The Effect of Pressure on Cyclizations. The Ring-Size Dependent Reaction Volumes of the Cyclization of 1-Alkenes to Cycloalkanes. Experimental Measurement of Activation and Reaction Volumes of the Intramolecular Diels−Alder Reaction of 1,3,8-Nonatriene and 1,3,9-Decatriene. Temperature Dependence of Activation and Reaction Volumes

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Received November 17, 1997. Revised Manuscript Received April 28, 1998

Abstract: The volumes of reaction determined for the hypothetical cyclization of 1-alkenes to cycloalkanes decrease continuously from the formation of cyclopropane ($\Delta V^R = -5.5$ cm^3 mol^{-1}) up to the formation of cyclodecane ($\Delta V^R = -32.3$ cm^3 mol^{-1}) and seem to be constant for the larger rings. The analysis of the packing coefficients ($\eta = V_W/V$) leads to the conclusion that this ring-size dependent decrease in volume results from the different packing of cyclic and acyclic compounds rather than from the changes in their intrinsic molecular volumes. The investigation of the intramolecular Diels−Alder reactions of (*E*)-1,3,8-nonatriene (*E*)-**1** and (*E*)-1,3,9-decatriene (*E*)-**2** leading to the bicyclo[4.3.0]nonenes *cis*- and *trans*-**4** ($\Delta V^{\ddagger}/\Delta V^R$ [cm^3 mol^{-1}] −24.8/−32.0 and −24.8/−28.5, respectively) or bicyclo[4.4.0]decenes *cis*- and *trans*-**6** (−37.6/−45.4 and −35.0/−37.4, respectively) confirms the ring-size dependence of the activation and reaction volumes. The dependence of the effect of pressure from the number of newly forming rings is illustrated with the thermolysis of (*Z*)-1,3,8-nonatriene (*Z*)-**1** in which an intramolecular Diels−Alder reaction leading to bicyclo[4.3.0]nonene *cis*-**4** competes with a sigmatropic [1,5] hydrogen shift leading to (*E*,*Z*)-1,5,7-nonatriene **7**. The use of high pressure causes a reversal of selectivity.

Introduction

Pressure in the range of 1−20 kbar (units of pressure: 1 kbar = 100 MPa = 14503.8 psi = 986.92 atm) strongly influences the rate and equilibrium position of many chemical reactions. Processes accompanied by a decrease in volume are accelerated by pressure (volume of activation: $\Delta V^{\ddagger} < 0$) and the equilibria are shifted toward the side of products (volume of reaction: $\Delta V^R < 0$), while those accompanied by an increase in volume are retarded ($\Delta V^{\ddagger} > 0$) and the equilibria are shifted toward the side of reactants ($\Delta V^R > 0$).[1] Many Diels−Alder [4 + 2]cycloadditions are accelerated under high pressure, and this effect is frequently exploited in synthetic work.[2] The volumes of activation, which can be determined from the dependence of the reaction rate on pressure, are usually highly negative ($\Delta V^{\ddagger} \approx -25$ to -45 cm^3 mol^{-1}). Sometimes they are even smaller (i.e., more negative) than the corresponding volumes of reaction ($\Delta V^R \approx -30$ to -40 cm^3 mol^{-1}, $\Delta V^{\ddagger}/\Delta V^R \geq 1$).[3] Within the scope of the transition state theory, volumes of activation are considered to be a measure of the partial molar volume of the transition state ($V^{\ddagger} = \Delta V^{\ddagger} + \Sigma V$ (reactants)). Accordingly the transition-state volume of these reactions are close to or even smaller than the product volumes. In the case of concerted pericyclic cycloadditions competing with stepwise cycloadditions proceeding via diradical intermediates, relatively large differences in their volumes of activation ($\Delta\Delta V^{\ddagger} = \Delta V^{\ddagger}$(pericyclic) $- \Delta V^{\ddagger}$(stepwise) ≈ -10 cm^3 mol^{-1}) are observed. At high pressure, this has the effect of an increased selectivity in favor of the pericyclic process.[4] Examples are the dimerizations of chloroprene,[5] 1,3-cyclohexadiene,[6] and 1,3-butadiene.[4] The preference for the pericyclic reactions at high pressure are explained with the packing coefficients which are defined as the ratio of the intrinsic molar volume, the so-called van der Waals volumes, to the partial molar volumes (ground state: η

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[1] Monographs: (a) Isaacs, N. S. *Liquid-Phase High-Pressure Chemistry*; John Wiley: Chichester, 1981. (b) *Organic High-Pressure Chemistry*; le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988. (c) *Organic Synthesis at High Pressure*; Matsumoto, K., Morrin Acheson, R., Eds.; John Wiley: New York, 1991. (d) *High-Pressure Techniques in Chemistry and Physics, a Practical Approach*; Holzapfel, W. B., Isaacs, N. S., Eds.; Oxford University Press: Oxford, 1997. (e) *Chemistry under Extreme or Non-Classical Conditions*; van Eldik, R., Hubbard, C. D., Eds.; Wiley: New York, Spektrum, Heidelberg, 1997. (f) Klärner, F.-G.; Diedrich, M. K. The effect of pressure on reactions of dienes and polyenes, Chapter I.I In *The chemistry of functional groups, the chemistry of dienes and polyenes*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1997; Vol. 1.

[2] Reviews: (a) Matsumoto, K.; Sera, A.; Uchida, T. *Synthesis* **1985**, 1. (b) Matsumoto, K.; Sera, A. *Synthesis* **1985**, 999. (c) Ciobanu, M.; Matsumoto, K. *Liebigs Ann./Recueil* **1997**, 623−635.

[3] Reviews: (a) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407−489. (b) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549−688. (c) le Noble, W. J.; Kelm, H. *Angew. Chem.* **1980**, *92*, 887−904; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 841. (d) le Noble, W. J. *Chem. Zeit* **1983**, *17*, 152−162. (e) Jenner, G. *J. Chem. Soc., Faraday Trans I* **1985**, *81*, 2437−2460. (f) Klärner, F.-G. *Chem. Zeit* **1989**, *23*, 53−63. (g) Klärner, F.-G.; Ruster, V.; Zimny, B.; Hochstrate, D. *High-Pressure Res.* **1991**, *7*, 133. (h) Isaacs, N. S. *Tetrahedron* **1991**, *47*, 8463−8497.

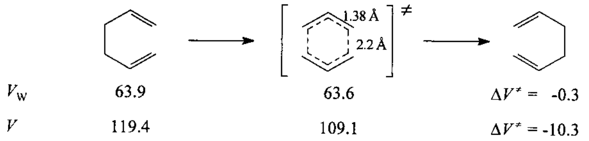
[4] Klärner, F.-G.; Krawczyk, B.; Ruster, V.; Deiters, U. K. *J. Am. Chem. Soc.* **1994**, *116*, 7646−7656.

[5] Stewart, C. A., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 635−637.

[6] Klärner, F.-G.; Dogan, B. M.; Ermer, O.; Doering, W. von E.; Cohen, M. P. *Angew. Chem.* **1986**, *98*, 109−111 *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 108−110.

