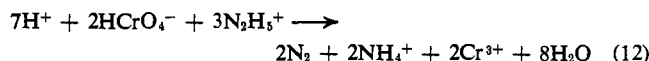


Mn(III) and Cr(III) it interrupts a pathway involving Cr(VI) + Cr(IV) → 2Cr(V), thus halving the rate of disappearance of Cr(VI) when Cr(VI) is present in excess. In excess N<sub>2</sub>H<sub>5</sub><sup>+</sup>, Mn(II) interrupted a path involving 2Cr(IV) → Cr(V) + Cr(III) which would not affect the rate of Cr(VI) disappearance.

In the presence of Mn(II) the stoichiometry is altered to



Evidently Cr(IV) cannot oxidize N<sub>2</sub>H<sub>5</sub><sup>+</sup> before Cr(IV) reacts with other species or disproportionates. A re-analysis of Figure 2, ref 6, leads us now to propose that Cr(IV) disproportionates in the absence of Mn<sup>2+</sup> when either Cr(VI) or N<sub>2</sub>H<sub>5</sub><sup>+</sup> is in excess. The halving of the rate in excess Cr(VI) can be shown to be an artifact of the change in stoichiometry shown by eq 12. Thus trapping of Cr(IV) by Cr(VI) in the absence of Mn(II) is no longer necessary to explain the results. In the presence of excess Cr(VI), it is [N<sub>2</sub>H<sub>5</sub><sup>+</sup>] which changes significantly during a run. Figure 2, ref 6, shows that *t*<sub>1/2</sub> is halved when Mn<sup>2+</sup> is present. Therefore, when no Mn<sup>2+</sup> is present (using eq 3)

$$\frac{d[\text{N}_2\text{H}_5^+]}{dt} = k_1[\text{Cr(VI)}][\text{N}_2\text{H}_5^+] = \frac{3}{4} \frac{d[\text{Cr(VI)}]}{dt}$$

When Mn<sup>2+</sup> is present (using eq 12)

$$\frac{d[\text{N}_2\text{H}_5^+]}{dt} = 2k_1[\text{Cr(VI)}][\text{N}_2\text{H}_5^+] = \frac{3}{2} \frac{d[\text{Cr(VI)}]}{dt}$$

$$\frac{d[\text{Cr(VI)}]}{dt} = \frac{4k_1}{3} [\text{Cr(VI)}][\text{N}_2\text{H}_5^+]$$

in both cases. Thus the "slower" rate in presence of Mn<sup>2+</sup> is an artifact of the change in stoichiometry and faster consumption of N<sub>2</sub>H<sub>5</sub><sup>+</sup>.

The oxidations of NH<sub>3</sub>OH<sup>+</sup> and NH<sub>3</sub>NH<sub>2</sub><sup>+</sup> are notable in that each requires two equivalent oxidation involving electron pair transfer to Cr(VI) involving a bridging atom. Neither appears to trap Cr(IV). While NH<sub>3</sub>OH<sup>+</sup> forms a bridge to Cr(VI) exclusively through the oxygen atom,<sup>11</sup> it forms a weaker complex than NH<sub>3</sub>NH<sub>2</sub><sup>+</sup> consistent with the generally greater donor ability of >N: over >O:. However, most possible N complexes with Cr(VI) cannot be studied due to saturation of N atoms with protons as in NH<sub>4</sub><sup>+</sup> and RNH<sub>3</sub><sup>+</sup>, whereas oxygen in potential ligands virtually always has a pair of electrons free to form dative bonds.

**Acknowledgment.** The authors wish to thank the National Institutes of Health and the National Science Foundation for support of this research.

## Application of the Principle of Least Motion to Organic Reactions. III.<sup>1,2</sup> Eliminations, Enolizations, and Homo-enolizations

Oswald S. Tee,\*<sup>3a</sup> Julianna A. Altmann,<sup>3b</sup> and Keith Yates<sup>3b</sup>

*Contribution from the Departments of Chemistry, Sir George Williams University, Montreal 107, Quebec, Canada, and the University of Toronto, Toronto, Ontario, Canada M5S 1A1. Received August 18, 1973*

**Abstract:** Using the PLM approach developed previously calculations of the stereochemical paths involving the least motion of atoms have been carried out for 15 further reactant-product systems. These include: 1,2-, 1,3-, and 1,4-eliminations, acetylene formation, allene formation, enolizations, homo-enolizations, a concerted 1,2-hydride shift, and epoxidation. Again there is remarkable agreement with available experimental observations. The only major discrepancy with experiment is in the 1,3-elimination of 2-norbornyl tosylates for which a truly concerted process may not apply.

