Photochemical Hydrogen Abstraction Reactions Proceeding through Five-Membered Transition States. Product Control through Restriction of Rotation in Diradical Intermediates[1,2]

John R. Scheffer,* Barry M. Jennings, and John P. Louwerens

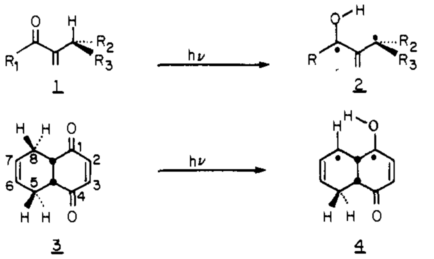
Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada. *Received February 23, 1976*

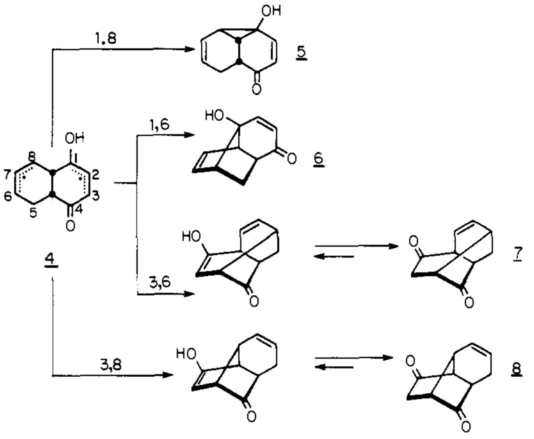
Abstract: The photochemistry of the 4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (**3**) ring system has been studied and the effect of placing substituents at certain positions assessed. For substrates possessing hydrogen atoms at C(5) and C(8) trans to the bridgehead substituents, two primary photochemical processes are observed: (1) allylic [i.e., C(5) or C(8)] hydrogen abstraction by the adjacent oxygen atom through a five-membered transition state and (2) allylic hydrogen abstraction by enone carbon through a six-membered transition state [i.e., abstraction of a C(5) hydrogen by C(2) or a C(8) hydrogen by C(3)]. Process 2 has so far been observed only for substrates with alkyl substitution at C(2) and C(3), indicating it may involve π,π^* excited states. Stern–Volmer quenching studies show process 1 to be singlet derived (unquenchable), whereas process 2 is triplet derived. Methyl or phenyl substitution at C(2) renders the allylic C(5) and C(8) hydrogens nonequivalent, and photolysis of these substrates proceeds in accord with expectations based on formation of the more stable diradical intermediate. Due to the cis ring junction stereochemistry, the diradicals formed via processes 1 and 2 can undergo interannular collapse to afford novel tricyclic photoproducts of general structure **6, 7,** and **8**. However, the exclusive formation of specific photoproduct types in the photolysis of bridgehead-substituted systems is in accord with the idea that hydrogen abstraction occurs via a single conformational isomer to give a diradical species of the same conformation and that this species is restricted to this conformation prior to closure by bulky or very polar bridgehead groups but rapidly equilibrated when the bridgehead groups are hydrogen. Finally, replacing the abstractable allylic hydrogens by methyl groups blocks both hydrogen-abstraction processes 1 and 2. In these cases irradiation brings about the unusual (for these systems) processes of intramolecular oxetane formation and (in one instance) 2 + 2 cage photoproduct formation.

Introduction

Organic chemistry is replete with reactions which proceed through five-membered transition states. This is particularly true of ring closure or cyclization reactions, and it is well established that five-membered rings are usually formed more rapidly than six in a wide variety of cases.[3] However, just the reverse is true for intramolecular hydrogen-transfer processes. Hydride[4] and hydrogen atom[5] shifts through five-membered transition states are extremely rare, whereas the corresponding six-membered transition state processes are commonplace. This reactivity pattern is followed in excited state reactions as well. For example, the intramolecular abstraction of a γ-hydrogen atom by an excited carbonyl group through a six-membered transition state (Norrish type II reaction) is one of the most ubiquitous and well studied of photochemical reactions. However, the analogous β or five-membered transition state photochemical hydrogen abstraction process is, by comparison, virtually unknown.[6] Only two types of molecular systems have been found to date which are generally capable of photochemical β-hydrogen abstraction. These are the α-methylene ketones **1** studied by Agosta and co-workers[7] and the 4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone system **3** with which we have been concerned.[8]

In this paper we describe the continuation of our studies aimed at effecting a full understanding of the factors controlling the novel **3** → **4** photoprocess. These include (1) the effect that placing methyl and phenyl substituents at C(2) has on the regioselectivity of β-hydrogen abstraction, (2) the effect of introducing methyl, nitrile, and carbomethoxy bridgehead (C(4a) and C(8a)) substituents, (3) the effect of introducing and varying the configuration of methyl substituents at C(5) and C(8), and (4) Stern–Volmer quenching studies. In addition to being of mechanistic interest, these studies promised to provide facile syntheses of unusual strained polycyclic small ring systems since, as a result of its cis ring fusion, diradical intermediate **4** is, in principle, capable of "interannular" biradical collapse to give products **5–8**. Our previous work had indeed provided examples of ring systems **6, 7,** and **8**. A second goal of our research was hence to ascertain how factors 1 to 3 above are important in controlling the partitioning of diradical **4** between photoproducts **5–8**.[9]





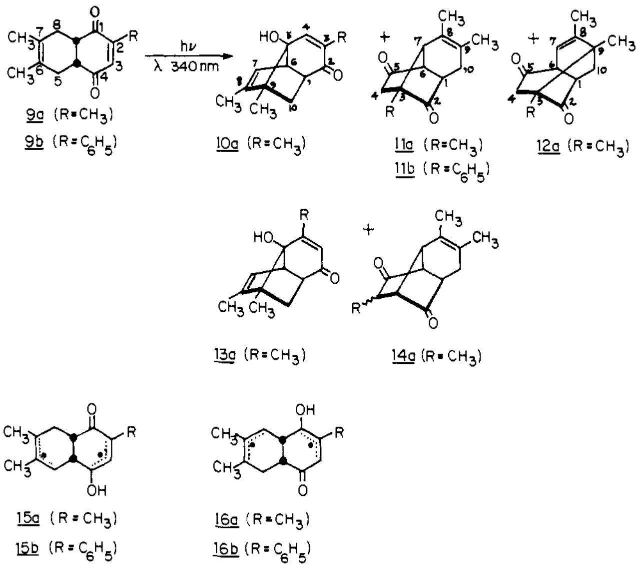
Results

Regioselectivity of β-Hydrogen Abstraction. The addition of methyl-*p*-benzoquinone and phenyl-*p*-benzoquinone to 2,3-dimethylbutadiene afforded the tetrahydro-1,4-naph-

Table I. Relative Photoproduct Ratios in Photolysis of **9a**

Solvent	10a	11a	12a	13a	14a
Benzene	3.8	1.0	2.6	3.4	
tert-Butyl alcohol	1.0	9.6		3.0	1.0

Scheme I



thoquinones **9a** and **9b**, respectively (Scheme I),[10] in which the β-hydrogen atoms at C(5) are no longer equivalent by symmetry to those at C(8). Of the two possible diradicals resulting from intramolecular β-hydrogen transfer, those of type **15** [abstraction from C(5)] are expected to be more stable than those of structure **16** [abstraction from C(8)]. Given the reasonable assumption that diradicals **15** and **16** collapse at comparable rates, one would then expect that the products arising from intermediate **15a** (i.e., **10a–12a**) should predominate over those formed from **16a** (**13a** and **14a**). Reference to Table I shows that this is exactly the experimental result in both benzene and *tert*-butyl alcohol.[11] In the case of **9b**, irradiation gave only **11b**, albeit in relatively low yield (35%). Product **11b** is again indicative of preferential formation of diradical type **15b**, but the argument is less compelling in this case due to the extensive photodestruction of starting material involved.

