

Figure 2. ^1H NMR spectrum (183 K, 250 Mhz) obtained by irradiation (192 K) of a CD_2Cl_2 solution of trione **3**. The major resonances are due to **1**. Small peaks near δ 6.3, 3.9, and 3.7 are due to unreacted **3** (\sim 5–10%). The small peaks near δ 3.8 and 3.6 are associated with an impurity whose formation can be suppressed by degassing the sample before irradiation.

The asymmetric stretching vibration of **2** is predicted^{6b} to produce an absorption band near 1745 cm^{-1} , and the "carbonyl" bands at 1846 and 1795 cm^{-1} observed in the photolysate at first aroused our hopes that both **1** and **2** had indeed been generated. However, only **1** is formed, and neither band is in fact associated with **2**, since irradiation of $3-d_6$ under the same matrix-isolated conditions gave rise to an unstable species with a strong FT-IR absorption at 1808 cm^{-1} and a weak one at 1861 cm^{-1} . Since **2** contains no hydrogen, the observed deuterium perturbation is inconsistent with **2** as the carrier of the spectrum. The splitting observed in the undeuterated transient is reasonably ascribed to a Fermi resonance⁹ in the spectrum of norbornadienone **1**. Similar smooth bisdecarbonylations are observed under matrix-isolated conditions in the photolyses of the 7,8-dihydro and 9-deoxy analogues of **3**, which lead, respectively, to norbornenone and norbornadiene. Again, only CO rather than C_2O_2 is formed.

Norbornadienone **1** can also be prepared in a polyethylene matrix, in which it is stable up to about 200 K. Photolysis of a CD_2Cl_2 solution of **3** at 192 K causes efficient conversion to **1**, whose ^1H NMR spectrum (Figure 2) shows only two absorptions: δ 6.72 (pseudo-t, 4 H, $J = 2\text{ Hz}$) and 4.08 (quintet, 2 H, $J = 2\text{ Hz}$). The ^{13}C spectrum shows three absorptions: δ 194.9 (s), 132.3 (d), and 55.4 (d). Norbornadienone decomposes to benzene and CO at higher temperature and has a half-life at 213 K of 25 min. From a study of the kinetics of decomposition (NMR), the activation parameters ΔG^\ddagger (300K) and E_a , 15 and 16 ± 2.5 kcal/mol, respectively, and $\log A = 13.0 \pm 1.8$ (A in s^{-1}), were obtained.¹⁰ The ΔG^\ddagger value seems to be the lowest yet measured for a cycloreversion. The experimental ΔG^\ddagger value now may be compared with theoretical predictions^{5a} of 21.5 and 25.7 kcal/mol derived, respectively, from MINDO/3 and MNDO calculations.

Free norbornadienone behaves similarly to the transient species implicated^{5c} in the photochemistry of its $\text{Fe}(\text{CO})_3$ complex, which forms 9,10-diphenylanthracene when generated in the presence of diphenylisobenzofuran. The same product now has been observed from the furan and **1** in the metal-free system.¹¹ Further studies of the chemistry of **1** are in progress.

The empirical correlation of Figure 1, slightly modified to incorporate the observed value for **1**, would seem to offer reliable predictions in the range covered by experiment to date. We hope

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(10) The E_a and $\log A$ values were obtained over the temperature range 200–213 K.

(11) Photolysis of a solution of **3** in Et_2O at -90°C was followed by treatment with cold ethereal diphenylisobenzofuran. Workup^{5c} gave 9,10-diphenylanthracene, recognized by its fluorescence and identified by 250-Mhz ^1H NMR spectroscopic comparison with an authentic sample.

to extend the correlation by further experiments to permit more firmly based predictions for substances of still lower stability, including C_2O_2 .

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Registry No. **1**, 22773-11-1; **3**, 96866-88-5; diethyl (*endo,endo*)-7,7-diethoxy-2,3-norborn-5-endicarboxylate, 96866-89-6; *endo*-9,9-diethoxytricyclo[4.2.1.0^{2,5}]non-7-en-3,4-dione, 96866-90-9; diethyl maleate, 141-05-9; 5,5-diethoxycyclopentadiene, 2931-32-0; 9,10-diphenylanthracene, 1499-10-1; diphenylisobenzofuran, 5471-63-6.

Supplementary Material Available: Data on ΔH_f^\ddagger and ΔG_f^\ddagger for 17 cycloreversions (7 pages). Ordering information is given on any current masthead page.

