Table I. Kinetic Data for $AgNO_3$ on Metal Oxide Crystals

Material	Φ_{lim}	C_L, M	K, $M^{-1\,a}$
ZnO	0.3–0.6	0.2–0.6	3.5–0
TiO_2	0.03–0.10	1×10^{-3} to 2×10^{-2}	970–0

[a] Calculated from eq 8; the largest value is obtained with the smallest Φ_{lim} when $\phi = 1$.

C_{Ag^+}, Φ_{lim} is the limiting yield at high C_{Ag^+}, and C_L is a constant. The parameters Φ_{lim} and C_L vary considerably for different crystals, largely depending on surface preparation (Table I). However, the concentration dependence, eq 1, is applicable in every case.

The Stern–Volmer concentration dependence may be obtained from the following reaction scheme

$$C + h\nu \xrightarrow{\phi} e^-_{(s)} + p \qquad (2)$$

$$e^-_{(s)} + Ag^+_{(s)} \xrightarrow{k_3} Ag_{(s)} \qquad (3)$$

$$e^-_{(s)} \xrightarrow{k_4} \text{nonreactive state} \qquad (4)$$

In this scheme, it is visualized that excitation of crystal C produces surface electrons $e^-_{(s)}$ with an efficiency ϕ; these electrons then react with silver $Ag^+_{(s)}$ at the solid–liquid interface. Thus

$$\Phi = \phi k_3 N_{Ag^+}/(k_4 + k_3 N_{Ag^+}) \qquad (5)$$

where N_{Ag^+} is the surface concentration of silver ions. Equation 5 is sufficient to describe our experimental results, if N_{Ag^+} is proportional to C_{Ag^+} and $\Phi_{\mathrm{lim}} = \phi < 1$. This condition ($\phi < 1$) requires a surface barrier to photoelectron transport. The effect of such a barrier and, hence, the value of ϕ depend on substrate properties such as trapping and recombination of photogenerated charge carriers.

A more general derivation of eq 1 is obtained if discrete ion effects in the solution region at the interface are considered. A Langmuir adsorption isotherm with equilibrium constant K and N_s sites/cm^2 can be used to describe the relationship of concentration of adsorbed silver ions to the solution Ag^+ concentration. This assumption and the use of eq 5 yield the Stern–Volmer dependence, eq 1, immediately with

$$\Phi_{\mathrm{lim}} = \phi[1 - k_4/(k_4 + k_3 N_s)] \qquad (6)$$

and

$$C_L = k_4/(k_4 + k_3 N_s)K \qquad (7)$$

Moreover

$$K = (1/C_L)(1 - \Phi_{\mathrm{lim}}/\phi) \qquad (8)$$

Note that for this treatment it is not necessary to invoke the above-mentioned surface barrier to electron transport. The quantities C_L and Φ_{lim} are experimentally determined (Table I). However, since ϕ has not been measured, only a range of K values can be calculated for each material (note that $\Phi_{\mathrm{lim}} \leq \phi \leq 1$). These values of K, also listed in Table I, suggest that adsorption of Ag^+ on ZnO may be considerably weaker than on TiO_2.

The measured quantum yields for the reduction of Ag^+ at the surface of TiO_2 and ZnO single crystals and the determination of Ag^+ concentration dependencies have provided information regarding the material properties of the two oxides. It may be anticipated that in the limiting region of high silver concentration the quantum yield should be determined by the substrate properties, *e.g.*, eq 6. One such property is the concentration of electron trap levels (impurity sites, lattice vacancies, etc.) in the material. The presence of these traps in the bulk material could affect the value of ϕ, while location on the surface could contribute to deactivation *via* reaction 4 (*i.e.*, increases the value of k_4). The near-unity value of Φ_{lim} for ZnO implies that there is little or no effect on the surface reduction of Ag^+ from either bulk or surface electron traps. However, the low limiting yields for TiO_2 could be the result of deactivation of photoelectrons by stable electron trap levels. It is not possible to specify whether these traps are in the bulk or at the surface, but their influence on the photoreactivity is consistent with literature reports in which large differences in electron trap distribution were observed after various surface treatments.[8] It may be concluded then that the differences in reactivity for the TiO_2 crystals that we examined resulted from differences in trap distribution induced during surface preparation.

Acknowledgment. This work was supported by the U. S. Air Force under Contract F04701-71-C-0172.

(8) A. K. Ghosh, F. G. Wakim, and R. R. Addiss, Jr., *Phys. Rev.*, **184**, 979 (1969).

