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Solution Photochemistry. XIII.[1] Hydrogen Abstraction Reactions Proceeding through Five-Membered Transition States. Mechanistic Studies Indicating Conformational Control[2]

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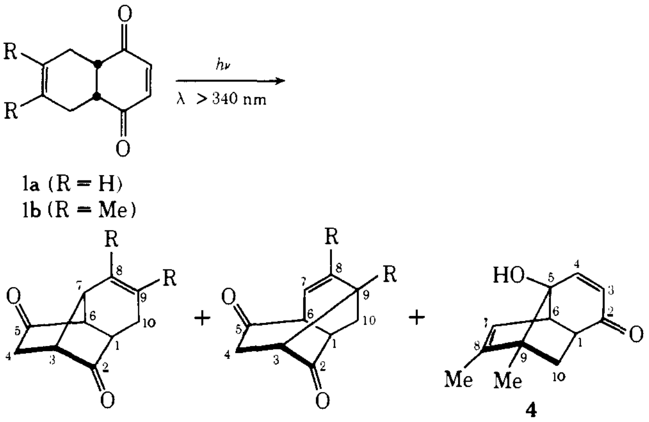
Abstract: The photochemistry of a variety of substituted acyclic 1,3-diene-*p*-quinone Diels–Alder adducts has been investigated. Irradiation of these systems in their long wavelength absorption bands leads to novel tricyclic ring systems in moderate to good yields. Derivatives of the following basic ring systems are produced in this way: tricyclo[4.4.0.$0^{2,8}$]decane, tricyclo[4.4.0.$0^{2,9}$]decane, tricyclo[4.4.0.$0^{3,9}$]decane, and tricyclo[5.3.1.$0^{2,7}$]undecane. The ratio in which the products are formed is generally solvent dependent. Deuterium labeling studies indicate that, in most instances, the major primary process in the photochemistry of substituted butadiene-*p*-benzoquinone Diels–Alder adducts consists of abstraction of a β-hydrogen atom by the excited carbonyl oxygen. The products are then derived from carbon–carbon bond formation in the bis(allylic) radical so produced. For unsymmetrical adducts, in which the β-hydrogen atoms are nonequivalent, abstraction occurs in accord with expectations based on the formation of the more stable diradical intermediate. However, exceptions to these reactivity patterns are found when the adducts possess either (a) C_5 and/or C_8 substituents (R = Me or Ph) or (b) bridgehead methyl substituents. In the former case, exclusive γ-hydrogen abstraction by oxygen is observed when R = Me, and when R = Ph the molecule is photochemically inert. In the case of the unsymmetrical piperylene-benzoquinone adduct (R = Me, R′ = H), β-hydrogen abstraction competes only poorly with γ-hydrogen abstraction. On the other hand, bridgehead methyl substitution brings about partial suppression of the β-hydrogen abstraction reaction in favor of a process tentatively concluded to involve γ-hydrogen abstraction by excited enone carbon. In general, these reactivity differences are interpreted as being due to the effects of the substituents on the ground state conformations of the basic tetrahydro-1,4-naphthoquinone ring system involved. The tricyclic photoproducts found in this study are nearly all thermally and/or photochemically labile and undergo unusual sigmatropic rearrangements whose mechanisms are discussed. In addition, the resemblance of the various tricyclic photoproducts formed in these reactions to naturally occurring sesquiterpenes is noted, and, finally, possible explanations are advanced for the variations in photoproduct ratios with solvent.

The endo Diels–Alder adducts of *p*-benzoquinone with cyclic 1,3-dienes are well known[4] to give cage products upon photolysis via internal 2 + 2 cycloaddition. However, prior to our work, no determined effort had been made to study the photochemistry of Diels–Alder adducts of *p*-benzoquinone with *acyclic* 1,3-dienes.[5] We report in this paper that these adducts, possessing the tetrahydro-1,4-naphthoquinone ring system, do not undergo intramolecular cycloaddition upon photolysis but rather take part in a remarkably general rearrangement leading to novel tricyclic ring systems. In addition, we report experiments which establish that these rearrangements are initiated by the rarely observed process of intramolecular β-hydrogen atom abstraction, i.e., abstraction through a five-membered transition state.

Results and Discussion

Photolysis of Diels–Alder Adducts of *p*-Benzoquinone with Butadiene (1a) and 2,3-Dimethylbutadiene (1b). In agreement with previous reports,[5] photolysis of the 1,3-butadiene-*p*-benzoquinone Diels–Alder adduct **1a** (Scheme I) through Pyrex in a variety of solvents led only to intractable polymeric material. However, selective n → π^* excitation of **1a** in benzene (uv_{max} 370 nm, ϵ 67)[6] using a Corning 7380 glass filter (transmitting $\lambda \geq 340$ nm) gave material whose crude ir spectrum showed weak absorptions in the 5.7 μ region indicating the presence of the cyclopentanone chromophore. This material was freed from polymer by passage through a short chromatography column containing neutral alumina (chloroform eluent) and the resulting mixture analyzed by GLPC which showed the presence of two

Scheme I



1a (R = H)
1b (R = Me)

2a (R = H)
2b (R = Me)

3a (R = H)
3b (R = Me)

4
(only for R = Me)

volatile components in the ratio of 1:7. These products comprised approximately 10% of the crude photolysate. The volatile photoproducts were isolated by preparative GLPC and shown (vide infra) to have the structures **2a** (minor) and **3a** (major). Interestingly, photolysis of **1a** in 80:20 *tert*-butyl alcohol-benzene under otherwise identical conditions led to a reversal of the **2a**:**3a** ratio of 5:1. The use of hexane, methanol, or acetonitrile led to vanishingly small quantities of **2a** and **3a**.

The structure of photoproduct **2a**, mp 67.5-68.5°, was indicated by the following partial spectroscopic data: a 5.72 μ carbonyl ir absorption, a two proton vinyl hydrogen multiplet centered at τ 4.15, and a broad uv$_{\max}$ (MeOH) at 293 nm (ϵ 17). Hydrogenation over palladium on charcoal gave the noncrystalline dihydro derivative, ir (CHCl$_3$) 5.71 (C=O) μ; uv$_{\max}$ (MeOH) 288 nm (ϵ 48). The structure of **2a** was ultimately secured by a direct method, single-crystal X-ray structure determination, the details of which have been published elsewhere.[7]

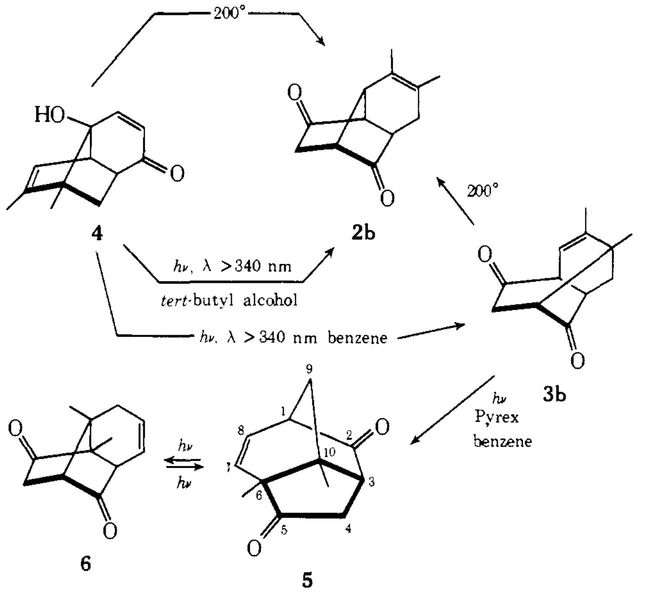
The structure of photoproduct **3a**, mp 147-150°, rests in part on ir (KBr) carbonyl absorptions at 5.68 and 5.80 μ and uv$_{\max}$ (MeOH) at 296 (ϵ 260) and 310 (ϵ 230) nm characteristic of β,γ-unsaturated ketones.[8] The 220-MHz NMR spectrum, while complex, supports the structure. The vinyl hydrogens appear essentially as triplets centered at τ 3.39 and 4.07 with a mutual coupling of 8 Hz. The C$_4$ methylene protons (τ 6.90 and 7.69) are near-doublets with a geminal coupling of 17 Hz. The large exo-endo chemical shift difference is similar to that observed for the α-methylene protons of camphor.[9] The C$_{10}$ methylene protons appear at τ 8.04 and 8.40 with a geminal coupling of 12 Hz; both are essentially doublets with smaller vicinal couplings. The C$_6$ methine appears as a clean triplet, J = 7 Hz at τ 6.66. The remaining methine protons give complex multiplets centered at τ 6.81, 7.37, and 7.56. Hydrogenation of **3a** over palladium on charcoal gave the dihydro derivative, mp 151-152°, ir (CHCl$_3$) 5.70 and 5.81 (C=O) μ with no NMR vinyl hydrogen signals. The uv$_{\max}$ (MeOH) of 292 nm (ϵ 55) corroborates the assignment of a β,γ-unsaturated ketone chromophore to **3a**.

Irradiation of the 2,3-dimethylbutadiene-*p*-benzoquinone Diels-Alder adduct **1b** under identical conditions led to the analogous photoproducts **2b** and **3b**. In addition a third product was isolated in this case, the novel enone alcohol **4**. As before, the relative yields of these photoproducts were solvent dependent; happily, the absolute yields were much greater. In benzene products **3b** (mp 77-78°) and **4** (mp 93-94°) were formed in yields of 35 and 22%, respectively; photoisomer **2b** was present in only trace amounts. In *tert*-butyl alcohol, ene-dione **2b**, mp 84-85°, was the major (80% isolated yield) product while isomers **3b** and **4** were present in a combined yield of less than 5%. The quantum yield for the appearance of photoisomer **2b** in *tert*-butyl alcohol was determined to be 0.12 (ferrioxalate actinometry).

The structures of **2b** and **3b** follow from the similarity of their spectra to the corresponding nonmethylated photoproducts **2a** and **3a**. Compound **2b** showed the following: ir (CHCl$_3$) 5.72 μ; NMR (CDCl$_3$) τ 8.29 (m, 3, CH$_3$), 8.41 (m, 3, CH$_3$), and no vinyl hydrogens. Photoisomer **3b** showed ir (CHCl$_3$) 5.69 and 5.81 (C=O) μ; NMR (CDCl$_3$) τ 8.63 (s, 3, C$_9$ CH$_3$), 8.13 (d, 3, J = 2 Hz, C$_8$ CH$_3$), and 4.48 (m, 1, vinyl); uv$_{\max}$ (MeOH) 292 (ϵ 220) and sh 310 nm (ϵ 200).[8] Photoproduct **4** exhibited the following spectra: ir (CCl$_4$) 2.8 (weak, OH), and 5.90 (C=O) μ; NMR (CCl$_4$) τ 8.90 (s, 3, C$_9$ CH$_3$), 8.50 (d, 2, J = 5 Hz), 8.20 (d, 3, J = 2 Hz, C$_8$ CH$_3$), 7.76 (m, 2, OH and methine, OH disappears upon addition of D$_2$O), 6.98 (d, 1, J = 3 Hz, C$_6$ methine), 4.38 (m, 1, C$_7$ vinyl), 4.15 (d, 1, J = 10 Hz, C$_3$ vinyl), and 3.35 (d, 1, J = 10 Hz, C$_4$ vinyl); uv$_{\max}$ (MeOH) 242 (ϵ 4000) and sh 330 nm (ϵ 30).

The structures of photoproducts **2a** and **3a** as well as of **2b**, **3b**, and **4** were interrelated in a remarkable series of thermal and photochemical reactions which are outlined in Scheme II. These studies serve to confirm the assigned structures.