The structures of photoproducts **10a–14a** and **11b** were assigned on the basis of their spectral data. Based on our previous experience[8] with analogous ring systems, it has become apparent that each photoproduct type displays two or three general and characteristic spectral features which uniquely identify it. These features will be summarized at this point; full spectral data are given in the Experimental Section. The generalities which follow rest ultimately on x-ray crystal structure data.[8]

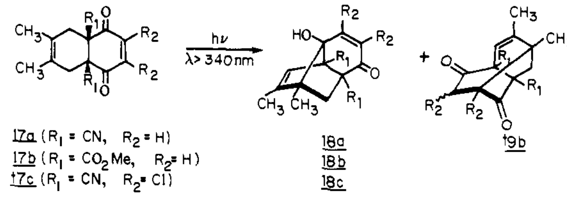
So-called enone-alcohols of type **10a** and **13a** are characterized by α,β-unsaturated carbonyl stretching frequencies near 5.95 μ and weak OH absorptions at 2.80 μ. The absorptions for both **10a** and **13a** were 5.93 and 2.80 μ. Particularly diagnostic of the enone-alcohol structure is a broad doublet in the NMR at approximately τ 7. This signal is attributed to the methine hydrogen at C(6) and was located at τ 7.05 in compound **10a** and τ 7.00 in **13a**. Photoproduct **10a** was clearly distinguishable from **13a** by the chemical shift of the vinyl hydrogen on the α,β-unsaturated double bond. This signal appeared at τ 3.61 in **10a** as compared with τ 4.29 in **13a**, the difference being due to the well-known[12] deshielding experienced by the β-vinyl hydrogens of α,β-unsaturated carbonyl compounds. Similarly the α,β-unsaturated vinyl methyl signal in **13a** comes at lower field (τ 8.06) than the corresponding signal in **10a** (τ 8.22).

Turning now to photoisomers **11a, 11b,** and **14a,** previous experience has shown that ring systems of this type exhibit infrared carbonyl stretching frequencies in the range 5.72 ± 0.02 μ. In line with this were the absorptions at 5.70 μ for **11a** and **11b** and 5.72 μ for **14a**. Compound **11a** could easily be differentiated from **14a** by the presence in the latter of a three-proton doublet at τ 8.95 (J = 7.5 Hz) due to the methyl group at C(4); the tertiary methyl group in **11a** appeared as a sharp singlet at τ 8.84. Ene-dione **11b** was assigned as having the bridgehead phenyl structure since its NMR showed no resonances below τ 6.88 in the benzylic region of the spectrum. For example, the benzylic hydrogens of dibenzyl ketone appear at τ 6.3.[13]

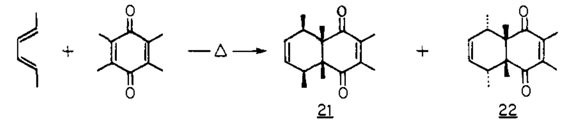
Finally, photoproducts of general structure **12a** are particularly easy to identify. For one thing they possess double infrared carbonyl stretching frequencies at 5.70 ± 0.02 and 5.80 ± 0.02 μ due to the five- and six-membered ketone groups, respectively. Photoisomer **12a** exhibited peaks at 5.68 and 5.80 μ. Secondly, **12a** and analogues are β,γ-unsaturated ketones and as such display the typically[14] strong n,π^* uv spectra associated with this chromophore. Compound **12a** showed uv (MeOH) 294 (ϵ 481) and 307 nm (ϵ 426). The position of the R = CH_3 group in **12a** was assigned as shown based on the observation of two sharp tertiary methyl singlets in the NMR at τ 8.73 and 9.02.

The Effect of Introducing Bridgehead Substituents. Our initial studies in this area were with substrates **17a–17c** formed from the Diels-Alder addition of 2,3-dimethylbutadiene to 2,3-dicyanobenzoquinone, 2,3-dicarbomethoxybenzoquinone, and 2,3-dichloro-5,6-dicyanobenzoquinone, respectively (Scheme II).[15] Irradiation of these compounds gave moderate yields of the corresponding enone–alcohols **18a–18c** analogous to photoproducts **10a** and **13a**. Only in the case of **17b** was any other photoproduct type obtained, that being **19b** analogous to **12a**. The **18b**:**19b** ratio varied with time from approximately 1:1 after 2.5 h to near 1:7 after 5 h. The photochemical conversion of **18b** to **19b** has precedent in our previous work.[8] The total yield in each of the above photolyses was 50 to 70%. The structure of enone-alcohol **18a** was established unequivocally by x-ray crystallography[16] while the structures of photoproducts **18b, 18c,** and **19b** were deduced from their spectra which are given in the Experimental Section.

Scheme II

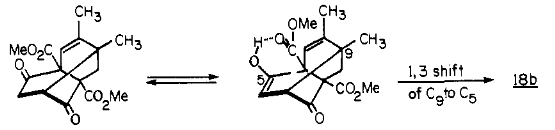


As part of the proof of structure of photoproduct **19b** it was subjected to thermolysis. The novel result was that sealed tube thermolysis of **19b** at 190 °C for 3.5 h afforded a high yield of enone-alcohol **18b**. Analogous ring systems lacking bridgehead ester groups (e.g., **12a**) undergo 1,3 shifts of C(3) from C(9) to C(5).[8] An explanation of these results which accounts for the difference in behavior between systems such as **12a** and **19b** is that in the latter case, rearrangement [1,3 shift of C(9)]



occurs through the enol form **20** which is stabilized by hydrogen bonding not available to the enol of **12a**.

The Effect of Introducing Substituents at C(5) and C(8). The Diels-Alder reaction of duroquinone with *trans,trans*-2,4-hexadiene gave two adducts, **21** and **22**, resulting from exo and



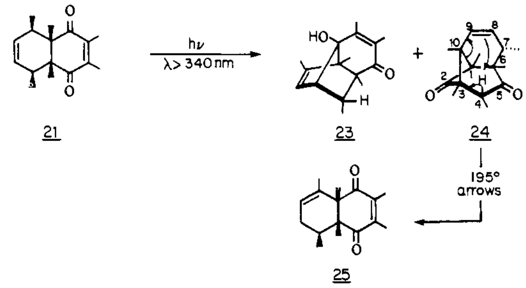
19b

20

endo addition, respectively. The stereochemical assignments were based on (a) the observed thermodynamic preference for adduct **21** (exo stereochemistry normally favored[17]) and the kinetic preference for adduct **22** (endo stereochemistry favored[17]), and (b) the difference in chemical shift of the C(5) and C(8) allylic protons in **21** (τ 7.17, two proton quartet, J = 7 Hz) and **22** (τ 7.85, two proton quartet, J = 7 Hz), which may be attributed to the anisotropic deshielding effect of the adjacent cis carbonyl groups on these protons in Diels-Alder adduct **21**.[18] A similar but less pronounced NMR deshielding effect was noted for the C(5)/C(8) methyl groups in **22** (τ 9.02, doublet, J = 7 Hz) relative to those in **21** (τ 9.12, doublet, J = 7 Hz).

Irradiation of adduct **21** in benzene gave a 1:2 ratio of photoproducts **23** and **24** in 80% overall isolated yield (Scheme III). The structure of photoproduct **23** (stereochemistry at C(10) assumed) was deduced from its spectral data which are given in the Experimental Section. Photoproduct **24**, however, represents a much less common product type, having been observed only once before in tetrahydro-1,4-naphthoquinone photochemistry.[8] Of primary importance in the structural assignment was the NMR spectrum of **24** showing methyl singlets at τ 8.98, 9.01, 9.03, and 9.09 as well as methyl doublets (J = 7.5 Hz, stereochemistry at C(4) and C(7) assumed) at τ 8.98 and 9.02. The C(4) methine proton appeared as a clean quartet (J = 7.5 Hz) at τ 7.30, and the vinyl hydrogens appeared basically as an AB quartet ($J_{8,9}$ = 10 Hz) with smaller couplings ($J_{7,9}$ = 5.5 Hz, $J_{7,8}$ = 1.5 Hz) superimposed. Also revealing was the infrared spectrum of **24** with carbonyl absorptions at 5.66 (cyclobutanone) and 5.85 μ (cyclohexanone). Further evidence for structure **24** was found in its thermal (195 °C, sealed tube) conversion into diene-dione **25** (Scheme III). An analogous retro-ene (arrows) reaction was recently observed.[8]

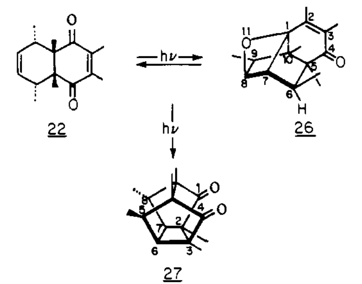
Scheme III



21 23 24 25

In contrast to the results of photolysis of exo adduct **21**, irradiation of benzene solutions of endo adduct **22** led to the formation of two products subsequently identified as the intramolecular oxetane **26** and the cage compound **27** (Scheme IV). GLC showed that **26** was formed rapidly until the **22**:**26** ratio reached ca. 1:2; thereafter this ratio did not change, and cage diketone **27** was slowly formed at the expense of both **22** and **26** until it remained as the sole product. Workup of the reaction at this point thus allowed for the isolation of near-quantitative yields of **27**.

