ethyl acetate–cyclohexane to give 1.60 g (90%) of a nearly 1:1 mixture of C(4) epimeric alcohols, mp 130–140 °C. Repeated recrystallization of this mixture eventually afforded pure **2c** as colorless needles, mp 156–157 °C: IR (KBr) 3500 (OH) and 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.18 (s, 3 H), 1.32 (s, 3 H), 1.49 (br s, 3 H, C(6) or C(7) CH_3), 1.62 (br s, 3 H, C(6) or C(7) CH_3), 1.67 (s, 1 H, exchangeable, OH), 1.78 (br s, 3 H, C(2) CH_3), 1.95 (br s, 3 H, C(3) CH_3), 2.44–2.57 (m, 1 H), 1.46–1.99 (multiplicity unknown, 3 H, signals buried beneath methyl resonances); mass spectrum parent *m/e* 262.

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 78.00; H, 10.00.

2,3,4aα,8aα-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (4). Butadiene (3.96 g, 6.0 mL, 73.2 mmol) was collected in a Carius tube cooled in dry ice–acetone. To this 3.0 g (18.3 mmol) of duroquinone and a few crystals of hydroquinone were added. The tube was sealed and heated to 177 °C for 24 h. After cooling (liquid nitrogen), the tube was opened and the red-orange semisolid was removed with chloroform, the mixture filtered, and the filtered solid (durohydroquinone) washed with more chloroform. The chloroform was removed in vacuo; the dark red liquid was taken up in hexane and filtered once again, and the resulting hexane solution was reconcentrated in vacuo. This material was sub-

(25) Schuster, D. I.; Nuñez, I. M.; Chan, C. B. *Tetrahedron Lett.* **1981**, *22*, 1187–1190; Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928–2929.

(26) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963**, 3012–3028.

jected to Kugelrohr distillation at 90–100 °C (0.01 mmHg) to give a light yellow liquid. At this stage duroquinone (as the major impurity) could be separated by column chromatography on silica gel using 5% ethyl acetate–petroleum ether (60–90 °C) as the eluting solvent. This provided compound **4** as a liquid which could be crystallized by mixing it with ca. half its volume of hexane and cooling overnight in the freezer. Rapid filtration of the resulting solid mass while still cold gave about 1.2 g (30%) of light yellow crystals. A second similar recrystallization gave ca. 1.0 g of **4**, mp 51.5–53 °C, which was sufficiently pure for further work. The analytically pure material has mp 55–55.5 °C: IR (CCl_4) 1690 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.11 (s, 6 H, C(4a) and C(8a) CH_3), 1.58–2.76 (m, 4 H, CH_2), 1.93 (s, 6 H, C(2) and C(3) CH_3), 5.56 (br s, 2 H, vinyls); mass spectrum parent *m/e* 218.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.30; H, 8.34.

2,3,4aα,8aα-Tetramethyl-1-oxy-4a,5,8,8a-tetrahydronaphthoquin-4β-ol (5a) and -4α-ol (5b). To a solution of 655 mg (3 mmol) of ene-dione **4** in 5 mL of methanol at 0 °C was added dropwise a solution of 76 mg (2 mmol) of sodium borohydride in 2 mL of cold methanol over a period of 5 min with stirring. Stirring was continued for 2 h during which time the solution was slowly allowed to come to room temperature. Methanol was removed in vacuo to afford a solid residue which was mixed with saturated aqueous ammonium chloride solution and extracted with ether. The combined organic layers were washed with brine and water, dried over magnesium sulfate, and concentrated in vacuo to afford a mixture of cyclohexenones **5a** and **5b** which were separated by silica gel column chromatography using 12% ethyl acetate–toluene as the eluting solvent. This gave 205 mg (31%) of **5a** and 416 mg (63%) of **5b**.

Compound **5a**, mp 115–116 °C (*n*-hexane), showed IR (KBr) 3440 (OH) and 1645 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.04 (s, 3 H, C(4a) or C(8a) CH_3), 1.18 (s, 3 H, C(4a) or C(8a) CH_3), 1.70 (s, 1 H, exchangeable, OH), 1.80 (br s, 3 H, C(2) CH_3), 1.98 (br s, 3 H, C(3) CH_3), 2.56–2.90 (m, 1 H), 4.35 (br s, 1 H, C(4) CH), 1.55–2.34 (m, 3 H, partially submerged beneath methyl resonances), 5.50–5.70 (m, 2 H, vinyls); UV ($CHCl_3$) n $\rightarrow$ π^* λ_{max} 324 (ϵ 65) and 345 nm (sh, ϵ 46); mass spectrum parent *m/e* 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.12; H, 9.06.

