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Geometric requirements for the photolysis of aryloxiranes and cyclic carbonate esters

Sorana Linder, Katherine White, Mandelin Palmer, Benny Arney and Rick White*

Department of Chemistry, Sam Houston State University, Huntsville, TX 77341, USA

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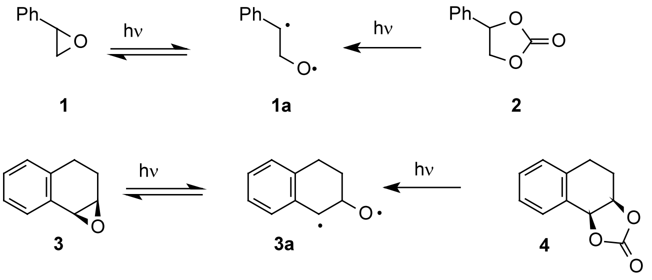
Abstract—The photolysis of *trans*-β-methylstyrene oxide proceeds smoothly, but neither the corresponding *cis*-isomer nor β,β-dimethylstyrene oxide are photochemically active. Moreover, although styrene glycol carbonate undergoes photolysis to extrude carbon dioxide, the β,β-dimethylstyrene glycol carbonate is photochemically unreactive. These results are explained by looking at the energies required to obtain a conformation in which the plane of the aromatic ring is orthogonal to the orbitals of the epoxide moiety. © 2002 Elsevier Science Ltd. All rights reserved.

The photochemistry of monoaryloxiranes has been generally described as occurring via cleavage of the benzylic carbon–oxygen bond to generate a 1,3-diradical such as seen in the photolysis of styrene oxide (**1**)[1] and tetrahydronaphalene oxide (**3**).[2] The same intermediate has been formed via extrusion of carbon dioxide from the corresponding cyclic carbonate esters such as styrene glycol carbonate (**2**)[3] and 1,2,3,4-tetrahydronaphalene carbonate (**4**).[4] These are summarized in Scheme 1.

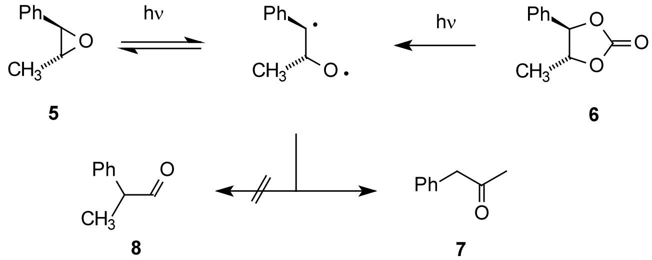
The intermediate 1,3-diradicals can undergo a 1,2-hydrogen migration, or a 1,2-aryl migration.[5] We were interested in 1,2-alkyl migrations in these systems since alkyl migrations in radical systems are rare, although they have been reported.[6] The photolysis[7] of either *trans*-β-methylstyrene oxide (**5**) or *trans*-β-methylstyrene glycol carbonate (**6**) for 1 h resulted in the formation of the 1,3-diradical leading to phenylacetone (**7**) in 20–25% conversion with none of the methyl migration product **8** being detected and is shown in Scheme 2.



Scheme 1.

However, the photolysis of the corresponding *cis*-β-methylstyrene oxide (**9**) resulted in no reaction as shown in Scheme 3. This puzzled us as to why the *trans* isomer was reactive, yet the *cis* isomer was not, even though their UV spectra were virtually identical. Moreover, the irradiation of either β,β-dimethyl styrene oxide **10** or β,β-dimethyl styrene glycol carbonate **11** resulted in no detectable reaction even after 2 h. We were puzzled as to why **5** and **6** were photoreactive, yet **9**, **10** and carbonate **11** were relatively inactive.

Photochemical reaction at the benzylic carbon–oxygen bond in aryl oxiranes requires the interaction of the electronically excited π-system with the bonding/antibinding orbitals of the carbon–oxygen bond. This interaction is a symmetry-controlled function of the dihedral angle (θ) between the aryl plane and the car-



Scheme 2.

