and the nicotinamide rings are stacked, one above the other. The T_1 data for NAD at 0.4 and 0.2 M at pH 7 corroborates this model. In both cases the relaxation rates of corresponding carbons in the adenine and nicotinamide portions of the molecule are similar, suggesting that the molecule reorients as a whole with little differential segmental motion between the two bases. It has been suggested that a lowering of the pH would diminish the intramolecular base stacking[9] through repulsion of the two positively charged rings which would provide the nicotinamide and adenine moieties the opportunity to move independently of each other and thus to have different effective correlation times. The data taken from the 0.4 M, pH 2 sample of NAD show no evidence of such independent segmental motion of the two rings confirming that NAD exists in aggregates of sufficient size to preclude a detectable amount of differential motion at the 0.4 M concentration. The data taken at 0.2 M and pH 2, however, do give some evidence for differential segmental motion. Note that the values for T_1 at N-2 and N-5 are somewhat longer than the T_1 values of the corresponding protonated carbons in the adenine rings (A-2 and A-8). Likewise, the T_1's for N-1' and N-4' are longer than for A-1' and A-4'. These data suggest that there is greater ring separation with protonation at the lower concentration and that differential motion of the two

rings becomes important as the aggregation of molecules decreases.

The concentration and pH data obtained by means of relaxation time studies on NAD and AMP have revealed details on molecule aggregation and differential segmental motion in two important biological compounds. Extrapolation of these data to lower and more typical biological concentrations suggests that even more significant results on segmental motion might be obtainable. Such studies would require isotopic labeling such as used by Blumenstein and Raftery[17] or improved instrumental techniques.[23] It is anticipated that the structure and dynamics of substrate binding to enzymes would also be amenable to T_1 studies.

(23) Such data have been obtained as specifically labeled enzymes in this laboratory and these data will appear shortly. In addition, A. Allerhand, R. F. Childen, R. A. Goodman, E. Oldfield, and X. Ysern, American Laboratory, November, 1972, p 19, have demonstrated the utilities of employing large sample tubes in the investigation of biological compounds.

Determination of the Fluxional Barrier in Semibullvalene by Proton and Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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Abstract: The ^{1}H and ^{13}C nmr spectra of semibullvalene are temperature dependent in the range of -100 to $-170°$. Rate constants were obtained at seven different temperatures by comparisons of calculated with experimental ^{1}H spectra. The free energy of activation for the degenerate Cope rearrangement in semibullvalene is 5.5 $\pm$ 0.1 kcal/mol at $-140°$; the enthalpy and entropy of activation are 4.8 $\pm$ 0.2 kcal/mol and -5.4 ± 3 eu, respectively. Semibullvalene has the lowest barrier of any presently known compound capable of undergoing the Cope rearrangement.

Nuclear magnetic resonance (nmr) has proved to be a powerful tool for the determination of barriers in molecules with fluctuating bonds. Fluxional molecules include the norcaradiene–cycloheptatriene system,[2] various annulenes,[3] and homotropilidenes.[4] The

bridged homotropilidenes, such as bullvalene (I),[5] dihydrobullvalene (II),[6] barbaralane (III),[7] and semibullvalene (IV),[8] are of particular interest. In these

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(2) E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965); **93**, 2207 (1971); G. E. Hall and J. D. Roberts, *ibid.*, **93**, 2203 (1971); E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Günther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).

(3) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 103 (1971).

(4) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) H. Günther, J. B. Pawliczek, J. Ulmen, and W. Grimme, *Angew. Chem., Int. Ed. Engl.*, **11**, 517 (1972).

(5) (a) Reference 4a; (b) G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **6**, 414 (1967); (c) M. Saunders, *Tetrahedron Lett.*, 1699 (1963); (d) A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965).

(6) (a) R. Merenyi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964); (b) ref 5b.

