

**Figure 2.** With  $T_h$  symmetry there are five unique symmetry-related sets of C–C bonds in the  $C_{60}$  framework (A, B, C, D, E). The average values of these bonds are shown and were determined using distances obtained for both independent molecules. These bonds had the following ranges of values (Å): A, 1.490 (11)–1.508 (12); B, 1.446 (13)–1.511 (13); C, 1.366 (13)–1.427 (11); D, 1.453 (12)–1.503 (11); E, 1.392 (13)–1.455 (11). There are eight unique angles subtended by bonds A, B, C, D, and E (deg): AB = 117.5 (±0.9), range 115.3 (8)–119.1 (7); BB = 104.5 (±0.9), range 102.9 (8)–106.0 (8); BC = 122.1 (±0.9), range 119.1 (9)–123.4 (9); BE = 109.6 (±0.8), range 107.8 (9)–110.8 (8); CD = 120.2 (±0.8), range 118.2 (8)–120.9 (8); CE (attached to B) = 119.2 (±0.8), range 117.7 (9)–121.0 (10); CE (attached to D) = 120.7 (±0.8), range 119.1 (9)–122.1 (8); DE = 107.8 (±0.7), range 106.5 (8)–109.1 (9).

(each bound in a dihapto manner) and having overall  $T_h$  point group symmetry (ignoring the ethyl groups). X-ray crystallographic results on  $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$  confirmed this.<sup>7</sup> The accuracy of this structure<sup>7</sup> is much improved compared to previous  $C_{60}$  structures.<sup>2,3</sup> The asymmetric unit consists of two half-molecules on different inversion centers that generate two independent molecules (Figure 1). Both molecules are essentially identical with differences in the ethyl group orientations and in the twisting and bending of the  $[(C_2H_5)_3P]_2Pt$  groups about the Pt–alkene bonds; because of this twisting, each molecular core deviates slightly from perfect  $T_h$  point group symmetry. Relative to free  $C_{60}$ , coordination of Pt lengthens the attached and adjacent C–C bonds (bonds A and B in Figure 2) which approach values of typical C–C single bonds. Bonds D are also lengthened, and we propose these are forced to stretch owing to both the lengthening of the A bonds which are parallel to it and the lengthening of the B bonds which could also exert a net strain parallel to D. As in  $C_{60}$  itself, bond-length alternation (for which there is evidence experimentally and theoretically)<sup>2,3,8</sup> persists in the eight six-membered rings composed of bonds C and E (planar to within  $\leq 0.019$  Å). Bonds C (exo to the five-membered rings) are shortest leading to the favored resonance form depicted in Figure 2. For comparison, in  $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})$  the two distinct bond types averaged to 1.39 (±0.04) and 1.44 (±0.04) Å.<sup>3</sup>

The octahedral array of platinum atoms in this structure is readily understood. All evidence to date suggests that for metal complexation the bonds between two fused six-membered rings

in  $C_{60}$  are the most reactive, these bonds being shorter and having the most double bond character.<sup>2,3,8</sup> There are a total of 30 such six–six ring fusions in  $C_{60}$ . Binding of a  $[(C_2H_5)_3P]_2Pt$  group at one of these bonds sterically protects four of the surrounding six–six ring junctions. Thus, placing six  $[(C_2H_5)_3P]_2Pt$  groups on  $C_{60}$  essentially blocks all of the remaining 24 six–six ring bonds to further attack by platinum.

In conclusion,  $C_{60}$  can be substituted multiple times by electron-rich reagents, and a total of at least 12 carbon atoms of the  $C_{60}$  framework can participate in bonding. These results suggest that the geometry of substitution about  $C_{60}$  is controlled in this case by the special electronic structure of  $C_{60}$  (with localization of double bonds between the six–six ring fusions) and the size of the  $[(C_2H_5)_3P]_2Pt$  groups. We are investigating the geometry of the less-substituted  $C_{60}$  derivatives which are the intermediates leading up to this novel compound.

