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A Temperature-, Multiplicity-, and Phase-Dependent Photorearrangement

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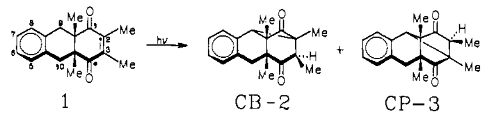
Abstract: The photochemistry of 2,3,4a,9a-tetramethyl-*cis*-4a,9a,9,10-tetrahydro-1,4-anthracenedione (**1**) has been found to be temperature-, multiplicity-, and phase-dependent. Direct irradiation at low temperatures in isotropic liquid phases gives predominantly photoproduct CP-**3**, whereas photolysis in solution at higher temperatures gives mainly CB-**2**. Sensitization/quenching studies show that **2** is triplet-derived and **3** is singlet-derived. From the linear plot of the natural logarithm of the **2**/**3** ratio vs. $1/T$, the value of $[E_a(\text{triplet}) - E_a(\text{singlet})]$ is calculated to be 4.5 kcal/mol. Similar behavior was found for 2,3,4a,6,7,8a-hexamethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthalenedione (**7**). Photolysis of crystals of enedione **1** gives only product **2**, regardless of the temperature employed. The X-ray crystal structure of **1** reveals the reasons for this specificity. An overall mechanistic scheme that explains both the solid state and solution results is presented and discussed.

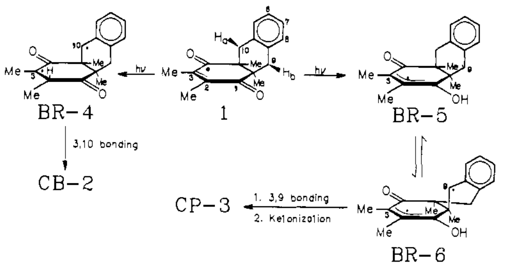
The situation whereby a molecule reacts to give two products that are isomeric with the starting material is not uncommon in organic photochemistry, and it has been observed in many instances that the photoproduct ratio depends on some experimental variable in the photolysis procedure such as temperature,[1] phase change,[2] or the presence of photosensitizers (multiplicity).[3] It is rare, however, that a reaction is found in which *all three* of these factors come into play simultaneously, but we have discovered exactly such a case. This paper reports a photorearrangement that can be diverted in one direction by direct irradiation at low temperatures in isotropic liquid phases and can be forced in a different direction by the use of higher temperatures and/or triplet energy photosensitizers (liquid phase) or by direct irradiation in the crystalline phase.

The compound studied was 2,3,4a,9a-tetramethyl-*cis*-4a,9a,9,10-tetrahydro-1,4-anthracenedione (**1**, Scheme I), mp 84–85 °C, prepared by the reaction between duroquinone and *o*-quinodimethane.[4] Irradiation of this material in acetonitrile in a conventional immersion well apparatus using a 450-W Hanovia lamp fitted with a uranium glass filter ($\lambda > 330$ nm) afforded mixtures of the cyclobutyl (CB) ketone **2** (96%) and the cyclopentyl (CP) ketone **3** (4%). Under the same conditions in methanol, the CB:CP ratio was 76:24. When the methanol irradiation was conducted in the presence of 1 molar equiv of benzophenone as a triplet energy sensitizer, cyclobutanone **2** became virtually the sole detectable product. This was corroborated by quenching studies using 2,5-dimethyl-2,4-hexadiene. The Stern–Volmer plot (Figure 1) shows that CB formation is quenched by the diene ($k_q\tau = 9.85$ M^{-1}) but that formation of the CP photoproduct is unaffected.

