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Effect of Pressure on the Rates of Sigmatropic Shifts. Volume as an Indication of a Wide Mechanistic Range

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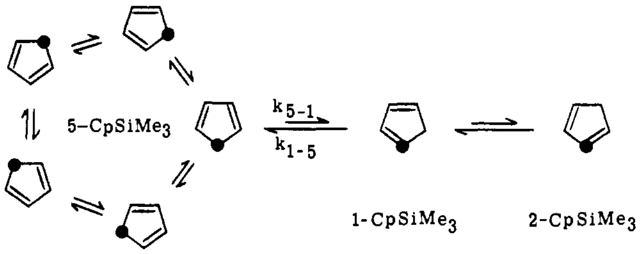
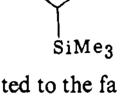
Abstract: The volume profiles of the several degenerate or near-degenerate sigmatropic shifts investigated here exhibit minima, as shown by the pressure-induced enhancements of the rates. This rules our predissociation to diradicals in each of these instances. In the case of hydrogen migration in 5-(trimethylsilyl)cyclopentadiene in $CDCl_3$ at 30 °C, the minimum is deep at -26.5 cm^3/mol; this observation virtually requires that considerable charge separation characterize the transition state. This conclusion is supported by a substantial solvent effect on the rate; the presence of a few percent Me_2SO increases the rate severalfold. The trimethylsilyl group in the same molecule in benzene at 68 °C migrates with an activation volume of -12.5 cm^3/mol; charge separation is much more minor, and probably opposite in sense. In 5-formylpentamethylcyclopentadiene in a benzene–Freon mixture at -4 °C, the minimum amounts to only -4 cm^3/mol; in that instance, there is no evidence for charge separation at all, and the contraction can be accounted for by the displacement feature of the circumambulation alone. Bullvalene is almost unaffected by pressure at 19.8 °C in carbon disulfide altogether ($\Delta V^{\ast} = -0.5$ cm^3/mol), in contrast to species known to undergo slow Cope rearrangements. This finding supports the view that in the fast, degenerate Cope rearrangements, bond cleavage is just about on an even keel with bond formation, and discourages hopes that homoaromaticity might be induced in semibullvalene by the application of extreme pressure. It is concluded from these and other data already in the literature that symmetry-allowed sigmatropic shifts may occur by a wide variety of mechanisms, ranging from highly dipolar, bound transition states to complete dissociation into radical pairs.

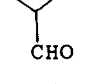
The very large accelerations by pressure and the correspondingly large, negative activation volumes of the Diels–Alder reaction have long been known.[2] Their exploitation for synthetic purposes has begun,[3] as has the exploration of pressure effects in other types of cycloaddition.[4] By contrast, relatively little is known about the pressure sensitivities of other pericyclic reactions,[5] although some of these rival the cycloaddition in ubiquity and the potential for synthetic application of pressure is present in those cases also. We have now made a study of several sigmatropic shifts and report our results herein.

Scheme I



At the outset, we were attracted by shifts that are degenerate, the obvious reasons being that the transition-state location is halfway by virtue of symmetry and that the activation volume is not subject to the prejudice of a large reaction volume. The choice of substrates 5-(trimethylsilyl)cyclopentadiene (5-$CpSiMe_3$),[6] 5-formylpentamethylcyclopentadiene,[7] and bullvalene[8] was related to the fact that the degenerate shifts had already been described as exceptionally facile, so that there is no need for the high temperatures that may easily cloud the interpretation of the high-pressure data; in fact, the NMR spectra exhibit coalescence near room temperature, so that is was possible to make use of the high-pressure NMR recently developed in the Lausanne laboratory.[9] The nondegenerate hydrogen shift of 5-$CpSiMe_3$ is much slower, but still fast enough that its rate can be conveniently followed in the conventional manner near room temperature. A further reason for our choices was that in spite of the careful





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(1) (a) Buffalo; (b) Lausanne; (c) Stony Brook.