Scheme IV



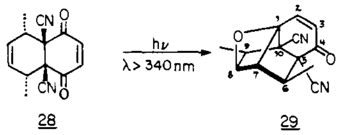
22 26 27

The structures of photoisomers **26** and **27** rest on their spectral data. Cage compound **27** exhibited the following simple NMR spectrum consistent with its symmetry: τ 7.40 (quartet, 2, J = 7 Hz, C(5) and C(8) methines), 7.60 (singlet, 2, C(6) and C(7) methines), 8.97 (singlet, 6, CH_3), 9.07 (singlet, 6, CH_3), and 9.33 (doublet, 6, J = 7 Hz, C(5) and C(8) CH_3). Also informative was the ir spectrum showing carbonyl peaks at 5.68 and 5.75 μ. Similar split carbonyl peaks have been observed in analogous C(5)-C(8) bridged cage compounds.[19]

Oxetane **26** showed an α,β-unsaturated carbonyl ir stretch (KBr) at 6.04 μ and exhibited the following definitive NMR spectrum (CCl_4): τ 5.64 (doublet, 1, J = 4 Hz, C(8) methine), 7.40 (doublet, 1, J = 4 Hz, C(7) methine), 7.78 (quartet, 1, J = 7 Hz, C(6) or C(9) methine), 8.03 (broad singlet, 3, vinyl CH_3), 8.33 (broad singlet, 3, vinyl CH_3), 8.35 (quartet, 1, J = 7.5 Hz, C(6) or C(9) methine, 8.97 (singlet, 3, C(5) or C(10) CH_3), 9.01 (doublet, 3, J = 7 Hz, C(6) or C(9) CH_3), 9.30 (singlet, 3, C(5) or C(10) CH_3), and 9.46 (doublet, 3, J = 7.5 Hz, C(6) or C(9) CH_3).

A second example of intramolecular oxetane formation was found in the photolysis of Diels-Alder adduct **28** (Scheme V).

Scheme V



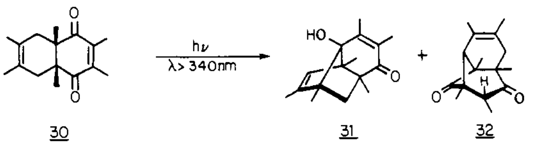
28 29

Irradiation of this material in either benzene or *tert*-butyl alcohol gave ca. 60% isolated yields of crystalline oxetane **29** after column chromatography. Unlike the photolysis of adduct **22**, no cage diketone product could be detected. Independent irradiation of **29** for extended periods gave no reaction.

The NMR spectrum of oxetane **29** was very similar to that of oxetane **26** and consisted of signals at τ 2.46 (doublet, 1, J = 10 Hz, C(2) vinyl), 3.73 (doublet, 1, J = 10 Hz, C(3) vinyl), 5.23 (doublet, 1, J = 4 Hz, C(8) methine), 6.83 (doublet, 1, J = 4 Hz, C(7) methine), 7.11 (quartet, 1, J = 7 Hz, C(6) or C(9) methine), 7.35 (quartet, 1, J = 7.5 Hz, C(6) or C(9) methine), 8.60 (doublet, 3, J = 7 Hz, C(6) or C(9) methyl), and 9.05 (doublet, 3, J = 7.5 Hz, C(6) or C(9) methyl). Ultimate proof of structure for photoproduct **29** came from a single crystal x-ray structure determination, the details of which will be published elsewhere.[16] This study fully corroborated the structure assigned.

Stern-Volmer Quenching Studies. The reaction chosen for study was the irradiation of the duroquinone-2,3-dimethylbutadiene Diels-Alder adduct **30** (Scheme VI). Previous work had shown that this reaction cleanly and reproducibly gives rise to photoproducts **31** and **32** (ratio 1:2) in 80% overall iso-

Scheme VI



30 31 32

lated yield.[8] The process is thus exactly analogous to the **21** to **23** + **24** photoreaction described in the present work. Kinetic studies were of interest for these reactions since it seemed likely (see Discussion section) that the enone-alcohol photoproduct type represented by **31** and **23** was formed via a mechanism completely different from that which gave rise to the cyclobutanone containing photoproduct type exemplified by **32** and **24**. The possibility of differential quenching of discrete excited states was thus raised.

Initial quantum yield studies in the absence of quencher were carried out in benzene at 366 nm using an apparatus similar to that described by McCullough et al.[20] Under these conditions the quantum yields for appearance of enone-alcohol **31** and cyclobutanone **32** were 0.066 ± 0.003 and 0.089 ± 0.003, respectively. These values were invariant within experimental error over a starting adduct **30** concentration range of 0.008 to 0.06 M. Since it appears[21] that the triplet energy of the ene-dione chromophore of Diels-Alder adduct **30** is approximately 58 kcal/mol, 1,3-cyclohexadiene (E_T = 52.4 kcal/mol)[22] was chosen as a quencher. Due to the fact that 1,3 dienes (acyclic) are known to react photochemically with *p*-benzoquinones,[23] it was deemed desirable to carry out parallel quenching runs with *trans*-stilbene (E_T = 50 kcal/mol)[24] as a quencher. The results of these experiments, plotted as Φ_0/Φ vs. quencher concentration, are shown in Figure 1. The upward curvature of the points in the quenching of the formation of **32** by 1,3-cyclohexadiene above 0.1 M can reasonably be attributed to nearest-neighbor quenching.[25] For both 1,3-cyclohexadiene and *trans*-stilbene, triplet-triplet energy transfer was verified as the quenching mechanism by the observation of GLC peaks due to cyclohexadiene dimers and *cis*-stilbene, respectively. The results thus indicate that photoproduct **31** is formed through a singlet (unquenchable) excited state, whereas the cyclobutanone product **32** arises via the intermediacy of a triplet excited state. These points will be elaborated in the Discussion section.

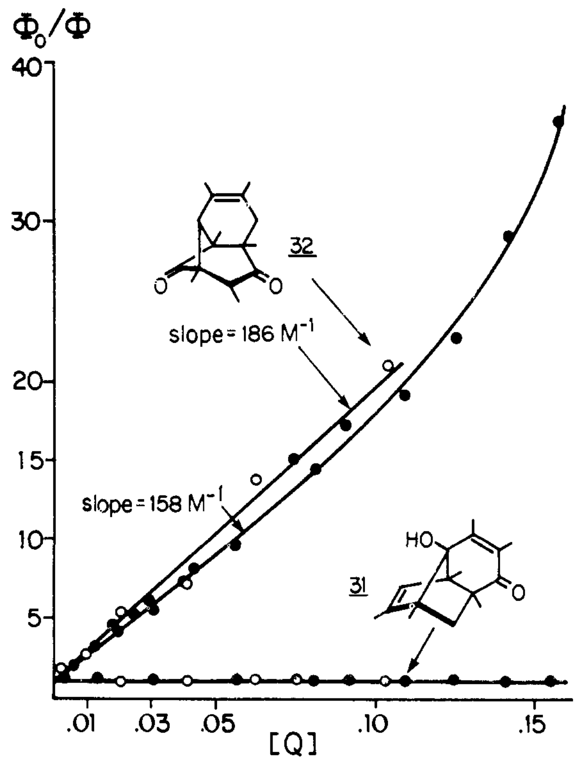
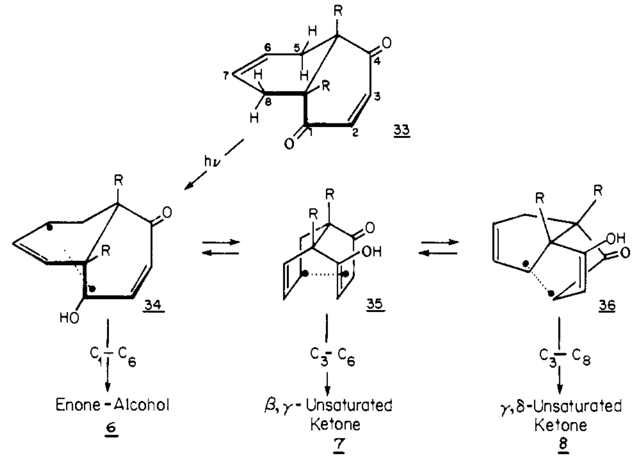


Figure 1. A plot of Φ_0/Φ for the appearance of **31** and **32** vs. quencher concentration in the photoreaction **30** → **31** + **32**. The concentration of starting material **30** was 0.015 M, and the quenchers used were 1,3-cyclohexadiene (●) and *trans*-stilbene (○).