Scheme I



Scheme II



As outlined in Scheme I, the CB photoproduct is formed via six-membered transition-state transfer of a benzylic hydrogen from C(10) to C(2) [or C(9) to C(3)] followed by C(3)···C(10) [or C(2)···C(9)] bonding; CP is produced by five-membered transition state abstraction by oxygen of a benzylic hydrogen atom [H(9) to O(1) or H(10) to O(4)] followed by C(3)···C(9) or C(2)···C(10) bonding and ketonization of the resulting enol. Both processes have precedent in previous work from our laboratory.[5]

In conducting the photolysis under different experimental conditions, we noted a puzzling variation in photoproduct ratio that could not be reconciled until we discovered that the process is temperature-dependent. Thus, as the temperature is lowered, the amount of product CP increases at the expense of CB. The temperature dependence was studied quantitatively over the range −40 to +20 °C by using a pulsed nitrogen laser ($\lambda = 337$ nm) as the light source. When the data were plotted as ln (CB/CP) vs. $1/T$ (Figure 2), a good straight line was obtained. This result is consistent with two competing first-order processes that have different activation energies, the slope of the straight line giving ΔE_a. In the case of compound **1**, $[E_a(\text{CB}) - E_a(\text{CP})] = 4.5$ kcal/mol.

Nitrogen laser irradiation of *crystals* of enedione **1** gave only CB photoproduct, regardless of the temperature used. In order to understand the reasons for this behavior, we determined the crystal and molecular structure of **1** by direct method X-ray diffraction studies. Crystals of **1** are monoclinic, space group *Cc*, $a = 6.877$ (2) Å, $b = 22.377$ (3) Å, $c = 9.972$ (3) Å, $\beta = 101.68$ (1)°, $Z = 4$. The structure was refined to a final R of 0.037 for 821 reflections with $I > 3\sigma(I)$. Full details will be published separately.

Figure 3 is a stereo diagram of enedione **1** in its solid-state conformation. Both the enedione ring and the central ring are in approximate half-chair conformations. It is apparent from this

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(1) The photochemistry of dienes and trienes has been found to be generally temperature-dependent. For reviews, see: Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* **1973**, *33*, 197. Dauben, W. G.; McInnis, E. L.; Michno, D. M. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 15.

(2) For a review on the differences between unimolecular photorearrangements in solution and the crystalline state, see: Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283. See, also: Appel, W. K.; Jiang, Z. Q.; Scheffer, J. R.; Walsh, L. *J. Am. Chem. Soc.* **1983**, *105*, 5354.

(3) The photochemistry of β,γ-unsaturated ketones is generally multiplicity-dependent. For reviews, see: (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Fortschr. Chem. Forsch* **1975**, *54*, 73. (c) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (d) Schaffner, K. *Tetrahedron* **1976**, *32*, 641. (e) Schuster, D. I. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 232–279. The di-π-methane rearrangement is also multiplicity-dependent. For a review of this reaction, see: Zimmerman, H. E. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 16.

(4) Askari, S.; Lee, S.; Perkins, R. R.; Scheffer, J. R. *Can. J. Chem.* **1985**, *63*, 3526.

(5) (a) Scheffer, J. R.; Bhandari, K. S.; Gayler, R. E.; Wostradowski, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 2178. (b) Scheffer, J. R.; Jennings, B. M.; Louwerens, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 7040. (c) Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163.

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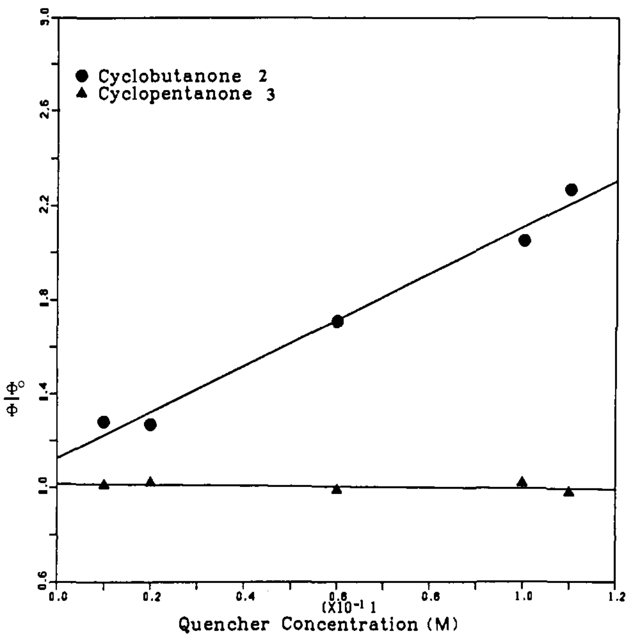


Figure 1. Stern–Volmer quenching plot for enedione **1**.

