Chiral Induction in photochemical reactions 10. The principle of isoinversion: A model of stereoselection developed from the diastereoselectivity of the Paterno-Buchi reaction

5 AUTHORS, INCLUDING:

Helmut Buschmann
RWTH Aachen University
89 PUBLICATIONS **1,920** CITATIONS

SEE PROFILE

Norbert Hoffmann
French National Centre for Scientific Research
107 PUBLICATIONS **2,268** CITATIONS

SEE PROFILE

Chiral Induction in Photochemical Reactions. 10.[1] The Principle of Isoinversion: A Model of Stereoselection Developed from the Diastereoselectivity of the Paternò-Büchi Reaction

Helmut Buschmann, Hans-Dieter Scharf,*,[†] Norbert Hoffmann, Martin Wolfgang Plath, and Jan Runsink

Contribution from the Institut für Organische Chemie der RWTH Aachen Prof.-Pirlet-Strasse 1, D-5100 Aachen, Federal Republic of Germany. Received July 25, 1988. Revised Manuscript Received February 1, 1989

Abstract: In the Paternò-Büchi reaction of the chiral phenylglyoxalates **a–c** with cyclic olefins **3–6**, the diastereomeric oxetanes **3–6a–c** and **3–6a′–c′** are formed *endo*-phenyl selectively in high chemical yields. The temperature dependence of the diastereoselectivity yields two linear functions in the corresponding Eyring diagrams. Two sets of activation parameters ($\Delta\Delta H^*_1$ and $\Delta\Delta S^*_1$, and $\Delta\Delta H^*_2$ and $\Delta\Delta S^*_2$) are derived from each Eyring diagram. There exists a linear correlation between the new parameters $\delta\Delta\Delta H^*$ and $\delta\Delta\Delta S^*$, which we call the principle of isoinversion. Furthermore isoselective relationships were observed in the Eyring plots with regard to the change of the chiral auxiliary and the change of olefins. These isoselective relationships as well as the principle of isoinversion allow a mechanistic description of the diastereoselection in the Paternò-Büchi reaction with cyclic olefins.

The Paternò-Büchi reaction[2] is one of the best known photoreactions[3,4] not only because of its preparative interest (e.g. "photoaldolization")[5] but also as a very useful example for studying the selection processes in bimolecular photochemical reactions. The addition of ^{3}(nπ)*-excited chiral α-keto esters (type 1) to electron-rich olefins leads in high chemical yields to the diastereomeric oxetanes **2** and **2′** shown in reaction 1.[6,7]
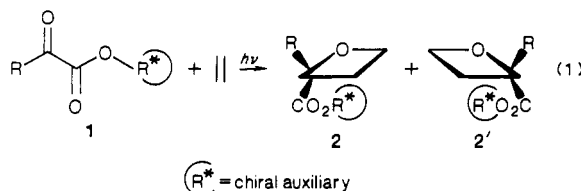
$\textcircled{R}^*$ = chiral auxiliary

During our systematic investigation of the chiral induction observable in this reaction,[7,8] we found that the following items determine the degree of stereoselection: the structure of the chiral auxiliary R*-OH,[7,8,9] the nature of the substituent R in the α-keto moiety,[7,10] the olefinic partner, and the reaction conditions (solvent,[11] addition of metal ions,[11] and in particular the reaction temperature[7b,8]).

Neither the irradiation time nor the concentration of the reactants have any significant influence on the product distribution. Hitherto temperature dependences of diastereoselective photochemical processes have been investigated only in a few cases.[12] Primarily we observed the dependence of temperature in diastereo- and regioselection[13] processes in the systems of tetramethylethylene and 1,1′-diethoxyethylene and chiral α-keto esters,[7,8] respectively.

Table I. Structures[7,8] of the Applied Cyclic Olefins **3–6** and Chiral Phenylglyoxalates **a–c**[a]

cyclic olefin	chiral phenylglyoxalate	excess and minor oxetane
3	**a**	3a - c 4a - c 5a - c 6a - c
4	**b**	
5	**c**	3a′ - c′ 4a′ - c′ 5a′ - c′ 6a′ - c′
6		

[a] The numbering of the oxetane is composed of the olefin number and the letter of the phenylglyoxalate. The minor isomer is indicated with a prime. The phenylglyoxalates **b** and **c** were used in racemic form. There are no different results by using the enantiomerically pure phenylglyoxalates.

The ln *P* values were found to be linearly dependent on the reciprocal of temperature according to the Eyring formalism:[14]

$$\ln P = \frac{-\Delta\Delta H^*}{R}\frac{1}{T} + \frac{\Delta\Delta S^*}{R} \qquad (2)$$

[†] Dedicated to the memory of David Ginsburg.