Scheme II



Thus sealed tube thermolysis of **3b** at 200° gave a high yield of **2b**. Similar thermolysis of **3a** quantitatively afforded **2a**. These reactions did not occur under the GLPC conditions used in analyzing and/or separating the photolysis mixtures. These reactions represent formally disallowed 1,3-suprafacial sigmatropic rearrangements,[10,11] and may be interpreted in terms of either a diradical mechanism or a concerted mechanism under the influence of subjacent orbital control.[12] In addition, thermolysis of **4** at 200° for 5 hr gave a 70% isolated yield of isomer **2b**, the formal result of an allowed [3,3] suprafacial sigmatropic rearrangement.[10] Again the evidence does not allow a decision to be made between concerted and diradical mechanisms although the remoteness of the ends of the 1,5-diene (oxy-Cope) system in **4** can be argued to favor the latter interpretation.[13]

Interestingly, photolysis of **4** gives **2b** in *tert*-butyl alcohol and **3b** in benzene. That **3b** is nevertheless a primary photoproduct in the photolysis of **1b** was demonstrated by a time dependence study which showed the buildup of both **3b** and **4** at comparable rates without an appreciable induction period for the formation of **3b**. Similarly, the rate at which enone-alcohol **4** is converted to **2b** in *tert*-butyl alcohol (approximately $1/20$ the rate of the **1b** to **2b** conversion) indicates that **4** is not an important intermediate in the formation of **2b** from **1b** in this solvent. The fact that the photochemistry of **4** exhibits exactly the same solvent dependence as in the case of **1b** argues for a common intermediate in both cases and mitigates against the likelihood that the photochemical conversion of **4** to **3b** in benzene is concerted even though this process represents an excited state symmetry allowed 1,3-suprafacial shift.[14]

Finally we turn to the novel photochemistry of compound **3b**. Irradiation (100-W Hanovia) of a 5 × 10^{-3} *M* benzene solution of **3b** through Pyrex slowly gave rise to a single new photoproduct subsequently shown to have the structure **5**. After 8 hr, starting material had disappeared, and further irradiation gradually led to a second new compound **6** at the expense of **5** until, after 48 hr, the **5**:**6** ratio was time invariant at 1:1.9. Photoproducts **5** and **6** were easily separable by preparative GLPC and could be isolated in this way in a combined yield of 50%. That the final **5**:**6** = 1:1.9 ratio is the result of a true photochemical equilibrium was shown by irradiation of pure samples of both **5** and **6**. Each gave rise to the same **5**:**6** = 1:1.9 mixture within experimental error; no **3b** could be detected in either of these photolyses.

The structures of photoisomers **5** (sealed tube mp 166-168°) and **6** (sealed tube mp 184-187° dec) were assigned on the basis of the following spectral data: for **5**, ir (CCl_4) 5.73 (C=O) μ; NMR (CCl_4) τ 4.07 (m, 1, C_8 vinyl, collapses to a doublet, J = 9 Hz upon irradiation of the C_1 methine multiplet at τ 7.00), 4.78 (d, 1, J = 9 Hz, C_7 vinyl), 7.00 (m, 1, C_1 methine), 7.71 (m, 3), 8.27 (m, 2), 8.88 (s, 3, CH_3), and 8.95 (s, 3, CH_3); uv$_{max}$ (MeOH) 292 (ϵ 460), sh 285 (ϵ 400), and sh 307 nm (ϵ 410); for **6**, ir (CCl_4) 5.70 (C=O) μ; NMR (CCl_4) τ 4.17 (m, 2, vinyls), 7.38-7.90 (m, 6), 9.04 (s, 3, CM_3), and 9.07 (s, 3, CH_3); uv$_{max}$ (MeOH) 290 nm (ϵ 110). The uv spectra of **5** and **6** are again characteristic of the β,γ-unsaturated ketone chromophore.[8] As is reasonable, ene-dione **5**, which is doubly β,γ-unsaturated, has the more intense absorption. The uv spectra of dihydro **5** and **6** (see Experimental Section) are in accord with these assignments.

The photochemical **3b** → **5** and **5** ⇄ **6** conversions have ample literature precedent and are examples of a process which appears to be remarkably general for β,γ-unsaturated ketones in their excited singlet states, namely, 1,3-acyl migration.[15] Singlet excited states are implicated in our reactions as well since piperylene failed to significantly affect their rates or product ratios, and the use of common triplet energy sensitizers led either to no reaction or to polymer formation. It is amusing to note that thermolysis and photolysis of **3b** give rise to isomers (**2b** and **6**) coincidentally possessing identical ring systems but with different methyl substitution patterns and double bond positions.

Mechanism Studies. A possible mechanism for the conversion of Diels-Alder adduct **1b** into photoproducts **2b**, **3b**, and **4** (as well as for the

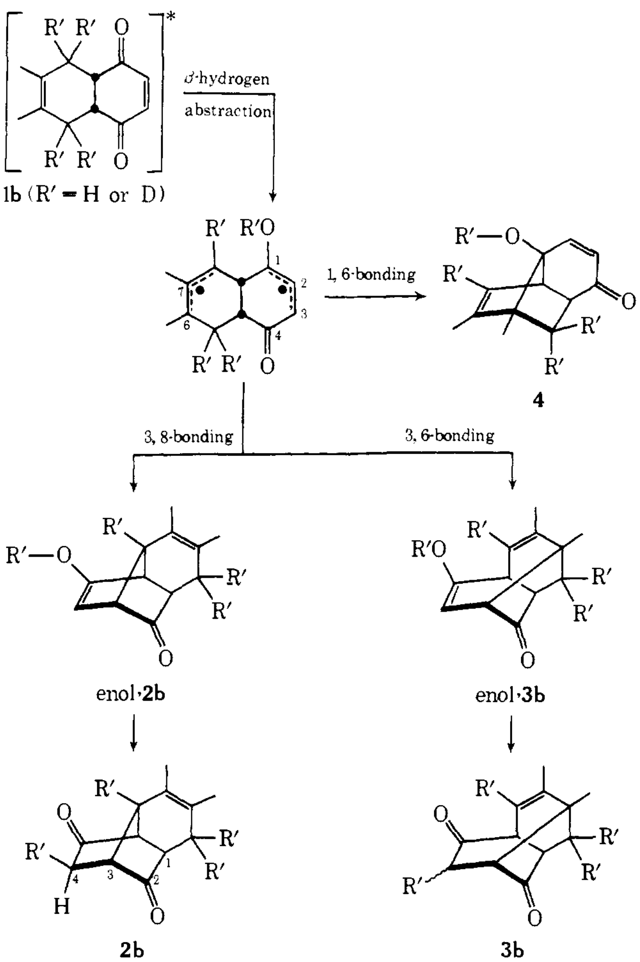
$$\mathbf{1a} \xrightarrow{h\nu} \mathbf{2a} + \mathbf{3a}$$

conversion) is outlined in Scheme III. This mechanism involves, as its primary photochemical step, the unusual and (when this work was begun) virtually unprecedented process of intramolecular β-hydrogen abstraction. The bisallylic radical so produced can then undergo carbon-carbon bond formation as indicated thanks to the cis ring junction stereochemistry; this produces **4** directly and **2b** and **3b** through their respective enol forms.

Thus in order to test for the intermediacy of enol-**2b** in this reaction, adduct **1b** (R′ = H) was irradiated in *tert*-butyl alcohol-*O-d*.[16] The ene-dione **2b** obtained in this way (80% yield of crystalline material) was 92% monodeuterated at the C_4 exo position as shown by NMR and mass spectrometry. The NMR spectrum of the photochemically deuterated material was identical with the NMR spectrum exhibited when ene-dione **2b** (R′ = H) was treated with base in D_2O. The preferential base-catalyzed exo deuteration of bicyclo[2.2.1]heptan-2-ones and 2,5-diones is now well known, and the reasons for this stereoselectivity have been discussed.[17]

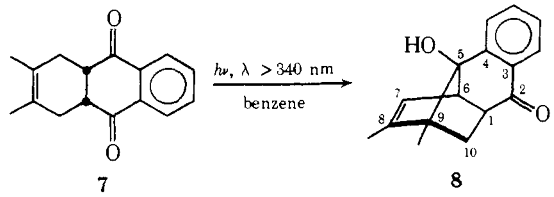
In order to provide evidence on the intermediacy of enol-**3b** (ene-dione **3b** is the major product of the photolysis of **1b** in benzene), tetradeuterated Diels-Alder adduct **1b** (R′ = D) (Scheme III) was prepared and photolyzed in anhydrous benzene. This photolysis resulted in a 60% yield of crystalline **3b** (R′ = D) after column chromatography; neither photoproduct **2b** nor photoisomer **4** were isolated in this experiment. The difference in total deuterium content between **1b** (R′ = D) and **3b** (R′ = D) was 8.4% (mass spectrometry), again strongly supporting the proposed mechanism. The 8.4% deuterium loss corresponds to a 66% deuterium incorporation at C_4 of ene-dione **3b** assuming no deuterium is lost from the other positions; the observation of an intramolecular deuterium incorporation of less than 100% is not unexpected.[18] The NMR spectrum of **3b** (R′ = D) is in agreement with the mass spectral results and conclusions (see Experimental Section).

Scheme III



Photolysis of the 1,4-Naphthoquinone-2,3-Dimethylbutadiene Diels-Alder Adduct 7. In order to test the generality of the photochemical reactions of **1a** and **1b**, we next turned our attention to a study of the irradiation of the 1,4-naphthoquinone-2,3-dimethylbutadiene Diels-Alder adduct **7** (Scheme IV). Photolysis of **7** in benzene gave a single product, the keto alcohol **8**, which could be isolated in 43% yield by column chromatography. This material, mp 126.0-126.5°, exhibited the following spectral data from which its structure was deduced: ir ($CHCl_3$) 2.80 (OH) and 5.91 (C=O) μ; NMR ($CDCl_3$) τ 1.94-2.72 (m, 4, aromatics), 4.24 (broad s, 1 vinyl), 6.76 (d, 1, J = 3 Hz, C_6 methine), 7.20 (shift dependent on concentration, broad s, 1, OH), 7.40 (d of d, 1, J = 3 and 11 Hz, C_1 methine), 8.14 (d, 3, J = 1.5 Hz, C_8 CH_3), 8.45 (d of d, 1, J = 8 and 13

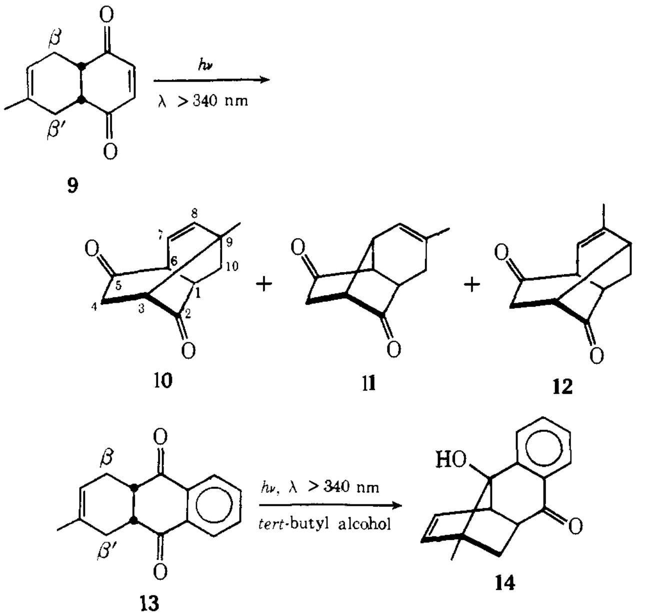
Scheme IV



Hz, C_{10} endo H), 8.66 (d of d, 1, J = 3 and 13 Hz, C_{10} exo H), and 8.97 (s, 3, C_9 CH_3). These assignments, with corroborating spin decoupling studies, are described more fully in the Experimental Section, uv_{max} (MeOH) 247 (ϵ 6700) and 286 nm (ϵ 1900). As can be seen photoproduct **8** is analogous to the product **4** obtained from the photolysis of **1b**. However, unlike **4**, ketone-alcohol **8** was thermally stable up to 245°. The exclusive formation of **8** from **7** is again consistent with the mechanism shown in Scheme III in that neither 3,6 nor 3,8 carbon-carbon bond formation would be expected from the C_2-C_3 benzo-substituted diradical intermediate.