(2) The first Diels–Alder reaction to be studies under high pressure was the dimerization of cyclopentadiene (Raistrick, B.; Sapiro, R. H.; Newitt, D. M. *J. Chem. Soc.* **1939**, 1761). We take passing note here of the common but mistaken impression that the question of concertedness of this reaction was first broached by Walling in 1958 on the basis of a comparison of the activation and reaction volumes of isoprene dimerization and that the controversy that followed—instigated by Benson and Berson—was finally solved by Eckert in 1970 (see, for example: Walling, C.; Peisach, J. *J. Am. Chem. Soc.* **1958**, *80*, 5819. Benson, S. W.; Berson, J. A. *Ibid.* **1964**, *86*, 259. Grieger, R. A.; Eckert, C. A. *Ibid.* **1970**, *92*, 2918, 7149). However, this criterion had already been invented by Gonikberg in 1949 and successfully applied by him to Newitt's data complemented by his own (Gonikberg, M. G.; Vereshchagin, L. F. *Zh. Fiz. Khim.* **1949**, *23*, 1447). News of this advance was not available in the English language literature until the translation of Gonikberg's book in 1963 (Gonikberg, M. G. "Chemical Equlibrium and Reaction Rates at High Pressure", Engl. Transl., Israel Program for Scientific Translations, Jerusalem, 1963).

(3) Seguchi, K.; Sera, A.; Maruyama, K. *Tetrahedron Lett.* **1973**, 1585. Dauben, W. G.; Kozikowski, A. P. *J. Am. Chem. Soc.* **1974**, *96*, 3664. Jenner, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *87*, 186.

(4) Asano, T.; le Noble, W. *Chem. Rev.* **1978**, *78*, 407. Recent new investigations in this area include an intramolecular Diels–Alder reaction (Isaacs, N. S.; Van Der Beeke, P. *Tetrahedron Lett.* **1982**, *23*, 2147), [2 + 2] dipolar cycloadditions (von Jouanne, J.; Kelm, H.; Huisgen, R. *J. Am. Chem. Soc.* **1979**, *101*, 151. Sasaki, M.; Tsuzuki, H.; Osugi, J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1596), a concerted, thermal [2 + 2] cycloaddition (Wiering, P. G.; Steinberg, H. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 267), a [2 + 2] photocycloaddition (Hamann, S. D.; Linton, M.; Sasse, W. H. F. *Aust. J. Chem.* **1980**, *33*, 1419), dipolar [2 + 3] cycloadditions (Kamernitzky, A. V.; Levina, I. S.; Mortikova, E. I.; Shitkin, V. M.; El'-yanov, B. S. *Tetrahedron* **1977**, *33*, 2135. Rice, J. E.; Okamoto, Y. *J. Org. Chem.* **1981**, *46*, 446. Dicken, C. M.; DeShong, P. *J. Org. Chem.* **1982**, *47*, 2047), a cyclotrimerization (Koppes, W. M.; Adolph, H. G. *J. Org. Chem.* **1981**, *46*, 406), and applications in heterocyclic synthesis (Matsumoto, K.; Uchida, T.; Acheson, R. M. *Heterocycles* **1981**, *16*, 1367).

(5) (a) Ene reaction: Papadopoulos, M.; Jenner, G. *Tetrahedron Lett.* **1981**, *22*, 2773. (b) Electrocyclic ring opening and closure: Mündnich, R.; Plieninger, H.; Vogler, H. *Tetrahedron* **1977**, *33*, 2661. Mündnich, R.; Plieninger, H. *Tetrahedron* **1978**, *34*, 887. (c) Neutral sigmatropic shifts: le Noble, W. J.; Daka, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5961 and references given there, especially to Claisen and Cope rearrangements. (d) Wagner–Meerwein rearrangement: le Noble, W. J.; Bitterman, S.; Staub, P.; Meyer, F. K.; Merbach, A. E. *J. Org. Chem.* **1979**, *44*, 3263.

(6) Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1965**, *4*, 313.

(7) Bushby, R. J.; Jones D. W. *J. Chem. Soc. Chem. Commun.* **1979**, 688.

(8) Merényi, R.; Oth, J. F. M.; Schröder, G. *Chem. Ber.* **1964**, *97*, 3150.

(9) (a) Earl, W. L.; Vanni, H.; Merbach, A. E. *J. Magn. Reson.*, **1978**, *30*, 571. (b) Monnerat, A.; Moore, P.; Newman, K. E.; Merbach, A. E. *Inorg. Chim. Acta* **1981**, *47*, 139.

