Organic Photochemistry in the Solid State. The Distance and Geometric Requirements for Intramolecular Hydrogen Abstraction Reactions. Structure–Reactivity Relationships Based on X-Ray Crystallographic Data[1]

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Abstract: The solid state photochemistry of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone and eight of its substituted derivatives has been investigated and the results have been correlated with x-ray crystal structure data for eight of the nine compounds. Regardless of substitution pattern, all of the substrates possess a common solid state "twist" conformation in which the cyclohexene moiety exists in a half-chair form cis fused to a nearly planar cyclohex-2-ene-1,4-dione ring. Despite their identical conformations, identical reactivities were not observed for the nine substrates. Five took part in intramolecular hydrogen abstraction processes, three underwent topochemically controlled bimolecular [2 + 2] ene–dione double bond photocycloaddition, and one gave rise to internal oxetane formation. The x-ray data showed that bimolecular [2 + 2] photoaddition occurred only when the crystal lattice was such that adjacent molecules were oriented so that the reacting double bonds were parallel with center to center distances of less than ca. 4.1 Å; failing that, unimolecular photoprocesses prevailed. Two intramolecular hydrogen abstraction reactions were observed: (1) abstraction by carbonyl oxygen through a five-membered transition state, and (2) abstraction by double bond carbon via a six-membered transition state. Both processes are facile in the solid state owing to favorable geometric and distance factors. The structural parameters associated with these abstractions are summarized and are compared to values previously estimated in the literature. This reveals that abstraction can take place over distances considerably greater than heretofore considered favorable, and the data suggest that with favorable geometry these distances can be at least as great as the sum of the van der Waals radii of the abstracting and abstracted atoms. The excited states giving rise to the two hydrogen abstraction processes are tentatively identified, and the general validity of formulating ground state structure–excited state reactivity relationships for these states is discussed. Equally important to the observation of the internal solid state hydrogen transfer reactions is the fact that the biradical intermediates produced by abstraction can collapse directly to stable products without the necessity for conformational isomerization. This is predicated on the reasonable assumption that the biradical has the same basic conformation as its ground state precursor. Intramolecular photochemical oxetane formation is observed only for the one substrate which has no neighbors in position to afford [2 + 2] photodimers and for which internal hydrogen abstraction is made geometrically impossible by replacement of the normally abstractable allylic hydrogen atoms by methyl groups. The fact that internal oxetane formation is geometrically feasible but undetected for all the other substrates tested indicates that it is the least favored of the solid state photoreactions. Finally, the close similarity observed between the solid state and the solution results for certain of the substrates (excluding those compounds which photodimerize in the solid state) strongly indicates reaction via the twist conformation in solution as well as in the solid, with any differences between the two arising from the freedom of motion in solution of the initially formed biradical intermediates.

The construction of detailed structure–reactivity relationships for the reactions of conformationally mobile organic molecules in solution or the gas phase is complicated by our inability to accurately determine their precise prereaction shapes and orientations with respect to their neighbors in these phases. The combination of organic solid state chemistry and x-ray crystallography, on the other hand, has proved to be an extremely powerful tool for structure–reactivity correlations[3-10] owing to the facts that (a) one has, via x-ray crystallography, a method to essentially "photograph" (in stereo, no less!) the reacting molecule and its surroundings, and (b) owing to the restraints on diffusion and rotation imposed by the crystal lattice on its constituents, reactions in the solid state tend to occur with a minimum of atomic and molecular motion.[11]

These lattice restraints exert two major types of influence on reactions occurring in the solid state. (1) Insofar as the molecules making up the lattice are held in specific conformations which in turn predispose the molecules to specific reaction pathways, solid state reactions will differ from those observed for the same molecules in solution or the gas phase if these conformations are either not present or are involved in rapid conformational isomerism with other reactive conformers in the liquid or gaseous state. These effects can play a role in both bimolecular and unimolecular processes, although they may be expected to be of particular importance for *intramolecular* reactions which are often more sensitive to conformational changes than bimolecular processes. (2) If the molecular packing in the crystal is such that adjacent molecules are favorably oriented with respect to one another for reaction to occur, then we may expect that this reaction will predominate in the solid state in contrast to more mobile phases where different geometries of approach may be favored leading to different products. These principles will apply of course to *intermolecular* reactions.

Up to the present time, nearly all organic photochemical studies in the solid state have dealt with reactions falling under category (2), specifically, lattice-controlled [2 + 2][3] and [4 + 4][10] photodimerizations. The use of the solid state method for the investigation of conformation-dependent unimolecular photoprocesses is essentially unreported.[12] In the present paper we report the first example of such a study. The reaction chosen for investigation was that of intramolecular photochemical hydrogen abstraction by excited carbonyl oxygen, one of the most ubiquitous of solution and/or gas phase photoprocesses. The present solid state results provide definitive information, heretofore lacking, on the distances over which intramolecular hydrogen abstraction can occur and on the preferred reaction geometries. In addition, since certain of the substrates investigated were found to undergo intermolecular photoprocesses, the results reported in this work allow interesting conclusions to be drawn concerning the factors which govern unimolecular vs. bimolecular reactions in the solid state.

Results and Discussion

The substrates chosen for study all possess the basic *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone ring structure **1** (Scheme I) and are in general readily available via the

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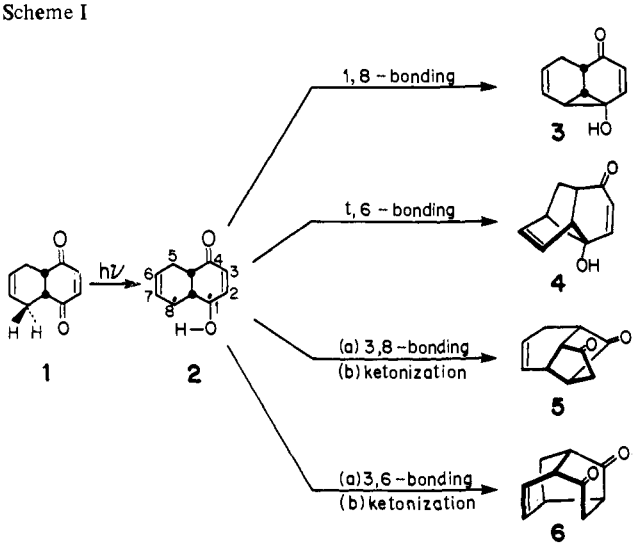
Scheme I



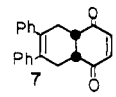
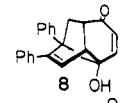
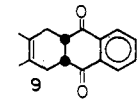
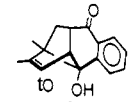
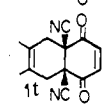
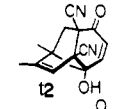
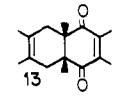
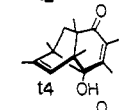
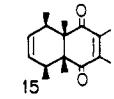
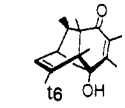
Diels–Alder reaction between various substituted *p*-benzoquinones and acyclic 1,3-dienes. They were chosen for two basic reasons: (1) Their solution phase photochemistry has been extensively studied and shown to be intramolecular in nature as well as conformation dependent.[13] (2) Nearly all of the substrates prepared were moderately high melting solids with crystal modifications which appeared suitable for x-ray crystallography.

Our previous work[13] on the solution phase photochemistry of the *cis*-tetrahydronaphthoquinone system **1** showed that the major course of reaction was intramolecular allylic hydrogen abstraction by the carbonyl oxygen through a five-membered transition state to give the (presumably) diradical species **2** (Scheme I) which, because of its cis ring junction stereochemistry, is capable of interannular biradical collapse to give the novel tricyclic ring systems **3–6**. Although no examples of keto alcohol **3** have yet been isolated,[13] the other three photoproduct types have routinely been observed in our solution results; in some instances all three may be formed from the same precursor tetrahydronaphthoquinone. An additional point of interest in our study of the solid state photochemistry of **1** and its analogues was thus raised, namely, the extent to which crystal lattice forces would influence not only the primary photochemical step in the reaction sequence but also the subsequent behavior of any biradical (e.g., **2**) or other metastable intermediate along the reaction pathway.

General Experimental Procedure. A useful preliminary test to determine whether or not (as well as how) a given substrate would react photochemically in the solid state was to irradiate potassium bromide pellets of the compound in question and follow the course of the reaction by infrared spectroscopy. Despite suggestions that the results obtained for reactions occurring in KBr pellets and pure crystals are not comparable,[3a,11f] we found a good correlation between the two methods in the nine compounds investigated in this project.

