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CYCLOPROPANOL FORMATION VIA β-HYDROGEN ATOM ABSTRACTION: THE FIVE MEMBERED TRANSITION STATE ANALOGUE OF THE NORRISH TYPE II REACTION

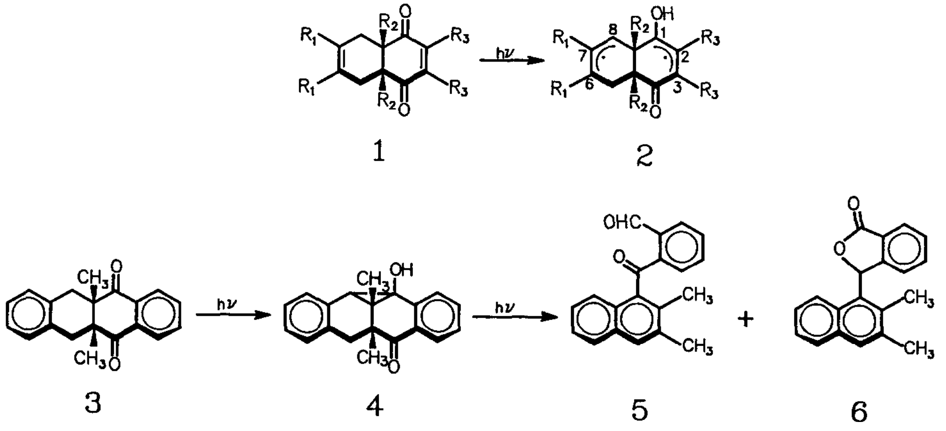
Sara Ariel, Syed H. Askari, John R. Scheffer* and James Trotter*
Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1Y6

Abstract

Solution phase photolysis of the Diels-Alder adduct **3** formed between o-quinodimethane and 2,3-dimethyl-1,4-naphthoquinone affords, via β-hydrogen atom abstraction and closure of the resulting 1,3-biradical, the cyclopropanol **4**. The cyclopropanol itself undergoes secondary photolysis initiated by a novel ring opening process. Irradiation of crystals of adduct **3** affords no detectable photoproducts. The crystal and molecular structure of **3** reveals that cyclopropanol formation in the solid state would involve prohibitive non-bonded steric interactions between lattice neighbors.

Photolysis of ketones possessing both β and γ-hydrogen atoms invariably leads to abstraction of the latter, a process known as the Norrish type II reaction.[1] In fact, only when favored by exceptional stereoelectronic factors is β-hydrogen abstraction ever seen, one example being the conversion of diene-diones of general structure **1** into the bis-allylic biradicals **2** (Scheme I).[2] Of the four possible modes of collapse of this biradical, only 1,8-bonding or cyclopropanol formation (cf., cyclobutanol formation in the Norrish type II reaction) has not been observed. In this communication we report that (1) cyclopropanol formation can be brought about by suitable choice of substituents, (2) cyclopropanol formation is not permitted in the solid state for reasons which can be understood from the crystal and molecular structure of the reactant, and (3) the cyclopropanol itself undergoes an intriguing, secondary photorearrangement.

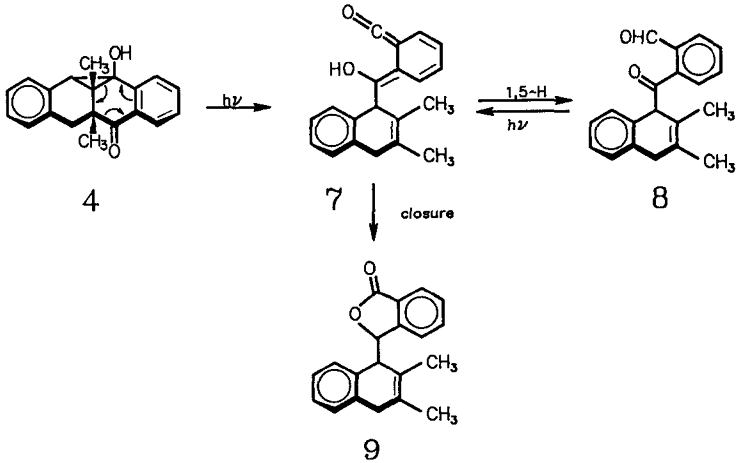
Scheme I.