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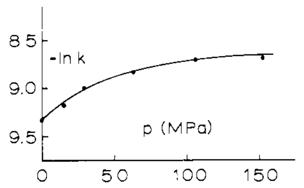


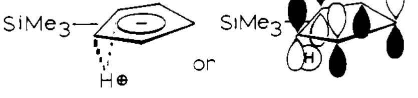
Figure 1. Effect of pressure on the rate of the 1,5-hydrogen shift in 5-CpSiMe$_3$ in CDCl$_3$ at 30 °C. The rate constants are values of $(k_{5-1} + k_{1-5})$ in s^{-1}.

studies reported earlier and quoted below, questions concerning the mechanism have not been completely dispelled.

Results and Discussion

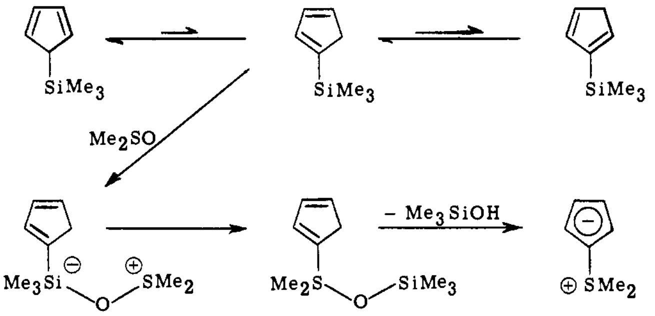
The reactions of 5-CpSiMe$_3$ to be discussed first are summarized in Scheme I (the dot represents the SiMe$_3$-substituted carbon). So far as the equilibrium composition is concerned, we concur with Ashe,[10] who reported a ratio of 5-:1-:2-CpSiMe$_3$ of 90:7:3, respectively, in C$_6$D$_6$; this fact could be readily ascertained since the proton NMR signals of the SiMe$_3$ group exhibit base-line separation. Since benzene cannot be used at high pressure (because of its high freezing point), we employed CDCl$_3$ thereafter, although this has the disadvantage that the 1- and 2-isomers then have identical SiMe$_3$ chemical shifts. The 5-isomer in this solvent is present to the extent of 87%.

Starting with pure 5-isomer (obtained by means of a partial melting procedure) in CDCl$_3$ at 30 °C and using the SiMe$_3$ peaks for analysis, we were able to measure $(k_{5-1} + k_{1-5})$. The fact that the conversion of the 1- to the 2-isomer was ignored did not seriously affect the outcome; straight lines were obtained through 9–12 points, with correlation coefficients from 0.97 to 0.99. The result is that $k_{5-1} + k_{1-5} = 8.7 \times 10^{-5}$ s^{-1}, in reasonable agreement with Ashe's result of 7×10^{-5} s^{-1} in C$_6$D$_6$.[10] This procedure was then repeated at several pressures to 150 MPa (~1500 atm); the results are portrayed in Figure 1. When the activation volume is calculated in the usual way[11] and with the assumption that K (k_{5-1}/k_{1-5}) is unaffected by pressure, the result is (-26.5 ± 1.5) cm^3/mol; a nonlinear regression analysis[12] that searches for the best values of the rate constants as well as of K led to the same value for the activation volume and to an appraisal of K as 0.146 ± 0.025. These results may be summarized by saying that $\Delta V^{\ddagger}$ equals -26 cm^3/mol in either direction and that $\Delta V = (0 \pm 3)$ cm^3/mol. This is an astonishingly large contraction for a reaction of which the principal volume-controlling features are similar to those of displacements occurring without net charge development or neutralization; $\Delta V^{\ddagger}$ is generally[13] found to be -5 to -10 cm^3/mol in such reactions. We see no way to avoid concluding from this deep minimum that substantial charge separation is occurring. We picture the transition state as resembling that of hydride shifts in carbonium ion rearrangements, i.e., as essentially an edge-protonated cyclopentadienide anion. The special stability of the



core of this species and the imposed nonlinear CHC group in the transition state[14] do not permit extrapolation of this mechanism to 1,5-hydrogen shifts in noncyclic 1,3-dienes.

Scheme II



Essentially the same proposal was made by Mironov et al.,[15] but only on the grounds that it seemed reasonable and was not ruled out by their extensive methyl substituent studies. McLean showed that the reactions are intramolecular except in the presence of strong bases[16] and that a 5-methyl substituent accelerates the reaction;[17] this supports Mironov's postulate in that this is expected if a hybridization change from sp^3 to sp^2 occurs. Upon finding that 5-halogen substitution decreases the rate, Breslow[18] argued that the charge separation must be in the opposite sense, but he conceded that his results would also have been anticipated on the basis of rehybridization.