The system chosen by Hine<sup>4</sup> to illustrate the principle of least motion (PLM) as applied to atoms was a prototypical 1,2-elimination, namely, the transformation of ethyl chloride into ethylene. Calculation of the minimum sum of the squares of the atomic displacements<sup>4</sup> (*E*<sub>min</sub>)<sup>1</sup> for the syn and anti modes of this elimination gave results favoring the latter.<sup>1,4</sup> Subsequently, a more general method of calculation was

devised<sup>1</sup> and applied<sup>1,2</sup> to a variety of reactions which could have, in principle, more than one stereochemical pathway. The results obtained agreed remarkably well with experimental observations and with more sophisticated theoretical models.<sup>1,2</sup>

In the present paper we explore further the applicability of the method to the stereochemistry of various types of elimination, enolization, homo-enolization, a concerted 1,2-hydride shift, and epoxidation. The method of calculation has been described previously<sup>1,2</sup> and does not need further elaboration. Molecular geometries were calculated either from published

(1) Part I: O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

(2) Part II: O. S. Tee and K. Yates, *J. Amer. Chem. Soc.*, **94**, 3074 (1972).

(3) (a) Sir George Williams University; (b) University of Toronto.

(4) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

structural data or from estimates<sup>5</sup> based upon suitable models.

## Results and Discussion

**1,2-Eliminations.** Early experimental work on the stereochemistry of 1,2-eliminations often utilized cyclohexane derivatives, and it was on the basis of such studies that the requirement of the antiperiplanarity of the leaving groups was suggested.<sup>6</sup> PLM calculations on the conversion of ethyl chloride to ethylene showed a preference for the anti mode of elimination.<sup>1,4</sup> Calculations have now been carried out for elimination from a cyclohexane derivative producing cyclohexene in order to see if this preference is retained. To cover most eventualities various conformers of the reactant and the product were considered. The results obtained are shown in Table I.

**Table I.** Variation of  $E_{\min}$  with the Modes of Elimination from Cyclohexane Derivatives

Elimination type	Reaction	$E_{\min}$ , Å <sup>2</sup>
Anti-diaxial		0.610
Syn-clinal diequatorial		7.36
Syn-clinal axial-equatorial		3.64
Anti-clinal diaxial		0.938
Syn-clinal diequatorial		8.86
Syn-clinal axial-equatorial		4.64
Anti-clinal		2.20
Syn (1)		2.23
Syn (2)		1.10

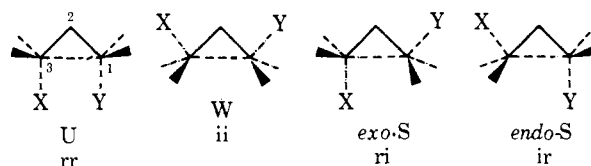
Of the three possible modes of elimination from a chair conformer the results indicate a preference for the anti-diaxial mode. Similarly for the reaction from a

(5) It was found in earlier work<sup>2</sup> that while small changes in molecular geometry affect the values of  $E_{\min}$  somewhat the indicated preference remained unaltered. Consequently, the choice of molecular parameters for calculating geometries is not critical, although one attempts to be as realistic as possible. In general the values of  $E_{\min}$  for two different stereochemical pathways are sufficiently different that their relative magnitude is insensitive to small changes in the molecular parameters.

(6) (a) D. H. R. Barton and W. J. Roesenfelder, *J. Chem. Soc.*, 1048 (1951); (d) E. D. Hughes, C. K. Ingold, and I. Rose, *ibid.*, 3839 (1953); (c) S. J. Cristol and N. L. Hause, *J. Amer. Chem. Soc.*, 74, 2193 (1952); (d) D. Y. Curtin, R. D. Stolow, and W. Maya, *ibid.*, 81, 3330 (1959); (e) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, 1, 225 (1962); (f) D. V. Banthorpe, "Elimination Reactions," Elsevier, Amsterdam, 1963.

symmetrical twist conformer the anti mode is preferred. On the other hand, for elimination from a boat conformation of a cyclohexane derivative leading to cyclohexene in a similar conformation, a syn mode is favored as might be anticipated in view of the dihedral angles between the potential leaving groups. The suggestion remains, therefore, that under normal circumstances an anti mode of elimination is preferred, and only in the unlikely event<sup>7</sup> that the reactant cyclohexane derivative is constrained to utilize a boat conformation will a syn mode become competitive.

