space group $P\bar{3}1c$ and share the following molecular details: the metal ion is coplanar with the NSi_2 plane of each of the three ligands and the silicon atoms of each of the ligands are tilted out of the MN_3 plane by about 50°. For all but the compounds of Sc, Nd, Eu, and Yb, the metal lies in the N_3 plane, whereas for the lanthanide compounds it is out of the N_3 plane by about 0.4 Å.

As before, subtraction of the appropriate values for the metal ion radius from $R(M-N)$ should yield an effective ionic radius for the ligand if the bonding is predominantly ionic. This is the case: the effective ionic radius of the silylamide ligand is constant at 1.47 (3) Å (see Figure 7a). For the purpose of such calculations, the ligand is considered to donate one electron pair to the metal and the remaining pair is involved in bonding to the silicon atoms. These complexes are therefore formally three-coordinate. Suggestions[70] that the "short" M–N bond lengths in these compounds should be attributed to metal-to-ligand back bonding are clearly unwarranted. The previous analysis did not take into account the change in the effective size of the metal ions with coordination number, which in the case of three-coordinate silylamides is especially pronounced. We believe that the molecular details of these structures are satisfactorily explained by a purely ionic description of the M–N bond. In this light, the tilt of the silicon atoms out of the MN_3 plane is due to steric crowding, and the M–N bond lengths are determined simply by balancing the opposing factors of steric crowding and the attractive force between the metal and the ligands.

(72) R. A. Andersen, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 17, 2317 (1978).

The lanthanides' displacement out of the N_3 plane is best attributed to packing forces in the solid. This view is supported by the infrared spectra, where the characteristic pyramidal bands of the scandium compound in the solid state collapse to the characteristic planar band in the solution spectrum.[70]

Concluding Remarks

We have developed a formalism, based only on structure, within which to address the question of the predominant mode of bonding in organometallic complexes of the lanthanide and actinide elements. The formalism considers the general structural features and the metal coordination number for a series of structurally related compounds. We have shown that an ionic model can explain these features as observed in organoactinides and -lanthanides well, while the same model does not work well in the d-metal MCp_2 metallocenes, where covalent bonding often predominantes. We have also shown that the ionic model can explain the observed structures of tris(silylamide) complexes of metals from all over the periodic table.

While we caution that structural variations are not usually very sensitive to small changes in bonding and alternative definitions of "ionic" and "covalent" based on other physical methods may well lead to different conclusions within such formalisms, we conclude that within the limits of our structural criteria the bonding in organoactinides and -lanthanides is ionic.

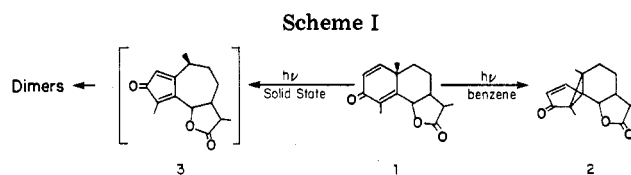# Crystal Lattice Control of Unimolecular Photorearrangements

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Many unimolecular organic photorearrangements take place by mechanisms requiring drastic conformational and configurational changes along the reaction coordinate. Consider, for example, the motions required in the complex conversion of santonin (1) to its well-known photoisomer lumisantonin (2) (Scheme I).

Equally obvious is the idea that physical restraints on a given set of atomic and molecular motions, by means as yet unspecified, can prevent these motions

John (Jerry) Scheffer was born in Missoula, Montana, in 1939 and raised in Minot, North Dakota. He received his B.Sc. and M.Sc. degrees at the University of Chicago, working with N. C. Yang, and obtained his Ph.D. degree in 1966 under the supervision of Howard Zimmerman at the University of Wisconsin. After a postdoctoral year at Yale University with Harry Wasserman, he joined the faculty at the University of British Columbia where he is currently Associate Professor. The 1973–1974 academic year was spent with Horst Prinzbach at Freiburg University under the aegis of a Guggenheim Fellowship. His current research interests include organic photochemistry, both in solution and the solid state, the chemistry of novel polycyclic ring systems of theoretical and biological interest, and the mechanisms of carbanionic rearrangements.

Scheme I

and lead to alternative reaction pathways. These "less motion" pathways, while possessing higher activation energies as compared to the unrestricted cases, nevertheless represent viable alternatives for the dissipation of the excess energy of the initially photoexcited systems. This situation is encountered, for example, in the triplet-state photochemistry of olefins: irradiation of unrestricted olefins (acyclic, exocyclic, larger ring cyclic) leads to radiationless decay via twisting about the carbon–carbon double bond, whereas photolysis of compounds in which the double bond is incorporated within a small and/or rigid ring system (for which

geometric isomerization is impossible) leads to different photoreactivity, e.g., photocycloaddition, hydrogen abstraction, di-π-methane rearrangement, etc. This type of restriction of molecular and atomic motion along a particular reaction coordinate may be termed *internal* in nature; that is, the restraints are incorporated within the molecular architecture of the system itself.

Much less common, however, is the case in which a normally favorable unimolecular reaction pathway is prevented by *external* restraints to the motions required. What sort of restraints fall under this latter heading? If molecules in dilute solution are viewed as essentially unrestrained externally, media which in principle can exert external restraints include micellar systems, monolayer assemblies, inclusion complexes, liquid crystals, glassy matrixes, and crystalline phases. These "ordered" media have the common feature that the weak forces (solvation, hydrogen bonding, electrostatic interactions, van der Waals forces, etc.) which cause the substrate ordering at the same time reduce or restrict the freedom of motion of the substrate both prior to and during reaction.

Of these media, the best defined (owing in large part to the powerful technique of X-ray crystallography) is the crystalline state. The crystalline state of organic systems is characterized by relatively large intermolecular forces which effectively restrict the rotational and translational motions of the constituent molecules.