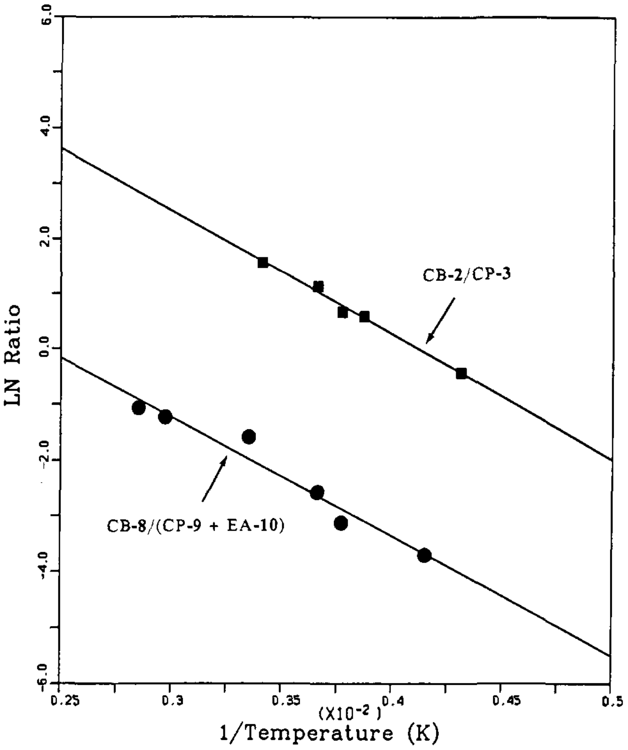


Figure 2. Temperature-dependence of photoproduct ratios.

conformation that CB and CP formation involve abstraction of different benzylic hydrogens. As outlined in Scheme II, abstraction of H_a by C(2) leads to CB, and transfer of H_b to O(1) gives CP. Both hydrogen-transfer processes are feasible geometrically. The $H_a \cdots C(2)$ distance is 2.75 Å with $\tau_c = 50.7°$ and $\Delta_c = 74°$.[6] The $H_b \cdots O(1)$ distance is 2.43 Å, $\tau_O = 2.7°$ and $\Delta_O = 84.9°$.[6] These values lie well within the limits established for such processes.[5c] Why then is only CB photoproduct formed in the solid state? The answer is that the second step of the rearrangement, biradical closure, is permitted in the solid state for CB but not for CP. Closure to give CB occurs from a biradical (**4**, Scheme II) that has the same conformation as the reactant **1**. The C(3)$\cdots$C(10) distance in **1** is 3.13 Å. In contrast, the initial biradical **5** leading to CP is incapable of C(3)$\cdots$C(9) bonding. The C(3)$\cdots$C(9) distance (for **1**) is 4.36 Å. Thus formation of CP requires a half-chair to half-chair conformational isomerization of biradical **5** to biradical **6**. This motion is too great to be accommodated by the crystal lattice, and so CP photoproduct is not observed in the solid state. No such restrictions exist in solution, however, and CP *is* formed in this medium. The C(3)$\cdots$C(9) distance in **6** may be approximated by the C(2)$\cdots$C(10) distance in **1**, which is 3.31 Å.