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Solution Photochemistry. VIII. Novel Rearrangements of Some Substituted Butadiene–Benzoquinone Diels–Alder Adducts[1,2]

Sir:

In a previous paper[3] we showed that n → π* excitation of the butadiene-*p*-benzoquinone Diels–Alder adduct **1** leads to formation of the novel tricyclic ene-diones **2** and **3** (Scheme I). As an extension of this work, we would like to report in the present communication that (a) photolysis of the 2,3-dimethylbutadiene–benzoquinone adduct **4** (*cf.* Scheme I) leads to products analogous to **2** and **3** (*i.e.*, **5** and **6**) and in addition gives rise to the unusual tricyclic enone alcohol **7**, (b) the ratio in which these three products are formed is remarkably solvent dependent, (c) the structure of **7** provides corroborative evidence for the mechanism postulated previously,[3] (d) deuterium labeling studies are also in accord with this mechanism, (e) the photoproducts undergo novel thermal and photochemical interconversions, and (f) irradiation of the *trans,trans*-2,4-hexadiene-*p*-benzoquinone Diels–Alder adduct **8** does *not* give products analogous to **5**, **6**, or **7**, but yields instead the unique photoproduct **9**.

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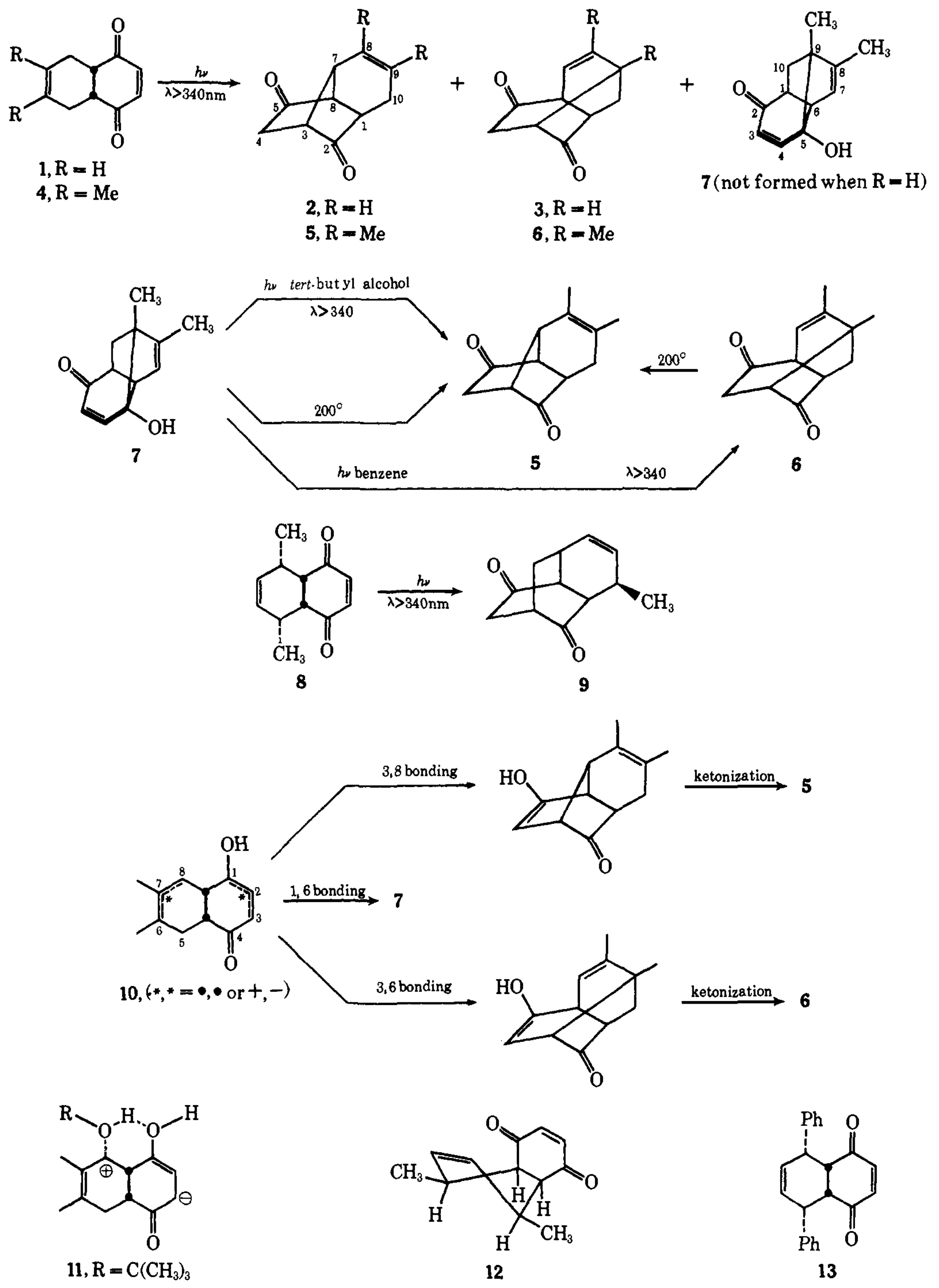
(1) For Part VII, see J. R. Scheffer, R. A. Wostradowski, and K. C. Dooley, *Chem. Commun.*, 1217 (1971).

