Tetrahedron Letters, Vol.30, No.5, pp 527-530, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

ANALYSIS OF NORRISH TYPE II REACTIONS BY MOLECULAR MECHANICS METHODOLOGY[1]

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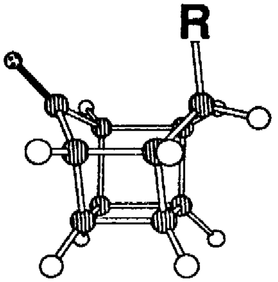
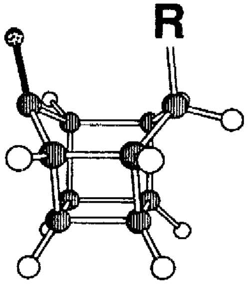
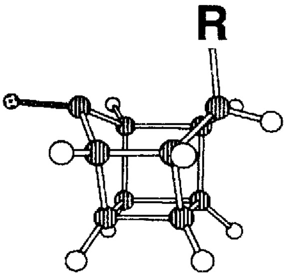
Force field parameters have been developed that reproduce the triplet state *ab initio* geometries of two ketones. Transition state energies and geometries have been computed for a variety of Norrish Type II reactions. A correlation has been found between overall reaction and transition state strain energy.

Although intramolecular hydrogen abstraction reactions of excited carbonyl groups have been extensively studied, detailed geometric and stereoelectronic requirements have not been systematically developed.[2] Recent computational results have provided insight into the behavior of simple systems,[3] e.g. butanal[4] but computations of larger and more complex structures by *ab initio* methodology are impractical. An appealing alternative would be to utilize force field methodology given the ease of application to complex molecules.[5] In this report we outline the development of a parameter set designed to evaluate "strain energies" of transition structures for intramolecular hydrogen abstractions and demonstrate its utility in diverse systems. The first objective was to develop force field parameters for excited states of alkanones so that strain energy could be computed for the initial states. Our approach to this phase of the problem was to use *ab initio* methods (STO-3G basis set)[6] to calculate the geometry of the excited triplet states of pentacyclodecanones **1** and **2** (C_s symmetry). These molecules were chosen because it was anticipated that steric and strain effects would be prominent and the importance of individual parameters would be highlighted as a result.

Four low energy structures were located that we have labelled *syn* and *anti* forms. The carbonyl groups were non-planar in all cases having the out-of-plane angles shown below. Methyl hydrogen atoms existed in staggered conformations in both forms. We then developed MM2 parameters that duplicated the structures of all four isomers. The major changes from standard ground state parameters included use of a lengthened $C{=}O^*$ bond (1.40 Å) and reduced out-of-plane force constants for the carbonyl groups [K_b = 0.13 mdyne Å/deg^2). The latter modification corresponds to reduced double bond character in the excited states and allows for pyramidalization at these centers. The agreement between the two sets of structures is excellent as shown by the comparisons of the out-of-plane angles and, *inter alia*, the carbonyl-methyl hydrogen distances in *syn*-2* (2.08, 3.64 Å).

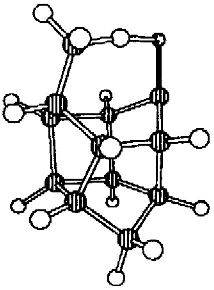






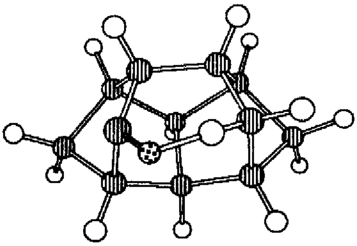
		syn-**1***	*syn*-**2***	*anti*-**1***	*anti*-**2***
1 R = H	*ab initio*	-37.3°	-31.2°	41.0°	42.9°
2 R = CH_3	MM2	-33.2°	-31.0°	42.8°	42.1°