The pure crystal irradiations themselves were carried out in a special variable temperature, evacuable apparatus which is described in the Experimental Section. The crystals were grown on the surface (gold plated) of the inner reaction vessel by slow (1–2 days) evaporation of solutions of the substrate under investigation. The last traces of solvent were removed by pumping on the sample (10^{-3}–10^{-2} Torr) for 1–2 h prior to photolysis, and this vacuum was maintained during the irradiation in order to exclude oxygen. The reaction temperature was chosen so as to be well below the eutectic temperature of the reaction mixture. This temperature was determined by differential scanning calorimetry on samples of varying composition prepared by mixing the reaction mixtures and starting materials in differing amounts.

Table I. Substrates, Photoproducts, and Molecular Parameters in Solid State Enone–Alcohol Formation

Substrate	Photoproduct	H_β–O, Å	τ_0[a]	Δ_0[b]	C_1–C_6, Å
		2.46	3°	81.3°	3.51
		2.57	5°	80.7°	3.46
		2.58	8°	83.6°	3.38
		2.47	0°	85.1°	3.35
		2.26	1°	86.4°	3.33

[a] For a definition of τ_0 see Figure 2. [b] The angle formed between the carbonyl carbon, the carbonyl oxygen, and the hydrogen being abstracted.

All samples were irradiated at wavelengths above 340 nm by means of passing the output of a 450-W Hanovia medium-pressure mercury lamp through an interposed sheet of Corning 7380 filter glass. This wavelength excites the low intensity (ϵ <150), near-visible absorption band common to all the compounds studied.[14] Conversions were generally kept low (<30%) so as to avoid complete destruction of the parent lattice and possible resulting loss of topochemical control, although in most instances near-complete conversions and high chemical yields could be achieved without noticeable loss of specificity or change in product ratios.

Concomitant with the photochemical studies, the crystal and molecular structure of each of the substrate tetrahydronaphthoquinones was determined by direct methods. This indispensible portion of the project was elegantly and expeditiously carried out by Trotter and Phillips.[15] All of the x-ray crystal structure data which follow and which are used to explain the solid state results are drawn from this work.

The nine compounds studied in this project fall into four subgroups based on the differences observed in their solid state photoreactivities. As we will show, these reactivity differences do not arise from conformational differences among the substrates, but rather from differences in their *intermolecular* contacts and crystal lattice packing arrangements as well as differences in their substitution patterns. Each of the four subgroups will be described and discussed in turn.

Enone–Alcohol Formation. Five of the nine substrates studied in this work gave so-called enone–alcohol photoproducts of general type **4** (Scheme I) upon irradiation in the solid state. The actual starting material and photoproduct structures are shown in Table I. In the case of tetrahydronaphthoquinones **7, 9,** and **11,** the corresponding enone–alcohols **8, 10,** and **12** were the only photoproducts isolated. Similar results were observed for **9** and **11** in solution,[13b] but irradiation of substrate **7** in solution gave both enone–alcohol **8** and diketone **17** (Scheme II) in the ratio of 3:1.

In the case of substrates **13** and **15,** the enone–alcohols **14** and **16** were minor products both upon irradiation in the solid state as well as in solution; the major photoproduct in each photolysis possessed the so-called cyclobutanone structure (**20** and **21,** respectively) shown in Table III. The ratios of enone–alcohol to cyclobutanone photoproducts obtained by

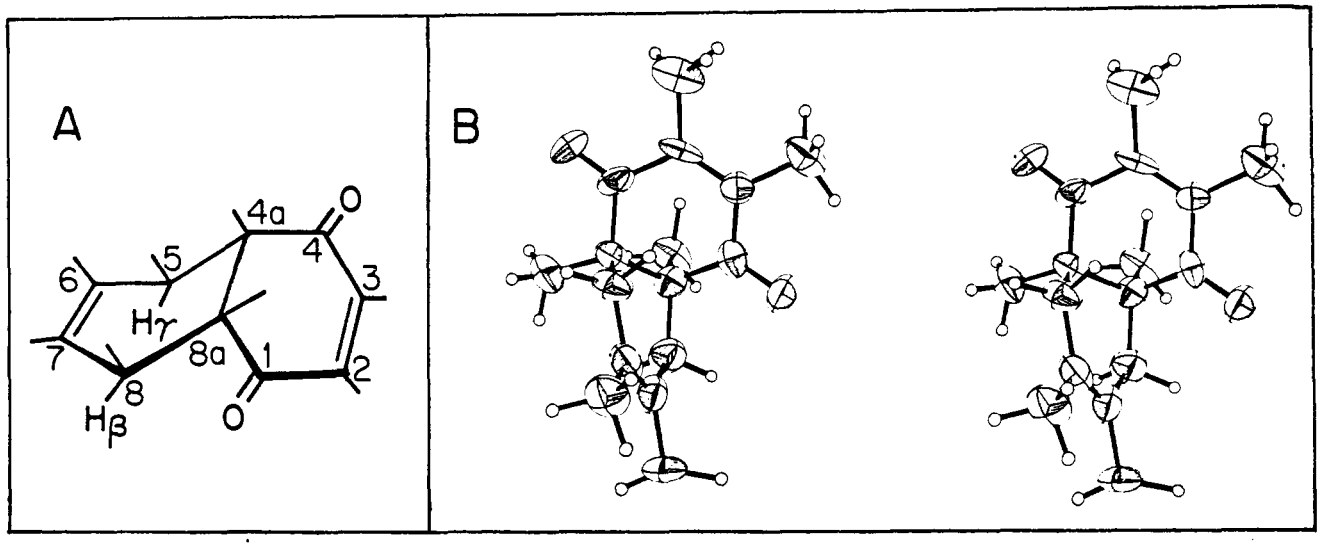
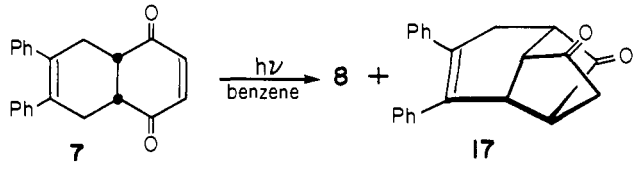


Figure 1. (A) So-called twist conformation common to all substrates studied. (B) Stereodrawing of substrate **13** in the solid state. Taken from ref 15d.

Table II. Enone-Alcohol to Cyclobutanone Ratio from Irradiation of Substrates **13** and **15** in Various Media

Substrate	Medium	Temp, °C	Enone-alcohol to cyclo butanone ratio
13	Solid state	−30	**14:20** = 2:3
13	Ether solution	−30	**14:20** = 1:2
15	Solid state	−30	**16:21** = 1:2
15	Benzene solution	Ambient	**16:21** = 1:2

Scheme II



irradiation of **13** and **15** in the various media are summarized in Table II. A discussion of the possible reasons why cyclobutanone formation occurs in these photolyses and not in the irradiations of **7**, **9**, and **11** is deferred to the next section.

During these chemical studies, the x-ray crystal structures of substrates **7**, **9**, **11**, **13**, and **15** were determined by Trotter and Phillips.[15a-e] All five of these compounds, and indeed all eight of the compounds studied in this project whose x-ray crystal structures were determined, had identical conformations in the crystalline state with only minor differences in the various bond lengths and bond angles. This common conformation, which we term the "twist" conformation to distinguish it from conformations having eclipsed ring junction groups or hydrogen atoms, is shown generally in Figure 1A. A specific example, taken from ref 15d, is shown in Figure 1B, which is a computer-drawn stereoview of tetrahydronaphthoquinone **13** in the solid state. As can be seen, the molecules adopt a conformation in which the cyclohexene ring exists in a half-chair form cis fused to a nearly planar cyclohex-2-ene-1,4-dione moiety.

With the aid of Figure 1A it is easy to see how enone-alcohol type photoproducts (**8**, **10**, **12**, **14**, and **16**) are formed in the solid state. Of the four allylic hydrogen atoms at C_5 and C_8, only the hydrogen marked H_β is in a favorable position, both stereochemically and proximally, to be abstracted by oxygen, specifically the oxygen attached to C_1. Table I lists these H_β to oxygen distances for the five substrates studied; they range from 2.26 to 2.58 Å. All other allylic hydrogen to O_1 distances

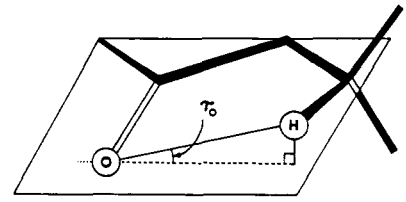


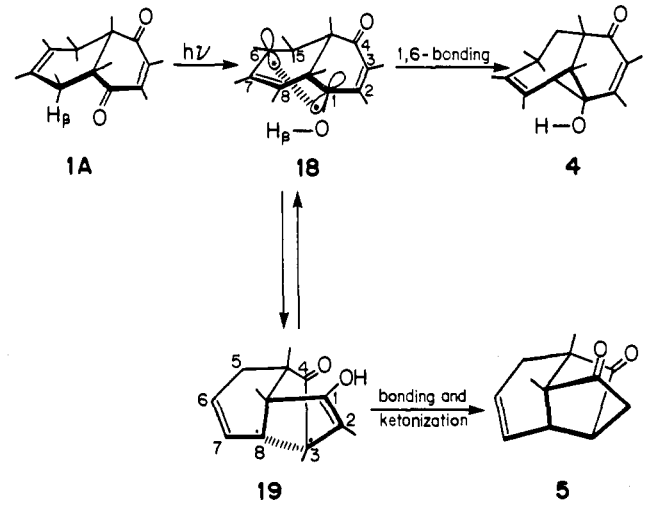
Figure 2. Definition of angle τ_0 referred to in Table I.

are greater than 3.28 Å with unfavorable abstraction geometries.