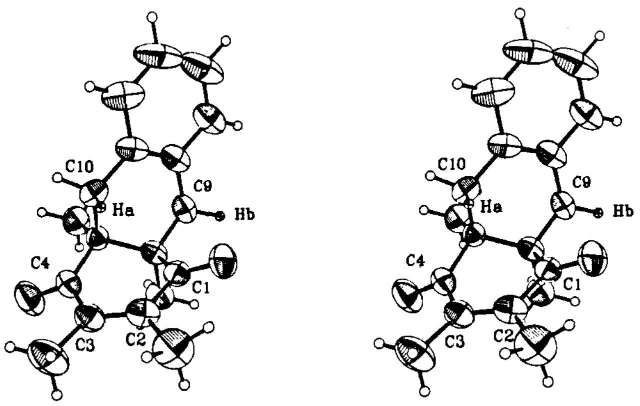
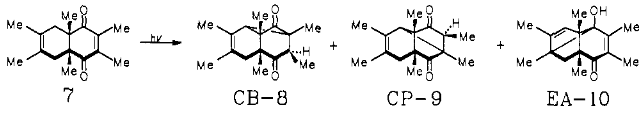


Figure 3. Stereodiagram showing solid-state conformation of enedione **1**.

Scheme III



A possible sequence of steps followed in the photorearrangement of **1** to CB and CP is shown below. The intermediacy of enol **3** (step 4) was verified by trapping in MeOD. It seems likely[7] that

$$\mathbf{1}\ (S_0) \rightarrow \mathbf{1}\ (S_1) \tag{1}$$

$$\mathbf{1}\ (S_1) \xrightarrow{k_2} \text{BR-}\mathbf{5} \xrightarrow{k_{-2}} \mathbf{1}\ (S_0) \tag{2}$$

$$\text{BR-}\mathbf{5} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{BR-}\mathbf{6} \tag{3}$$

$$\text{BR-}\mathbf{6} \xrightarrow[k_4]{} \text{enol } \mathbf{3} \rightarrow \text{CP-}\mathbf{3} \tag{4}$$

$$\mathbf{1}\ (S_1) \xrightarrow[k_5]{} \mathbf{1}\ (T_1) \tag{5}$$

$$\mathbf{1}\ (T_1) \xrightarrow[k_6]{} \text{BR-}\mathbf{4} \tag{6}$$

$$\text{BR-}\mathbf{4} \xrightarrow[k_7]{} \text{CB-}\mathbf{2} \tag{7}$$

$$\mathbf{1}\ (T_1) \xrightarrow[k_8]{} \mathbf{1}\ (S_0) \tag{8}$$

the hydrogen abstraction processes (steps 2 and 6) are important contributors to ΔE_a, with step 2 having the lower activation energy, owing in part to the fact that S_1 has a higher excitation energy than T_1[8] as well as to the greater resonance stabilization of bi-

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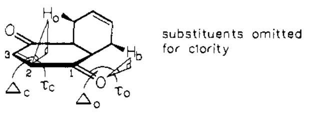
[6] As illustrated below, τ_c is the angle between the $C(2) \cdots H_a$ vector and its projection on the plane of the C(2)–C(3) double bond; Δ_c is the C(3)–C(2)$\cdots H_a$ angle. τ_O is the angle between the O(1)$\cdots H_b$ vector and its projection on the plane of the carbonyl group; Δ_O is the C(1)–O(1)$\cdots H_b$ angle.



[7] Making the reasonable assumptions (for purposes of linearity of the Arrhenius plot) that $k_3 \ll k_{-2}$ and $k_6 \ll k_8$, the proposed mechanism predicts that ΔE_a is equal to the sum of the activation energies for reactions 5, 6, and −2 minus the sum of the activation energies for processes 2, 3, 4, and 8. Of these, we consider the activation energies associated with steps 2, 3, and 6 as likely to be most important.