(7) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(8) (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969); (c) J. Meinwald and D. Schmidt, *ibid.*, **91**, 5877 (1969); (d) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

compounds, determinations of kinetic parameters for degenerate Cope rearrangements (*e.g.*, IVa ⇌ IVb) are not complicated by the interference of conformational isomers as in the unbridged compounds, homotropilidene[4] and 2,4,6,8-tetramethylhomotropilidene.[9]

An attempt[8a,b] to measure the rate of the Cope rearrangement in semibullvalene showed that the 60-MHz proton spectrum of this compound remained unchanged down to −110°; unlike the nmr spectrum of I,[5c] II,[6a] and III,[7] and it was suggested[8a,b] that the barrier to the Cope rearrangement in IV must be much lower than the corresponding barriers in I, II, and III. Consideration was given to the possibility that the structure of semibullvalene might be that of the bishomobenzene IV⧧, but evidence against this structure as the ground

I, X = CH=CH   IV
II, X = CH₂CH₂
III, X = CH₂

IVa   IVb   IV⧧
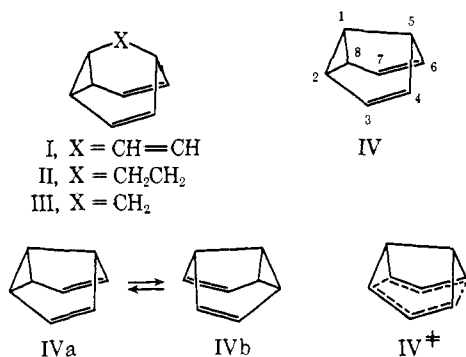
state was adduced from uv spectroscopy and from chemical shift arguments.[8a,b] An electron diffraction study[10] suggests that the ground state of semibullvalene has only C_s symmetry and that the double bonds are localized. Furthermore, it has been shown by low-temperature nmr studies that octamethylsemibullvalene has (at best) a structure of C_s symmetry and thus cannot be an octamethyl derivative of bishomobenzene structure IV⧧.[11]

The nature of semibullvalene has also been investigated by the quantum mechanical MINDO/2 method,[12] which showed that the ground state has only C_s symmetry. The barrier for the Cope rearrangement initially was calculated to be 2.8 kcal/mol,[12a] but, in a later paper, this value was modified to 3.6 kcal/mol.[12b] Because of the interest in homoaromaticity,[13] calculations[14] have also been carried out on the possible effects of substituents on this barrier, with the aim of finding compounds which might have a negative barrier for the Cope rearrangement; such compounds would, of course, have ground states derived from bishomobenzene. An experimental determination of the barrier in semibullvalene itself would test the reliability of theoretical calculations and would provide a calibration point for calculations of substituent effects on the barrier to the Cope rearrangement. Although the theoretical calculations previously mentioned suggest that the barrier in semibullvalene itself would be too small to measure by nmr line-shape methods, a conclusion which

has received some acceptance,[15,16] our feeling was that the calculated barrier might well be too low. Thus, a reinvestigation of the nmr spectra of semibullvalene was considered desirable, especially since the previous nmr work[8a,b] was carried out at a low spectrometer frequency and spectra were not obtained below −110°.

Experimental Section

The synthesis of semibullvalene (IV) was accomplished as described in the literature.[8c,d]

The proton nmr spectra of IV were recorded on a superconducting solenoid nmr spectometer[17] operating at 59 kG. The proton spectra were obtained in a frequency-sweep mode on a 0.04% solution of IV in CCl₂F₂. The ¹³C spectra were acquired as free induction decay signals, which were then Fourier transformed.[18] An accumulation of 1000 to 2000 transients was required to obtain a satisfactory signal-to-noise ratio for a 1.5% solution of IV in CCl₂F₂ at low temperatures.

Theoretical spectra were calculated by means of a computer program provided by Professor Saunders[5c] and modified by M. Henrichs and W. L. Larson to run on the IBM 360/91 of the Campus Computer Network of UCLA. The plotted spectra were obtained on a Calcomp plotter.

Nmr Results and Discussion

Proton Chemical Shifts. The 251-MHz proton spectra of semibullvalene (IV) recorded at various temperatures are shown in Figure 1. At −103°, the spectrum shows three time-averaged resonances (δ 2.98, 4.17, and 5.07), which have previously been assigned[8] to $H_{1,5}$, $H_{2,4,6,8}$, and $H_{3,7}$, respectively. The spectrum at −167° consists of five resonances, as expected for semibullvalene undergoing the Cope rearrangement slowly on the nmr time scale. The rearrangement leads to the following exchanges of proton chemical shifts.