Photolysis of Unsymmetrical Diels-Alder Adducts. Substituent Effects. It was next of interest to determine the regioselectivity of β-hydrogen abstraction by studying the photochemistry of unsymmetrical Diels-Alder adducts such as **9** and **13** (Scheme V). Considerations of methyl substituent effects on allyl radical stability[19] indicated that β-hydrogen abstraction might be favored over β' abstraction in both **9** and **13**. This was indeed found to be the case. Photolysis of Diels-Alder adduct **9** in benzene or *tert*-butyl alcohol gave high yields of photoproducts **10**, **11**, and **12** in the relative ratios shown in Table I. Reference to Table I indicates that the products of β-hydrogen abstraction (**10** and **11**) are formed in preference to **12**, the product of β' hydrogen abstraction, in both benzene (**10** + **11**:**12** = 4:1) and *tert*-butyl alcohol (**10** + **11**:**12** = 7:1). Similarly, photolysis of the isoprene-1,4-naphthoquinone Diels-Alder adduct **13** gave isomer **14** as the sole isolable (preparative GLPC) product in low yield. Again, **14** is the product derived from β rather than β' hydrogen abstraction.[20]

Scheme V

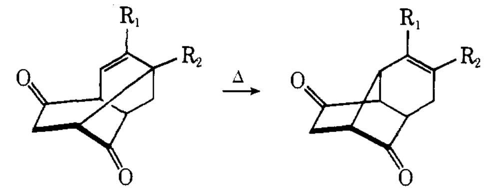


The structures of photoproducts **10**, **11**, **12**, and **14** were assigned on the basis of their spectral characteristics (see Experimental Section) which were similar to those of the analogous photoproducts obtained previously. Again indicative of structure was the finding that sealed tube thermolysis (168°, 16 hr) of ene-dione **10** quantitatively afforded **11**, and similar thermolysis (185°, 22 hr) of **12** gave the previously unobserved isomer **15** in 95% yield. These reactions are outlined in Scheme VI.

Table I. Relative Product Ratios Obtained in Photolysis of 9

Solvent	10:11:12
Benzene	5 3 2
tert-Butyl alcohol	7 1

Scheme VI

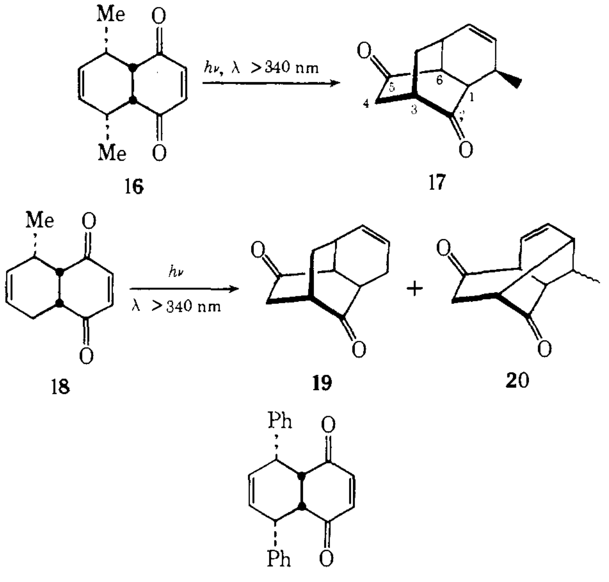


10 (R_1 = H, R_2 = Me) 12 (R_1 = Me, R_2 = H)

11 (R_1 = H, R_2 = Me) 15 (R_1 = Me, R_2 = H)

The Effect of Substituents at C_5 and C_8; β- vs. γ-Hydrogen Abstraction. Our initial efforts aimed at assessing the influence of substituents at C_5 and C_8 on the photochemistry of these systems centered around the *trans,trans*-2,4-hexadiene-benzoquinone Diels-Alder adduct **16**.[21] Irradiation of this material proved to be unique; none of the previously observed photoproduct types was formed. Photolysis of **16** in a variety of solvents with light of $\lambda \geq 340$ nm led to 20-30% yields of the unusual ene-dione **17** (Scheme VII).

Scheme VII



The structure of photoisomer **17** rests on spectral data, deuterium exchange studies, and on the spectra of its dihydro derivative. Compound **17**, mp 80-80.5°, showed ir 5.78 (C=O) μ and uv_{max} (MeOH) 291 nm (ϵ 56). Significant features of the NMR spectrum were (a) a two proton multiplet at τ 4.1-4.6 due to the vinyl hydrogens and (b) a three proton methyl doublet at τ 8.7 (J = 7 Hz). The stereochemistry at C_{10}, while not known with certainty, is very likely as shown since there is no reason to suspect epimerization of the methyl groups of **16**. Mild base-catalyzed deuterium exchange of compound **17** resulted in the replacement of two hydrogens, and hydrogenation gave the dihydro derivative, mp 84.5-85.0°, whose NMR spectrum showed a striking one proton pentuplet at τ 7.34. This signal is attributed to the C_3 methine which models reveal forms nearly equal angles with its four nonequivalent neighboring protons.

The mechanism by which photoproduct **17** arises very likely involves γ-hydrogen abstraction from one of the methyl groups followed by intramolecular cyclization to the enol form of **17** and ketonization. In agreement with this mechanism photolysis of adduct **16** in *tert*-butyl alcohol-*O-d* gave C_4-deuterated **17**. However, the deuterium incorporation was low (30%) as shown by mass spectrometry and NMR spectroscopy. The reasons for this low value are not known although this result is not without precedent.[22]

It was next of interest to determine the extent to which β-hydrogen abstraction can compete with γ-hydrogen abstraction in these systems. To this end the irradiation of the *trans*-piperylene-*p*-benzoquinone adduct **18** was investigated. Photolysis of adduct **18** in either benzene or *tert*-butyl alcohol resulted in the low yield formation of enediones **19** and **20** in the ratio of 7:1 (Scheme VII). The structures of **19** and **20** follow from the similarity of their spectra to analogous systems previously prepared (see Experimental Section). Thus secondary β-hydrogen abstraction can apparently compete only poorly with the statistically favored process of γ-hydrogen abstraction in adduct **18** despite the fact that the former should be electronically favored over the latter; here again factors other than the actual hydrogen abstraction rate may influence the relative yields of final products.[20]

In this regard it is interesting to note that in neither adduct **16** nor in **18** were the products of tertiary β (allylic) hydrogen abstraction observed. This was also found to be the case for Diels-Alder adduct **21** (Scheme VII). This molecule, which possesses no abstractable γ-hydrogens, was photochemically inert under a variety of conditions despite the fact that its β-hydrogens are tertiary, allylic, and benzylic which should greatly facilitate their abstraction.[20]

Conformational analysis reveals a possible reason for the failure of adducts **16** and **21** to take part in β-hydrogen abstraction. The basic butadiene-benzoquinone Diels-Alder adduct (X = Y = H) has five more or less well-defined conformers, A-E, shown in Scheme VIII. Also included in Scheme VIII are the "accessible" β-hydrogen (X or Y) to oxygen distances in each conformer as measured with Dreiding models; those distances which are ≥ 3.5 Å with an unfavorable relative β-hydrogen-oxygen geometry are not shown. As can be seen, when X = H and Y = CH_3 or Ph (as in **16** and **21**, respectively), only in conformations A and B is the X hydrogen accessible. However, for Diels-Alder adducts **16** and **21**, conformations A and B are destabilized by Y-Y (i.e., methyl-methyl or phenyl-phenyl) nonbonded interactions. In addition, β-hydrogen abstraction of X = H in conformers A and B breaks a C-H bond which is nearly orthogonal to the adjacent carbon-carbon double bond p orbitals, thus eliminating incipient allyl radical stability. Instead, in the case of adduct **16** (X = H, Y = CH_3), γ-hydrogen abstraction from the methyl group occurs, likely from either conformation D or E, since in these conformers the methyl groups are pseudo-equatorial and the methyl hydrogen to oxygen distance can be as little as 1.4 Å.[23] Similar reasoning allows the tentative conclusion that, in the Diels-Alder adducts which have no C_5 or C_8 substituents (e.g., **1b**), it is the Y hydrogen which is preferentially abstracted, although evidence is lacking on this point at the present time.

Scheme VIII

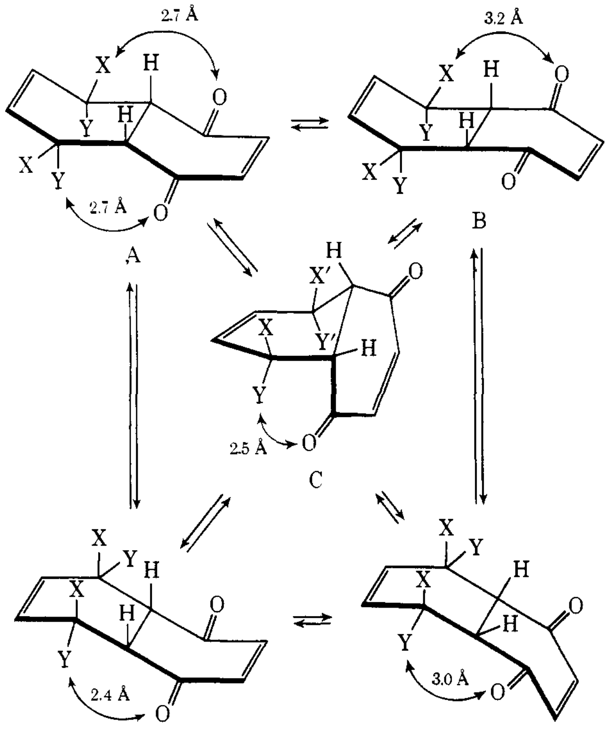
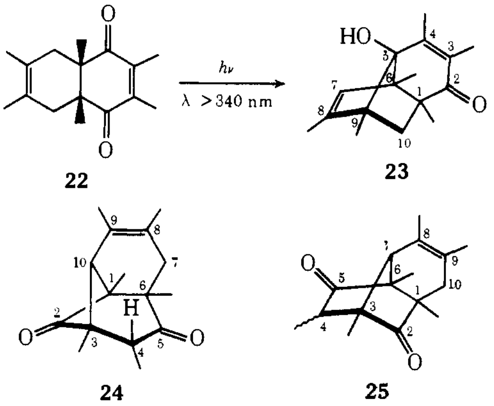


Table II. Relative Product Ratios Obtained in Photolysis of **22**

Solvent	23 :	24 :	25
Benzene	0.5	1	
tert-Butyl alcohol	1.1	1	
Acetonitrile	4	1	
Methanol	13	1	2
1:1 dioxane-water	30	1	6

α,β-Unsaturated Double Bond Substitution and Bridgehead Substitution; β-Hydrogen Abstraction by Oxygen vs. γ-Hydrogen Abstraction by Carbon. It was next of interest to determine what effects, if any, methyl substituents in other positions have on the photochemistry of these systems. To this end the duroquinone-2,3-dimethylbutadiene Diels-Alder adduct **22** was prepared and irradiated (Scheme IX).

Scheme IX



The photochemistry of **22** was again solvent dependent; three products, **23**, **24**, and **25**, were formed in varying amounts depending on the solvent as outlined in Table II. The total yield from preparative runs in benzene was 70%.