(1) Pelzer, R.; Jütten, P.; Scharf, H.-D. *Chem. Ber.* **1989**, *122*, 487.
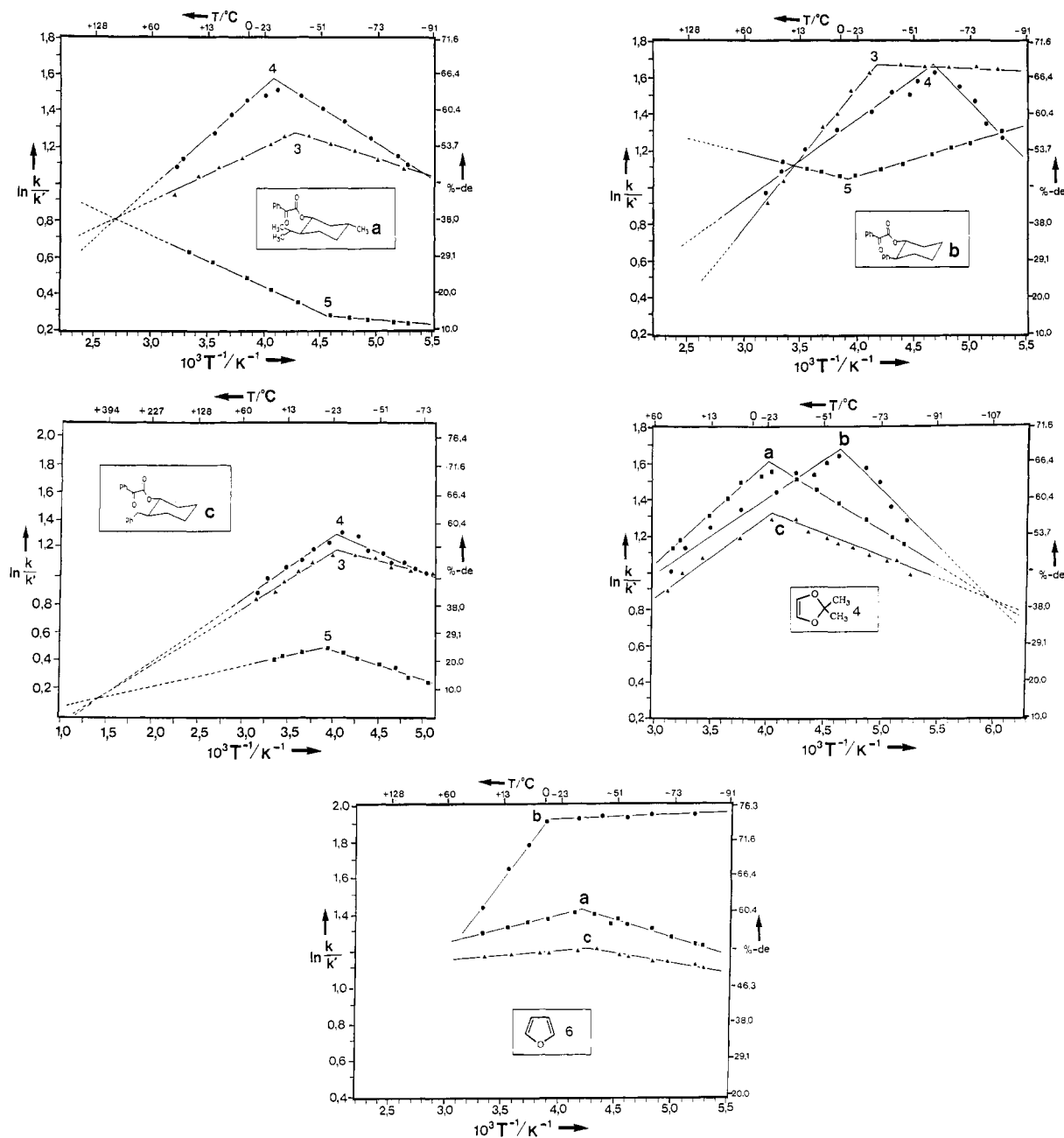
Figure 1. Eyring plots and isoselective temperatures, T_{iso} (evaluated according to Giese[15]), for the following systems: (i) phenylglyoxalate a/dioxols 3–5, T_{iso} = 378 K (top, left); (ii) phenylglyoxalate b/dioxols 3–5, T_{iso} = 287 K (top, right); (iii) phenylglyoxalate c/dioxols 3–5, T_{iso} = 752 K (middle, left); (iv) phenylglyoxalate a–c/dioxols 4, T_{iso} = 162 K (middle, right); and (v) phenylglyoxalate a–c/furan (6) (bottom).

where $P = k$(excess oxetane)/k'(minor oxetane) = I(excess oxetane)/I'(minor oxetane),[13] k and k' are rate constants of the

overall reaction 1 for the formation of diastereomeric and regioisomeric oxetanes, respectively, and I and I' are the intensity

(2) (a) Paternò, E.; Chieffi, G. *Gazz. Chim. Ital.* **1909**, *39*, 341. (b) Büchi, G.; Inman, C. G.; Lipinsky, E. S. *J. Am. Chem. Soc.* **1954**, *76*, 4327.

(3) (a) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301. (b) Jones, G. II *Organic Photochemistry*; Padwa, A. Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 1. (c) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255. (d) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 3819. (e) Carless, H. A. J. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1983, p 425. (f) Braun, M. *Nachr. Chem., Tech. Lab.* **1985**, *33*, 213. (g) Wilson, K. M. *Organic Photochemistry*; Padwa, A. Ed.; Marcel Dekker: New York, 1985; Vol. 7, p 339. (h) Rau, H. *Chem. Rev.* **1983**, *83*, 535. (i) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(4) (a) Turro, N. J. *Modern Molecular Photochemsitry*; The Benjamin/Cummings Publishing Company, Inc.; Menlo Park, CA, 1978. (b) Turro, N. J.; Wriede, P. A. *J. Am. Chem. Soc.* **1970**, *92*, 320. (c) Turro, N. J.; et al. *Acc. Chem. Res.* **1972**, *5*, 92. (d) Turro, N. J. *Pure Appl. Chem.* **1971**, *27*, 679. (e) Dalton, J. C.; Turro, N. J. *Ann. Rev. Phys. Chem.* **1970**, *71*, 499.

(5) (a) Araki, Y. *Carbohydr. Res.* **1977**, *58*, C4–C6. (b) Araki, Y. *J. Chem. Soc., Perkin Trans 1* **1981**, *12*. (c) Schreiber, S. L. *Science* **1985**, *227*, 857. (d) Schreiber, S. L. *J. Am. Chem. Soc.* **1983**, *105*, 660. (e) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1983**, *105*, 6723. (f) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1984**, *106*, 4186. (g) Schreiber, S. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1984**, *106*, 7200. (h) Nehrings, A.; Scharf, H.-D.; Runsink, J. *Angew. Chem.* **1985**, *97*, 882; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 877. (i) Weuthen, M.; Scharf, H.-D.; Runsink, J.; Vaßen, R. *Chem. Ber.* **1988**, *121*, 971. (j) Kožluk, T.; Zamojski, A. *Tetrahedron* **1983**, *39*, 805.