$$H_1 \rightleftharpoons H_5$$

$$H_{2,8} \rightleftharpoons H_{4,6}$$

$$H_{3,7} \rightleftharpoons H_{3,7}$$
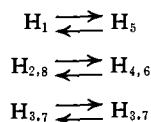
The $H_{3,7}$ protons give rise to a single chemical shift at all temperatures, as expected. The chemical shifts of the $H_{2,8}$ and $H_{4,6}$ protons are assigned as shown in Table I on the basis of the expected chemical shifts of olefinic and cyclopropyl protons. The assignments of H_1 and H_5 are not completely trivial because of the comparatively small chemical-shift difference (0.3 ppm) between these protons. Since H_1 is a cyclopropyl proton whereas H_5 is allylic to two double bonds and is not part of a cyclopropane ring, it is reasonable to assign the low-field component of the $H_{1,5}$ doublet to the H_5 proton and the high-field component to the H_1 proton. The same order of chemical shifts for the corresponding protons in dihydrobullvalene (II) has been reported.[6a]

A comparison of the chemical shifts in semibullvalene (IV) with the corresponding shifts in bullvalene (I),[5b] dihydrobullvalene (II),[6a] barbaralane (III),[7] and bicyclo[3.1.0]hexene-2 (V)[19] is instructive. As shown in Table II, the chemical shifts of the olefinic protons in

(9) L. Birladeanu, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, 92, 6387 (1970).

(10) Y. C. Wang and S. H. Bauer, *J. Amer. Chem. Soc.*, 94, 5651 (1972).

(11) F. A. L. Anet and G. Schenck, *Tetrahedon Lett.*, 4237 (1970).

(12) M. J. S. Dewar and W. W. Schoeller, *J. Amer. Chem. Soc.*, 93, 1481 (1971); M. J. S. Dewar and D. H. Lo, *ibid.*, 93, 7201 (1971).

(13) S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).

(14) R. Hoffmann and W. D. Stohrer, *J. Amer. Chem. Soc.*, 93, 6941 (1971).

(15) R. M. Moriarty, C. Yeh, E. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, 94, 9229 (1972).

(16) R. K. Russell, L. A. Paquette, L. G. Greifenstein, and J. B. Lambert, *Tetrahedron Lett.*, 2855 (1973).

(17) F. A. L. Anet, G. W. Buchanan, and C. H. Bradley, paper presented at the 11th Experimental Nuclear Magnetic Resonance Conference, Pittsburgh, Pa., April 1970.

(18) F. A. L. Anet, V. J. Basus, C. H. Bradley, and A. Cheng, paper presented at the 12th Experimental Nuclear Magnetic Resonance Conference, Fla., February 1971.

(19) P. K. Freeman, M. F. Grostic, aud F. A. Raymond, *J. Org. Chem.*, 30, 771 (1965).

Table I. Assignments of Proton and Carbon-13 Chemical Shifts of Semibullvalene

Temp, °C	Chemical shifts, ppm from TMS Proton	Carbon-13	Assignments[a]
−95	2.98	50.7	1, 5
	4.17	87.2	2, 4, 6, 8
	5.05	121.7[b]	3, 7
−160	2.79	42.2	2, 8
	2.83	48.0	1
	3.16	53.1	5
	5.08	121.7[b]	3, 7
	5.59	131.8[c]	4, 6

[a] The numbering system is shown on structure IV. [b] This resonance overlaps with the high-field component of the ^{13}C triplet of the solvent CCl_2F_2, as evidenced from the relative intensities of the triplet in the temperature range investigated. [c] This resonance overlaps with the low-field component of the solvent triplet in the slow-exchange region (cf. footnote b of this table).

Table II. Proton Nmr Data for I to V

Compd	Proton chemical shifts B[a]	C[b]	O[c]	Ref
Bullvalene (I)	2.2	2.2	5.7	5b
Dihydrobullvalene (II)	2.2	1.6	5.7	6a
Barbaralane (III)	2.3[d]	2.2[d]	5.6	7
Semibullvalene (IV)	3.2	2.8	5.0 and 5.6	This work
Bicyclo[3.1.0]-hexene-2 (V)		1.67[e]	5.4 and 5.9	19

[a] Saturated bridged proton. [b] Cyclopropane protons. [c] Olefinic protons. [d] The chemical shift of the allylic C protons was calculated from the time-averaged shift (3.9 ppm) and the chemical-shift separation (205 Hz at 60 MHz) of the $H_{2,6}$ protons. Similarly, the chemical shift of the B proton was obtained from the chemical shift of the C protons and the time-averaged shift (2.27 ppm) of the $H_{1,5}$ protons. [e] Methine allylic cyclopropyl proton.

