J. Org. Chem. **1994**, *59*, 7061–7066

Modeling of Norrish Type II Reactions by Semiempirical and *ab Initio* Methodology

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Received June 1, 1994®

A detailed computational analysis of hydrogen abstraction reactions by carbonyl triplet states for the formaldehyde:methane reaction and the intramolecular butanal reaction has been made. From a comparison of several semiempirical methods with *ab initio* results (UMP2/6-311+G**), it was concluded that use of the UHF/MINDO/3 Hamiltonian leads to a good description of the geometry of the carbonyl triplet states and the transition structures for hydrogen abstraction reactions. This methodology was used to survey the energetics of several intramolecular hydrogen abstraction reactions.

Introduction

This work was initiated in response to a need to develop a comprehensive means to model Norrish/Yang Type II photoreactions of complex carbonyl systems. Although there are hundreds of examples of these reactions in the literature, relatively few quantitative modeling studies have been undertaken.[1] Early attempts to model hydrogen abstraction reactions by excited carbonyl systems ranged from approximations based on the stereoelectronic properties of half-filled p orbitals to calculations using perturbation theory and *ab initio* SCF-CI methods.[1,2] Dewar and Doubleday in 1978 derived a detailed description of the singlet and triplet state intramolecular hydrogen abstraction reactions of butanal using the MINDO/3 SCF method and configuration interaction.[3] Chandra *et al.*[4] extended this treatment to include 2-pentanone, 2-hexanone, and 5-methyl-2-hexanone. Morrison and Severance[5] and Houk and coworkers[6] used *ab initio* methods to model triplet hydrogen abstraction reactions of aldehydes and the Norrish/Yang reaction of triplet butanal. Although calculated activation energy barriers (MP2/6-31G*//3-21G) were as much as 5 kcal/mol greater than the experimental barriers, it appeared likely that these results could be improved by use of more extended basis sets and inclusion of higher level electron correlation. Unfortunately, application of high level *ab initio* methodology to systems with >6–7 heavy atoms rapidly becomes impractical with the available hardware.

In view of this, we recently developed a molecular mechanics force field method to model Norrish/Yang Type II reactions of large molecules.[7–9] This protocol simulates the experimentally determined nonplanar geometry of triplet alkanones and models the transition structure as a pseudominimum.[10] Following the approach developed by Houk and co-workers,[11] force constants are approximated for partial O•H* and C•H* bonds, and stereoelectronic requirements of hydrogen abstraction are modeled by torsional forces corresponding to Cα—C=O•H* assemblages in the transition structures. Although this approach has been applied successfully to many different molecules,[8,9] the inherent limitations of molecular mechanics methodology for transition structure modeling[10] prompted us to explore approaches based on higher level theory. Given the size and complexity of the systems of interest, it appeared that only semiempirical methods can serve this end. It should be noted that none of these methods has been parameterized for open shell or excited states and that results based on single determinant theory suffer from the lack of electron correlation. In this paper, the utility of several of these methods is surveyed to determine which of them best describes the geometry of triplet alkanones and transition structures for hydrogen abstraction reactions. Decisive comparisons have been made between the *ab initio* calculated geometries of the hydrogen abstraction stages of the methane:triplet formaldehyde and triplet butanal reactions with those calculated by various semiempirical methods. In the second phase of this work, MINDO/3 activation enthalpies have been calculated for several Norrish/Yang Type II photoreactions of triplet ketones with up to 20 heavy atoms. The results are compared with experimentally determined reactivities of these systems.

Computational Methods

Coordinates for semiempirical calculations of triplet alkanones and transition structures were generated by molecular mechanics methods.[9] The default routines in MOPAC version 6.00[12] were used for full optimizations of geometry and computation of heats of formation using the keyword PRECISE. Unless otherwise noted, all optimizations were UHF calculations. Geometry opti-

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® Abstract published in *Advance ACS Abstracts,* October 15, 1994.

[1] For a review, see: Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227.

[2] (a) Chandra, A. K. *J. Photochem.* **1979**, *11*, 347. (b) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. (c) Bigot, B. *Isr. J. Chem.* **1983**, *23*, 116.