Compound **5b**, mp 118.5–119 °C (*n*-hexane), showed IR (KBr) 3470 (OH) and 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.92 (s, 3 H, C(4a) or C(8a) CH_3), 1.16 (s, 3 H, C(4a) or C(8a) CH_3), 1.76 (s, 1 H, exchangeable, OH), 1.80 (br s, 3 H, C(2) CH_3), 1.99 (br s, 3 H, C(3) CH_3), 2.18–2.54 (m, 2 H), 4.41 (br s, 1 H, C(4) CH), 5.46–5.90 (m, 2 H, vinyls), 1.56–2.06 (multiplicity unknown, 2 H, signals buried beneath methyl resonances); UV ($CHCl_3$) n $\rightarrow$ π^* λ_{max} 324 (ϵ 66) and 345 nm (sh, ϵ 43); mass spectrum parent *m/e* 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.28; H, 9.19.

2,3,6,7-Tetramethyl-1-oxy-4aα,5,8,8aα-tetrahydronaphthoquin-4β-ol (8). Substrate **8** was prepared by sodium borohydride reduction of ene-dione **7**[27] in the presence of ammonium chloride following the general procedure of Cavill and Quinn.[28] To a suspension at 0 °C of 387 mg (1.77 mmol) of compound **7** in 10 mL of methanol containing 49 mg (0.92 mmol) of ammonium chloride was added dropwise a solution of 33 mg (0.87 mmol) of sodium borohydride in 2 mL of cold methanol over a period of 5 min. Stirring was continued for 1.5 h at 0 °C and the solution then diluted with saturated aqueous sodium chloride and extracted with chloroform. The chloroform extracts were combined, washed with water, dried, and concentrated in vacuo to afford the 4β-ol derivative **8** in 75% yield. Compound **8**, mp 138–138.5 °C (cyclohexane), showed IR (KBr) 3380 (OH) and 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.58 (br s, 3 H, C(6) or C(7) CH_3), 1.65 (br s, 3 H, C(6) or C(7) CH_3), 1.78 (s, 3 H, C(2) CH_3), 2.00 (s, 3 H, C(3) CH_3), 2.00 (s, 1 H, exchangeable, OH), 2.46–2.84 (m, 3 H), 4.62 (br s, 1 H, C(4) CH), 1.16–2.22 (multiplicity unknown, 3 H, signals buried beneath methyl resonances); UV ($CHCl_3$) n $\rightarrow$ π^* λ_{max} 318 nm (ϵ 53); mass spectrum parent *m/e* 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.39; H, 8.99.

2,3-Dimethyl-4aα,5,8,8aα-tetrahydro-1,4-naphthoquinone (10). A mixture of 3.0 g (22.1 mmol) of 2,3-dimethyl-*p*-benzoquinone[29] and 6 mL (80.7 mmol) of 1,3-butadiene was sealed in a Pyrex tube at −78 °C and then heated at 90 °C for 6 h. Excess butadiene was removed in vacuo to afford an oily residue which crystallized. Recrystallization from cyclohexane gave needles, 3.16 g (75%), mp 76–76.5 °C: IR (KBr) 1665 (C=O) and 1620 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 2.00 (s, 6 H, C(2) and C(3) CH_3), 1.90–2.68 (m, 4 H, C(5) and C(8) CH_2), 3.10–3.38 (m, 2 H, C(4a) and C(8a) CH), 5.72 (m, 2 H, vinyls); mass spectrum parent *m/e* 190.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 76.00; H, 7.60.

2,3-Dimethyl-1-oxy-4aα,5,8,8aα-tetrahydronaphthoquin-4β-ol (11). This compound, mp 109.5–110.5 °C (cyclohexane), was prepared from ene-dione **10** in 67% yield by the same procedure used for the synthesis of 4β-ol **8**: IR (KBr) 3360 (OH) and 1665 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.81 (br s, 3 H, C(2) CH_3), 2.01 (br s, 3 H, C(3) CH_3), 2.12 (s, 1 H, exchangeable, OH), 1.70–2.38 (m, 3 H), 2.54–3.0 (m, 3 H), 4.70 (br s, 1 H, C(4) CH), 5.50–5.90 (m, 2 H, vinyls); UV ($CHCl_3$) n $\rightarrow$ π^* λ_{max} 317 nm (ϵ 46); mass spectrum parent *m/e* 192.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.17; H, 8.49.