compounds I to V range from 5 to 6 ppm with the $H_{3,7}$ protons of semibullvalene having the highest field shift. The resonances of the olefinic protons in semibullvalene, unlike those of the olefinic protons in I to III, are nicely resolved and have a chemical-shift difference of 0.6 ppm. Interestingly, an appreciable chemical-shift separation is also found for the olefinic protons of V, although individual assignments of these olefinic protons have not been made. The cyclopropyl chemical shifts of II, III, and IV are substantially different from one another and appear to be correlated to the length of the chain bridging the homotropilidene system, but the actual origin of these differences is not clear.

Carbon-13 Chemical Shifts. The ^{13}C spectrum of semibullvalene at room temperature has been reported[20] and consists of three resonances at 50.0, 86.5, and 120.4 ppm assigned to the carbons $C_{1,5}$, $C_{2,4,6,8}$, and $C_{3,7}$, respectively. The ^{13}C results of semibullvalene in the present study, as summarized in Table I, indicate that the $C_{1,5}$ and $C_{2,4,6,8}$ resonances, like the corresponding proton resonances, are 1 : 1 doublets at low temperatures and that the $C_{3,7}$ resonance remains as a single line at all temperatures. The assignments of the $C_{2,8}$ and $C_{4,6}$ carbons are based on the expected chemical shifts of cyclopropyl and olefinic carbons. The C_1 and C_5 resonances are separated by only 5.8 ppm, and their assignments are based on the fact that cyclopropyl carbons generally resonate at higher fields than allylic carbons.[21]

(20) W. Wenkert, E. W. Hagaman, L. A. Paquette, R. E. Wingard, and R. K. Russell, J. Chem. Soc., Chem. Commun., 135 (1973).
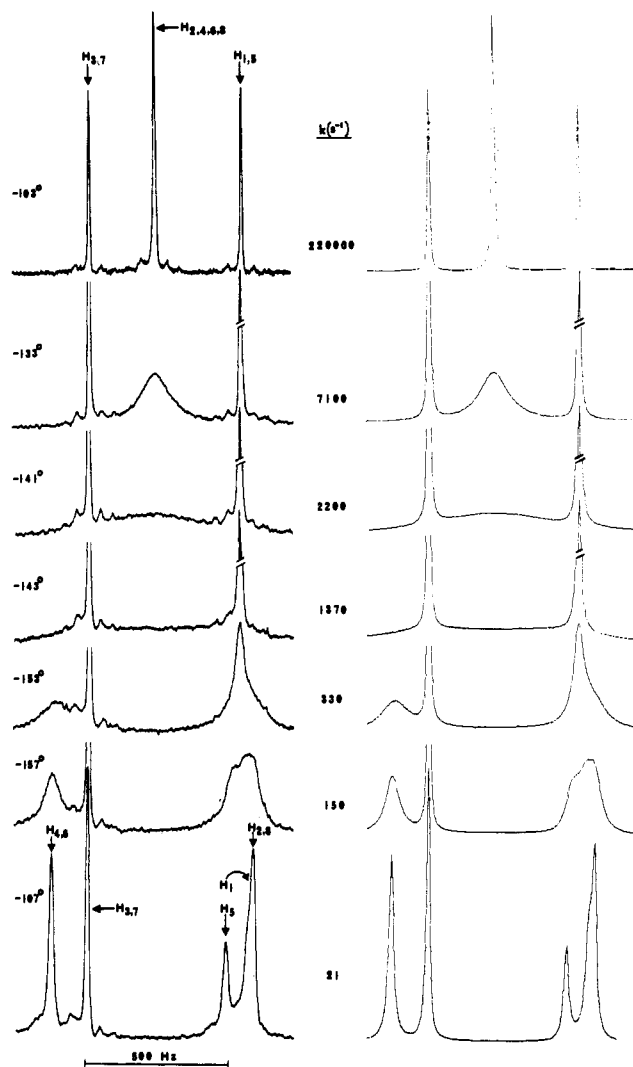

Figure 1. Left: 251-MHz proton nmr spectra of semibullvalene (IV) in CCl_2F_2 at various temperatures. Right: calculated line shapes for various values of the rate constant for the degenerate Cope rearrangement in semibullvalene.