S0002-7863(97)03936-X CCC: $15.00

Scheme 1[a]



[a] All volumes are given in $cm^3\ mol^{-1}$. The structural parameters necessary for the calculation of the van der Waals volume for the transition structure (TS) were taken from *ab initio* calculations. The partial molar volume for the TS was calculated from the equation $V(\text{TS}) = V_W(\text{TS})/\eta(\text{cyclohexene})$; $\eta \equiv V_W/V = 0.5829$ (cyclohexene).

$= V_W/V$, transition state: $\eta^{\ddagger} = \Delta V_W^{\ddagger}/V^{\ddagger}$).[7] The cyclic transition states of pericyclic reactions exhibit larger packing coefficients $\eta^{\ddagger}$ than the acyclic transition states of the corresponding stepwise processes, in agreement with differences in the packing coefficients of cyclic and acyclic ground states.

Many pericyclic rearrangements such as Cope rearrangements,[8,9] electrocyclizations,[9] and intramolecular Diels−Alder reactions[9,10] show a pressure-induced acceleration which is also characterized by negative volumes of activation. As before, the effect of pressure on the pericyclic rearrangements, which is usually smaller than that on the intermolecular cycloadditions, can be explained by assuming larger packing coefficients for the cyclic transition states than for the acyclic reactants.[9] This may be illustrated by the degenerate Cope rearrangement of parent 1,5-hexadiene. The van der Waals volumes calculated for 1,5-hexadiene and the pericyclic transition state are approximately the same (Scheme 1). This is understandable since in the symmetrical transition state the bond breaking and bond making have proceeded to the same extent so that the effects of the two processes on the van der Waals volume compensate, and no great overall effect of pressure on the Cope rearrangement is to be expected. However, it is reasonable to assume that the transition state, because of its cyclic geometry, exhibits a larger packing coefficient than the acyclic starting material, and therefore the volume of activation should be negative. The volume of activation of the degenerate Cope rearrangement of 1,5-hexadiene can be estimated to be approximately $\Delta V^{\ddagger} \approx -10$ $cm^3\ mol^{-1}$ if the packing coefficient of cyclohexene[4,7b] is used for the unknown packing coefficient of the transition state. In fact, negative activation volumes of the expected magnitude were found for several Cope rearrangements, related Claisen rearrangements, and the electrocyclization of the (*Z*)-1,3,5-hexatriene to 1,3-cyclohexadiene involving the formation of a new six-membered ring in each transition state.[8,9]

In intramolecular Diels−Alder reactions, two new rings are formed. There are examples of relatively large pressure-induced accelerations comparable to the acceleration observed in intermolecular cycloadditions which can be exploited for preparative purposes.[10] All the hitherto studied systems contain polar groups and are, therefore, not very suitable for the analysis of the relation between pressure effect and ring formation. The strong solvent dependence of the activation volume observed for the intramolecular Diels−Alder reaction[10b] indicates that other effects than ring formation, for example electrostriction, may also be important for the size of the activation volume. To analyze the effect of ring-size and ring-number on the activation and reaction volumes in cyclizations, we investigated the pressure effect on the intramolecular Diels−Alder reactions of the pure hydrocarbons (*E*)- and (*Z*)-1,3,8-nonatriene (*E*)-**1**, (*Z*)-**1**, and (*E*)-1,3,9-decatrienes (*E*)-**2** in which electrostriction caused by polar substituents cannot occur. Furthermore, the reaction volumes of the hypothetical cyclization of 1-alkenes to the corresponding cycloalkanes ($(CH_2)_n$, $n = 3-13$) were determined from the molar volumes of starting materials and products and provide a systematic elucidation of the relationship between volume and ring-size.

Ring-Size Dependence of the Reactions Volumes of the Cyclization of 1-Alkenes to Cycloalkanes. A first hint for the ring-size dependence of volume data came from the observation, that the ring-enlargement of *cis*-1,2-divinylcyclobutane to 1,5-cyclooctadiene and *trans*-1,2-divinylcyclobutane to 1,5-cyclooctadiene and 4-vinylcyclohexene shows highly negative reaction volumes ($\Delta V^R = -12.8$, -9.6, and -17.4 $cm^3\ mol^{-1}$, respectively[11]). This means that the ring-enlargement from a four- to a six- and finally eight-membered ring is accompanied by a substantial decrease in volumes. The volumes of reaction calculated for the hypothetical cyclizations of 1-alkenes from their partial volumes ($\Delta V^R = V(\text{cycloalkane}) - V(\text{1-alkene})$) confirm this trend. The partial molar volumes V(1-alkene) and V(cycloalkane) were determined for the 1-alkenes (from 1-hexene to 1-decene) and for the cycloalkanes (from cyclopentane to cyclotridecane[12]) by the concentration-dependent measurement of their densities in hexane solution as described in the Experimental Section.

The partial molar volumes V of the mentioned 1-alkenes in hexane do not differ significantly (within the limits of ± 0.5 $cm^3\ mol^{-1}$) from the molar volume ($V_M = M/d$) of the neat compounds and the values $V_{M(calc)}$ calculated by the use of Exner increments[13] (Table 3). For this reason, we used $V_{M(calc)}$ of 1-alkenes for the calculation of the reaction volumes ΔV^R listed in Table 1. Most of the cycloalkanes mentioned above are commercially available. Exceptions are cyclononane, cycloundecane, and cyclotridecane which were synthesized starting from the corresponding commercially available cycloalkanones either by ring-expansion and reduction (cyclononane from cyclooc-

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[7] Asano, T.; le Noble, W. J. *Rev. Phys. Soc. Jpn*. **1973**, *43*, 82−91. (b) Yoshimura, Y.; Osugi, J.; Nakahara, M. *Bull. Chem. Soc. Jpn*. **1983**, 56, 680−683. (c) Yoshimura, Y.; Osugi, J.; Nakahara, M. *J. Am. Chem. Soc*. **1983**, *105*, 5414−5418. (d) Firestone, R. A.; Smith, G. M. *Chem. Ber*. **1989**, *122*, 1089−1094. (f) The van der Waals volumes V_W can be calculated by the computer program MOLVOL: Artschwager-Perl, U. *Cycloadditionen unter hohem Druck*, Ph.D. Dissertation, Ruhr-Universität Bochum, 1989 (Prof. Dr. F.-G. Klärner, Research Director). This program uses the Cartesian coordinates of a molecular structure resulting from a force field or quantum mechanical calculations and can be obtained on request. V_W of ground states can also be calculated from tables of group contributions to the van der Waals volumes published by A. Bondi, *J. Chem. Phys.* **1964**, *68*, 441−451.

[8] Walling, C.; Naiman, M. *J. Am. Chem. Soc*. **1962**, *84*, 2628−2632. (b) Stashina, G. A.; Vasil'vitskaya, E. N.; Gamalevich, G. D.; El'yanov, B. S. Serebryakow, E. P.; Zhulin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim*. **1986**, 329; *Chem Abstr*. **1986**, 224412q.

[9] Diedrich, M. K. Hochstrate, D.; Klärner, F.-G.; Zimny, B. *Angew. Chem*. **1994**, *106*, 1135−1137; *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 1079−1081.