Discussion

The results presented can be nicely accommodated within a common framework if one makes the unifying assumption that in solution tetrahydro-1,4-naphthoquinones exist mainly in twist conformation **33** (Scheme VII) and that their photochemistry involves the reaction of excited states and the initial formation of diradical intermediates with this same basic shape. In connection with solid state photochemical studies, we have had occasion to examine the x-ray crystal structure of eight variously substituted 4a*β*,5,8,8a*β*-tetrahydro-1,4-naphthoquinones including most of the substrates used in the present work.[26] It was found that regardless of the presence or absence of bridgehead or other substituents, all eight crystallized in "twist" conformation **33** with only relatively small differences in bond lengths and torsion angles among them. This plus the fact that it is experimentally found[27] that conformationally mobile systems generally crystallize in their most stable conformations lends strong support to the argument that twist conformer **33** is the major one present in solution at room temperature.

Scheme VII



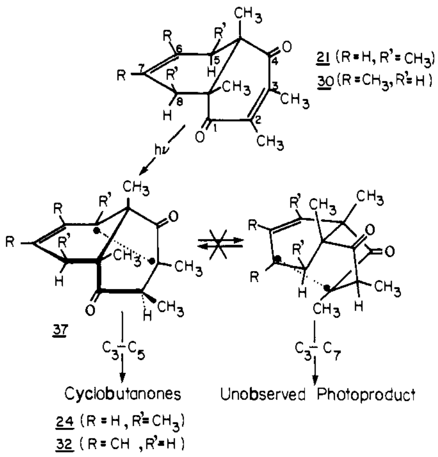
Abstraction of the "endo" *β*-hydrogen atom from C(8) by the excited C(1) carbonyl oxygen (oxygen to hydrogen distance in the crystalline state 2.26 to 2.58 Å)[26] thus gives rise to the diradical species **34** with the same conformation as its precursor 33. This intermediate is ideally set up to undergo C(1) to C(6) bonding to give enone-alcohol (type **6**, e.g., **10a**, **13a**, **18a–c**, **23**, and **31**) products. However, C(3) to C(6) bonding)leading to photoproducts of general structure **7**, e.g., **12a** and **19b**) and C(3) to C(8) closure (giving products analogous to **8**, e.g., **11a**, **11b**, and **14a**) require conformational isomerism to **35** and **36**, respectively, each of which involves either formation of, or rotation through, an eclipsed bridgehead R group arrangement. *It is our contention that bulky bridgehead groups, particularly methyl groups, restrict this conformational isomerism during the excited state and diradical lifetimes involved, and that in effect the diradical intermediate is frozen in conformation* **34** *from which only enone-alcohol,* **6**, *formation is possible.*

This hypothesis is well in accord with experimental observation for substrates with bridgehead methyl substitution. Thus *β*-hydrogen abstraction in the duroquinone adducts **21** and **30** leads only to the corresponding enone-alcohols **23** and **31**, respectively. (The mechanism of the formation of the cyclobutanone containing photoproducts **24** and **32** will be discussed separately.) No such restrictions apply to systems possessing bridgehead hydrogen atom substitution, however. For example, substrates **9a** and **9b** form all three photoproduct types upon irradiation, indicating that conformational isomerism can successfully compete with diradical closure. Several other examples of similar behavior were observed in our earlier work.[8]

The situation with respect to carbomethoxy and cyano bridgehead substitution is less clear-cut. It will be recalled that the bridgehead diester **17b** afforded products of type **8** (i.e., **19b**) as well as the enone-alcohol **18b** upon irradiation, whereas only the latter type of product was isolated in the photolysis of the dicyano bridgehead substituted adducts **17a** and **17c**. Apparently then, bridgehead R = CN substitution is more effective than ester substitution at restricting the **34** ⇄ **35** ⇄ **36** equilibrium (dipole-dipole repulsion?), although this conclusion must be regarded as tentative in view of the relatively large amounts of photodecomposition (30-50%) observed in these latter three systems.

The same general type of reasoning can be applied to the formation of the cyclobutanone-containing photoproducts **24** and **32** from adducts **21** and **30**, respectively. We previously presented preliminary evidence[8] (of a negative nature) that this type of photoisomer is produced via a mechanism involving transfer of a C(5) [or C(8)] allylic hydrogen atom through a six-membered transition state to the excited C(2) [or C(3)] double bond carbon atom, followed by C(3)-C(5) [or C(2) -C(8)] ring closure (Scheme VIII). The results described in this paper strongly support this mechanism. First of all, the twist conformers of **21** and **30** (Scheme VIII) are ideally arranged to undergo the postulated hydrogen-transfer process. The C(5) endo hydrogen to C(2) carbon distances in the crystalline state of adducts **21** and **30** are 2.70 and 2.89 Å, respectively,[26] close to the sum of the van der Waals radii involved,[28] and hence indicative of the feasibility of this type of transfer. Secondly, the cyclobutanone containing photoproducts **24** and **32** are again those expected from a "frozen" (by virtue of its bridgehead methyl substituents) diradical **37** possessing the same basic twist conformation as the starting substrates. Bonding between C(3) and C(7) is impossible without ring flipping of conformer **37** and hence is not observed.

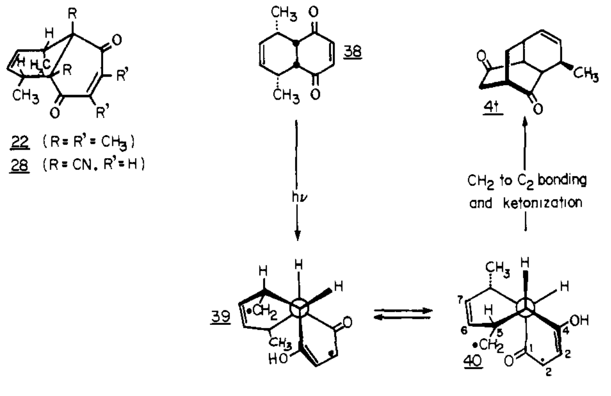
Scheme VIII



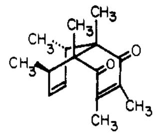
Finally the suggestion that adducts **21** and **30** react via two distinct mechanisms (β-hydrogen abstraction by oxygen leading to **23** and **31** vs. γ-hydrogen abstraction by carbon leading to **24** and **32**) is supported by the Stern-Volmer quenching results which show the former process to be singlet derived and the latter triplet derived. While the reasons for this singlet-triplet reactivity difference are not known at the present time, it is interesting to note that in their work on β-hydrogen abstraction in α-methylene ketones, Agosta and co-workers[29] have found a similar preference for reaction via singlet excited states. In addition, in those cases in which it has been studied, hydrogen abstraction by the β carbon of an α,β-unsaturated ketone has been found to be a triplet state process, very likely π,π*.[30] In view of this and of the well-known[31] effect of enone double bond methyl groups in lowering the energy of the $(\pi,\pi^*)^3$, we tentatively suggest that the reactive triplet states of adducts **21** and **30** are also largely π,π* in nature. Unfortunately, adduct **30** does not phosphoresce (EPA glass, 77 K) thus precluding direct determination of the nature or lifetime of its triplet. Nevertheless, from the slopes of the Stern-Volmer plots of the quenching of the formation of diketone **32** (see Figure 1), and with the assumptions that (a) quenching is diffusion controlled (k_q in benzene ca. 6×10^9 M^{-1} s^{-1}) and (b) that the process of γ-hydrogen abstraction by enone carbon is the fastest (by at least an order of magnitude) triplet state deactivation process, an upper limit of ca. 3.5×10^7 s^{-1} may be estimated for the rate constant for the abstraction. This is about an order of magnitude less than the rate constant for triplet state allylic γ-hydrogen abstraction by oxygen in 1-phenyl-5-hexen-1-one.[32]

We turn now to a discussion of the possible reasons for the different photochemical behavior observed for the endo Diels-Alder adducts **22** and **28**, namely intramolecular oxetane formation (**26** and **29**, respectively), and in the case of adduct **22**, cage compound **27** formation. Again these reactions are explicable in terms of the twist conformation shown in Scheme IX. As can be seen, this conformation does not allow intramolecular C(5) or C(8) allylic hydrogen abstraction to take place. It might be argued that γ-hydrogen abstraction from the C(5) methyl group by the C(4) carbonyl oxygen will, as a result, be favored. Indeed, just this mode of reaction was observed[8] for Diels-Alder adduct **38** (Scheme IX). Irradiation of **38** gave moderate yields of tricyclic diketone **41** resulting from C(5) methyl γ-hydrogen abstraction, followed by bonding of the methylene radical so produced to C(2) and ketonization.[8] However, this reaction requires conformational isomerism of the first-formed diradical **39** into **40** due to the remoteness of the radical centers in **39**. The reason then that adducts **22** and **28** do not form photoproducts analogous to **41** is that the **39** ⇄ **40** type of conformational isomerism is restricted by the bridgehead substituents. If formed, the bridgehead substituted species analogous to **39** likely revert to starting material via reverse hydrogen transfer.[32]

Scheme IX



Thwarted in their attempts to take part in hydrogen-abstraction processes, the excited states of adducts **22** and **28** seek an alternative reaction pathway, that of intramolecular oxetane formation, a common *inter*molecular reaction for the closely related *p*-benzoquinone system.[33] The twist conformations of adducts **22** and **28** are ideally suited for this reaction since the reacting carbon-carbon and carbon-oxygen double bond moieties are held in close proximity. Oxetane formation is photoreversible in the case of **22** but not in the case of **28**. This allows the slow, irreversible formation of cage compound **27** in the former case but not in the latter. While direct evidence is lacking on this point at the present time, it seems most reasonable to assume that the cage photoproduct is formed through conformation **42** (see below) which, although of higher energy than the twist conformation, is undoubtedly present in small amounts in the equilibrium mixture. Thus only a very special set of circumstances appears to allow cage product formation, namely (a) blocking of the normally favored hydrogen-abstraction processes and (b) reversibility of the second-favored process of intramolecular oxetane formation. The extension of these ideas plus the chemistry of the unusual cage compound **27** are under active investigation.