Parameters for evaluating energies of transition structures were developed from considerations of the corresponding geometry for butanal triplet and from force constants involved in the closely related Barton reaction.[4,7] For example, the optimal angles for $C{=}O^*\text{--}H$ and $O^*\text{--}H\text{--}C$ were taken as 101.0° and 170.5°, respectively. A parameter required to describe the dependency of hydrogen abstraction rates on the dihedral angle defined by the atoms $C{-}C{=}O^*\text{--}H$ was also incorporated. Inclusion of this term accounts for the facility of hydrogen abstraction reactions when the hydrogen lies near the n-orbital in the carbonyl plane and the high barrier predicted when the hydrogen atom lies in the Π-realm.[4,8] To accomplish this objective we included a variable parameter (V_2) in the torsion equation for this grouping that reaches a maximum when the torsion angle is 90° and is minimal at 0°. We report here results using three values of V_2 (0.0, 7.5, and 15 kcal/mol) that illustrate the sensitivity of the calculations to this parameter. We calculate values of 2.7, 2.7, and 2.8 kcal/mol, respectively, for the "strain energy" required to achieve the Norrish Type II transition state geometry, starting from the energy-minimized pre-aligned triplet state geometry of pentanone. With these values as references we can compare transition state strain energies for other more complex ketones, both reactive and unreactive, to determine whether correlations can be developed between strain energy and reactivity. It is instructive to compare the results found for cyclodecanone which does not undergo either Type II elimination or cyclobutanol formation with those for cycloundecanone, a reactive ketone.[9] Calculated transition state strain energies for these two systems are 3.7, 5.2, and **5.4** kcal/mol for the 10-membered system and 2.1, 3.3, and **3.5** kcal/mol for the 11-membered ring. The importance of the non-zero two-fold term V_2, is clear from these results and is particularly evident in the results with the transition states **3** and **4** shown for two "unreactive" polycyclic ketones. Consistent with the recent findings that *syn*-11-alkyl-pentacycloundecan-8-ones[1] were shown to be photochemically stable, we calculate transition state strain energies of 0.2, 5.1, and **7.2** kcal/mol for **3**. The calculated transition strain energies for the transition state **4** of the ketone studied by Sugiyama, *et al*, are: 0.3, 4.0, and **5.5** kcal/mol .



syn-Pentacycloundecanone
Transition State

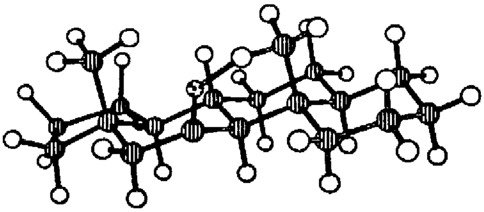
3



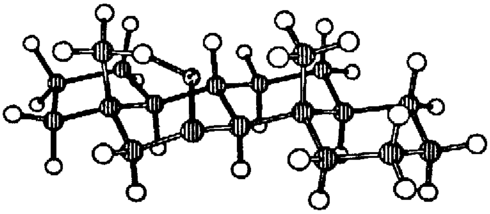
Pentacycloundecanone
Transition State

4

Lastly, we examined the energetics of some steroidal ketone photoreactions that are known to lead to cyclobutanol formation selectively by abstraction of hydrogen atoms from C-19 as opposed to the similarly sited C-18 methyl group. For abstractions at C-19 we find values of 3.9, 3.9, and **3.9** kcal/mol. On the other hand, abstraction at C-18 leads to values of 4.9, 7.2, and **8.0** kcal/mol.



Steroid C 19 Transition State



Steroid C 18 Transition State

Thus, we have found that the ease of intramolecular hydrogen abstractions can be related to the strain energy of the transition states, and a distinction was found between reactive (SE < 3.9 kcal/mol) and unreactive (SE > 5.0 kcal/mol) systems. Our parameters were developed strictly for carbonyl triplet states; however, the reactive state is not always known and may include contributions from singlet states. In addition, revertibility of hydrogen abstraction may lead to misleading conclusions about overall reactivity in extreme cases. Despite these drawbacks, this approach appears to be useful in predicting reactivity. We are currently refining the parameters and plan to test them more extensively in similar comparisons and to test them in our own experimental work.

Acknowledgment. We are grateful to K. N. Houk for access to unpublished data and for helpful suggestions. We also thank J. D. Westbrook for computational assistance and J. Kohn for assistance with manuscript preparation.

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(Received in USA 20 October 1988)