Molecular Mechanics Explorations with 1,2-Dioxetanes

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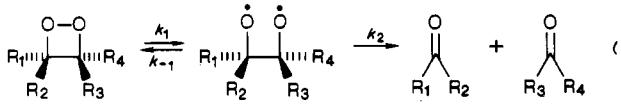
Molecular mechanics (MM2) force field parameters were developed for dioxetanes, based on heats of formation of alkyl-substituted dioxetanes and dialkyl peroxides, which can be readily calculated by the Benson additivity method. Further fitting was made to some reported OCCO dihedral angles of dioxetanes and dialkyl peroxides. MM2 calculations were also made on the 1,4-dioxybutane biradicals corresponding to the dioxetanes and some noticeable differences were observed between the Benson and MM2 heats of formation, and the origin of these differences was sought. Several correlations were attempted between E_a and $\Delta G^{\ddagger}$ for the thermolysis of dioxetanes and the MM2 derived heats of formation, strain energy, and geometries of dioxetanes and biradicals. The better correlations were between $\Delta G^{\ddagger}$ and the dioxetane strain energy, the biradical strain energy, and $(\angle OCCO)^2$ of the dioxetane. On the basis of the correlations of $\Delta G^{\ddagger}$ between both dioxetane and biradical strain energy, it was concluded that the transition structure was intermediate between the dioxetane and biradical. This was further supported by a slope of 0.60 in the correlation of $\Delta G^{\ddagger}$ with the difference in strain energies between the gauche biradicals and the dioxetanes. Comparisons were made between Benson thermochemical kinetic calculations of E_a for dioxetane thermolysis and MM2 derived data. The spread in calculated E_a values between dioxetane and tetramethyldioxetane by the Benson method is not as large as observed experimentally, while there is essentially no difference in the calculated E_a values for these dioxetanes by the MM2 method. A possible reason for this compression in the spread of calculated E_a values is that the back activation energy may not be constant as is assumed by the thermochemical kinetic method. With MM2 data, this proposal was supported in terms of a correlation between calculated E_{-1} values and the Taft steric substituent constant.

Several years ago we used the thermochemical kinetic method of Benson[1] to estimate activation parameters for the thermolysis of 1,2-dioxetane and its methylated derivatives.[2] Arrhenius activation energies are evaluated from eq 1, based on the stepwise mechanism as given in eq 2.

$$E_a = \Delta H^\circ_{1,-1} + E_{-1} \quad (1)$$



Here, $\Delta H^\circ_{1,-1}$ is the difference between the heats of formation of the biradical and the dioxetane and E_{-1} is the activation energy of the back reaction to re-form the dioxetane from the biradical. Heats of formation of the biradical and the dioxetane are calculated by the group additivity method to give $\Delta H^\circ_{1,-1}$, and an observed E_a value for one dioxetane is used to obtain E_{-1}. Then other dioxetane E_a values are obtained from eq 1 with this constant E_{-1} value and calculated $\Delta H^\circ_{1,-1}$ values. The trend to larger activation energies with increased methylation that is observed experimentally was qualitatively followed in the calculated activation energies. More recently Adam and Baader[3] have determined activation parameters for the entire series of methylated dioxetanes as well as the parent dioxetane. Again, both the calculated and experimental activation energies increased with increased methylation, but the spread in calculated activation energies with increased methylation is too small. That is, the calculated activation energy is too large for dioxetane, while it is too small for tetramethyl-1,2-dioxetane. The reason for this difference between calculated and observed activation energies is uncertain. There is sufficient evidence that for simply substituted dioxetanes[3] the mechanism of thermolysis is either a stepwise biradical process or, if concerted, it has the kinetic characteristics of a biradical process. Thus, the biradical mechanism of eq 2, upon which the calculations are based, should be a reasonable model. The difficulty in calculating mutually satisfactory E_a values for dioxetane and tetramethyldioxetane from eq 1 could reside in $\Delta H^\circ_{1,-1}$, where the cis and gauche corrections are most suspect. Also, there is the question as to whether or not E_{-1} is a constant in eq 1 as is assumed by the thermochemical kinetic method. This too could be responsible for the small spread in calculated E_a values for dioxetane and tetramethyldioxetane.

Molecular mechanics is an attractive alternative method that can be used to obtain the necessary thermodynamic quantities to calculate E_a from eq 1.[4] By this means, it may be possible to avoid some of the uncertainties in calculating heats of formation, where cis and gauche corrections are involved. Furthermore, it may be possible to find empirical correlations between activation energy or free energy of activation and physical properties from molecular mechanics calculations, such as strain energy.[5] For example, correlations of rates or free energies of activation of solvolysis reactions,[5a–h] thermolysis of azoalkanes,[5h] thermolysis of peresters,[5h,i] homolysis of C–C bonds,[5i–l] and hydrogen atom abstraction[5m] have been made from physical properties derived from molecular mechanics calculations. Unfortunately, not all of the molecular mechanics force field parameters for dioxetanes were available at the inception of this work. Our first task was to develop a set of these parameters for dioxetanes. The necessary parameters to calculate thermodynamic and structural quantities of dioxetanes by the MM2 molecular mechanics program of Allinger[4] are reported here. Correlations between activation energy and the MM2 output

(1) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York, 1976.
(2) O'Neal, H. E.; Richardson, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553; **1971**, *93*, 1828.
(3) Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410.
(4) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177, American Chemical Society: Washington, DC, 1982.
(5) (a) Schneider, H.-J.; Becker, N.; Schmidt, A.; Thomas, F. *J. Org. Chem.* **1986**, *51*, 3602. (b) Bentley, T. W. *Ibid.* **1985**, *50*, 5852. (c) Schneider, H.-J.; Schmidt, G.; Thomas, F. *J. Am. Chem. Soc.* **1983**, *105*, 3556. (d) Osawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1. (e) Schneider, H.-J.; Thomas, F. *J. Am. Chem. Soc.* **1980**, *102*, 1424. (f) Osawa, E.; Engler, E. M.; Godleski, S. A.; Inamota, Y.; Kent, G. J.; Kausch, M.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 984. (g) Lomas, J. S.; Pham, K. L.; Dubois, J. E. *Ibid*, **1979**, *44*, 1647. (h) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189. (i) Ruchardt, C.; Golzke, V.; Range, G. *Chem. Ber.* **1981**, *114*, 2769. (j) Ruchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429. (k) Lomas, J. S. *J. Org. Chem.* **1985**, *50*, 4294. (l) Lomas, J. S.; Dubois, J. E. *Ibid.* **1982**, *47*, 4505. (m) Koch, V. R.; Gleicher, G. J. *J. Am. Chem. Soc.* **1971**, *93*, 1657. Detar, D. F. *J. Org. Chem.* **1987**, *52*, 1851.