^{13}C chemical shifts of semibullvalene (IV) shown in Table I can in fact be used to confirm the chemical-shift assignments for the carbons in 4,6-tetramethylenesemibullvalene (VI),[20] which has a structure similar to that

VI
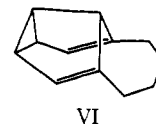
of IV and has a very small equilibrium constant for tautomerism at room temperature. Thus, it is not surprising that the individual shifts of the nonolefinic methine carbons in IV and VI are very similar. Because of the substituent effects, the olefinic carbons in these two compounds have different shifts.

Proton Dynamic Nmr Spectra of Semibullvalene. The $H_{3,7}$ protons of semibullvalene remain at the same site during the Cope rearrangement, and therefore these protons should exhibit a single chemical shift at all temperatures as is indeed observed (Figure 1). The

(21) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.

only dynamic nmr effect expected in the band of these nuclei arises from unequal coupling to other protons in semibullvalene. For example, at high temperature the spectrum depends on the average of J_{23} and J_{34} but not on the individual values of these coupling constants, whereas at low temperatures the spectrum does depend on the individual values of J_{23} and J_{34}. Since these coupling constants are quite small, and their differences even smaller, dynamic nmr effects on $H_{3,7}$ should be almost negligible. In fact, the band of $H_{3,7}$ has a very complex splitting pattern at room temperature, and below $-100°$ it is an unresolved band whose width at half-height changes from 7 Hz at $-100°$ to 13 Hz at $-167°$. The increase in the width of the $H_{3,7}$ line over the temperature range -100 to $-167°$ is attributed mainly to dipole–dipole relaxation, which become more effective at low temperatures because of increased solvent viscosity.

The $H_{2,4,6,8}$ protons appear as a time-averaged resonance at $-100°$ and higher temperatures. As the temperature is lowered, this resonance exhibits appreciable broadening because the exchange of $H_{2,8}$ and $H_{4,6}$ proton is no longer extremely rapid on the nmr time scale. Below $-143°$, a separation into two peaks takes place, and, at $-167°$, the chemical-shift difference is 700 Hz. The $H_{1,5}$ band splits into two peaks below $-155°$. The difference between this coalescence temperature and that for the $H_{2,4,6,8}$ protons reflects the much smaller chemical-shift separation (80 Hz) of the H_1 and H_5 protons than that of the $H_{4,6}$ and $H_{2,8}$ protons (700 Hz).

A strict line-shape analysis of a system of coupled spins requires the application of density matrix methods.[22] However, for semibullvalene, this method is hardly feasible, because the molecule has eight protons, and a very long computation time is expected. Furthermore, resolved spin–spin splittings are not observed in the spectra at low temperatures because of dipole–dipole relaxation, and therefore it is not possible to obtain the coupling constants, which are required by the density matrix treatment. Fortunately, the chemical shifts are very much larger than the coupling constants in semibullvalene, and it is therefore possible to use a treatment based on the modified Bloch's equations[23,24] to calculate line shapes.

Line widths for all the resonances in semibullvalene due to spin–spin couplings, magnetic field inhomogeneities, and dipole–dipole relaxation were assumed to be equal to the observed line width of the $H_{3,7}$ peak, which should show negligible dynamic nmr effects. Since the difference in proton spin–spin couplings is expected to be small, the above assumptions are reasonable. At intermediate temperatures, the exchange broadening of the $H_{2,4,6,8}$ signal is quite large, and spin–spin couplings would have almost no effects on the line shape.

Exchange rate constants for the Cope rearrangement in semibullvalene at several temperatures were determined by visual matchings of the experimental with theoretical spectra (see Figure 1). A simple visual allowance for the presence of spinning side bands in the experimental spectra was made in the matchings of

(22) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).
(23) H. S. Gutowsky, D. L. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).
(24) C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

theoretical with experimental spectra. The temperature variation of the chemical shifts was found to be small (1 to 6 Hz) from -100 to $-167°$, and no chemical-shift correction was applied.