Also included in Table I are values of τ_0, the angle subtended by the oxygen to H_β vector and its projection on the plane of the C_1 carbonyl group. This is shown in Figure 2. These values of τ_0 are all close to 0°, i.e., the hydrogen being abstracted is essentially coplanar with the carbonyl group, an ideal arrangement for abstractions involving n,π* excited states in which the new oxygen-hydrogen bond is formed using the half-occupied n orbital on oxygen which also lies in the plane of the carbonyl group.[16]

Abstraction will thus lead to a species (**18**, Scheme III), most

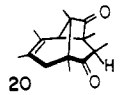
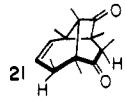
Scheme III[a]



[a] Substituents omitted for clarity.

economically formulated as a diradical in analogy to the Norrish type II reaction, having basically the same "twist" conformation as its ground state precursor.[17] It now becomes

Table III. Substrates, Photoproducts, and Molecular Parameters in Solid State Cyclobutanone Formation

Substrate	Photoproduct	H_γ–C_2, Å	τ_C[a]	Δ_C[b]	C_3–C_5, Å
13	 20	2.89	52°	72.6°	3.17
15	 21	2.66	50°	74.4°	3.17

[a] Angle subtended by the C_2 to H_γ vector and its projection on the plane of the C_2–C_3 double bond. [b] Angle formed between C_2, C_3, and H_γ.

apparent why enone–alcohol formation is such a prominent process in the solid state photochemistry of tetrahydronaphthoquinones. *Not only is the hydrogen abstraction leading to this product favorable in the solid state, but the biradical intermediate thus formed is ideally arranged to undergo biradical collapse to product.* Thus the geometrically favorable process of C_1 to C_6 bonding in biradical **18** leads directly to enone–alcohol photoproduct.

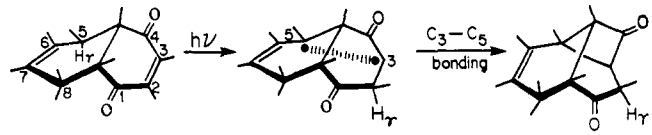
Table I lists the C_1 to C_6 distances for the five substrates which react in this manner; they range from 3.33 to 3.51 Å. Other biradical bonding possibilities, e.g., C_3 to C_8 and C_3 to C_6, involve longer interatomic distances (>3.86 Å) as well as much poorer orbital overlap. Of course the interatomic distances in the biradical intermediate **18** will be different from the corresponding distances in its precursor, but owing to the fact that these two species should have basically the same shape as the result of crystal lattice restraints, it is entirely reasonable to suggest that the relative interatomic separations (C_1–$C_6 \ll C_3$–C_6) should be similar for both.

These solid state results also provide evidence on another point, namely, they offer further insight into the mechanism by which diketones of general structure **5** (Scheme I) are formed in solution. These photoproducts result from C_3–C_8 bonding in the bisallylic radical **2** followed by ketonization of the resulting enol. As we have seen, however, if this species has the "twist" conformation **18** (Scheme III), C_3–C_8 bonding is impossible. In order to bring these two centers into bonding proximity, biradical **18** must undergo a ring flip (a ring A cyclohexene half-chair → half-chair interconversion) to conformer **19** (Scheme III). We thus have an explanation for why photoproduct **17** (analogous to **5**) is formed in solution but not in the solid state. *Its formation requires a biradical conformation which is accessible in solution but which is prevented by crystal lattice restraints in the solid state.*

Cyclobutanone Formation. As mentioned (vide supra), two of the substrates (**13** and **15**) which give enone–alcohol type photoproducts upon irradiation in the solid state also give cyclobutanone photoproducts having structures **20** and **21**, respectively (Table III). The ratios of enone–alcohol to cyclobutanone products in these photolyses, both in the solid state and in solution, are given in Table II.

As in the case of enone–alcohol formation, we can unambiguously correlate the solid state tetrahydronaphthoquinone conformation (cf. Figure 1A) with the formation of cyclobutanone photoproducts **20** and **21**. We suggest that this occurs through a six-membered transition state hydrogen (presumably atom) transfer of H_γ to C_2 followed by C_3–C_5 bonding in the biradical **22** so produced as outlined in Scheme IV. Thus an exactly analogous situation prevails in cyclobutanone formation as in the earlier solid state results, namely, *the "twist" conformation permits facile intramolecular hydrogen transfer giving rise to an intermediate which is ideally set up to collapse directly to product.* Both the H_γ to C_2 (2.66 and 2.89 Å) and C_3 to C_5 (3.17 Å) interatomic distances support this interpretation.[18]

Scheme IV[a]



1A 22 23

[a] Substituents omitted for clarity.

We come now to a discussion of the possible reasons for the lack of cyclobutanone formation in the photochemistry of substrates **7** and **11**.[20] While we can only speculate at the present time, the answer may be similar to that advanced for the analogous solution results,[13b] that is, that enone–alcohol formation originates from a different excited state (singlet) (exciton?)[21] from that which gives rise to cyclobutanone photoproducts (triplet). It seems likely, at least in solution, that these excited states are $(n,\pi^*)^1$ and $(\pi,\pi^*)^3$, respectively, the $(\pi,\pi^*)^3$ being formed fastest[22] from $(n,\pi^*)^1$ and having a lower energy relative to the $(n,\pi^*)^3$ as the result of ene–dione double bond methyl substitution. For a more thorough discussion of this point, see ref 13b. In this view the formation of both product types from a common substrate would reflect the competition between intersystem crossing and reaction of the initially formed singlet. The answer to this question will have to await solid state quenching experiments similar in principle (but more difficult in practice) to those carried out on substrate **13** in solution.[13b] The finding of two different hydrogen abstraction processes leading to two different biradical intermediates in the solid state *is* in agreement with this dual excited state concept, however.

Geometric and Distance Requirements for Intramolecular Hydrogen Abstraction Processes. The distances over which we find abstraction can occur range from 2.26 to 2.58 Å for abstraction by oxygen and 2.66 to 2.89 Å for abstraction by carbon. These distances are considerably greater than those generally supposed to be favorable.[23] This likely stems in part from experimental[24] and theoretical[25] work on the distance and stereochemical requirements for the closely related mass spectrometric McLafferty rearrangement (intramolecular γ-hydrogen abstraction by ionized carbonyl oxygen) which indicated that abstraction did not occur at distances greater than 1.8 Å and angles of τ_0 larger than ca. 50° with angles close to 0° being much preferred.

With regard to the analogous photochemical process (Norrish type II reaction), there are instances of γ-hydrogen abstraction by oxygen occurring over distances as great as 2.2 Å (measured on molecular models[26]) albeit with reduced hydrogen abstraction rate constant. In view of these results and our own, we would like to suggest that intramolecular hydrogen abstraction by oxygen can, in favorable instances, occur over distances at least as great as the sum of the van der Waals radii of the atoms involved. Using the van der Waals radius for oxygen, $\bar{r}_w(O)$, as 1.52 Å and $\bar{r}_w(H)$ as 1.20 Å from the recent calculations of Bondi[27] yields a van der Waals sum of 2.72 Å for abstraction of a hydrogen atom by oxygen. This is well in accord with the data in Table I in which the β-hydrogen abstraction distances range from 2.26 to 2.58 Å and the angle τ_0 is very close to the ideal of 0°.

In addition to the angle τ_0, a second angle Δ_0 must be considered whose value will be critical for efficient hydrogen abstraction by oxygen. We define Δ_0 as the angle formed between the carbonyl carbon, the carbonyl oxygen, and the hydrogen being abstracted. Since the atomic orbital on oxygen involved in the abstraction process (the n orbital) is largely 2p-like in character,[28] the optimum angle Δ_0 for hydrogen abstraction should be close to 90°. Table I gives the Δ_0 values observed in

this work. As can be seen, they range from 80.7° to 86.4°, again very close to ideal for abstraction.

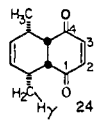
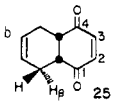
While the process of intramolecular γ-hydrogen abstraction by a double bond carbon atom in an excited enone chromophore is much less common in organic photochemistry than abstractions by excited carbonyl oxygen atoms,[29] our limited data (Table III) suggest that here too a reasonable guide to the distances over which abstraction can be expected is at least equal to the sum of the van der Waals radii of carbon and hydrogen. Since $\bar{r}_w(C) = 1.70$ Å and $\bar{r}_w(H) = 1.20$ Å,[27] this sum is 2.90 Å, which is again in good accord with the crystallographic distances of 2.89 and 2.66 Å for **13** and **15**, respectively.