Generally, organic compounds crystallize in a single, lowest energy conformation. As yet it has not been possible to predict in a general and simple way the preferred molecular packing arrangement for organic systems. With reference once again to olefinic systems, it is noteworthy that external crystal lattice restraints are apparently *not* sufficient to prevent cis,trans photoisomerization, particularly in the cases of sterically hindered acyclic olefins whose ground states deviate significantly from planarity.[1]

During the past 4 years, my co-workers and I have investigated the effects of crystal lattice restraints on the photochemistry of organic systems which undergo more complex unimolecular photorearrangements in solution. That such a program of research might yield interesting and unusual results was indicated in a pioneering paper by Matsuura and co-workers on the irradiation of santonin (1) in the solid state.[2] In contrast to the solution results, these authors found that photolysis of polycrystalline samples of santonin gives rise to *no* lumisantonin (2), but rather leads to products assumed to result from the formation and subsequent dimerization of the cyclopentadienone 3 (Scheme I). The structure–reactivity relationships involved in these latter transformations remain unclear and warrant further study.

Product Studies: Irradiation of Acyclic 1,3-Diene/p-Quinone Diels–Alder Adducts in the Solid State

Adducts of Duroquinone with 1,3-Dienes. Our initial efforts in the area of solid state photochemistry were centered around the Diels–Alder adducts formed between acyclic 1,3-dienes and p-quinones. Our extensive work on the *solution* photochemistry of these

Scheme II
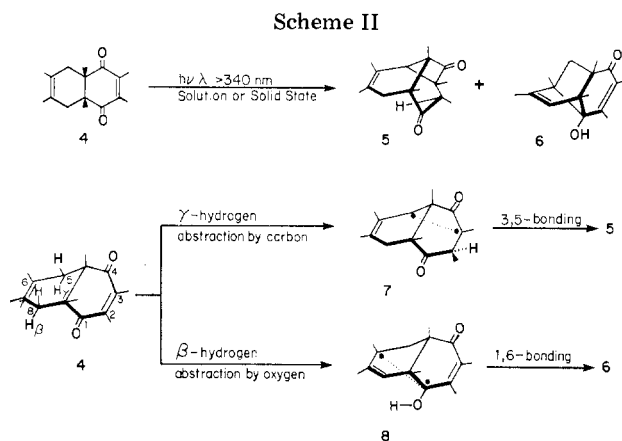
systems had shown the utilization of two main reaction pathways depending upon the substituent pattern present in the starting Diels–Alder adducts.[3] (1) For adducts formed between duroquinone and 1,3-dienes (e.g., the 2,3-dimethylbutadiene adduct 4, Scheme II), irradiation in solution affords, as major products, cyclobutanones having the general structure exemplified by 5. A minor photoproduct with the structure 6 (ratio of **5:6** = 2:1) was also formed in the solution photolysis of 4.

Formation of these photoproducts appears at first sight to require drastic molecular reorganization of 4, and it was thus intriguing to discover that irradiation of compound 4 in the *solid state* gives exactly the same two photoproducts in the identical 2:1 ratio as found in solution.[4] This apparent paradox was resolved by determination of the shape of adduct 4 in the solid state by X-ray crystallography.[5] This showed that 4 exists in a conformation which can be represented by a structure (Scheme II) in which the cyclohexene ring adopts a half-chair conformation and is cis fused to a nearly planar ene dione ring. The key feature of this finding is that this conformation is uniquely and beautifully consistent with the solid-state results. The formation of cyclobutanone 5 can be understood as proceeding via transfer of allylic hydrogen atom H_γ to C-2 of the ene dione chromophore followed by bonding of C-3 to C-5 in the resulting biradical species 7. On the other hand, the mechanism by which enone alcohol 6 is formed can be seen to involve initial abstraction of H_β by the C-1 carbonyl oxygen atom through a five-membered transition state to afford biradical 8 which in turn can close to 6. The success of these competing solid-state photoprocesses is thus seen to depend on two factors: (1) the molecule exists in a geometry favorable for the intramolecular hydrogen transfers, and (2) the intermediate species formed by abstraction are ideally arranged to undergo biradical collapse to products. Note particularly that photoproducts 5 and 6 have shapes basically similar to that of the reactant 4.

We shall see further examples of this phenomenon in later sections of this Account. Results exactly parallel to those described above were observed for the duro-

(1) M. D. Cohen, *Angew. Chem., Int. Ed. Engl.*, 14, 386 (1975).
(2) T. Matsuura, Y. Sata, and K. Ogura, *Tetrahedron Lett.*, 4627 (1968).

(3) (a) J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. A. Wostradowski, *J. Am. Chem. Soc.*, 97, 2178 (1975); (b) J. R. Scheffer, B. M. Jennings, and J. P. Louwerens, *ibid.*, 98, 7040 (1976).
(4) A. A. Dzakpasu, S. E. V. Phillips, J. R. Scheffer, and J. Trotter, *J. Am. Chem. Soc.*, 96, 6049 (1976); (b) J. R. Scheffer and A. A. Dzakpasu, *ibid.*, 100, 2163 (1978).
(5) S. E. V. Phillips and J. Trotter, *Acta Crystallogr., Sect. B*, 32, 3088 (1976).

Scheme III

quinone/*trans,trans*-2,4-hexadiene Diels–Alder adduct 9.[4b]
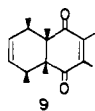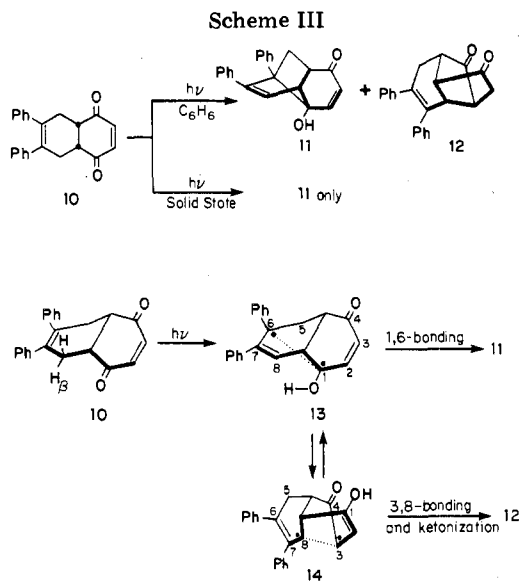
Photolysis of the *p*-Benzoquinone/2,3-Diphenylbutadiene Adduct. A second facet of our solid-state studies is exemplified by the photolysis of the Diels–Alder adduct 10 formed between *p*-benzoquinone and 2,3-diphenylbutadiene (Scheme III). Irradiation of 10 in solution gives products 11 and 12 in the ratio 3:1. Note that no cyclobutanone-type photoproducts (cf. 5) are observed in this case. Possible reasons for this are discussed in ref 4b. In contrast, photolysis of 10 in the *solid state* leads only to the enone alcohol 11; no diketone 12 is formed. Note also that the enone alcohol 11 is analogous to that isolated previously (i.e., 6). Why this difference in product ratios between the two media?