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Experimental Section

General. Ir spectra were obtained using a Perkin-Elmer 137 spectrophotometer. NMR spectra were recorded with either Varian T-60, HA-100, or XL-100 spectrometers using tetramethylsilane as an internal standard. Mass spectra were obtained on either a direct inlet AEI MS-9 or an Atlas CH4-B instrument at 70 eV, and uv spectra were measured on a Unicam SP-800 B spectrophotometer. Melting points were taken on either a Thomas-Hoover capillary apparatus or a Fisher-Johns hot stage apparatus and are uncorrected. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda, whom we thank. For GLC Varian-Aerograph 90-P3 and Autoprep Model A700 instruments were used with helium as the carrier gas. The following columns were used: column A, 5 ft × 0.25 in. stainless steel, 20% DEGS on 60/80 Chromosorb W; column B, 5 ft × 0.25 in. stainless steel, 10% FFAP on 60/80 Chromosorb W; column C, 7 ft × 0.25 in. stainless steel, 10% OV-1 on 60/80 Chromosorb W. Internal standards were not used in GLC monitoring of qualitative photolyses since it has been found that isomeric photoproducts of the type encountered in this work have identical thermal conductivities within experimental error (±10%). All photolysis solvents were purified by standard procedures and distilled before use. All photolysis solutions were thoroughly deoxygenated prior to irradiation with either Canadian Liquid Air argon (<5 ppm oxygen) or with L grade high-purity nitrogen. Preparative photolyses were performed by means of a 450-W medium pressure Hanovia Type L lamp placed in a water-cooled quartz immersion well. Interposed between the lamp and reaction vessel was a 15 × 15 cm plate of Corning No. 7380 glass (transmitting light of $\lambda > 340$ nm) which was cooled by a stream of air. The reaction vessel, surrounded by aluminum foil so as to receive the maximum amount of light, was placed 6 to 10 in. from the lamp. For silica gel column chromatography, columns were slurry packed in the eluting solvent with silica gel <0.08 mm from E. Merck AG and eluted under 5-10 psi nitrogen pressure.

Quantum Yield Measurements. The apparatus used was essentially identical with that reported by Bowman, Chamberlain, Huang, and McCullough.[20] We thank Professor McCullough for advice and help in its assembly. Light output and absorption were monitored by ferrioxalate actinometry.[34] Uv measurements were made on a Cary Model 15 recording spectrophotometer. The solutions to be photolyzed were thoroughly degassed prior to photolysis by four freeze-pump-thaw cycles using Argon as the purging gas. Stirring was accomplished by 1 × 0.2 cm Teflon coated magnetic bars placed inside the sample and reference cells. The monochromator was set at 366 nm with an inlet slit width of 5.4 mm and an exit slit width of 3 mm giving a band pass of 22 nm at half-peak height.[35] For all GLC operations involving the measurement of quantum yields, a Varian-Aerograph Model 1520 B instrument with a flame ionization detector was used. The column employed was 10 ft × ⅛ in. stainless steel packed with 20% DEGS on 60/80 Chromosorb W and operated at 135 °C with a helium flow rate of 30 ml/min. Peak area quantitation was by means of a Disc Chart Integrator Model 201-B fitted to the recorder. Biphenyl was used as the internal standard and was added after photolysis. Calibration curves were constructed for the response of the detector to each of the photoproducts **31** and **32** plus internal standard.

Irradiation of 2,6,7-Trimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (9a). Adduct **9a** was prepared by the method of Bergmann and Bergmann,[9] mp 89-91 °C (lit.[9] mp 93-94 °C). A solution of 804 mg (3.94 mmol) of **9a** in 250 ml of benzene was irradiated with light of wavelength >340 nm. The reaction was monitored by GLC (column A, 175 °C, helium flow 160 ml/min) which showed a rapid buildup of four new products. After 6.5 h, all starting material had reacted, and the ratio of products was **10a**:**11a**:**12a**:**13a** = 3.8:1:2.6:3.4. Isolation of the products was achieved by preparative GLC using the same column and conditions as above. All were collected as colorless oils which crystalllized on standing and were characterized by the following data.

5-Hydroxy-3,8,9-trimethyltricyclo[4.4.0.$0^{5,9}$]deca-3,7-dien-2-one (**10a**): mp (68 °C petroleum ether) 90-91.5 °C; ir (CCl_4) 2.78 (OH) and 5.93 (C=O) μ; NMR (CCl_4) τ 3.61 (m, 1, C_4 vinyl), 4.43 (m, 1, C(7) vinyl), 7.05 (m, 1, C(6) methine), 7.6-7.9 (m, 1, C(1) methine), 7.70 (s, 1, OH), 8.22 (br s, 6, C(3) and C(8) methyls), 8.6 (m, 2, C(10) methylenes), 8.91 (s, 3, C(9) methyl); uv (MeOH) 244 (6200) and 325 nm (58); mass spectrum (70 eV) *m/e* parent 204.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.25; H, 7.79.

3,8,9-Trimethyltricyclo[4.4.0.$0^{3,7}$]dec-8-ene-2,5-dione (**11a**): mp (68 °C petroleum ether) 69-70 °C; ir (CCl_4) 5.70 (C=O) μ; NMR (CCl_4) τ 7.40 (m, 1, C(6) methine), 7.5-7.65 (m, 2), 7.65-7.8 (m, 2), 7.79 (dd, 1, J = 18 Hz, 1 Hz, C(4) exo H), 8.01 (d, 1, J = 18 Hz, C(4) endo H), 8.28 (br s, 3, C(8) or C(9) methyl), 8.38 (br s, 3, C(8) or C(9) methyl), 8.84 (s, 3, C(3) methyl); uv (MeOH) 286 nm (78); mass spectrum (70 eV) *m/e* parent 204.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.15; H, 7.92.

3,8,9-Trimethyltricyclo[4.4.0.$0^{3,9}$]dec-7-ene-2,5-dione (**12a**): mp (68 °C petroleum ether) 108.5-109.5 °C; ir (CCl_4) 5.68 and 5.80 (C=O) μ; NMR (CCl_4) τ 4.42 (br d, 1, J = 7 Hz, C(7) vinyl), 6.77 (dd, 1, $J_{6,7}$ = 7 Hz, $J_{1,6}$ = 8 Hz, C(6) methine), 7.14 (d, 1, J = 17.5 Hz, C(4) exo H) 7.35 (dt, 1, $J_{1,6}$ = 8 Hz, $J_{1,10}$ = 2 Hz, C(1) methine), 8.12 (d, 3, J = 1.5 Hz, C(8) methyl), 8.15 (d, 1, J = 17.5 Hz, C(4) endo H), 8.3-8.7 (m, 2, C(10) methylenes), 8.73 (s, 3, C(9) methyl), 9.02 (s, 3, C(3) methyl); uv (MeOH) 294 (481) sh 307 nm (426): mass spectrum (70 eV) *m/e* parent 204.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.53: H, 7.85.

5-Hydroxy-4,8,9-trimethyltricyclo[4.4.0.$0^{5,9}$]deca-3,7-dien-2-one (**13a**): mp (68 °C petroleum ether) 92.5-93 °C; ir (CCl_4) 2.80 (OH) and 5.93 (C=O) μ; NMR (CCl_4) τ 4.29 (m, 1, C(3) vinyl), 4.36 (m, 1, C(7) vinyl), 7.00 (d, 1, J = 3 Hz, C(6) methine), 7.51 (s, 1, OH). 7.83 (m, 1, C(1) methine), 8.06 (d, 3, J = 1.5 Hz, C(4) methyl), 8.20 (d, 3, J = 1.5 Hz, C(8) methyl), 8.47 and 8.52 (each a singlet, 2, C(10) methylenes), 8.86 (s, 3, C(9) methyl); uv (MeOH) 244 (6100) and a long tailing shoulder from 310 to 355 nm (ϵ 51 at 325 nm); mass spectrum (70 eV) *m/e* parent 204.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.23; H, 7.77.