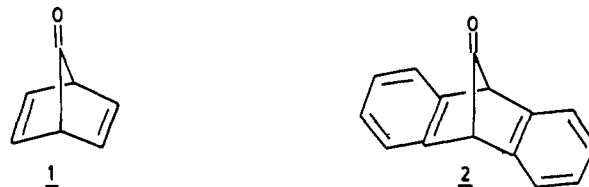
Photochemical Generation and Direct Observation of 7-Norbornadienone

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The novel ketone 7-norbornadienone (bicyclo[2.2.1]hepta-2,5-dien-7-one, **1**) holds a key position in the lore of cheletropic



reactions,¹ yet this elusive molecule has not been previously observed.² Landesberg and Sieczkowski³ have reported suggestive evidence for the intermediacy of **1** in photolysis or oxidation of its iron tricarbonyl complex, although the molecule eluded spectroscopic detection. Warrenner and co-workers⁴ recently reported observation of a highly substituted derivative of **1** which decarbonylated above -30°C . In contrast, dibenzo derivatives of **1**, such as **2**, are modestly stable at room temperature.^{5,6} On the basis of semiempirical calculations, Dewar and Chantranupong⁷ have predicted that **1** should have an activation barrier of 21.4 kcal/mol (MINDO/3; 25.6 by MNDO; at 300 K) toward cheletropic loss of CO. We now wish to report the generation of **1** from two independent precursors, its spectroscopic observation, and details of its reactivity.⁸

Our approach to **1** was based on known reactions of norbornadienes⁹ and quadricyclanes¹⁰ with triazolinediones. Azo

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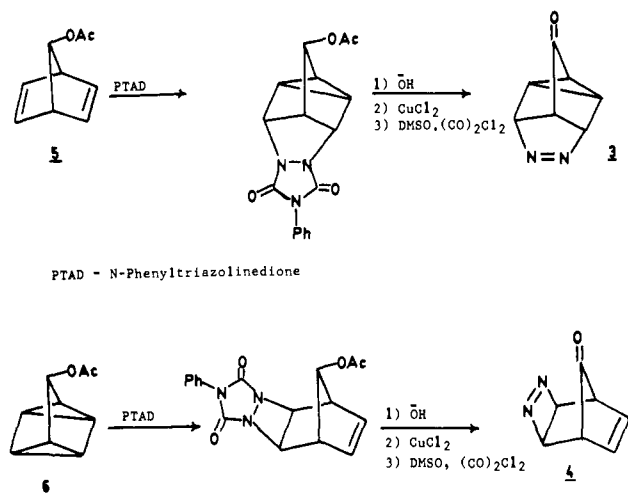
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Scheme I



compounds **3** and **4** were synthesized as shown in Scheme I, from known acetates **5** and **6**.¹¹ The crystalline azo compounds **3** and **4** were completely characterized spectroscopically.¹²

Irradiation ($\lambda > 340$ nm) of **3** in an argon matrix at 10 K gave benzene,¹³ CO,¹³ quadricyclanone,¹³ and a small amount of a new species with IR absorptions in the carbonyl region. Similar results were obtained with **4**, although qualitatively less benzene and CO and more quadricyclanone and unknown compound were formed. Although product bands overlapped the carbonyl absorptions of starting material, the unknown's absorptions remained after all other **3** and **4** absorptions were destroyed. Better spectra (vide infra) were obtained from photolyses of **3** and **4** in 3-methylpentane matrices, in which the new species was the major product observed. The photoproduct bands were shown to arise from a common thermally labile species. Irradiation ($\lambda > 340$ nm) at 77 K of a Nujol mull of **3** painted onto the cold-tip CsI window gave mainly the unknown's IR bands at 1861, 1790, 1314, 1198, 811, 714, and 570 cm^{-1} and only traces of benzene and quadricyclanone. Warming the mull to 220 K caused smooth decay of these absorptions and concurrent growth of benzene bands.

These results suggest that the new IR absorptions are due to 7-norbornadienone (**1**) and that this species is stable at temperatures where solution NMR is possible. In particular, two carbonyl absorptions at ca. 1860 and 1790 cm^{-1} are in general characteristic for 7-norbornenones^{12,14,15} and are similarly seen in the iron tricarbonyl derivative of **1**.³ Confirmation came from low-temperature ¹H NMR. Irradiation ($\lambda > 340$ nm) of **3** at 77 K in toluene-*d*₈, followed by ¹H NMR at 195 K, gave conversion mainly to a product with absorptions at δ 6.09 and 3.53 in the integrated ratio of 2:1 (Figure 1). Similar results were obtained from **4**, although photolysis was much slower, and complete conversion of starting material was more difficult. Warming to 230 K caused rapid, quantitative conversion of the photoproduct to benzene (by ¹H NMR).