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**Supplementary Material Available:** Details of X-ray crystallographic analysis and tables of atomic coordinates, bond distances and angles, and thermal parameters (14 pages); listings of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

### Amine Photoredox Reactions: A Photoinduced “Methylene Shuttle” Initiated via Two-Electron Oxidation of a Tertiary Amine by Anthraquinone

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The photooxidation of tertiary amines by excited electron acceptors is generally indicated to occur by a sequence of electron-transfer quenching (SET), proton transfer, and electron transfer.<sup>1–10</sup> Although examples of rather clean reactivity to afford net two-electron products such as enamines or iminium ions are known,<sup>4–12</sup> these reactions often give complex mixtures and evidence for a variety of radical intermediates. The formation of oxidation products (enamines and/or secondary amines) which are themselves good donors frequently frustrates utilization of this reaction for preparative purposes. In the present paper we report an example of a tertiary amine photooxidation in which selective net two-electron oxidation of the amine leads to novel products in excellent yield and efficiency via self-condensation of highly reactive two-electron redox intermediates.

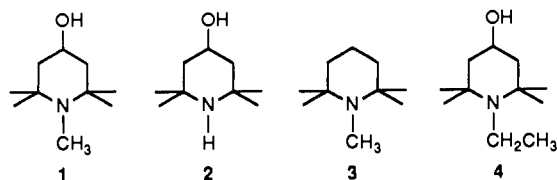
Previous investigations have established that irradiation of 9,10-anthraquinone (AQ) in the presence of potential reductants

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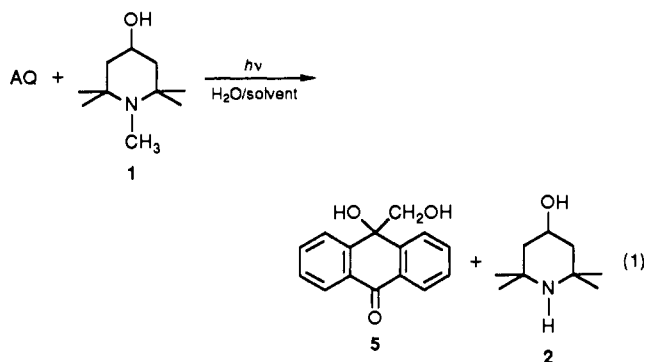
(7) Crystal data:  $C_{132}H_{180}Pt_6$ ; dark red parallelepiped,  $\approx 0.12 \times 0.26 \times 0.39$  mm; triclinic,  $P1$  (No. 2);  $a = 14.841$  (3) Å,  $b = 15.419$  (1) Å,  $c = 30.882$  (2) Å,  $\alpha = 95.25$  (1)°,  $\beta = 98.74$  (1)°,  $\gamma = 112.20$  (1)° (from 25 reflections);  $Z = 2$ ;  $V = 6380.9$  Å<sup>3</sup>;  $T = -70$  °C;  $FW = 3309.12$ ;  $D_c = 1.722$  g/cm<sup>3</sup>; final  $R = 0.043$ ,  $R_w = 0.033$ . For bond distances, numbers in parentheses are the estimated standard deviations. An error which contains “±” notation is the standard deviation of the calculated average of a number of bond measurements.

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such as amines or alcohols leads to the formation of the corresponding hydroquinone (AQH)<sub>2</sub>.<sup>11-17</sup> This has been confirmed in our studies; irradiation of AQ (>313 nm) with ethanol or formaldehyde in freeze-pump-thaw degassed acetonitrile solutions (0.1% H<sub>2</sub>O) leads to the formation of AQH<sub>2</sub>; the conversion can be easily followed by the growth of AQH<sub>2</sub> at 380 nm with an isosbestic point at 348 nm and its characteristic fluorescence. However, when AQ is irradiated under these conditions with cyclic amines 1-4, quite different behavior is observed. Although all