[10] Isaacs, N. S.; van der Beeke, P. G. *J. Chem. Soc., Perkin. Trans. 2* **1982**, 1205−1208. (b) Buback, M.; Gerke, K.; Ott, C.; Tietze, L. F. *Chem. Ber*. **1994**, *127*, 2241−2248. (c) Buback, M.; Abeln, J.; Hübsch, T.; Ott, C.; Tietze, L. F. *Liebigs Ann*. **1995**, *1*, 9−12. (d) Heiner, T.; Michalski, S.; Gerke, K.; Kuchta, G.; Buback, M.; de Meijere, A. *Synlett* **1995**, 355. (e) Harwood: L. M.; Leening, S. A.; Isaacs, N. S.; Jones, G.; Pickard, J.; Thomas, R. M.; Wetkin, D. *Tetrahedron Lett*. **1988**, *29*, 5017−5020. (f) Burrell, S. J.; Derone, A. E:, Edenborough, M. S.; Harwood: L. M.; Leening, S. A.; Isaacs, N. S. *Tetrahedron Lett* **1985**, 26, 2229−2232.

[11] Doering, W. von E.; Birladeanu, L.; Sarma, K.; Teles, J. H.; Klärner, F.-G.; Gehrke, J.-S. *J. Am. Chem. Soc*. **1994**, *116*, 4289−4297.

[12] With the exception of cycloundecane the amount prepared by ring contraction of cyclododecanone was too small for an exact measurement of the concentration-dependent density of the hexane solution. In Figure 1 the molar volume calculated from the density of neat cycloundecane (V(neat) $= M/d = 154.3/0.8596 = 179.5$ $cm^3\ mol^{-1}$) was used. *Beilstein Handbuch der Organischen Chemie*; Springer-Verlag: Berlin, 1963; suppl. 3, Vol. 5, p 142.

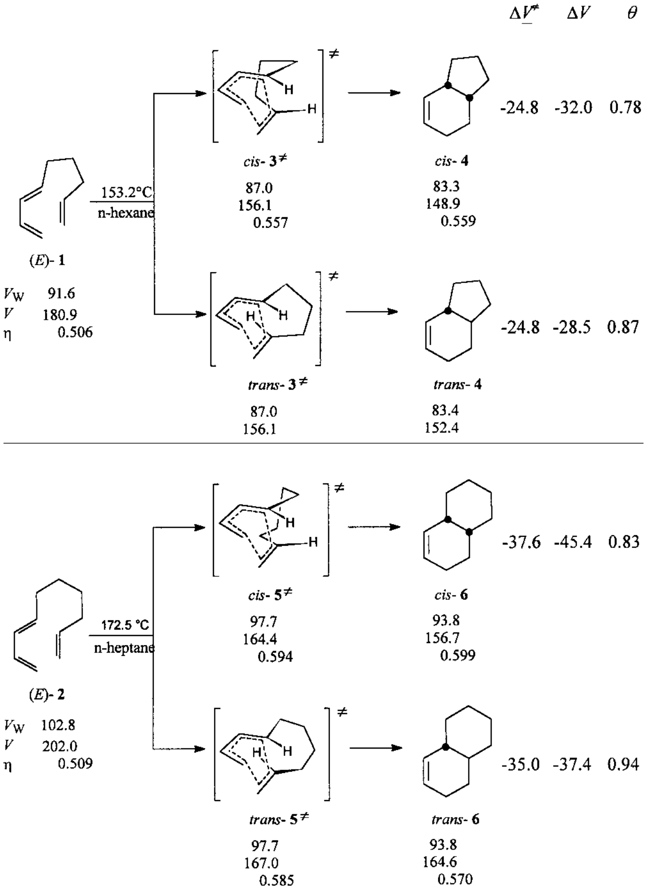
[13] Exner, O. *Empirical Calculations of Molar Volumes*; Chapter 2, pp 19−49 in (1b).

Table 1. Volume of Reaction (ΔV^R), van der Waals Volumes of Reaction (ΔV_W), Enthalpies, Entropies, and Gibbs Enthalpy of Reaction Calculated for the Hypothetical Cyclizations of 1-Alkenes to Cycloalkanes by Means of the Corresponding Thermodynamics Parameters

1-alkene → cycloalkane	ΔV_W[a]	ΔV^R [a]	ΔH[b]	ΔS[c]	ΔG[b]
C_3H_6	−1.7	−5.5	7.86	−7.0	9.95
C_4H_8	−2.5	−6.6	6.43	−10.3	9.50
C_5H_{10}	−3.8	−14.7	−13.46	−13.1	−9.56
C_6H_{12}	−4.4	−16.5	−19.47	−21.0	−13.21
C_7H_{14}	−4.7	−21.2	−13.41	−19.6	−7.57
C_8H_{16}	−4.9	−25.6	−9.88	−18.8	−4.28
C_9H_{18}	−4.7	−30.9			
$C_{10}H_{20}$	−4.6	−32.3			
$C_{12}H_{24}$	−4.7	−32.8			
$C_{13}H_{26}$	−4.7	−32.3			
$C_nH_{2n} + C_nH_{2n+2} \rightarrow C_{2n}H_{4n+2}$[d]	−4.6	−27.6			

[a] $cm^3\ mol^{-1}$. V(n-alkene) calculated by the use of Exner increments. V(cycloalkane) determined from density measurements in n-hexane. [b] $kcal\ mol^{-1}$. [c] $cal\ mol^{-1}\ K^{-1}$. [d] Intermolecular addition of 1-alkene to n-alkane.

Table 2. Volume Data of the Intramolecular Diels−Alder Reactions of Nonatriene (E)-**1** and Decatriene (E)-**2**[a]



[a] All volumes are given in $cm^3\ mol^{-1}$ and related to the reaction temperatures at 153.2 and 172.5 °C, respectively, $\eta = V_W/V$ is the packing coefficient, and $\theta = \Delta V^{\neq}/\Delta V$ is the ratio of activation volume to reaction volume.

tanone and cyclotridecane from cyclododecanone) or by ring-contraction and reduction (cycloundecane from cyclododecanone) as described in the literature.[14] In the case of the cycloalkanes the differences between the partial molar volumes in n-hexane solution and molar volume of the neat compounds are larger (up to ±4 $cm^3\ mol^{-1}$) than in the case of the 1-alkenes. For the calculation of the reaction volumes (Table 1) we used the partial molar volumes determined for the homologous sequence of cycloalkanes (from cyclopentane to cyclotridecane with exception of cycloundecane[12]) in n-hexane and the molar volume of cyclopropane and cyclobutane calculated by the use of Exner increments. The partial molar volumes obtained here for the cycloalkanes can also be used to extend the list of *"special structural correction terms for ring closure"* reported by Exner[13] to calculate molar volumes of cyclic compounds by the use of the increments (Supporting Information: Table 1). The van der Waals reaction volumes ($\Delta V_W = V_W$(cycloalkane) − V_W(1-alkene)), also listed in Table 1, were obtained from the van der Waals volumes of the cycloalkanes and 1-alkenes which were determined by numerical integration employing the individual molecular geometries calculated by force field.[7f] Since the van der Waals volumes of conformational isomers do not differ substantially from each other, only the conformations of minimum energy were used in these calculations.