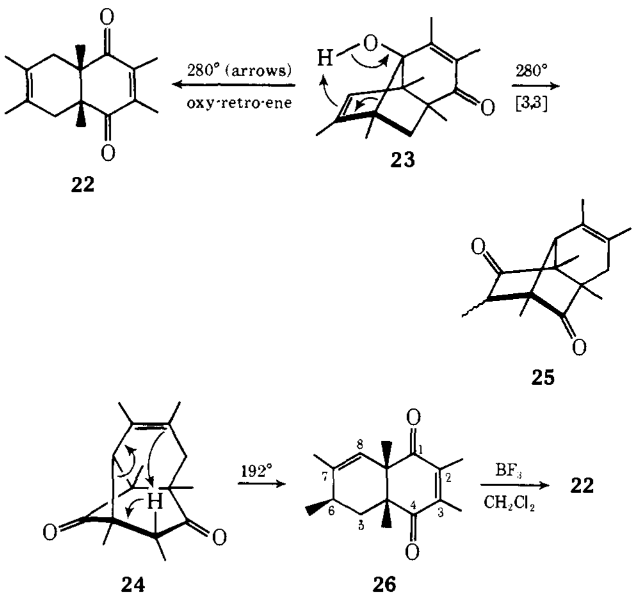
Photoproducts **24** and **25** were shown to be primary photoproducts by appropriate control experiments. For example, photolysis of **23** gave neither **24** nor **25** under conditions which completely convert Diels-Alder adduct **22** into isomers **23-25**. Prolonged photolysis of **23** resulted in its disappearance with, however, no GLPC volatile products being formed.

Ene-dione **24** represents a novel and previously unobserved photoproduct type in this study. Its structure was assigned on the basis of the following information: uv$_{max}$ (MeOH) 300 nm (ϵ 70); ir (CCl_4) 5.67 (cyclobutanone) and 5.85 (cyclohexanone) μ; NMR (CCl_4) τ 7,57 (q, 1, J = 7.5 Hz, C_4 methine), 7.9-8,1 (m, 3, C_7 CH_2 and C_{10} methine), 8,25-8.40 (m, 6, vinyl methyls), 8,78 (s, 3, CH_3), 8.95 (s, 3, CH_3), 8.95 (d, 3, J = 7.5 Hz, C_4 CH_3), and 9.03 (s, 3, CH_3). In addition, the thermal rearrangement of **24** (vide infra) is in accord with this assignment.

In view of the unusual structure of **24**, it was deemed possible that **23** might also possess a heretofore unobserved structure, although the spectral data (see Experimental Section) were in accord with the structure shown. Accordingly a direct method, single-crystal X-ray structure determination was carried out on **23** which fully supported (R = 0.061 for 1774 observed reflections) the assignment given.[24] The structure of ene-dione **25** was assigned on the basis of its spectral properties (see Experimental Section) which were similar to those of photoproducts **2a** and **2b**.

The thermochemistry of these photoproducts again proved to be interesting and informative (Scheme X).

Scheme X

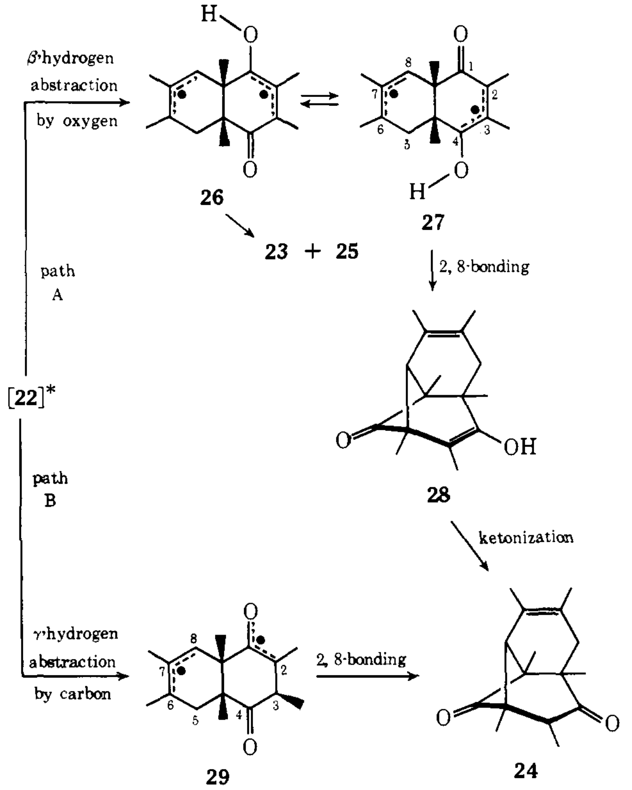


Sealed tube thermolysis of enone-alcohol **23** at 280° resulted in a formal [3,3] sigmatropic rearrangement and gave ene-dione **25** in 53% isolated yield. This reaction is entirely analogous to the **4** → **2b** conversion and serves to verify the structure assigned to **25**. A second product of this reaction could also be isolated in 20% yield and proved to be starting adduct **22**. A variety of mechanisms are conceivable for this latter transformation, one of which is the oxy-retro-ene process[25] shown by the arrows in Scheme X.

In addition, heating neat samples of ene-dione **24** at 192° for 16 hr afforded the interesting product **26** in 92% yield. The structure of this material follows straightforwardly from its spectra[26] as well as from its quantitative boron trifluoride catalyzed isomerization to the starting Diels-Alder adduct **22**. The reaction of **24** giving **26** may be thought of as a novel example of a retro-ene reaction[25] (cf. arrows). Models indicate the steric feasibility of this pathway provided the hydrogen being transferred is syn to the double bond as drawn. Although this position is likely epimerizable under the thermal reaction conditions, the configuration of **24** shown is in accord with its probable mechanism of photochemical formation from **22** (vide infra). Less concerted mechanisms for the **24** → **26** transformation may also be readily envisaged.

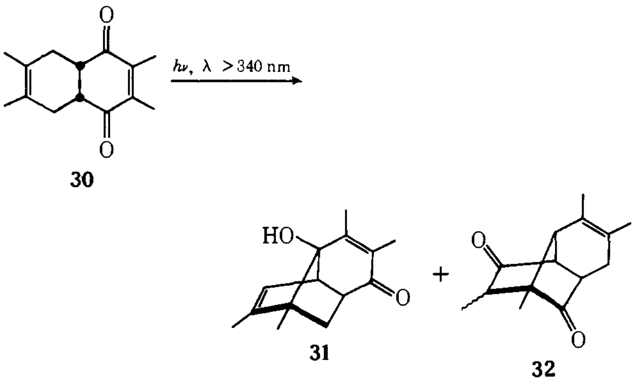
The photochemistry of the duroquinone-2,3-dimethylbutadiene Diels-Alder adduct **22** thus diverges from that of the adducts previously investigated. While the mechanism shown in Scheme III can explain the formation of photoproducts **23** and **25**, the production of **24** from **22** requires further discussion. At least two mechanisms, A and B (Scheme XI), appear conceivable. The first of these, path A, again involves initial β-hydrogen abstraction followed by a prototropic shift to give intermediate **27**.[27] The rearrangement is then completed by intramolecular bonding to give enol **28** and ketonization. The second pathway, path B, involves direct γ-hydrogen abstraction from C_8 by the excited C_3 enone carbon atom. This process has analogy in the photochemistry of certain substituted cyclopentenones and cyclohexenones.[28] In theory, pathways A and B should be distinguishable by deuterium labeling studies since path A involves the intermediacy of enol **28** while path B does not. Accordingly, Diels-Alder adduct **22** was irradiated in deuterated protic solvents. Photolysis of **22** in either *tert*-butyl alcohol-*O-d* or 1:1 dioxane-D_2O led to ene-dione **24** containing no trace of deuterium (NMR, mass spectrometry) whereas, as expected, the photoproduct **25** isolated in these runs contained exactly one deuterium atom per molecule in the C_4 position. These experiments thus provisionally rule out pathway A for the formation of **24**, although caution must always be exercised in interpreting such negative results.[29]

Scheme XI



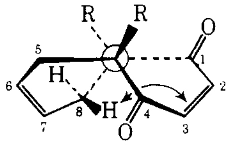
Since the divergent photochemical behavior of Diels-Alder adduct **22** appeared to be due to either (a) ene-dione double bond methyl substitution or (b) bridgehead methyl substitution, the photochemistry of Diels-Alder adduct **30**, which has only double bond substitution, was investigated (Scheme XII). The interesting result was that irradiation of

Scheme XII



adduct **30** gave only the photoproducts **31** and **32** typical of β-hydrogen atom abstraction by oxygen. As before, the **31**:**32** photoproduct ratio was solvent dependent. In benzene, enone-alcohol **31** was virtually the sole product, while in *tert*-butyl alcohol, ene-dione **32** is the eventual major product. However, by following the course of the photolysis of **30** in *tert*-butyl alcohol (GLPC) and by independent photolyses of **31** in benzene and *tert*-butyl alcohol, it could be shown (a) that photoproduct **32** arises mainly through secondary photolysis of **31** and (b) that **31** is photostable in benzene. In the case of adduct **30**, then, enone-alcohol **31** is the primary photoproduct both in benzene and *tert*-butyl alcohol, and the variation in product ratio with solvent merely reflects the relative rate of rearrangement of **31** to **32** in the two solvents. This is not the case for the solvent effects described previously, for example, in the photolysis of the 2,3-dimethylbutadiene-benzoquinone Diels-Alder adduct **1b**.

It thus appears, from a comparison of the photochemistry of the Diels-Alder adducts **22** and **30**, that bridgehead substitution, not ene-dione double bond substitution, plays a major role in determining the nature of the photoproducts produced in these systems. This reactivity may again be rationalized with the aid of conformational analysis. It seems entirely reasonable that of the five conformers discussed previously (Scheme VIII), conformer C will be favored by bridgehead substitution since only in this conformation are the bridgehead substituents noneclipsed. The result of conformation C is to bring the C_3 enone carbon into relatively close proximity (2.6 Å) with the "inner" C_8 allylic hydrogen thus facilitating the process of γ-hydrogen abstraction by enone carbon previously suggested for the formation of photoproduct **24**.

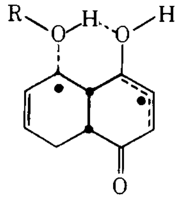


C

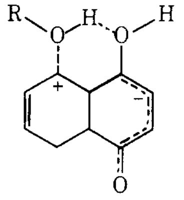
Solvent Effects. We have noted throughout this paper the nearly general dependence of photoproduct ratio on solvent. About the only safe generalization in this regard appears to be that, for the Diels-Alder adducts of benzoquinone with butadiene (**1a**), isoprene (**9**), and 2,3-dimethylbutadiene (**1b**), C_6 is the preferred ring A bonding terminus in nonpolar solvents (benzene) while C_8 is the preferred bonding site in *tert*-butyl alcohol.

The present evidence allows only speculation concerning the possible reasons for these solvent effects. With regard to the preference for C_3-C_6 bonding in benzene following β-hydrogen abstraction, it is conceivable that this is the kinetically preferred pathway while the nearly exclusive occurrence of C_3-C_8 bonding in *tert*-butyl alcohol represents thermodynamic control. While there seems little doubt that the final products of C_3-C_8 bonding are thermodynamically more stable than the products resulting from C_3-C_6 bonding (cf. the nearly quantitative thermal isomerizations of **3a**, **3b**, **10**, and **12** to **2a**, **2b**, **11**, and **15**, respectively), this explanation requires the unusual supposition that the formation of the enol from C_3-C_6 bonding is reversible in *tert*-butyl alcohol and not in benzene.