Solution Photolyses. The following procedure for the solution photolysis of substrate **2a** is typical. A solution of 100 mg (0.40 mmol) of naphthoquinol **2a** in 170 mL of reagent grade benzene was placed in a standard, water-cooled immersion well apparatus, degassed with high-purity nitrogen for 2 h, and irradiated from within using a 450-W Hanovia lamp fitted with a uranium glass filter sleeve (transmitting $\lambda > 330$ nm). The photolysis was monitored by TLC (silica gel, 15% ethyl acetate–toluene) and continued until this showed no remaining starting material (2.5 h). Removal of benzene in vacuo and passage of the residue through an approximately 2.5 × 5 cm column of silica gel (chloroform eluent) afforded 96 mg (96%) of crystalline ketol **3a**. Recrystallization from petroleum ether gave 79 mg of colorless needles, sealed tube mp 152–153 °C. A second crop (6 mg, mp 147–151 °C) was recovered from the mother liquor: IR (KBr) 1730 (C=O) and 3450 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.72 (d, 1 H, J = 13 Hz), 0.88 (s, 3 H), 0.93 (s, 3 H), 0.96 (s, 3 H), 1.01 (s, 3 H), 1.03 (s, 3 H), 1.06 (s, 3 H), 1.46 (d, 1 H, J = 13 Hz), 1.56 (s, 1 H, exchangeable, OH), 1.90 (d, 1 H, J = 13 Hz), 2.14 (d, 1 H, J = 13 Hz), 3.16 (s, 1 H, C*H*OH); mass spectrum parent *m/e* 248.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.67; H, 9.75.

Similar photolysis of 100 mg (0.40 mmol) of naphthoquinol **2b** for 2.5 h afforded cyclic hemiacetal **3b**, sealed tube mp 198–199 °C (95% ethanol), in 95% isolated yield. Compound **3b** showed IR (KBr) 3333 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.79 (s, 3 H), 0.88 (s, 3 H), 0.89 (s, 3 H), 0.90 (s, 3 H), 0.93 (s, 3 H), 1.03 (s, 3 H), 1.51 (d, 1 H, J = 13 Hz), 1.57 (d, 1 H, J = 13 Hz), 2.89 (s, 1 H, exchangeable, OH), 3.46 (s, 1 H, C*H*OH), 0.80–1.07 (multiplicity unknown, 2 H, signals partially obscured by methyl resonances); mass spectrum parent *m/e* 248.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.40; H, 9.56.

Irradiation of 58 mg (0.22 mmol) of substrate **2c** by the standard procedure for 1.7 h afforded 54 mg (93%) of cyclic hemiacetal **3c**, mp 132–134 °C (*n*-hexane): IR (KBr) 3350 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.75 (s, 3 H), 0.77 (s, 3 H), 0.84 (s, 3 H), 0.87 (s, 6 H), 0.91 (s, 3 H), 0.99 (d, 1 H, J = 13 Hz), 1.03 (s, 3 H), 1.49 (br d, 2 H, J = 13 Hz), 2.80 (br s, 1 H, exchangeable, OH), ca. 0.8 (multiplicity unknown, 1 H, signal partially obscured by methyl resonances); mass spectrum parent *m/e* 262.

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. found: C, 78.04; H, 9.86.

Photolysis of 95 mg (0.43 mmol) of naphthoquinol **5a** by the standard procedure for 2.5 h afforded 90% of ketol **6a**, mp 141–142 °C (*n*-hexane): IR (KBr) 3450 (OH) and 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 1.09 (s, 3 H), 1.12 (s, 3 H), 1.59 (s, 1 H, exchangeable, OH), 1.68 (dd, 1 H, J = 12 and 5 Hz), 1.85 (d, 1 H, J = 12 Hz), 2.05 (d, 1 H, J = 12 Hz), 2.25 (dd, 1 H, J = 9.5 and 5 Hz), 2.45 (dd, 1 H, J = 9.5 and 5 Hz), 3.14 (s, 1 H, C*H*OH), 1.04–1.15 (multiplicity unknown, 1 H, signal partially obscured by methyl resonances); mass spectrum parent *m/e* 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. found: C, 76.53; H, 9.30.

A small amount (6%) of the solid-state photoproduct, ketol **18**, could be isolated in this photolysis by column chromatography (silica gel, 12% ethyl acetate–toluene) of the mother liquors from recrystallization of **6a**.