The answer to this question is straightforward once we know the shape adopted by the starting material 10 in the solid state. The X-ray crystal structure of 10 gives us this information.[6] The conformation of 10 in the crystalline phase is, with minor variations, identical with that of substrate 4. In fact, all of the quinone/acyclic diene adducts we have investigated to date (nine compounds) have this basic "twist" conformation in the solid state. This conformation is also quite certainly the major one present in solution, and we thus suggest (Scheme III) that reaction occurs from the same conformation 10 in solution as in the crystal and that the difference in results stems from the freedom of motion available to the biradical intermediate 13 formed by β-hydrogen abstraction. The argument proceeds as follows: biradical 13 will be formed in the same twist conformation as its precursor 10 and can undergo biradical collapse directly to enone alcohol 11, both in solution and in the solid state. However, formation of diketone 12 from biradical 13 is sterically impossible (examination of molecular models will quickly convince the reader of this) and requires an intervening cyclo-

(6) S. E. V. Phillips and J. Trotter, *Acta Crystallogr., Sect. B*, **32**, 3098 (1976).

Table I
Substrates, Photoproducts, and Molecular Parameters in Solid-State Hydrogen Abstraction Reactions

Diels–Alder adduct Photolysed	Enone–Alcohol Photoproduct	$H_\beta - O_1$, Å	τ_0^a	Δ_0^b	Cyclobutanone Photoproduct	$H_\gamma - C_2$, Å	τ_c^c	Δ_c^d
	11	2.46	3°	81.3°	not formed			
		2.57	5°	80.7°	not formed			
		2.58	8°	83.6°	not formed			
	6	2.47	0°	85.1°	5	2.89 Å	52°	72.6°
		2.26	1°	86.4°		2.66 Å	50°	74.4°

[a] Degree by which H_β is out of coplanarity with mean plane of the C-1 carbonyl group. [b] Angle formed between C-1, O-1, and H_β. [c] Degree by which H_γ is out of coplanarity with mean plane of C-2 to C-3 double bond. [d] Angle formed between C-3, C-2, and H_γ.

hexene half-chair to half-chair ring flip to give biradical 14. This motion is allowed in solution but prevented by crystal lattice restraints in the solid; hence photoproduct 12 is observed only in solution. Both Quinkert and co-workers[7] and Aoyama et. al.[8] have advanced similar arguments to explain the solution vs. solid-state product ratio differences observed upon irradiation of the 1,3-diphenyl-2-indanone and *N,N*-dialkyl α-oxo amide systems respectively. Finally, the reason substrate 4 (Scheme II) gives *identical* photoproduct ratios in solution and the solid state is that the bridgehead methyl substituents retard the solution-phase ring flipping of intermediates 7 and 8 relative to biradical collapse.

Quantitative Aspects: Crystallographic Distances and Angles Involved in Unimolecular Photoreactions in the Solid State

All of the photoreactions discussed thus far have been initiated by intramolecular hydrogen atom abstraction. It is instructive to tabulate for each the value of the distance between the abstracted hydrogen and the abstracting atom as well as the geometric relationship between these centers as determined by X-ray crystallography. Table I summarizes these data for the five substrates which take part in photoinitiated solid-state β-hydrogen abstraction by carbonyl oxygen (leading to enone alcohol formation) as well as the two Diels–Alder adducts which undergo γ-hydrogen abstraction by enone carbon to give cyclobutanone-type photoproducts.

The parameters in Table I do not represent the actual distances and angles involved at the moment of photochemical reaction since the crystallographic values of course refer to the situation in the ground electronic state. Nonetheless the data in Table I afford insight into the factors which favor these reactions. This is particularly the case for the β-hydrogen abstractions by oxygen, since it seems likely[9] that the carbonyl moiety

(7) G. Quinkert, T. Tabata, E. A. J. Hickman, and W. Dobrat, *Angew. Chem., Int. Ed. Engl.*, **10**, 198 (1971).
(8) H. Aoyama, T. Hasegawa, and Y. Omote, *J. Am. Chem. Soc.*, **101**, 5343 (1979).

of enones (and therefore presumably also of enediones) retains its basic ground-state geometry upon photoexcitation. Even for the hydrogen atom abstractions by enone carbon, the crystallographic H_γ to C-2 distances may fairly accurately represent the excited-state situation since the twisting about the enone carbon–carbon double bond, which accompanies formation of the reactive $(\pi,\pi^*)^3$ state,[9] should primarily affect only τ_c. In fact, such twisting may actually *facilitate* abstraction by tilting the abstracting C-2 2p atomic orbital more directly toward H_γ, i.e., by increasing the value of τ_c more toward the ideal of 90°.

The distances over which hydrogen abstraction occurs in the systems studied range from 2.26 to 2.58 Å when oxygen is the abstracting atom and from 2.66 to 2.89 Å for carbon. These values are consistent with the fact that carbon has a greater van der Waals radius (1.70 Å) than oxygen (1.52 Å).[10] We suggest, on consideration of the measured crystallographic parameters, that intramolecular hydrogen abstractions can occur over distances which approach the sum of the van der Waals radii of the atoms involved. Since hydrogen has a van der Waals radius of 1.20 Å,[10] these sums are 2.72 Å for oxygen and hydrogen and 2.90 Å for carbon and hydrogen. These values are considerably greater than those previously assumed on the basis of calculations and/or molecular models.[11] We shall encounter additional examples of hydrogen abstractions which adhere to these van der Waals radii sum guidelines in later sections of this Account.