One aspect of the Mironov transition-state model is that the solvent effect on the rate is surprisingly modest.[19] It occurred to us that perhaps the use of a dipolar solvent that is also a powerful H-bond acceptor would show a much more pronounced acceleration, and the choice fell on Me$_2$SO-d_6. It was found that 5-CpSiMe$_3$ reacts[20] very rapidly with this solvent to give the known dimethylsulfonium *S*-ylide.[21] An NMR spectrum taken immediately after dissolution suggested that final product formation was not yet complete and implicated the presence of at least one transient intermediate. Studies with dilute solutions of Me$_2$SO-d_6 in CDCl$_3$ then showed that the pathway producing the ylide is as indicated in Scheme II. Since the required, initial intermediacy of 1-CpSiMe$_3$ is crucial to our argument, we must briefly digress here is describe the support for this initial step.

A solution of initially pure 5-CpSiMe$_3$ in CDCl$_3$ containing 6.25% Me$_2$SO-d_6 has an NMR spectrum showing only a single peak in the SiMe$_3$ region at δ −0.05. As this peak declines in intensity relative to a cyclohexane standard, a new peak grows in a δ 0.15. This peak increases, levels off, and declines again as a third peak grows in at δ 0.10, and the same thing happens to it as a fourth and final peak evolves at δ +0.05. The sequence

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(10) Ashe, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 1233. We note in passing the exceptional nature of the trimethylsilyl group compared to alkyl groups in that it strongly favors the 5-position; thus, methyl seeks out only the 1- and 2-positions (~4:5, respectively; see ref 15). See also: Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766, who report that ΔG for the process XCH$_2$—CH=CH$_2$ ⇄ XCH=CH—CH$_3$ is negative with all of the 57 substituents studied.

(11) le Noble, W. J. *J. Am. Chem. Soc.* **1963**, *85*, 1470.

(12) Deming, W. C. "Statistical Adjusment of Data"; Wiley: New York, 1943; Chapter 9. We translated this analysis into BASIC; the program searches for the best values of the rate constant as well as of K and estimates the standard derivations of the adjustable parameters.

(13) Isaacs, N. S. "Liquid Phase High Pressure Chemistry"; Wiley: New York, 1981.

(14) Kwart, H.; Brechbiel, M. W.; Acheson, R. M.; Ward, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4671.

(15) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939. The proposal was quoted but not endorsed by: Roth, W. R. *Tetrahedron Lett.* **1964**, 1009. See also: Mironov, V. A.; Fedorovich, A. D.; Akhrem, A. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 1272. These authors contended, however, that this description does not imply charge separation.

(16) McLean, S.; Haynes, P. *Tetrahedron Lett.* **1964**, 2385 (1964); *Tetrahedron* **1965**, *21*, 2329.

(17) McLean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555.

(18) Breslow, R.; Hoffman, J. M.; Perchonock, C. *Tetrahedron Lett.* **1973**, 3723. The authors did not comment on the fact that the rate-retarding effect increased in the order Cl, Br, I. Other pertient investigations on sigmatropic shifts in cyclopentadienes and indenes have been reported (Berson, J. A.; Aspelin, G. B. *Tetrahedron* **1964**, *20*, 2694. Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 650. Wawzonek, S.; Friedrich, B. H. *J. Org. Chem.* **1972**, *37*, 2520. Mason, J. G.; Youssef, A. K.; Ogliaruso, M. A. *J. Org. Chem.* **1975**, *40*, 3015).

(19) The rate in CCl$_4$ is only about 3 times that in the gas phase and that in acetone is only about 4 times faster (Roth, W. R. *Tetrahedron Lett.* **1964**, 1009).

(20) McLean, S.; Reed, G. W. B. *Can. J. Chem.* **1970**, *48*, 3110. We were at first unaware that these authors had already studied this reaction and identified the product.