We reasoned that by converting the 2,3 and 6,7 aliphatic double bonds of **1** into aromatic double bonds, closure of the resulting biradical would be restricted to the 1,8 positions. The starting material required to test this hypothesis, diketone **3**, was prepared by trapping o-quinodimethane with 2,3-dimethyl-1,4-naphthoquinone.[3] As anticipated, irradiation of acetonitrile solutions of **3** through Pyrex followed by column chromatography afforded moderate yields (35%) of cyclopropanol **4**.[4] GC analysis of the photolysis reaction mixture prior to column chromatography revealed the presence of several other volatile components. By the appropriate control studies, these photoproducts were shown to be the result of secondary photolysis of cyclopropanol **4**. Further column chromatography permitted the isolation of small amounts of two of these substances, the keto-aldehyde **5** (9%),[4] and the lactone **6** (22%).[4]

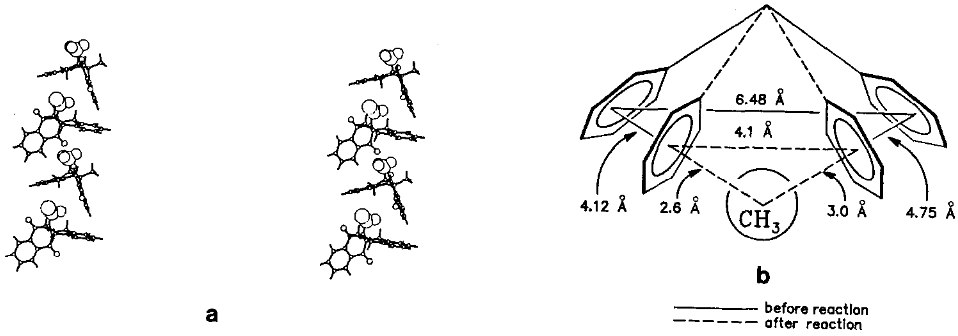
As outlined in Scheme II, we view the formation of photoproducts **5** and **6** as resulting from a novel ring opening of cyclopropanol **4** to give the ketene-enol intermediate **7** followed by 1,5-hydrogen transfer to afford **8** or closure to yield **9**. Products **5** and **6** are then formed by oxidation during workup of the dihydronaphthalene derivatives **8** and **9**, respectively. The GC peaks due to **6** increase with increasing irradiation time while those due to **5** and **4** decrease proportionately, indicating that **8** can revert photochemically to **7**. Independent irradiation of keto-aldehyde **5** showed that it too undergoes photoenolization to afford lactone **6** in high yield.[5] There is exact literature precedent for this process in the photorearrangement of o-phthalaldehyde to phthalide via a ketene-enol intermediate.[6]

Scheme II.



Previous work from our laboratory has shown that crystalline ene-diones of general structure **1** undergo photolytic hydrogen abstraction followed by biradical closure in the <u>solid state</u> as well as in solution.[7] However, when crystals of diketone **3** were irradiated, no new products of any kind could be detected. In order to understand this puzzling inertness, the crystal and molecular structure of **3** was determined. Crystals of **3** are triclinic, space group $P\bar{1}$, $a = 9.907$, $b = 12.094$, $c = 13.049$ Å, $\alpha = 80.54$, $\beta = 85.03$, $\gamma = 89.73^\circ$, $Z = 4$. The structure was solved by direct methods from 4600 observed reflections and refined to a final R of 0.045.[8] The results show that there are two independent molecules with very slightly different conformations in the asymmetric unit. The molecules pack in stacks consisting of alternating conformers. A stereodiagram of a molecular stack is shown in Figure 1a. A notable feature, which we feel explains the lack of cyclopropanol formation in the solid state, is evident in the view shown.[9] A methyl group of a lower molecule projects directly into the space between the two aromatic rings of an upper molecule. Cyclopropanol formation requires that these two rings move considerably closer together, and this is prevented by the presence of the methyl group. The location of the methyl group with respect to the two aromatic rings is illustrated in Figure 1b. In the reactant 3, the center to center distance between the two rings is 6.48 Å, and the intruding methyl carbon to aromatic center distances are 4.12 and 4.75 Å.[10] After reaction, the conformationally rigid cyclopropanol 4 has an aromatic center to center distance of 4.1 Å as estimated from Dreiding models. Assuming an identical methyl group location, the distances between the intruding carbon and the aromatic centers in photoproduct 4 are reduced to 2.6 and 3.0 Å, respectively. These distances are too short to accommodate the methyl group. Methyl groups have van der Waals radii of 2.0 Å,[11] and when this is added to the van der Waals half "thickness" of an aromatic ring (1.7 Å), the sum of 3.7 Å clearly indicates the prohibitive steric compression[12] accompanying cyclopropanol formation.

Figure 1. Crystal Lattice Steric Effects.