[8] The importance of excited state energetics in determining the rate of hydrogen abstraction reactions has been discussed by Turro (Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 365–366).

radical **5** compared to biradical **4**. The proposed mechanism suggests that ΔE_a would be even greater than 4.5 kcal/mol were it not for the requirement that biradical **5** isomerize to biradical **6** prior to closure. This conformational isomerization undoubtedly has a significant activation energy.[9] Finally we note that, in the solid state, the process with the greater overall activation energy dominates completely, even at low temperatures (−40 °C). As mentioned above, this is due to the restriction of step 3 by the rigid crystalline medium and requires that biradical **5** revert to starting material in the solid state. Reversion to S_0 is predicted on theoretical grounds to be particularly important for hydrogen abstraction reactions occurring through the singlet manifold.[10]

In many respects, the solution phase[5a,b] and solid-state[5c] photochemistry of 2,3,4a,6,7,8a-hexamethyl-*cis*-4a,5,8,8a-tetrahydro-1,4-naphthalenedione (**7**, Scheme III) parallels that of enedione **1**. Both give triplet-derived CB type photoproducts (**2** and **8**) as well as singlet-derived CP products (**3** and **9**). Photoproduct **9**, however, is a very minor component of the room temperature photolysis mixture, its place being taken by the enone alcohol (EA) **10** (also singlet-derived).[5b] The formation of EA photoproduct in the case of **1** requires interruption of aromaticity and is therefore not observed. We also note that formation of **10** can occur without half-chair to half-chair conformational isomerization and can thus take place in the solid state. Indeed, irradiation of crystals of **7** leads to mixtures of photoproducts **8** and **10**.[5c]

After finding that the solution phase photochemistry of **1** is temperature-dependent, we decided to investigate the temperature-dependence of the photorearrangement of enedione **7**. Behavior very similar to that of **1** was found. The lower portion of Figure 2 shows a plot of ln [**8**/(**9** + **10**)] [i.e., ln (triplet photoproduct/sum of singlet photoproducts)] vs. $1/T$ between −32 °C and +78 °C. The excellent straight line obtained has a slope nearly the same as that found for enedione **1**, and the [E_a(triplet) − E_a(singlet)] difference so calculated is 4.2 kcal/mol compared to 4.5 kcal/mol for **1**.

Why do S_1 and T_1 (likely n,π^* and π,π^* in nature, respectively[5b]) react differently? One contributing factor may be the preference for triplet excited states to give biradical intermediates that have a greater separation between the radical centers than the biradical intermediates formed from singlet excited states.[11] As Michl has shown,[10] this stems from the zwitterionic character of singlet biradicals in which radical separation has to overcome coulombic attractive forces. Comparing biradicals **4** and **5** (Scheme II), it can be seen that the radical centers in the latter (which is singlet-derived) can approach each other more closely (two bond separation) than they can in the triplet-derived biradical **4** (minimum three bond separation). These correlations are consistent with what is known concerning the photochemical hydrogen atom abstraction reactions of α,β-unsaturated ketones, namely that π,π^* excited states favor abstraction by the β-carbon atom and that n,π^* excited states lead to hydrogen atom abstraction by oxygen.[12] The predilection of ketone n,π^* excited states to engage in hydrogen atom abstraction through the use of the oxygen n-orbital is well established.[13]

Experimental Section

General Methods. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. Infrared (IR) spectra were determined on a Perkin-Elmer 710B instrument by using KBr discs and are reported as ν_{max} in cm^{-1}. Proton nuclear magnetic resonance (NMR) spectra were recorded either on a Bruker WH-400 or Varian XL 300 instrument by using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Signal positions are given in δ, and the multiplicities, integrated areas, coupling constants, and assignments are indicated in brackets. Mass spectra (MS) were recorded with a Kratos MS-50 instrument operating at 70 eV. Gas chromatography–mass spectrometry (GCMS) was carried out on Kratos MS-80RFA and Carlo Erba 4160 instruments by the departmental mass spectral services; the relative intensity of each ion is given in parenthesis. Analytical gas chromatography (GC) was carried out on a Hewlett-Packard Model 5890 instrument by using a 15-m DB-1 capillary column with He as the carrier gas. Elemental analyses were carried out by the departmental microanalyst, P. Borda. Spectral grade solvents were used directly as obtained; for quantum yield purposes, however, solvents were purified by well-established procedures.[14] Photolyses were carried out either with a Molectron UV-22 pulsed nitrogen laser (λ = 337 nm, 330 mW average power) or with a 450-W Hanovia medium pressure mercury lamp. In the latter case, the desired wavelength was achieved by using either a Pyrex (λ > 290 nm) or uranium glass (λ > 330 nm) filter sleeve. The samples were degassed by bubbling nitrogen through the solution for 1 h prior to photolysis. The quantum yields were determined in a merry-go-round apparatus[15] at 313 nm by using valerophenone actinometry. Nonadecane and tetradecane were used as internal standards. The adduct **7** was prepared by the Diels–Alder reaction between 2,3-dimethylbutadiene and duroquinone.[5a,16]