(6) (a) Zamojski, A.; Jarosz, S. *Tetrahedron* **1982**, *38*, 1447; *Ibid* **1982**, *38*, 1453. (b) Jarosz, S. *Wiad. Chem.* **1983**, *37*, 167. (c) Gotthard, H.; Lenz, W. *Angew. Chem.* **1979**, *91*, 926; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 868.

(7) (a) Koch, H.; Runsink, J.; Scharf, H.-D. *Tetrahedron Lett.* **1983**, 3217. (b) Koch, H.; Runsink, J.; Scharf, H.-D.; Leismann, H. *Chem. Ber.* **1985**, *118*, 1485. (c) Runsink, J.; Koch, H.; Scharf, H.-D.; Nehrings, A. *J. Chem. Soc., Perkin Trans. 2* **1988**, 49. (d) Weuthen, M. Dissertation, RWTH Aachen, 1987. (e) Mitrowski, K. J. Dissertation, RWTH Aachen, 1988. (f) Vaßen, R. Dissertation, RWTH Aachen, 1988.

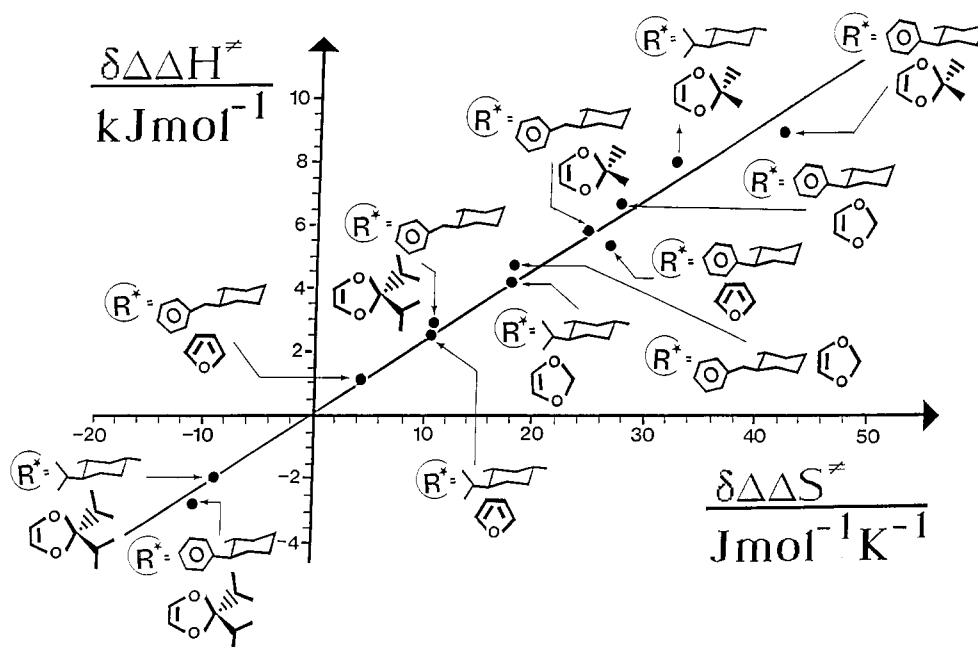(8) Koch, H. Dissertation, RWTH Aachen, 1984.

Figure 2. $\delta\Delta\Delta H^{\neq}/\delta\Delta\Delta S^{\neq}$ diagram.

of relevant signals in ^{13}C NMR spectra of the diastereomeric and regioisomeric mixture, respectively.

Furthermore, we observed an isoselective relationship, like Giese[15] found in carbene and simple radical reactions. In our early investigations the influence of temperature was not uniform on the regio- and diastereoselection. Diastereoselection may increase, but alternatively it may be constant or even decrease with decreasing temperature, contrary to common opinion.

Results and Discussion

In the present paper we study the temperature dependence of the reaction between the cyclic olefins **3–6** and the chiral phenylglyoxalates **a–c** (Scheme I, Table I). Substituted cyclohexanols

---

(9) Buschmann, H.; Scharf, H.-D. *Tetrahedron Lett.* Submitted for publication.

(10) Pelzer, R.; Scharf, H.-D.; Buschmann, H.; Runsink, J. *Chem. Ber.* In press.

(11) Hoffmann, N. Diplomarbeit, RWTH Aachen, 1986.

(12) (a) Vanest, J.-M.; Martin, R. H. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 113. (b) Lange, G. L.; Decicco, C.; Lee, M. *Tetrahedron Lett.* **1987**, 2833. (c) Pete, J.-P.; Hénin, F.; Mortezaei, R.; Muzart, J.; Piva, O. *Pure Appl. Chem.* **1986**, *58*, 1257. (d) Demuth, M. *Pure Appl. Chem.* **1986**, *58*, 1233. (e) Demuth, M.; Palomer, A.; Sluma, H.-D.; Dey, A. K.; Krüger, C.; Tsay, Y.-H. *Angew. Chem.* **1986**, *98*, 1093; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1117.

(13) (a) The diastereo- and regioselectivity is defined according to D. Seebach; Seebach, D. *Angew. Chem.* **1979**, *91*, 259; *Angew Chem., Int. Ed. Engl.* **1979**, *18*, 239. (b) The diastereoselectivity of the reaction is characterized by the de value of the excess oxetane:

$$\% \ de = \frac{c - c'}{c + c'} 100 = \frac{\sum\limits_{i=1}^{n}(I_i - I_i')/(I_i + I_i')}{n} 100$$

where c and c' are the concentration of the excess and minor oxetane, respectively, in the diastereomeric mixture, and n is the number of evaluated signal pairs in the ^{13}C NMR spectra ($n = 14$–16).