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the National Research Council and the University of British Columbia is also gratefully acknowledged.

(3) J. R. Scheffer, J. Trotter, R. A. Wostradowski, C. S. Gibbons, and K. Bhandari, *J. Amer. Chem. Soc.*, **93**, 3813 (1971).

Scheme I



The Diels–Alder adducts 4 and 8 were prepared by literature procedures[4] and irradiated in their n → π* bands (370 nm) using light of λ > 340 nm (Corning 7380 filter). In the case of adduct 4 the ensuing photochemical reaction was markedly solvent dependent; in *tert*-butyl alcohol the major product was ene–dione 5, mp 84–85°, isolated in 80% yield. Photoproducts 6 and 7 were formed in only trace amounts in this photolysis as indicated by glpc. In contrast, photolysis of 4 in benzene followed by column chromatography on silica gel afforded ene–dione 6, mp 77–78°, and keto alcohol 7, mp 92–93°, in isolated yields of 35 and 22%, respectively; photoisomer 5 was present in amounts too small to be recovered.

The structures of photoproducts 5 and 6 followed from the similarity of their spectra[5,6] to the analogous nonmethylated photoproducts 2 and 3. Photoisomer 7 exhibited the following spectral characteristics: ir (CCl_4) 2.8 (weak, OH) and 5.90 μ (C=O); nmr (CCl_4) τ 8.90 (s, 3, C_9CH_3), 8.50 (d, 2, J = 5 Hz), 8.20 (d, 3, J = 2 Hz, C_8CH_3), 7.76 (m, 2, OH and methine, OH

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[4] Adduct 4: A. Mandelbaum and M. Cais, *J. Org. Chem.*, 27, 2243 (1962); adduct 8: H. v. Euler, H. Hasselquist, and A. Glaser, *Ark. Kemi*, 3, 49 (1951). The stereochemistry of adduct 8 follows from its mode of synthesis and its nmr spectrum.

[5] All new compounds described gave satisfactory elemental analyses and mass spectral parent peaks.

[6] Isomer 5 showed: ir ($CHCl_3$) 5.72 μ (C=O); nmr ($CDCl_3$) τ 8.29 (m, 3, CH_3), 8.41 (m, 3, CH_3), and no vinyl hydrogens. Photoproduct 6 showed: ir ($CHCl_3$) 5.69 and 5.81 μ (C=O); nmr ($CDCl_3$) τ 8.63 (s, 3, C_9CH_3), 8.13 (d, 3, J = 2 Hz, C_8CH_3), and 4.48 (m, 1, vinyl H); n → π* uv max (MeOH) 292 (ε 220), sh 310 nm (ε 200).

disappears upon addition of D_2O), 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).

In addition, the structures of these photoproducts were indicated by a series of intriguing thermal and photochemical interconversions. Thus, sealed tube thermolysis of **6** at 200° gave a high yield of **5**. Analogous behavior was previously observed[3] for compounds **2** and **3**. Furthermore, sealed tube thermolysis of **7** at 200° for 5 hr gave a 70% isolated yield of isomer **5**, and photolysis of **7** in benzene ($\lambda > 340$ nm) afforded an 80% yield of **6**. That **6** is nevertheless a primary photoproduct of Diels–Alder adduct **4** in benzene was demonstrated by a time-dependence study which showed the build-up of both **6** and **7** at comparable rates without an induction period for the formation of **6**. Remarkably, photolysis of **7** in *tert*-butyl alcohol gave a high yield of photoisomer **5**. These reactions are summarized in Scheme I.

In contrast to the results of photolysis of Diels–Alder adduct **4**, irradiation of either benzene or *tert*-butyl alcohol solutions of Diels–Alder adduct **8** afforded, after column chromatography on neutral alumina, a 30% yield of the tricyclic product **9**, mp 80–80.5°, which possesses the basic patchouli alcohol[7] and seychellene[8] ring system. The structure of this material followed from its spectral characteristics: ir (CCl_4) 5.79 μ (C=O); nmr ($CDCl_3$) τ 4.1–4.6 (m, 2, vinyl H), 7.2–7.7 (m, 7), 7.7–8.4 (m, 2), and 8.7 (d, 3, J = 7 Hz, CH_3); $n \rightarrow \pi^*$ uv max (MeOH) 291 nm (ϵ 56); prolonged base-catalyzed deuterium exchange afforded replacement of only two hydrogens as shown by nmr.