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* Corresponding author. Tel.: 936-294-1060; fax: 936-294-4996; e-mail: chm_rcw@shsu.edu

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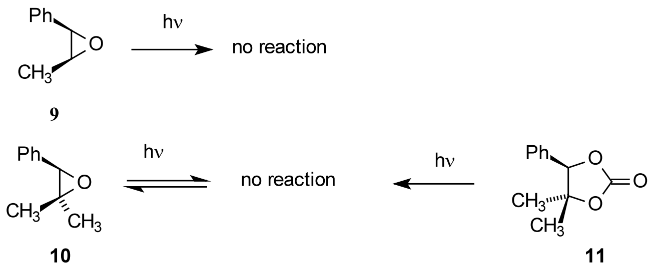

Scheme 3.

bon–oxygen bond. The observed positional dependence of reactivity caused us to suspect that van der Waals repulsions between the substituents on the oxirane moiety with the *ortho* aryl hydrogens were preventing the necessary orbital alignment for charge density transfer into the antibonding orbitals of the benzylic carbon–oxygen bond. We examined the calculated energy profile compounds **1**, **5**, **9**, and **10** as a function of rotation about the phenyl–oxirane bond using HF/3-21G(*) optimized geometries with the dihedral (θ) to five (5) degree increments. This is outlined in Fig. 1. Compounds <u>1</u> and <u>5</u> display virtually identical profiles with moderately restricted rotation (barrier ≈ 5.7 and 6.0 kcal/mol, respectively) as expected because of the geometric isolation of the *trans*-beta position from the aryl group. This finding agrees well with the similar photochemical reactivity observed for <u>1</u> and <u>5</u>. Compounds <u>9</u> and <u>10</u> exhibited significantly greater barriers to rotation (9.8 and 10.2 kcal/mol, respectively) reflecting the greater interaction of the *cis*-beta substituents with the *ortho* aryl hydrogens. Just as important as the increased height of the barrier is its position from $\theta \approx 50$–120°, which is the most critical range for effective electronic interaction with the excited aryl π system. Conformations in this range are approaching a potential energy maximum and should expectedly possess low residence times.

Calculation of a population distribution graph of the fraction of molecules (logarithmic scale) with sufficient internal energy versus dihedral angle clearly illustrates the drastic reduction (as much as 10^{-3}) in the fraction of energetically viable molecules in the region of greatest probability of reaction. These calculated results strongly suggest a dramatic decrease in the expected photochemical reactivity of the benzylic oxirane ring in the presence of a *cis*-beta substituent, which is clearly expressed in the observed photo-inactivity of compound <u>10</u> (Fig. 2).

These results explain the variation of photoreactivity of aryloxiranes and aryl carbonate esters and also match well with a recent investigation into the structure of phenylcyclopropane[8] which showed, that the lowest energy conformation of phenylcyclopropane was one in which the cyclopropane ring was orthogonal to the plane containing the aromatic ring.

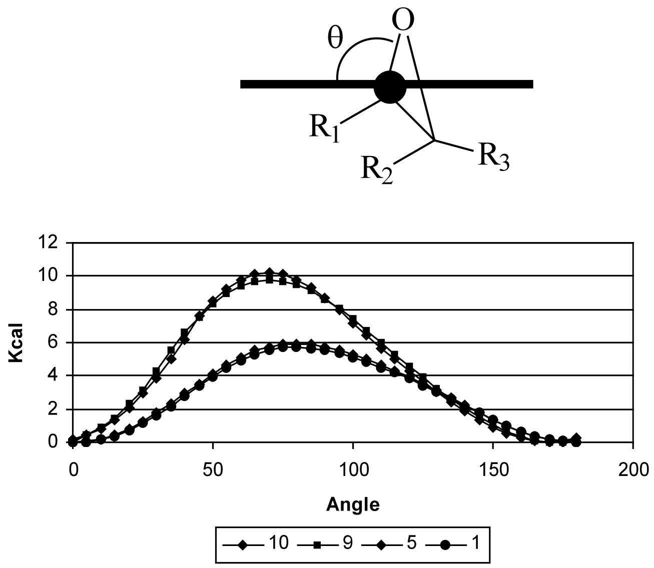

Figure 1. Energy profile HF/3-21G(*).

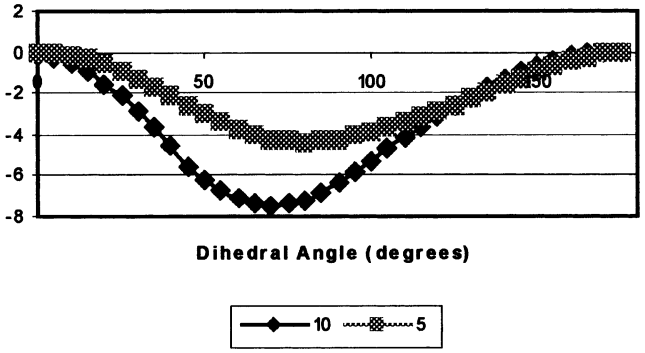

Figure 2. Normalized population distribution.

Acknowledgements

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