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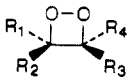
Table I. Basis Set of Dioxetanes and the Resulting MM2 Output Parameters[a]



no.	R_1	R_2	R_3	R_4	E_a(obs)[b]	$\Delta G^{\ddagger}$(obs)[c]	$\Delta H_f°$(Benson)[d]	$\Delta H_f°$-(MM2)	diff	E_{strain}(D)[e]	∠OCCO, deg
1	H	H	H	H	22.7	23.2	0.0	1.06	1.06	27.14	0.59
2	Me	H	H	H	22.8	23.3	−9.18	−8.30	0.88	27.12	6.49
3	Me	Me	H	H	24.5	24.3	−18.66	−17.88	0.78	27.06	4.06
4	Me	H	Me	H	24.1	24.0	−18.36	−17.75	0.61	26.99	9.42
5	Me	H	H	Me	24.8	24.2	−17.36	−17.17	0.19	27.87	0.05
6	Me	Me	Me	H	26.0	25.0	−26.84	−26.46	0.38	27.82	9.55
7	Me	Me	Me	Me	27.8	26.2	−35.32	−34.54	0.78	29.26	11.47
8	Et	Et	Et	Et	30.8	27.5	−49.66	−49.78	−0.12	34.39	16.47
9	Me	Me	Me	*n*-Bu	25.3	25.6	−48.91	−48.79	0.12	30.20	15.32
10	Et	H	H	Et	24.5	24.0	−26.60	−26.82	−0.22	28.11	7.14
11	Et	H	Et	H	24.9	24.4	−27.60	−27.98	−0.38	27.05	10.24
12	*n*-Pr	H	H	*n*-Pr	24.5	24.0	−36.48	−37.07	−0.59	27.95	0.43
13	*n*-Pr	H	*n*-Pr	H	25.0	24.4	−37.48	−38.12	−0.64	26.90	10.26
14	*n*-Bu	H	H	*n*-Bu	24.6	24.4	−46.34	−47.22	−0.88	27.89	7.42
15	*n*-Bu	H	*n*-Bu	H	25.1	24.6	−47.34	−48.31	−0.97	26.79	10.75
16	Et	Et	H	H	24.9	24.4	−26.12	−26.21	−0.09	28.92	1.13
17	Me	Me	Et	H	24.7	24.6	−31.47	−31.46	0.01	27.90	10.15
18	Me	Et	H	H	24.5	24.0	−22.42	−21.94	0.48	28.10	5.54
19	Me	*n*-Pr	H	H	24.6	24.1	−27.33	−27.01	0.32	28.07	4.80
20	Me	*n*-Bu	H	H	24.4	24.1	−32.26	−31.64	0.62	28.49	6.44
21	Me	*i*-Pr	H	H	25.0	24.4	−27.76	−28.29	−0.53	28.93	7.88
22	Me	*t*-Bu	H	H	25.8	25.1	−34.12	−34.04	0.08	31.23	5.60
									av ±0.49		

[a] kcal/mol. [b] References 3 and 6. [c] 60 °C. [d] Reference 1. [e] D indicates dioxetane.

Table II. Basis Set of Dialkyl Peroxides and the Resulting MM2 Output Parameters[a]

R_1OOR_2

no.	R_1	R_2	$\Delta H_f°$-(Benson)[b]	$\Delta H_f°$-(MM2)	diff	∠OCCO, deg
1P	Me	Me	−30.0	−29.07	0.93	119.01
2P	Et	Et	−46.1	−46.38	−0.28	179.45
3P	*i*-Pr	*i*-Pr	−63.1	−64.23	−1.13	177.92
4P	*t*-Bu	*t*-Bu	−81.5[b]	−82.73	−1.23	166.18
5P	*t*-Bu	*n*-Bu	−73.3	−73.87	−0.57	177.27
6P	*t*-Bu	Me	−55.3	−55.89	−0.59	174.75
7P	*t*-Bu	Et	−63.4	−64.38	−0.98	177.22
8P	*t*-Bu	*i*-Pr	−72.3	−73.45	−1.15	179.01
9P	Et	*i*-Pr	−54.2	−55.27	−1.07	170.61
10P	Me	Et	−37.3	−38.00	−0.70	179.40
11P	Me	*i*-Pr	−46.1	−46.85	−0.75	173.16
12P	Me	3-heptyl	−65.3	−64.75	0.55	172.26
					av ±0.83	

[a] kcal/mol. [b] Reference 1.

quantities are tested and finally, the calculation of E_a from eq 1 by means of MM2 data is considered with respect to E_a values derived from the Benson additivity method.

Results

There is a scarcity of thermodynamic or structural data available for dioxetanes or dialkyl peroxides that can be used to generate the required MM2 parameters for these compounds. In order to obtain the necessary MM2 parameters, we carried out a multilinear regression fit between calculated heats of formation[1] and the MM2 bending and torsional parameters that were required. Basis sets of dioxetanes and dialkyl peroxides, as given in Tables I and II, were used for this purpose. Only simple alkyl groups were used in the basis sets in order to minimize problems in the calculation of the heats of formation. Finally, parameterization was done with the aid of reported dihedral OCCO angles in dimethyl peroxide,[6] di-*tert*-butyl peroxide,[7] dispiro[tricyclo[3.3.1.1^{3,7}]decane-2,3′-[1,2]dioxetane-4′,2″-tricyclo[3.3.1.1^{3,7}]decane,[8] and *trans*-2,3-bis(bromomethyl)-2,3-dimethyl-1,2-dioxetane.[9] The MM2 calculations were performed on a PC/AT with the program PCMODEL[10] and were checked for selected compounds with

Table III. MM2 Parameters for Dioxetanes and Dialkyl Peroxides

torsional	V_1	V_2	V_3
∠CCCO	0.100	0.100	0.180[a]
∠COOC	0.300	−1.00	0.300
∠CCOO	0.390	0.593	0.403
∠COOLp	0.000	0.000	0.000[a]
∠LpOOLp	0.000	0.000	0.000[a]
∠COOC(4-ring)	0.130	0.314	1.55
∠CCOO(4-ring)	0.130	0.314	1.55
∠OCCO(4-ring)	0.130	0.314	1.55

bending	k_B	θ, deg
∠COLp	0.350	105.16[a]
∠OOLp	0.350	103.26[a]
∠LpOLp	0.240	131.00[a]
∠CCO	0.700	107.50[a]
∠COO	0.770	104.00
∠COO(4-ring)	0.500	104.00
∠CCO(4-ring)	0.530	107.40[a]

O–O bond enthalpy = 12.8 kcal/mol (normal); (32.3 kcal/mol, strainless)[b]

[a] Reference 11. [b] Calculated from BE(O–O,SL) = E_{strain} + ∑BE(n) − ∑BE(SL), where BE is bond enthalpy, SL strainless, and n is normal. The Allinger values for ∑BE(n) and ∑BE(SL) are used. The BE(O–O, SL) value reported in this table is an averaged of the basis set dioxetanes given in Table I.