An attractive possibility for the photochemical conversion of Diels–Alder adduct **4** into products **5**, **6**, and **7** involves initial formation of the resonance-stabilized intermediate **10** *via* a virtually unprecedented[9] carbon–oxygen β-hydrogen transfer. Bonding of species **10** as indicated in Scheme I would then lead directly to photoproduct **7** and to the enol forms of compounds **5** and **6**. The intermediacy of these enol forms is supported by the finding that photolysis of Diels–Alder adduct **4** in *tert*-butyl alcohol-*O-d* led to photoisomer **5** with one deuterium atom substituted exclusively in the exo-4 position.[10] The same product was obtained by mild base-catalyzed deuterium exchange of proteo ketone **5**.[11]

The source of the remarkable product dependence on solvent in the photolysis of **4** is less clear-cut. Explanations invoking the intermediacy of photoproducts **6** and/or **7** in the conversion of **4** to **5** in *tert*-butyl alcohol were ruled out by appropriate control experiments. The possibility exists that in *tert*-butyl alcohol, a zwitterionic intermediate such as **11**, stabilized by hydrogen bonding and solvation of the positive charge at C_8, may be responsible for the preferential formation of photoproduct **5** *via* 3,8 bonding. The reaction in benzene on the other hand could then be interpreted as occurring (through either a zwitterionic or a diradical intermediate) by preferential bond formation at the inductively stabilized C_6 position to give photoisomers **6** and **7**. Similar arguments can be brought to bear on the photochemical conversion of **7** to **5** in *tert*-butyl alcohol which in all probability also occurs *via* species **11**. Further studies on this point are planned.[12]

As pointed out previously,[3] the thermal conversions of **3** to **2**, and in this study, of **6** to **5**, are likely to be nonconcerted.[13,14] On the other hand, the photochemical reaction of **7** giving **6** in benzene and the thermal **7** to **5** conversion are formal examples of allowed [1,3] and [3,3] suprafacial sigmatropic rearrangements, respectively.[13] Whether these concerted pathways are in fact followed is uncertain in view of the probable low activation energies required for the corresponding nonconcerted processes.[15]

Finally, the difference in photochemical reactivity between Diels–Alder adducts **4** and **8** should be discussed. Possibly this difference (β-hydrogen abstraction *vs.* γ-hydrogen abstraction) is due to the inaccessibility of the β-hydrogens for abstraction in the preferred conformation of Diels–Alder adduct **8** (*cf.* structure **12**). An alternative conformation which brings the β-hydrogen atoms and the carbonyl groups into proximity introduces a severe methyl–methyl bowsprit–flagpole-like interaction. In support of these ideas is the finding that the Diels–Alder adduct **13**[16] is completely inert under the conditions used for the photolysis of adducts **4** and **8**.

Further product, mechanistic, and photophysical studies with a variety of quinone–diene adducts are in progress.

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[7] G. Büchi, W. D. MacLeod, Jr., and J. Padilla O., *J. Amer. Chem. Soc.*, **86**, 4438 (1964).

[8] G. Wolff and G. Ourisson, *Tetrahedron*, **25**, 4903 (1969).

[9] See A. Padwa and W. Eisenhardt (*J. Amer. Chem. Soc.*, **93**, 1400 (1971)) for a possible example.

[10] The extent, position, and stereochemistry of the deuterium substitution were proved by nmr and mass spectrometry; details will be published in the full paper.

[11] For other examples of preferential exo exchange in bicyclo[2.2.1]-heptan-2-ones, see T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 1448 (1970), and references cited therein.

[12] Explanations for these solvent effects based on n,π^* (benzene) – π,π^* (*tert*-butyl alcohol) reactivity differences cannot be ruled out at the present time although it is difficult to see how these differences can be interpreted in terms of mechanism. Furthermore, if Diels–Alder adducts **1** and **4** resemble *p*-benzoquinone in the relative positioning of their n,π^* and π,π^* excited states (n,π^* much lower in both the singlet and the triplet, *cf.* H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967), and references cited therein), it is unlikely that a change to polar solvents will cause a level reversal. Emission spectroscopic studies and sensitization-quenching experiments are in progress to resolve these points.

[13] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[14] J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

[15] A reaction analogous to the photochemical **7** → **6** conversion has recently been reported and shown to be nonconcerted, *i.e.*, nonstereospecific: R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970).

[16] Y. Lepage, *Bull. Soc. Chim. Fr.*, 2019 (1963).

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Trapping by Mercaptans of the Biradical Intermediates in Type II Photoelimination

Sir:

Although the massed evidence for the intermediacy of 1,4 biradicals in triplet-state type II photoelimination processes is compelling,[1] no successful attempt to trap such a biradical has yet been reported,[2] despite

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[1] P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

[2] A nitroso compound traps a radical species produced by irradia-