With regard to the preferred geometry for hydrogen abstraction by sp^2-hybridized carbon, we may once again expect that this will be governed by the spatial characteristics of the atomic orbital to which the abstracted hydrogen becomes bonded. In the case of carbon this is the 2p orbital which, in the ground state, is orthogonal to the plane of the carbon–carbon double bond and forms an angle of 90° with the double bond axis. Thus with τ_C defined as the angle subtended by the abstracting carbon to abstracted hydrogen vector and its projection on the plane of the double bond and Δ_C equal to the angle formed between the axis of the double bond and the abstracted hydrogen (cf. Table III), the optimum carbon–hydrogen abstraction geometry should approach $\tau_C = 90°$ and $\Delta_C = 90°$ if the reactive excited state has the same shape as the ground state.[30]

This raises the critical point that till now we have assumed that it is the *ground state* molecular shape which can be correlated with *excited state* behavior. While it seems certain that the gross molecular conformation remains essentially unchanged in the solid state in going from ground state to excited state to biradical intermediate, it seems equally likely that these transformations can be accompanied by slight bond expansions and contractions as well as small angle deformations attending excitation and atom rehybridization. For α,β-unsaturated carbonyl compounds there is general agreement[31] that the $(n,\pi^*)^1$ excited state remains essentially planar and the $(\pi,\pi^*)^3$ excited state seeks an equilibrium geometry in which the β carbon is twisted relative to the original enone plane. In both instances the carbon–carbon and carbon–oxygen double bonds as well as the single bond joining them experience slight (≤0.1 Å) expansions. Since it seems likely (vide supra) that the solid state processes of β-hydrogen abstraction by oxygen and γ-hydrogen abstraction by carbon originate from these same $(n,\pi^*)^1$ and $(\pi,\pi^*)^3$ excited states, respectively, our ground state structure–excited state reactivity correlations appear well founded, particularly for the former process in which the ground and excited states very likely have essentially identical geometries. This conclusion is based on the reasonable assumption that the 2-ene-1,4-dione system in our substrates experiences twisting and stretching modes upon excitation similar to those of the parent[31] 2-en-1-one chromophore. With regard to the process of γ-hydrogen abstraction by carbon in substrates **13** and **15**, twisting around the ene–dione carbon–carbon double bond in the $(\pi,\pi^*)^3$ state may actually *facilitate* the reaction by tilting the abstracting C_2 2p atomic orbital more directly toward the γ hydrogen undergoing abstraction. In fact, a reasonable[31] 45° twist, when added to the ground state τ_C of ca. 50°, would, in effect, bring about an excited τ_C^* of 95°, nearly ideal for abstraction by carbon. Twisting in the opposite direction would, of course, result in an unreactive excited state with τ_C^* effectively near 0°. Twisting should not, however, greatly affect the excited state H_γ to C_2 distances nor the angle Δ_C, and these values may be considered valid for both the ground and $(\pi,\pi^*)^3$ states.

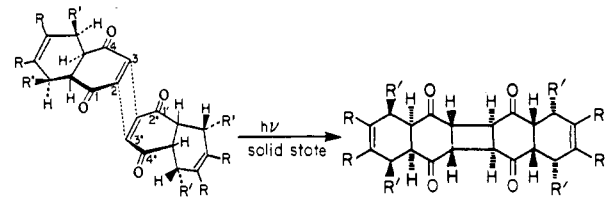
Intermolecular [2 + 2] Photodimerization. Three of the *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinones studied in this project were found to undergo intermolecular ene–dione double bond [2 + 2] dimerization upon irradiation in the solid state. These are the substrates **24, 25,** and **26** shown in Scheme V.

Table IV. Substrates and Molecular Parameters in Solid State Intermolecular [2 + 2] Photodimerizations

Substrate	H_γ–O_1, Å	H_β–O_1, Å	τ_0	Δ_0	Intermolecular C_2–C_3 double bond separation,[a] Å
	2.38	No abstractable β hydrogen	15°	101.4°	4.04
[b] 	No abstractable γ hydrogen	2.49 (A) 2.42 (B)	4° 3°	80.8° 79.5°	5.27 (A-A) 3.76 (B-B)

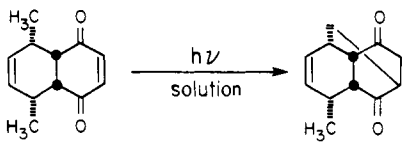
[a] C_2–C_3 to C_2'–C_3' center to center distance between neighboring molecules. Refer to Scheme V. [b] Unit cell contains two independent molecular types, **25**A and **25**B. See Figure 3 and discussion in text.

Scheme V



24 (R=H, R'=Me)
25 (R=R'=H)
26 (R=Me, R'=H)

27a (R=H, R'=Me)
27b (R=R'=H)
27c (R=Me, R'=H)



24 **28**

The photodimers all have the same basic stereochemistry shown by formula **27**, the detailed structure for each being established by x-ray crystallography.[15f,h]

In our previous solution work,[13a] we have shown that irradiation of substrates **25** and **26** leads only to internal hydrogen abstraction processes analogous to those described in the preceding sections. In addition we showed in this work that photolysis of substrate **24** in solution also leads to internal hydrogen abstraction, in this case abstraction of a methyl group hydrogen to give, after biradical collapse and ketonization, the interesting diketone **28** (Scheme V). Hence the observation of bimolecular reactions for **24, 25,** and **26** in the solid state represents completely new chemistry for the tetrahydronaphthoquinone system.[32]

The question at this point was thus whether this reactivity difference was due primarily to a solid state conformation disfavoring intramolecular hydrogen abstraction or to a particularly favorable intermolecular crystal packing arrangement favoring dimerization. Evidence that the latter situation prevails was obtained from the x-ray crystal structures of substrates **24** and **25**.[15f,g] Crystals of **26** were unfortunately not suitable for analysis. Overall, compounds **24** and **25** possessed the same "twist" conformation common to all the tetrahydro-1,4-naphthoquinones studied (cf. Figure 1A). Table IV

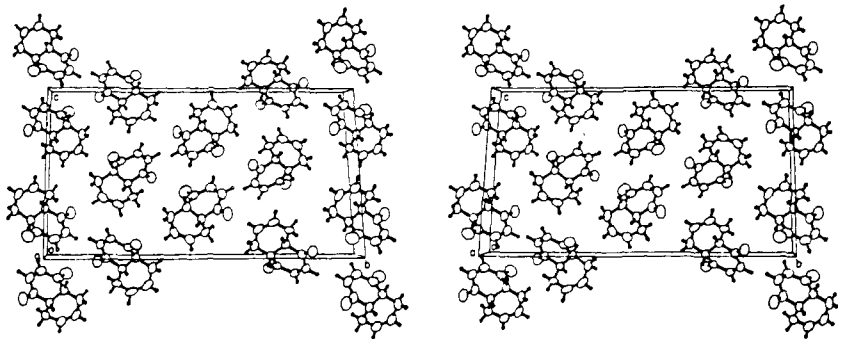


Figure 3. Stereodiagram of unit cell of substrate **25**.

records the solid state hydrogen to oxygen distances for the abstraction processes observed in solution for substrates **24** and **25**. As can be seen, these distances are well within the guideline of the van der Waals radii sum (ca. 2.7 Å) previously suggested for hydrogen abstraction by carbonyl oxygen. Similarly the values of τ_0 and Δ_0 are very close to those of previously studied systems which do undergo internal solid state hydrogen abstraction.

However, a major crystallographic difference between substrates **24** and **25** on the one hand and adducts **7, 9, 11, 13,** and **15** on the other was the presence in the former group of a particularly close and parallel approach of the C_2–C_3 double bonds of neighboring molecules. The center to center intermolecular double bond distances for substrates **24** and **25** are given in Table IV. Note that for tetrahydronaphthoquinone **25** the unit cell contains equal proportions of two independent molecular types **25A** and **25B**. Only for the latter is the intermolecular double bond separation (3.76 Å) favorable for dimerization. Figure 3 shows a stereodrawing of the unit cell of substrate **25** reproduced from ref 15g. As can be seen, layers of **25A** alternate with those of **25B**. Molecules of type A form an axial repeat pattern (5.27 Å) with essentially no intermolecular double bond overlap, whereas molecules of type B occur in pairs related by a center of symmetry. In this arrangement the double bonds of adjacent molecules are parallel but offset with C_2 of one molecule directly above C_2' of the other. The C_2 to C_2' contact is the shortest intermolecular distance and measures 3.35 Å; the center to center distance is, as mentioned, 3.76 Å.