[3] Dewar, M. J. S.; Doubleday, C. *J. Am. Chem. Soc.* **1978**, *100*, 4935.

[4] Sengupta, D.; Sumathi, R.; Chandra, A. K. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 149.

[5] (a) Severance, D.; Morrison, H. *Chem. Phys. Lett.* **1989**, *163*, 545. (b) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231.

[6] Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508.

[7] Sauers, R. R.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1989**, 527.

[8] Sauers, R. R.; Huang, S.-Y. *Tetrahedron Lett.* **1990**, 5709.

[9] Sauers, R. R.; Stevenson, T. *J. Org. Chem.* **1992**, *57*, 671.

[10] For a discussion of the use of molecular mechanics methods to locate transition structures, see: Jensen, F. *J. Am. Chem. Soc.* **1992**, *114*, 1596.

[11] Eksterowicz, J. E.; Houk, K. N. *Chem. Rev.* **1993**, *93*, 2439.

[12] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1307.

0022-3263/94/1959-7061$04.50/0

mizations of transition structures used the nonlinear least-squares (NLLSQ) minimization routine. The resulting transition structures were subjected to normal coordinate analyses, and in each case only one negative eigenvalue was found. *Ab initio* SCF calculations were executed with the GAUSSIAN 92 program, revision C.4,[13] using analytic energy gradients. All structures were fully optimized using the default gradient and convergence criteria. Select structures were further characterized by normal coordinate analyses as noted in the tables. For transition structures, first-order saddle points were located which displayed one imaginary frequency corresponding to one negative eigenvalue. The degree of spin contamination for triplet configurations was less than 6% in all cases.

Results and Discussion

Initially, we focused our attention on triplet pentanone and the corresponding transition structure for intramolecular hydrogen abstraction at the γ-position. This approach was prompted by the conclusions reached by Chandra *et al.*,[4] who carried out extensive calculations of several alkanones by means of MINDO/3 methods. These authors concluded that Norrish Type II reactions proceed in two stages: (a) rotation of the lowest energy conformation of the triplet state to another "conformer" in which the reacting centers are relatively close; (b) formation of the transition structure for abstraction by further approach of the abstractable hydrogen toward the oxygen. Upon examination of structures that were reported for the 2-pentanone triplet reaction [$\Delta(\Delta H)$ = −7.729 kcal/mol and −9.77 kcal/mol], we found that they are neither real minima nor first-order saddle points. When these structures were reoptimized using the more rigorous convergence criteria invoked by the keyword PRECISE, they led to a conformer of the triplet of 2-pentanone with energy −13.7 kcal/mol (Table 1). Furthermore, normal coordinate analyses of these structures gave rise to several negative frequencies. In view of this, they have no real physical significance and we believe that the hypothesis based on these species serves no useful purpose in the analysis of Type II reactions. We extended this evaluation of the Type II process for 2-pentanone with several other semiempirical methods and found that none of them is totally satisfactory in terms of the accuracy of structural parameters and relative energies (Table 1). For example, experimental measurements of alkanone triplet states show that they are significantly puckered with carbonyl out-of-plane (OOP) angles of 35−40°.[14] Of the semiempirical methods, only MINDO/3 calculations lead to comparable OOP angles. The semiempirical methods all lead to an "early" transition structure with respect to the bond-breaking/bond-making process involving the abstracted H-atom in contrast to the reported *ab initio* calculated data for triplet formaldehyde:methane and triplet butanal systems: 1.19 Å (H-O) and 1.35 Å (C-H).[5,6] In addition, calculated $\Delta H^{\ddagger}$ energies are 4−26 kcal/mol higher than experimental values.

