

TRANSANNULAR INTERACTIONS IN HEXACYCLO[6.6.0.0.<sup>2,6</sup>.<sup>3,13</sup>.<sup>4,11</sup>.<sup>5,9</sup>]TETRADECA-10,14-DIONE

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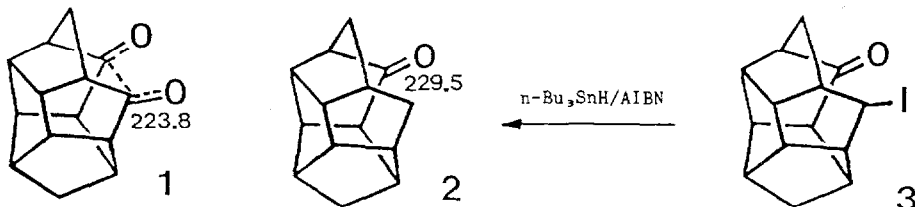
**Summary:** Transannular interaction between the two carbonyl groups of the titled compound is evidenced by C-13 NMR, X-ray and chemical reactions. Photolysis in isopropanol or tetrahydrofuran induces a pinacol-type reductive coupling between the two carbonyl groups.

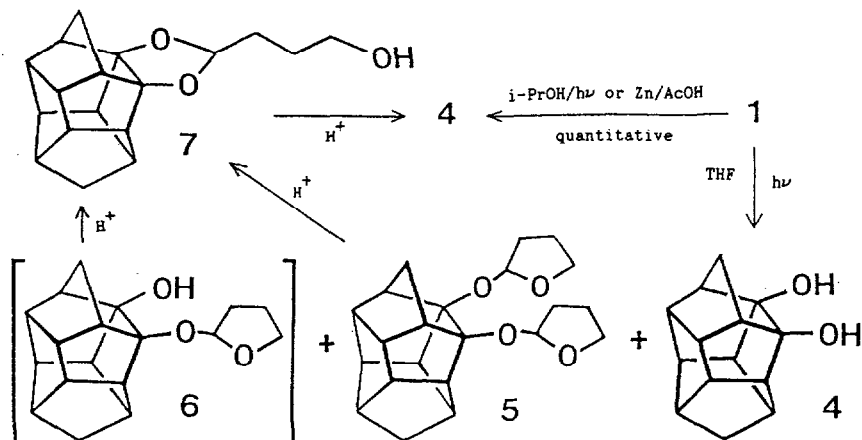
Nonbonding interactions between proximately located functional groups have subtle yet significant influences on many chemical as well as biological reactions. The interaction between  $\pi$  orbitals is of special interest. The titled compound, (1)<sup>1</sup>, consisting of a pair of closely located carbonyl groups, provides a good model for the analysis of such type of interaction.<sup>2</sup> The distance between the facing carbonyl carbons is measured to be 2.88 Å by X-ray diffraction analysis of a single crystal.<sup>3</sup> Considering that the  $\pi$  lobes of a double bond extend to a distance of ca. 1.7 Å above and below the nodal plane, a significant orbital overlap between the two CO groups is expected.

The presence of such interaction is disclosed by <sup>13</sup>C NMR<sup>4</sup>: The CO chemical shift in 1 is measured to be 5.7 ppm upfield ( $\delta$  223.8 ppm) compared with that of the monoketone 2 ( $\delta$  229.5 ppm), the reference compound synthesized from the iodide 3<sup>1</sup> with n-Bu<sub>3</sub>SnH/AIBN in nearly a quantitative yield.<sup>5</sup> This variation in chemical shift is believed to be induced by electronic delocalization across the two CO groups.

An intramolecular pinacol-type reductive coupling occurred readily upon treatment of 1 with zinc in acetic acid. Photochemistry of 1 shows similar results, i.e. an excellent yield of the diol 4<sup>5</sup> is produced under UV irradiation in the presence of isopropanol. Both processes may have gone through a ketyl radical intermediate which couples with the adjacent CO to produce an oxa-radical.

The presence of oxa-radicals in photochemical processes can be better illustrated in the following reaction in tetrahydrofuran (THF). Under UV light in THF, compound 1 was converted into three major products, the diol 4 (11%), the bis-THF-adduct 5 (21%), and the





alcohol 7 (60%).<sup>5</sup> The alcohol 7 is likely derived from the mono-THF-adduct 6 during the isolation process through silica gel chromatographic column, as it was obtained by partial hydrolysis of 5. Complete hydrolyses of both 5 and 7 give 4 in quantitative yields. The formation of 5 and 6 witnessed the coupling of the oxa-radical with THF radical. The long lifetime of the oxa-radical may be attributed to transannular orbital delocalization.

#### References and notes

1. T.J. Chow, T.-K. Wu, *J. Org. Chem.* 1988, **53**, 1102.
2. (a) V. Balaji, K.D. Jordan, R. Gleiter, G. Jahne, G. Muller, *J. Am. Chem. Soc.* 1985, **107**, 7321; (b) T. Mori, K.H. Yang, K. Kimoto, H. Nozaki, *Tet. Lett.* 1970, 2419; (c) W.T. Borden, T. Ravindranathan, *J. Org. Chem.* 1971, **36**, 4125.
3. Single crystal X-ray diffraction data of 1 will be published elsewhere.
4. (a) R. Bishop, G.-H. Lee, *Aust. J. Chem.* 1987, **40**, 249; (b) R. Bishop, *ibid*, 1984, **37**, 319; (c) Y. Senda, J.-i. Ishiyama, S. Imaizumi, *J. Chem. Soc. Perkin II* 1981, 90.
5. 2: <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ=1.14 (1H, dd, J=3.5, 15), 1.67 (2H, s), 1.9-2.0 (2H, m), 2.25 (1H, d, J=12), 2.38 (2H, m), 2.52-2.78 (6H, m), 2.95-3.03 (2H, m); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ=35.0, 45.5, 46.6, 47.3, 48.2, 48.7, 50.1, 52.1, 54.0, 54.4, 56.7, 57.0, 57.3, 229.5.  
4: <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ=1.74 (3H, m), 2.02 (1H, d, J=11), 2.45 (9H, m), 2.72 (1H, m), 2.80 (2H, -OH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ=39.3, 42.5, 46.8, 49.5, 50.3, 51.4, 54.7, 56.9, 95.8; MS: m/z 216 (M<sup>+</sup>, 100%), 167 (30), 129 (30), 105 (38), 91 (44).  
5: <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ=23.3 (t, THF), 24.0 (t, THF), 30.5 (t, THF), 32.2 (t, THF), 39.3 (t), 43.0 (t), 49.1 (d), 49.5 (d), 50.2 (d), 50.7 (2C, d), 52.1 (d), 66.6 (2C, t, THF), 103.5 (d, THF), 104.8 (s), 104.9 (d, THF); MS: m/z 285 (M<sup>+</sup>-THF, 11%), 240 (6), 227 (100), 253 (4); IR (CDCl<sub>3</sub>): ν=3019 cm<sup>-1</sup>, 1526, 1478, 1217, 1046, 1031, 929.  
7: <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ=26.8, 30.6, 39.4, 43.0, 49.1, 49.5, 50.3, 50.7, 50.75, 52.1, 62.7, 104.9, 104.95; MS: m/z 286 (M<sup>+</sup>, 0.5%), 254 (1.4), 240 (2), 227 (100), 216 (14).

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