**1,3-Eliminations.** The formation of a cyclopropane by a concerted 1,3-elimination can formally occur with either retention (r) or inversion (i) of configuration at each of the reacting centers ( $C_3$  and  $C_1$ ). Of the various possibilities for the transition state geometry four have been selected as most likely (designated as U, W, *exo-S* and *endo-S*) by Nickon and Werstiuk.<sup>9</sup>



PLM calculations were carried out for the conversion of a 1,3-disubstituted propane to cyclopropane having either double retention (rr), double inversion (ii), or retention and inversion (ri or ir)<sup>10</sup> of the configurations at  $C_1$  and  $C_3$ . For each type of potential product values of  $E_{\min}$  were calculated considering 28 distinct conformations of the reactant obtained by various combinations of rotations about the C-C bonds. The lowest values obtained (Chart I) correspond exactly to the

**Chart I**

Configurations in the product	Transition state	$E_{\min}$ , Å <sup>2</sup>
rr	U	3.30
ii	W	0.71
ri	<i>exo-S</i>	1.59
ir	<i>endo-S</i>	1.59

conformations implied by the transition state geometries illustrated above, *i.e.*, in all three cases<sup>10</sup> the leaving groups, X and Y, and the three carbons ( $C_1$ ,  $C_2$ ,  $C_3$ ) should be coplanar. The results clearly favor a W transition state, and an *exo-S* (or *endo-S*) is preferred over a U transition state.

In the main, base-catalyzed 1,3-eliminations give products corresponding to a W transition state,<sup>11</sup> but as Bordwell has pointed out<sup>11</sup> the stereoselectivity is usually not high. A case where a W transition state is not favored is the 1,3-elimination from 2-norbornyl tosylates studied by Nickon and Werstiuk.<sup>12</sup> They found that for both 2-*exo*- and the 2-*endo*-norbornyl

(7) Unlikely, since the boat conformation is higher in energy than either the chair or twist conformations and is considered to be a transition state between two twist forms.<sup>8</sup>

(8) (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, 89, 7036, 7043, 7047 (1967); (b) H. M. Pickett and H. L. Strauss, *ibid.*, 92, 7281 (1970).

(9) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, 89, 3914 (1967).

(10) In the definition of *exo-S* and *endo-S* the leaving group Y is taken to be more electronegative than X.<sup>9</sup> Since the present PLM calculations do not include the moieties being eliminated,<sup>1,2,4</sup> we are not able to distinguish between these two modes.

(11) A recent review may be found in F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, 95, 3585 (1973).

(12) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, 89, 3915, 3917 (1967).

tosylates the 6-endo hydrogen is lost preferentially.<sup>12</sup> This result corresponds to a preference of *exo-S* over *W* and *U* over *endo-S* geometries. However, in neither instance was the preference high.<sup>12</sup> Both of these observations are contrary to those expected on the basis of our results, and it was not immediately clear whether this was due to the insufficiency of the PLM method or of a geometric peculiarity of the norbornyl system. To check the latter of these possibilities, calculations were carried out for a norbornyl system undergoing 1,3-elimination to give nortricyclene. The results obtained (Chart II) for the four possible transition states<sup>10</sup> are in

Chart II

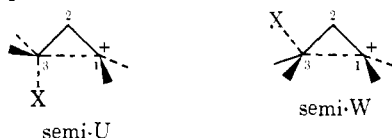
Transition state	$E_{\min}$ , Å <sup>2</sup>
W-like	3.27
<i>exo-S</i> -like	6.78
<i>endo-S</i> -like	6.78
U-like	10.07

the same order as was found for the calculations on a simple propane-cyclopropane system and opposite to that found experimentally.<sup>12</sup> It is quite possible, however, that the mechanisms operating in this<sup>12</sup> and other norbornyl systems<sup>13</sup> may not be concerted but might involve cationic intermediates.<sup>11</sup>

Bordwell<sup>11,14</sup> suggests that most, if not all, 1,2- and 1,3-eliminations formerly considered to be concerted may involve prior formation of a carbanion. However, the intermediacy of a carbanion does not necessarily affect the applicability of the present and earlier<sup>1,4</sup> PLM calculations, providing a pyramidal carbanion does not undergo rotation and/or inversion before expulsion of the leaving group.

Cristol<sup>15</sup> studied the 1,3-addition of bromine to a quadricyclene dicarboxylic acid and concluded that it proceeds *via* a *W*-like transition state. PLM calculations carried out for a 1,3-addition to quadricyclene to give a nortricyclene derivative showed the same preferences found for the norbornane-nortricyclene system described earlier.