Table 1. Calculated Transition Structure Geometry/Reaction $\Delta H^{\ddagger}$ for 2-Pentanone Triplet H-Abstractions

	extended 2-pentanone triplet		transition structure			
method	OOP[a]	ΔH_f[b]	C-H*[c]	O-H*[c]	ΔH_f[b]	$\Delta H^{\ddagger}$[b]
AM1	0.16	−10.9	1.253	1.334	6.12	17.0
AM1[d]	3.8	−2.09	1.218	1.373	14.6	16.7
MNDO	2.87	−15.4	1.263	1.306	18.2	33.6
PM3	3.36	−11.0	1.304	1.274	7.07	18.1
MINDO/3	35.2	−13.8	1.253	1.452	−2.75	11.0
MINDO/3[e]	30.2	−1.42	1.14	1.545	8.84	10.2
MINDO/3[d]	22.9	−1.03	1.14	1.53	8.23	9.2

[a] Oxygen out-of-plane angle in degrees. [b] kcal/mol. [c] Bond distance in Å. [d] RHF; CI = 5. [e] RHF.

In an effort to resolve these discrepancies, semiempirical calculations were carried out on triplet butanal and the corresponding transition structure for the intramolecular hydrogen abstraction reaction for comparisons with literature *ab initio* values (Table 2). MINDO/3 calculations led to the most highly puckered triplet state (OOP = 36.6°) and transition structure (OOP = 36.8°), but O-H* and C-H* lengths were still not consistent with the *ab initio* values (UHF/3-21G basis set[6]). It is likely that these distances will be dependent on basis set and electron correlation effects since the triplet ketone and the biradical intermediate should have different amounts of interaction between the radical centers. In order to determine the dependency of the position of the transition structure on the reaction coordinate, we carried out extensive *ab initio* calculations on butanal triplet and the transition structure for hydrogen abstracton at the γ-carbon.[15]

The results (Table 2) show a shift toward an earlier transition structure when going from the 6-31G* basis set, which includes second-order (d-type) polarization functions on the heavy atoms, to the 6-31G**, which adds first-order (p-type) functions to the hydrogens. Addition of diffuse functions (6-311+G**), which are important in processes where lone pair electrons become bonding electrons, resulted in an even earlier transition structure. In accord with the above expectations, the most dramatic shift in the position of the transition structure was seen when second-order Møller−Plesset theory (MP2) was used to include effects of electron correlation.

Examination of all of the available data shows that the calculated O-H* and C-H* bond lengths changed from 1.191 and 1.353 Å (UHF/3-21G[6]), respectively, to 1.323 and 1.210 Å (UMP2/6-311+G**), in fair agreement with most of the semiempirical results. In all cases, the computed *ab initio* triplet states and transition structures were significantly puckered about the carbonyl center (44°), in good agreement with the MINDO/3 structures. In addition, the MINDO/3 calculated value for $\Delta H^{\ddagger}$ is closest to the highest level *ab initio* value.

We confirmed these findings by similar comparisons of the geometry and energies associated with the hydrogen abstraction reaction of the triplet formaldehyde: methane system (Tables 3 and 4).[16] Upon inclusion of p,d functions (see above) and electron correlation (UMP2/

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(13) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(14) (a) Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1990**, *94*, 4425. (b) Shah, A. K.; Moule, D. C. *Spectrochim. Acta* **1978**, *34A*, 749. (c) Jensen, P.; Bunker. P. R. *J. Mol. Spectrosc.* **1982**, *94*, 114.

(15) For a general description and discussion of basis sets, see: Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*; Gaussian: Pittsburgh, 1993; pp 110−111.

(16) Recent calculations by Hadad *et al.* (Hadad, C. M.; Foresman, J. B.; Wiberg, K. B. *J. Phys. Chem.* **1993**, *97*, 4293) using CIS methodology lead to similar results with the exception of the out-of-plane angles.

Table 2. Butanal Triplet and Transition Structure Geometry and $\Delta H^{\ddagger}(E_{act})$