The volumes of reaction (ΔV^R) calculated for the hypothetical cyclizations of 1-alkene to the corresponding cycloalkane (Table 1) decrease continuously from the formation of the three-membered ring ($\Delta V^R = -5.5\ cm^3\ mol^{-1}$) up to the formation of the ten-membered ring ($\Delta V^R = -32.3\ cm^3\ mol^{-1}$) and, then, seem to be constant for the larger rings. In contrast to this finding the van der Waals volumes of reaction (ΔV_W) are approximately equal, with the exceptions of the cyclopropane, cyclobutane, and cyclopentane formation. In the larger systems they are almost independent of the ring-size and cannot explain the dramatic decrease found for the volumes of reaction. In Figure 1 the packing coefficients ($\eta = V_W/V$) of the cycloalkanes (from C_5H_{10} to $C_{13}H_{26}$) are compared with those of the 1-alkenes and n-alkanes following the procedure of Nakahara et al.[7c] to plot η against V_W. Accordingly, the packing coefficients of the cycloalkanes are larger and exhibit a steeper slope (up to C_9H_{18}) than those of the acyclic compounds. Therefore, the ring-size dependent decrease in volume observed for the cyclizations of the 1-alkenes to the cycloalkanes results from the different packing of the cyclic and open-chained compounds rather than from the changes in their intrinsic molecular volumes.

A simple explanation may come from the assumption that the empty space between the single molecules, which can be attributed to the so-called void volume and expansion volume required for the thermally induced motions and collisions of the molecules in the liquid state, as pointed out by Asano and le Noble[7a] already in 1973, is reduced by the ring-closure of an open chain largely due to the restriction of rotational degrees of freedom during the cyclization. Apparently, the larger the ring is, the more degrees of freedom have to be restricted during the cyclization, resulting in the observed ring-size dependent volume contraction. An upper limit of this effect seems to be the formation of cyclodecane. The increasing conformational flexibility in the rings larger than $C_{10}H_{20}$ obviously requires a larger volume, which compensates the volume contracting effect of ring-closure so that the volume of reaction observed for the

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(14) Cyclooctanone was converted to cyclononane by condensation with ethyl cyanoacetate, 1,3-dipolar cycloaddition of diazomethane to the condensation product, thermally induced ring-expansion of the 1,3-dipolar cycloadduct under N_2 elimination, and alkaline hydrolysis leading to cyclononanone which was reduced by $NaBH_3CN$ in DMF and sulfolane. Cyclotridecane was prepared by the same route starting from cyclododecanone. Saunier, Y.-M.; Danion-Bougot, R.; Danion, D.; Cariée, R. *J. Chem. Res. (S)* **1978**, 436−437. Hutchins, R. O.; Milewski, C. A.; Maryanoff, B. E. *J. Am. Chem. Soc.* **1973**, *95*, 3662−3668. (b) Cyclododecanone was converted to cycloundecane by bromination leading to 2,12-dibromocyclododecanone followed by Favorskii rearrangement leading to the ethyl cycloundec-1-en-1-carboxylate which was degradated to cycloundecanone by treatment with NaN_3 in concentrated H_2SO_4 (Schmidt reaction). Cycloundecanone was reduced to cycloundecane by $NaBH_3CN$ as described above. Rappe, C.; Adeström, R. *Acta Chem. Scand.* **1965**, *19*, 383−389; Rappe C. *Acta Chem. Scand.* **1966**, *20*, 862−870.

Table 3. Partial Molar Volumes (V) at 20 °C in *n*-Hexane; k_0 Derived from Their Temperature Dependencies between 20 and 70 °C; Molar Volumes ($V_M = M/d$) Determined from the Densities of the Neat Compounds, Calculated ($V_{M(calc)}$) by the Use of Exner Increments; van der Waals Volumes (V_W); and Packing Coefficients $\eta = V_W/V$

compound	V^a	$k_0 \cdot 10^3$ [K^{-1}]	$V_M{}^a$	$V_{M(calc)}{}^a$	$V_W{}^a$	η
n-hexane[b]	130.4	1.549	130.7	130.5	69.6	0.5340
n-heptane	146.2	1.367	146.6	146.7	79.2	0.5464
n-octane	161.6			162.9	90.4	0.5598
n-nonane	177.4	1.164	178.7	179.1	100.7	0.5676
n-decane	192.2			195.3	111.2	0.5782
n-undecane	209.3			211.5	121.3	0.5793
n-dodecane	225.6	1.023	227.5	227.7	131.9	0.5847
1-hexene	124.4	1.576	124.9	124.8	66.9	0.5377
1-heptene	141.0	1.399	140.7	141.0	77.3	0.5592
1-octene	156.3					0.5610
1-octene[c]	159.4	1.266	156.8	157.2	87.7	0.5499
1-octene[d]	158.9					0.5516
1-nonene	171.8	1.173	173.1	173.4	97.9	0.5790
1-decene	186.5	1.117	189.3	189.6	108.4	0.5814
cyclopentane	93.8	1.502	94.2	95.5	52.8	0.5545
cyclohexane	108.3	1.322	108.1	110.0	62.5	0.5774
cycloheptane	119.8	1.131	121.0	122.9	72.6	0.5995
cyclooctane	132.1					0.6268
cyclooctane[c]	138.2	1.040	134.3		82.8	0.5991
cyclooctane[d]	136.1					0.6086
cyclononane	142.4				93.3	0.6656
cyclodecane	157.3	0.920	162.4		103.8	0.6564
cycloundecane	163.4		179.5		114.0	0.7093
cyclododecane	189.2				121.2	0.6577
cyclotridecane	205.9				134.7	0.6608
(*Z*)-**10**[e]	105.4	1.43			61.2	0.5820
12[e]	94.9	1.10			57.0	0.5980
(*E*)-**1**[b]	158.2	1.08			91.6	0.5790
cis-**4**[b]	132.0	0.96			83.3	0.6310
trans-**4**[b]	135.1	–[f]			83.3	0.6170
(*E*)-**2**[b]	174.2	1.05			102.8	0.5900
cis-**6**[b]	142.2	0.67			93.8	0.6600
trans-**6**[b]	146.6	0.81			93.8	0.6400

[a] In $cm^3\ mol^{-1}$. [b] In *n*-heptane. [c] In CH_2Cl_2. [d] In 2-propanol. [e] In toluene. [f] This value was not determined because of the shortage of *trans*-**4**. For the extrapolation of V (*trans*-**4**) to reaction temperature (Table 4) κ_0 (*cis*-**4**) is used.

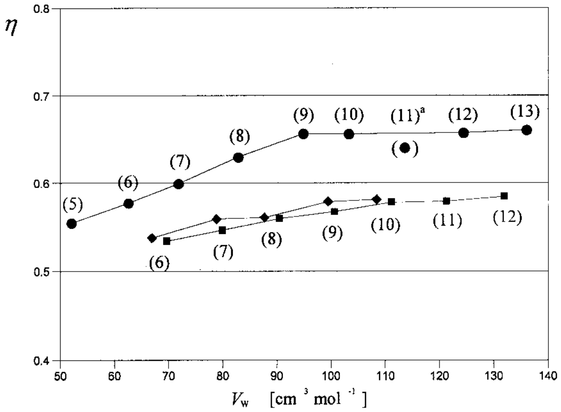

Figure 1. The plot of the packing coefficients η of cycloalkanes from C_5 to C_{13} (●), 1-alkenes from C_6 to C_{10} (◆) and *n*-alkanes from C_6 to C_{12} (■) against their van der Waals volumes V_W. Superscript a represents calculated from V(neat).