(6) Adam, W.; Cilento, G. *Chemical and Biological Generation of Excited States*; Academic Press: New York, 1982.

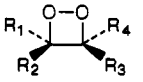
(7) Haas, B.; Oberhammer, H. *J. Am. Chem. Soc.* **1984**, *106*, 6146.

(8) Rademacher, P.; Elling, W. *Liebigs Ann. Chem.* **1979**, 1473.

(9) Adam, W.; Arias, L. A.; Zahn, A.; Zinner, K. *Tetrahedron Lett.* **1982**, 3251.

(10) PCMODEL, Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076. PCMODEL is modified version of C. Still's (Columbia University) MODEL program (VAX version 1.1) modified by Kosta Steliou (University of Montreal) and adapted to the IBM-PC by M. Mark Midland (University of California, Riverside) and worked on further by K. E. Gilbert and J. J. Gajewski (Indiana University).

Table IV. MM2 Output Parameters for Miscellaneous Dioxetanes[a]



no.	R_1	R_2	R_3	R_4	E_a(obs)[b]	$\Delta G^{\ddagger}$(obs)[c]	$\Delta H_f°$(MM2)	E_{strain}(D)[d]	∠OCCO, deg
23	$BrCH_2$	Me	$BrCH_2$	Me	27.6	26.2	−23.09	33.16	16.04[e]
24	Me	Me	Me	CH_2Br	28.4	26.2	−29.77	30.26	14.23
25	EtO	H	H	EtO	23.6	23.1	−96.97	24.70	5.98
26	Me	Me	MeCO	H	26.4	24.3	−56.89	28.26	11.65
27	Me	Ph	H	H	22.9	23.8	125.30	28.38	7.66
28	$PhCH_2$	$PhCH_2$	H	H	24.2	24.2	256.59	29.31	8.44
29	Ad–		Ad–		34.6	33.0	−40.80	56.41	21.92[f]
30	H	$-(CH_2)_4-$		H	22.5	22.4	−19.34	27.15	16.95
31	$-(CH_2)_5-$		$-(CH_2)_5-$		27.7	26.3	−48.75	30.04	13.78
32	Me	$-(CH_2)_4-$		Me	25.7	24.3	−36.78	28.76	19.07
33		$-(CH_2)_4-$			26.3	25.3	−28.19	33.34	7.99
		$(CH_2)_3$							
34		$-(CH_2)_5-$			29.8	27.9	−28.15	39.13	12.63
		$(CH_2)_3$							
35					35.6	32.8	−36.85	62.66	22.56

[a] kcal/mol. [b] Reference 6. [c] 60 °C. [d] D indicates dioxetane. [e] Experimental ∠OCCO(X-ray), 15.3°, ref 9. [f] Experimental ∠OCCO(X-ray), 21.3°, ref 9.

the Allinger QCPE MM2 1977 program installed on a CDC Cyber-750 and with the Molecular Design Ltd. version of MM2. Population (POP = $0.35(n - 1) + 0.30$) and torsional (TOR = $0.36n$) corrections were made to the heats of formation of alkyl-substituted dioxetanes, where n is the number of n-butane torsions.[4]

The MM2 parameters that were generated, along with some key parameters reported by Allinger[11] are given in Table III. With these parameters, MM2 calculations on the miscellaneous dioxetanes given in Table IV were made and the last three columns give the MM2 results. In order to carry out thermochemical kinetic calculations with eq 1, where MM2 calculated values of $\Delta H°_{-1,-1}$ are used, it was necessary to perform MM2 calculations on the dioxy biradicals that correspond to the dioxetanes in Tables I and IV. The results of these MM2 calculations on anti and gauche biradical conformations are given in Table V. The biradical structures were typically generated by deleting the O–O bond in the dioxetane with the PCMODEL program. The MM2 C–O• bond enthalpy term is unknown and PCMODEL uses the alcohol/ether bond enthalpy, so that the calculated heats of formation are erroneous. To these calculated heats of formation from PCMODEL was added a correction of 53.74 kcal/mol so as to give the best average fit to the Benson heats of formation of biradicals **1B–7B**.

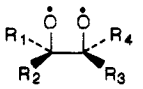
It is seen that the difference between the MM2 and Benson heats of formation is on the average greater for the biradicals than for the dioxetanes. Since these differences could arise from different gauche corrections in the Benson and MM2 calculations, it was of interest to deduce them from the MM2 calculations of gauche and anti biradicals and to compare these values with those used in the Benson method. From the heats of formation of gauche and anti **1B** in Table V, the gauche O,O ($G_{O,O}$) correction of 0.07 kcal/mol is obtained. In anti **4B**, the gauche corrections are $[G_{C,C} + 2G_{C,O}]$, while in gauche **4B** the corrections are $[G_{C,C} + G_{O,O}]$. The difference between these corrections ($g - a = G_{O,O} - 2G_{C,O}$) equals the difference in the heats of formation of the two conformers ($\Delta\Delta H_f(g - a) = -4.63 - (-3.73) = -0.90$ kcal/mol). With this relationship and the previous value for $G_{O,O}$ of 0.07 kcal/mol, one obtains $G_{C,O} = 0.49$ kcal/mol. In a similar manner, one obtains $G_{C,C} = 0.55$ kcal/mol with the preceding gauche corrections and the anti and gauche conformers of **5B**. For comparison, the Benson and (MM2) values are (in kcal/mol): $G_{O,O} = 0.3$ (0.07), $G_{C,O} = 0.3$ (0.49), and $G_{C,C} = 1.0$ (0.55). The overall lower gauche corrections in the MM2 calculation will then cause biradical heats of formation to be lower in sterically more congested molecules relative to the Benson values. In other words, there will be a smaller spread in biradical heats of formation due to gauche corrections by the MM2 calculations as compared to Benson calculations. This will cause a similar trend in $\Delta H_{1,-1}$ of eq 1 so that, based on the gauche corrections in biradical alone, the spread in E_a value for dioxetanes will be smaller by the MM2 calculations.