(14) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

(15) (a) Giese, B. *Angew. Chem.* **1977**, *89*, 162; *Angew. Chem.*, Int. *Ed. Engl.* **1977**, *16*, 125. (b) Giese, B. *Acc. Chem. Res.* **1984**, *17*, 438. (c) Giese, B.; Meister, J. *Angew. Chem.* **1978**, *90*, 636; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 595. (d) Giese, B.; Lee, W.-B.; Meister, J. *Liebigs Ann. Chem.* **1980**, *725*. (e) Giese, B.; Lee, W.-B. *Angew. Chem.* **1980**, *92*, 864; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 835. (f) Giese, B.; Lee, W.-B.; Neumann, C. *Angew. Chem.* **1982**, *94*, 320; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 310. (g) Giese, B. *Angew. Chem.* **1976**, *88*, 159; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 173. (h) Giese, B. *Angew. Chem.* **1976**, *88*, 161; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 174. (i) Giese, B. *Angew. Chem.* **1976**, *88*, 723; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 688.

Scheme I. The Oxetane Formation and the Corresponding 1,4-Biradical Intermediates[a]
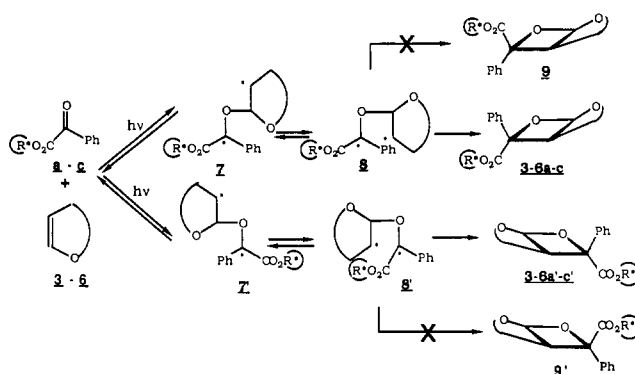
[a] Most probably the trans-1,4-biradical **7,7'** is formed first, but for ring closure the cis-configurated biradical **8, 8'** is necessary.

were included as chiral auxiliaries. They produce diastereomeric excesses in the medium range (de values[13b] between 30% and 70%), where the determination of the activation parameters $\Delta\Delta H^*$ and $\Delta\Delta S^*$, from temperature-dependent measurements of the diastereomeric excess, is optimal. In each of the oxetanes **3–6a–c** and **3–6a'–c'**, the phenyl ring and the olefinic moiety are cis to each other (*endo*-phenyl structure).[7,8] Toluene was used as solvent in the photochemical reactions except in cases in which neat furan **6** was used as olefinic partner because of its lower reactivity. The results are presented in Eyring plots (Figure 1, parts i–v). Each plot is characterized by a point of inversion. The corresponding temperature is called the "inversion temperature", T_{inv}, of the system. Obviously the dominance of the partial selection steps varies as a consequence of the change of enthalpy and entropy influence. Furthermore, strict linearity on both sides of the inversion point was found. Generally the transition regions are quite narrow. In two examples the transition region is broadened (**4a,a'** and **4c,c'**) however.

In the high-temperature range ($T > T_{inv}$), points of isoselectivity[15] exist with regard to the variation of the dioxols **3–5** for a given auxiliary (Figure 1 parts i–iii). In the low-temperature area ($T < T_{inv}$) an isoselective point with regard to the variation of the phenylglyoxalates **a–c** for a given olefin is observed (Figure 1iv). The inversion temperature reveals two sets of parameters of activation ($\Delta\Delta H^*_1$ and $\Delta\Delta S^*_1$, and $\Delta\Delta H^*_2$ and $\Delta\Delta S^*_2$) for each system, corresponding to a change of dominance of partial selection

5370 *J. Am. Chem. Soc., Vol. 111, No. 14, 1989*

Buschmann et al.

$$\ln\frac{k}{k'} = -\frac{\Delta\Delta H^{\neq}}{R}\cdot\frac{1}{T} + \frac{\Delta\Delta S^{\neq}}{R}$$

$$\delta\Delta\Delta G^{\neq} = \delta\Delta\Delta H^{\neq} - T\,\delta\Delta\Delta S^{\neq}$$
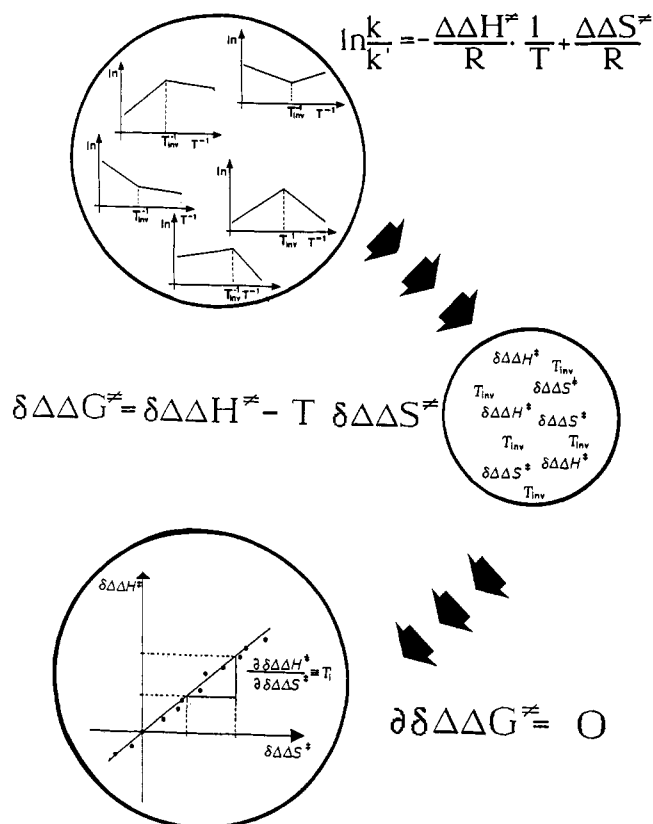
$$\partial\delta\Delta\Delta G^{\neq} = 0$$

Figure 3. A schematic presentation of the derivation of the isoinversion temperature T_i.