In 1,3-eliminations involving prior formation of a carbonium ion the stereochemistry of one of the reacting centers (the nucleofugal center,  $C_1$ ) is lost before ring closure. Therefore, only two stereochemical alternatives are possible for the transition state of the ring-forming step. The semi-*U* transition state involves



retention of configuration at the electrofugal center ( $C_3$ ), whereas the semi-*W* transition state involves inversion at that center. In relation to these two possibilities, PLM calculations were performed for the conversion of the *n*-propyl cation to cyclopropane having either retention or inversion of configuration at  $C_3$ . For both types of product values of  $E_{\min}$  were calculated considering 49 rotational isomers of the reactant cation derived from rotations about both C-C bonds, and minimum values of  $E_{\min}$  were located which correspond exactly to the conformations of the reactant implied by transition states illustrated above; *i.e.*, in both cases the leaving

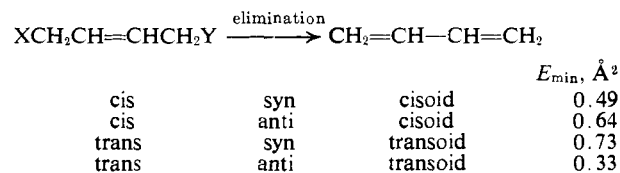
(13) N. H. Werstiuk, *Chem. Commun.*, 1499 (1970), and references therein.

(14) F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

(15) S. J. Cristol and R. T. Lalonde, *J. Amer. Chem. Soc.*, **80**, 4355 (1958).

group X should be coplanar with three carbons and this plane should be perpendicular to the one containing the bonds around the trigonal center ( $C_1$ ). Over-all the results favor a semi-*W* ( $E_{\min} = 0.92$  Å<sup>2</sup>) over a semi-*U* transition state ( $E_{\min} = 2.30$  Å<sup>2</sup>). Calculations carried out for the formation of nortricyclene from the 2-norbornyl cation also showed a preference for a semi-*W* transition state. For the loss of 6-*exo* hydrogen  $E_{\min} = 4.57$  Å<sup>2</sup>, whereas for loss of the 6-*endo* hydrogen  $E_{\min} = 8.05$  Å<sup>2</sup>. These results again conflict with some of the experimental findings,<sup>12,13,16</sup> but it must be borne in mind that the nature of the cation involved in these systems is not known with certainty.

**1,4-Eliminations.** The view has been expressed<sup>17</sup> that PLM would predict that 1,4-eliminations (or additions) should generally be anti. The simplest system in which a 1,4-conjugate elimination<sup>18</sup> could occur is in the conversion of a 1,4-disubstituted-2-butene to butadiene. By a syn or anti elimination a *cis*- or *trans*-2-butene derivative might be converted to butadiene in a *cisoid* or *transoid* configuration. PLM calculations were performed for the four basic possibilities listed



above. The results show a preference for a *syn* 1,4-elimination from a *cis*-2-butene, and for an *anti* elimination from a *trans*-2-butene.

Experimental work on 1,4-eliminations favors the *syn* mode.<sup>18</sup> However, the substrates that have been used<sup>18</sup> are all structurally related to a *cis*-2-butene derivative for which PLM favors a *syn* elimination. We are not aware of any experimental work in which the stereochemical preference of 1,4-elimination from a *trans*-2-butene-like system has been investigated and for which PLM suggests that an *anti* mode would be favored. 1,4-Additions to 1,3-dienes exhibit a *syn* preference,<sup>19</sup> but again a *cisoid*-diene/*cis*-olefin system was involved.

**Acetylene Formation.** In earlier work<sup>1</sup> it was found that PLM calculations favored an *anti* over a *syn* mode of 1,2-elimination leading to acetylene. Furthermore, it was suggested that from the PLM viewpoint the effect of a simple substituent such as a methyl group would be such as to enhance the preference for the *anti* mode of elimination.<sup>20</sup> To test this suggestion values of  $E_{\min}$

(16) N. H. Werstiuk and I. Vancas, *Can. J. Chem.*, **48**, 3963 (1970).

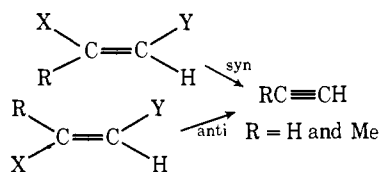
(17) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968). The comment we are referring to is on page 302 of this reference.

(18) (a) S. J. Cristol, W. Barasch, and C. H. Tieman, *J. Amer. Chem. Soc.*, **77**, 583 (1955); (b) P. B. D. de la Mare, R. Koenigsberger, and J. S. Lomas, *J. Chem. Soc. B.*, 834 (1966); (c) however, for a recent reappraisal, see S. J. Cristol, *Accounts Chem. Res.*, **4**, 393 (1971).

(19) G. S. Hammond and J. Warkentin, *J. Amer. Chem. Soc.*, **83**, 2554 (1961).

(20) One of the referees expressed the view that this point is obvious and thus is not worthy of consideration. This was originally our view also. However, from calculations carried out on the rearrangement ethylcarbene-propylene (J. A. Altman, M.S. Thesis, Sir George Williams University, 1973) *vs.* those on methylcarbene-ethylene<sup>2</sup> it became clear that the effect of a methyl group on these calculations is not always that which ones intuition suggests. In the case cited the extra methyl group caused a change in the stereochemical preference exhibited by the PLM calculations. In other respects also intuition is not always a safe guide. For example, a least motion pathway may be one proceeding with inversion of configuration and not with retention as one expects intuitively.