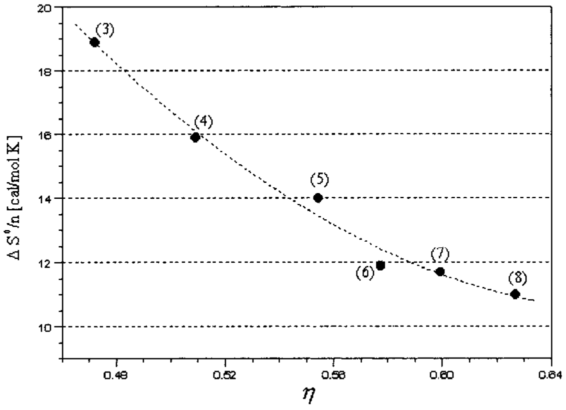

Figure 2. The plot of the entropy of formation of cycloalkanes, from $(CH_2)_3$ to $(CH_2)_8$, per CH_2 group, $\Delta S°/n = \Delta S°\ (CH_2)$, against their packing coefficients $\eta = \eta(CH_2)_n = V_W(CH_2)_n/V(CH_2)_n = \eta(CH_2)$.

formation of these larger rings remains constant. It is interesting to note that the ΔV^R values do not correlate with any other thermodynamic parameter such as enthalpy, entropy, or Gibbs enthalpy of reaction included in Table 1 for the formation of cyclopropane to cyclooctane.[15] From these parameters the entropy of reaction should reflect best the restriction of degrees of freedom assumed for the explanation of the volume contractions. As expected, the entropy of reaction decreases from the formation of cyclopropane to that of cyclohexane but increases again for the formation of the larger rings, cycloheptane and cyclooctane. Accordingly, the entropy parameter seems to be more sensitive and responds to the conformational flexibility of the forming ring at an earlier state than the volume parameter. A better correlation is found between the entropies of formation of the cycloalkanes related each to one CH_2 group ($\Delta S_f^0(CH_2) = \Delta S_f^0(CH_2)_n/n$) and their packing coefficients, η-$(CH_2)_n$, shown in Figure 2. This indicates that there is a relation between the entropy of formation and the packing coefficient of the cycloalkanes in the liquid state as expected from the given explanation. The $\Delta S_f^0(CH_2)$ values, decreasing continuously

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(15) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R:, O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279–324.

Table 4. Pressure Dependencies of the Rate Constants of the Intramolecular Diels–Alder Reactions: (a) (*E*)-**1** → *cis*-**4** (k_1), (*E*)-**1** → *trans*-**4** (k_2) at 153.2 °C in *n*-Hexane and (b) (*E*)-**2** → *cis*-**6** (k_1), (*E*)-**2** → *trans*-**6** (k_2) at 172.5 °C in *n*-Heptane[a]

(a)	*p* [bar]	$k_1 \cdot 10^6$ [s^{-1}]	$k_2 \cdot 10^6$ [s^{-1}]	(b)	*p* [bar]	$k_1 \cdot 10^6$ [s^{-1}]	$k_2 \cdot 10^6$ [s^{-1}]
	210	7.57 ± 0.36	2.51 ± 0.36		200	9.97 ± 0.17	8.60 ± 0.17
	400	8.93 ± 0.23	3.14 ± 0.23		500	13.8 ± 0.7	11.4 ± 0.7
	800	11.5 ± 0.2	3.88 ± 0.22		800	17.2 ± 6.3	14.2 ± 6.3
	1100	13.6 ± 0.3	4.49 ± 0.29		1120	22.8 ± 0.5	18.5 ± 0.5
	1600	18.1 ± 0.7	6.01 ± 0.68		1690	28.6 ± 1.9	23.2 ± 1.8
	3100	36.8 ± 1.0	12.8 ± 1.0		2500	41.8 ± 1.9	33.3 ± 1.8
	4600	61.3 ± 1.5	20.6 ± 1.3				
	$\Delta V^{\neq}$:	−(24.8 ± 0.3)	−(24.8 ± 0.8)		$\Delta V^{\neq}$:	−(37.6 ± 1.6)	−(35.0 ± 1.3)

[a] The volumes of activation ($\Delta V^{\ddagger}$) in [cm^3 mol^{-1}] were calculated from these pressure dependencies by the use of the quadratic equation $\ln k(p) = a + b \cdot p + c \cdot p^2$; $a = \ln k(p = 0)$; $\Delta V^{\ddagger} = -bRT$.

with increasing ring-size, correlate very nicely with the packing coefficients of the cycloalkanes which are identical in each case to that of one single ring CH$_2$ group: $\eta(\mathrm{CH_2})_n = \mathrm{V_W}(\mathrm{CH_2})_n/V(\mathrm{CH_2})_n \triangleq \eta(\mathrm{CH_2})$. In the homologous sequence of *n*-alkanes, however, the entropy of formation per CH$_2$ group ($\Delta S^0_\mathrm{f}(\mathrm{CH_2}) = 9.5$ cal mol^{-1} K^{-1}) as well as the packing coefficient per CH$_2$ group ($\eta(\mathrm{CH_2}) = V_\mathrm{W}(\mathrm{CH_2})/V(\mathrm{CH_2}) = 10.4/16.2 = 0.64$) remains constant.

Provided that the activation volumes depend similarly on the ring-size, the formation of larger rings should be dramatically accelerated by pressure. The comparison between the cyclization of 1-alkenes and the intermolecular addition of 1-alkenes to *n*-alkanes (Table 1) shows that in the case of the larger rings the intramolecular cyclization should be competitive to or even be favored over the intermolecular addition. Thus, the application of high pressure should be a favorable method for the synthesis of medium- and large-sized rings. The high-pressure synthesis of macrocycles reported by Jurczak et al.[16] may benefit inter alia from this effect. Another example is the synthesis of macrocycles by the sequence of inter- and intramolecular Diels–Alder reactions which only succeed at high pressure.[17] As a first test for the ring-size dependence of activation volumes we examined the intramolecular Diels–Alder reactions of (*E*)-1,3,8-nonatriene (*E*)-**1** and (*E*)-1,3,9-decatriene (*E*)-**2** in which a new five- and a six-membered ring or two new six-membered rings are formed.

The Volume Profiles of the Intramolecular Diels–Alder Reactions of (*E*)-1,3,8-Nonatriene and (*E*)-1,3,9-Decatriene. Recently, the experimental measurement of the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) of the intramolecular Diels–Alder reactions of (*E*)-**1** and (*E*)-**2** leading to the bicyclo[4.3.0]nonen *cis*-**4** and *trans*-**4** or the bicyclo[4.4.0]decenes *cis*-**6** and *trans*-**6** were reported[18] and led to the conclusion that all these reactions are pericyclic processes involving bicyclic transition states. All intramolecular Diels–Alder reactions show a pressure-induced acceleration. From the pressure dependencies of the rate constants (Table 4) the activation volumes (Table 2) were determined to be highly negative. The product ratio (*cis*-**4**:*trans*-**4**) is not noticeably pressure-dependent and, hence, the activation volumes for the formation of both cycloadducts are equal ($\Delta\Delta V^{\ddagger} \approx 0$ cm^3 mol^{-1}), whereas the relatively small but significant pressure dependence of the product ratio (*cis*-**6**:*trans*-**6**) corresponds to a difference in the activation volumes of $\Delta\Delta V^{\ddagger} = -2.6$ cm^3 mol^{-1} in favor of *cis*-**6**.