Table III gives the rate constants for the Cope re-

Table III. Rate Data for the Cope Rearrangement in Semibullvalene

Temp, °C	Rate constants, sec⁻¹
-103	*ca.* 220,000
-133	7,100
-141	2,200
-143	1,370
-153	330
-157	150
-167	*ca.* 20

arrangement in semibullvalene at temperatures from -167 to $-103°$. The activation energy (E_a), obtained by a least-squares treatment on these data, is 5.1 ± 0.2 kcal/mol. The free energy of activation ($\Delta G^{\ddagger}$) at $-143°$ is 5.5 ± 0.1 kcal/mol, while the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation are 4.8 ± 0.2 kcal/mol and -5.4 ± 3 eu, respectively. The rate constants at at -103 and $-167°$ given in Table III were not used to obtain the activation parameters quoted above because the spectra at these temperatures consist of relatively sharp lines, and the neglect of coupling constants could lead to appreciable errors.

Barriers for Cope Rearrangements. The free energies of activation for Cope rearrangements in some systems with *cis*-divinylcyclopropane moieties are listed in Table IV. We choose the free energy barriers ($\Delta G^{\ddagger}$) for

Table IV. Free Energies of Activation ($\Delta G^{\ddagger}$) in Some Systems with *cis*-Divinylcyclopropane Moieties

Compd	$\Delta G^{\ddagger}$, kcal/mol	Temp, °C	Ref
cis-Divinylcyclopropane	*ca.* 20	5 to 20	*c*
Homotropilidene	13.7[a]	-35	4b
2,4,6,8-Tetramethyl-homotropilidene	13.6[b]	0	9
Bullvalene (I)	12.8[b]	100	5d
Dihydrobullvalene (II)	9.5[b]	-40	6
Barbaralane (III)	7.8[b]	-77	7
Barbaralone	9.6[b]	-55	*d*
Protonated barbaralone	>13.8	-5	*e*
Semibullvalene (IV)	5.5	-143	This work
Octamethylsemibullvalene	6.4	-141	11
Semibullvalene–tungsten pentacarbonyl	12.0	0	15

[a] Calculated from $\Delta H^{\ddagger}$ (11.8 kcal/mol) and $\Delta S^{\ddagger}$ (-8 eu) given in ref 4b. [b] Reference 11. [c] J. M. Brown, B. T. Golding, and J. J. Stofks, *J. Chem. Soc., Chem. Commun.*, 319 (1973). [d] J. B. Lambert, *Tetrahedron Lett.*, 1901 (1963). [e] P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4454 (1970).

comparisons because the values can be determined quite accurately from nmr data. The enthalpy of activation and the entropy of activation, on the other hand, are obtained from the temperature dependence of $\Delta G^{\ddagger}$ and are frequently afflicted with large systematic errors.[25] In the bridged homotropilidenes, bullvalene
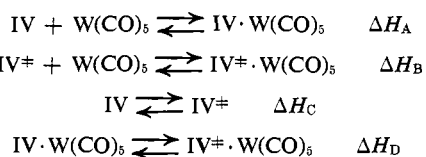
(25) F. A. L. Anet and R. Anet in "Determination of Organic Structure by Physical Methods," Vol. 3, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, p 344.

(I), dihydrobullvalene (II), barbaralane (III), and semibullvalene (IV), the entropies of activation ($\Delta S^{\ddagger}$) for Cope rearrangements should be close to zero, since the ground states and the transition states are both fairly rigid. Reported entropies of activation, in fact, are -0.4[26] and -4.8[5b] eu for I and 11.0,[5b] 11.5,[27] and -5.4 eu for II, III, and IV, respectively. The diversity in $\Delta S^{\ddagger}$ suggests that the entropies of activation, and therefore also the enthalpies of activation, are not very reliable.

Hoffmann and Stohrer have used extended Hückel calculations[14] to study substituent effects on the activation energy for the Cope rearrangement in semibullvalene. Their calculations show that electron releasing substituents at positions 1, 5 or electron withdrawing substituents at 2, 4, 6, 8 should decrease the activation energy. These conclusions are in agreement with the decreasing barriers in the series: protonated barbaralone > barbaralone > barbaralane (see Table IV).

The barrier height for rearrangement in semibullvalene–tungsten pentacarbonyl has been reported[15] to be 12 kcal/mol (Table IV). It was suggested[15] that the metal plays the role of an electron-releasing substituent, which should increase the barrier for the rearrangement. However, the metal binds to two carbons in the ground state, but a different binding scheme could well occur in the transition state for this rearrangement. For example, the metal could be bonded in a symmetrical fashion to three carbons.