	triplet state	transition structure					
method	OOP[a]	OOP[a]	C-H*[b]	O-H*[b]	C-O-H[c]	C-C-O-H*[d]	$\Delta H^{\ddagger}$[e]
MINDO/3	36.6	36.8	1.159	1.436	112.5	17.65	13.0
MNDO	0.2	2.4	1.267	1.307	108.9	2.94	34.1
PM3	20.7	8.2	1.284	1.299	108.7	5.34	18.9
AM1	1.9	4.5	1.259	1.330	109.5	4.10	31.5
UHF/3-21G	n.a.[i]	n.a.	1.353	1.191	101.0	n.a.	32.5[f,g]
UHF/6-31G*	44.4	41.4	1.323	1.209	105.3	24.22	36.2[f]
UHF/6-31G**	43.8	40.8	1.305	1.215	105.5	23.88	34.1[f]
UHF/6-311+G**	43.5	40.3	1.300	1.222	105.4	23.73	33.3[f]
UMP2/6-31G*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	14.0[f,g]
UMP2/6-31G**[h]	46.0	42.8	1.217	1.299	105.0	25.25	14.9[f]
UMP2/6-311+G**	45.6	42.5	1.210	1.323	104.5	25.97	13.3[f]

[a] Oxygen out-of-plane angle in degrees. [b] Bond distance in Å. [c] Bond angle in degrees. [d] Torsion angle in degrees. [e] kcal/mol. [f] Electronic E_{act}. [g] Reference 6. [h] Normal coordinate analysis. [i] n.a. = not available.

Table 3. Comparisons of Transition Structure Geometry/Total Energy for Triplet Formaldehyde:Methane Abstraction

geometric parameters	UHF/6-31G*	UHF/6-31G**	UHF/6-311+G**	UHF/6-311++G**	UMP2/6-31G**	UMP2/6-311+G**
O-H[a]	1.193	1.198	1.207	1.207	1.259	1.283
C-H[a]	1.319	1.305	1.298	1.298	1.221	1.211
C-O-H*[b]	108.1	108.2	108.4	108.4	107.6	107.5
O-C-H*[b]	177.1	176.6	177.3	177.2	172.0	172.9
H-C-O-H*[c]	28.0	26.96	26.21	26.20	26.56	24.85
electronic energy[d]	−153.93011[e,f]	−153.94360	−153.98440	−153.98453	−154.39201	−154.46744[g]

[a] Bond length in Å. [b] Bond angle in degrees. [c] Torsion angle in degrees. [d] In hartree units. [e] Reference 5a. [f] Reference 6. [g] Normal coordinate analysis.

Table 4. Transition Structure Geometry for Triplet Formaldehyde:Methane Abstraction

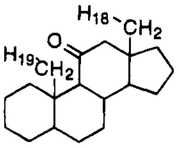
geometric parameters	MINDO/3	AM1	PM3	MNDO
O-H*[a]	1.367	1.279	1.235	1.278
C-H*[a]	1.148	1.247	1.251	1.264
C-O-H*[b]	121.6	111.7	113.2	114.4
O-C-H*[b]	175.2	173.2	178.9	175.7
H-C-O-H*[c]	32.13	1.32	1.29	0.006

[a] Bond length in Å. [b] Bond angle in degrees. [c] Torsion angle in degrees.

6-311+G**) in the basis sets, the transition structure shifts from a "late" to an "early" one: O-H* 1.177 Å (UHF/3-21G)[5b] → 1.283 Å (UMP2/6-311+G**); and C-H* 1.350 Å (UHF/3-21G)[5b] → 1.211 Å (UMP2/6-311+G**). MINDO/3 reproduces the early transition structure fairly closely except for the C-O-H* angle.

An early transition structure is consistent with the experimental results of Bibart *et al.*,[17] who evaluated intramolecular hydrogen abstraction rates for primary, secondary, and tertiary systems from triplet quenching data in *n*-heptane. The narrow spread in reactivity, 1:15:95, respectively, is reminiscent of the reactivity trends found in free radical hydrogen abstraction reactions by highly reactive species, e.g. trichloromethyl or phenyl radicals.[18]

In view of the above results, we chose to examine a more extended series of Type II photoreactions by means of the MINDO/3 Hamiltonian for which we report computed activation enthalpies $\Delta H^{\ddagger}$ [$\Delta H_{f(\text{transition state})} - \Delta H_{f(\text{triplet state})}$]. Our expectation was that the relative $\Delta H^{\ddagger}$ values would have predictive value since most of the ketones under comparison are fairly rigid and differences in entropic contributions would be minimal.[19] Initially, we discuss MINDO/3 calculated $\Delta H^{\ddagger}$ values (Table 5) for hydrogen abstractions in the systems **1**−**5** that were examined earlier by molecular mechanics methodology[7−9] because these molecules span a wide range of behavior and structure and represent useful reference points.