Standard irradiation of 220 mg (1 mmol) of substrate **5b** in 180 mL of benzene for 4.5 h followed by concentration in vacuo and recrystallization of the solid residue from *n*-hexane afforded 156 mg (71%) of cyclic hemiacetal **6b**, mp 189–190 °C: IR (KBr) 3330 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.93 (s, 6 H), 1.04 (s, 3 H), 1.06 (s, 3 H), 1.22 (m, 2 H), 1.43 (d, 1 H, J = 14 Hz), 1.47 (d, 1 H, J = 14 Hz), 2.02 (m, 2 H), 2.83 (br s, 1 H, exchangeable, OH), 3.44 (s, 1 H, C*H*OH); mass spectrum parent *m/e* 220.

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Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.17; H, 9.24.

The mother liquors from the recrystallization of **6b** were concentrated in vacuo, dissolved in a minimum amount of methylene chloride and set aside overnight at −15 °C whereupon large crystals (53 mg, 24%) of photoproduct **19** were deposited. This material, whose structure was determined by X-ray crystallography,[11] proved to be identical with the major photoproduct obtained by irradiation of substrate **5b** in the solid state (vide infra).

Photolysis of 100 mg (0.45 mmol) of naphthoquinol **8** by the usual procedure for 3.8 h followed by removal of benzene in vacuo and recrystallization of the solid residue from petroleum ether afforded 95 mg (95%) of ketol **9**, sealed tube mp 300 °C dec: IR (KBr) 3435 (OH) and 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.86 (s, 3 H), 0.96 (s, 3 H), 0.97 (s, 3 H), 1.07 (s, 3 H), 1.68 (s, 1 H, exchangeable, OH), 1.68 (br d, 1 H, J = 12 Hz), 2.04 (d, 1 H, J = 12 Hz), 2.14 (d, 1 H, J = 12 Hz), 2.43 (br s, 2 H), 3.69 (br s, 1 H, C*H*OH), 0.9–1.0 (multiplicity unknown, 1 H, signal partially obscured by methyl resonances); mass spectrum parent m/e 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.10; H, 9.17.

Irradiation (24 h) of 128 mg (0.67 mmol) of cyclohexenone **11** in 170 mL of benzene using the standard procedure followed by flash chromatography on silica gel afforded 126 mg (98%) of keto-alcohol **12** as a homogeneous oil which crystallized upon trituration with *n*-hexane. Recrystallization from *n*-hexane gave needles, sealed tube mp 173–174 °C: IR (KBr) 3425 (OH) and 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.01 (s, 3 H), 1.13 (s, 3 H), 1.31 (dt, 1 H, J = 13 and 4 Hz), 1.63 (s, 1 H, exchangeable, OH), 1.89 (dt, 1 H, J = 13 and 4 Hz), 2.01 (quasi t, 2 H, J = 13 Hz), 2.25-2.34 (m, 1 H), 2.34–2.44 (m, 1 H), 2.44–2.53 (m, 2 H), 3.61 (s, 1 H, C*H*OH); mass spectrum parent m/e 192.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.13; H, 8.60.

1,3,4,6,8,9-Hexamethyltetracyclo[4.4.0.0^{3,9}.0^{4,8}]decane-2,5-dione (13a). A solution of 190 mg (0.77 mmol) of ketol **3a** and 253 mg (1.17 mmol) of pyridinium chlorochromate (Aldrich) in 20 mL of methylene chloride was refluxed for 9 h, a second portion (121 mg, 0.56 mmol) of oxidant added, and refluxing continued for an additional 12 h. After filtration through Florisil, the solvent was removed in vacuo to afford 182 mg (97%) of solid diketone **13a**. Recrystallization from *n*-hexane gave large needles, sealed tube mp 137.5–138.5 °C: IR (KBr) 1740 and 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.93 (s, 6 H), 1.03 (s, 6 H), 1.09 (s, 6 H), 2.42 (d, 2 H, J = 13 Hz, endo CH_2), 1.02 (d, 2 H, J = 13 Hz, exo CH_2); proton-decoupled ^{13}C NMR ($CDCl_3$) δ 7.31 (CH_3), 14.30 (CH_3), 16.25 (CH_3), 42.23, 43.03, 51.02, 54.45, and 215.77 (C=O); mass spectrum parent m/e 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.20; H, 9.08.