Also important for efficient abstraction is a favorable geometric relationship between the abstracting atomic orbital and the hydrogen being abstracted. This condition is nearly ideally met in the β-hydrogen abstractions by oxygen encountered in our work. As summarized in Table I, the β-hydrogen atom in each case is situated within a few degrees of the mean plane of the abstracting carbonyl group, a perfect arrangement for the now well-established[12] involvement in hydrogen abstractions of the $n \rightarrow \pi^*$ derived half-filled oxygen n orbital which also lies in this plane. The values of Δ_o for these systems (approaching 90°; cf. Table I) are also nearly ideal for carbonyl oxygen n-orbital participation.
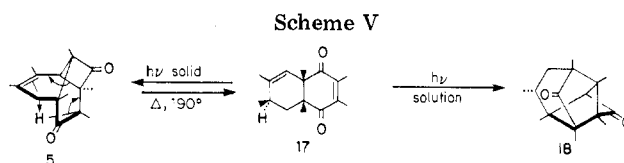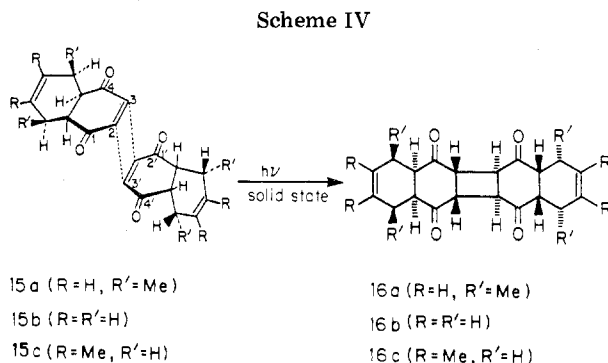
Aoyama and co-workers[8] have recently reported very interesting solid-phase studies of intramolecular six-membered transition state (type II) hydrogen abstractions by oxygen in the *N,N*-dialkyl α-oxo amide system. However, the absence of X-ray crystal structure data for their substrates precludes quantitative comparison

(9) (a) J. J. McCullough, H. Ohorodnyk, and D. P. Santry, *Chem. Commun.*, 570 (1969); (b) D. A. Haner and D. A. Dows, *J. Mol. Spectrosc.*, 34, 296 (1970); (c) G. Marsh, D. R. Kearns, and K. Schaffner, *J. Am. Chem. Soc.*, 93, 3129 (1971); (d) R. R. Birge, W. C. Pringle, and P. A. Leermakers, *ibid.*, 93, 6715 (1971); (e) R. R. Birge and P. A. Leermakers, *ibid.*, 93, 6726 (1971); (f) *ibid.*, 94, 8105 (1972); (g) A. Devaquet, *ibid.*, 94, 5160 (1972); N. C. Baird and R. M. West, *Mol. Photochem.*, 5, 209 (1973). See, however, C. E. Dykstra, *J. Am. Chem. Soc.*, 98, 7182 (1976), and C. R. Jones and D. R. Kearns, *ibid.*, 99, 344 (1977), for indications that the $^3(\pi,\pi^*)$ state of enones may be planar.

(10) A. Bondi, *J. Phys. Chem.*, 68, 441 (1964). See also J. T. Edward, *J. Chem. Educ.*, 47, 261 (1970).

(11) For example, Winnik assumes a spherical "reactive volume" for the carbonyl group in intramolecular photochemical hydrogen-abstraction reactions and finds that values of its radius ranging from ca. 1.7 to 2.1 Å are best in accord with theoretical calculations of C_{eff}, the effective concentration of hydrocarbon chain elements containing abstractable hydrogen atoms with the reactive volume. See M. A. Winnik, *Acc. Chem. Res.*, 10, 173 (1977), and references cited therein.

(12) N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, CA, 1978, Chapter 10.

Scheme IV

15a (R=H, R'=Me)   16a (R=H, R'=Me)
15b (R=R'=H)   16b (R=R'=H)
15c (R=Me, R'=H)   16c (R=Me, R'=H)

Scheme V

with our results on the corresponding five-membered transition-state process.

Competing Unimolecular and Bimolecular Processes in the Solid State

A great deal of work has been published in recent years on the roles that crystal lattice restraints and packing arrangements play in *bimolecular* photochemical processes.[13] The type of reaction which has been investigated most extensively is $[_\pi 2_s + _\pi 2_s]$ cycloaddition. It has been established[13] that the success of this process in the solid state requires a packing arrangement in which the reacting double bonds are parallel to one another with mean interplanar distances of $< \sim 4.1$ Å. When these conditions are met, photocycloaddition occurs in such a way that the intrinsic and relative geometries of the reacting double bonds in the crystal lattice are retained in the cyclobutane product; such processes are said to be topochemically controlled.[14]
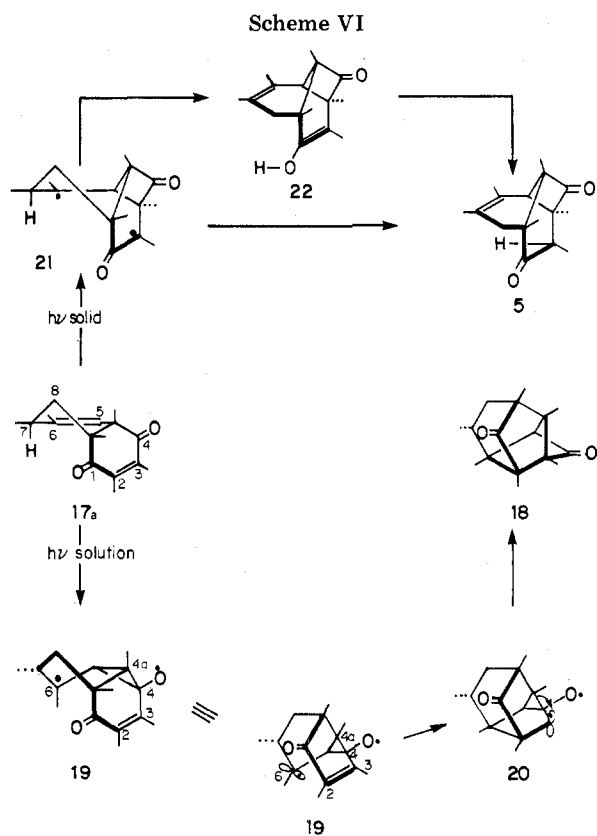
Three of the nine tetrahydronaphthoquinone systems whose solid-state photochemistry we have investigated undergo similar topochemically controlled intermolecular processes (15a–c). The exclusive photoproducts are the dimers 16a–c respectively, formed via [2 + 2] photocycloaddition between the enedione double bonds of adjacent molecules (Scheme IV).[15] Scheme IV also shows the parallel, slightly offset orientation of the reacting double bonds (center to center distances ≤4.04 Å) within the molecular crystal lattice as determined by X-ray crystallography. Of the nine tetrahydronaphthoquinones studied, this close parallel approach is unique to substrates 15a–c.