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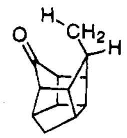

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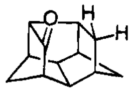

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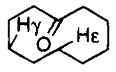

4, 5

Jeger and co-workers provided several examples of phototransformations of 11-ketosteroid systems in which the predominant reaction involved intramolecular cyclobutanol formation *via* abstraction of the C_{19} hydrogen atom followed by cyclization.[20] These systems represent ideal models for computational analysis because intramolecular comparisons are likely to be more accurate than comparisons between separate molecular assemblies. We modeled these structures with framework **1** and calculated MINDO/3 energies for the triplet state of ketone **1** and the two competing transition structures for hydrogen abstraction. H-atom abstraction from carbon 18 was found to have an activation enthalpy 14 kcal/mol higher than that for abstraction from C_{19}, a result that is consistent with the experimental observation of complete hydrogen abstraction at C_{19}. It is interesting to note that the reaction at C_{19} has a smaller calculated $\Delta H^{\ddagger}$ than that for the 2-pentanone triplet (11.0 kcal/mol).

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(17) Bibart, C. H.; Rockley, M. G.; Wettack, F. S. *J. Am. Chem. Soc.* **1969**, *91*, 2802.

(18) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 783.

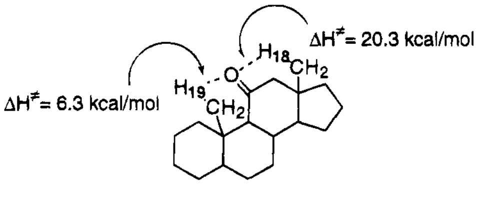
(19) Lewis *et al.* (Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100) have suggested rate factors of 5−8 for each internal rotation which must be frozen in the transition state. In most of the systems discussed, no bond rotations need to be frozen.

(20) Zink, P. M.; Wolf, H. R.; Muller, E. P.; Schweizer, W. B.; Jeger, O. *Helv. Chim. Acta* **1976**, *59*, 32.

Table 5. MINDO/3 Transition Structures and H-Abstraction $\Delta H^{\ddagger}$

	ketone triplet			transition structure				
ketone	C=O* [a]	OOP[b]	$\Delta H_f{}^{c,d}$		C-H* [a]	O-H* [a]	ΔH_f	$\Delta H^{\ddagger}$ [c]
1	1.27	37.7	35.6	**18-TS**	1.19	1.35	55.9	20.3
				19-TS	1.16	1.44	41.9	6.3
2	1.24	44.6	96.8	**2-TS**	1.20	1.31	123.5	26.7
3	1.24	44.1	104.5	**3-TS**	1.18	1.36	123.8	19.3
4	1.27	22.2	−27.2	**4-TS**	1.18	1.37	−7.9	19.3
5	1.28	23.5	−26.9	**5-TS**	1.17	1.46	−13.9	13.0
6	1.26	41.4	4.70	**6-TS**	1.28	1.50	11.2	6.5
7	1.26	38.7	87.9	**7-TS**	1.16	1.41	100.2	12.3
8	1.26	22.7	49.2	**8-TS**	1.16	1.40	64.8	15.6
9	1.25	42.4	73.8	**9-TS**	1.18	1.38	93.4	19.6
10 (R = H)	1.27	27.5	1.72	**13**	1.15	1.46	10.38	8.66
12 (R = H)	1.27	23.7	2.62	**14**	1.15	1.46	11.92	9.30
15	1.27	27.2	−41.0	**16-TS**	1.18	1.42	−24.4	16.6
	1.21	0.2						

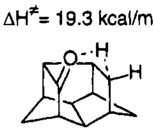
[a] Bond length in Å. [b] Out-of-plane carbonyl angle in degrees. [c] kcal/mol. [d] Lower energy conformer.