steps. The new parameters $\delta\Delta\Delta H^{\neq}$ and $\delta\Delta\Delta S^{\neq}$ are derived according to eq 3 and 4. Table II presents the inversion temper-

$$\delta\Delta\Delta H^{\neq} = \Delta\Delta H^{\neq}_{2} - \Delta\Delta H^{\neq}_{1} \qquad (3)$$

$$\Delta\Delta H^{\neq}_{1},\ T > T_{inv}$$

$$\Delta\Delta H^{\neq}_{2},\ T < T_{inv}$$

$$\delta\Delta\Delta S^{\neq} = \Delta\Delta S^{\neq}_{2} - \Delta\Delta S^{\neq}_{1} \qquad (4)$$

$$\Delta\Delta S^{\neq}_{1},\ T > T_{inv}$$

$$\Delta\Delta S^{\neq}_{2},\ T < T_{inv}$$

atures T_{inv} and the parameters of activation $\Delta\Delta H^{\neq}_{1,2}$ and $\Delta\Delta S^{\neq}_{1,2}$ as well as the $\delta\Delta\Delta H^{\neq}$ and $\delta\Delta\Delta S^{\neq}$ values. The inversion temperatures range from 213 to 265 K. No correlation is found between the T_{inv}^{-1} values and the corresponding $\ln k/k'$ values, but strict linearity exists in the enthalpy/entropy diagram (correlation factor >0.99) for the obtained $\delta\Delta\Delta H^{\neq}$ and $\delta\Delta\Delta S^{\neq}$ values. The regression line passes through the origin of the coordinate (Figure 2). The observed principle, shown in Figure 2, is obviously of general importance for diastereoselection in the Paternò–Büchi reaction. It gives evidence for the existence of the dominance change of the two partial selection steps (Figures 5 and 6) in the investigated reaction type. This principle is independent of the de values achieved in this reaction. We call the linear correlation in the $\delta\Delta\Delta H^{\neq}/\delta\Delta\Delta S^{\neq}$ diagram (Figure 2) the "principle of isoinversion". The slope of the regression line has the dimension of a temperature, which we define as "isoinversion temperature", T_i (eq 5). This T_i is a characteristic parameter of the dominance

$$T_i = \frac{\partial\,\delta\Delta\Delta H^{\neq}}{\partial\,\delta\Delta\Delta S^{\neq}} = 230\ \text{K} \qquad (5)$$

change of diastereoselection steps in the Paternò–Büchi reaction with cyclic olefins (Figure 3). Solvent dependences as well as viscosity effects were not investigated in detail. However, toluene
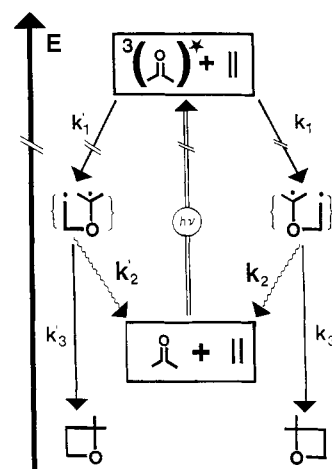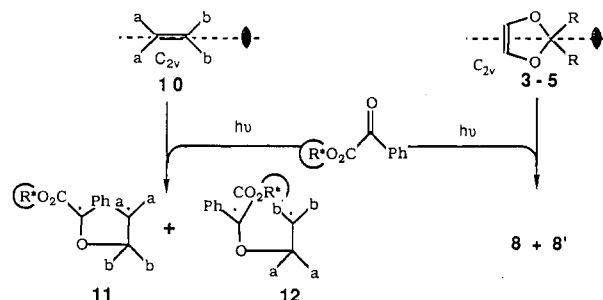

Figure 4. A simplified kinetic scheme of the diastereoselective oxetane formation in the Paternò–Büchi reaction (k_2 and k_2' as well as k_3 and k_3' include intersystem crossing steps).

Scheme II. Olefins of C_{2v} Symmetry Having a C_2 Axis Parallel or Perpendicular to the Double Bond

and furan yield values of $\delta\Delta\Delta H^{\neq}$ and $\delta\Delta\Delta S^{\neq}$ which are in accordance with the relationship in Figure 2.

Mechanism of Stereoselection

The photochemical diastereoselective oxetane formation could therefore be described by the following simple scheme (Figure 4): The initial step is a $^1(n\pi)^*$ excitation of the keto carbonyl function. By intersystem crossing a part of the excitation energy is lost and the system passes into the $^3(n\pi)^*$ state of lower energy. The existence of an exciplex intermediate in the Paternò–Büchi reaction is frequently discussed in literature[3] but hitherto without conclusive proof.[16] Subsequent to the release of most of the excitation energy the 1,4-biradical intermediate is formed. This intermediate has been trapped by radical species[18] and established by transient analytical methods.[3c,d] An important influence on the degree of energy dissipation is exerted by the substituent R in **1**.[8,10] The phenyl group was found to be very efficient in this matter. It stabilizes the 1,4-biradical intermediate. The intermediate **8** or **8'** (Scheme I) has only two possibilities to react. It may either undergo ring closure to the oxetane or dissociate to the reactants (retrocleavage). There is no indication for an equilibrium between the diastereomeric 1,4-biradicals (Figures 4 and 5). By reexcitation the system joins the reaction cycle again. In this way the retrocleavage establishes a "photon-driven selection pump", which consequently produces diastereoselectivity. The

(16) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neusberger, K. R.; Wrighton, M.; Zafiriou, O. L.; Chapman, O. C. *Organic Photochemistry*; Marcel Dekker: New York, 1978, Vol. 3, p 1.

(17) (a) Ooms, P.; Hartmann, W. *Tetrahedron Lett.* **1987**, 4271. (b) Schroeter, S. M.; Orlando, C. M. *J. Org. Chem.* **1969**, *34*, 1181. (c) Schroeter, S. M. *J. Org. Chem.* **1969**, *34*, 1188. (d) Schroeter, S. M. *J. Chem. Soc., Chem. Commun.* **1969**, *12*. (e) Dürr, H.; Heitkämpfer, P.; Herbst, P. *Synthesis* **1972**, 261.