These results are interesting in view of the fact that the X-ray crystal structure of, e.g., 15b reveals that it should be capable of solid-state intramolecular hydrogen abstraction identical with that observed previously (H_β to O = 2.42 and 2.49 Å, $\tau_o = 4°$ and 3°, and $\Delta_o =$

(13) G. M. J. Schmidt, *Pure Appl. Chem.*, 27, 647 (1971).

(14) These results led to the development of the well-known topochemical principle which states that reactions in organic crystals tend to occur with a minimum of atomic and molecular motion. See, for example, M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1996 (1964), as well as a more recent discussion by Cohen.[1]

(15) The structure of these photodimers was established by X-ray crystallography: (a) S. E. V. Phillips and J. Trotter, *Acta Crystallogr., Sect. B*, 33, 984 (1977); (b) *ibid.*, 33, 991 (1977).

Scheme VI

21
hν solid

22
H—O

5

8
7 6
H
5
O 4
1
2 3

17a
hν solution

18

19
6
O
O
2
4a
O
4
3

≡

O
6
4a
2
O·
3

→

O
O·
20

19

80.8° and 79.5°).[16]   Therefore adoption of a crystal packing arrangement favorable for bimolecular reaction can overcome the advantageous entropy effects which normally favor unimolecular reactivity. These results also emphasize that knowledge of the packing arrangement of substrates in the solid state is essential for making sound photochemical predictions.

Irradiation of a β,γ-Unsaturated Ketone in the Solid State

The cyclobutanone 5, upon thermolysis at 190°, undergoes a retro-ene reaction (arrows, Scheme V) affording high yields of the crystalline β,γ-unsaturated ketone 17.[3a] The unusual chromophoric system present in 17 prompted a study of its photochemistry. A remarkable finding was that irradiation of 17 in solution gives results completely different from those obtained when 17 is photolyzed in the solid state. In solution, diketone 18 is the exclusive photoproduct, while in the solid phase, cyclobutanone 5 is nearly quantitatively regenerated upon photolysis (Scheme V).[17]

In order to understand these transformations better, we again turned to X-ray crystallography. The X-ray crystal structure of substrate 17 revealed that it exists in conformation 17a as shown in Scheme VI.[18] Note particularly, in accord with the principle that organic molecules generally crystallize in their most stable conformations, that this conformation places the bulky methyl group at C-7 in the pseudoequatorial rather than the pseudoaxial position. This is a critical point in the

solid-state photorearrangement.

First, however, we turn to a discussion of the probable mechanism of the solution lumiprocess. Almost certainly this also involves conformation 17a. We suggest (Scheme VI) that 17a behaves as a typical $^3(\pi,\pi^*)$ excited β,γ-unsaturated ketone; that is, it undergoes the first step of the well-known[19] oxa-di-π-methane rearrangement which consists of carbonyl carbon/vinyl bridging to give, in the case of 17a, species 19. At this point, while the exact *sequence* of steps followed is not certain, it is clear that diketone 18 can be formed by (a) cleavage of the C-4 to C-4a bond, (b) bonding of C-4a to C-3, and (c) bonding of C-6 to C-2. One possible sequence, initiated by step c, is illustrated in Scheme VI. Space does not permit a detailed comparison of the relative merits of alternative sequences. Furthermore, for the purposes of this Account, the point of the preceding mechanistic discussion is not the timing of the steps involved but rather the realization that the formation of photoproduct 18 involves a complex series of sterically demanding steps, each of which involves substantial atomic motion and molecular deformation and leads to a final product whose shape bears little resemblance to that of its progenitor. As we shall see, this is *not* the case for the solid-state photorearrangement. This basic difference is very likely the key factor which explains the different results obtained in the two media.

Turning now to the irradiation of substrate 17 in the solid state, we might think that formation of the final photoproduct 5 would also require motions which should be prohibited by the crystal lattice. However, a different perspective of cyclobutanone 5 (Scheme VI) reveals that 5 in fact has a shape very similar to the conformation 17a adopted by the starting material in the solid state. The formation of 5 is envisaged as occurring via initial C-3 to C-5 bond formation in 17a to give species 21 followed by intramolecular transfer of the pseudoaxial hydrogen at C-7 to C-2, either directly or through the intermediacy of enol 22. The feasibility of this process is indicated first by the fact that the shape of 17a is such that the back lobes of the 2p orbitals at C-3 and C-5 are pointing nearly directly at one another with an interatomic separation of 3.12 Å, well below the sum of the van der Waals radii for two carbon atoms (3.40 Å). Second (as mentioned earlier), the configuration at C-7 is uniquely favorable for the intramolecular hydrogen transfer which completes the rearrangement. The H-7 to O-1 separation in 17a is 2.64 Å with $\tau_o = 28.5°$ and $\Delta_o = 84.7°$.