The volumes of reaction included in Table 2 were calculated by means of the partial molar volumes of both reactants and all cycloadducts determined from their densities in *n*-hexane and *n*-heptane, respectively. From temperature-dependent density measurements between 20 and 70 °C the temperature coefficients κ_0 related to $T_0 = 20$ °C were calculated following the procedure reported by El'yanov et al.[19] (Table 3). By the use of these κ_0 values the partial molar volume ($V_\mathrm{T} = V_0[1 + \kappa_0(T - T_0)]$) and, hence, the volumes of reaction related to the temperatures of reaction can be calculated which are comparable with the volumes of activation obtained from the kinetic measurements at these temperatures. The structures required for the calculation of the van der Waals volumes (Table 2) were obtained by force-field calculations (for the reactants and cycloadducts) and by ab initio calculations (for the transition structures).[18]

From the data compiled in Table 2 the following conclusions can be drawn: The volumes of activation and reaction of the intramolecular Diels–Alder reaction of nonatriene (*E*)-**1** and decatriene (*E*)-**2** are highly negative, comparably to those of the intermolecular Diels–Alder reactions.[1–3] Obviously, the intramolecular formation of two rings starting from an acyclic chain causes a similar contraction in volume as the intermolecular formation of one ring starting from two chains. The packing coefficients calculated for the bicyclic transition structures are substantially larger than those of the acyclic reactants. In agreement with the intermolecular Diels–Alder reactions they are approximately equal to and in some cases even larger than those of the corresponding bicyclic products. Finally, the activation volumes found for the intramolecular Diels–Alder reactions of decatriene (*E*)-**2** leading to *cis*-**6** and *trans*-**6** are, indeed, more negative by −13 and −10 cm^3 mol^{-1} than those found for the corresponding reactions of nonatriene (*E*)-**1** leading to *cis*-**4** and *trans*-**4**, respectively. Similar differences of −13 and −9 cm^3 mol^{-1} are also observed for the corresponding volumes of reaction. These results can be regarded as a first evidence that the relationship between ring-size and volume is also valid for activation volumes of cyclizations.[20] Furthermore, this ring-size effect may explain why the activation volumes found for the formation of three-

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[16] Jurczak, J.; Pietraskiewicz, M. *Top. Curr. Chem.* **1986**, *130*, 185–204; Salanski, P.; Ostaszewski, R.; Jurczak, J. *High-Pressure Res.* **1994**, *13*, 35-; Jurczak, J.; Ostaszewski, R.; Salanski, P.; Stankiewicz, T. *Tetrahedron* **1993**, *49*, 1471–1477.

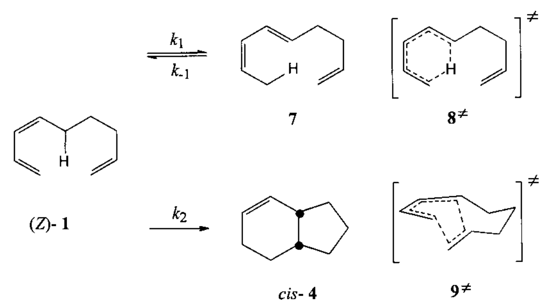
[17] Kohnke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem.* **1987**, *99*, 941–943; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 892-; (b) Kohnke, F. H.; Stoddart, J. F. *Pure Appl. Chem.* **1989**, *61*, 1581–1586. (c) Ashton, P. R.; Brown, G. R.; Isaacs, N. S.; Guiffrida, D.; Kohnke, F. H.; Mathias, J. P.; Slawin, A. M. Z.; Smith, D. R.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 6330–6353. (d) Mathias, J. P.; Stoddart, J. F. *Chem. Soc. Rev.* **1992**, *21*, 215–225. (e) Benkhoff, J.; Boese, R.; Klärner, F.-G.; Wigger, A. E. *Tetrahedron Lett.* **1994**, *35*, 73–76.

[18] Diedrich, M. K.; Klärner, F.-G.; Beno, B. R.; Houk, K. N.; Senderowitz, H.; Still. W. C. *J. Am. Chem. Soc.* **1997**, *119*, 10255–10259.

[19] El'yanov, B. S.; Gonikberg, E. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 172–191; El'yanov, B. S.; Vasylvitskaya, E. M. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 169–183.

[20] The volumes of activation show a similar trend as the entropies of activation (*E*)-**1** → *cis*-**4** : $\Delta S^{\ddagger}$[eu] = −25.21, *E*-**1** → *trans*-**4**: −23.97, (*E*)-**2** → *cis*-**6**: −29.32, (*E*)-**2** → *trans*-**6**: −29.10.

Scheme 2[a]



[a] (a) Gas-phase thermolysis of (*Z*)-**1**: $k_1 = (1.07 \pm 0.19)\cdot 10^{11}$ $s^{-1}\cdot\exp[-(32.95 \pm 0.15)$ kcal $mol^{-1}/RT]$. 232 °C: $\Delta H^{\ddagger}$ (31.95 ± 0.15) kcal mol^{-1}; $\Delta S^{\ddagger} = (-11.1 \pm 0.3)$ cal mol^{-1} K^{-1}. $k_{-1} = (2.19 \pm 1.14)\cdot 10^{11}$ $s^{-1}\cdot\exp[-(36.18 \pm 0.51)$ kcal $mol^{-1}/RT]$. 232 °C: $\Delta H^{\ddagger}$ (35.18 ± 0.51) kcal mol^{-1}; $\Delta S^{\ddagger} = (-9.7 \pm 1.0)$ cal mol^{-1} K^{-1}. $k_2 = (1.70 \pm 0.3)\cdot 10^{8}$ $s^{-1}\cdot\exp[-(28.38 \pm 0.17)$ kcal $mol^{-1}/RT]$. 232 °C: $\Delta H^{\ddagger}$ (27.38 ± 0.17) kcal mol^{-1}; $\Delta S^{\ddagger} = (-23.9 \pm 0.3)$ cal mol^{-1} K^{-1}. (b) Pressure-dependence of the thermolysis of (*Z*)-**1** at 150.2 °C in *n*-pentane for 24 h: 1 bar, 80.2% (*Z*)-**1**, 13.7% **7**, 6.1% *cis*-**4**; 7.7 kbar, 5.5% (*Z*)-**1**, 18.2% **7**, 76.4% *cis*-**4**.

membered rings in cheleotropic reactions[21] are substantially less negative than those found for the formation of five- and six-membered rings in 1,3-dipolar cycloadditions[22] or Diels−Alder reactions.[23]