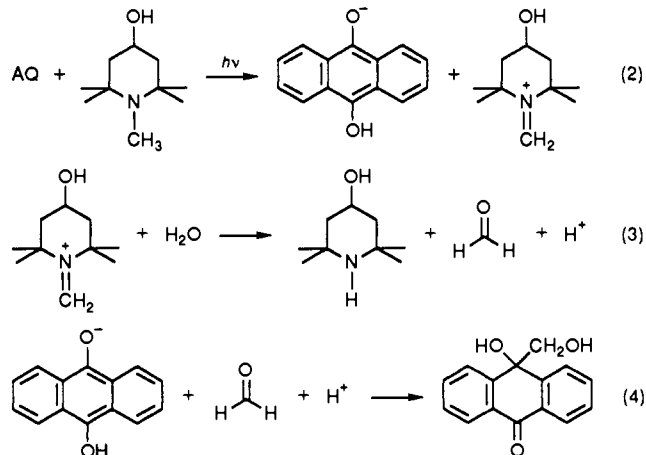


these amines are good reductants (irreversible peak potentials for oxidation in acetonitrile ranging from -0.98 to -1.22 V vs SCE; diffusion-controlled fluorescence quenching of 9,10-dicyanoanthracene in acetonitrile<sup>18</sup>), no net reaction is observed for 2 and 4 while 1 and 3 give efficient net photoreaction. Irradiation of a 1:1 mixture of AQ and 1 (ca.  $5 \times 10^{-3}$  M) leads to the formation of two major products in good chemical yield (>90% by NMR analysis or >80% in terms of isolated 5). These products were readily characterized by proton NMR and determined to be dealkylated amine 2 and the hydroxymethyl adduct of AQ, 9-hydroxy-9-(hydroxymethyl)anthrone (5)<sup>19</sup> (eq 1). The reaction proceeds smoothly in several other solvents (acetone, benzene, and methylene chloride) but only very slowly in methanol; an identical reaction is observed between AQ and 3.



While AQH<sub>2</sub> is not obtained as a final product under irradiation of AQ with 1 or 3, its characteristic fluorescence and absorption can be observed during the course of the photoconversion of AQ to 5. If the irradiation is interrupted and the spectrum measured immediately, the characteristic absorption of AQH<sub>2</sub> at 380 nm is observed; it decays nonexponentially ( $\tau_{1/2} \sim 15$ -20 min) in what is clearly a dark process concomitant with formation of 5. The overall reaction according to eq 1 thus consists of a photochemical

stage ( $\Phi = 0.25$ -0.46 for the disappearance of AQ<sup>20</sup>) resulting in formation of AQH<sub>2</sub> (or AQH<sup>-</sup>, its conjugate base) and a dark process in which 5 is generated. The structure of 5 suggests that it could arise via an aldol condensation of AQH<sup>-</sup> with formaldehyde, which could be generated from hydrolysis of a photo-generated iminium via eqs 2-4.<sup>21</sup> Accordingly we find that



synthetic AQH<sub>2</sub>, added to a solution of formaldehyde ( $1.3 \times 10^{-2}$  M) in the presence of base,<sup>22</sup> is converted to 5 following second-order kinetics consistent with the rate of the "dark phase" of the photoreaction described above.

These results are novel in several ways. Although anthrone-type products have been previously found as products from photoredox reactions of anthraquinone,<sup>23-25</sup> their formation in these cases has been attributed to addition via radical intermediates. Interestingly, we find AQH<sup>-</sup> does not condense with acetone or benzaldehyde and, accordingly, neither of these inhibit or divert the observed photoreaction. The unreactivity of amines 2 and 4 is probably not due to a lack of excited-state quenching of AQ but rather to the impedance of subsequent steps. In accord with evidence from other studies<sup>10-17</sup> with structurally similar donor-acceptor pairs, we suggest the photoreaction (eq 2), which results in a net hydride transfer, occurs by a sequence of electron-proton transfer for AQ/1 and AQ/3.<sup>26</sup> The semiquinone radical may be converted to AQH<sub>2</sub>, by either secondary electron transfer within the radical pair<sup>27</sup> or via disproportionation. In the case of amine 2, the lack

(20) The quantum yields of photoreduction of AQ are dependent on the concentration of amine.  $\Phi = 0.37$  in the presence of 0.01 M of 1;  $\Phi = 0.46$  in the presence of 0.10 M of 1;  $\Phi = 0.25$  in the presence of 1.00 M of 1.

(21) Formaldehyde can be observed by <sup>1</sup>H NMR (singlet at  $\delta$  9.60 ppm in CD<sub>3</sub>CN) immediately after the photolysis of the reaction mixture, and it disappears with the concurrent formation of 5 on the same time scale as the overall dark reaction.

(22) A referee has suggested that the condensation could also be accounted for in terms of a Mannich reaction. Although the conditions in the "dark phase" (presence of a secondary amine, carbonyl, and nucleophile) do not preclude a Mannich reaction, we think an aldol condensation is more likely since we find anthrahydroquinone condenses with formaldehyde when either sodium hydroxide or tertiary amine 1 are employed as the base. No reaction is observed when AQH<sub>2</sub> and formaldehyde are mixed in the absence of base.