Several correlations were attempted between the MM2 output data and the Arrhenius activation energy and the free energy of activation. Correlations with the free energy of activation have an advantage in that they are directly related to the experimental rate constants. In contrast, the experimental rate constants are effectively subdivided into the Arrhenius activation energy and the log A term. This subdivision is a potential source of error in the Arrhenius activation energy. For this reason, correlations were made with both of these activation energies. Where biradicals are involved in the MM2 correlation parameter, such as in the strain energy of the biradical (E_{strain}(B)) and in ΔE_{strain}(B – D), the correlations can be based on either the lowest energy or the gauche conformation biradical. Correlations with gauche biradicals would reflect the conformation of the biradical that is initially produced upon thermolysis of the dioxetane according to the biradical mechanism. Tables VI and VIII report correlations with the lowest energy biradical, which may be either anti or gauche. Note that some of correlations that are given in this table are independent of the biradical conformation. In Tables VII and IX, correlations are given with gauche biradicals. If one considers the error in the activation energies, which is typically ±0.5 to 1.0 kcal/mol within a given laboratory and this may be even higher between different laboratories, some of the correlations are very good. The best indicator of the correlation is $S_{y,x}$, the standard deviation of y (either E_a or $\Delta g^{\ddagger}$) on x (the MM2 parameter), since the correlation coefficient (r) is dependent on the slope of the correlation.[12] Correlations

(11) Allinger, N. L., updated parameters, 6/18/87.

(12) Davis, W. H.; Pryor, W. A. *J. Chem. Ed.* **1976**, *53*, 270.

Table V. MM2 Output Parameters for Dioxy Biradicals[a]



no.	R_1	R_2	R_3	R_4	$\Delta H_f°$(Benson)[b]	$\Delta H_f°$(MM2)	diff	E_{strain}(B)[c]	∠OCCO, deg
1B	H	H	H	H	12.2	14.13	1.93	-3.13	179.75
					12.5	14.20	1.70	-3.05	65.36
2B	Me	H	H	H	4.12	4.52	0.40	-3.41	176.46
					4.12	4.33	0.21	-3.59	64.21
3B	Me	Me	H	H	-5.72	-5.11	0.61	-3.51	179.68
					-5.72	-5.83	-0.11	-4.23	61.09
4B	Me	H	Me	H	-3.66	-3.73	-0.07	-2.32	169.68
					-3.66	-4.63	-0.97	-3.23	62.16
5B	Me	H	H	Me	-3.96	-4.85	-0.89	-3.45	179.09
					-2.96	-4.72	-1.76	-3.32	62.35
6B	Me	Me	Me	H	-11.94	-13.31	-1.37	-2.38	173.38
					-11.94	-13.81	-1.87	-2.88	52.58
7B	Me	Me	Me	Me	-19.92	-21.40	-1.48	0.94	174.96
					-19.22	-21.99	-2.77	-1.53	50.81
8B	Et	Et	Et	Et	-33.04	-31.41	1.63	9.42	173.23
					-32.34	-32.14	0.20	8.70	68.91
9B	Me	Me	Me	*n*-Bu	-33.41	-34.94	-1.53	0.70	172.07
					-32.71	-35.25	-2.54	0.40	62.55
10B	Et	H	H	Et	-13.22	-14.56	-1.34	-2.97	179.93
					-12.22	-13.99	-1.77	-2.40	65.57
11B	Et	H	Et	H	-12.22	-13.54	-1.32	-1.95	170.87
					-12.92	-14.33	-1.41	-2.75	63.33
12B	*n*-Pr	H	H	*n*-Pr	-23.08	-24.71	-1.63	-3.03	179.88
					-22.08	-24.18	-2.10	-2.50	65.78
13B	*n*-Pr	H	*n*-Pr	H	-22.08	-23.70	-1.62	-2.02	173.26
					-22.78	-24.72	-1.94	-3.04	82.22
14B	*n*-Bu	H	H	*n*-Bu	-32.94	-34.86	-1.92	-3.10	179.63
					-31.94	-34.33	-2.39	-2.56	65.20
15B	*n*-Bu	H	*n*-Bu	H	-31.94	-34.20	-2.26	-2.43	172.91
					-32.64	-34.80	-2.16	-3.03	65.53
16B	Et	Et	H	H	-12.12	-12.64	-0.52	-0.85	175.52
					-12.12	-12.56	-0.44	-0.77	65.71
17B	Me	Me	Et	H	-16.57	-18.64	-2.07	-2.61	177.03
					-16.57	-18.61	-2.04	-2.59	66.18
18B	Me	Et	H	H	-8.49	-9.06	-0.57	-2.36	179.49
					-8.49	-9.09	-0.60	-2.40	61.36
19B	Me	*n*-Pr	H	H	-13.42	-14.0	-0.68	-2.36	178.58
					-13.42	-14.16	-0.74	-2.42	62.65
20B	Me	*n*-Bu	H	H	-18.45	-19.20	-0.75	-2.41	179.51
					-18.45	-19.21	-0.76	-2.43	61.99
21B	Me	*i*-Pr	H	H	-14.24	-14.46	-0.22	-0.58	176.15
					-14.24	-14.35	-0.11	-0.47	55.91
22B	Me	*t*-Bu	H	H	-19.92	-19.27	0.65	2.66	179.00
					-19.2	-19.17	0.75	2.76	49.29
							av -1.76		
23B	$BrCH_2$	Me	$BrCH_2$	Me		-6.78		5.08	169.05
						-6.75		5.12	42.34
24B	Me	Me	Me	CH_2Br		-14.57		1.07	173.70
						-14.81		0.82	64.21
25B	EtO	H	H	EtO		-84.04		-5.44	179.59
						-85.05		-6.45	65.47
26B	Me	Me	MeCO	H		-42.23		-1.47	178.18
						-43.22		-2.45	57.01
27B	Me	Ph	H	H		140.59		-0.73	178.89
						139.97		-1.34	57.31
28B	$PhCH_2$	$PhCH_2$	H	H		270.14		-1.53	179.63
						270.30		-1.36	51.63
29B	-Ad[d]			Ad[d]		-21.31		31.52	178.63
						-13.88		38.95	40.64
30B	H	$(CH_2)_4$		H		-4.20		-2.10	56.41
31B	$(CH_2)_5$		$(CH_2)_5$			-29.30		5.11	179.49
						-29.70		4.70	59.70
32B	Me	$(CH_2)_4$		Me		-20.99		0.16	52.47
33B		$-(CH_2)_4-$				-9.47		7.68	45.28
		$(CH_2)_3$							
34B		$-(CH_2)_5-$				-7.60		15.30	32.56
		$(CH_2)_3$							
35B						-18.67		36.46	178.51
						-8.91		46.22	40.56

[a] kcal/mol. [b] Reference 1. [c] B indicates biradical. [d] Ad indicates adamantyl.