The crystallographic packing arrangement of substrate **24** is exactly analogous to that of compound **25** with one important difference: The unit cell in the case of **24** is made up entirely of type B molecules.[15f] The center to center double bond distance of 4.04 Å is slightly longer than that for **25B**. In contrast, tetrahydronaphthoquinones **7, 9, 11, 13,** and **15** have nearest-neighbor double bond center to center distances greater than 5.16 Å in each case.

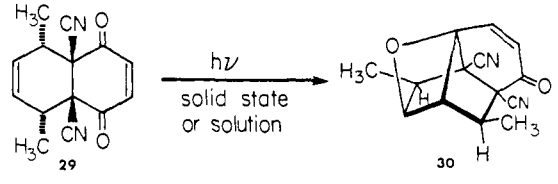
We thus conclude that the deciding factor favoring solid state photodimerization over intramolecular hydrogen abstraction in the case of substrates **24** and **25** (and probably also **26**) is the close and geometrically favorable approach of the reacting double bonds enforced by the crystal lattice for these systems.[34] This view is supported by the fact that these dimerizations are topochemically controlled, i.e., the photodimers **27a** and **27b** result from the least motion process of C_2 to C_3' and C_3 to C_2' bonding and maintain the relative and intrinsic stereochemistry possessed by the monomer pairs in the substrate lattice. This result is of course reminiscent of the well-known cinnamic acid [2 + 2] photodimerizations studied by Schmidt et al.[3] which were also shown to be topochemically controlled. Interesting too is the close similarity between our work and that of Schmidt on the distance and geometric requirements for intermolecular [2 + 2] photodimerization. Schmidt and co-workers found that a parallel approach with a center to center double bond distance of less than 4.2 Å was required for solid state photodimerization. Beyond this limit no reaction occurred. The limits for our substrates (4.1 Å) are very similar, the only difference being that beyond this distance, unimolecular photoprocesses (intramolecular hydrogen abstraction) take over.

One final interesting point concerns the yields expected in the photodimerization of substrate **25**. The x-ray crystal structure of this material (Figure 3) suggests that only half of the molecules in the solid state (type B) are in a position to photodimerize to the observed product **27b**. Dimerization within the A stack is impossible, and bonding between type A and type B molecules (closest center to center double bond approach, 6.29 Å) is very unlikely owing to the offset and near-orthogonal arrangement of the ene–dione double bonds of adjacent molecules. Furthermore, the stereochemistry of the observed photoproduct **27b** cannot be achieved by any A to B dimerization process in which the reacting monomers maintain their relative lattice positions even allowing for free rotation after initial C_3(A) to C_2'(B) or C_2(A) to C_3'(B) bond formation. The result is, therefore, that the maximum yield of photodimer **27b** is predicted to be 50%. This, however, was not found to be the case experimentally. In five runs ranging from 16 to 94% conversion, the chemical yields of dimer **27b** averaged 87%.

The reasons for this behavior are not clear at the present time. One possibility is that following dimerization in the B stack, the boundaries between the reacted and unreacted regions of the crystal are akin to dislocation sites since molecules here may have orientations different from those located elsewhere in the crystal lattice. These defect regions may be sites for non-topochemically controlled reaction in the crystal as they are thought to be in the photodimerization of certain 9-substituted anthracenes.[10] The continued formation of dimer **27b** past 50% yield could then be ascribed, as in the 9-substituted anthracene photodimerizations, to preferential formation of the least sterically hindered product.[35]

Intramolecular Oxetane Formation. Irradiation of crystalline samples of tetrahydro-1,4-naphthoquinone **29** gave the intramolecular oxetane **30** as the sole product (Scheme VI).

Scheme VI



Identical results were obtained when **29** was photolyzed in solution.[13b] The structure of oxetane **30** was established by x-ray crystallography.[15j]

The course of this reaction clearly involves bonding in **29** of C_1 to C_6 and O_1 to C_7. In order to delineate the geometric and

distance parameters associated with this reaction as well as to understand why substrate **29** behaves differently from the previously studied systems, its x-ray crystal structure was also determined.[15i] Again, the conformation of **29** was found to conform very closely to the "twist" arrangement shown in Figure 1A which is apparently general for the *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone system.

One difference between the crystal packing arrangement in compound **29** and that of substrates **24** and **25** (preceding section) is the long (6.02 Å) center to center intermolecular C_2–C_3 to C_2'–C_3' double bond contact in the former. It is thus not surprising that **29** fails to dimerize upon photolysis in the solid state.

Figure 4 contains a partial drawing of substrate **29** showing the arrangement of the reacting C=O and C=C double bonds in the solid state. It seems unlikely that this relative geometry will change significantly upon excitation since the carbonyl group of the enone chromophore is expected to retain its original planar ground state configuration in each of the $(n,\pi^*)^1$, $(n,\pi^*)^3$, and $(\pi,\pi^*)^3$ excited states.[31]

Three structural parameters serve to characterize this arrangement. They are the C_1 to C_6 and O_1 to C_7 distances and the angle θ, defined as the angle formed between the planes orthogonal to the plane of the C_1=O_1 carbonyl group and the plane of the C_6–C_7 double bond. This angle is, of course, the angle formed between the interacting 2p atomic orbitals.[36] The values of these parameters are C_1 to C_6, 3.37 Å; O_1 to C_7, 3.20 Å; and θ = 99.2°. The center to center carbonyl double bond distance in **29** is 3.20 Å. It is interesting to note that the C_1 to C_6 and O_1 to C_7 distances quoted above are again within the limits of the sums of the van der Waals radii of the atoms involved. For carbon to carbon this sum is 3.40 Å, and for carbon to oxygen it is 3.22 Å, both remarkably close to the experimentally observed values. Rabinovich and Schmidt[37] have shown that *intermolecular* oxetane formation is possible in the solid state over center to center carbonyl double bond distances as great as 3.70 Å.

The question next arises as to why internal oxetane formation is not observed in the tetrahydronaphthoquinone substrates **7, 9, 11, 13, 15, 24,** and **25**. The center to center C=O to C=C distances for these substrates range from a high of 3.45 Å for **7** to a low of 3.26 Å for **11** with the remaining compounds having intermediate values. These distances do not seem sufficiently longer than the 3.20 Å observed for naphthoquinone **29** to account for the observed lack of oxetane formation. Similarly the values of the angle θ for these substrates fall within a range of 97.3 to 87.1°, again insufficiently different from 99.2° (for **29**) to be significant in terms of reactivity.

We thus suggest that this reactivity difference is simply a matter of competitive rates, i.e., that internal oxetane formation of the type **29** → **30** is associated with an intrinsically low overall rate constant compared to the processes of β-hydrogen abstraction by oxygen (e.g., **7** → **8**) and γ-hydrogen abstraction by carbon (e.g., **13** → **20**). These latter two favored processes are, of course, sterically impossible from the twist conformation of substrate **29**, and this accounts for the occurrence of the least favored reaction of oxetane formation in this case. Arnold[38] has noted a similar trend of preference for hydrogen abstraction over oxetane formation (intermolecular, however) in the photochemistry of carbonyl compounds with accessible hydrogen atoms. Abstraction by oxygen of a methyl group γ hydrogen in **29** is, as in the case of substrate **24**, possible but unlikely to lead to new products owing to the inability of the resulting diradical to isomerize in the solid state to a conformation in which closure is possible.[34]

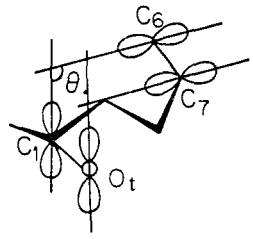


Figure 4. Relative C_1=O_1 and C_6=C_7 geometry in twist conformation of tetrahydro-1,4-naphthoquinones.

Summary

We suggest that the interatomic distances over which intramolecular hydrogen abstraction can occur are at least as great as the sum of the van der Waals radii of the abstracting and abstracted atoms. For α,β-unsaturated carbonyl compounds in their n,π^* excited states, abstraction by oxygen is geometrically favored when $\tau_0 = 0°$ and $\Delta_0 = 90°$ (see text for definitions of τ_0 and Δ_0). A direct correlation between excited state and ground state geometry is possible in this case since all available evidence indicates that very little change of shape occurs upon $n \rightarrow \pi^*$ excitation of the enone (and presumably the ene-dione) chromophore.

The preferred excited state geometry for abstraction of hydrogen by enone carbon through a $(\pi,\pi^*)^3$ excited state is expected to be $\tau_C^* = 90°$ and $\Delta_C^* = 90°$. The values of these parameters may differ from the corresponding ground state values (τ_C and Δ_C) owing to the fact that the enone double bond is very likely twisted in the $(\pi,\pi^*)^3$ state relative to the ground state.