The rearrangement in the tungsten pentacarbonyl complex of semibullvalene is, in our view, best interpreted in terms of a transition state that has the tungsten bonded to three carbons of the bishomobenzene form of semibullvalene (IV‡). Consider the following formal transformations

$$IV + W(CO)_5 \rightleftharpoons IV \cdot W(CO)_5 \quad \Delta H_A$$

$$IV^{\ddagger} + W(CO)_5 \rightleftharpoons IV^{\ddagger} \cdot W(CO)_5 \quad \Delta H_B$$

$$IV \rightleftharpoons IV^{\ddagger} \quad \Delta H_C$$

$$IV \cdot W(CO)_5 \rightleftharpoons IV^{\ddagger} \cdot W(CO)_5 \quad \Delta H_D$$

where $IV \cdot W(CO)_5$ and $IV^{\ddagger} \cdot W(CO)_5$ are tungsten pentacarbonyl complexes of IV and IV‡, respectively. For ΔH_C we use the enthalpy of activation for the Cope rearrangement of semibullvalene as determined in the present work. For ΔH_D we use the free energy of activation reported for the rearrangement of semibullvalene–tungsten pentacarbonyl and this should be a very good approximation for reasons stated earlier. It follows that $\Delta H_B - \Delta H_A = \Delta H_D - \Delta H_C = 12 - 4.8 = 7.2$ kcal/mol. Therefore, semibullvalene forms a more stable complex with $W(CO)_5$ than does the bishomo-

benzene form of this compound, and the difference in the heats of complexation is 7.2 kcal/mol.

In compounds II to IV, the barrier for the Cope rearrangement increases substantially with the length of the bridge linking the two ends of the homotropilidene system (Table IV). An examination of framework molecular models (Prentice-Hall) reveals that the overlaps between p orbitals on C_4 and C_6 should decrease as the size of the bridge is increased. This decreased overlap should result in a raising of the energy of the bishomobenzene structure, and thus to a larger barrier, as observed.

Octamethylsemibullvalene[11] has a free energy barrier of 0.9 kcal/mol higher than semibullvalene itself for the Cope rearrangement (Table III). The methyl groups on carbons 2, 4, 6, 8, according to the extended Hückel calculations,[14] should increase the barrier, while those on carbons 1 and 5 should decrease the barrier. Since the molecule is crowded with methyl groups, steric effects may be important in determining the barrier height in this compound. It is interesting that while semibullvalene and octamethylsemibullvalene have different barrier heights, homotropilidene and 2,4,6,8-tetramethylhomotropilidene have very similar barriers. Semibullvalene has the lowest barrier of any presently known compound capable of undergoing the Cope rearrangement.

The activation energies of the hypothetical compounds 2,4,6,8-tetracyanosemibullvalene (VII), 1,5-difluorosemibullvalene (VIII), and 1,5-difluoro-2,4,6,8-tetracyanosemibullvalene (IX) have been calculated by Hoffmann and Stohrer to be -0.34, -0.39, and -0.59 eV, respectively, relative to the activation energy of semibullvalene.[14] If we use the activation energy of 5.1 kcal/mol determined experimentally for semibullvalene, the activation energies of VII, VIII, and IX can be deduced to be -2.8, -4.0, and -8.7 kcal/mol, respectively, and the ground states of these compounds should be bishomobenzene structures.

At present, no molecule having a bishomobenzene structure as the ground state is known. Vogel and coworkers have synthesized a compound for which a formal semibullvalene structure can be written, but they have shown that the molecule is actually a bridged annulene, 1,6:8,13-ethanediylidene[14]annulene.[28] Thus, the delocalization in the formal semibullvalene moiety of this compound does not lead just to a bishomobenzene structure but proceeds to a fully aromatic 14 π-electron system.

(26) Calulated from the activation parameters given in ref 5d.

(27) Footnote 27 of ref 5b.

(28) E. Vogel, U. H. Brinker, K. Nachtkamp, J. Wassen, and K. Müllen, *Angew. Chem.*, **85**, 760 (1973); H. Günther, H. Schmickler, U. H. Brinker, K. Nachtkamp, J. Wassen, and E. Vogel, *ibid.*, **85**, 762 (1973).