The ¹H NMR spectrum confirms the common generation of **1** from **3** and **4**. Careful warming experiments gave activation parameters for decarbonylation of **1**. Temperatures were calibrated by internal capillary MeOH samples.¹⁶ Arrhenius

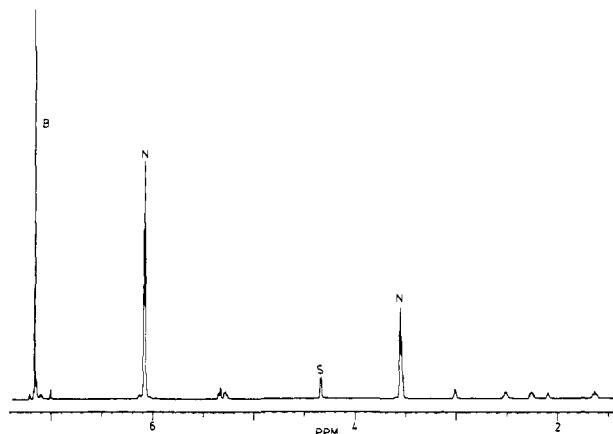
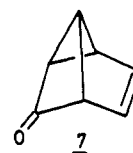


Figure 1. ¹H NMR (270 MHz, toluene-*d*₈) obtained at 195 K after irradiation of **3** at 77 K. Peaks labeled N are due to **1**, and benzene is labeled B. Multiplets at 5.34, 5.28, 3.0, 2.52, 2.25, and 1.6 ppm are tentatively assigned to tricyclic ketone **7**. The peak labeled S is due to residual starting material, and the peak at 2.10 is from solvent.

treatment of decomposition rates over the temperature range 198–218 K gives $E_a = 17 \pm 2$ kcal/mol and $\log A$ (s^{-1}) = 14 ± 2 . These numbers predict that **1** will have a half-life of only 0.03 s at 20 °C, consistent with previous foiled synthesis attempts.² While these values are somewhat lower than predicted by theory,⁷ they are in line with reasonable extrapolation from **2**,^{5,6} the previously reported substituted derivative,⁴ and tricyclo[3.2.1.0^{2,4}]oct-6-en-8-ones.¹⁷

Several other aspects of the photochemistry of **3** and **4** are of interest. The amount of benzene formation is strongly dependent on matrix material. In argon at 10 K, benzene is the major product from both **3** and **4**, whereas in 3-methylpentane under identical conditions, only a small amount of benzene is formed (by IR). Ketone **1** is stable at these wavelengths. Although the reasons for this dramatic medium effect are unknown, these results suggest caution in comparisons of argon matrix photochemistry with experiments in other media. As seen in Figure 1, another minor product is formed in the photolysis of **3**. The same product is formed from **4**, and it is formed in greater amounts in more polar solvents. The species has only limited stability at room temperature, rapidly giving polymer and uncharacterizable products. The NMR and IR spectra and the stability of the unknown species to visible irradiation are not consistent with a diazo compound.¹⁸ Comparison of the observed chemical shift values to those for known saturated analogues¹⁹ suggests that this species may be the unknown C₇H₆O isomer **7**. This ketone could



logically arise from rearrangement of intermediate biradicals in the azo decompositions.^{20,21} This possibility is being addressed, and investigation of other "aromatic plus stable fragment" compounds is in progress.²²

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Registry No. 1, 22773-11-1; 3, 96866-57-8; 4, 87380-97-0; 5, 13426-49-8; 6, 35825-94-6; 7-acetoxy-3,5-(4-phenyl-3,5-dioxotetrahydro-1,2,4-triazol-1,2-diyl)tricyclo[2.2.1.0^{2,6}]heptane, 96866-58-9; 7-acetoxy-5,6-(4-phenyl-3,5-dioxotetrahydro-1,2,4-triazol-1,2-diyl)bicyclo[2.2.1]hept-2-ene, 96866-59-0.

One-Electron Reduction of Anthraquinone by Hydroxide Ion in Aprotic Media

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In acetonitrile or dimethyl sulfoxide hydroxide ion reacts rapidly and reversibly with 9,10-anthraquinone and 2-ethylanthraquinone to form an adduct that subsequently reacts more slowly and irreversibly with a second quinone molecule to form near-stoichiometric amounts of the semiquinone anion radical. Several reports¹⁻⁷ have suggested that hydroxide ion is an electron donor toward quinones and other electron acceptors, but the extent and nature of the electron-transfer process have not been determined. The process also yields oxidants (presumably hydrogen peroxide),¹⁻⁷ and phenol has been isolated from systems that contain added benzene.^{3,4}

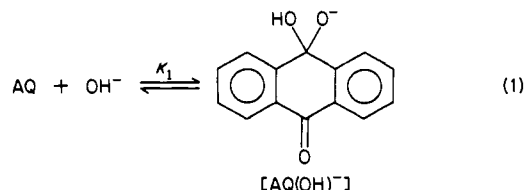
Characterization of the electron transfer from OH⁻ to quinones is significant because (1) the reaction produces radical products from nonradical reactants, (2) the effectiveness of alkaline wood pulping with anthraquinone (AQ) additives is believed to result from the production of AQ^{-•} and AQ²⁻, which function as soluble electron-transfer catalysts,⁸ and (3) there are several proposals⁹⁻¹² that quinones (Q) can accept a single electron to form Q^{-•}, which reacts with O₂ to form O₂^{-•}.