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(26) Although both singlet and triplet can be quenched in an exergonic process by amines 1-4, the lack of fluorescence from AQ and a relatively long lived triplet state suggests that the observed reaction results from SET quenching of the latter. Laser flash photolysis studies indicate that quenching of the triplet ( $\tau_0 \sim 2.3$  ns) results in rapid formation (timescale < 130 ns) of products absorbing strongly at 400 nm where AQ<sup>-</sup>, AQH, and AQH<sup>-</sup> all show similar strong absorption.

(27) Other mechanisms such as electron-proton transfer followed by diffusion disproportionation and second electron transfer cannot be excluded. However, the secondary electron transfer within the radical pair is favorable by about 25 kcal/mol. The reduction potential of iminium ion is around 1.0 eV vs SCE.<sup>28</sup> The oxidation potential of hydroquinone is around 0.0 eV vs SCE.<sup>29</sup>

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(18) 9,10-Dicyanoanthracene has an almost identical reduction potential to AQ in acetonitrile; application of the Weller equation indicates that quenching of both singlet and triplet AQ by 1-4 should be highly favorable ( $-\Delta G_{et} = 1.1$ -1.5 V) in each case.

(19) Spectroscopic and elemental analysis of isolated 5: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.26 (2 H, d, ArH), 7.93 (2 H, d, ArH), 7.69 (2 H, t, ArH), 7.53 (2 H, t, ArH), 3.62 (2 H, d, -CH<sub>2</sub>-OH), 3.07 (1 H, s, -OH), 1.87 (1 H, t, -CH<sub>2</sub>-OH). Upon addition of D<sub>2</sub>O, the signals at  $\delta$  3.07 and 1.87 ppm disappeared and the signal at  $\delta$  3.62 ppm becomes a broad singlet. <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  184.7, 147.2, 134.1, 132.6, 128.8, 127.2, 127.0, 74.8, 73.9. UV (CH<sub>3</sub>CN):  $\lambda_{max} = 274$  nm (15400). Anal. Found: C, 74.51; H, 5.03. Calcd: C, 74.99; H, 5.03.

of an  $\alpha$ -proton inhibits further reaction, therefore no net reaction occurs. Although **4** possesses  $\alpha$ -protons, stereoelectronic considerations suggest that the kinetic acidity of  $\alpha$ -protons in the cation radical of **4** may be greatly reduced compared to those of **1** and **3** since the lone pair orbital on nitrogen atom should not be aligned parallel to the  $\alpha$  C-H bond in the former. This alignment, which can occur readily for **1** and **3**, is indicated by MMX calculations to result in delocalization of the positive charge to the  $\alpha$  C-H bonds and subsequently to enhanced kinetic acidity.<sup>30-32</sup> Perhaps of most significance in the present study is the finding that the reactive metastable products generated via the photoprocess (eq 2) are so cleanly converted via the subsequent "methylene shuttle" to **2** and **5**. The key is hydrolysis of the reactive iminium ion and efficient interception of the formaldehyde generated. Interestingly we find that irradiation of AQ and **1** or **3** in rigorously dry degassed benzene solution leads only to metastable products which return to starting materials in a dark reaction.<sup>33</sup>

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### Unusual Reorganization Reactions of 3-Azabicyclo[3.3.1]nonanes

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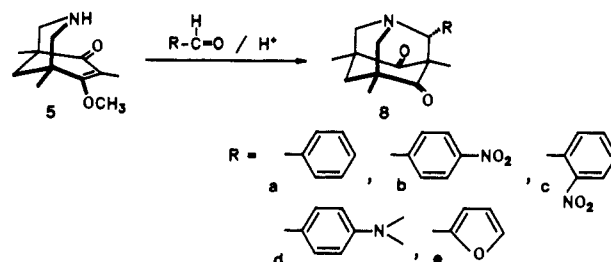
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Functionalized 3-azabicyclo[3.3.1]nonanes are studied intensively because of their pharmaceutical use<sup>1</sup> and their application as an important structure in the field of molecular recognition.<sup>2</sup> The basic step in our synthetic approach is a regiospecific Grob fragmentation of easily accessible 1-azaadamantane derivatives. We observe a surprising and fascinating self-organization of a key intermediate. The analysis of this remarkable reaction initiated a facile preparation of  $\alpha$ -substituted 1-azaadamantanes, which may be of interest as concave bases.<sup>3</sup>