Photolysis of adduct **9a** in *tert*-butyl alcohol under otherwise identical conditions led to the formation of **10a**, **11a**, **13a** and to a new photoisomer **14a** in the relative proportions shown in Table I (text). Compound **14a**, mp 78-79 °C, was characterized as 4,8,9-trimethyltricyclo[4.4.0.$0^{3,7}$]dec-8-ene-2,5-dione on the basis of the following data: ir (KBr) 5.72 (C=O) μ; NMR ($CDCl_3$) τ 6.9-7.1 (m, 1, C(3) methine), 7.2-7.3 (m, 1, C(6) methine), 7.4-7.6 (m, 2) 7.6-7.8 (m, 3), 8.27 (br s, 3, C(8) or C(9) methyl), 8.39 (br s, 3, C(8) or C(9) methyl), 8.95 (d, 3, J = 7.5 Hz, C(4) methyl); uv (MeOH) 283 nm (78); mass spectrum (70 eV) *m/e* parent 204.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.23; H, 7.82.

Irradiation of 6,7-Dimethyl-2-phenyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (9b). Adduct **9b** was prepared by the method of Bergmann and Bergmann,[9] mp 108-110 °C (lit.[9] mp 113-114 °C). A solution of 211 mg (0.8 mmol) of **9b** in 50 ml of benzene was irradiated with light of wavelength >340 nm. The reaction was monitored by ir spectroscopy which showed a rapid change in the fingerprint region accompanied by a more gradual buildup of a 5.70 μ carbonyl peak until after 18.5 h, it was virtually the only carbonyl signal present. Evaporation of solvent followed by column chromatography (silica gel, 15% ethyl acetate-benzene) resulted in 95 mg (45%) of homogeneous pale-yellow oil. A second chromatography (silica gel, chloroform) yielded 83 mg of oil which crystallized on standing. Recrystallization from ether-petroleum ether (38 °C) gave 70 mg (33%) of 8,9-dimethyl-3-phenyltricyclo[4.4.0.$0^{3,7}$]dec-8-ene-2,5-dione (**11b**) as colorless crystals, mp 109-110 °C, identified on the basis of the following data: ir (CCl_4) 5.70 (C=O) μ; NMR ($CDCl_3$) τ 2.64 (s, 5, phenyl), 7.06 (dd, 1, J = 18 Hz, 1.5 Hz, C(4) exo H), 7.23 (br s, 1), 7.2–7.4 (m, 2), 7.50 (br s, 2), 7.62 (d, 1, J = 18 Hz, C(4) endo H), 8.32 (s, 3, C(8) or C(9) methyl), 8.69 (s, 3, C(8) or C(9) methyl); uv (MeOH) a long featureless absorption, ϵ at 252 nm 800, at 290 nm 140; mass spectrum (70 eV) *m/e* parent 266.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.09; H, 6.73.

Irradiation of 4aβ,8aβ-Dicyano-6,7-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (17a). This material was prepared by the method of Ansell, et al.,[15] mp 158–159 °C (lit.[15] mp 157–158 °C). A solution of 485 mg (2 mmol) of adduct **17a** in 250 ml of 10% v/v benzene-*tert*-butyl alcohol (to prevent freezing) was irradiated at λ >340 nm as before and the reaction followed by GLC (column C, 180 °C, 160 ml/min) which showed no starting material remaining after 3 h. Evaporation of solvents left a pale-brown residue which, on trituration with benzene followed by filtration, left 265 mg of colorless solid. Recrystallization of the solid from acetone–petroleum ether (68 °C) gave 240 mg (50%) of 1,6-dicyano-8,9-dimethyl-5-hydroxytricyclo[4.4.0.0^{5,9}]deca-3,7-dien-2-one (**18a**) as colorless crystals, mp 188–190 °C, which showed the following spectral characteristics: ir (KBr) 2.90 (OH), 4.41 (weak, CN), and 5.87 (C=O) μ; NMR (acetone-d_6) τ 2.99 (d, 1, J = 10 Hz, C(4) vinyl), 3.69 (d, 1, J = 10 Hz, C(3) vinyl), 4.07 (m, 1, C(7) vinyl), 7.19 (s, 1, disappears on adding D_2O, OH), 7.67 (d, 1, J = 13 Hz, one of C(10) methylenes), 7.7–8.2 (m, other C_{10} methylene and acetone resonances), 8.03 (d, 3, J = 1.5 Hz, C(8) methyl), 8.73 (s, 3, C(9) methyl); uv (MeOH) 239 (3800), tailing absorption (ϵ at 315 nm, 141); mass spectrum (70 eV) *m/e* parent 240.

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.87; H, 4.96; N, 11.63.

Column chromatography (silica gel, 33% ethyl acetate–benzene) of the benzene soluble material afforded 175 mg of an unidentified photoproduct whose NMR and mass spectra indicated that one molecule of *tert*-butyl alcohol had been incorporated. This material was not further investigated.

Irradiation of 4aβ,8aβ-Dicarbomethoxy-6,7-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (17b). This adduct was prepared by the method of Ansell and Nash,[15] mp 132–133.5 °C (lit.[15] mp 132–135 °C). A solution of 190 mg (0.62 mmol) of **17b** in 50 ml of benzene was irradiated for 5 h, after which the uv spectrum of the reaction mixture remained unchanged. Evaporation of solvent in vacuo resulted in a residue which showed two main components on TLC (silica gel, 40% ethyl acetate–benzene). Column chromatography on silica gel using the same solvent system gave 110 mg (58%) of enedione **19b** and 15 mg (8%) of enone–alcohol **18b**, both as colorless solids. In a second experiment, a solution of 80 mg (0.26 mmol) of **17b** in 40 ml of benzene was irradiated for a shorter length of time (2.5 h). Workup as above gave 28 mg (35%) of **19b** and 24 mg (30%) of **17b**. These structures were assigned on the basis of the following data:

1,6-Dicarbomethoxy-8,9-dimethyl-5-hydroxytricyclo[4.4.0.0^{5,9}]deca-3,7-dien-2-one (**18b**), mp 158.5–159 °C (benzene–petroleum ether, 68 °C), showed ir (KBr) 2.92 (OH), 5.80, and 5.90 (C=O) μ; NMR ($CDCl_3$) τ 3.41 (d, 1, J = 10 Hz, C(4) vinyl), 3.78 (d, 1, J = 10 Hz, C(3) vinyl), 4.17 (m, 1, C(7) vinyl), 6.27 (s, 6, carbomethoxy methyls), 7.22 (s, 1, disappears on adding D_2O, OH), 8.03 (br s, 2, C(10) methylenes), 8.19 (d, 3, J = 1.5 Hz, C(8) methyl), 8.86 (s, 3, C(9) methyl), the C(3) and C(4) vinyl hydrogen resonance shifts were calculated;[36] uv (MeOH) 241 (3630) plus long tail with ϵ at 325 nm of 50; mass spectrum (70 eV) *m/e* parent 306.

Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.85; H, 5.89.

1,6-Dicarbomethoxy-8,9-dimethyltricyclo[4.4.0.0^{3,9}]dec-7-ene-2,5-dione (**19b**), mp 96.5–97 °C (benzene–petroleum ether, 68 °C), showed ir (KBr) 5.58, 5.72, 5.78, and 5.86 (C=O) μ; NMR ($CDCl_3$) τ 3.51 (m, 1, C(7) vinyl), 6.22 and 6.26 (each s, 6, C(1) and C(6) carbomethoxy methyls), 6.2–6.4 (m, 1, C(3) methine), 7.32 (dd, 1, J = 5 Hz, 16 Hz, C(4) exo H), 7.53 (dd, 1, J = 4 Hz, 16 Hz, C(4) endo H), 7.76 (d, 1, J = 14 Hz, C(10) H), 8.12 (d, 3, J = 1 Hz, C(8) methyl), 8.14 (d, 1, J = 14 Hz, C(10) H), 8.75 (s, 3, C(9) methyl); the chemical shifts of the C(4) exo and endo protons and the C(10) methylenes were calculated;[36] uv (MeOH) 300 (165) and 313 nm (134); mass spectrum (70 eV) *m/e* parent 306.

Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 63.03; H, 5.89.