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

1. Reviews: (a) P.J. Wagner, Acc. Chem. Res., 16, 461 (1983); (b) P.J. Wagner in "Molecular Rearrangements in Ground and Excited States," P. de Mayo, Ed., Wiley-Interscience, New York, 1980, Ch. 20; (c) P.J. Wagner, Acc. Chem. Res., 4, 168 (1971).
2. (a) J.R. Scheffer, K.S. Bhandari, R.E. Gayler and R.A. Wostradowski, J. Am. Chem. Soc., 97, 2178 (1975); (b) J.R. Scheffer, B.M. Jennings and J.P. Louwerens, J. Am. Chem. Soc., 98, 7040 (1976).
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4. Cyclopropanol 4: mp 158-159°; IR (KBr) 3435 (OH) and 1660 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$,

400 MHz) δ 7.01-6.06 (m, 8H, aromatics), 3.81 (s, 1H, cyclopropyl H), 3.06 (AB q, 2H, J = 18 Hz, CH_2), 2.31 (s, 1H, exchangeable, OH), 0.89 (s, 3H, CH_3), 0.79 (s, 3H, CH_3); mass spectrum m/e (relative intensity) 290 (M^+, 38), 262 (53), 247 (32), 229 (21), 215 (13), 157 (50), 142 (39), 134 (100), 130 (50), 115 (31), 105 (52), 77 (34); Anal. calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.54; H, 6.31. Keto-aldehyde 5: mp 138-139°; IR (KBr) 1682 (HC=O) and 1650 (ArC=O) cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 10.80 (s, 1H, CHO), 8.1-7.15 (m, 9H, aromatics), 2.47 (s, 3H, CH_3), 2.25 (s, 3H, CH_3); mass spectrum m/e (relative intensity) 288 (M^+, 66), 273 (100), 259 (16), 243 (25), 215 (20), 155 (14), 104 (18); Anal. calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.39; H, 5.54. Lactone 6: mp 142-143°; IR (KBr) 1742 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, 27°) 8.3-6.9 (m, 10 H, aromatics plus methine), 2.68 (s, 1.5 H, CH_3), 2.55 (s, 1.5 H, CH_3), 2.36 (s, 1.5 H, CH_3), 1.86 (s, 1.5 H, CH_3). This spectrum indicates a 1:1 mixture of conformers in slow equilibrium. Fast exchange is achieved at 90° as indicated by the following ^{13}C NMR spectrum (DMSO-d_6, 100.6 MHz): δ 170.1 (C=O), 150.7, 135.6, 135.5, 134.7, 132.3, 129.9, 129.2, 128.0, 127.2, 126.1, 125.9, 125.7, 125.1, 124.9, 122.5, 122.2 (aromatics), 79.4 (methine carbon), 20.7 and 15.7 (methyls). At 25°, the peaks at 79.4, 20.7 and 15.7 ppm are broad doublets. Mass spectrum m/e (relative intensity) 288 (M^+, 100), 273 (58), 243 (75), 229 (80), 215 (22), 202 (21), 183 (25), 157 (30), 133 (30), 104 (62); Anal. calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.04; H, 5.50.

5. This is an unusual reaction in that α-naphthyl ketones usually have lowest triplet states which are π,π^* in character and are therefore poor hydrogen atom abstractors. (a) G.S. Hammond and P.A. Leermakers, J. Am. Chem. Soc., 84, 207 (1962); (b) P.J. Wagner and G.S. Hammond, Adv. Photochem., 5, 21 (1968); (c) N.J. Turro and C.G. Lee, Mol. Photochem., 4, 427 (1972).
6. S.P. Pappas and J.E. Blackwell, Jr., Tetrahedron Lett., 3337 (1968) and references cited therein.
7. J.R. Scheffer and A.A. Dzakpasu, J. Am. Chem. Soc., 100, 2163 (1978).
8. S. Ariel and J. Trotter, *manuscript in preparation.*
9. One possible explanation for the lack of photoreactivity of diketone 3 in the solid state is that its conformations are not suitable for β-hydrogen atom abstraction. However, the abstraction distance (2.51/2.54 Å) and the angular parameters (τ = 35.1°/42.0° and Δ = 81.0°/81.0°) in the case of 3 are very similar to the values for other ene-diones which do react in the crystalline phase.[7]
10. These values are for one of the two independent molecules present in the asymmetric unit. The other molecule has an interaromatic center to center distance of 6.52 Å and methyl carbon to benzene center distances of 4.12 and 4.68 Å.
11. A. Bondi, J. Phys. Chem., 68, 441 (1964).
12. For other examples of steric compression effects in organic solid state chemistry, see S. Ariel, S. Askari, J.R. Scheffer, J. Trotter and L. Walsh in "Organic Phototransformations in Nonhomogeneous Media," M.A. Fox, Ed., ACS Symposium Series 278, American Chemical Society, Washington, D.C., 1985, Ch. 15.

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