Chem. Soc., following paper in this issue.

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

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(7) (a) Scheffer, J. R.; Bhandari, K. S.; Gayler, R. E.; Wostradowski, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 2178–2189. (b) Scheffer, J. R.; Jennings, B. M.; Louwerens, J. P. *Ibid.* **1976**, *98*, 7040–7048. (c) Scheffer, J. R.; Dzakpasu, A. A. *Ibid.* **1978**, *100*, 2163–2173.

(8) Only when all other competing reaction modes are blocked by substituents is internal [2 + 2] cycloaddition observed for tetrahydro-1,4-naphthoquinones of general structure **1**. See Scheffer, J. R.; Jennings, B. M. *J. Chem. Soc., Chem. Commun.* **1975**, 609–610.

(9) Intramolecular excited-state carbonyl (acceptor)-amine (donor) charge-transfer interactions leading to internal hydrogen abstractions are well established. See for example (a) Padwa, A. *Acc. Chem. Res.* **1971**, *4*, 48–57. (b) Padwa, A.; Eisenhardt, W.; Gruber, R.; Pashayan, D. *J. Am. Chem. Soc.* **1971**, *93*, 6998–7005. (c) Wagner, P.J.; Kemppainen, A. E.; Jellinek, T. *Ibid.*, **1972**, *94*, 7512–7519. (d) Coyle, J. D.; Kingston, D. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1475–1479. (e) Wagner, P. J.; Ersfeld, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4515–4518. (f) Coyle, J. D.; Kingston, D. H. *Tetrahedron Lett.* **1976**, 4525–4528. (g) Wagner, P. J.; Scheve, B. J. *J. Am. Chem. Soc.* **1977**, *99*, 1858–1863. (h) Coyle, J. D.; Newport, G. L. *Tetrahedron Lett.*, **1977**, 899–902. (i) Coyle, J. D.; Newport, G. L. *J. Chem. Soc., Perkin II*, 1978, 133–137. The fact that amines and di-, tri-, and tetrasubstituted alkenes have similar ionization potentials lends support to the idea that intramolecular charge-transfer exciplex formation may be important in the photochemistry of **1b** and related compounds.

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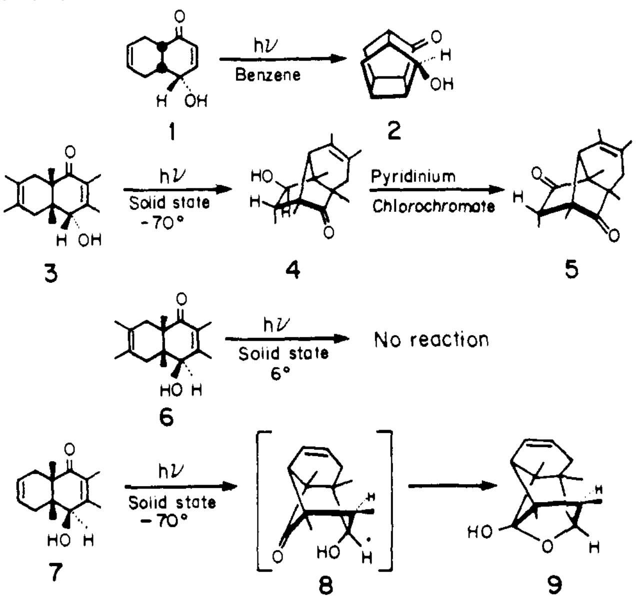
Crystal Lattice Control of Unimolecular Photorearrangements. Differences in Cyclohexenone Photochemistry in Solution and the Solid State. Solid-State Results

Sir:

In the preceding communication[1] we outlined the solution phase photochemistry of 4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol (**1**, Scheme I) and five of its substituted analogues. This consisted, in every case, of intramolecular [2 + 2] photocycloaddition to yield the corresponding tetracyclo[5.3.0.0^{2,6}.0^{4,9}]decane derivatives (e.g., **2**). In this paper we describe the different results obtained when three of these same tetrahydronaphthoquinols were irradiated in the solid state. In addition, we report the crystal and molecular structure of each of the three substrates as determined by single crystal X-ray diffraction methods. These studies establish that the solid phase photoreactions are crystal lattice-controlled, least motion processes and lead to the novel conclusion that the solid state/solution reactivity differences are the result of reaction from different conformational isomers in the two media.

Scheme I



The compounds studied were the tetrahydronaphthoquinols **3**, **6**, and **7** prepared via sodium borohydride reduction of the corresponding ene-diones.[1] Irradiation[2] ($\lambda > 330$ nm) of polycrystalline samples of these substrates led to the results outlined in Scheme I, that is formation of photoproducts **4** and **9** from **3** and **7** respectively and no reaction in the case of tetrahydronaphthoquinol **6**. Accompanying products **4** and **9** were traces (<5%) of the corresponding intramolecular [2 + 2] solution photoproducts.[1] We attribute their formation to reaction at defect sites and/or regions of local melting. Photoisomer **4** was identified by oxidation (pyridinium chlorochromate, 95%) to the known[3] diketone **5**. The relative stereochemistry of **4** at the hydroxyl-bearing carbon atom and the adjacent center follows from a vicinal coupling constant of 4 Hz. Photoproduct **9** was identified by a single crystal, direct method X-ray structure determination, current $R = 0.082$.[4] It is undoubtedly formed by cyclization of the keto-alcohol **8** which could not be isolated. Evidence which indicates that this hemiacetal formation occurs even in the solid state comes from experiments involving irradiation of potassium bromide pellets of **7**. Infrared spectra of the irradiated pellet at various intervals showed only peaks due to **7** and **9**; no absorptions corresponding to the cyclobutanone carbonyl stretching frequency (ca. 1780 cm^{-1}) were observed.