Thermal Rearrangement of Diketone 19b. Diketone **19b** (20 mg, 0.065 mmol) was placed in a sealed ampule and heated for 3.5 h at 190 °C. The golden product was dissolved in chloroform and chromatographed through a short column of alumina (chloroform) giving 19 mg of slightly impure enone-alcohol **18b**. A second chromatography on silica gel (40% ethyl acetate–benzene) gave 10 mg (50%) of pure enone-alcohol **18b** whose ir and NMR spectra were identical with those of samples previously obtained by photochemical methods.

Preparation and Irradiation of 2,3-Dichloro-4aβ,8aβ-dicyano-6,7-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (17c). To a solution of 4.16 g (0.018 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 100 ml of methanol was added 1.5 g (0.019 mol) of 2,3-dimethyl-1,3-butadiene. The reaction mixture rapidly became green in color and slightly warm. After allowing the solution to stand at room temperature for 1 h, solvent was evaporated to give a greenish-brown residue. Recrystallization from methanol resulted in 4.5 g (81%) of green colored crystals of **17c**, mp 178–179 °C, identified by the following properties: ir (KBr) 5.82 (C=O) μ; NMR ($CDCl_3$) τ 7.23 (s, 4, C(5) and C(8) methylenes), 8.28 (s, 6, vinyl methyls); uv (MeOH) 270 nm (6000) and a long featureless absorption from 300 to 360 nm (ϵ at 340 nm, 400); mass spectrum (70 eV) *m/e* parent 308, 310, 312.

Anal. Calcd for $C_{14}H_{10}Cl_2N_2O_2$: C, 54.39; H, 3.26; Cl, 22.94; N, 9.06. Found: C, 54.58; H, 3.26; Cl, 22.70; N, 9.18.

A solution of 600 mg (2 mmol) of **17c** in 300 ml of *tert*-butyl alcohol was irradiated and the course of the reaction monitored by GLC (column C, 180 °C, 180 ml/min) which showed complete reaction of starting material after 24 h. Evaporation of the now yellow solution resulted in a reddish residue which was dissolved in 100 ml of ether and washed with 4 × 15 ml of water, 4 × 15 ml of sodium bicarbonate, and 4 × 15 ml of water again. After drying (sodium sulfate), the ether was evaporated to give 400 mg of pale-yellow solid. Two recrystallizations from methanol–water gave 250 mg (42%) of colorless needles, mp 226–228 °C, identified as 3,4-dichloro-1,6-dicyano-8,9-dimethyl-5-hydroxytricyclo[4.4.0.0^{5,9}]deca-3,7-dien-2-one (**18c**) on the basis of the following data: ir (KBr) 2.92 (OH) and 5.90 (C=O) μ; NMR (acetone-d_6) τ 4.07 (m, 1, C(7) vinyl), 7.07 (br s, 1, disappears on adding D_2O, OH), 7.47 and 7.81 (each d, 2, J = 14 Hz, C(10) methylenes), 8.02 (d, 3, J = 1.5 Hz, C(8) methyl), 8.67 (s, 3, C(9) methyl). The τ values for the C(10) methylenes were calculated;[36] uv (MeOH) 265 nm (9100); mass spectrum (70 eV) *m/e* parent 308, 310, 312. A sample was sublimed at 190 °C and 0.01 Torr to give an analytical sample.

Anal. Calcd for $C_{14}H_{10}Cl_2N_2O_2$: C, 54.39; H, 3.26; Cl, 22.94; N, 9.06. Found: C, 54.13; H, 3.15; Cl, 22.92; N, 8.76.

Preparation of the Duroquinone-2,4-Hexadiene Diels–Alder Adducts 21 and 22. A mixture of 1.6 g (9.8 mmol) of duroquinone, 2 g (24.4 mmol) of freshly distilled *trans,trans*-2,4-hexadiene and a few crystals of hydroquinone was heated in a sealed Pyrex tube at 190 °C for 20 h. The resulting dark-brown gum (after removal of excess diene) was extracted with refluxing methanol, and the methanol extracts were concentrated and subjected to preparative GLC (column A, 160 °C, 160 ml/min) to yield 120 mg (5%) of 2,3,4aβ,5β,8β,8aβ-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (**21**) which, upon recrystallization from low boiling petroleum ether, formed pale-yellow needles, mp 103–104 °C, and exhibited the following properties: uv (MeOH) 251 (8700) and 340 nm (70); ir (KBr) 5.99 (C=O) and 6.13 (C=C) μ; NMR (CCl_4) τ 4.58 (s, 2, vinyls), 7.17 (q, 2, J = 7 Hz, C(5) and C(8) methines), 8.07 (s, 6, C(2) and C(3) methyls), 8.93 (s, 6, C(4a) and C(8a) methyls), 9.12 (d, 6, J = 7 Hz, C(5) and C(8) methyls); mass spectrum (70 eV) *m/e* parent 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.75; H, 9.11.

To obtain the endo adduct **22**, an identical mixture was placed in a sealed Pyrex tube and heated at 140 °C for 40 h. The mixture was cooled and then extracted with hot petroleum ether (68 °C). After filtration and concentration, the solution was chilled in the freezer whereupon a crop of unreacted duroquinone precipitated. After a second filtration and further concentration, the solution was again chilled whereupon 400 mg of yellow solid, mp 40–42 °C, was deposited. This solid was collected by suction filtration and recrystallized twice more from a small amount of petroleum ether (68 °C). In this way, 246 mg (10%) of 2,3,4aβ,5α,8α,8aβ-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (**22**) could be isolated. This material had a mp of 47–50 °C and was found to be suitable for photolysis. An analytical sample could be obtained by preparative GLC (column A, 170 °C, 150 ml/min) followed by recrystallization from 68 °C petroleum ether. Adduct **22** was thus obtained as pale-yellow needles, mp 57–58 °C, uv (benzene) 350 nm (83); ir (KBr) 5.94 and 6.00 (C═O) μ; NMR (CCl_4) τ 4.57 (s, 2, vinyls), 7.85 (q, 2, J = 7 Hz, C(5) and C(8) methines), 8.10 (s, 6, C(2) and C(3) methyls), 8.81 (s, 6, C(4a) and C(8a) methyls), 9.02 (d, 6, J = 7 Hz, C(5) and C(8) methyls); mass spectrum (70 eV) *m/e* parent 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.96; H, 8.86.

Irradiation of Adduct 21. A solution of 110 mg (0.49 mmol) of adduct **21** in 50 ml of benzene was irradiated in the usual way and the reaction monitored by GLC which showed the formation of two new products. After 3 h, starting material had completely reacted, and the two products **23** and **24** remained in a ratio of 1:2. Evaporation of solvent followed by column chromatography on silica gel (10% ethyl acetate–benzene) afforded 62 mg (56%) of **24** and 27 mg (24.5%) of **23** whose structures were assigned on the basis of the following information:

1,3,4,6,7,10-Hexamethyl-5-hydroxytricyclo[4.4.0.0^{5,9}]deca-3,7-dien-2-one (**23**) (stereochemistry at C(10) assumed), mp 156.5–157 °C (68 °C petroleum ether), showed uv (MeOH) 247 nm (5700) and a broad featureless absorption with an ϵ of 175 at 340 nm; ir (KBr) 2.88 (OH) and 6.05 (C═O) μ; NMR (CCl_4) τ 4.15 (m, 1, vinyl), 7.45 (dd, 1, $J_{8,9}$ = 3 Hz, $J_{9,10}$ = 3 Hz, C(9) methine), 7.67 (s, 1, disappears on adding D_2O, OH), 7.79 (m, 1, C(10) methine), 8.16 (s, 3, C(3) methyl), 8.25 (br s, 6, C(4) and C(7) methyls), 9.20 (s, 3, C(1) methyl), 9.29 (d, 3, J = 7 Hz, C(10) methyl), 9.34 (s, 3, C(6) methyl); mass spectrum (70 eV) *m/e* parent 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.01; H, 9.01.

1,3,4,6,7,10-Hexamethyltricyclo[4.4.0.0^{3,10}]dec-8-ene-2,5-dione (**24**) (stereochemistry at C(4) and C(7) assumed), colorless oil, showed uv (MeOH) 290 nm (68); ir (film) 5.66 and 5.85 (C═O) μ; NMR ($CDCl_3$) τ 4.03 (dd, 1, $J_{8,9}$ = 10 Hz, $J_{7,8}$ = 5.5 Hz, C(8) vinyl), 4.49 (dd, 1, $J_{8,9}$ = 10 Hz, $J_{7,9}$ = 1.5 Hz, C(9) vinyl), 7.30 (q, 1, J = 7.5 Hz, C(4) methine), 7.82 (m, 1, C(7) methine), 8.98 (s, 3, methyl), 8.98 (d, 3, J = 7.5 Hz, C(4) methyl), 9.01 (s, 3, methyl), 9.02 (d, 3, J = 7.5 Hz, C(7) methyl), 9.03 (s, 3, methyl), 9.09 (s, 3, methyl). Irradiation at τ 7.30 leads to the collapse of the doublet at τ 8.98 to a singlet. Irradiation at τ 7.82 leads to the collapse of the doublet at τ 9.02 to a singlet and to simplification of the vinyl signals to an AB system with a mutual coupling constant of 10 Hz; mass spectrum (70 eV) *m/e* parent 246. Distillation (Kugelrohr) at 0.01 Torr and 65 °C yielded an analytically pure sample.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.30; H, 9.20.