(18) (a) Wilson, R. M.; Wunderly, S. W. *J. Chem. Soc., Chem. Commun.* **1974**, 461. (b) Adam, W.; Kliem, U.; Luccini, V. *Liebigs Ann. Chem.* **1988**, 869.
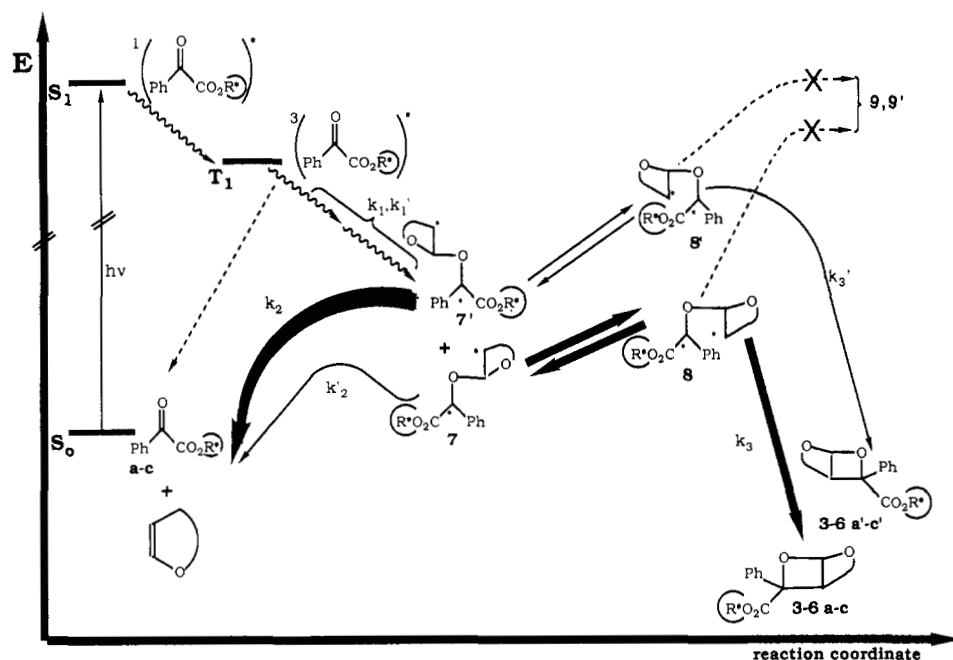
Chiral Induction in Photochemical Reactions

J. Am. Chem. Soc., Vol. 111, No. 14, 1989 5371

Figure 5. The structural relationship in the different selection steps of the Paternò–Büchi reaction with cyclic olefins.

difference in quantum yields between decay and the rate of oxetane formation gives evidence of the retrocleavage, since no side reactions can be detected [$\Phi = 0.39 \pm 0.01$ (oxetane formation), $\Phi = 0.61 \pm 0.01$ (retrocleavage)].[7f,8] Noncyclic olefins **10** having C_{2v} symmetry with a C_2 axis parallel to the double bond yield 1,4-biradical intermediates **11** and **12** without any new chiral center. This type of olefins generates regioisomeric oxetanes[7b,c,8,17] (Scheme II). Contrarily, C_{2v} symmetric olefins having a C_2 axis perpendicular to the double bond (cyclic olefins **3–5**) form 1,4-biradical intermediates **8** and **8'** with a new chiral center. Furan (**6**) as a cyclic olefin generates a new chiral center in the 1,4-biradical intermediate too, but exclusively the diastereometric oxetanes **6a–c** and **6a'–c'** are formed regioselectively in this particular case.[5] Because of the *endo*-phenyl structure in the oxetanes, all further chiral centers of the oxetane are determined by the first one in the 1,4-biradical intermediate. After formation of the intermediate, further diastereoselectivity control is now a consequence of the retrocleavage cycle. In the 1,4-biradical intermediate, energetically unfavored conformations predominantly undergo retrocleavage instead of ring closure to oxetanes. In this model diastereoselection is produced on two levels: (1) The preferred formation of the diastereomeric 1,4-biradical intermediate **8**, which leads to the excess oxetane and (2) The preferred cleavage of the energetically unfavored diastereomeric intermediate **8'** to the reactants (retrocleavage) or the preferred oxetane formation of the energetically favored intermediate **8**.

The existence of inversion temperatures T_{inv} implicates that each temperature region has its dominant selection step. This matter can be presented according to Figure 5. The kinetic description (eq 8) of the reaction (Figures 4 and 5) is evaluated from the

$$c\left(\begin{array}{c}\cdot\ \ \cdot\\ \mathrm{O}\_\!\!\rule{8pt}{0.5pt}\end{array}\right) = \frac{k_1}{k_2 + k_3}\, c\left(\left(\begin{array}{c}^3\\ \mathrm{O}\end{array}\right)^* + \|\right) \qquad (6)$$

$$c\left(\begin{array}{c}\Box\\ \mathrm{O}\end{array}\right) = k_3 \int_0^t c\left(\begin{array}{c}\cdot\ \ \cdot\\ \mathrm{O}\_\!\!\rule{8pt}{0.5pt}\end{array}\right) dt \qquad (7)$$

$$\frac{c\left(\begin{array}{c}\Box\\ \mathrm{O}\end{array}\right)}{c'\left(\begin{array}{c}\Box\\ \mathrm{O}\end{array}\right)} = \frac{k_1 k_3}{k_1' k_3'} \frac{(k_2' + k_3')}{(k_2 + k_3)} \qquad (8)$$

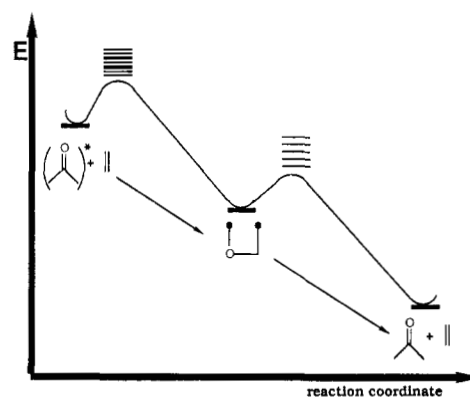steady-state assumption for the diastereomeric 1,4-biradical in-