(21) Behringer, H.; Scheidl, F. *Tetrahedron Lett.* **1965**, 1757. Yoshida, Z.; Yoneda, S.; Hazama, M. *J. Chem. Soc., Chem. Commun.* **1971**, 716. Ernstbrunner, E. E.; Lloyd, D. *Chem. Ind.* (*London*), **1971**, *13*, 1332.

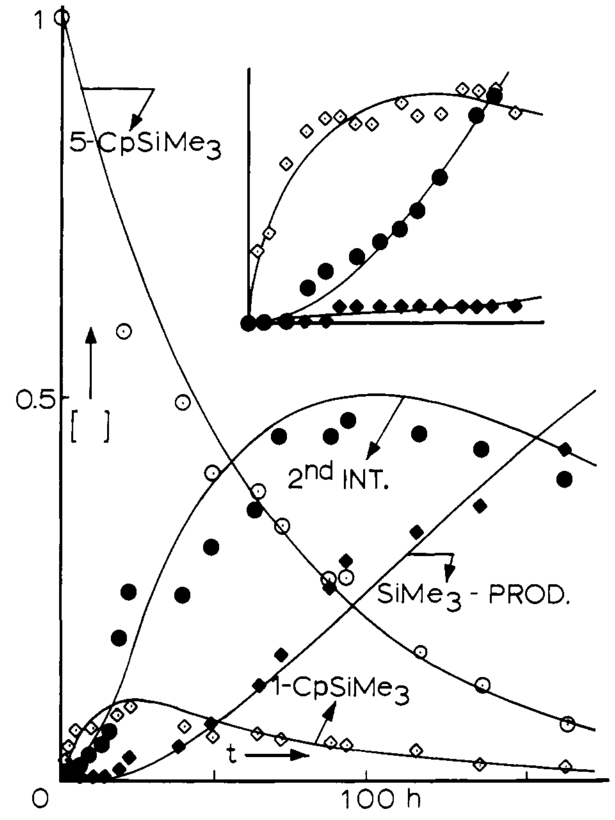


Figure 2. Change in peak intensities in the $SiMe_3$ region upon reaction of 5-$CpSiMe_3$ with Me_2SO-d_6. The first intermediate was identified as 1-$CpSiMe_3$. The curves are calculated for best fit on the basis of a sequence of three consecutive first-order reactions. The inset shows the early changes in another run in greater detail.

of events is graphically illustrated in Figure 2. The solid-line curves shown in the figure were estimated by means of pairwise Deming iterations[12] on the basis of assumed values of the rate constants as they appear in the integrated rate expressions[22] for a system of three consecutive reactions; they clearly fit quite well. The assignment of the first intermediate as 1-$CpSiMe_3$ is assured by the observation that the allylic signal of this species grows and declines apace. The nature of the second intermediate is not really known to us,[23] but the important point is that 1-$CpSiMe_3$ is the first intermediate and that the rate k_{5-1} can be measured in the presence of Me_2SO.

The result is that this rate constant is increased by a factor of 1.9 if 1% Me_2sO is present, of 3 if 5% Me_2SO is present, and of 12 in the presence of 15% Me_2SO (at higher concentrations of Me_2SO the changes occur too rapidly to allow a guarantee to be made that 1-$CpSiMe_3$ is still the first intermediate).

We believe that this large and specific solvent effect supports the Mironov model of the transition state and conclude that the effect of 5-substituents in this reaction is best analyzed in terms of hybridization changes. We also note in passing that the solvent effect does not support the possibility[18] of a substantial tunnelling correction; at 1% Me_2SO, most of the substrate should be H-bonded to the cosolvent, and this encumbrance of the migrating atom should *suppress* the assistance of tunnelling.

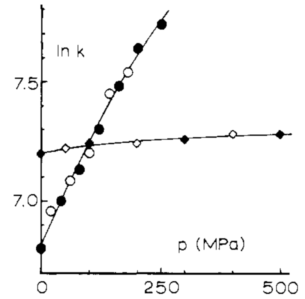


Figure 3. Effect of pressure on the degenerate sigmatropic shifts in 5-$CpSiMe_3$ (circles) and in bullvalene (squares). The filled points are taken with pressure increasing; clearly, the effect is reversible.