Photolysis of Enedione 1 in Acetonitrile and Methanol. A solution of enedione **1** (0.40 g, 1.49 mmol) in 250 mL of acetonitrile was photolyzed for 2 h through a Pyrex filter by using a 450-W Hanovia medium pressure mercury lamp. A GC trace of the reaction mixture showed that only two volatile products were present in 96% and 4% yields. A similar irradiation using methanol as the solvent afforded the same two products in 76% and 24% yields according to GC. The solvent was removed in vacuo, and the resulting mixture was purified by flash column chromatography with use of petroleum ether(30–60 °C):EtOAc (9:1, v/v) as the eluting solvent. The major product corresponding to rf 0.61 was isolated and recrystallized from low boiling petroleum ether to yield large, colorless prisms identified as cyclobutanone **2**: mp 89.5–90 °C; IR (KBr) 1745 and 1700 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (m, 4 H, aromatics), 3.01 (s, 1 H, benzylic CH), 2.81 (AB q, 2 H, J = 16 Hz, benzylic CH_2), 2.23 (q, 1 H, J = 8 Hz, $-CHCH_3$), 1.33 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.05 (d, 3 H, J = 8 Hz, $-CHCH_3$); when the quartet at δ 2.23 is irradiated, the doublet at δ 1.05 collapses to a singlet; mass spectrum *m/e* (rel intensity), 268 (M^+, 10), 240 (22), 225 (8), 197 (7), 157 (100), 156 (34), 142 (22), 83 (19), 55 (13); X-ray crystallography confirms the structure and stereochemistry assigned.[17] Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.46; H, 7.43.

The other photoproduct corresponding to rf 0.57 was also isolated by chromatography and recrystallized from low boiling petroleum ether to afford colorless needles identified as CP-3: mp 133–34 °C; IR (KBr) 1735 (C═O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (m, 4 H, aromatics), 2.92 (s, 1 H, benzylic CH), 2.80 (AB q, 2 H, J = 16 Hz, benzylic CH_2), 2.32 (q, 1 H, J = 8 Hz, $-CHCH_3$), 1.07 (s, 3 H, CH_3), 0.95 (d, 3 H, J = 8 Hz, $-CHCH_3$), 0.92 (s, 3 H, CH_3); mass spectrum *m/e* (rel intensity), 268 (M^+, 66), 240 (3), 225 (14), 197 (13), 157 (65), 156 (100), 142 (22), 141 (22), 115 (9). The methyl group stereochemistry in **3** is assigned on the basis of the well known preferential exo protonation of the enolate anions of bicyclo[2.2.1]heptan-2-ones and 2,5-diones.[18] Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.50; H, 7.44.