Figure 1A illustrates the spectra for AQ and for the product solution from the combination of 1.5 OH⁻ per AQ at -20 °C. The spectrum has a broad band at 268 nm but not the 323-nm band for AQ nor those for AQ^{-•} (543, 506, 408, and 388 nm). When it is warmed, the solution turns red with formation of AQ^{-•} (Figure 1A).

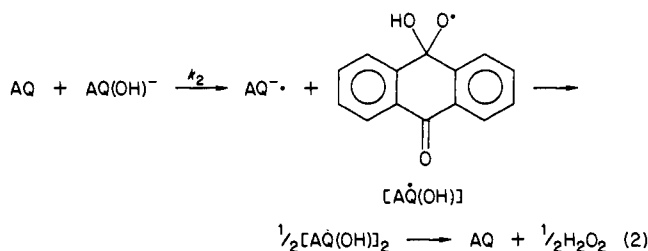
The addition of 1.3 M Bu₄N(OH) in MeOH (or 1 M aqueous NaOH) to 1-100 mM anthraquinone (AQ) or 2-ethylanthraquinone (2-EtAQ) in MeCN or Me₂SO results in the almost stoichiometric (80-98%) formation of AQ^{-•} or 2-EtAQ^{-•}.¹³ Figure 1B indicates the initial rate for the formation of AQ^{-•} from the combination of OH⁻ and AQ as a function of the mole ratio for OH⁻ relative to AQ.¹⁴

When 2 equiv of AQ (1 mM) is combined with 0.5 mM OH⁻ the product solution contains equal amounts of AQ^{-•} and AQ and no O₂, O₂^{-•}, or OH⁻. A voltammogram for the product solution exhibits an anodic peak at 2.1 V vs. SCE, which is characteristic of H₂O₂ and corresponds to the peak current for 0.2 mM H₂O₂. Addition of excess acid (HClO₄) to the product solution results in the oxidation of all of the AQ^{-•} to AQ (probably by H₂O₂).

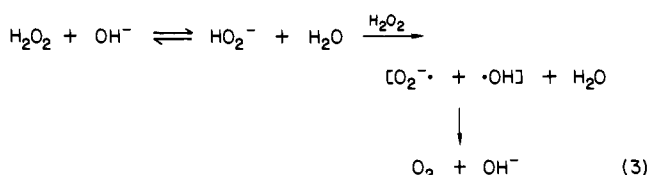
The low-temperature electrochemical¹³ and UV-visible spectral data (Figure 1A) provide compelling evidence that AQ reacts with OH⁻ to form an addition complex [AQ(OH)]⁻¹⁵



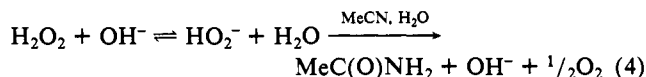
that AQ^{-•} is formed in a second slower electron-transfer step with another AQ.



Control experiments establish that the addition of OH⁻ to H₂O₂ in MeCN causes it to decompose by two different pathways. One forms water and dioxygen¹⁶



the other forms acetamide and dioxygen:^{17,18}



Because only trace amounts of acetamide are detected, the dominant pathway for hydrogen peroxide decomposition in the present

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(13) When OH⁻ is added to a solution of AQ in MeCN or Me₂SO the limiting current for reduction of quinone at a PtRDE decreases immediately. The decrease is proportional to the amount of OH⁻ added with a stoichiometry of 1:1 OH⁻/AQ. After 3-10 min the initial (OH⁻)-AQ adduct is converted to AQ^{-•} and AQ. At 0 °C in MeCN the addition of OH⁻ to AQ causes the reversible one-electron reduction couples for AQ (-0.58 and -1.12 V vs. NHE) to be diminished and replaced by an irreversible reduction peak at -1.28 V. When the solution is warmed it yields AQ^{-•}.

(14) The rate of increase for the 543-nm absorption band of AQ^{-•} was measured after the rapid combination (~3 s) of AQ (1 mM) with increasing mole ratios of (Bu₄N)OH (1 M in MeOH) in MeCN at 25 ± 1 °C.

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