A second explanation involves the possibility that in *tert*-butyl alcohol, the ring A unpaired electron of the diradical formed via β-hydrogen abstraction is essentially "localized" at C_8 due to interaction (of an unspecified nature) with the adjacent solvated hydroxyl group thus leading to preferential C_3-C_8 bonding. This explanation, shown schematically in structure **33**, has loose analogy in the work of Hart and Love[30] on the effect of "remote" hydroxyl and acetate substituents on the regiospecificity of the di-π-methane rearrangement. A related explanation would invoke the specifically solvated zwitterion **34**.[31]



33



34

In accord with these ideas involving the solvation of an intermediate diradical or zwitterion is the finding, previously discussed, that photolysis of enone-alcohol **4** (Scheme II) leads to photoproduct **2b** in *tert*-butyl alcohol and to photoisomer **3b** in benzene although at slower rates than when adduct **1b** is the starting material. The observation of identical solvent effects in the photolysis of both **1b** and **4** argues for a common intermediate in each solvent, i.e., the species **33** or **34** (with appropriate methyl groups) in *tert*-butyl alcohol leading to 3,8-bonding and the corresponding unsolvated species in benzene leading to preferential 3,6-bonding.[32]

Finally, the possibility that the solvent changes the nature of the reactive excited states involved in these processes in an unusual and yet unknown way cannot, at present, be ruled out.

Concluding Remarks

The process of β-hydrogen atom abstraction by carbonyl oxygen is a surprisingly rare event in organic photochemistry. Prior to the initiation of this work, such hydrogen atom transfers were virtually unknown.[33] Recently Cormier, Schreiber, and Agosta[34] have provided examples of such a process in the photochemistry of some α-methylene ketones. In these cases β-hydrogen abstraction occurs only if the β-hydrogen atom is tertiary (or secondary and adjacent to an ether functionality) and α to the methylene double bond. The diradical resulting from abstraction is thus a derivative of the very stable (~34 kcal/mol delocalization energy) trimethylene methane species. These facts, plus the work reported in this paper, indicate that photochemical β-hydrogen atom abstraction reactions proceed only when the diradical species so formed is extensively resonance stabilized. A further indication of this in the case of our Diels-Alder adducts is the finding that the presence of the C_2-C_3 ene-dione double bond is apparently necessary for β-hydrogen abstraction to occur. Prolonged photolysis of *cis*-2,3,4a,5,8,8a-hexahydro-1,4-naphthoquinone (from the zinc-acetic acid reduction of the butadiene-benzoquinone Diels-Alder adduct[35]) results in no reaction. Presumably the extra stabilization energy afforded the diradical intermediate (Scheme III) by this double bond facilitates the process of β-hydrogen abstraction. In addition, the altered shape and flexibility of the dione six-membered ring may be of consequence in this regard. Interestingly, photolysis of the fully saturated system, *cis*-decalin-1,4-dione, has recently been shown to result in γ-hydrogen abstraction from C_6 followed by cyclobutanol formation.[36] The relatively high activation energy associated with five-membered transition state hydrogen atom abstraction reactions by oxygen is further indicated by the fact that such processes have never been observed in the ground state (e.g., the Barton reaction) despite the apparent accessibility of suitable β-hydrogens.[37]

The competition between photochemical γ- and δ-hydrogen abstraction as well as the relative rates of γ-hydrogen abstraction in a variety of systems has been analyzed in terms of transition state torsional strain and relative oxygen-hydrogen distances.[38] Similar arguments may be applied to the process of β-hydrogen abstraction. For the case of 2-pentanone, β-hydrogen atom abstraction must occur over ground state distances of 2.2 Å (planar, eclipsed transition state) to 2.7 Å (bisected transition state). The corresponding γ-hydrogen to oxygen distances in 2-pentanone are 1.1 Å (eclipsed) and 1.8 Å (skew).[39]

In addition, β-hydrogen abstraction in the case of the Diels-Alder adducts reported in this paper may be facilitated by the relative rigidity of the ring systems involved which leads to favorable entropic contributions to the transition state for the abstraction process.[23]

Finally, we point out the similarity of many of the tricyclic photoproducts obtained in this study to existing naturally occurring tricyclic sesquiterpenes. For example, the basic tricyclo[4.4.0.0^{2,8}]decane ring system of photoproduct types **2b** and **4** occurs in the sesquiterpenes copacamphor[40] and sativene[41] while the tricyclo[5.3.1.0^{2,7}]undecane ring system of photoproduct **17** is found in patchouli alcohol[42] and seychellene.[43] The potential synthetic utility of these photochemical reactions is thus indicated.

Experimental Section[44]

Photolysis of the Butadiene-Benzoquinone Adduct 1a. The adduct **1a** was prepared by the method of van Tamelin et al.[35] This material (500 mg, 3.08 mmol) in 250 ml of benzene was irradiated using apparatus 1.[44] The reaction was followed by uv which showed the disappearance of the 370-nm $n \rightarrow \pi^*$ band after 48 hr. Removal of benzene in vacuo and passage of the crude mixture through a short column of neutral alumina (chloroform eluent) yielded a mixture of photoisomers **2a** and **3a**. Analysis of this mixture by GLPC (column A, 170°, 140 ml/min) showed the **2a**:**3a** ratio to be 1:7 with **2a** having the longer retention time. Preparative GLPC of this mixture (same conditions as above) afforded 50 mg (10%) of isomer **3a**, mp 147-150° after recrystallization from ether-hexane. Compound **2a** was collected in very small quantities (~1%) and recrystallized as above, mp 67.5-68.5°. Larger amounts of **2a** could be obtained by photolysis of **1a** exactly as above in *tert*-butyl alcohol-benzene (80:20 v/v). The photolysis was complete in 10 hr. The **2a**:**3a** ratio in this case was 5:1, and the yield of crystalline **2a** obtained via identical workup was 10%.

The full NMR data for ene-dione **2a** is as follows: (CCl_4) τ 4.15 (m, 2), 7.00 (m, 1), 7.23 (m, 1), 7.34 (m, 1), 7.57 (m, 3), 7.72 (m, 1), and 7.90 (m, 1). Isomer **2a** also showed a mass spectrum parent (70 eV) at *m/e* 162.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.15; H, 6.17. Found: C, 74.04; H, 6.22.

The spectral data for product **3a** are given in the text. In addition **3a** showed a mass spectrum parent (70 eV) at *m/e* 162.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.15; H, 6.17. Found: C, 74.08; H, 6.32.

Hydrogenation of Photoproduct 2a. Photoisomer **2a** (45 mg, 0.28 mmol) in 10 ml of ethyl acetate was hydrogenated at atmospheric pressure over 10% palladium on charcoal. Filtration, removal of ethyl acetate in vacuo, and bulb to bulb Kugelrohr distillation at 55° and 0.05 mm gave 37 mg (82%) of dihydro **2a** as a colorless oil, uv$_{max}$ (MeOH) 288 nm (ϵ 48); ir ($CHCl_3$) 5.71 (C=O) μ; NMR (CCl_4) showed no vinyl hydrogens.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.16; H, 7.31. Found: C, 72.86; H, 7.32.

Hydrogenation of Photoproduct 3a. Compound **3a** (35 mg, 0.22 mmol) was hydrogenated exactly as above. Filtration and removal of ethyl acetate in vacuo gave solid dihydro **3a**. Recrystallization from low boiling petroleum ether afforded 30 mg (85%) of fine white needles, mp 151-152°, uv$_{max}$ (MeOH) 292 nm (ϵ 55); ir ($CHCl_3$) 5.70 and 5.81 (C=O) μ; NMR (CCl_4) showed no vinyl hydrogens.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.16; H, 7.31. Found: C, 73.23; H, 7.41.

Photolysis of the 2,3-Dimethylbutadiene-Benzoquinone Diels-Alder Adduct 1b. This adduct was prepared by the method of Mandelbaum and Cais.[45] Irradiation of 1.0 g of **1b** in 400 ml of benzene (method 1) was complete after 35-40 hr. Removal of benzene in vacuo and silica gel chromatography[44] of the residue (chloroform eluent) resulted in the clean separation of photoproducts **3b** and **4** which were isolated in the yields of 35 and 22%, respectively.

Ene-dione **3b** was obtained as colorless crystals, mp 77-78° from ether-hexane, mass spectrum parent (70 eV) *m/e* 190, spectral data in text.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.52; H, 7.27.

Enone alcohol **4** gave colorless crystals, mp 93-94° from ether-hexane, mass spectrum parent (70 eV) *m/e* 190, spectral data in text.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.77; H, 7.44.

Irradiation of 1.0 g of **1b** in 400 ml of 80:20 (v/v) *tert*-butyl alcohol-benzene for 30-35 hr in apparatus 1 followed by removal of solvent in vacuo gave 1 g of an oily residue. Short path Kugelrohr distillation of this material at 88-90° and 0.05 mm gave 0.80 g (80%) of crystalline photoproduct **2b**, mp 84-85° (ether-hexane), ir ($CHCl_3$) 5.72 (C=O) μ; NMR ($CDCl_3$) τ 6.88 (m, 1), 7.22 (m, 1), 7.45 (m, 2), 7.53 (d of d, 1, J = 18 and 5 Hz), 7.61 (m, 2), 7.81 (d of d, 1, J = 18 and 2 Hz), 8.29 (m, 3, CH_3), and 8.41 (m, 3, CH_3); mass spectrum parent (70 eV) *m/e* 190.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.72; H, 7.30.

Thermolysis of Photoproducts 3a and 3b. Ene-dione **3a** (15 mg) was heated in a sealed Pyrex tube at 200° for 4 hr. GLPC (column A, 170°, 140 ml/min) of the dark reaction mixture showed **2a** as the only volatile product. A collected sample was identical (ir) with photochemically generated **2a**.

Ene-dione **3b** (15 mg) was thermolyzed as above for 3 hr. Chloroform elution through a short column of neutral alumina and evaporation of the solvent gave a crystalline residue. Recrystallization (ether-hexane) afforded 9.5 mg (62%) of pure material which was identical (GLPC retention time, mp, mmp, and ir) to the photoproduct **2b**.

Thermolysis of Photoproduct 4. The enone-alcohol **4** was thermolyzed as above at 200° for 5 hr. GLPC showed only one volatile product corresponding in retention time to isomer **2b**. Passage of the crude thermolysate through a neutral alumina column with chloroform and removal of chloroform in vacuo gave 70% of a crystalline compound which proved to be **2b** (mp, ir).

Photolysis of Enone-Alcohol 4. Enone-alcohol 4 (50 mg) in 25 ml of benzene was irradiated (apparatus 1) for 40 hr and followed by GLPC. A new peak corresponding in retention time to that of **3b** was observed to grow throughout the photolysis. Removal of benzene in vacuo followed by silica gel column chromatography (chloroform) gave 39 mg (78%) of crystalline **3b** identical in every respect (mp, mmp, ir) with previous samples.

Identical photolysis of **4** (50 mg) in 25 ml of *tert*-butyl alcohol slowly gave rise to isomer **2b** as shown by GLPC. Some **4** remained even after 40 hr. Removal of *tert*-butyl alcohol in vacuo followed by Kugelrohr short path distillation (88-90°, 0.05 mm) gave 40 mg (80%) of crystalline material which was identical (mp, mmp, ir) with authentic **2b**.

Photolysis of Ene-Dione 3b. A solution of 30 mg of this material in 30 ml of benzene was irradiated through Pyrex by method 2 (100-W Hanovia) and followed by GLPC (column B, 150°, 150 ml/min). During 8 hr, starting material gradually disappeared and was replaced by a new GLPC peak due to photoisomer **5**. Continued irradiation led to a second new GLPC peak, that of **6**, at the expense of **5** until after 48 hr the **5**:**6** ratio was time invariant at 1:1.9.

Simultaneous irradiation of 23 mg of **3b** in 10 ml of benzene in one Pyrex tube and 23 mg of **3b** dissolved in 10 ml of 8:2 (v/v) benzene-piperylene in another gave identical results.