The reactivity differences found among the *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone substrates studied in this work are *not* due to differences in their molecular conformations in the solid state; the substrates possess a common (twist) conformation. The bimolecular process of [2 + 2] photodimerization becomes favored over the unimolecular process of internal hydrogen abstraction when the crystal lattice is such that the two double bonds involved in dimerization are held together in an arrangement favorable for reaction, i.e., parallel (but offset) with a center to center distance of less than ca. 4.1 Å.

In the case of one substrate for which both intramolecular hydrogen abstraction and intermolecular dimerization are impossible owing to substituent and crystal packing effects, respectively, internal oxetane formation becomes the sole observed solid state photoprocess. This reaction is made possible by a close (3.20 Å) C=O to C=C contact in the common twist conformation and involves the unusual (for oxetane formation involving electron-rich alkenes) geometry of approach of near-orthogonal end to end π bond overlap. The fact that this reaction is geometrically feasible but undetected for all the other substrates studied indicates that it is the least favored of the solid state photoreactions discovered in this work.

Finally, in view of the general observation that organic molecules crystallize in their most stable, lowest energy conformations, it seems reasonable to suggest that the twist conformation is also important in the *solution* photochemistry of tetrahydro-1,4-naphthoquinones. This view is strengthened by the close similarity observed between the solution and solid state results for certain of the substrates (excluding those compounds which photodimerize in the solid state). Two general mechanisms thus exist for any solid state–solution state unimolecular reactivity differences which may appear: (1) reaction in solution via a minor, unfavorable conformation, and (2) initial formation in solution of a conformationally mobile intermediate which, because of its freedom of motion, is capable of modes of reaction not available to the immobilized solid state biradical. The present work most likely provides examples of the latter phenomenon.

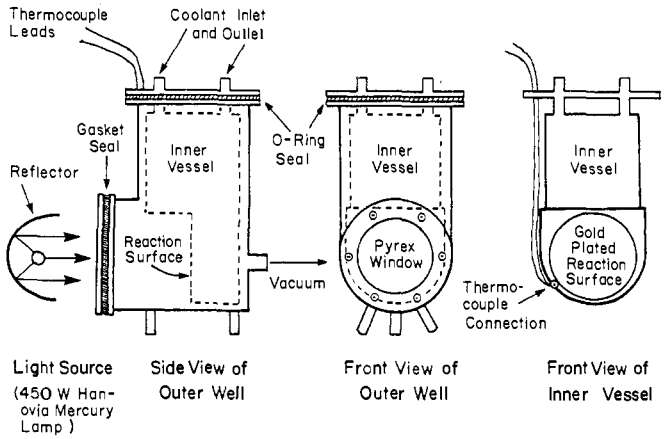


Figure 5. Apparatus for solid state irradiations.

Experimental Section

General. Eutectic temperatures were determined by differential thermal analysis using a Perkin-Elmer DSC-1B. In each case, both the crude reaction mixture and varying compositions of crude reaction mixture and added starting material were analyzed until a sharp melting transition was observed. The calibration-corrected results were as follows (mixture, eutectic temperature): **7** and **8**, 151 °C; **9** and **10**, 126 °C; **11** and **12**, 119 °C; **13**, **14**, and **20**, −16 °C; **15**, **16**, and **21**, 61 °C; **24** and **27a**, 53 °C; **25** and **27b**, 49 °C; **26** and **27c**, 110 °C; **29** and **30**, 124 °C. Melting points were obtained on either a Fisher-Johns hot-stage apparatus or on the Perkin-Elmer DSC-1B. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. ^{1}H NMR spectra were recorded with either a Varian T-60, HA-100, or XL-100 spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on a direct inlet Varian Atlas MAT CH 4-B or AEI MS-9 at 70 eV. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda. GLC analyses were carried out on Varian Aerograph 90-P and Varian Autoprep A-700 instruments connected to Honeywell 15 strip chart recorders. The carrier gas was helium. In quantitative GLC analyses, an internal standardization procedure was used. Peak areas were calculated from height times width at half-height measurements. Analytical TLC was done on strips of aluminum backed silica gel 60F-254 (thickness 0.2–0.25 mm) available from E. Merck. Preparative TLC was carried out using 20 × 20 cm glass plates coated with silica gel GF-254 (thickness 0.7–0.8 mm). For column chromatography, slurry packed columns of silica gel 60 (particles size < 0.063 mm) from E. Merck or neutral aluminum oxide activity grade 1 from Woelm were used. The silica gel columns were eluted under 5–10 psi pressure of nitrogen. All solvents used were distilled and normally stored over molecular sieve Linde type 4A. All photolysis solutions were degassed before and during photolysis using either Canadian Liquid Air argon (<5 ppm oxygen) or high-purity L grade nitrogen. All photolyses in solution were by external irradiation using a 450-W Hanovia mercury lamp. Unless otherwise stated, irradiation of solids was carried out in vacuo in the specially designed apparatus described below. KBr pellets for spectroscopic as well as for preliminary photochemical studies were prepared with 1–2 mg of sample per 250 mg of dried KBr using a Perkin-Elmer potassium bromide evacuable die 186-0002 and a Carver laboratory press Model B at a pressing load of ca. 20 000 psi.

Apparatus for Solid State Irradiations. The solid state reactor, shown in Figure 5, consists of two main parts, an inner vessel and an outer well. The inner vessel consists of a double-walled cylindrical brass drum having a lower flat surface which is gold plated and serves as the reaction surface on which crystals are grown. One of the two junctions of a copper–constantan thermocouple is soldered near the edge of the reaction surface and protected from direct radiation by an aluminum foil roof. The second junction of the thermocouple (reference junction) is kept in a slurry of ice during operations. The inner vessel fits into an outer well also made of brass and having a Pyrex window to allow for external irradiation of crystals on the reaction surface. The two-component system is made airtight by means of an O-ring seal and is evacuable. The rest of the apparatus consists of an Ultra Kryomat K-80 DW which cools and circulates a coolant through the inner vessel, a digital microvoltmeter for the thermocouple terminals, a water-cooled 450-W Hanovia mercury lamp and power source, an air-cooled Corning glass filter (no. 7380 for λ >340 nm and no. 3850 for λ >355 nm) interposed between the lamp and the Pyrex window of the reactor, and finally a polished reflector for directing the lamp output into the reaction vessel.

Irradiation of 6,7-Diphenyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (7) in the Solid State. Substrate **7** (mp 163.0–164.5 °C) was prepared by the method of Allen, Eliot, and Bell[39] using *p*-benzoquinone and 2,3-diphenyl-1,3-butadiene prepared by the procedure of Iwai and Ide.[40]

Crystals of compound **7** (50.0 mg) were irradiated (λ >340 nm) at 0.05 Torr between −10.4 and −9.8 °C for 15 min. The recovered material balance was 94%. Preparative TLC (silica gel, 15% ethyl acetate–benzene) of the mixture gave 41.3 mg of residual starting material and 5.8 mg of a new product subsequently shown to have the structure **8**. The extent of reaction, based on recovered starting material, was 17% and the yield of product was 67%. Upon extended irradiation (>2 h), small amounts of a second photoproduct subsequently identified as ene–dione **17** began to appear. This material was formed at the expense of enone–alcohol **8**, and a separate control experiment verified that photolysis of **8** in the solid state does afford diketone **17**.

Enone–alcohol **8** was obtained as white needles, mp 189.5–190.0 °C, from acetone–hexane and identified on the basis of the following data: IR (KBr) 2.92 (OH), 5.97 μ (C=O); NMR ($CDCl_3$) δ 7.17 (m, 10 H, phenyls), 6.44 (d, J = 10 Hz, 1 H, C_2 vinyl), 6.30 (d, J = 3 Hz, 1 H, C_9 vinyl), 6.01 (dd, J = 10 and 2 Hz, 1 H, C_3 vinyl), 3.45 (d, J = 3 Hz, 1 H, C_{10} methine), 2.73 (s, 1 H, disappears upon adding D_2O, OH), 2.65 (m, 2 H, C_6 methylenes), 2.13 (dd, J = 14 and 9 Hz, 1 H, C_5 methine); mass spectrum parent *m/e* 314.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.06; H, 5.87.

Photoproduct **17** crystallized as colorless needles, mp 170.5–171.5 °C, from acetone–hexane and was identified as 2,3-diphenyltricyclo[5.3.0.0^{5,10}]dec-2-ene-6,9-dione on the basis of the following information: IR (KBr) 5.73 (C=O) and 6.25 μ (C=C); NMR ($CDCl_3$) δ 7.23–6.87 (m, 10 H, aromatics), 3.23 (m, 2 H, C_7 and C_{10} methines), 3.07 (m, 1 H, C_5 methine), 2.83 (m, 3 H, C_1 methine and C_4 methylenes), 2.49 (calcd,[41] dd, J = 20 and 5 Hz, 1 H, C_8 exo), and 2.30 (calcd,[41] dd, J = 20 and 1.5 Hz, 1 H, C_8 endo). Six drops of a 2 N solution of KOH in D_2O was added to the NMR sample of **17**. The tube was periodically shaken. A spectrum recorded after 12 h showed no changes. However, after 4.5 days, the δ 2.49 resonances attributed to the C_8 exo proton had disappeared, the dd resonance due to the C_8 endo proton had collapsed to a broad singlet at δ 2.31, and the small splitting of the multiplet at δ 3.23 was no longer present. The remainder of the spectrum remained unchanged. Selective exo exchange in bicyclo[2.2.1]heptan-2-ones and related compounds is well established.[42] Mass spectrum parent *m/e* 314.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.95; H, 5.71.