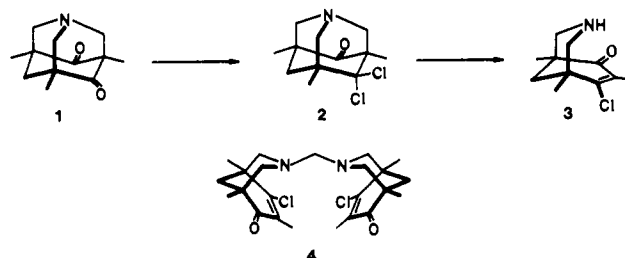
Refluxing a solution of the diketone **1**<sup>4</sup> (available from standard chemicals in two steps: methyl methacrylate, 3-pentanone, hexamethylenetetramine) for 12 h in thionyl chloride yields the derivative **2**. Specifically, only one of the carbonyl groups reacts and is dichlorinated. **2** can be isolated and characterized, but by application of special conditions during the workup [(1) aqueous ammonia, 25%; (2) methanol/NaOH; (3) concentrated hydrochloric acid], a Grob fragmentation<sup>5</sup> is induced. The chlorine axial to the carbocyclic ring (*exo*-chloride) probably acts as the leaving group.

The regiospecificity of this fragmentation is remarkable but not surprising. The  $\alpha,\beta$ -unsaturated derivative **3** is isolated ex-

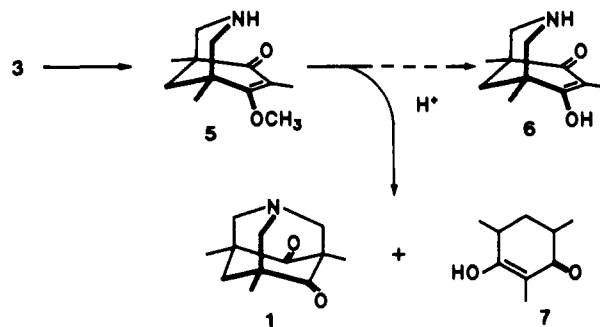


**Figure 1.** Synthesis of  $\alpha$ -substituted 1-azaadamantanediones **8a-e** from **5** (only one of two possible enantiomers is shown).

clusively (TLC; NMR; 90% yield); the possible (alternative) fragmentation to the  $\beta,\gamma$ -unsaturated product is not observed.



**3** is an interesting and versatile synthetic building block. The NMR data verify the chair conformation of the piperidine part of the bicycle. The  $^4J$  (*W*) couplings observed are in good agreement with the depicted rigid conformation of **3** and help to establish the geometry of the molecular cleft in products of this type. This is of interest, because special derivatives may be useful in the field of molecular recognition.<sup>6</sup> For example, modified workup of the above reaction (80% aqueous ethanol, triethylamine) yields the dimer **4**, exclusively. Other dimers are easily available, too. **3** is not only a secondary amine (nucleophile) but also a vinylogous acid chloride (diminished reactivity, probably because of the geometry of the compound). The cooperation of both functional groups establishes a variety of chemical applications.<sup>6</sup> Treatment of **3** with  $\text{CH}_3\text{O}^-$  yields the vinylogous ester **5** (addition-elimination reaction), which we planned to hydrolyze for generating the reactive bicycle **6**. While **3** is surprisingly stable toward acids, the ester **5** immediately reacts with hydrochloric acid at room temperature. The vinylogous acid **6**, however, is not the product; the diketone **1** is isolated instead. This results from



a remarkable and surprising self-organization, probably of the intermediate **6** in acidic medium (retro-Mannich/Mannich reaction). The optimized yield of this reaction does not exceed 62%.<sup>7</sup>

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- (6) Rebeck, J. J., Jr.; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245. Langhals, M. Dissertation, University of Bielefeld, 1990. Unlike the interesting derivatives of Kemp's acid, several sites of **3** are functionalized. <sup>13</sup>C NMR data of **3** (75 MHz, CDCl<sub>3</sub>):  $\delta$  13.22 (q), 21.32 (q), 24.79 (q), 40.52 (s), 40.56 (s), 47.40 (t), 50.96 (t), 53.84 (t), 136.87 (s), 157.65 (s), 200.20 (s). The total assignment of the <sup>1</sup>H NMR data (300 MHz) succeeds by conventional methods and analysis of the COSY spectra.