Irradiation of 27 mg of **3b** in 20 ml of benzene containing 102 mg of benzophenone through a number 3850 Corning glass filter (transmitting λ >355 nm) for 65 hr resulted in the formation of traces of **5** (GLPC). However, identical results were obtained in a parallel experiment in which the benzophenone was omitted. Irradiation of **3b** in 20 ml of acetone using a 253.7-nm mercury lamp resulted in the complete disappearance of starting material within 3 hr with no GLPC volatile products being formed.

Compounds **5** and **6** could be easily isolated in 50% overall yield by preparative GLPC (column C, 170°, 120 ml/min) of solutions photolyzed so as to give a 1:1 = **5**:**6** ratio. The physical and spectral data for **5** and **6** are given in the text. Both **5** and **6** showed mass spectral parent peaks (70 eV) at *m/e* 190.

Anal. Calcd for compound **5** ($C_{12}H_{14}O_2$): C, 75.76; H, 7.42. Found: C, 75.59; H, 7.45.

Anal. Calcd for compound **6** ($C_{12}H_{14}O_2$): C, 75.76; H, 7.42. Found: C, 75.88; H, 7.43.

Irradiation of Isomers 5 and 6. Ene-dione **5** (22 mg) in 18 ml of benzene was irradiated through Pyrex by method 2 (450-W Hanovia). After 3 hr the **5**:**6** ratio was constant at 1:1.8 as shown by GLPC. The ir and NMR spectra of collected samples were identical with previous spectra. Photolysis of ene-dione **6** (27 mg) in 20 ml of benzene exactly as above also led to a **5**:**6** ratio of 1:1.8. Ir and NMR spectra were again superimposable.

Hydrogenation of Photoisomers 5 and 6. Ene-dione **5** (30 mg) in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure over 10% palladium on charcoal. Filtration, removal of the ethyl acetate in vacuo, and recrystallization of the solid residue from ether-hexane gave pure dihydro **5**, mp (sealed tube) 225° dec, uv$_{max}$ (MeOH) 293 nm (ϵ 54); ir ($CHCl_3$) 5.72 (C=O) μ; NMR (CCl_4) no vinyl hydrogens.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.71; H, 8.25.

Identical hydrogenation of photoproduct **6** and workup as above afforded pure dihydro **6**, mp (sealed tube) 211-212.5°, uv$_{max}$ (MeOH) 292 nm (ϵ 39); ir ($CHCl_3$) 5.70 (C=O) μ; NMR (CCl_4) no vinyl hydrogens.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.69; H, 8.43.

Photolysis of the Benzoquinone–2,3-Dimethylbutadiene Diels–Alder Adduct 1b in *tert*-Butyl Alcohol-*O-d*. Diels-Alder adduct **1b** (50 mg) was dissolved in 5 ml of *tert*-butyl alcohol-*O-d* and photolyzed by method 1 until no starting material remained. Workup as previously described gave 40 mg (80%) of colorless photoproduct **2b**; mp 82-83°, ir ($CHCl_3$) 5.72 (C=O) μ; NMR ($CDCl_3$) τ 7.0 (broad s, 1), 7.33 (m, 1), 7.45 (m, 1), 7.62 (m, 1), 7.75 (m, 2), 7.87 (broad t, 1, C_4 endo H), 8.31 (m, 3, CH_3), and 8.41 (m, 3, CH_3). The doublet of doublets at τ 7.53 in undeuterated **2b**, likely due to the C_4 exo proton, was absent. The mass spectrum parent (70 eV) appeared at *m/e* 191, the relative intensity of which indicated 92.2% deuterium content.[46] Photolysis of **2b** exactly as above gave only recovered undeuterated **2b**.

A mixture of 10 mg of photoproduct **2b**, 3 mg of potassium hydroxide, 4 drops of deuterium oxide, and 0.7 ml of $CDCl_3$ was placed in an NMR tube, and the contents were shaken at room temperature for 3 hr. The NMR spectrum of this mixture was found to be identical with that reported above.

Preparation of 2,3-Dimethylbutadiene-*1,1,4,4-d₄*. This material was prepared by the general method of Cope, Berchtold, and Ross[47] which involves sulfolene formation, base-catalyzed deuteration, and thermal cleavage to the deuterated diene. The requisite 3,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide was prepared by the method of Grummit, Ardis, and Fick,[48] mp 135° (lit.[48] 135°). The deuteration was carried out as follows. A mixture of sulfolene (3.6 g, 0.05 mol), dioxane (30 ml), deuterium oxide (5 ml), and potassium *tert*-butoxide (0.56 g, 0.005 mole) was refluxed for a period of 20 hr. The reaction mixture was cooled and acidified with hydrochloric acid. The volume was reduced to about 10 ml by evaporation in vacuo and the reaction mixture was then extracted with chloroform twice in 30-ml portions. The dried (Na_2SO_4) chloroform extract was concentrated in vacuo to give a white solid which recrystallized from water to yield 3.4 g (94%) of colorless crystals: mp 129-130°; NMR ($CDCl_3$) τ 6.30 (s, 0.5, unexchanged CH_2) and 8.30 (s, 6, CH_3). Mass spectrometry (70 eV) indicated a total deuterium content of 89%.[46]

Thermal cracking of this material to the deuterated butadiene was accomplished as follows. The deuterated sulfolene from above (1.5 g, 0.01 mol) was placed in a long-necked round-bottom flask which was in turn connected to a U-tube immersed in an ice bath. The flask together with its long neck was heated to 170° in a Kugelrohr apparatus oven. The desired deuterated butadiene was trapped in the U-tube in the form of a colorless liquid while sulfur dioxide escaped. Distillation of the trapped residue at 74-75° gave 0.67 g (80%) of tetradeuterio-2,3-dimethyl-1,3-butadiene whose NMR showed peaks at τ 5.0 (d, 0.5, unexchanged vinyl H) and 8.18 (s, 6, CH_3).

Preparation and Photolysis of the 2,3-Dimethylbutadiene-*1,1,4,4-d₄* Benzoquinone Diels–Alder Adduct 1b (R′ = D). Following the procedure of Mandelbaum and Cais,[45] Diels-Alder adduct **1b** (R′ = D) was obtained from the tetradeuteriobutadiene prepared above and benzoquinone as pale yellow needles, mp 110-111°. The NMR spectrum showed τ 3.40 (s, 2, vinyl), 6.85 (s, 2), and 8.40 (s, 6, CH_3). From the mass spectrum (70 eV, parent *m/e* 194), the extent of deuteration was determined[46] to be 88.2%. A second preparation gave material with 83.5% total deuterium content.

A sample (100 mg) of this latter material in 80 ml of benzene (pretreated with D_2O, azeotropically distilled, and redistilled from sodium) was photolyzed to completion by method 1. Workup as previously described gave 60 mg (60%) of crystalline photoproduct **3b** (R′ = D), NMR ($CDCl_3$) τ 6.71 (d, 1, J = 7 Hz), 7.0 (d of d, 0.4, J = 18 and 2 Hz, C_4-exo H), 7.33 (d, 1, J = 7 Hz), 7.67 (d of d, 1, J = 18 and 5 Hz, C_4-endo H), 7.95 (m, 1), 8.12 (s, 3, CH_3), and 8.62 (s, 3, CH_3). In agreement with these NMR data, the mass spectrum of **3b** (R′ = D) indicated a total deuterium content of 75.1%.

As expected, photolysis of **1b** (R′ = D) (88.2% total deuterium content) in *tert*-butyl alcohol gave photoproduct **2b** (77%) with a total deuterium content of 68.2% and the C_4-exo proton intact.

Photolysis of the 1,4-Naphthoquinone–2,3-Dimethylbutadiene Diels–Alder Adduct 7. Diels-Alder adduct **7** was prepared by the method of Allen and Bell.[49] A solution of 1.0 g of **7** in 400 ml of benzene was irradiated (method 2) for 15 hr. The reaction mixture was concentrated under vacuum and subjected to silica gel column chromatography with 5% acetone-chloroform elution. In this way 410 mg of adduct **7** and 257 mg (43% based on unrecovered starting material) of keto alcohol **8** were isolated. Recrystallization (hexane) and sublimation (100°, 0.02 mm) of the latter gave material melting at 126.0-126.5°. With reference to the NMR reported in the text, the following spin decoupling experiments were carried out: Irradiation of the C_7 vinyl proton (τ 4.24) led to a collapse of the C_6 proton doublet (τ 6.75) to a singlet. Irradiation of the C_1 methine signal (τ 7.4) converted the signals at τ 8.45 and 8.66 (C_{10} endo and exo protons, respectively) to an AB quartet with J = 13 Hz. Mass spectrum parent (70 eV) *m/e* 240.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.98; H, 6.71. Found: C, 80.01; H, 6.90.

Photolysis of the Isoprene–Benzoquinone Diels–Alder Adduct 9. A solution of 515 mg of adduct **9**[50] in 250 ml of benzene was irradiated by method 2 and followed by the decrease in intensity of the 350-nm uv absorption band which indicated nearly complete reaction after 15 hr. Analysis of the resulting mixture on GLPC (column D, 157°, 150 ml/min) indicated the presence of three products subsequently shown to have structures **10**, **11**, and **12** in the ratio of 5:3:2, respectively. An otherwise identical photolysis in *tert*-butyl alcohol gave only ene-diones **11** and **12** in the ratio 7:1. The photoproducts were isolated in the form of colorless liquids by preparative GLPC (column C, 145°, 150 ml/min), and analytical samples were prepared by short path Kugelrohr distillation.

Ene-dione **10** exhibited ir ($CHCl_3$) 5.68 (C=O) and 5.80 (C=O) μ; NMR ($CDCl_3$) τ 3.69 (d of d, 1, J = 8 and 1 Hz, vinyl), 4.11 (d of d, 1, J = 8 and 6 Hz, vinyl) 6.63 (broad t, 1), 6.80 (d of d, 1, J = 18 and 2 Hz, C_4 exo H), 7.18-7.38 (m, 1), 7.65 (broad d of d, 1, J = 18 and 5 Hz, C_4 endo H), 7.83-7.97 (m, 1), 8.34 (broad d, 2, J = 1.5 Hz), and 8.60 (s, 3, CH_3); uv$_{max}$ (MeOH) 296 (ϵ 300), 310 nm (shoulder);[51] mass spectrum parent (70 eV) *m/e* 176.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.80; H, 6.79.

Photoproduct **11** showed ir ($CHCl_3$) 5.72 (C=O) μ; NMR ($CDCl_3$) τ 4.3-4.5 (symmetric m, 1, vinyl), 6.9-7.0 (symmetric m, 1), 7.1-7.3 (m, 2), 7.4-7.5 (m, 1), 7.56 (d of d, 1, J = 18 and 4 Hz, C_4 exo H, exchangeable), 7.6-7.7 (m, 2), 7.78 (d of d, 1, J = 18 and 1 Hz, C_4 endo H), and 8.35 (broad s, 3, CH_3); uv$_{max}$ (MeOH) 288 nm (ϵ 61); mass spectrum parent (70 eV) *m/e* 176.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.75; H, 6.70.

Photoproduct **12** gave the following data: ir ($CHCl_3$) 5.70 (C=O) and 5.84 (C=O) μ; NMR ($CDCl_3$) τ 4.47 (symmetric m, 1, vinyl), 6.67 (broad t, 1, J = 7 Hz), 6.0-7.8 (m, 6), 8.06 (d, 3, J

= 1.5 Hz, CH_3), and 8.39 (broad d, 2, J = 12 Hz). Irradiation of the τ 4.47 vinyl multiplet caused the collapse of the τ 6.67 triplet to a doublet with J = 7 Hz and conversion of the methyl doublet to a singlet. The uv spectrum (MeOH) was again indicative[51] with a max at 295 nm (ϵ 330) and a shoulder at 305 nm. The mass spectrum parent (70 eV) appeared at m/e 176.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.08; H, 6.84.