Table VI. Correlations between $\Delta G^{\ddagger}_{obs}$ and MM2 Output Parameters for the Lowest Energy Biradial Conformation

MM2 parameter[b]	correlation equation[c]	r	$S_{y\cdot x}$	notes
1. E_{strain}(D)	$\Delta G^{\ddagger} = (0.278 \pm 0.016)E_{strain}(D) + 16.6 \pm 0.5$	0.949	±0.72	*a*
2. E_{strain}(B)	$\Delta G^{\ddagger} = (0.233 \pm 0.013)E_{strain}(B) + 24.8 \pm 0.1$	0.953	±0.69	*a*
3. ΔE_{strain}(B − D)	$\Delta G^{\ddagger} = (0.782 \pm 0.133)\Delta E_{strain}(B - D) + 48.1 \pm 3.9$	0.715	±1.60	*a*
4. ΔE_{strain}(B − D)	$\Delta G^{\ddagger} = (0.443 \pm 0.079)\Delta E_{strain}(B - D) + 37.8 \pm 2.3$	0.709	±0.84	*a, d*
5. ∠(OCCO) = ω	$\Delta G^{\ddagger} = (0.344 \pm 0.044)\omega + 22.1 \pm 0.5$	0.818	±1.35	
6. ω^2	$\Delta G^{\ddagger} = (0.0174 \pm 0.0012)\omega^2 + 3.3 \pm 0.2$	0.933	±0.84	
7. $\cos^2 \omega$	$\Delta G^{\ddagger} = (-59.9 \pm 4.3) \cos^2 \omega + 83.1 \pm 4.2$	0.930	±0.86	

[a] Corrected for Ph ring strain as calculated by PCMODEL (11.57 kcal/mol/Ph). Corrections made for **27** and **2**. [b] D = dioxetane and B = biradical. [c] $\Delta G^{\ddagger}$ at 60 °C. [d] Dropped **23**.

Table VII. Correlations between $\Delta G^{\ddagger}_{obs}$ and MM2 Output Parameters for Gauche Biradicals

MM2 parameter[b]	correlation equation[c]	r	$S_{y\cdot x}$	notes
1. E_{strain}(B)	$\Delta G^{\ddagger} = (0.216 \pm 0.012)E_{strain}(B) + 24.8 \pm 0.1$	0.956	±0.67	*a*
2. ΔE_{strain}(B − D)	$\Delta G^{\ddagger} = (0.600 \pm 0.044)\Delta E_{strain}(B - D) + 42.4 \pm 1.3$	0.921	±0.89	

[a] Corrected for Ph ring strain as calculated by PCMODEL (11.57 kcal/mol/Ph). Correction made for **27** and **28**. [b] D = dioxetane and B = biradical. [c] $\Delta G^{\ddagger}$ at 60 °C.

Table VIII. Correlations between Arrhenius Activation Energy (E_a) and MM2 Output Parameters for the Lowest Energy Biradical Conformation

	MM2 parameter[b]	correlation equation	r	$S_{y\cdot x}$	notes
1.	E_{strain}(D)	$E_a = (0.339 \pm 0.030)E_{strain}(D) + 15.5 \pm 0.9$	0.892	±1.34	*a*
2.	E_{strain}(B)	$E_a = (0.289 \pm 0.023)E_{strain}(B) + 25.5 \pm 0.2$	0.910	±1.23	*a*
3.	ΔE_{strain}(B − D)	$E_a = (0.703 \pm 0.134)\Delta E_{strain}(B - D) + 46.1 \pm 4.0$	0.686	±1.42	
4.	∠OCCO = ω	$E_a = (0.460 \pm 0.054)\omega + 21.9 \pm 0.6$	0.839	±1.66	
5.	ω^2	$E_a = (0.0226 \pm 0.0017)\omega^2 + 23.5 \pm 0.3$	0.928	±1.13	
6.	$\cos^2 \omega$	$E_a = (-77.7 \pm 5.8) \cos^2 \omega + 101.2 \pm 5.6$	0.927	±1.14	

[a] Corrected for Ph ring strain as calculated by PCMODEL (11.57 kcal/mol/Ph). Correction made for **27** and **28**. [b] D = dioxetane and B = biradical.

Table IX. Correlations between Arrhenius Activation Energy (E_a) and MM2 Output Parameters for Gauche Biradicals

MM2 parameter[b]	correlation equation	r	$S_{y\cdot x}$	notes
1. E_{strain}(B)	$E_a = (0.265 \pm 0.022)E_{strain}(B) + 25.5 \pm 0.2$	0.901	±1.29	*a*
2. ΔE_{strain}(B − D)	$E_a = (0.748 \pm 0.069)\Delta E_{strain}(B - D) + 47.5 \pm 2.0$	0.884	±1.38	

[a] Corrected for Ph ring strain as calculated by PCMODEL (11.57 kcal/mol/Ph). Corrections made for **27** and **2**. [b] D = dioxetane and B = biradical.

with the free energy of activation are also somewhat better than those with the Arrhenius activation energy, which may be due to the reasons given above. It can also be noted that correlations with gauche biradicals, where differences between biradical and dioxetane values are taken, are better than those with lowest energy biradicals. Agreement between the OCCO dihedral angle in dioxetane and methyl dioxetane as calculated by MM2 (0.59° and 6.5°, respectively) and by the GAUSSIAN 82 ab initio molecular orbital program[13] at the 3-21G* level (0.0° and 8.0°, respectively) is good. From the MM2 calculations and these two ab initio molecular orbital calculations, it appears that the out-of-plane bending mode of the dioxetane ring is of low energy, at small angles, since subtle changes in structure cause noticeable changes in ∠OCCO. For example, substitution of one methyl group changes ∠OCCO by about 6–8°, according to these calculations. Also the *cis*-2,3-dialkyl isomers with methyl and *n*-propyl groups show nearly zero degree OCCO angles, while the *cis*-diethyl isomer OCCO angle is about 7°.