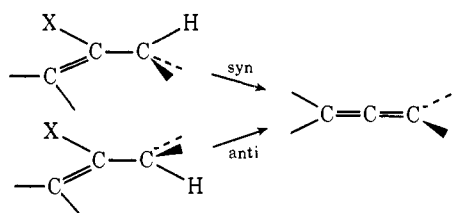
were calculated for syn and anti eliminations from a 2-halopropene to give propyne.<sup>21</sup>



Product	$E_{\min}$ , Å <sup>2</sup>		difference
	syn	anti	
R = H <sup>1</sup>	1.24	0.32	0.92
R = Me	2.92	0.56	2.36

As may be seen from the results above, the earlier suggestion<sup>1</sup> is borne out in that the difference in  $E_{\min}$  for the two modes is markedly greater when R = Me.

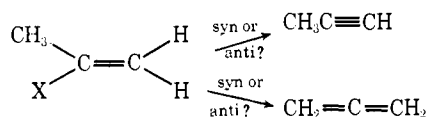
**Allene Formation.** Elimination from a 2-halopropene could also lead to allene. Values of  $E_{\min}$  were calculated for the formation of a syn and an anti



product from various conformations of the reactant derived from rotations about the C-C bond. Minimum values of  $E_{\min}$  were found corresponding exactly to a pure syn elimination ( $E_{\min} = 2.09$  Å<sup>2</sup>) and to a pure anti elimination ( $E_{\min} = 0.71$  Å<sup>2</sup>) as illustrated above. These results clearly favor the anti mode of elimination.

Experimentally, it is not known for certain which mode is favored, although it is assumed to be the anti mode.<sup>22</sup>

**Acetylene Formation vs. Allene Formation.** Based on the assumption that allene formation occurs preferentially by the anti mode, Staley and Doherty have arrived at an order of ease of elimination to give an acetylene or an allene. Their order (mode-product) is: *anti*-acetylene > *anti*-allene  $\gg$  *syn*-acetylene.<sup>23</sup> The relative position of syn formation of an allene is not known. This order of reactivity is reflected very well by the PLM results outlined in the two previous sections. Combining the two sets of calculated values of  $E_{\min}$  gives the predicted order of ease of elimination: *anti*-acetylene ( $E_{\min} = 0.56$  Å<sup>2</sup>) > *anti*-allene (0.71 Å<sup>2</sup>)  $\gg$  *syn*-allene (2.09 Å<sup>2</sup>) > *syn*-acetylene (2.92 Å<sup>2</sup>).



**Enolization.** Earlier<sup>1</sup> the conformational preference for proton abstraction from the carbon adjacent to a carbonyl group was studied using acetaldehyde as the model substrate, and the results indicated that enolization would involve least motion of atoms for a rotamer

(21) In the calculations it was assumed that in going from reactant to product there is no rotation about the Me-C bond. Under these circumstances the values of  $E_{\min}$  quoted are independent of the rotation of the methyl group.

(22) S. W. Staley and R. F. Doherty, *Chem. Commun.*, 288 (1969).

(23) For the particular system that they studied<sup>22</sup> the relative rates were 66,000:1,500:1, respectively.

having the departing hydrogen perpendicular to the trigonal plane. It was felt that the addition of a methyl group, as in acetone, would not affect this result.<sup>1,20</sup>

Calculations have now been carried out to ascertain the effect of an extra methyl group on the earlier PLM results. The results obtained for the enolization of acetone together with those for acetaldehyde are given in Table II. As previously,  $\beta$  is the dihedral angle

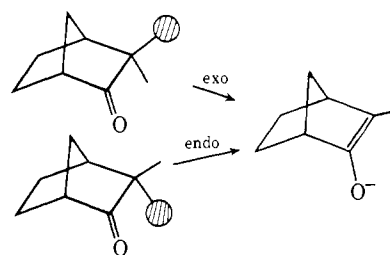
**Table II.** Variation of  $E_{\min}$  with Dihedral Angle for the Enolization of Acetaldehyde and Acetone

$\beta$ , deg	$E_{\min}$ , Å <sup>2</sup>		Difference
	Acetaldehyde <sup>a</sup>	Acetone <sup>b</sup>	
0	2.38	3.37	0.99
30	1.18	1.76	0.58
60	0.42	0.64	0.22
90	0.17	0.23	0.06
120	0.44	0.62	0.18
150	1.20	1.71	0.51
180	2.39	3.30	0.91

<sup>a</sup> O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969). <sup>b</sup> These values assume that there is no rotation of the nonenolizing methyl group during the reaction. Under these circumstances the values of  $E_{\min}$  are independent of the rotation of this methyl group.

between the leaving hydrogen and the carbonyl oxygen.<sup>1</sup> It is evident from the results that the effect of the extra methyl group is to enhance the least motion preference for proton abstraction perpendicular ( $\beta = 90^\circ$ ) to the plane of the trigonal system.