The X-ray crystal structures[4] of starting substrates **3** ($R = 0.043$), **6** ($R = 0.041$), and **7** (current $R = 0.048$) showed that all three adopt conformations which can be approximately described as consisting of a half-chair cyclohexene ring cis-fused to a second half-chair cyclohexenone moiety. There are two non-equivalent ring flipped conformations of this type for each substrate, one in which the hydroxyl group is pseudoequatorial and one in which it is pseudoaxial. The crystallographic results show that the conformation with the hydroxyl group pseudoequatorial is present exclusively in each case. Figure 1 shows a computer drawn stereodiagram of this conformation for substrate **3**.

The result of this conformational preference is that substrates **6** and **7** (hydroxyl group syn to bridgehead methyls)

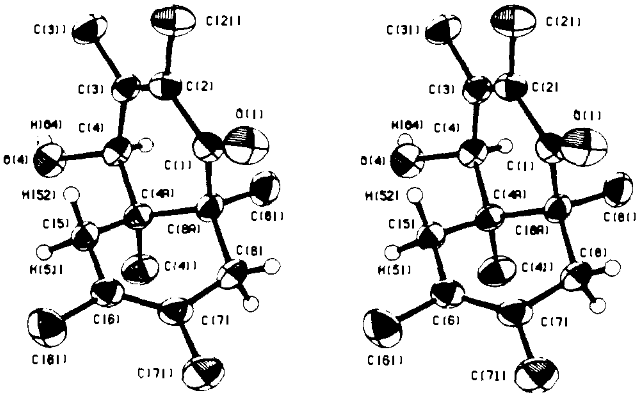


Figure 1. Stereodiagram of the conformation of tetrahydro-1,4-naphthoquinol **3** in the solid state. The methyl hydrogen atoms are omitted for clarity.

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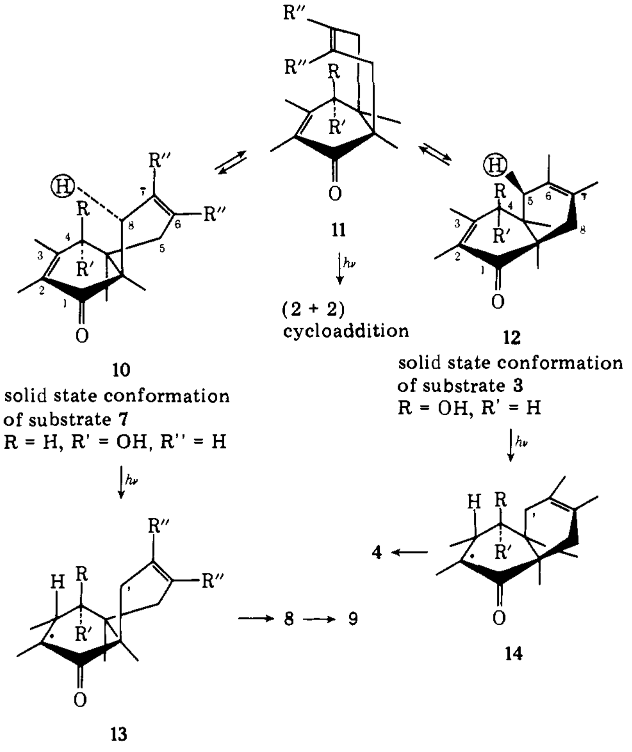
Scheme II[a]



adopt a conformation different from that adopted by **3** (hydroxyl group anti to bridgehead methyls). These differences are shown by structures **10** and **12** in Scheme II. With this information we are now in a position to understand the solid state photochemical results. Photoproduct **9** arises from conformer **10** via a six-membered transition state allylic hydrogen atom transfer from C(8) to C(3) followed by C(2) to C(8) bonding of the resulting biradical **13**. On the other hand, photoproduct **4** is formed through conformer **12** by means of a C(5) to C(3) hydrogen atom transfer (five-membered transition state![5]) and subsequent C(2) to C(5) bonding in **14**.