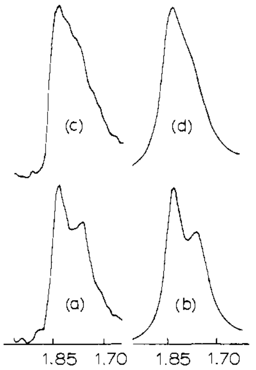
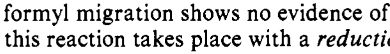


Figure 4. Methyl resonance of 5-formylpentamethylcyclopentadiene: (a) observed, 0.1 MPa; (b) calculated, $k = 20$ s^{-1}; (c) observed, 240 MPa; (d) calculated, $k = 30$ s^{-1}.

The effect of pressure on the degenerate migration of the $SiMe_3$ group was determined at 68 °C over a 250-MPa range by means of neat, fully equilibrated mixtures of the three isomers. The rate measurements were based on the line shapes of the vinylic and allylic protons of the 5-isomer; the other isomers do not interfere. The results are portrayed in Figure 3. Similarly, the activation volume for the degenerate formyl shift in 5-formylpentamethylcyclopentadiene was determined at −4 °C by means of line-shape analysis of the merging methyl signals; two of the spectra are shown in Figure 4. The pressure-induced spectral changes are completely reversible. The $\Delta V^{\neq}$ values for these two reactions were found to be −12.5 and −4 cm^3/mol, respectively. These results are consistent with the transition-state representations



The main conclusion that can be drawn is that there is far less charge development in these reactions than in the hydrogen migration discussed above. It is common for displacement reactions (both bimolecular and internal, and both ionic and free radical) to display small negative activation volumes of perhaps −5 to −10 cm^3/mol. This leads us to suggest that the silyl migration may be accompanied by a minor degree of charge separation. The formyl migration shows no evidence of this; it may even be that this reaction takes place with a *reduction* in overall dipole moment. Minor volume effects due to changes in hybridization and strain are also conceivable, and this makes further comparison and dissection unprofitable.

The degenerate Cope rearrangement of bullvalene was of great interest to us in this connection. Relatively few slow, nondegenerate [3,3] rearrangements have as yet been studied under pressure, but the known results on the average amount to perhaps −10 cm^3/mol.[4] It had been our hope[24] that if this value also applies to the exceedingly rapid degenerate shift in semibullvalene, the work term $p\Delta V$ might (at the very high but now routinely available pressures of several GPa) suffice to offset the residual free energy of activation of about 5 kcal/mol altogether, thus stabilizing the

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[22] Rodinguin, N. M.; Rodiguina, E. N. "Consecutive Chemical Reactions"; Engl. Transl., Schneider, R. F., Ed.; Elsevier: New York, 1964; p 9 ff.

[23] Nor did we investigate whether the final $SiMe_3$ peak is that of trimethylsilanol or hexamethyldisiloxane. McLean assumed[18] it is the latter, but there is also a report describing silanols as moderately stable in the presence of Me_2SO (Hampton, J. F.; Lacefield, C. W.; Hyde, J. F. *Inorg. Chem.* **1965**, *4*, 1659).

[24] le Noble, W. J.; Miller, A. R.; Hamann, S. D. *J. Org. Chem.* **1977**, *42*, 338.

bishomobenzene transition-state structure as the high-pressure form of semibullvalene. However, knowledge of isotope effects emerging in recent years[25] has begun to suggest that, in these superrapid cases, bond making and breaking become more and more evenly matched and, hence, that the minimum in the volume profiles might not be as deep as we supposed. The actual test with semibullvalene is still some time away (both the need for UV or Raman appraisal and the little-noted thermal instability of semibullvalene aggravate the experimental difficulty of the problem), but we must now report that the interim result with the much slower bullvalene at 19.8 °C is quite discouraging. There is barely a minimum at all! The activation voluem in this case is only −0.5 cm^3/mol (Figure 3). Thus, this seems to dash hopes that high pressure might be the route to homoaromaticity and supports Gajewski's notion that strain relief can impart dissociative character upon Cope transition states.

We conclude as follows. As in the case of cycloadditions where a range of activation volumes is now known from −7[26] to −50[27] cm^3/mol, the effect of pressure is also highly variable in the case of sigmatropic shifts, where the range is now from +10 to −30 cm^3/mol.[5c] In both instances, it has to date proved possible to understand individual variations and to correlate them with conclusions drawn from entirely different approaches. Thus, in the present case of 5-CpSiMe$_3$, the hydrogen migration apparently involves a bound zwitterionic state according to both solvent effect and volume profile; with bullvalene, both the pressure and isotope effects suggest a rather loose diradical-like transition state.