1,3,4,6-Tetramethyltetracyclo[4.4.0.0^{3,9}.0^{4,8}]decane-2,5-dione (13b). To a stirred suspension of 50 mg (0.23 mmol) of pyridinium chlorochromate and 25 mg (0.3 mmol) of anhydrous sodium acetate in 2 mL of anhydrous methylene chloride was added 30 mg (0.14 mmol) of ketol **6a** in 1 mL of methylene chloride. After stirring for 10 h at room temperature, the reaction mixture was diluted with 15 mL of anhydrous ether and filtered through Florisil. Evaporation of the solvent left 27 mg (91%) of crystalline diketone **13b**. Recrystallization from *n*-hexane afforded large cubes, mp 122–123 °C: IR (KBr) 1750 and 1728 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.08 (s, 6 H), 1.38 (d, 2 H, J = 13 Hz, exo CH_2), 2.42 (d, 2 H, J = 13 Hz, endo CH_2), 2.76 (m, 2 H); mass spectrum parent m/e 218.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.08; H, 8.43.

Independent Synthesis of Photoproduct 3b by Sodium Borohydride Reduction of Diketone 13a. A solution of 33 mg (0.13 mmol) of diketone **13a** and 3 mg (0.08 mmol) of sodium borohydride in 3 mL of 95% ethanol was stirred for 3.5 h at room temperature, acidified with acetic acid, diluted with cyclohexane, and evaporated to dryness in vacuo. The residue was dissolved in chloroform and washed with aqueous sodium carbonate and brine, dried over magnesium sulfate, and concentrated in vacuo to yield 30 mg (90%) of crystalline hemiacetal **3b** whose IR and NMR spectra were identical with those of **3b** obtained from the photolysis of naphthoquinol **2b**.

Independent Synthesis of Photoproduct 3c by Reaction of Diketone 13a with Methyllithium. To a stirred solution of 40 mg (0.16 mmol) of diketone **13a** in 1.5 mL of anhydrous, freshly distilled THF was added 0.25 mL (0.30 mmol) of a 1.2 M solution of methyllithium in ether at −78 °C under nitrogen. After stirring for 1 h at −78 °C, the reaction was quenched with excess aqueous ammonium chloride solution and extracted with ether. The combined ether extracts were dried and concentrated in vacuo; the solid residue was recrystallized from *n*-hexane to afford 32 mg (75%) of hemiacetal **3c** whose melting point, IR, and NMR were identical with those of **3c** obtained from the solution photolysis of substrate **2c**.

Preparation of Diketone Hydrate 14.[7] A mixture of 147 mg (0.6 mmol) of diketone **13a** and 4.0 g of 10% amalgamated zinc in 3 mL of concentrated hydrochloric acid, 9 mL of water, and 15 mL of THF was momentarily brought to reflux and then stirred at room temperature for 18 h. The resulting solution was diluted with 30 mL of brine, decanted, and extracted with chloroform. After washing with dilute aqueous sodium bicarbonate and brine solutions, the combined chloroform extracts were dried ($MgSO_4$) and concentrated in vacuo; the solid residue was recrystallized from ethyl acetate–hexane to afford 143 mg (96%) of hydrate **14**, mp 143–144 °C: IR (KBr) 3500 and 3250 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.79 (s, 6 H), 0.87 (s, 6 H), 0.90 (s, 6 H), 1.00 (d, 2 H, J = 12 Hz, exo CH_2), 1.50 (d, 2 H, J = 12 Hz, endo CH_2), 4.79 (s, 2 H, exchangeable, OH); proton-decoupled ^{13}C NMR (Me_2SO-d_6) δ 13.47 (CH_3), 14.61 (CH_3), 19.38 (CH_3), 41.56, 41.86, 49.37, 53.37, and 109.41 (hydrate carbons); mass spectrum parent m/e 264.

Anal. Calcd for $C_{10}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.44; H, 9.26.