Discussion

The Benson method of approximating activation energy with the aid of eq 1 is still convenient for dioxetanes which contain simple substituent groups. However, for unusual substituents where unique but unknown strain corrections are needed, the use of one of the better correlation equations in Tables VI–IX is recommended. The easiest option is to use those correlations based on the MM2 calculation of the dioxetane solely, i.e., a correlation of E_a or $\Delta G^{\ddagger}$ with E_{strain}(D), ω(OCCO)^2, or $\cos^2 \omega$. The standard deviation of $\Delta G^{\ddagger}$ on these parameters ranges from ±0.7 to ±0.9 kcal/mol, while the corresponding range for E_a is ±1.1 to ±1.3 kcal/mol.

It can be noted that correlations of activation energies with either E_{strain}(D) or E_{strain}(B) have positive slopes such that increasing these strain energies increases the activation energy. The increase in E_a with increasing E_{strain}(D) suggests that the activated complex is reactant-like, while the positive correlation of E_a with E_{strain}(B) suggests a biradical-like activated complex. This gives a composite picture that is consistent with what is known about the thermolysis of simply substituted dioxetanes.[14] For ex-

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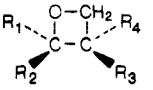
ample, Schneider and co-workers[5a] have observed linear correlations between the free energy of activation for solvolysis of cyclic tosylates and the difference in strain energy between the carbocation intermediate and reactant. Molecular mechanics calculations were used to obtain the strain energies where the cycloalkanone was used as a model for the carbocation and the methylcycloalkane was the model for the tosylate reactant. It was pointed out by these workers that for sterically controlled reactions, the slope in these correlations will approach one if the transition structure is intermediate- or product-like, while the slope will approach zero if the transition structure is reactant-like. From Table VII, it is seen that such a correlation between $\Delta G^{\ddagger}$ and ΔE_{strain}(B – D) gives a slope of 0.60, which is consistent with the picture that the transition-state structure is intermediate in character between the dioxetane reactant and the biradical intermediate. It was proposed that dioxetanes may decompose with a twisting mode so that the OCCO dihedral angle may be related to E_a and $\Delta G^{\ddagger}$,[14l,15] however, this has been questioned.[9,16] As seen from Tables VI and VIII, correlations involving the OCCO dihedral are quite good, where an increase in this angle corresponds to an increase in the activation energy. An increase in the OCCO dihedral angle is expected to increase the strain in the dioxetane ring, so this correlation is consistent with the positive correlation between E_a and E_{strain}(D).

It has been suggested that geminal alkyl substitution effects the stability of dioxetanes, as measured by E_a,[14k,17] more than cis substitution. The stability of dioxetanes can now be pursued from the basis of the MM2 strain energy. Two pairs of dioxetanes from Table I can be compared, for methyl-substituted dioxetanes **3** and **5** (ΔE_{strain}(D)(Gem – cis) = –0.8) and for ethyl-substituted dioxetanes **16** and **10** (ΔE_{strain}(D)(gem –cis) = +0.8). For the larger ethyl groups, it does appear that geminal substitution increases the dioxetane strain energy more than cis substitution; however, this is reversed with the smaller methyl groups.

There has also been question about cis effects in dioxetanes. For example, it was suggested that the cis isomer is more stable than the trans isomer with small substituent groups such as methyl, based on the Arrhenius activation energy.[3,18] Again, if one consults Table I, the difference in strain energy (cis – trans) for the following pairs of dioxetanes is the following (kcal/mol): **5** – **4** (0.88), **10** – **11** (1.06), **12** – **13** (1.05), and **14** – **15** (1.10); av 1.0 ± 0.1. Based on the MM2 strain energy, the cis correction used in the Benson heat of formation calculation of dioxetanes cannot be neglected, and it is approximately 1.0 kcal/mol for all the *n*-alkyl groups including methyl. The cis effect as measured by the strain energy is not unique to dioxetanes or the MM2 parameters that are used here for dioxetanes. A similar observation is found with oxetanes, where only the Allinger parameters are used. The results are given in Table X, where it is seen that the cis effect for oxetanes is similar to that observed with dioxetanes. Although a better fit of calculated E_a values by eq 1 to observed values was observed by neglecting the cis correction in methylated dioxetanes,[3] this procedure does not seem to be justified. The inclusion of the cis correction

Table X. Cis Effects in Oxetanes[a]



R_1	R_2	R_3	R_4	E_{strain} (MM2)[b]	ΔE_{strain} (cis – trans)[b]
Me	H	H	Me	24.92	
					0.80
Me	H	Me	H	24.12	
Et	H	H	Et	25.31	
					0.99
Et	H	Et	H	24.32	
Me	H	H	Et	25.23	
					0.94
Me	H	Et	H	24.29	

[a] Calculated with Allinger's parameters. [b] kcal/mol.

in the Benson calculation then gives a spread in calculated E_a values of only 3.6 kcal/mol compared to 5.1 kcal/mol that is observed for the methylated dioxetanes as seen in Table XI.