Thermolysis of Ene-Diones 10 and 12. Thermolysis (168°) of 10 mg of ene-dione **10** in a sealed Pyrex tube for 16 hr followed by filtration through a small column of neutral alumina (chloroform eluent) gave 10 mg of ene-dione **11** (identical NMR spectrum).

Photoproduct **12** (15 mg) was similarly heated at 185° for 22 hr. Filtration through silica gel with chloroform yielded 14 mg (95%) of ene-dione **15** as a colorless liquid: ir ($CHCl_3$) 5.70 (C=O) μ; NMR ($CDCl_3$) 4.62 (m, 1, vinyl), 6.8-6.9 (m, 1), 7.16-7.27 (m, 1), 7.33-7.65 (m, 5), 7.78 (d of d, 1, J = 18 and 1 Hz, C_4 endo H), and 8.23 (m, 3, CH_3); uv$_{max}$ (MeOH) 290 nm (ϵ 80); mass spectrum parent (70 eV) m/e 176.

Photolysis of the Isoprene-1,4-Naphthoquinone Diels-Alder Adduct 13. Diels-Alder adduct **13** was prepared according to the procedure of Diels, Alder, and Stein.[52] A solution of 315 mg of this material in 135 ml of *tert*-butyl alcohol and 15 ml of benzene was irradiated (method 2) for 21 hr. Silica gel column chromatography (chloroform) gave 80 mg of material consisting largely of photoproduct **14**. A small sample of this material, isolated with difficulty (due to thermal instability) by preparative GLPC showed the following spectral data: ir (CCl_4) 5.86 (C=O) μ; NMR (CCl_4) τ 2.0-2.8 (m, 4, aromatic), 3.6-4.0 (m, 2, vinyls), 6.6-6.8 (m, 1), 7.4 (s, 1, OH, exchangeable with addition of D_2O), 7.6 (d of d, 1, J = 8 and 3 Hz), 8.3-8.6 (m, 2) and 8.9 (s, 1, CH_3); mass spectrum parent (70 eV) m/e 226.

Photolysis of the *trans,trans*-2,4-Hexadiene-Benzoquinone Diels-Alder Adduct 16. A solution of 1.0 g of Diels-Alder adduct **16**, prepared by the method of Euler, Hasselquist, and Glaser,[50] in 400 ml of benzene was irradiated using method 1 for 121 hr after which time the 371-nm uv absorption of **16** had disappeared. GLPC (column D, 170°, 150 ml/min) of the dark brown reaction mixture revealed only one major volatile product. Chromatography of this material on neutral alumina (chloroform eluent) gave photoproduct **17** as a yellow oil. Crystallization from hexane afforded 274 mg (26%) of **17**, mp 75.5-78.5°. Two recrystallizations gave analytically pure material melting at 80.0-80.5°: ir (CCl_4) 5.78 (C=O) μ; NMR ($CDCl_3$) τ 4.1-4.6 (m, 2, vinyls), 7.2-7.7 (m, 7), 7.7-8.4 (m, 2), and 8.7 (d, 3, J = 7 Hz, CH_3); uv$_{max}$ (MeOH) 291 nm (ϵ 56); mass spectrum parent (70 eV) m/e 190.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.50; H, 7.32.

Hydrogenation of Photoproduct 17. A solution of 93 mg of ene-dione **17** in 25 ml of ethyl acetate was hydrogenated over 20 mg of 10% palladium on charcoal at atmospheric pressure. Hydrogen uptake was complete within 1 hr. The reaction mixture was filtered through Celite to give 92 mg (99%) of crystalline dihydro **17**, mp 84.5-85.0° after recrystallization from low boiling petroleum ether: ir (CCl_4) 5.80 (C=O) μ; NMR (CCl_4 and $CDCl_3$) τ 7.34 (pentuplet, 1, J = 3 Hz, C_3 methine), 7.5-7.8 (m, 5), 7.8-8.8 (m, 7), 8.82 (d, 3, J = 6.5 Hz, CH_3); uv$_{max}$ (MeOH) 293 nm (ϵ 51); mass spectrum parent (70 eV) m/e 192.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.86; H, 8.52.

Photolysis of the *trans,trans*-2,4-Hexadiene-Benzoquinone Diels-Alder Adduct 16 in *tert*-Butyl Alcohol-*O-d*. A solution of 89 mg of Diels-Alder adduct **16** in 7.5 ml of *tert*-butyl alcohol-*O-d* was irradiated using method 2 and the reaction monitored by uv at 371 nm which showed the disappearance of starting material after 2.5 hr. Passage of the crude photolysate through a 4 × 1 cm column of neutral alumina (chloroform eluent) resulted in the isolation of 28 mg of crystalline photoproduct **17** whose NMR spectrum was consistent with partial deuteration at C_4 as shown by the decrease of the integral of the multiplet at $\tau \sim 7.5$. (Base-catalyzed deuterium exchange of proteo-**17** resulted in the exchange of two hydrogens at $\tau \sim 7.5$.) From the mass spectrum (70 eV), the extent of photochemical deuterium incorporation was determined[46] to be 30%.

Photolysis of the Piperylene-Benzoquinone Diels-Alder Adduct 18. A solution of 0.75 g of Diels-Alder adduct **18**[53] in 200 ml of *tert*-butyl alcohol was irradiated using method 1 and the reaction followed by TLC (15% ethyl acetate-benzene) which showed the disappearance of starting material after 12 hr. GLPC analysis (column A, 160°, 120 ml/min) indicated the presence of two photoproducts in the ratio of 7:1 which were assigned structures **19** and **20**, respectively, on the basis of the spectral data given below (isolation by preparative GLPC, column E, 170°).

Ene-dione **19**, mp 75-76° (ether-hexane), showed ir (CCl_4) 5.79 (C=O) μ; NMR (CCl_4) τ 4.0-4.6 (m, 2, vinyl), 7.2-7.8 (m, 8), 7.9-8.2 (m, 2); uv$_{max}$ (MeOH) 285 nm (ϵ 60); mass spectrum parent (70 eV) m/e 176.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.17; H, 7.01.

Photoproduct **20**, a colorless liquid, showed ir (CCl_4) 5.67 and 5.79 (C=O) μ; NMR ($CDCl_3$) τ 3.3 (broad t, 1, J = 8 Hz, vinyl), 4.1 (broad t, 1, J = 7 Hz, vinyl), 6.4-6.8 (m, 1), 6.8-8.4 (m, 6), and 9.0 (d, 3, J = 8 Hz, CH_3); uv$_{max}$ (MeOH) 296 nm (ϵ 440);[51] mass spectrum parent (70 eV) m/e 176.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.72; H, 7.00.

Attempted Photolysis of Diels-Alder Adduct 21. Diels-Adler adduct **21** was prepared by the method of Lepage.[54] Photolysis (method 1) of 250-mg samples of this material in either benzene or *tert*-butyl alcohol for periods of up to 48 hr resulted in no product formation, and in each case over 90% of the starting material could be recovered unchanged.

Photolysis of the Duroquinone-2,3-Dimethylbutadiene Diels-Alder Adduct 22. Diels-Alder adduct **22** was prepared by the method of Ansell, Nash, and Wilson.[55] A solution of 0.80 g of this material in 300 ml of benzene was irradiated using method 1 for 6 hr. Silica gel column chromatography (8% ethyl acetate-benzene eluent) gave 182 mg (23%) of enone alcohol **23**, mp (hexane) 101-102°, and 369 mg (46%) of liquid ene-dione **24**. Photolysis of **22** in other solvents gave the results shown in Table II of the text (GLPC analysis with column A, 145°, 150 ml/min plus spectra of collected samples). The enone alcohol **23** was irradiated in *tert*-butyl alcohol under identical conditions and shown to be photostable for periods of time during which Diels-Alder adduct **22** reacted completely. Prolonged photolysis of **23** led to nonvolatile polymer-like material.

Photolysis of adduct **22** in methanol or water-dioxane mixtures led to small quantities of a third photoproduct, ene-dione **25**, which could also be isolated by silica gel column chromatography as above.

Photoisomer **23** exhibited the following spectra: ir (CCl_4) 2.69 (OH) and 5.98 (C=O) μ; NMR (CCl_4) τ 4.62 (m, 1, vinyl), 7.79 (broad, s, 1, OH, disappears with D_2O), 8.12-8.16 (m, 3, CH_3), 8.20-8.26 (m, 6, CH_3), 8.43 (d, 1, J = 12.5 Hz, $C_{10}H$), 8.92 (s, 3, CH_3), 9.03 (d, 1, J = 12.5 Hz, $C_{10}H$), 9.14 (s, 3, CH_3), and 9.20 (s, 3, CH_3); uv$_{max}$ (MeOH) 251 (ϵ 7.42 × 10^3), 325 nm (ϵ 58); mass spectrum parent (70 eV) m/e 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.80; H, 9.02.

The spectral data for photoproduct **24** are given in the text. Mass spectrum parent (70 eV) m/e 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.80; H, 9.13.

Minor photoproduct **25**, a colorless liquid, showed ir (CCl_4) 5.72 (C=O) μ; NMR (CCl_4) τ 7.93 (broad s, 1, C_7 methine), 7.99 (q, 1, J = 7 Hz, C_4 methine), 8.05-8.15 (m, 2, C_{10} CH_2), 8.24-8.34 (m, 3, CH_3), 8.39 (broad s, 3, CH_3), 8.87 (s, 3, CH_3), 9.05 (s, 3, CH_3), 9.17 (d, 3, J = 7 Hz, C_4 CH_3), and 9.28 (s, 3, CH_3). Deuterium exchange in the NMR tube (CCl_4-D_2O-KOH) led to the disappearance of the quartet at τ 7.99 and to the formation of a broad singlet at τ 9.17. Uv$_{max}$ (MeOH) 292 nm (ϵ 70); mass spectrum parent (70 eV) m/e 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.78; H, 8.98.

Thermolysis of Enone Alcohol 23. Photoproduct **23** (60 mg) was heated for 2 hr at 280° in a sealed Pyrex tube. Silica gel column chromatography (8% ethyl acetate-benzene) afforded 12 mg (20%) of Diels-Alder adduct **22** plus 32 mg (53%) of ene-dione **25**. All spectra were identical with those of previously prepared samples.

Thermolysis of Ene-Dione 24. Photoproduct **24** (26 mg) was heated (192°) for 16 hr in a sealed Pyrex tube. The slightly brown product was chromatographed (silica gel-chloroform) to yield 24 mg (92%) of a homogeneous (GLPC, column A, 150°, 150 ml/min) yellow oil. Crystallization from hexane gave compound **26** as yellow needles, mp 53.0-53.5°, whose spectra are described in the text.[26] Mass spectrum parent (70 eV) *m/e* 246.

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.99; H, 9.03.

Boron Trifluoride-Catalyzed Isomerization of 26. A solution of 21 mg of diene-dione **26** in 4 ml of methylene chloride was saturated with gaseous boron trifluoride and stirred for 30 min at room temperature. Water (5 ml) and excess solid sodium bicarbonate were then added to the brown reaction solution, and the resulting mixture was extracted with chloroform. Removal of chloroform in vacuo gave 21 mg (100%) of partially crystalline Diels-Alder adduct **22**. Recrystallization from hexane gave material whose ir and NMR spectra were identical with those of an authentic sample.