Synthesis of Cyclic Ethers 15a and 15b. A solution of 390 mg (1.77 mmol) of keto-alcohol **9** in 8 mL of anhydrous pyridine was cooled to 0 °C and 2.0 g (11.6 mmol) of *p*-toluenesulfonyl chloride added. After standing at 5 °C for 12 days, the reaction mixture was poured onto ice and stirred for 10 min; the precipitate was filtered, washed with water and petroleum ether, and then dried over P_2O_5 to afford 407 mg (61%) of crude keto-tosylate. Without further purification, 377 mg (1.01 mmol) of this material was suspended in 12 mL of methanol, the mixture cooled to 0 °C, and a solution of 77 mg (2.03 mmol) of sodium borohydride in 3 mL of cold methanol added over a period of 5 min. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 6 h. The solution was acidified with glacial acetic acid, diluted with water, and extracted with ether. The combined ether extracts were washed with aqueous sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated by fractional distillation at atmospheric pressure to give an oil which crystallized. Sublimation at 75–79 °C and 100 mm afforded 117 mg (57%) of cyclic ether **15a**, sealed tube mp 259.5–261 °C dec: IR (KBr) 1000 and 1015 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ 0.88 (s, 6 H), 0.91 (s, 6 H), 1.03 (br d, 2 H, J = 12 Hz, exo CH_2), 1.51 (d, 2 H, J = 12 Hz, endo CH_2), 2.26 (br s, 2 H), 4.23 (m, 2 H, C*H*–O); proton-decoupled ^{13}C NMR ($CDCl_3$) δ 11.41 (CH_3), 16.04 (CH_3), 32.51, 40.13, 43.99, 53.27, and 92.36 (*CH*–O) ppm; mass spectrum parent m/e 204.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.54; H, 9.90.

Analogous tosylation of ketol **12** followed by sodium borohydride reduction led to cyclic ether **15b**, sealed tube mp 128.5–130 °C: IR (KBr) 995 and 1020 cm^{-1} (C–O); ^1H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.28 (br d, 2 H, J = 13 Hz), 1.43 (d, 2 H, J = 13 Hz), 2.10 (br s, 2 H), 2.31 (br s, 2 H), 4.20 (m, 2 H, C*H*-O); proton-decoupled ^{13}C NMR ($CDCl_3$) δ 15.27 (CH_3), 23.07, 38.74, 41.96, 52.01, and 91.25 (*CH*-O) ppm; mass spectrum parent m/e 176.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.88; H, 9.17.

Solid-State Photolysis of Naphthoquinol 2a. As described in the text, preparative solid-state photolyses were carried out either on the inner surface of an immersion well apparatus (method A) or by using Pyrex glass plate "sandwiches" sealed in polyethylene bags (method B). Low-conversison, analytical runs were performed using the sealed capillary tube method. Naphthoquinol **2a** (70 mg, 0.28 mmol) was irradiated through a uranium glass filter sleeve (λ >330 nm) by method A at −74 °C under nitrogen for 2.1 h. Column chromatography (silica gel, 20% ethyl acetate–toluene) afforded 39 mg of starting material **2a** and 25 mg (81% based on unrecovered starting material) of a new photoproduct subsequently shown to have structure **16**. Gas chromatography of the crude reaction mixture indicated approximately 4% of a peak with the same retention time as solution photoproduct **3a**. Ketol **16**, sealed tube mp 121.5–122.5 °C (*n*-hexane), showed IR (KBr) 3465 (OH) and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.87 (s, 3 H), 0.88 (d, 3 H, J = 7 Hz, C(4) CH_3), 0.96 (s, 3 H), 1.03 (s, 3 H), 1.54 (br s, 3 H, C(8) or C(9) CH_3), 1.65 (s, 1 H, exchangeable, OH), 1.65 (br s, 3 H, C(8) or C(9) CH_3), 1.6–1.75 (m, 1 H, C(4) CH), 1.82 (d, 1 H, J = 16 Hz, one of C(10) CH_2), 2.02 (d, 1 H, J = 16 Hz, one of C(10) CH_2), 2.20 (s, 1 H, C(7) CH), 3.60 (d, 1 H, J = 4 Hz, C(5) CH); mass spectrum parent m/e 248.

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.49; H, 9.59.

Solid-State Photolysis of Substrate 2b. Prolonged irradiation (λ >330 nm) of polycrystalline samples of naphthoquinol **2b** by either method A or method B at several different temperatures invariably afforded es-

sentially complete recovery of starting material; TLC, IR, and gas chromatography indicated no significant accumulation of any new photoproducts.

Solid-State Photolysis of Substrate 2c. A 4-mg crystal of naphthoquinol **2c** was irradiated via the sealed-tube method through a Pyrex filter for 12 h at −20 °C using a 450-W Hanovia lamp as the light source. Gas chromatography of the reaction mixture revealed two photoproducts and no remaining starting material. The combined material from five such runs (19 mg) was subjected to preparative TLC (0.5 mm silica gel, 20% ethyl acetate–toluene) to afford 13 mg (68%) of ketol **17** and 3.5 mg (18%) of cage hemiacetal **3c**. Photoproduct **17**, mp 145–146 °C (*n*-hexane–ether), showed IR (KBr) 3430 (OH) and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.74 (d, 3 H, J = 8 Hz, C(4) CH_3), 0.96 (s, 3 H), 1.01 (s, 3 H), 1.13 (s, 3 H), 1.32 (s, 3 H), 1.54 (br s, 3 H, C(8) or C(9) CH_3), 1.64 (br s, 3 H, C(8) or C(9) CH_3), 1.57 (s, 1 H, exchangeable, OH), 1.69 (q, 1 H, J = 8 Hz, C(4) CH), 1.88 (s, 1 H, C(7) CH), 1.75 (d, 1 H, J = 18 Hz, one of C(10) CH_2), 2.07 (d, 1 H, J = 18 Hz, one of C(10) CH_2); mass spectrum parent m/e 262.