Sensitization Studies. A 0.1 M solution of the adduct **1** and a 1.0 M solution of benzophenone in methanol were prepared. By diluting these two solutions to the desired concentration, five solutions with different concentrations of the sensitizer and a constant 10^{-2} M concentration of adduct **1** were prepared. All were photolyzed by using the 450-W lamp fitted with a uranium glass filter. The results were as follows (sensitizer

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(9) Temperature-dependent NMR studies on enediones similar to **1** have established ΔG^* values of ca. 9 kcal/mol. Ariel, S.; Scheffer, J. R.; Trotter, J.; Wong, Y.-F. *Tetrahedron Lett.* **1983**, *24*, 4555. The proposed mechanism also very neatly explains why no cyclobutanone type photoproducts are obtained when enediones that lack bridge-head methyl groups are photolyzed in solution. The explanation is that the activation energy for singlet biradical isomerization is low for these compounds, which results in a large ΔE_a; thus only the lower activation energy cyclopentanone type photoproducts are observed.

(10) Michl, J. *Mol. Photochem.* **1972**, *4*, 243 and 257.

(11) Zimmerman and Factor (Zimmerman, H. E.; Factor, R. E. *Tetrahedron Suppl.* (*9*) **1981**, 125) have analyzed the reactions of diradicals as being either "large K" or "small K" in nature, K being the exchange integral (or approximately half the singlet–triplet splitting) for the reacting species. Small K processes are predicted to be preferred by singlet states, whereas large K reactions are preferred by triplets. According to this approach, reactions with separated diradical centers tend to be of the large K (triplet) variety.

(12) Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928.

(13) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978, Chapter 10.

(14) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1982.

(15) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; Chapter 14.

(16) Ansell, M. F.; Nash, B. W.; Wilson, D. A. *J. Chem. Soc.* **1963**, 3012.

(17) Ariel, S.; Askari, S. H.; Scheffer, J. R.; Trotter, J.; Wireko, F. *Acta Crystallogr.*, in press.

(18) Werstiuk, N. H.; Taillefer, R. *Can. J. Chem.* **1970**, *48*, 3966.

concentration, percent conversion, CB-**2**:CP-**3**): 0.0 M, 4%, 76:24; 0.2 M, 33%, 94:6: 0.4 M, 36%, 95:5; 0.8 M, 53%, 97:3; 1.0 M, 74%, 98:2.

Deuterium Labeling Study. A 0.1 M solution of adduct **1** in methanol-*O-d* was photolyzed with the 450-W lamp for 30 min with use of the uranium glass filter. The resulting photoproduct mixture was analyzed by GCMS, which showed that the peak corresponding to CP-**3** had incorporated deuterium to the extent of 55% after correction for the M + 1 peak.

Photolysis of Enedione 1 at Low Temperatures in Acetonitrile. Photolysis of the adduct **1** at a series of temperatures below room temperature was carried out by using the nitrogen laser. A solution of enedione **1** (0.1 M) in acetonitrile/water (50:1, v/v) was used in all cases. The desired temperature was achieved by selecting an appropriate solvent/dry ice mixture[19] or by ice and ice/salt mixtures. The adduct **1**, in a transparent dewar flask containing the coolant, was photolyzed for 5-10 min, and the products were analyzed by GC. The results obtained are shown in the upper portion of Figure 2 (text).

Crystal Photolysis of Enedione 1. When a single crystal or a polycrystalline sample of adduct **1** was photolyzed at room temperature for up to 20 min by using the nitrogen laser (5% conversion), the only product observed by GC was cyclobutanone **2**. When the irradiation was continued for longer periods of time (1-1.5 h, ca. 30% conversion), the crystal partially melted, and GC showed the formation of both photoproducts in a **2**:**3** = 30:1 ratio. Laser photolysis (50 min) of a single crystal maintained at -41 °C afforded only CB-**2**.

Variable Temperature Photolysis of Enedione 7 in Acetonitrile. As before, 0.1 M solutions of the adduct **7**, maintained at the desired temperature in an appropriate solvent/dry ice or ice/salt bath, were photolyzed for 5-10 min with the nitrogen laser. Temperatures above room temperature were achieved by immersing the photolysis sample in a refluxing organic solvent of appropriate boiling point. Since all three photoproducts had been isolated and characterized previously,[5] no attempt was made to isolate them in this study. The reaction mixtures were analyzed by GC with the results shown in the lower part of Figure 2 (text).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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[19] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; Chapter 16.