Photolysis of the Duroquinone-2,3-Dimethylbutadiene Diels-Alder Adduct 22 in Deuterated Protic Solvents. A solution of 91 mg of Diels-Alder adduct **22** in 7 ml of anhydrous dioxane and 5 ml of deuterium oxide was irradiated using method 2 for 5.9 hr. Three products, corresponding in TLC behavior and GLPC retention times to photoisomers **23**, **24**, and **25**, were observed in the ratio of 33:1:6, respectively (column A, 170°, 60 ml/min). Photoproducts **24** and **25** were isolated in small amounts by silica gel column chromatography using 8% ethyl acetate-benzene as the eluting solvent. The NMR spectrum of photoproduct **25** obtained in this way was identical in every respect with the spectrum observed when proteo-ene-dione **25** was subjected to base-catalyzed deuterium exchange as previously described. The NMR spectrum of photoproduct **24**, however, showed no trace of deuterium incorporation and was identical with that previously observed.

Irradiation of adduct **22** (110 mg) in 8 ml of *tert*-butyl alcohol-*O-d* and 1 ml of benzene followed by identical workup gave 21 mg of ene-dione **24** whose NMR and mass spectra showed absolutely no deuterium incorporation.

Photolysis of the 2,3-Dimethylbutadiene-2,3-Dimethyl-*p*-benzoquinone Diels-Alder Adduct 30. Diels-Alder adduct **30** was prepared as described by Fieser and Chang.[56] This material (0.60 g) in 200 ml of benzene was irradiated by method 2 and followed by GLPC (column A, 165°, 150 ml/min) which showed the formation of essentially only one photoproduct. After 6.5 hr the reaction was stopped and the crude photolysate subjected to column chromatography on silica gel (eluting solvent 20% ethyl acetate-benzene). This procedure gave 137 mg (23%) of material, mp 55-56°, which was assigned the structure **31** on the basis of the following data: ir ($CHCl_3$) 2.80 (weak, OH) and 6.00 (C=O) μ; NMR ($CDCl_3$) τ 4.42 (m, 1, vinyl), 7.13 (d, 1, J = 3 Hz), 7.70 (s, 1, OH, disappears on adding D_2O), 7.84 (m, 1), 8.15 (s, 3, vinyl CH_3), 8.25 (broad s, 3, vinyl CH_3), 8.30 (s, 3, vinyl CH_3), 8.59 (d, 1, J = 3 Hz), 8.65 (s, 1), and 8.93 (s, 3, CH_3); uv$_{max}$ (MeOH) 252 (ϵ 8600) and 325 nm (ϵ 80); mass spectrum parent (70 eV) *m/e* 218.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.10; H, 8.44.

Irradiation of 150 mg of adduct **30** in 25 ml of *tert*-butyl alcohol as described above led to the formation of enone-alcohol **31** plus a new photoproduct subsequently assigned the structure **32**. The **31**:**32** ratio decreased with increasing length of irradiation indicating that ene-dione **32** was being formed at the expense of enone-alcohol **31**. After 19 hr, the **31**:**32** ratio was ca. 1:5.5. Both products were isolated by preparative GLPC (column A, 165°, 150 ml/min) and identified by their spectra. Photoisomer **32**, mp 78-80°, showed ir ($CHCl_3$) 5.73 (C=O) μ; NMR ($CDCl_3$) τ 7.37 (m, 1), 7.70 (m, 4), 7.85 (m, 1), 8.25 (s, 3, vinyl CH_3), 8.37 (s, 3, vinyl CH_3), 8.88 (s, 3, CH_3), 9.13 (d, 3, J = 7 Hz, C_4 CH_3); mass spectrum parent (70 eV) *m/e* 218.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.80; H, 8.36.

Photolysis of enone-alcohol **31** under conditions identical with those described above led to ene-dione **32** in *tert*-butyl alcohol (proved by GLPC retention time); irradiation in benzene led to no measurable (GLPC) reaction.

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(14) A reaction analogous to the photochemical conversion of **4** to **3b** has been reported and shown to be nonconcerted, i.e., nonstereospecific: R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *J. Am. Chem. Soc.*, **95**, 4346 (1973).

(15) See D. I. Schuster, G. R. Underwood, and T. P. Knudson, *J. Am. Chem. Soc.*, **93**, 4304 (1971), and K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *ibid.*, **94**, 6233 (1972), for leading references and attempts to explain this phenomenon.

(16) This experiment cannot provide evidence on the intermediacy of enol-**3b** since **3b** is formed in only trace amounts in *tert*-butyl alcohol.

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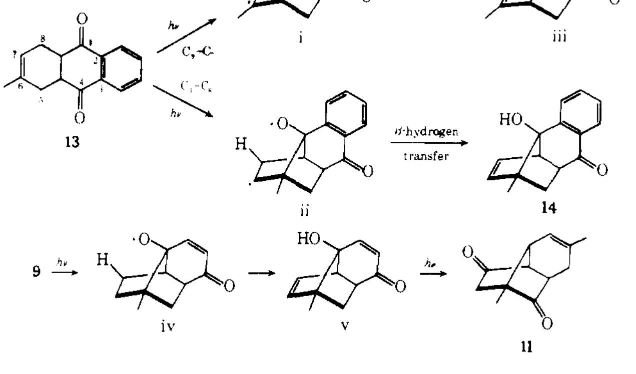

in photochemical hydrogen abstraction reactions, at least in the Norrish type II reactions of phenyl alkyl ketones, due primarily to the possibility and unknown rate of reverse hydrogen transfer, the observed photochemistry of Diels–Alder adducts **9** and **13** does suggest that β-hydrogen abstraction *precedes* carbon–carbon bond formation in these systems. For example, a mechanism involving initial C_1–C_6 or C_4–C_7 bond formation in **13** followed by intramolecular β-hydrogen transfer would be expected to lead to the unobserved photoproduct iii since the diradical i should be formed in preference to ii. Similarly in the case of adduct **9**, a mechanism involving the intermediate formation of v followed by rapid photorearrangement to **11** in *tert*-butyl alcohol (cf. the **4** to **2b** conversion) is unlikely since it requires the initial formation of iv, the *less* stable of the two possible diradical intermediates.

(21) While Diels–Alder adduct **16** has been reported several times in the literature (see Experimental Section for references), its stereochemistry has apparently never been rigorously determined. The stereochemistry assumed for **16** in this paper is based on (a) the preference for stereospecific cis–endo addition in Diels–Alder reactions and (b) the structure of the photoproduct **17** which can only arise from an adduct of the stereochemistry shown. The same is true of adducts **18** and **21** (Scheme VII).

(22) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **86**, 3602 (1964).

(23) For further examples of conformational control of intramolecular photochemical hydrogen abstraction reactions, see F. D. Lewis, R. W. Johnson, and D. R. Kory, *J. Am. Chem. Soc.*, **95**, 6470 (1973), and references cited therein.

(24) J. Trotter and C. A. Bear, *J. Chem. Soc., Perkin Trans. 2*, 330 (1974).

(25) For a review see H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

(26) Compound **26**, mp 53–53.5°, showed uv$_{max}$ (MeOH) 247 (ϵ 12,000) and 356 nm (ϵ 84); ir (CCl_4) 5.99 (C=O) μ; NMR (CCl_4) τ 4.97 (m, 1, vinyl), 7.58–7.93 (m, 2), 8.03–8.13 (m, 6, C_2 and C_3 CH_3), 8.40–8.45 (m, 3, C_7 CH_3), 8.63–8.87 (m, 1), 8.84 (s, 3, CH_3), 8.98 (d, 3, $J = 7.5$ Hz, C_6 CH_3), and 9.00 (s, 3, CH_3). The stereochemistry at C_6 is assumed and is based on the proposed mechanism.

(27) The analogous rearrangement of a semiquinone free radical has recently been suggested. S. Farid, *Chem. Commun.*, 303 (1970). Formation of **27** by direct C_8 hydrogen abstraction by the C_4 oxygen is conceivable although perhaps less likely in view of the relatively long distances (>3.1 Å) involved.

(28) (a) W. Herz and M. G. Nair, *J. Am. Chem. Soc.*, **89**, 5474 (1967); (b) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *ibid.*, **94**, 7797 (1972); (c) A. B. Smith, III, and W. C. Agosta, *ibid.*, **95**, 1961 (1973); (d) A. Marchesini, U. M. Pagnoni, and A. Pinetti, *Tetrahedron Lett.*, 4299 (1973).

(29) Lack of deuterium incorporation into photoproduct **24** due to steric hindrance of exchange in enol **28** is unlikely in view of the fact that the enolate of **24** is apparently readily formed and undergoes rearrangement. On the other hand attempted acid-catalyzed deuteration of **24** was unsuccessful under conditions (0.05 *M* DCl in 1:1 dioxane-D_2O, 11 days, 60°) which brings about deuteration of the tertiary position of 2-methylcyclohexanone in less than 1 hr. Higher temperatures (100°) or increased acid concentration (1 *M*) leads to the conversion of **24** into numerous products.

(30) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **95**, 4592 (1973). For a similar effect, see I. Murata and Y. Sugihara, *Tetrahedron Lett.*, 3785 (1972).

(31) Zwitterions resulting from intramolecular β-hydrogen atom abstraction by excited carbonyl oxygen have been tentatively suggested by N. J. Turro and T-J. Lee, *J. Am. Chem. Soc.*, **92**, 7467 (1970).

(32) A referee has suggested that the increased effective size of the hydroxyl group in hydrogen bonding solvents such as *tert*-butyl alcohol (cf. E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **4**, 761 (1965)) may alter the preferred conformation of **33** or **34** relative to the corresponding unsolvated species and hence lead to a difference in the preferred mode of collapse.

(33) For tentative suggestions along these lines in reactions for which alternative mechanisms are also reasonable, see ref 31 and also P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963). The β-hydrogen transfers in the photochemistry of aroylaziridines and aroylazetidines are likely proton, not hydrogen atom transfers; cf. A. Padwa and R. Gruber, *ibid.*, **92**, 107 (1970); A. Padwa and W. Eisenhardt, *ibid.*, **93**, 1400 (1971). For a reaction which can be similarly interpreted see H. J. Roth and M. H. El Rale, *Tetrahedron Lett.*, 2445 (1970).

(34) R. A. Cormier, W. L. Schreiber, and W. C. Agosta, *J. Am. Chem. Soc.*, **95**, 4873 (1973). For a related example see P. Gull, H. Wehrli, and O. Jeger, *Helv. Chim. Acta*, **54**, 2158 (1971). In addition D. S. L. Blackwell and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 130 (1973) have reported β-hydrogen abstraction in the case of a thio ketone.

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(36) N. Sugiyama, K. Yamada, and H. Aoyama, *J. Chem. Soc. C*, 830 (1971).

(37) R. H. Hesse, *Adv. Free-Radical Chem.*, **3**, 83 (1969).

(38) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Am. Chem. Soc.*, **94**, 4292 (1972); P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *ibid.*, **94**, 7500 (1972).

(39) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Am. Chem. Soc.*, **90**, 7239 (1968).

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(41) P. de Mayo and R. E. Williams, *J. Am. Chem. Soc.*, **87**, 3275 (1965).

(42) G. Büchi, W. D. MacLeod, Jr., and J. Padilla O., *J. Am. Chem. Soc.*, **86**, 4438 (1964).

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(44) 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 CH-4-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. For GLPC 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, 10 ft × 0.25 in. stainless steel, 30% DEGS on 60/80 Chromosorb W; column D, 5 ft × 0.25 stainless steel, 30% DEGS on 60/80 Chromosorb W; column E, 20 ft × ⅜ in. aluminum, 5% DEGS on 60/80 Chromosorb W. Unless otherwise indicated, internal standards were not used. 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. Three general photolysis methods were used: (1) external irradiation from a distance of 1 ft through an interposed plate of Corning 7380 glass (transmitting $\lambda \geq 340$ nm) using a Westinghouse 275-W sun lamp, (2) external irradiation from a distance of 6 in. exactly as above only using a Hanovia 450-W light source, and (3) conventional immersion well photolysis using either water-cooled 450-W or 100-W Hanovia lamps and a Pyrex filter sleeve. 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.

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