The stereochemistry of enolization may best be studied in cyclic systems where the relative positions of the enolizable hydrogens are fixed. For example, experimental evidence for the assertion that the proton removal in enolization is most favorable perpendicular to the trigonal plane of the carbonyl group is derived from studies of a steroidal ketone.<sup>24a</sup> Also, Tidwell and coworkers<sup>24b,c</sup> have measured the relative rates of proton abstraction in some bicyclic ketones. For comparison with this latter work PLM calculations were performed for 3-exo and 3-endo proton abstraction from 2-norbornanone. The value of  $E_{\min}$  for exo abstraction (2.46 Å<sup>2</sup>) is much lower than that for endo

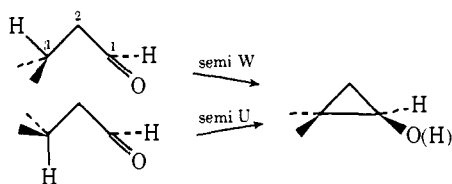


abstraction (5.94 Å<sup>2</sup>) and is in the same direction as the experimental results. Tidwell<sup>24b,c</sup> found that the ratio of base-catalyzed exchanges 3-exo:3-endo is 715:1.

**Homoenolization.**<sup>25</sup> The simplest molecule capable of undergoing this process is propionaldehyde, homoenolization of which would give cyclopropanol. The

(24) (a) E. J. Corey and R. A. Sneed, *J. Amer. Chem. Soc.*, **78**, 6269 (1956). The conclusions of these authors have been questioned in the light of more recent work. See F. G. Bordwell and R. G. Scamehorn, *ibid.*, **90**, 6749 (1968); (b) T. T. Tidwell, *ibid.*, **92**, 1448 (1970); (c) S. P. Jindal, S. S. Sohoni, and T. T. Tidwell, *Tetrahedron Lett.*, 779, 783 (1971).

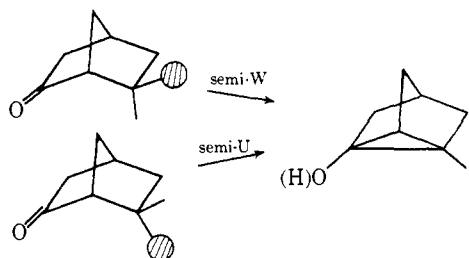
(25) A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **84**, 4604 (1962).



ring closure may occur with either retention or inversion of configuration at  $C_3$ , and by analogy with 1,3-eliminations (*vide supra*) the corresponding transition states may be designated semi-U or semi-W. For each of these possibilities values of  $E_{\min}$  were calculated for 49 conformations of the reactant arising from rotation about both C-C bonds. The lowest values of  $E_{\min}$  for retention and inversion of configuration are found for conformations in which the trigonal plane of the carbonyl is perpendicular to the plane comprising  $HC_3C_2C_1$ . Comparison of these lowest values favors reaction by a semi-W ( $0.97 \text{ \AA}^2$ ) rather than a semi-U transition state ( $2.40 \text{ \AA}^2$ ).<sup>26</sup>

Due to the free rotation about the C-C bonds it is difficult to study experimentally the stereochemistry of the homoenolization of open-chain compounds. However, the stereochemistry of the reverse process has been studied,<sup>27</sup> and it was found that in alkaline media the ring opening of a cyclopropanol derivative proceeded with inversion of configuration, *i.e.*, protonation of the incipient carbanion occurred from the more remote side. This result<sup>27</sup> implies that, in the microscopic reverse sense, homoenolization proceeds through a semi-W transition state. On the other hand, results obtained by DePuy<sup>27</sup> and by Nickon<sup>28</sup> from ring-opening experiments conducted in acidic media suggest a semi-U transition state. Here, however, the over-all stereochemical result may be prescribed by edge protonation of the cyclopropane ring.

Much of the experimental work on homoenolization has involved studies of bicyclic ketones. With this in mind calculations were also carried out for the homoenolization of 2-norbornanone in which 6-*exo* H



abstraction corresponds to a semi-W transition state and 6-*endo* H abstraction corresponds to a semi-U transition state. Again the results favor the former over the latter ( $E_{\min} = 4.63$  vs.  $8.11 \text{ \AA}^2$ ),<sup>29</sup> *i.e.*, preferential abstraction of the 6-*exo* proton. This finding is in accord with the experimental studies of Nickon, Werstiuk, and coworkers<sup>28</sup> for results obtained in basic

(26) Note that these values are very close to those found for the analogous conversions of the *n*-propyl cation to cyclopropane (*vide supra*).