A Benson-type calculation with eq 1 can be made from the MM2 biradical and dioxetane heats of formation as given in Table XII. What is curious about these calculations is that there is very little change in the calculated E_a values throughout the methylated series. It was pointed out above that a smaller spread in calculated E_a values is expected with MM2 data compared to the Benson method because of the overall smaller gauche corrections in the biradicals. In order to pursue the origin of the spread in E_a values in the methylated dioxetane series, the difference in activation energies between dioxetanes **7** and **1** (δE_a(**7** – **1**)) can be examined, where these values are 3.6, –0.6, and 5.1 kcal/mol, respectively, for the Benson calculation, the MM2 calculation, and the observed value. If one consults the "difference" columns in Table I and V, it is seen that the difference in heats of formation for gauche biradicals **7B** and **1B** by the Benson and MM2 methods is 4.47 kcal/mol (= 1.70 – (–2.77)), while the corresponding difference for dioxetanes **7** and **1** is only 0.28 kcal/mol (= 1.06 – 0.78). The major reason for the difference in δE_a(**7** – **1**) between the Benson and MM2 calculations with eq 1 is then to be found in the biradical heats of formation. Another question than can be asked is whether or not the 4.47 kcal/mol "difference" value above for biradicals **7B** and **1B** can be explained solely by different gauche interactions in the Benson and MM2 calculations. This can be tested by using the MM2 derived gauche interactions (see Results) in the Benson calculation. The difference between the Benson and the MM2 gauche interactions for the gauche$_{O,O}$ biradicals are the following (in kcal/mol): **1B** ($G_{O,O}$ = 0.3 – 0.07 = 0.2) and **7B** ($G_{O,O}$ + 2$G_{C,O}$ + $G_{C,C}$ = (0.3 – 0.07) + 2(0.3 – 0.49) + 3(1.0 – 0.55) = 1.2). The difference between these values is only 1.0 kcal/mol, which is not nearly enough to explain the 4.47 kcal/mol "difference" value. This means that the difference between the Benson and MM2 biradical heats of formation is because of an inherent difference in the Benson and MM2 methods, exclusive of just gauche corrections. In terms of the calculation of E_a with MM2 data for $\Delta H^{\circ}_{1,-1}$ from eq 1, a possible explanation for the nearly constant calculated E_a values is that E_{-1} is not constant, but increases with increasing bulk of the 2,3-substituents in the 1,4-dioxybutane biradical. To test this proposal, $\Delta H^{\circ}_{1,-1}$ was calculated from the MM2 heats of formation for dioxetanes **1**–**22** and the corresponding gauche biradicals, and with these values a calculated E_{-1} was obtained from observed E_a values by eq 1. Now a correlation was made between

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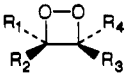
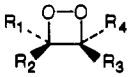
Table XI. Benson Thermochemical Kinetic Calculations for 1,2-Dioxetanes and the Corresponding Biradicals[a] (in Parentheses)



R_1	R_2	R_3	R_4	$\Delta H_f°$(Benson)[c]	$\Delta H°_{1,-1}$	E_a(calc)[b]	E_a(obs)
H	H	H	H	0.0 (12.5)	12.5	23.6	22.7
Me	H	H	H	-9.18 (4.12)	13.3	24.4	22.8
Me	Me	H	H	-18.66 (-5.72)	12.9	24.0	24.5
Me	H	Me	H	-18.36 (-3.66)	14.7	25.8	24.1
Me	H	H	Me	-17.36 (-2.96)	14.4	25.5	24.8
Me	Me	Me	H	-26.84 (-11.94)	14.9	≡26.0	26.0
Me	Me	Me	Me	-35.32 (-19.22)	16.1	27.2	27.8

[a] kcal/mol. [b] Referenced to E_a(obs) = 26.0 kcal/mol for trimethyl-1,2-dioxetane, so that E_{-1} = 11.1 kcal/mol. [c] With E_{strain}(ring) = 25.2 kcal/mol, $E_{cis\ C,C}$ = 1.0 kcal/mol in dioxetanes; and gauche = $gauche_{O,O}$ = 0.3 kcal/mol and $gauche_{C,C}$ = 1.0 kcal/mol in biradicals. $Gauche_{O,O}$ biradicals are used.

Table XII. Thermochemical Kinetic Calculations Based on MM2 Dioxetane and Biradical (in Parentheses) Heats of Formation for Methylated Derivatives[a]



R_1	R_2	R_3	R_4	$\Delta H_f°$(MM2)[c]	$\Delta H_f°_{1,-1}$	E_a(calc)[b]	E_a(obs)
H	H	H	H	1.06 (14.20)	13.14	26.5	22.7
Me	H	H	H	-8.30 (4.33)	12.63	26.0	22.8
Me	Me	H	H	-17.88 (-5.83)	12.05	25.4	24.5
Me	H	Me	H	-17.75 (-4.63)	13.12	26.5	24.1
Me	H	H	Me	-17.17 (-4.72)	12.45	25.8	24.8
Me	Me	Me	H	-26.46 (-13.81)	12.65	≡26.0	26.0
Me	Me	Me	Me	-34.54 (-21.99)	12.55	25.9	27.8

[a] kcal/mol. [b] Referenced to trimethyl-1,2-dioxetane, so that E_{-1} = 13.35 kcal/mol. [c] Gauche biradicals.

these calculated E_{-1} values and the sum of the Taft steric substituent constants.[19] The following correlation eq 3

$$E_{-1} = (-0.868 \pm 0.138)\sum E_s + 13.6 \pm 0.3 \qquad (3)$$

was obtained, where dioxetanes **9** and **22** were not included, and where r = 0.828, $S_{y.x}$ = ±0.7 kcal/mol. The observed E_a values for both of these dioxetanes appeared low compared to the predicted values. The reported E_a value of 25.3 kcal/mol for **9** does appear low for a tetrasubstituted dioxetane. Table XIII presents the calculated E_a values that are obtained from eq 3, eq 1, and the MM2 values for $\Delta H°_{1,-1}$. Although the predicted value of E_a for **7** is noticeably lower than the reported value, there is a noticeable improvement between observed and calculated E_a's for **8** with a variable E_{-1} (+0.7 kcal/mol) as compared to the standard Benson calculation (-2.4 kcal/mol). When MM2 heats of formation of dioxetanes and biradicals are used, it appears that steric effects come into play in the back reaction (E_{-1}). It seems likely that this is also the reason for the descrepancies between observed E_a and the standard Benson calculated values.

Conclusions. Use of the molecular mechanics (MM2) parameters reported here give certain correlation equations that can be employed to give reasonably good predictions of the Arrhenius activation energy and the free energy of activation. The correlation equations have an advantage over the standard Benson calculation of E_a in that activation energies of dioxetanes of unusual structures can be readily predicted from data based on MM2 calculations, while Benson calculations on such structures would be difficult or impossible. Probably the easiest approach to predicting activation energies of dioxetanes by MM2 calculations is to carry out the calculations on just the dioxetane and then to use the correlation equations based on the MM2 strain energy (E_{strain}) or OCCO dihedral angle of the dioxetane. Good estimates of activation energies can also be made by using eq 1 and 3, where $\Delta H°_{1,-1}$ is obtained from MM2 calculations. This method is of course more troublesome, since heats of formation for both the dioxetane and the biradical must be calculated by MM2. The ability to obtain good estimates of activation energies by this method suggests that steric effects play a consid-