1-TS

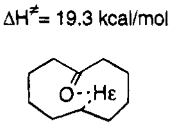
At the other extreme, the pentacyclic ketone **2** was predicted to be unreactive toward hydrogen atom transfer on the basis of the large increase in calculated MM2 steric strain as the transition structure is formed. The MINDO/3 calculated barrier ($\Delta H^{\ddagger}$ = 26.7 kcal/mol) is significantly higher than those described for Type II reactive systems. Consistent with these results are the detailed photochemical and photophysical studies of **2** and related compounds from which no evidence of triplet carbonyl: hydrogen abstractions could be found.[9]

The behavior of a hydroxy analog of pentacyclic ketone **3** has been widely cited as an example of a system whose unreactivity in the Norrish/Yang reaction is controlled by stereoelectronic factors.[21,22] Because MM2 calculations gave a steric energy increase only slightly higher than that found for the cyclodecanone-γ-H reaction, we considered this system borderline and were stimulated to undertake a more detailed computational study. Since the MINDO/3 calculated $\Delta H^{\ddagger}$ is 19.3 kcal/mol (**3-TS**), a value comparable to that obtained for the observable cyclodecanone-ϵ-H abstraction reaction, we investigated the photochemistry of **3** and found that it undergoes Type I cleavage upon irradiation in methanol.[23] In view of this, it cannot be stated unequivocally that the geometry of **3** precludes Type II reactions.

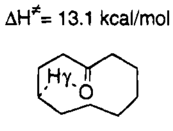


3-TS

Bernard and Yang observed the formation of 10-decalol upon irradiation of cyclodecanone in cyclohexane, the result of hydrogen abstraction at the ϵ-carbon.[24] Despite this fact, MM2 calculations led to the expectation that hydrogen abstraction at the γ-carbon would be preferred over abstractions at other sites.[8,25] Resolution of this conflict was provided by experiments that demonstrated that cyclodecanone photochemistry was solvent dependent. We found that the major product of irradiation in alcoholic solvents was bicyclo[6.2.0]decan-1-ol, the product of hydrogen abstraction at the γ-carbon. The experimental results reflect the fact that hydrogen abstractions are at least partially reversible in hydrocarbon solvents and that the observed products under those conditions are controlled mainly by thermodynamic factors. In hydroxylic solvents the hydrogen abstraction step is at least partially irreversible and the observed products are formed (predominantly) by kinetically controlled hydrogen abstractions. The MINDO/3 calculations shown below are in qualitative agreement with both the MM2 calculations and the experimental results.

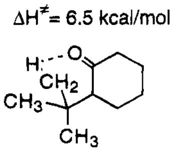


4-TS



5-TS

2-*tert*-Butylcyclohexanone (**6**) is an example of a prefolded model of 2-pentanone in that a hydrogen atom is inevitably positioned at nearly the correct geometry for abstraction. It is of interest that the calculated value of $\Delta H^{\ddagger}$ for hydrogen abstraction, 6.5 kcal/mol, is considerably less than that for 2-pentanone (11.1 kcal/mol). Consistent with these results, triplet ketone **6** undergoes Type II elimination with a rate constant of *ca.* 5×10^8 s^{-1} (methanol) *vs* $1.8{-}3.3 \times 10^6$ s^{-1} (acetonitrile−water)



6-TS

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[21] Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227.

[22] Sugiyama, N.; Nishio, T.; Yamada, K.; Aoyama, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1879.

[23] Unpublished results.

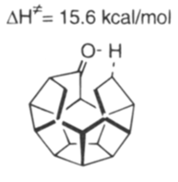
[24] (a) Barnard, M.; Yang, N. C. *Proc. Chem. Soc.* **1958**, 300. (b) Schulte-Elte, K. H.; Willhalm, B.; Thomas, A. F.; Stoll, M.; Ohloff, G. *Helv. Chim. Acta* **1971**, *54*, 1759.