(27) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Amer. Chem. Soc.*, **88**, 3347 (1966).

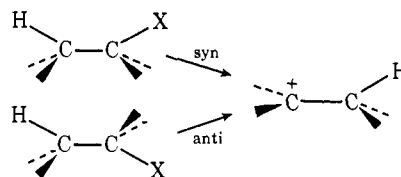
(28) (a) A. Nickon, J. L. Lambert, S. J. R. O. Williams, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **88**, 3354 (1966); (b) N. H. Werstiuk, *Can. J. Chem.*, **48**, 3966 (1970).

(29) Again note the similarities of these values to those found for the conversions of the 2-norbornyl cation to nortricyclene (*vide supra*).

media. Their results, however, from acidic media again suggest a semi-U transition state.

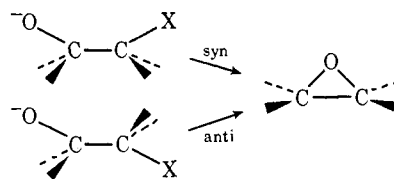
**Concerted 1,2-Hydride Shift.** The possible stereochemistry of a 1,2-hydride shift in the ethyl cation has been considered earlier from a least motion viewpoint.<sup>1</sup> If, however, the formation of the cation (*i.e.*, the loss of a leaving group) is concerted with the migration of the hydrogen, then two quite distinct processes may be envisaged: one in which the migrating hydrogen and the leaving group are syn-periplanar, and one in which they are anti-periplanar.

Both of these possibilities have now been considered in relation to PLM. Calculations were performed for various conformations of the reactant and product,<sup>30</sup> and minimum values of  $E_{\min}$  were found corresponding



exactly to the syn-periplanar and anti-periplanar migrations depicted above.<sup>30</sup> Over-all the PLM calculations favor anti- over syn-periplanar migration ( $2.33$  vs.  $3.09 \text{ \AA}^2$ ).<sup>31</sup> Intuitively, this might be anticipated because of the conceptual similarity to 1,2-eliminations and to epoxidation (see next section).

**Epoxidation.** Similar to the process just considered, the formation of ethylene oxide from 2-chloroethoxide ion could conceivably arise by displacement of  $Cl^-$  in



either a syn or anti process. Calculation of values of  $E_{\min}$  for various conformations of reactant for both types of process favored the anti-periplanar displacement ( $E_{\min} = 0.68 \text{ \AA}^2$ ) rather than the syn displacement ( $E_{\min} = 1.41 \text{ \AA}^2$ ). Such a conclusion was reached on the basis of experiment many years ago.<sup>32</sup>

## Conclusions

The results presented here extend considerably the apparent range of applicability of the PLM method previously described.<sup>1,2,4</sup> As was noted before,<sup>1,2</sup> there is very good agreement between the preferences suggested by the calculations of  $E_{\min}$  values and those observed experimentally or predicted by more sophisticated theoretical treatments. Of the 15 different reactant-product systems considered in the present paper only one gave a PLM prediction in major conflict with

(30) For each type of migration 49 different combinations of reactant and product conformations were considered. A minimum value for syn migration is found for the reactant having a dihedral angle of  $0^\circ$  between migrating H and leaving group and for the product having the migrated H in a plane perpendicular to the trigonal plane. The minimum value for anti migration occurs where the same dihedral angle in the reactant is  $180^\circ$ , and the product has the same configuration as previously described.

(31) Interestingly, these two numbers are respectively smaller and larger than that found previously ( $2.60 \text{ \AA}^2$ ) for migration in the discrete cation. See Table V of ref 1.

(32) (a) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **61**, 1576 (1939); (b) P. D. Bartlett, *ibid.*, **57**, 224 (1935).

experimental observation, this being in connection with 1,3-eliminations from 2-norbornyl tosylates for which a truly concerted process may not apply.

For only two of the 33 different systems considered in this and earlier papers<sup>1,2</sup> are there major discrepancies between the PLM result and experimental observation. In view of this high degree of agreement it is unlikely that the concordance is purely fortuitous. However, the apparent success of the PLM method does not necessarily imply that least motion of atoms is itself the factor which determines stereochemical pathways. It may well transpire that the least motion type of calculation, by virtue of its geometric constraints and

hence its implicit adherence to requirements of local symmetry, is successfully simulating some more important stereoelectronic factors.