These processes are seen, as in our previous unimolecular solid state results,[6] to be least motion in character, that is, relatively little molecular reorganization is required to initiate product formation via carbon-carbon bonding following hydrogen abstraction. With regard to the abstraction processes themselves, the C(3) to H(5) distance in **12** is 2.72 (2) Å, and the C(3) to H(8) distance in **10** is 2.84(4) Å. Both values are within the suggested[6a] van der Waals radii sum limit of 2.90 Å for abstraction of hydrogen by carbon.[7] Significantly, substrate **6**, which is photochemically unreactive and exists in conformation **10** (R'' = CH_3), has a C(3) to H(8) interatomic distance of 2.92 (2) Å, just outside the suggested limit. For all three substrates the angle τ_c,[6a] the degree to which the abstracted hydrogen atom lies outside the mean plane of the C(2)-C(3) double bond, is very close to 50°. Similarly, Δ_c, the C(2)-C(3)···H_{abs} angle, is nearly constant at 75°. The conclusion is thus that these geometric factors are not responsible for the lack of solid state reactivity of substrate **6**.

Finally we turn to a discussion of the factors which give rise to the observed solution/solid state reactivity differences. We suggest that internal [2 + 2] photocycloaddition does not occur from conformers **10** and **12** owing to the relatively large double bond separations involved (≥4.37(2) Å in every case) as well as their nonparallel orientations. Parallel double bond approach at distances of less than ca. 4.1 Å is a well-established prerequisite for successful *inter*molecular [2 + 2] photocycloadditions.[6a,8] On the other hand, in solution, where conformational equilibration is facile, small amounts of conformers which better fulfill these requirements (e.g., **11**) will be present. It is thus reasonable to suggest that rapid [2 + 2] photocycloaddition from these minor, higher energy conformers can predominate in solution. Perusal of the photochemical literature reveals a number of additional examples of systems which likely react via nonminimum energy conformations in solution and which might therefore exhibit different photobehavior in the solid state. We plan to continue our investigations along these lines.

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References and Notes

(1) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J.; Walsh, L. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Photolyses were carried out either in the apparatus previously described[6a] or by coating the inner surface of a conventional immersion well vessel with a thin film of crystals and irradiating from the inside in an oxygen-free atmosphere. Conversions were generally kept below 50%. Low temperatures were employed to avoid development of liquid phases during irradiation. Solution photolyses at −70 °C gave results identical with those observed at ambient temperatures.[1]

(3) Scheffer, J. R.; Bhandari, K. S.; Gayler, R. E.; Wostradowski, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 2178–2189.

(4) Greenhough, T. J.; Trotter, J., unpublished results. Full details of all X-ray crystal structure determinations will be published separately.

(5) This appears to be the first example of a five-membered transition state hydrogen abstraction process in which the abstracting atom is the olefinic carbon of a photoexcited alkene or enone chromophore. The corresponding six-membered transition state process, while rare in comparison with the Norrish type II reaction, is well established. (a) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129–6140. (b) Scully, F.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1973**, 529–530. (c) Hornback, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6773–6774. (d) Hornback, J. M. *Tetrahedron Lett.* **1976**, 3389–3392; (e) Padwa, A.; Chiacchio, U.; Hatanaka, N. *J. Am. Chem. Soc.* **1978**, *100*, 3928–3930. (f) Herz, W.; Iyer, V. S.; Nair, M.; Saltiel, J. *Ibid.* **1977**, *99*, 2704–2713. (g) Hasegawa, T.; Aoyama, H.; Omote, Y. *Tetrahedron Lett.* **1975**, 1901–1902. (h) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 3289–3295. (i) Smith, A. B., III; Agosta, W. C. *Ibid.* **1973**, *95*, 1961–1968. (j) Wolff, S.; Schreiber, W. L.; Smith, A. B., III; Agosta, W. C. *Ibid.* **1972**, *94*, 7797–7806. (k) Gloor, J.; Schaffner, K. *Helv. Chim. Acta* **1974**, *57*, 1815–1845. (l) Nobs, F.; Burger, U.; Schaffner, K. *Ibid.*, 1977, *60*, 1607–1628; (m) Ayral-Kaloustian, S.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 5984–5992.

(6) (a) Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163–2173. (b) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J. *Ibid.* **1979**, *101*, 213–215.

(7) Note that both hydrogen transfers found in this work involve abstraction by the β carbon of the α,β-unsaturated ketone system. This occurs despite the fact that the C(2)···H(8) distance (abstraction by the α carbon) in **10** is actually less [2.73 (4) Å] than the C(3)···H(8) distance of 2.84 Å corresponding to the observed β-abstraction process. For examples of photoreactions which involve intramolecular hydrogen abstraction by the α carbon of an α,β-unsaturated ketone system, see ref 5f, 5k, and 5l.

(8) Schmidt, G. M. J. *Pure Appl. Chem.* 1971, *27*, 647–678. See also Irngartinger et al. (Irngartinger, H.; Acker, R.-D.; Rebafka, W.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 674–675) for an example of an intramolecular [2 + 2] photocycloaddition involving close (~3 Å) parallel approach of the reacting double bonds.

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Hydrolysis of Phenyl Acetates with Capped β-Cyclodextrins: Reversion from Meta to Para Selectivity

Sir:

Modeling of enzymic reactions by use of natural[1] and artificial[2] compounds has been extensively studied in the past decade. One notable advantage of the use of artificial com-

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