Thermal Rearrangement of Diketone 24. Ene-dione **24** (21 mg, 0.09 mmol) was placed in a sealed ampule and thermolyzed for 21 h at 195 °C. The crude product was taken up in chloroform and chromatographed on 5 g of silica gel using chloroform as the eluting solvent. In this way, a slightly yellow oil was obtained, which was distilled at 70 °C and 0.01 Torr to give 13 mg (63%) of 2,3,4aβ,5,8β,8aβ-hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone (**25**) as a colorless oil. Distinguishing spectral features of **25** were as follows: uv (MeOH) 254 (11 000) and 352 nm (70); ir (film) 5.98 (C═O) μ; NMR (CCl_4) τ 4.50 (m, 1, vinyl), 8.07 (s, 6, vinyl methyls), 8.12 (br s, 3, vinyl methyl), 8.40 (center of br m, 1, C(8) methine), 8.75–9.25 (br m, 2, C(7) methylenes), 8.84 (s, 3, C(4a) methyl), 9.05 (s, 3, C(8a) methyl), 9.37 (d, 3, J = 6 Hz, C(8) methyl); mass spectrum (70 eV) *m/e* parent 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.16; H, 9.20.

Irradiation of Adduct 22. Adduct **22** (130 mg, 0.53 mmol) in 25 ml of benzene was irradiated as before with light of λ >340 nm. The reaction was monitored by GLC (column A, 170 °C, 150 ml/min) which showed the formation of two new products. One product, subsequently identified as the oxetane **26**, was observed to build up rapidly until it reached a constant ratio with **22** of ca. 1:1.9. The other product, cage compound **27**, formed more slowly at the expense of both **22** and **26**, until after 18 h of irradiation it was the only detectable product. Evaporation of the solvent yielded 110 mg of **27** as a pale-yellow solid which was recrystallized twice from 68 °C petroleum ether to give 80 mg of colorless crystals: mp 144–146 °C; ir (CCl_4) 5.68 and 5.75 (C═O) μ; NMR given in text; uv (MeOH) 227 (333), 299 (40), and 315 nm (33); mass spectrum (70 eV) *m/e* parent 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.82; H, 9.12.

In a second run, irradiation of a solution of 246 mg (1.0 mmol) of adduct **22** in 40 ml of benzene was interrupted after 4 h at which time the ratio of products was ca. **26**:**22**:**27** = 1:1.9:1.2. After evaporation of solvent, the residue was subjected to preparative GLC (column A, 170 °C, 150 ml/min) from which was isolated 14 mg of oxetane **26**, 46 mg of unreacted starting material, and 16 mg of cage compound **27**. Recrystallization of **26** from low-boiling petroleum ether yielded colorless crystals, mp 59.5–60 °C, deduced to be 2,3,5,6,9,10-hexamethyl-11-oxatetracyclo[6.2.1.0.^{1,7}0^{5,10}]undeca-2-ene-4-one on the basis of the following evidence: ir (KBr) 6.04 (C═O) μ; NMR given in text; uv (MeOH) 266 (6100) and 325 nm (240); mass spectrum (70 eV) *m/e* parent 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.18; H, 9.05.

Irradiation of Oxetane 26. A solution of 11.5 mg (0.047 mmol) of **26** in 4 ml of benzene was irradiated as usual, the reaction being monitored by GLC (column A, 170 °C, 150 ml/min) which showed the rapid buildup of **22** (after 30 min, ratio of **26**:**22** = 1:1.9). Then at longer irradiation times, cage compound **27** formed at the expense of both **26** and **22** until after 12 h it remained as the only product. The material isolated was identical with that obtained from the photolysis of **22** in benzene.

Preparation and Irradiation of 4aβ,8aβ-Dicyano-5α,8α-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (28). To a solution of 1 g (6.5 mmol) of 2,3-dicyano-1,4-benzoquinone[37] in 20 ml of benzene-ethanol (9:1 by volume) was added 1 g (12 mmol) of *trans,trans*-2,4-hexadiene. The mixture was allowed to stand at room temperature for 3 h. Evaporation of solvent and excess diene yielded 1.2 g of solid which, on recrystallization from methanol, gave 800 mg (52%) of adduct **28** as pale-yellow crystals, mp 155–156 °C. Spectral characteristics were as follows: ir (KBr) 4.43 (CN), 5.79 and 5.90 (C═O), and 6.23 (C═C) μ; NMR ($CDCl_3$) τ 3.01 (s, 2, C(2) and C(3) vinyls), 4.32 (s, 2, C(6) and C(7) vinyls), 6.85 (q, 2, J = 7 Hz, C(5) and C(8) methines), 8.69 (d, 6, J = 7 Hz, C(5) and C(8) methyls); uv (MeOH) 240 (6200), 352 nm (64); mass spectrum (70 eV) *m/e* parent 240.

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.29; H, 5.25; N, 11.39.

A solution of 412 mg (1.7 mmol) of **28** in 200 ml of benzene was irradiated as usual, the reaction being monitored by uv spectroscopy which showed complete disappearance of the 352 nm peak and a buildup of a new absorption at 330 nm after 5 h. Evaporation of solvent followed by column chromatography (silica gel, 30% ethyl acetate–benzene) yielded 253 mg of colorless oil which crystallized upon standing. Recrystallization from ether–petroleum ether (68 °C) gave 215 mg (52%) of colorless crystals, mp 137.5–139 °C. On the basis of the following data, the compound was identified as 5,10-dicyano-6,9-dimethyl-11-oxatetracyclo[6.2.1.0.^{1,7}0^{5,10}]undec-2-en-4-one (**29**): ir (KBr) 4.43 (CN) and 5.93 (C═O) μ; NMR given in text; uv (MeOH) 258 (3200) and 330 nm (66); mass spectrum (70 eV) *m/e* parent 240.

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.93; H, 5.10; N, 11.60.

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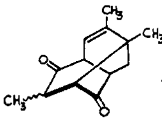

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Titration Properties of Homodinucleoside Monophosphates. Determination of Overlapping Ionization Constants and Intramolecular Stacking Equilibrium Quotients of ApA, CpC, GpG, and UpU

Naotake Ogasawara and Yasuo Inoue*

Contribution from the Department of Biophysics and Biochemistry, Faculty of Science, University of Tokyo, Hongo, Tokyo, Japan.

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Abstract: In order to study the effect of ionization (protonation or deprotonation) upon the base-base stacking properties of homoribodinucleotides, the overlapping pK values which differ by less than 2 were determined for four homodinucleoside monophosphates by means of a computer-assisted iterative least-squares treatment of spectrophotometric titration data. The pK of component nucleic acid base residues of the four homodimers in the fully unstacked conformation was approximated by $\frac{1}{4}[pK_{3'\text{-mononucleotide}} + pK_{5'\text{-mononucleotide}} + 2pK_{\text{nucleoside}}]$. These were used to estimate the intramolecular stacking equilibrium quotients for the dimers at neutral pH and for the half-ionized form. The proportion of stacked species in the half-ionized molecules of a homodimer is found to be almost the same as that in the corresponding un-ionized dimer and is even enhanced in the case of GpG with the protonated guanine in the 3′-linked nucleoside as compared to that of the neutral GpG.

Although the acid-base chemistry of nucleic acid bases is well known at the monomer level, protonation–deprotonation reactions of oligonucleotides have been much less investigated. Known examples include ApA,[1,2] ApU,[1] UpA,[1] CpC,[3,4] GpG,[5] GpU,[6] GpUp,[6] UpC,[7] and UpU[1,7] as well as some of higher oligomers.[3,8–10] The possibility of creating and stabilizing a half-protonated form of dinucleoside monophosphates[4,6,11,12] by interaction of two side-chain bases, one protonated and the other un-ionized, has prompted further study of the conformational characteristics of half-protonated homodinucleoside monophosphates. First, in this paper spectrophotometric titration of the diacidic bases (ApA, CpC, and GpG) and dibasic acids (GpG and UpU) was selected as the tool to investigate the molecular behavior. No macroscopic ionization constants