Experimental Section

An equilibrium mixture (~10 g) of the three position isomers of CpSiMe$_3$ was prepared as described,[28] and the pure 5-isomer (1–2 g) was isolated after 6–7 partial melting cycles; mp −19 °C (lit.[10] bp −19 °C). The SiMe$_3$ peaks of the 5-, 1-, and 2-siomers show up in C$_6$D$_6$ at δ −0.11, 0.19, and 0.14 (Varian HFT-80) in the ratio of 90:7:3, respectively, as found by Ashe.[10] In CDCl$_3$, the 5-isomer has a peak at δ −0.02, and the other two appear together at δ 0.18. The isomerization of 5-CpSiMe$_3$ to 1-CpSiMe$_3$ in CDCl$_3$ was monitored at 30 °C by means of the growing δ 0.18 peak in relation to an internal cyclohexane standard; integrated peaks A were used. Plotting ln $(A_\infty - A_0)$ vs. time gave good straight lines the slopes of which represent $k_{5-1} + k_{1-5}$; alternatively, use was made of a computer program that searched for the best values of this term and K.[12] The same experiment was done at several pressures up to 150 MPa in apparatus previously described.[11] Allowance was made for the heat of compression by considering the solution that had reached thermal equlibrium (after 5 min) at the starting point. The rate constants obtained were fitted via a least-squares procedure to $\ln k = a + bp + cp^2$, and $\Delta V^{\ddagger} = -bRT$. In CDCl$_3$ containing 6.25% Me$_2$SO-d_6 (by volume), a complex series of changes was seen in the SiMe$_3$ region; by comparing solutions of various Me$_2$SO concentrations, we could ascertain that the 5-isomer now appeared at δ −0.05, the other two isomers at δ 0.15, an intermediate at δ 0.10, and trimethylsilanol (or hexamethyldisiloxane) at δ 0.05. The rate constant k_{5-1} was measured as before, but now as a function of the Me$_2$SO concentration. In pure Me$_2$SO-d_6, CpSiMe$_3$ is converted into the dimethylsulfonium *S*-ylide virtually completely and immediately upon mixing.

A neat equilibrium mixture of the three isomers of CpSiMe$_3$ was studied by ^{1}H NMR as a function of temperature at ambient pressure. The vinyl region shows one broad singlet (4 H) at δ 6.6 at room temperature; another (1 H) is seen in the allyl region at δ 3.4. The former is resolved into an apparent quartet below 0 °C. At elevated temperatures, the two peaks broaden and coalesce; the vinyl and allyl protons of the 1- and 2-isomers are then clearly visible at δ 6.68 (d) and 6.91 (t), and δ 2.77 (d) and 2.72 (m), respectively. These peaks also allowed the identification of the 1-isomer as the first intermediate in the Me$_2$SO reaction described above. The rate constant of the degenerate SiMe$_3$ shift as a function of temperature was based on the line shape of the coalescing peaks; a plot of k vs. $1/T$ gave $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as 14.7 ± 0.8 kcal/mol and −2 ± 2 cal(mol deg), respectively. There was little or no change in K over the temperature range used (+27–+120 °C). A solution of the equilibrium mixture in benzene–Freon was then studied by means of NMR under high pressure[9] up to 250 MPa, and the rate constants were again determined by means of line-shape analysis.

5-Formylpentamethylcyclopentadiene was prepared as described by Bushby and Jones;[7] the degenerate equilibration was evaluated under pressure by means of line-shape analysis of the merging methyl peaks. A sample of bullvalene was obtained through the courtesy of Professor G. Schröder. $\Delta V^{\ddagger}$ was evaluated with a 350-mg sample in carbon disulfide at 19.8 °C, once again in the same way, over a pressure range of 500 MPa.

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Registry No. 5-CpSiMe$_3$, 3559-74-8; 1-CpSiMe$_3$, 29942-99-2; 2-CpSiMe$_3$, 29943-00-8; Me$_2$SO, 67-68-5; 5-CpMe$_5$CHO, 73057-50-8; 1-CpMe$_5$CHO, 85554-58-1; 2-CpMe$_5$CHO, 85554-59-2; bullvalene, 1005-51-2.

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