"Pagodane": The Efficient Synthesis of a Novel, Versatile Molecular Framework

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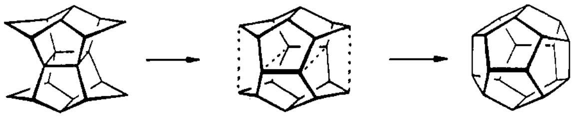
Abstract: The class of "pagodane" compounds constitutes a novel series of undecacyclic, strained, and chemically versatile carbon frameworks. In particular, the $C_{20}H_{20}$ [1.1.1.1]pagodane (**1**) and variously substituted derivatives thereof are principal precursors for structurally closely related dodecahedranes. The synthesis of **1** commences from isodrin **3** and consists of ca. 45 functional and structural modifications which are efficiently concentrated into 14 one-pot operations with an overall yield of 24%. Key steps in this reaction sequence are a benzo/benzo [6 + 6] photocycloaddition and a domino Diels-Alder reaction. Monochromatic irradiation (254 nm) of the dibenzo compound **18** led to a 7:3 equilibrium mixture of **18** with the *syn-o,o′*-dibenzene isomer **42**. The (unexpectedly high) thermal stability of the latter permitted the regiospecific addition of maleic anhydride to give rise to the pagodane framework **48** by two consecutive [4 + 2]-addition steps. From the diester **55** the parent hydrocarbon **1** as well as the 4,9-diketone **70** is prepared. Geometrical details of the face-to-face dibenzo compound **18**, the [6 + 6] photoisomer **42**, and the [1.1.1.1]pagodane derivative **55** are provided by X-ray structural determinations.

"Pagodane" is the trivial name we have coined for the highly complex, esthetically appealing $C_{20}H_{20}$ polyquinane **1**.[2] The obvious need for such a short-hand description can be readily understood in view of the von Baeyer/IUPAC and Chemical Abstracts nomenclature given in Chart I. Our interest in the [1.1.1.1]pagodane[3] system **1** arose primarily from its close relationship with the entirely pentagonal $C_{20}H_{20}$ structure, dodecahedrane **2**.[4]

Chart I



1 2

1: Undecacyclo[$9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.3^{16,20}$]eicosane.

2: Undecacyclo[$9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}$]eicosane.[5]

1: Perhydro-2,7,8b,3,4b,6-ethanediylidinedipentaleno[1,6-*ab*:1′,6′-*ef*]pentalene.

2: Perhydro-5,2,1,6,3,4-[2,3]butanyl[1,4]diylidenedipentaleno[2,1,6-*cde*:2′,1′,6′-*gha*]pentalene.

In both cases, the skeletons exhibit unusually high point group symmetries (i.e., D_{2h} vs. I_h), and each contains 12 cyclopentane units. Furthermore, as can be deduced at a glance from the IUPAC designation, both are undecacyclic with all 20 atoms making up the main ring and with all interconnections being of the same order. Consequently, the structural alterations required in going from **1** to **2** are limited to only the hydrogenolytic fission of two cyclobutane C-C bonds, with inversion of the cyclobutane

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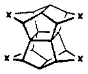
[1] (a) Universität Freiburg. (b) Ciba-Geigy AG. (c) Alexander von Humboldt Fellow, 1985-1986.

[2] (a) Fessner, W.-D.; Prinzbach, H.; Rihs, G. *Tetrahedron Lett.* **1983**, *24*, 5857-5860. (b) Fessner, W.-D. Ph.D. Dissertation, Universität Freiburg, 1986.

[3] The name "pagodane" represents the class of compounds based on the general structure (i) in which X symbolizes bridges of different nature and



i

lengths. The length of the bridges is given in square brackets placed in front of the name, according to their order in the IUPAC numbering scheme.

[4] Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446-5450.

[5] Eckroth, D. R. *J. Org. Chem.* **1967**, *32*, 3362-3365.

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