Photolysis of Naphthoquinone 7 in Benzene. Irradiation of solutions of substrate **7** in benzene (λ >340 nm, concentrations 1–2 mg/mL) afforded ca. 60% yields of mixtures of enone–alcohol **8** and diketone **17** whose ratios depended upon the length of photolysis due to the concomitant photoconversion of **8** to **17**. Independent photolysis of enone–alcohol **8** in benzene verified this. Exactly analogous rearrangements were observed in our previous solution studies.[13a] In contrast to the solid state results, an analytical time dependence study established that in solution, both **8** and **17** are primary photoproducts of **7**. The melting points and spectra of the products obtained in solution were identical with those reported above.

Irradiation of 2,3-Dimethyl-1,4,4aβ,9aβ-tetrahydro-9,10-anthraquinone (9) in the Solid State. Substrate **9** (mp 148–148.5 °C) was prepared from 1,4-naphthoquinone and 2,3-dimethylbutadiene using the method of Allen and Bell.[43]

Crystals of compound **9** (132 mg) were irradiated (λ >340 nm) in vacuo (0.02 Torr) between 8.3 and 10.0 °C for a total of 30.8 h. A pale yellow solid (132 mg, 100% material balance) was obtained. Preparative TLC on silica gel using 15% ethyl acetate–benzene as the eluting solvent afforded 58 mg of residual starting material **9** and 45 mg (60% of the known[13a] enone–alcohol **10**. This material was washed with hexane, dried, and sublimed at 103 °C and 0.03 Torr. Subsequent crystallization from acetone–benzene gave colorless crystals, mp 124.5–125.5 °C (lit.[13a] mp 126.0–126.5 °C). The spectral data for

10 were identical with those of an authentic sample prepared by photolyzing **9** in benzene.[13a]

Irradiation of 4aβ,8aβ-Dicyano-6,7-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (11) in the Solid State. Compound **11** (mp 156.5–157.5 °C) was prepared from 2,3-dicyano-1,4-benzoquinone[44] and 2,3-dimethyl-1,3-butadiene using the method of Ansell, Nash, and Wilson.[45]

Crystals of compound **11** (230 mg) were irradiated (λ >340 nm) at 0.01 Torr between 19.3 and 19.7 °C for 1.5 h. The reaction mixture which was retrieved from the reactor weighed 195 mg (85% recovery). To 22 mg of this mixture, 0.2 mL of a stock solution of benzophenone (internal standard) in chloroform was added. GLC analysis of this mixture was carried out on a 5 ft × 1/4 in. 10% OV-210 column at 175 °C and a flow rate of 160 mL/min. The detector response factor for **11** was determined to be 1.34. The percent conversion determined by this analysis was 34%.

The remainder of the reaction mixture (173 mg) was separated by preparative TLC (silica gel, 10% acetone–chloroform). This gave 109 mg of recovered starting material **11** and 57 mg of the known[13b] enone–alcohol **12** (91% yield). The yields from three other runs were 98, 94, and 87% at conversions of 19, 30, and 26%, respectively. The product from all the runs was combined and crystallized from acetone–hexane to give colorless crystals of **12**, mp 195–196 °C (lit.[13b] mp 188–190 °C). The spectra of enone–alcohol **12** obtained in this work were identical with those of an authentic sample.[13b]

Irradiation of 2,3,4aβ,6,7,8aβ-Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (13) in the Solid State. Substrate **13**, mp 113–114 °C, was prepared from duroquinone and 2,3-dimethylbutadiene by the method of Ansell, Nash, and Wilson.[46]

In a series of runs, crystals of compound **13** (40–80 mg) were irradiated at λ >355 nm in vacuo (0.03–0.10 Torr) at temperatures ranging from −23 to −34 °C for periods ranging from 1.5 to 24 h. The actual temperature fluctuation in any run was <3 °C. Recovery of material from the reactor was 78–94%. Each reaction mixture was analyzed by a quantitative GLC method using an aliquot of a stock solution of biphenyl as the internal standard. Analyses were carried out on a 5 ft × 1/4 in. column of 20% DEGS on 60/80 Chromosorb W operated at 150 °C and a flow rate of 150 mL/min. Retention times were 19.0 min for starting material **13** and 22.0 and 16.4 min for the known[13a] photoproducts **14** and **20**, respectively. The detector response factors for **20**, **13**, and **14** were found to be 1.5, 1.2, and 1.3, respectively. The combined GLC yield of the two products **14** and **20** was 62–88%, and the ratio **14**:**20** was invariant at 2:3 for conversions of **13** ranging from 41 to 88%.

Column chromatography (silica gel, 8% ethyl acetate–benzene) of the reaction mixtures afforded pure samples of the photoproducts. The order of elution was **13**, **20**, and **14**. Cyclobutanone **20** obtained in this way was purified by short-path vacuum distillation at 0.01 Torr at 65–70 °C using a Kugelrohr to give material melting at 24.5–26.0 °C whose spectra were identical with those of an authentic sample.[13a] Enone–alcohol **14** crystallized from petroleum ether as colorless needles, mp 101–102 °C (lit.[13a] mp 101–102 °C) and again gave spectra identical in every respect with those of an authentic sample.[13a]

Photolysis of Substrate 13 in Diethyl Ether below the Eutectic Temperature. A solution containing 87 mg of naphthoquinone **13** in 40 mL of anhydrous diethyl ether was deoxygenated and photolyzed between −31.5 and −29 °C for 6.5 h. The reaction mixture was analyzed by GLC using biphenyl as internal standard as in the preceding section. The calculated extent of reaction was 25% and the **14**:**20** ratio was 1:2. This ratio was invariant at 21, 52, and 63% conversions of starting material.

Irradiation of 2,3,4a,5,8,8a-Hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (15) in the Solid State. Substrate **15**, mp 104–105 °C, was prepared from duroquinone and *trans,trans*-2,4-hexadiene by the method of Scheffer, Jennings, and Louwerens.[13b]

Crystals of compound **15** (57 mg) were irradiated (λ >355 nm) at 0.005 Torr and between −32.4 and −31.7 °C for 5.6 h. The recovered material balance was 86%. A small amount of the photolysis mixture (5 mg) was used in GLC analysis (5 ft × 1/4 in. stainless steel column of 20% DEGS on A/W 60/80 mesh Chromosorb W at 150 °C and a flow of 100 mL/min). This showed two peaks due to a mixture of the known[13b] cyclobutanone **21** (retention time 16 min) and enone–alcohol **16** (retention time 22 min). The remainder of the reaction mixture was subjected to preparative TLC (silica gel, 8% ethyl acetate–benzene). This gave 12 mg of crystalline enone–alcohol **16** and 26 mg of liquid cyclobutanone **21**. The starting material **15**, which has the same R_f (TLC) and the same GLC retention time as product **21**, was found to be absent from the NMR sample of **21**. The conversion of starting material to photoproducts was thus 100%. The combined isolated yield of the two products was 85%, and the **16**:**21** ratio was 1:2.

In another run, 70 mg of crystals of adduct **15** were irradiated at 0.005 Torr and between −31.6 and −27.3 °C for 5 h. Recovery was 86%. A portion (29 mg) of this material was analyzed quantitatively by GLC. An aliquot of 0.2 mL of a stock solution of internal standard (173.2 mg of biphenyl in 10 mL of benzene) was added to the 29 mg and the resulting mixture analyzed under the GLC conditions described above. The detector response factors for **16** and **21** were 1.7 and 1.9, respectively. The combined GLC yield of the two products by this analysis was 86%, and the **16**:**21** ratio was 1:2.

Since substrate **15** and cyclobutanone **21** could not be separated by TLC or GLC, the amount of residual **15** in mixtures of **15** and **21** from low-conversion runs was determined by comparison of the integration of the δ 1.97 methyl NMR resonances of **15** to the integration of the resonances of added biphenyl as an internal standard. This analysis again showed the **16**:**21** ratio to be invariant at 1:2 at conversions of 29, 56, and 57%.