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.88; H, 10.00.

Solid-State Photolysis of Naphthoquinol 5a. Naphthoquinol **5a** (60 mg, 0.27 mmol) was photolyzed (λ >330 nm) at −70 °C for 9 h using method A and the resulting mixture dissolved in the minimum amount of boiling *n*-hexane. Upon cooling, 38 mg of crystalline starting material **5a** was deposited. Column chromatography of the mother liquor (silica gel, 12% ethyl acetate–toluene) afforded an additional 6 mg of **5a** (total recovery 73%) along with solution photoproduct **6a** (10 mg, 63% based on unrecovered starting material, identified by melting point and IR) and a new substance, ketol **18** (4 mg, 25%). Recrystallization of this latter material from *n*-hexane afforded needles, mp 109–110 °C: IR (KBr) 3500 (OH) and 1745 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.96 (s, 3 H), 1.01 (d, 3 H, J = 6 Hz), 1.07 (s, 6 H), 1.58 (s, 1 H, exchangeable, OH), 1.75–1.95 (m, 2 H), 2.15–2.35 (m, 2 H), 2.90 (d, 1 H, J = 6 Hz), 5.56–5.68 (m, 1 H, vinyl), 5.92–6.04 (m, 1 H, vinyl); mass spectrum parent m/e 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.35; H, 9.35.

Solid-State Photolysis of Naphthoquinol 5b. Naphthoquinol **5b** (210 mg, 0.95 mmol) was irradiated (λ >330 nm) by method A for 10 h at −70 °C. The reaction mixture was dissolved in a minimum amount of methylene chloride, and upon cooling in the refrigerator overnight, large cubes of photoproduct **19**, mp 157–158 °C, were deposited. This operation was repeated twice to afford a total of 89 mg (73% based on amount of starting material consumed) of hemiacetal **19**. Column chromatography of the mother liquors on silica gel (5% methanol–chloroform) gave 88 mg of unreacted starting material **5b** and 7 mg of solution photoproduct **6b**. Additional amounts of **19** could not be isolated by column chromatography owing to its decomposition on silica gel: IR **19** (KBr) 3300 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.88 (d, 3 H, J = 7 Hz, C(4) CH_3), 0.88 (s, 3 H), 0.96 (s, 3 H), 0.98 (s, 3 H), 1.89–1.98 (m, 2 H), 2.03 (d, 1 H, J = 7 Hz), 2.09 (q, 1 H, J = 7 Hz, C(4) CH), 2.75–3.20 (broad smear, 1 H, exchangeable, OH), 3.35 (s, 1 H, C*H*–O–), 5.54-5.65 (m, 1 H, vinyl), 5.81–5.93 (m, 1 H, vinyl); mass spectrum parent m/e 220; X-ray crystal structure.[11]

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.40; H, 9.21.

Solid-State Photolysis of Substrate 8. Naphthoquinol **8** (94 mg, 0.43 mmol) was photolyzed (λ >330 nm) under nitrogen by method A for 10 h at −40 °C. Column chromatography on silica gel (30% ethyl acetate–toluene) afforded 65 mg of starting cyclohexenone **8**, 22 mg (76% based on starting material consumed) of keto-alcohol **20** and 5 mg (17%) of solution photoproduct **9**. Recrystallization of compound **20** from *n*-hexane–benzene gave long needles, mp 116.5–117.5 °C: IR (KBr) 3475 (OH) and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.89 (d, 3 H, J = 7 Hz, C(4) CH_3), 1.02 (s, 3 H, C(3) CH_3), 1.55 (br s, 3 H, C(8) or C(9) CH_3), 1.67 (br s, 3 H, C(8) or C(9) CH_3), 1.71 (s, 1 H, exchangeable, OH), 1.75 (m, 1 H, C(4) CH), 2.06–2.19 (m, 2 H), 2.35 (br d, 1 H, J = 16 Hz, one of C(10) CH_2), 2.54 (s, 1 H), 2.22 (s, 1 H), 3.50 (d, 1 H, J = 3 Hz, C*H*OH); mass spectrum parent m/e 220.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.48; H, 9.25.