[25] Entropic differences may play a significant role in these competing reactions due to the highly flexible nature of the ring systems.

for the 2-pentanone triplet.[26] This reactivity difference is partly attributable to entropic factors since one-bond rotation in the 2-pentanone triplet must be frozen to generate a reactive conformation.[19]

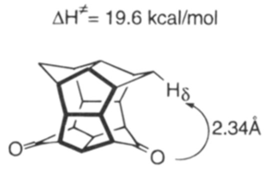
The ketones **7** and **8** were used by Paquette *et al.*[27] as key intermediates in synthetic approaches to dodecahedranes. Each of them undergoes intramolecular abstraction of remote hydrogen atoms followed by photocyclization to produce homocyclic systems. System **8** is an example of a reactive alkanone in which the abstractable hydrogen atom lies above the π-realm of the ground state carbonyl group. Despite this, the excited state is sufficiently flexible that the Cα—C=O*—H assemblage can easily attain an angle of *ca.* 19° in the transition structure for hydrogen abstraction. The calculated MINDO/3 values of $\Delta H^{\ddagger}$ for **7** and **8**, 12.3 and 15.6 kcal/mol, respectively, are commensurate with values for other reactive systems.

7-TS



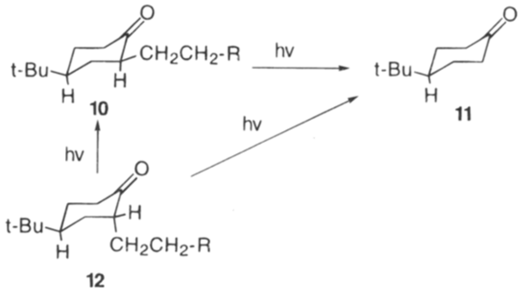
8-TS

Another interesting alkanone was recently examined by Prinzbach and co-workers,[28] who were seeking new routes to dodecahedranes *via* pagodanes. These authors examined the diketone **9** by molecular mechanics and noted that the ground state oxygen:δ-hydrogen distances were below the 2.7 Å "critical limit" defined by Scheffer *et al.* for successful intramolecular hydrogen abstractions in the solid phase.[29] This finding suggested that a double intramolecular H-transfer followed by cyclization would provide a useful synthetic entry into a novel ring system. On the other hand, the authors noted that the δ-hydrogen atoms are positioned nearly perpendicular to the (ground state) carbonyl plane and suggested that normal n,π^* carbonyl photochemistry might be inhibited as a consequence. It was reported that "No structural change at all could be accomplished" on irradiation of **9** at >280 nm in several different solvents, e.g. acetonitrile, isooctane, tetrahydrofuran; addition of *tert*-butyl alcohol was without effect. MINDO/3 calculations give rise to a $\Delta H^{\ddagger} \sim 20$ kcal/mol, a value not significantly different from that found for e-H-abstraction in cyclodecanone. It is likely that reversible Type I reactions and/or reversible hydrogen abstraction reactions are involved in the deactivation of triplet **9**. It is also possible that there is an unusually high barrier for *syn*−*anti* interconversion about the carbonyl triplet center. This would have the effect of prolonging the triplet lifetime in the unfavorable *anti*-conformation. We were unable to locate a minimum energy structure for the *syn*-conformation at the carbonyl triplet center.



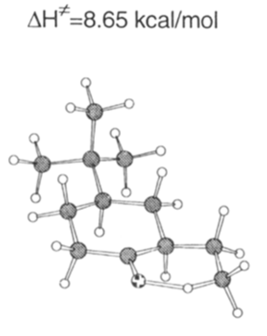
9

Scheme 1



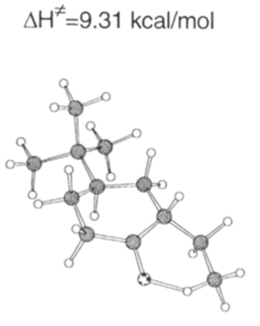
The energetics and structures of the photocleavage reactions of the epimeric 2-ethyl-4-*tert*-butylcyclohexanones **10** and **12** (R = H) were also examined. These isomers serve as models for the propyl analogs (R = CH_3) that have been widely cited as examples of Type II reactions that are controlled by stereoelectronic factors[30] since Type II product **11** was obtained more efficiently from **10** than from **12** [ratio of quantum yields *ca.* 10:1 in cyclohexane; see Scheme 1 (R = CH_3)].[30b]