Table XIII. Calculation of E_a from MM2 $\Delta\Delta H_f°$(B - D) and E_{-1} Equation Which Includes Steric Effects

no.	E_a(obs)	E_a(calc)[a]	$\Delta\Delta H_f°$-(B - D)$_{MM2}$[b]	E_{-1}(calc)[c]	$\sum E_s$
1	22.7	22.4	13.14	9.29	4.96
2	22.8	23.0	12.63	10.37	3.72
3	24.5	23.5	12.05	11.45	2.48
4	24.1	24.6	13.12	11.45	2.48
5	24.8	23.9	12.45	11.45	2.48
6	26.0	25.2	12.65	12.52	1.24
7	27.8	26.2	12.55	13.6	0.00
8	30.8	31.5	17.64	13.84	-0.28
10	24.5	24.4	12.83	11.57	2.34
11	24.9	25.2	13.65	11.57	2.34
12	24.5	25.0	12.89	12.07	1.76
12	24.5	25.0	12.89	12.07	1.76
13	25.0	25.5	13.40	12.07	1.76
14	24.6	25.0	12.89	12.12	1.70
15	25.1	25.6	13.51	12.12	1.70
16	24.9	25.2	13.65	11.57	2.34
17	24.7	25.4	12.85	12.58	1.17
18	24.5	24.4	12.85	11.51	2.41
19	24.6	24.6	12.85	11.76	2.12
20	24.4	24.2	12.43	11.79	2.09
21	25.0	25.8	13.94	11.86	2.01

[a] $E_a = \Delta\Delta H_f°(B - D)_{MM2} + E_{-1}$. [b] Gauche biradicals. [c] $E_{-1} = (-0.868 \pm 0.138)\sum E_a + 13.6 \pm 0.3$, r = 0.828, $S_{y.x}$ = ±0.7.

(19) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; John Wiley: New York, 1963; p 228.

erable role in the activation energy of the back reaction (E_{-1}).

The correlation equations of activation energy with E_{strain} or ∠OCCO of the dioxetane, as obtained from MM2, mean that increased strain in the dioxetane corresponds to higher activation energies. This suggests a reactant-like transition structure and the correlation of E_{strain} of the biradical further imposes biradical character in the transition structure. A transition-state structure that is intermediate in character between the dioxetane reactant and the biradical intermediate is also suggested by the slope of 0.60 in the correlation between $\Delta G^{\ddagger}$ and the difference in the gauche biradical and the dioxetane strain energies.

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Notes

[3,3]- and [1,3]-Sigmatropic Amino-Claisen Rearrangements of Electron-Rich Alkenes [1,3,1′,3′-Tetraallyl-2,2′-biimidazolidinylidenes]

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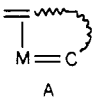
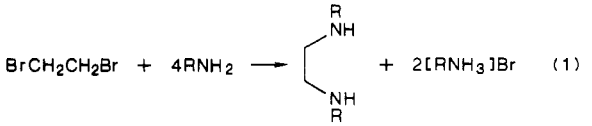
We have for some years used 1,3,1′,3′-tetrasubstituted 2,2′-biimidazolidinylidenes such as **1** as (i) sources of carbenemetal complexes M=CN(R)$(CH_2)_2$NR[1] or (ii) powerful reducing agents: **1** being oxidized successively to $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$.[2] The present study arose from a search for *R*-functionalized carbenemetal complexes. Allyls or but-3-enyls were considered to be particularly interesting, because such 1,3,1′,3′-tetrasubstituted 2,2′-biimidazolidinylidenes were anticipated to be capable of generating carbene(alkene)metal complexes A (the latter



A

are implicated in alkene metathesis); we shall report on such chemistry elsewhere. Compounds **1** are generally prepared from an *N,N′*-disubstituted 1,2-diaminoethane and the dimethyl acetal of dimethylformamide. We now show that using standard conditions [(a) in Scheme I] compounds **1** are accessible for R = crotyl (**1b**) or but-3-enyl (**1c**), whereas for R = allyl the rearranged product **2a** was obtained. Moreover, the similar [3,3]-sigmatropic amino-Claisen rearrangement product **2b** was isolated by heating **1b** [(b) in Scheme I], while photolysis [(c) in Scheme I] of **1b** gave not only **2b** but also the [1,3] rearrangement isomer **2b′**.

Two of the starting diamines are new and were prepared as shown in eq 1 [R = $CH_2CH{=}CHMe$ or $(CH_2)_2CH{=}CH_2$].



(1)

Because of their large size it was impractical to carry out molecular orbital calculation on allylic molecules of types **1** and **2**. The methyl analogues **1d** and **2d** were selected as appropriate models and MNDO was the MO method of choice.[3] This gave the following heats of formation: **1d** 204.6 kJ mol^{-1} and **2d** 168.1 kJ mol^{-1}, whence ΔH for the isomerization of gaseous 1,2,1′,2′-tetramethyl-2,2′-biimidazolidinylidene **1d** into the gaseous isomer **2d** is predicted to be −36.5 kJ mol^{-1}. (The heats of sublimation of **1d** and **2d** are expected to be similar.) To test further the validity of the MNDO method, we have demonstrated (Table I) that there is a good correlation between MNDO calculated and experimental geometrical parameters for **1d** (1, R = Me) (electron diffraction)[4] and **2e** (2, R = CH_2Ph) (X-ray);[5] experimental data for **2d** (2, R = Me) are not at hand.

The following conclusions emerge. (i) The tetraallylbiimidazolidinylidene **1a** (1, R = $CH_2CH{=}CH_2$) is not accessible under our reaction conditions [(a) in Scheme I] and if formed it spontaneously rearranges to the isomer **2a**. (ii) The thermal allylic isomerization **1** → **2** are believed to be intramolecular [3,3]-sigmatropic rearrangements, cf., the transition state B; because from **1b** (R = $CH_2CH{=}CHMe$) only one product **2b** [R = $CH_2CH{=}CHMe$, R′ = $CH(Me)CH{=}CH_2$] was obtained. (iii) The corresponding photochemical transformations are thought

(1) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185 and references therein.

(2) Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L.; Lappert, M. F.; Smith S. J. *J. Organomet. Chem.* **1986**, *310*, 21 and references therein.

(3) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898 and references therein. Calculations were carried out with full optimization of geometry.

(4) Lappert, M. F.; Spyropoulos, K.; Traetteberg, M. Unpublished results. Spyropoulos, K. D.Phil.Thesis, University of Sussex, 1985; the molecule has D_2 symmetry with a pyramidal configuration about nitrogen.

(5) Cetinkaya, E.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F. Unpublished work. Jasim, H. A. D.Phil. Thesis, University of Sussex, 1987. The molecule has each nitrogen in a nearly trigonal-planar configuration.

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