Solid-State Photolysis of Substrate 11. Naphthoquinol **11** reacted very slowly in the solid state. For example, using the solid-state apparatus described in ref 4, irradiation (5 h) (Pyrex, −22 °C) caused only 4% conversion to a mixture of photoproducts **12** and **21**. In order to accumulate sufficient material for characterization of photoproduct **21**, preparative runs were performed at 0 °C using method B despite the fact that approximately equal amounts of solution photoproduct **12** were also formed under these conditions. Ketol **21** was isolated by silica gel column chromatography (40% ethyl acetate–toluene) and exhibited the following physical and spectroscopic properties: mp 107.5–108.5 °C (hexane/acetone); IR (KBr) 1736 (C=O) and 3290 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.91 (d, 3 H, J = 8 Hz, C(4) CH_3), 1.04 (s, 3 H, C(3) CH_3), 1.70 (s, 1 H, exchangeable, OH), 1.58–1.93 (m, 1 H, C(4) CH), 2.10–2.44 (m, 4 H), 2.66–2.84 (m, 1 H), 3.57 (d, 1 H, J = 3 Hz, C(5) CH), 5.52–5.98 (m, 2 H, vinyls); UV ($CHCl_3$) n → π^* λ_{max} 294 nm (ϵ 29); mass spectrum parent m/e 192.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.88; H, 8.35.

Irradiation through Pyrex of a single crystal of **11** at −24 °C for 47 h (100-W lamp) resulted in a **21**:**12** ratio of 4.3:1 at a total conversion of approximately 4% as shown by gas chromatography.

Oxidation of Photoproducts 16 and 20. A CH_2Cl_2 solution of 100 mg (0.40 mmol) of keto-alcohol **16**, 51 mg of anhydrous sodium acetate, and 137 mg (0.64 mmol) of pyridinium chlorochromate was stirred for 24 h at room temperature. Filtration through Florisil followed by column chromatography on silica gel (10% ethyl acetate–toluene) afforded 94 mg (95%) of diketone **22a** as an oil. Kugelrohr distillation at 0.05 torr and 50–60 °C gave material whose IR, NMR, and mass spectra were identical with those of an authentic sample.[10]

In a similar fashion, 64 mg (0.29 mmol) of ketol **20** was oxidized in 87% yield to diketone **22b**, mp 91.5–92.5 °C, whose spectra were identical with those of an authentic sample prepared by solution photolysis of ene-dione **7**.[10]

Independent Synthesis of Photoproduct 17. To a stirred solution of 23 mg (0.09 mmol) of diketone **22a**[10] in 1 mL of anhydrous THF at −78 °C under nitrogen was added 0.15 mL (0.18 mmol) of 1.2 M methyllithium in ether. After 1 h at −78 °C, a second 0.15-mL portion of methyllithium was added and stirring was continued for an additional hour. Workup in the usual way followed by preparative TLC on silica gel (96% chloroform–acetone) afforded 8 mg (33%) of a white solid. Recrystallization from *n*-hexane gave material melting at 140–142 °C whose spectra were identical with those of photoproduct **17**.

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Registry No. 1, 49576-86-5; **2a**, 74069-47-9; **2b**, 74069-48-0; **2c**, 78872-20-5; **3a**, 74069-59-3; **3b**, 74069-57-1; **3c**, 86118-43-6; **4**, 74069-52-6; **5a**, 74069-55-9; **5b**, 74069-49-1; **6a**, 74069-64-0; **6b**, 74069-56-0; **7**, 55511-74-5; **8**, 86118-42-5; **9**, 86118-44-7; **10**, 81981-42-2; **11**, 81768-03-8; **12**, 86118-45-8; **13a**, 74069-60-6; **13b**, 86118-49-2; **14**, 79427-82-0; **15a**, 86118-50-5; **15b**, 86118-51-6; **16**, 74069-50-4; **17**, 78872-21-6; **18**, 86118-46-9; **19**, 74069-51-5; **20**, 86118-47-0; **21**, 86118-48-1; **22a**, 73395-58-1; butadiene, 106-99-0; duroquinone, 527-17-3; 2,3-dimethyl-*p*-benzoquinone, 526-86-3.