A second mechanistic possibility, which differs from that discussed above only in the sequence of the steps involved, has as its first step C-7 hydrogen abstraction by carbonyl oxygen which is then followed by C-3 to C-5 bond formation. This is deemed less likely in view of the likelihood that the reactive excited state of 17 is heavily $\pi \rightarrow \pi^*$ weighted. The reluctance of $\pi \rightarrow \pi^*$ excited states of carbonyl compounds to participate in intramolecular hydrogen abstraction reactions is well established.[12]

In summary, then, it appears that the solid-state/solution reactivity differences observed for 17 stem from

(16) Each parameter for 15 has two values owing to the fact that there are two independent molecules with very slightly different shapes in the unit cell.

(17) W. K. Appel, T. J. Greenhough, J. R. Scheffer, and J. Trotter, *J. Am. Chem. Soc.*, **101**, 213 (1979).

(18) T. J. Greenhough and J. Trotter, *Acta Crystallogr., Sect. B*, in press.

(19) (a) S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973); (b) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Fortschr. Chem. Forsch.*, **54**, 73 (1975); (c) K. N. Houk, *Chem. Rev.*, **76**, 1 (1976); (d) K. Schaffner, *Tetrahedron*, **32**, 641 (1976).

Scheme VII

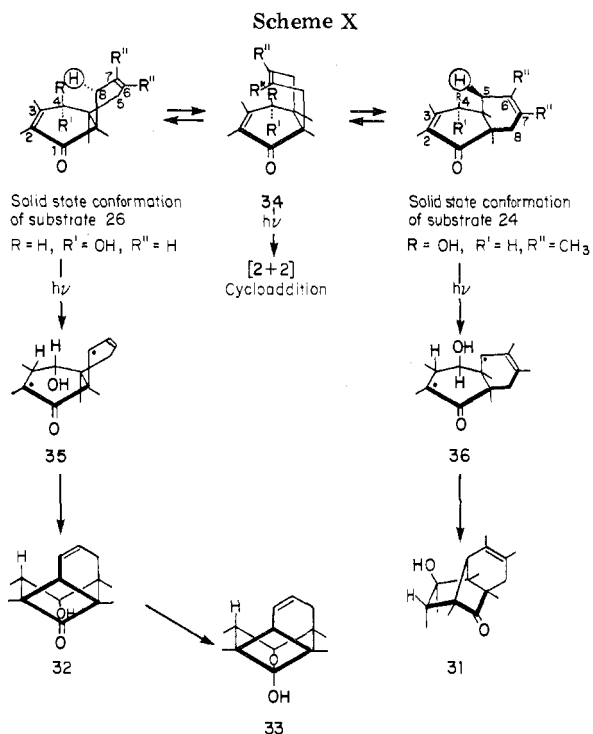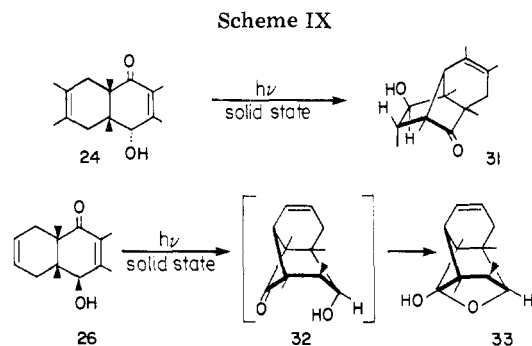**Scheme VIII**

Scheme IX

Scheme X
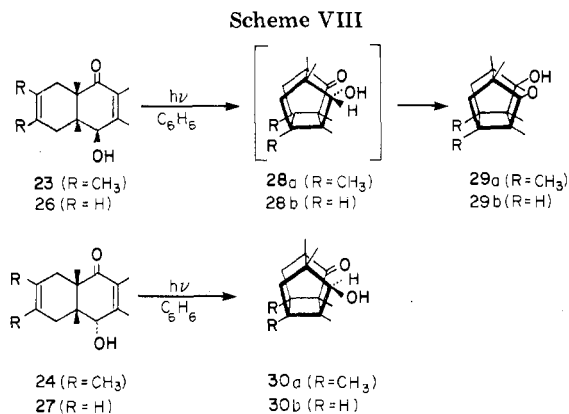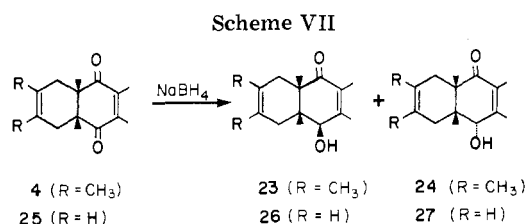
the fact that the motions required to form the normally favored solution photoproduct are too great to be permitted by the crystal lattice. This may be termed a "topochemically forbidden" reaction. As a result, a "less motion" pathway giving rise to a different photoproduct is observed in the solid state. Specifically, formation of **5** from **17a** requires only the relatively minor processes of rehybridization of carbon atoms 2, 3, 5, and 7 plus a decrease in the C-3 to C-5 contact; the basic molecular shape remains constant throughout the transformation.

Irradiation of Cyclohexenones in the Solid State

With the idea in mind that it would be interesting to compare the photochemistry of an enone chromophoric system with that of its ene dione counterpart, we turned next to an investigation of the photoreactivity of the 4a,5,8,8a-tetrahydro-1-naphthoquin-4-ol system which, following a suggestion by Dr. Kurt Schaffner of the Max Planck Institute, Mülheim, West Germany, is readily available by sodium borohydride reduction of the quinone/diene Diels–Alder adducts whose photochemistry is described above. For example, reduction of the duroquinone/2,3-dimethylbutadiene Diels–Alder adduct **4** leads to a mixture consisting of alcohols **23** (50%) and **24** (35%) (Scheme VII); similar results were obtained in the case of the duroquinone/butadiene adduct **25** with yields of reduction products **26** and **27** being 63% and 31%, respectively.