Figure 6. The "early" transition states for the two selection steps (formation of the 1,4-biradical intermediate and its retrocleavage) with their corresponding vibration states. Energetically close vibrational states in the transition states characterize an entropy determination, energetically wide vibrational states characterize an enthalpy determination according to Skell.[19]
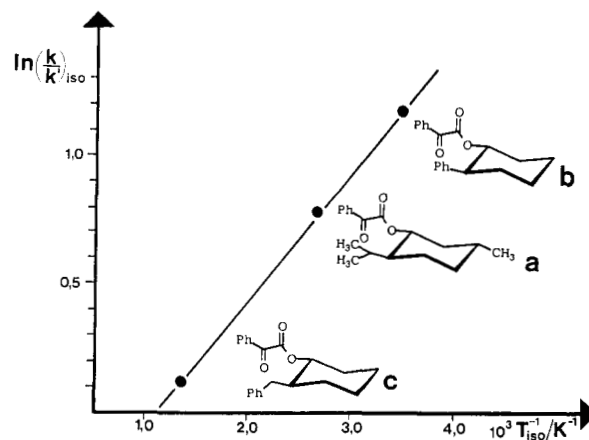
Figure 7. In $(k/k')_{iso}/T_{iso}$ diagram. The observed isoselective points for the auxiliaries **a–c** with regard to the variation of the dioxols **3–5** follow a linear course in the Eyring plot.

termediates **8** and **8'** and by application of the relationships 6 and 7. Rate constants of processes prior to the encounter of the reactants are negligible since they are identical for both diastereomers. They vanish therefore in the formalism 8–10. In the

5372 *J. Am. Chem. Soc., Vol. 111, No. 14, 1989*

Buschmann et al.

Table II. Inversion Temperature, T_{inv}, and Parameters of Activation, $\Delta\Delta H^{\ddagger}_1$, $\Delta\Delta S^{\ddagger}_1$ ($T > T_{inv}$), and $\Delta\Delta H^{\ddagger}_2$, $\Delta\Delta S^{\ddagger}_2$ ($T < T_{inv}$)

(R)*		$\Delta\Delta H^{\ddagger}_1$ $\Delta\Delta H^{\ddagger}_2$, kJ mol⁻¹	$\delta\Delta\Delta H^{\ddagger}$,[a] kJ mol⁻¹	$\Delta\Delta S^{\ddagger}_1$ $\Delta\Delta S^{\ddagger}_2$, J mol⁻¹ K⁻¹	$\delta\Delta\Delta S^{\ddagger}$,[a] J mol⁻¹ K⁻¹	T_{inv}, K (°C)
Ph	**3**	−6.32 / +0.33	6.65	−12.10 / +15.33	27.43	242 (−31)
	4	−3.58 / +5.32	8.90	−2.94 / +38.95	41.89	212 (−61)
	5	+1.25 / −1.50	−2.75	+14.23 / +3.42	−10.81	253 (−20)
	6	−6.98 / −0.17	6.81	−11.70 / +14.86	26.56	257 (−16)
Ph	**3**	−2.94 / +1.39	4.33	−2.06 / +15.59	17.65	245 (−28)
	4	−3.58 / +2.24	5.82	−3.69 / +20.04	23.73	245 (−28)
	5	−1.16 / +1.66	2.82	−0.48 / +10.19	10.67	265 (−8)
	6	−0.42 / +0.67	1.09	+8.40 / +12.70	4.30	249 (−24)
H₃C, H₃C, CH₃	**3**	−2.58 / +1.58	4.16	−0.24 / +17.56	17.80	234 (−40)
	4	−4.74 / +3.24	7.98	−5.86 / +26.41	32.27	247 (−26)
	5	+2.33 / +0.42	−1.91	+12.80 / +4.04	−8.76	218 (−55)
	6	−1.16 / +1.41	2.57	+7.09 / +17.54	10.45	229 (−44)

[a] The parameters $\delta\Delta\Delta H^{\ddagger}$ and $\delta\Delta\Delta S^{\ddagger}$ are derived from eq 3 and 4.

high-temperature region ($T > T_{inv}$), mostly enthalpy-determined selection is observed (Table II). This behavior is known for "early" transition states of bond cleavage in energy-rich reactants (the 1,4-biradical intermediates). This is in accordance to Skell[19] and Giese[15] (Figure 6). Contrarily, in the low-temperature region ($T < T_{inv}$) we observed mostly an entropy-determined selection for the formation of the 1,4-biradical intermediate from an energy-rich precursor. This is a bond-formation step due to an "early" transition state (the energy-rich precursor is the reactant). The correlation of the activation parameters to the selection steps is supported by the nature of the observed isoselectivities. Isoselective relationships for variation of olefins are found in the region

$T > T_{inv}$ and for variation of auxiliaries in the region $T < T_{inv}$. The diastereomeric excess in the high-temperature region ($T > T_{inv}$) is dominantly controlled by steric effects of the chiral auxiliaries, whereas in the low-temperature region ($T < T_{inv}$) the nature of the olefin becomes a dominating influence. Furthermore, in the high-temperature region we observe a strict linear relationship in the corresponding Eyring diagram of the isoselective points (Figure 7). Different isoselective points of a particular reaction indicate a slight variation of the basic selection mechanism.[15]

Keeping in mind that increasing temperature ($T > T_{inv}$, $k_2 > k_3$) favors the retrocleavage more than the bond formation, we obtain eq 9 as a limit expression for relationship 8. In the area $T < T_{inv}$ ($k_3 > k_2$) eq 8 simplifies to expression 10.