Analysis of the Activation Parameters of Competing Intramolecular Diels−Alder Reaction and Sigmatropic [1,5]-Hydrogen Shift in *Z*-1,3,8-Nonatriene. The Effect of Pressure on Competing Processes. A particularly instructive example is the thermolysis of (*Z*)-1,3,8-nonatriene (*Z*)-**1** in which an intramolecular Diels−Alder reaction leading to *cis*-**4** via a bicyclic transition state $\mathbf{9}^{\ddagger}$ competes with a sigmatropic [1,5]-hydrogen shift leading to (*E,Z)*-1,5,7-nonatriene **7** via a monocyclic transition state $\mathbf{8}^{\ddagger}$. On gas-phase thermolysis at temperatures between 200 and 265 °C under carefully controlled conditions excluding acid catalysis (*Z*)-**1** underwent clean rearrangement leading to a mixture of *cis*-**4** and **7** which could be separated by preparative GC. The structures of the isolated products were assigned either by comparison with an authentical sample or by their spectral properties as described in the Supporting Information. The temperature dependence of the rates of formation of *cis*-**4** and **7** was determined from the disappearance of the starting material (*Z*)-**1** and the product ratio *cis*-**4**/**7** with time (Supporting Information: Table 2). The Arrhenius parameters and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values derived from the temperature dependence of these rate constants are given in Scheme 2. Accordingly, the sigmatropic [1,5] hydrogen shift in (*Z*)-**1** turned out to be faster than the intramolecular Diels−Alder reaction. It is the dominating process in particular at the high temperatures despite its larger enthalpy of activation which is compensated by a less negative entropy of activation.

The use of high pressure allows a reversal of selectivity apparently because of the competition between monocyclic and bicyclic transition states $\mathbf{8}^{\ddagger}$ and $\mathbf{9}^{\ddagger}$, respectively. At 1 bar and 150 °C in *n*-pentane solution the [1,5]hydrogen shift of (*Z*)-**1** is preferred by a factor of 2.2 over the intramolecular Diels−Alder reaction. At 7.7 kbar and 150 °C the intramolecular Diels−Alder reaction is the favored process by a factor of 4.2. From the pressure dependence of the product ratio one can extrapolate that the difference in the activation volumes ($\Delta\Delta V^{\ddagger} = \Delta V^{\ddagger}(Z\text{-}\mathbf{1} \rightarrow cis\text{-}\mathbf{4}) - \Delta V^{\ddagger}(Z\text{-}\mathbf{1} \rightarrow \mathbf{7}) < [RT/(7700-1)]\cdot\ln(1/4.2\cdot 2.2) = -10$ cm^3 mol^{-1}) is comparable to those observed for pericyclic rearrangements involving monocyclic and bicyclic transition states, respectively.[9]

Conclusions

The packing coefficient, $\eta = V_W/V$, has been demonstrated to be a valuable tool for the explanation of the effect of pressure on many pericyclic reactions. The finding that η of cyclic structures is larger than that of the corresponding acyclic structures explains the negative activation volumes of many pericyclic rearrangements. The size of η depends on the number and size of the newly forming rings. This explains why, among others, intramolecular Diels−Alder reactions involving bicyclic transition states at high pressure are favored over rearrangements involving monocyclic transition states, and why the activation and reaction volumes of the intramolecular Diels−Alder reactions in (*E*)-1,3,9-decatriene (*E*)-**2**, in which two new six-membered rings are formed, are more negative than those of the corresponding reactions of (*E*)-1,3,8-nonatriene (*E*)-**1**, in which only a new five- and a new six-membered ring are formed. The restriction of rotational degrees of freedom during the cyclization of open chains is certainly the major contribution to the contraction of volume and, hence, the increase of the packing coefficients observed here for various ring-closure reactions. This assumption is supported by the correlation between $\eta(CH_2)_n$ and $\Delta S_f^0(CH_2)$ of the cycloalkanes (Figure 2).

Experimental Section

Measurement of Partial Molar Volumes. For each substance, the densities of solutions of six different concentrations are determined. Measurements are performed in a temperature range from 20 to 70 °C in steps of 5 °C. For each temperature, the value of ϕ_V (apparent molar volume of a substance at a given concentration) is calculated according to the following equation:

$$\phi_V = \frac{M}{d_0} - \frac{1000}{c}\cdot\frac{d - d_0}{d_0}$$

with c [mol L^{-1}], concentration of the solution; M [g mol^{-1}], molar mass of the solute; d [g cm^{-3}], density of the solution; d_0 [g cm^{-3}], density of the pure solvent.

The partial molar volume, V, is calculated by linear extrapolation of ϕ_V to a concentration $c = 0$. The κ_0 values included in Table 3 are derived from the temperature dependence of the partial molar volume by the use of the equation $V_T = V_0\cdot[1 + \kappa_0\cdot(T - T_0)]$, $T_0 = 20$ °C.

Kinetic Measurements

Thermolysis of (*E*)-1,3,8-Nonatriene ((*E*)-1) and (*E*)-1,3,9-Decatriene ((*E*)-2). Portions (8−10 mL each) of a solution of (*E*)-**1** (500 mg) or (*E*)-**2** (500 mg) and *n*-nonane (500 mg) or *n*-decane (500 mg) as internal standards in 50 mL of *n*-hexane or *n*-heptane are thermolyzed 153.2 and 172.5 °C, respectively, at different pressures given in Table 4. For each pressure, 5 to 7 samples are taken and analyzed by GC (column A, 70 °C, t_R (*n*-nonane) = 5.0 min, t_R ((*E*)-**1**) = 7.0 min, t_R (*trans*-**4**) = 10.2 min, t_R (*cis*-**4**) = 11.7 min; column A, 120 °C/10 min, 10 °C/min, 250 °C/2 min, t_R(*n*-decane) = 5.0 min, t_R((*E*)-**2**) = 6.3 min, t_R(*trans*-**6**) = 9.2 min, t_R(*cis*-**6**) = 10.6 min). The specific rate constants (Table 4) are calculated from the time dependence of the disappearance of (*E*)-**1** or (*E*)-**2** versus the internal standard and from the ratio of the forming bicyclic products by the use of the kinetic law for first-order irreversible reactions.

Gas Phase Thermolysis of (*Z*)-1,3,8-Nonatriene (*Z*-1). Portions (250−300 mL each) of *Z*-**1** and *n*-nonane as internal standard in

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[21] Turro, N. J.; Okamoto, M.; Gould, I. R.; Moss, R. A.; Lawrynowicz, W.; Hadel, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 4973−4976.

[22] Swieton, G.; von Jouanne, J.; Kelm, H.; Huisgen, R. *J. Org. Chem.* **1983**, *48*, 1035−1040. (b) Yoshimura, Y.; Osugi, J.; Nakahara, M. *J. Am. Chem. Soc.* **1983**, *105*, 5414−5418.

[23] Jenner, G. *New J. Chem.* **1991**, *15*, 897−899.

anhydrous *n*-pentane are thermolyzed at six temperatures between 200 and 265 °C. At each temperature the time dependence of the product ratio at least for 10 samples is analyzed by GC (column C, 50 °C, t_R (*n*-nonane) = 6.1 min, t_R (*Z*-**1**) = 9.5 min, t_R (**7**) = 11.9 min, t_R (*cis*-**4**) = 12.6 min). The specific rate constants (Supporting Information: Table 2) are derived from these ratios by numerical integration by the use of the Runge−Kutta procedure of fourth order and optimization by the use of the Marquardt method.[29]

Thermolysis of (*Z*)-1,3,8-Nonatriene ((*Z*)-1). Portions (100 μL each) of a solution of (*Z*)-**1** (50 μL) and *n*-nonane (50 μL) as internal standard in 5 mL of *n*-pentane are thermolyzed at 150.2 °C and at 1 bar and 7.7 kbar, respectively. The product ratios are analyzed by GC (column C, 50 °C, t_R(*n*-nonane) = 6.1 min t_R((*Z*)-**1**) = 9.5 min, t_R(**7**) = 11.9 min, t_R(*cis*-**4**) = 12.6 min).