The photochemistry found for these systems in the solid state was once again dramatically different from that observed in solution.[20] We first describe our solution results which are summarized in Scheme VIII. Both direct and benzophenone-sensitized irradiation (γ > 330 nm) of benzene solutions of the four tetrahydronaphthoquinols described above affords essentially quantitative yields of intramolecular [2 + 2] cycloaddition products having the tetracyclo-[5.3.0.0^{2,6}.0^{4,9}]decane ring skeleton. In the case of substrates **23** and **26**, the configuration at the hydroxyl-bearing carbon is such that the initially formed keto alcohols **28a** and **28b** immediately undergo internal hemiacetal formation, affording **29a** and **29b**, respectively. This is of course impossible in the case of the photoproducts **30a** and **30b**, with the result that these keto alcohols are isolated as such.

In contrast, irradiation of these substrates in the solid state gives no cage product formation. However (as found in solution), the nature of the photoproducts which are observed in the solid state depends on the hydroxyl group stereochemistry. The results obtained with **24** (α-OH) and **26** (β-OH) are representative and are summarized in Scheme IX. Irradiation of polycrystalline samples of **24** gives high yields of keto alcohol **31**, and similar photolysis of **26** leads essentially quantitatively to hemiacetal **33**.[21] As we shall see, **33** is formed via keto alcohol **32**.

Of numerous questions that arise from the chemistry outlined in Schemes VIII and IX, two are salient: (1) what factors give rise to the solution/solid-state reactivity differences observed, and (2) why do substrates **24** and **26** behave differently upon irradiation in the solid state? X-ray crystallography once again provides

(20) (a) W. K. Appel, T. J. Greenhough, J. R. Scheffer, J. Trotter, and L. Walsh, *J. Am. Chem. Soc.*, **102**, 1158 (1980); (b) *ibid.*, **102**, 1160 (1980).

(21) Structure(s) established by X-ray crystallography: T. J. Greenhough and J. Trotter, *Acta Crystallogr., Sect. B*, submitted for publication.

the answers. Scheme X shows the conformations adopted by cyclohexenones **24** and **26** in the solid state.[21] Although they are different, both can be described as consisting of a half-chair cyclohexene ring cis fused to a second half-chair-like cyclohexenone moiety. The difference between them stems from the fact that the hydroxyl group of each seeks the lower energy pseudoequatorial position. Since **24** and **26** have opposite configurations at the hydroxyl-bearing carbon atom, substrate **24** adopts a preferred conformation which is the ring-flipped counterpart of **26**.

We are now in a position to understand the solid-state results. Photoproduct **33** arises from conformer **26** 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 **35**. On the other hand, photoproduct **31** is formed through conformer **24** by means of a C-5 to C-3 allylic hydrogen transfer and subsequent C-2 to C-5 bonding in the species **36** so produced. Note that the hydrogen transfer in this latter instance involves a cyclic five-membered transition state. To the best of our knowledge, this is the first example of such a process in which carbon is the abstracting atom.
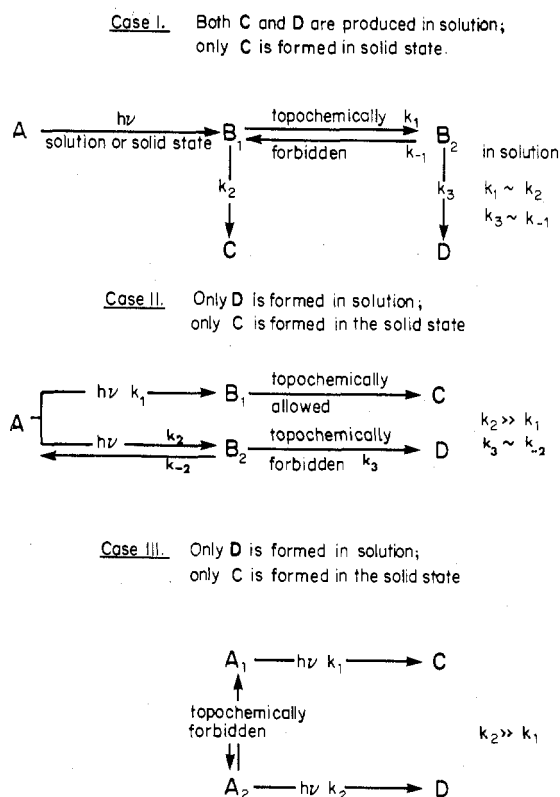
As in other cases discussed above, the course of events followed in the case of substrates **24** and **26** is seen to involve minimal molecular distortion and deformation. The hydrogen abstraction distances of 2.72 Å for **24** and 2.84 Å for **26** are both within the suggested 2.90 Å guideline for abstraction by carbon, and the values of the geometric parameters involved (for **24** $\tau_c = 53.2°$ and $\Delta_c = 78.5°$; for **26** $\tau_c = 48.8°$ and $\Delta_c = 71.5°$) are very similar to those measured for Diels–Alder adducts **4** and **9** (cf. Table I) which also take part in carbon abstraction. Equally important is the fact that the biradicals produced by abstraction (**35** and **36**) can close to products without necessity for an intervening major conformational change.

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 **24** and **26** owing to the relatively large double bond separations involved (≥4.37 Å in every case) as well as their nonparallel orientations. As pointed out earlier in this Account, 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.[13] On the other hand, in media where conformational equilibration is facile, small amounts of conformers which better fulfill these requirements (e.g., **34**) will be present. It is thus reasonable to suggest that rapid [2 + 2] photocycloaddition from these minor, higher energy conformers can predominate in solution.

Concluding Remarks

We have shown that solid-state unimolecular photorearrangements may differ from their solution-phase counterparts in three ways. (1) For systems which undergo identical primary photoprocesses in both media to give a common intermediate which then partitions itself among two or more products, the final product *ratios* may vary depending on the motions required in the partitioning steps. Specifically, a product requiring a major conformational change of the intermediate in its formation will be absent (topochemically forbidden) in the solid state. This situation is outlined in case I,

Scheme XI

Case I. Both C and D are produced in solution; only C is formed in solid state.