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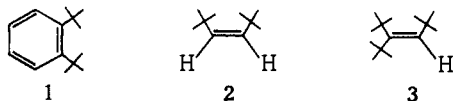
## Chemistry of *cis*- and *trans*-2,3-Di-*tert*-butylthiiranes (Episulfides). Some Observations on the Consequences of Steric Overcrowding in Small Ring Compounds

Peter Raynolds, Steven Zonnebelt, Silvia Bakker, and Richard M. Kellogg\*

Contribution from the Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands. Received November 27, 1973

**Abstract:** Chemical reactions of *cis*- and *trans*-2,3-di-*tert*-butylthiiranes (episulfides) have been investigated. The *cis* isomer has extra steric strain because of the interference of the bulky *tert*-butyl groups. One side of the molecule is exposed to attack by various reagents. The *trans* isomer, although probably less strained, is better shielded from attack on either side of the ring. The sulfoxides from both isomers have been prepared as well as an *S*-methylsulfonium salt from the *cis* isomer. Chlorine cleaves a sulfur-carbon bond of the *cis* isomer but gives a complex reaction with the *trans* isomer. Somewhat related behavior is seen with *tert*-butyl hypochlorite. Protonation of both the *cis* and *trans* isomers on the sulfur atom occurs in fluorosulfonic acid. In none of the derivatives prepared was there any evidence for ring opening to a presumably less strained 2-thia analog of an allyl cation. The *S*-methylsulfonium salt underwent ring opening in the expected *trans* fashion with a variety of nucleophiles (water, methanol, chloride, bromide). No evidence for initial attack on sulfur was forthcoming although precedent exists for this type of reaction.

A leitmotiv of organic chemistry is the juxtapositioning of *tert*-butyl groups. Classic examples in which these bulky substituents are positioned on adjacent trivalent carbon atoms are found in *o*-di-*tert*-butylbenzene (1),<sup>1</sup> *cis*-1,2-di-*tert*-butylethylene (2),<sup>2</sup> and 1,1,2-tri-



*tert*-butylethylene (3).<sup>3</sup> The steric crowding introduces undeniable strain (22.3 kcal/mol in **1** relative to the *para* isomer,<sup>1</sup> 10 kcal/mol in **2** relative to the *trans* isomer,<sup>4</sup> apparently unknown in **3**). Hope of discov-

ering the means by which such strain manifests itself in structural features, spectral properties, and chemical reactivity has provided a major impetus for the synthesis and examination of these types of compounds.<sup>5,6</sup>

Our own interest in this general area was stimulated when the *cis*- and *trans*-2,3-di-*tert*-butylthiiranes (episulfides) **4** and **5** became available to us through the routes in eq 1 and 2.<sup>7</sup> *tert*-Butyl groups and other bulky aliphatic substituents are often useful in stabilizing sensitive three-membered rings but in the examples reported thus far<sup>8</sup> the *tert*-butyl groups appear to be in the sterically

(5) The effects of the considerable steric interaction in these types of compounds are often remarkably muted. Available evidence suggests that in **1** there is no significant deviation from planarity of the  $\pi$  system;<sup>4d,6a</sup> the same holds true in *o*-di-*tert*-butylquinoxaline, the crystal structure of which has been determined.<sup>6b</sup> Bending from planarity of an aromatic system is accomplished in an [8]paracyclophane,<sup>6c</sup> however, and calculations indicate that mild deviations from planarity of the benzene ring require remarkably little energy.<sup>6d</sup> In **2** there appears to be no appreciable twisting of the carbon-carbon double bond.<sup>6e</sup>

(1) (a) For a compilation of references, see E. M. Arnett, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5889 (1967). (b) For *o*-di-*tert*-butyl aromatics, see Ae. de Groot and H. Wynberg, *J. Org. Chem.*, **31**, 3954 (1966). (c) For a discussion of much of the thought that led to interest in *o*-di-*tert*-butyl compounds, see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.

(2) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **81**, 1611 (1959).

(3) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 4125 (1970).

(4) (a) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958); (b) M. S. Newman, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 248; (c) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972); (d) M. B. Robin, G. N. Taylor, and N. A. Kuebler, *J. Org. Chem.*, **38**, 1049 (1973).

(6) (a) E. H. Wiebenga and E. Bouwhuis, *Tetrahedron*, **25**, 453 (1969); (b) G. J. Visser, A. Vos, Ae. de Groot, and H. Wynberg, *J. Amer. Chem. Soc.*, **90**, 3253 (1968); (c) M. G. Newton, T. J. Walter, and N. L. Allinger, *ibid.*, **94**, 5652 (1972); also C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (d) H. Wynberg, W. Nieuwpoort, and H. T. Jonkman, *Tetrahedron Lett.*, 4623 (1973); (e) M. B. Robin, G. N. Taylor, N. A. Kuebler, and R. D. Bach, *J. Org. Chem.*, **38**, 1049 (1973); see also N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972), and ref 6a.

(7) J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972).