(19) Skell, P. S.; Cholod, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 7131.

$$\frac{c\left(\begin{array}{c}\boxed{}\\ \text{O}{-}\end{array}\right)}{c'\left(\begin{array}{c}\boxed{}\\ {-}\text{O}\end{array}\right)} = \frac{k_1}{k_1'} \cdot \left(\frac{k_3 \cdot k_2'}{k_3' \cdot k_2}\right) \qquad (9)$$

$$\frac{c\left(\begin{array}{c}\boxed{}\\ \text{O}{-}\end{array}\right)}{c'\left(\begin{array}{c}\boxed{}\\ {-}\text{O}\end{array}\right)} = \frac{k_1}{k_1'} \qquad (10)$$

For the reaction of dioxol **5** in the high-temperature region an entropy-determined selection ($\Delta\Delta S^{\ddagger} \gg 0$, $\Delta\Delta H^{\ddagger} > 0$) is observed (Figure 1, Table II). According to Price and Hammett,[20] transition states ($\Delta G^{\ddagger}$) resulting from reactants with highly populated degrees of freedom as strongly influenced by entropy. The same considerations have to be made for comparisons of transition states from competitive reaction pathways ($\Delta\Delta G^{\ddagger}$). Nevertheless the selection mechanism corresponds to those described above, because these reactions belong to systems with isoselective points (Figures 1 and 7), which is characteristic for an identical basic mechanism.[15] Thus the matter of isoinversion is based on the same mechanistic pattern.

Conclusion

It is obvious that this observed competition between enthalpy- and entropy-determined partial selection steps in complex chemical systems may very likely be a general principle, which allows optimization of selectivity either by changing reaction temperature, by structural adaption of a system for a given temperature or by a combination of both.

Experimental Section

¹H NMR and ¹³C NMR spectra were recorded on a Varian VXR-300 in CDCl₃ as solvent and TMS as internal standard. The solvents and chemicals were purified by general methods.

Racemic *trans*-2-phenylcyclohexanol and *trans*-2-benzylcyclohexanol were synthesized from cyclohexene oxide and the corresponding Grignard

reagents according to ref 21. The optically pure alcohols were obtained by enzymatic racemic resolution.[22] (–)-Menthol was kindly provided by Haarmann & Reimer (Holzminden). The phenylglyoxalates a–c were synthesized by a modified Stadler method.[23] The dioxols **3** and **4** were obtained by Field's route; dioxol **5** was prepared by our method.[25] Furan (**6**) (Fa. Merck) was distilled under nitrogen and used without further purification.

All temperature-dependent irradiations were carried out under nitrogen in a photoreactor which was fitted with an immersion well (vacuum jacket, Pyrex glass) and a high pressure mercury lamp HPK 125 W (Philips). The photoreactor was plunged in a thermostated bath.

Irradiation of the Phenylglyoxalates a–c with the 2,2-Disubstituted 1,3-Dioxols 3–5. Solutions of the esters a–c (7 mmol) in toluene (200 mL, 0.035 M) were flushed with nitrogen in the photoreactor. The dioxols **3–5** (8 mmol, 0.04 M) were added after 30 min of thermostatisation. After 8 h of irradiation, the conversion was complete. The solvent was evaporated and the residue was dissolved in dichloromethane, percolated over 25 g of silica gel, and eluated with 250 mL of dichloromethane. The filtate was evaporated and the residue was dried in high vacuum. The diastereomeric oxetane mixtures were obtained as colorless syrups.

Irradiation of the Phenylglyoxalates a–c with Furan (6). The photoreactor was charged with the reaction solution (7 mmol of the respective ester a–c in 200 mL of furan (**6**), 0.035 M). After 30 min of thermostatisation under nitrogen, the solution was irradiated for 24 h. The furan adducts were obtained as white crystalline solids. The workup was the same as above.

Under the described reaction conditions no further byproducts were formed. The yield of oxetane was nearly quantitative. The diastereomeric ratio of the products was determined by ¹³C NMR spectra.[13] Depending on the system, 14–16 signals could be used for the determination of the de values. The values given in the Eyring plots (Figure 1, parts i–v) are the average values, which minimize the influence of different NOE and of spin-relaxation effects. Each point in the Eyring plots (Figure 1, parts i–v) was confirmed by three independent measurements.

(20) Price, F. P.; Hammett, L. P. *J. Am. Chem. Soc.* **1941**, *63*, 2387.

(21) Huynh, C.; Verguini-Boumechal, F.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, 1503.

(22) (a) Whitesell, J. K.; Chen, H.-H. Lawrence, R. M. *J. Org. Chem.* **1985**, *50*, 4664. (b) Whitesell, J. K.; Lawrence, R. M. *Chimica* **1986**, *40*, 318.

(23) (a) Stadler, P. A. *Helv. Chim. Acta* **1978**, *61*, 1675. (b) Herzog, H.; Scharf, H.-D. *Synthesis* **1986**, 420. (c) Buschmann, H.; Scharf, H.-D. *Synthesis* **1988**, 827.

(24) Field, N. D. *J. Am. Chem. Soc.* **1961**, *83*, 3504.

(25) Meier, L.; Scharf, H.-D. *Synthesis* **1987**, 517.

The Mechanism of Rearrangement of the Icosahedral Carboranes[1]

Shao-hai Wu* and Maitland Jones, Jr.*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received September 19, 1988. Revised Manuscript Received February 7, 1989

Abstract: The bridged *o*-carborane **5** rearranges on heating to all four possible isomers in which the three-carbon bridge spans adjacent positions. These are the new ortho isomer **6** and the three possible *m*-carboranes **7–9**. After 30 min at 450 ± 5 °C, the ratios of **5/6/7/8/9** = 39/16/5/16/25. The meta compounds do not interconvert under these conditions. Although the further rearrangement of **6** does take place, the ratio of the three meta compounds changes only slightly with time and can be summarized as **7/8/9** = 9/34/57. The formation of **9** as the major product is inconsistent with the popular "diamond–square–diamond" mechanism. The extended triangle rotation mechanism, which focuses on the preservation of triangular faces throughout the rearrangement, is suggested to rationalize both data from the literature and the results from the pyrolysis of **5**.

Framework rearrangements are characteristic of polyhedral boranes and heteroboranes, and there have been many attempts

to determine the mechanisms of these reactions.[2] The effort to provide a general mechanism capable of rationalizing all data and