The results of MINDO/3 calculations [$\Delta(\Delta H^{\ddagger}) = 0.66$ kcal/mol] suggest that the major difference in observed Type II reactivity is not due to enthalpy differences but may be entropic in origin or a consequence of a highly competitive Type I process from the axial isomer **12**. The MINDO/3 transition structure **13** derived from **10** utilizes chair-chair forms readily accessible from the most likely initial conformation, but the corresponding structure **14** derived from **12** is somewhat distorted and its attainment undoubtedly requires significant restriction of bond angle and rotational motions. In any event, it is clear that no simple stereoelectronic factor accounts for the difference in reactivity between **10** and **12**.



13

MINDO/3 transition structure from *cis*-isomer **10**



14

MINDO/3 transition structure from *trans*-isomer **12**

cis-2,5-Decalindione (**15**) represents a good example of a complex system that can be expeditiously analyzed by MINDO/3 methodology, but one whose Type II reactivity would be difficult to evaluate by an examination of

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[26] (a) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 7213. (b) Encinas, M. V.; Lissi, E. A.; Scaiano, J. C. *J. Phys. Chem.* **1980**, *84*, 948.

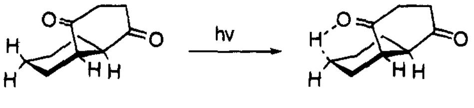
[27] (a) Paquette, L. A.; Weber, J. C.; Kobayashi, T. Mihayara, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8591. (b) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774.

[28] Lutz, G.; Pinkos, R.; Murty, B. A. R. C.; Spurr, P. R.; Fessner, W.-D.; Wörth, H. F.; Knothe, L.; Prinzbach, H. *Chem. Ber.* **1992**, *125*, 1741.

[29] Scheffer, J. R.; Trotter, J.; Omkaram, N.; Evans, S. V.; Ariel, S. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 169.

[30] (a) Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 2125. (b) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barlthrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 7213.

molecular models or other means. The formation of a cyclobutanol in this reaction is consistent with the calculations which give rise to a $\Delta H^{\ddagger}$ of 16.6 kcal/mol.[31]



15 **15-TS**

In summary, we have demonstrated that MINDO/3 methodology can be used to gain insights into Norrish Type II photoreactions by calculation of the $\Delta H^{\ddagger}$ associated with the hydrogen abstraction stage. It is no longer necessary to rely on structural features of ground states as indicators of triplet ketone reactivity since good approximations of the structure and energy of the triplet states and transition structures can be readily generated. Ketones with $\Delta H^{\ddagger}$ values in the range 6 to 19 kcal/mol are associated with reactive systems provided that side reactions do not intervene. Several ketones with $\Delta H^{\ddagger} \geq$ 20 kcal/mol do not undergo Norrish Type II reactions, at least in part, as a result of competitive Type I photocleavage.[9,19,20a] For the moment, we are unable to define a $\Delta H^{\ddagger}$ limit beyond which Type II photochemistry is effectively barred. We are extending these studies experimentally and computationally[32] by examination of untested ketones.

Acknowledgment. We thank K. Krogh-Jespersen for helpful advice, J. Pelaschier for technical help, and Prof. A. K. Chandra for comments concerning semiempirical calculations. We also acknowledge the Pittsburgh Supercomputing Center for allocation time on the Cray C90 (Grant No. CHE930027P).

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(31) Sugiyama, N.; Yamada, K.; Aoyama, H. *J. Chem. Soc. C* **1971**, 830.

(32) A referee has expressed concern that AM1 methods might be expected to give "more dependable" trends because they reproduce weak hydrogen bonds acccurately. This comment may or may not be relevant since the systems in question have one less electron. The fact that MINDO/3 includes some differential overlap may be an important factor in the observed correlations. For more detailed discussions of these methods and comparisons see: Stewart, J. J. P. *J. Computer-Aided Mol. Des.* **1990**, *4*, 1–105 and Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985; Chapter 4.