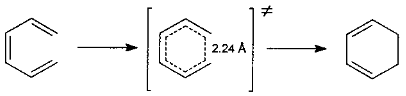
Thermolysis of (*Z*)-1,3,5-Hexatriene ((*Z*)-10). Portions (8−10 mL each) of a solution of (*Z*)-**10** (200 mg) and *n*-octane (200 mg) as internal standard in 40 mL of toluene are thermolyzed as described above. Three temperatures (108.1, 117.5, and 122.4 °C) and six different pressures (400, 800, 1200, 1600, 2000, and 2500 bar) at each temperature are chosen. For each temperature and pressure, 7 to 9 samples are taken and analyzed by GC (column A, 40 °C/5 min, 10 °C/min, 190 °C/10 min, t_R((*Z*)-**10**) = 6.7 min, t_R(**12**) = 7.5 min, t_R(*n*-octane) = 8.5 min). The specific rate constants (Supporting Information: Table 3) are calculated from the time dependence of the disappearance of hexatriene versus the internal standard by the use of the kinetic law for first-order irreversible reactions.

Acknowledgment. Dedicated to Professor William von Eggers Doering on the occasion of his 80th birthday. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. M.K.D. thanks the Graduiertenförderung des Landes Nordrhein-Westfalen and the WASAG Stiftung für Studiumsförderung for fellowships. We are grateful to Ms. Heike Wöll for performing major parts of the preparative work and to Mr. Heinz Bandmann for measuring the 300 MHz NMR spectra.

Appendix: Temperature Dependence of Volumes of Reaction and Activation

For a comparison of activation volumes with the corresponding reaction volumes it is necessary to determine both data at the same temperature which is, however, not feasible in most cases. The measurement of the pressure dependence of rate constants frequently requires a temperature different from that used for the determination of partial molar volumes of reactants and products (in general room temperature). Therefore, the activation volumes have to be extrapolated to room temperature or the reaction volumes, correspondingly, to the temperature of reaction. The measurement of the temperature dependence of activation volumes requires a large collection of experimental data. To the best of our knowledge only one case, the Diels−Alder [4 + 2]cyclodimerization of isoprene, has been reported where the temperature dependence of activation as well as reaction volume has been determined.[24] We have studied the temperature dependence of the activation volume of the electrocyclization of (*Z*)-1,3,5-hexadiene (*Z*)-**10** to 1,3-cyclohexadiene **12**. In the experimentally accessible temperature range between 100 and 122 °C no significant temperature dependence of the activation volumes have been observed within limits of experimental error (Table 5).

Table 5. Temperature Dependence of the Volumes of Reaction and Activation of Electrocyclization of (*Z*)-1,3,5-Hexatriene (*Z*)-**10** to 1,3-Cyclohexadiene **12**



(*Z*)- **10** **11≠** **12**

T [°C]	$\Delta V^{\ddagger\, a}$	$\Delta V^{R\, a}$	$\theta = \Delta V^{\ddagger}/\Delta V^{R}$
20.0		−10.5	
101.2	−(9.8 ± 0.2)	-14.3^{b}	0.69
108.1	−(10.8 ± 0.8)	-14.7^{b}	0.73
117.5	−(10.9 ± 2.2)	-15.1^{b}	0.72
122.4	−(10.7 ± 1.1)	-15.3^{b}	0.67

[a] In $cm^3\ mol^{-1}$. [b] Extrapolated by the use of $\kappa_0 = 4.34 \cdot 10^{-3}\ K^{-1}$.

Table 6. κ_0 Values for the Extrapolation of Volume of Reaction from the Temperature T_0 = 20 °C to the Temperature T

reaction	$\kappa_0 \cdot 10^3$ [K^{-1}]
1-hexene → cyclohexane	4.27
1-heptene → cycloheptane	4.22
1-octene → cyclooctane	3.75
1-nonene → cyclononane	3.92
1-decene → cyclodecane	3.45
1-hexene + *n*-hexane → *n*-dodecane	7.27
(*Z*)-**10** → **12**	4.34
(*E*)-**1** → *cis*-**4**	1.66
(*E*)-**2** → *cis*-**6**	2.73
(*E*)-**2** → *trans*-**6**	2.33
[4 + 2] cyclodimerization of isoprene	5.70^{a}
	$8.80^{a,b}$

[a] Values from the literature.[24] [b] From the temperature dependence of the activation volume.

With modern thermostated densimeters it is much easier to determine the temperature dependence of partial molar volumes and, hence, of reaction volumes. Compared to the kinetic measurements, the densities can be measured over a broader range of temperatures in most cases. From the temperature dependence of volumes of various reactions El'yanov et al.[19] extrapolated a generally applicable equation already mentioned ($\Delta V_T = \Delta V_0 \cdot [1 + \kappa_0 \cdot (T - T_0)]$ with $\kappa_0 = (4.43 \pm 0.48) \cdot 10^{-3}\ K^{-1}$ for T_0 = 20 °C).

The κ_0 values derived from the temperature dependencies of the volumes of reactions investigated in this work are summarized in Table 6. These κ_0 values vary to a larger extent than that given for the general constant κ_0 derived by El'yanov et al.[19] Therefore, one should use the El'yanov value for the extrapolation of activation and reaction volumes only as a first approximation. According to our experience the most convenient method for a comparison between activation and reaction volumes is to extrapolate the reaction volumes to the temperature of reaction by means of the temperature-dependent density measurements.

Supporting Information Available: Experimental procedures, table of special structural correction terms for the calculation of molar volumes V of cyclic compounds by the use of Exner increments, and tables of specific rate constants meassured for the reactions **7** $\rightleftharpoons$ (*Z*)-**1** → *cis*-**4** and (*Z*)-**10** → **12** at different temperatures and for different pressures (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(24) Rimmelin, J.; Jenner, G. *Tetrahedron* **1974**, *30*, 3081−3085.

(25) Grimme, W.; Schumachers, L.; Roth, W. R.; Breuckmann, R. *Chem. Ber.* **1981**, *114*, 3197−3208.

(26) Hwa, J. C. H.; Sims, H. *Organic Syntheses*; Wiley: New York, Collect. Vol. 5, pp 608−612.

(27) De Boer, Th. J.; Backer, H. J. *Organic Syntheses*; Wiley: New York, Collect. Vol. 4, pp 250−253.

(28) Wohllebe, J.; Garbisch, E. W. *Organic Syntheses*; Wiley: New York, Collect. Vol. 6, pp 368−371.

(29) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431−441. We thank Dr. R. Fink for a copy of the program KINETIK, which permits optimization by the Marquardt procedure of kinetic schemes with up to seven components.