Case II. Only D is formed in solution; only C is formed in the solid state

Case III. Only D is formed in solution; only C is formed in the solid state

Scheme XI, and applies to Diels–Alder adduct **10**.

(2) For substrates which undergo competing primary photoprocesses (both in solution and the solid state) to produce two different intermediates (case II), the results obtained in the solid state will differ from those observed in solution if the subsequent conversion of these intermediates to final products is topochemically allowed in one case and topochemically forbidden in the other. A further proviso is that in solution $k_2 \geq k_1$. In particular, if $k_2 \gg k_1$ (and $k_3 \sim k_{-2}$), only D will be formed in solution and only C in the solid state. This is the situation which applies to the β,γ-unsaturated ketone **17**. If $k_2 \sim k_1$, both C and D will be formed in solution and only C in the solid state. If $k_2 \ll k_1$, C will be the exclusive product both in solution and the solid state.

(3) Finally we have the situation outlined in case III in which the crystal lattice controls the equilibrium between two reactive conformers of the starting material. Only the lower energy conformer A_1 is present in the solid state. In solution A_1 is still the predominant conformer, but a small equilibrium concentration of A_2 is also present. For solid-state results to differ completely from those in solution, the requirement is that $k_2 \gg k_1$. This is the situation in the case of cyclohexenones **24** and **26**. Rate constant k_1 refers to the overall process of intramolecular hydrogen abstraction and biradical closure, and k_2 is the rate constant for intramolecular [2 + 2] photocycloaddition. As k_1 approaches k_2, increasing amounts of photoproduct C will be observed in solution until the $k_1 \gg k_2$ limit is reached, which will result in C being the sole product in both media.

The observation of unimolecular photorearrangements which differ in the solid state and solution greatly enlarges the scope of organic photochemistry. How

many of the literally hundreds of other well-characterized solution lumirearrangements will also be found to have totally different solid-state counterparts? Perusal of the photochemical literature reveals a number of systems which may be expected to exhibit case I or case II behavior. In addition, there are several examples of systems which likely react via nonminimum energy conformations in solution and which might therefore show different photobehavior in the solid state via case III mechanisms.

Not only is the synthetic potential of organic photochemistry enhanced by findings such as those reported in this Account, but with the use of X-ray crystallography, deeper insights into the mechanistic structure–

reactivity relationships involved in organic photorearrangements are possible. In short, studies of organic solid-state unimolecular photoprocesses are likely to provide fascinating and useful results for some time to come.

A van der Waals Picture of the Isotropic–Nematic Liquid Crystal Phase Transition

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Long-range orientationally ordered states of liquids composed of elongated, flat molecules have been known for almost a century.[1] The simplest fluid–fluid transition involving these "liquid crystal" systems takes place between the normal isotropic phase and a nematic state where the long molecular axes tend to lie along a preferred direction. But in the nematic state there is *no* long-range ordering of the centers of mass. Thus the system retains to a great extent many of the familiar properties, e.g., viscosity, characteristic of ordinary liquids. Only in the solid phase do we find long-range ordering of both the molecular orientations and centers of mass: hence the name "liquid crystal" for the nematic state.

In a liquid crystal, each molecule interacts with its neighbors via forces which depend on their mutual orientations. To "keep out of each other's way", i.e., to minimize repulsions, a parallel configuration is optimal; in addition this arrangement enhances the pair attractions. Recall that the thermodynamic free energy, A, is a balance between the total interaction energy, E, and the temperature-weighted entropy, TS; $A = E - TS$. Thus, at low enough temperature we expect that the lowering of E which comes about from parallel arrangements of molecules will become sufficient to offset

the decrease in S attendant upon this long-range alignment. The likelihood of this happening before the freezing (liquid → solid) temperature is reached depends of course on the intermolecular potential being properly anisotropic. The ultimate goal of any theory of liquid crystals must then be to account for why the phase diagrams for thousands of compounds include an "extra", orientationally ordered fluid, region whereas those for hundreds of thousands of others show only the usual fluid and solid phases.[2]

The transition between isotropic and nematic states is observed to be first order, but the differences in density (ρ), enthalpy (H), and entropy (S) between the coexisting phases are dramatically small. Consider, for example, the prototype liquid crystal forming molecule *p*-azoxyanisole (PAA) shown in Figure 1. When it is cooled below 408 K at atmospheric pressure, it undergoes a first-order transformation from the isotropic to nematic phase: the associated discontinuities are as small as $\Delta\rho/\bar{\rho} \approx 0.0035$, $\Delta H \approx 0.14$ kcal/mol, and $\Delta S \approx 0.34$ cal/(mol K).[3] (Here $\bar{\rho}$ is the average of the densities of the coexisting phases.) Upon further cooling of the nematic state it is transformed near $T = 390$ K to a solid; at the freezing transition the discontinuities are larger by one to two orders of magnitude—the values of $\Delta\rho/\bar{\rho}$, ΔH, and ΔS are 0.11, 7.1 kcal/mol, and 18 cal/(mol K).[4]

Descriptions of the isotropic–nematic transition have been largely phenomenological,[5] but recently there have

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(1) For mention of early work on liquid crystals, see the references given in the review by G. W. Gray, *Adv. Liquid Cryst.* **2**, 1 (1976).

(2) See, for example, the tabulations provided by D. Demus, H. Demus, and H. Zaschke, Flüssige-Kristallen in Tabellen (1974).

(3) W. Maier and A. Saupe, *Z. Naturforsch., A*, **14A**, 882 (1959); **15A**, 287 (1960), for $\Delta\rho/\bar{\rho}$; H. Arnold, *Z. Phys. Chem.* (Leipzig), **226**, 146 (1964), for ΔH and ΔS.

(4) B. Deloche, B. Cabane, and D. Jerome, *Mol. Cryst.*, **15**, 1975 (1971).