The photoproducts **16** (mp 158–159 °C, lit.[13b] mp 156.5–157 °C) and **21** had spectra identical with those of authentic samples.[13b]

Irradiation of 5α,8α-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (24) in the Solid State. Substrate **24** (mp 55–56 °C) was prepared by the method of Euler, Hasselquist, and Glaser.[47] Crystals of **24** (115 mg) were irradiated (λ >340 nm) at 0.03 Torr between −2.0 and −1.5 °C for 1 h. Recovery from the reactor was 98%. The resulting solid was washed three times with petroleum ether and the washings were stripped of solvent and dried in vacuo to give 43.2 mg of solid which was shown by TLC, NMR, and IR to be residual starting material **24**. The insoluble product was dried in vacuo to give 68 mg (95%) of dimer **27a**. The extent of reaction was 62%. Yields of **27a** at 17, 37, 56, 79, and 100% conversions ranged from 87 to 96%.

The crude photoproduct was crystallized from chloroform–hexane to give colorless plates suitable for single-crystal x-ray analysis.[15f] The IR of the recrystallized material was identical with that of the crude photoproduct. Dimer **27a** had mp 265.0 °C dec; IR (KBr) 5.82 and 5.90 μ (C=O); NMR ($CDCl_3$) δ 5.83 (s, 4 H, vinyls), 3.47 (s, 4 H, cyclobutane methines), 3.22 (dd, J = 3 and 2 Hz, 4 H, C_4, C_9, C_{14} and C_{19} methines), 2.50 (m, 4 H, C_5, C_8, C_{15} and C_{18} methines), 1.10 (d, J = 7 Hz, 12 H, methyls); mass spectrum parent *m/e* 380.

Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.48; H, 7.42.

Irradiation of 4a,5,8,8a-Tetrahydro-1,4-naphthoquinone (25) in the Solid State. Substrate **25** (mp 53.5–54 °C) was prepared from benzoquinone and butadiene using the method of van Tamelen, Shamma, Burgstahler, Wolinsky, Tamm, and Aldrich.[48]

Crystals of **25** (136 mg) were irradiated (λ >340 nm) at 0.01 Torr between 4.3 and 0.0 °C for 1 h. Recovery from the reactor was 92%. The solid obtained was washed with chloroform and the washings were concentrated and analyzed by TLC (silica gel, chloroform). Apart from a base spot, the only spot was that of starting material, **25**. Its identity was verified by IR. The chloroform-insoluble material, dimer **27b**, weighed 118 mg (92%). Yields of **27b** at 16, 19, 36, and 77% conversions of starting material ranged from 75 to 100%.

Photoproduct **27b** was crystallized from chloroform to give colorless plates, mp 280 ± 2 °C dec. The IR (KBr) of the crystallized material was identical with that of the crude product and showed 5.85 μ (C=O). NMR ($CDCl_3$) δ 5.70 (m, 4 H, vinyls), 3.64 (s, 4 H, cyclobutane methines), 3.20 (m, 4 H, C_4, C_9, C_{14}, and C_{19} bridgehead methines), 2.30 (m, 8 H, methylenes); mass spectrum parent *m/e* 324.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.22. Found: C, 73.88; H, 6.15.

The crystals of **27b** obtained by crystallizing from chloroform were too small and thin for single-crystal x-ray structure determination. Suitable crystals for this purpose[15h] were obtained by crystallizing from acetonitrile. The NMR spectrum of this latter material was identical with that of **27b** recrystallized from chloroform. There were slight differences in the IRs of KBr pellets of the two crystal samples, however. These differences are believed to be due to solid state IR differences attributable to intermolecular effects.[49]

Irradiation of 6,7-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphtho-

quinone (26) in the Solid State. Compound **26** (mp 115–116 °C) was prepared using the method of Mandelbaum and Cais.[50] Crystals of this material (93 mg) were irradiated in a covered Pyrex Petri dish for 0.4 h. The resulting solid was washed three times with chloroform and the washings were concentrated and analyzed by TLC (silica gel, chloroform). With the exception of a base spot, this showed only residual starting material. The dry weight of recovered **26** was 56 mg. The insoluble dimeric material, **27c**, was dried in vacuo. The crude yield was 36 mg (97%), and the percent conversion was 40%. Yields of **27c** at 25 and 61% conversions of starting material were 96 and 99%, respectively.

Recrystallization from chloroform afforded small, colorless plates, mp 265 °C dec. These crystals were too small for use in the x-ray structure determination. Larger single crystals for this purpose[15h] were obtained by recrystallization from acetonitrile. The IR of these crystals was identical in every respect with the corresponding spectra of the crude and chloroform-derived material.

IR (KBr) 5.85 μ (C=O); NMR ($CDCl_3$) δ 3.64 (s, 4 H, cyclobutane methines), 3.18 (m, 4 H, C_4, C_9, C_{14}, and C_{19} methines), 2.22 (m, 8 H, methylenes), and 1.66 (s, 12 H, methyls); mass spectrum parent *m/e* 380.

Anal. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.61; H, 7.29.

Irradiation of 4aβ,8aβ-Dicyano-5α,8α-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (29) in the Solid State. Substrate **29** (mp 153–154 °C) was prepared from 2,3-dicyanobenzoquinone and *trans,trans*-2,4-hexadiene as described by Scheffer, Jennings, and Louwerens.[13b]

Crystals of adduct **29** (172 mg) were photolyzed at 0.02 Torr between 7.2 and 8.3 °C for a total of 35 h. Recovery of material from the reaction vessel was 97%. Preparative TLC (silica gel, 30% ethyl acetate–benzene) gave 130 mg of residual starting material **29** and 27 mg (75%) of an oil which solidified. The yields from two other runs were 74 and 65%. The product from all runs was combined and recrystallized twice from ether–petroleum ether with a few drops of acetone to give colorless crystals of the known[13b] oxetane **30**, mp 138–139 °C (lit.[13b] mp 137.5–139 °C) whose spectra were identical with those of an authentic sample prepared by photolyzing **29** in benzene.[13b]

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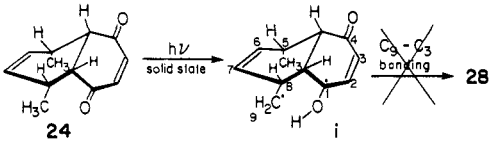
(34) Note in addition that diketone **28**, which is formed from **24** in solution via γ-hydrogen abstraction followed by C_9 to C_3 bonding and ketonization, cannot be formed in the solid state since the required biradical collapse is impossible from the twist conformation I. Formation of **28** requires an intervening half-chair–half-chair ring flip of biradical i which is possible in solution but not in the solid state.



(35) Assuming only cis stereochemistry at the four ring junctions, six diastereomeric dimers of substrate **25** are possible. They are anti-anti-anti, anti-anti-syn, syn-anti-syn, anti-syn-anti, anti-syn-syn, and syn-syn-syn. Of these, the anti-anti-anti dimer **27b** is clearly the least sterically congested and the syn-syn-syn isomer the most.
(36) It is interesting to note that the relative carbonyl double bond geometry shown in Figure 4 appears to favor involvement of the oxygen double bond 2p atomic orbital rather than its n orbital in interacting with and bonding to C_7. This is in contrast to the commonly accepted notion that the mechanism of oxetane formation between carbonyl compounds and electron-rich olefins involves the oxygen n orbital in exciplex and/or initial biradical formation. See N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975), and references cited therein.
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Synthesis and Crystal Structure of 2,3,4,5,6,7,8,9-Octahydro-2,2,5,5,8,8-hexamethyl-1*H*-benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]tripyrrolium Tribromide Dihydrate, $C_{18}H_{30}N_3^{3+}\cdot 3Br^-\cdot 2H_2O$[1]

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Abstract: A new trisquaternary ammonium compound, referred to as triquat tribromide dihydrate, has been synthesized from a mixture of hexabromomethylbenzene and anhydrous dimethylamine in anhydrous ethanol. The colorless product crystallizes in the centrosymmetric triclinic space group $P\bar{1}$-C^1_i with lattice parameters $a = 11.097 \pm 0.001$, $b = 13.502 \pm 0.001$, $c = 9.124 \pm 0.001$ Å, $\alpha = 92.87 \pm 0.01°$, $\beta = 111.37 \pm 0.01°$, and $\gamma = 66.08 \pm 0.01°$. The structure consists of discrete cations of nominal C_3 symmetry, two of which are held together electrostatically as a sandwich by a central network of bromide anions and water. The two halves of the resulting dimer are related by a crystallographic center of symmetry. At the center of the triply charged cation is a planar six-membered aromatic ring to which are attached three appreciably puckered five-membered (pyrrolium) rings. There are two methyl groups per nitrogen atom.

Introduction

There are very few tris- and tetrakisquaternary ammonium salts reported in the literature in which the charged nitrogen atoms are relatively close to each other in a molecule possessing rigidity and high symmetry.[4a,b] We wish to report the synthesis and characterization of 2,3,4,5,6,7,8,9-octahydro-2,2,5,5,8,8-hexamethyl-1*H*-benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]tripyrrolium tribromide dihydrate.

It had been recognized by Backer[4c] that hexabromometh-

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