

147. Comparative Study of the *Cope* Rearrangement of Hexa-1,5-diene and Barbaralane

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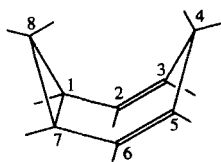
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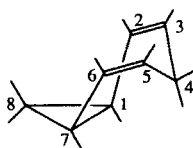
The classical rules for *Cope* rearrangements predict a transition state with chair form to be favored over the boat form. On the other hand, bridged homotropylidenes, which allow only a boat-form transition state by steric reasons, have extremely low barriers. A controversy about the correct pathway and the different possible intermediates and transition states of the reaction has gone on for years. In this work, the hypersurfaces of barbaralane, in comparison with the *boat*- and *chair*-form of hexa-1,5-diene, are computed by the *ab initio* CASSCF (6,6)/6-31G** method starting with UMP2/6-31G** natural orbitals (NO's). All three hypersurfaces show characteristic features, and, moreover differ from each other. A hitherto undiscussed intermediate, bicyclo[2.2.0]hexane, was localized on the *boat*-hexa-1,5-diene pathway. So it is noteworthy that our transition state for the *boat*-hexa-1,5-diene does not correspond to the transition states found by other authors for this conformation. The computed enthalpies of activation of *boat*- and *chair*-hexa-1,5-diene, and barbaralane are in good agreement with the experimental data.

Introduction. – *Oth* and *Schröder* [1] [2] in 1965 and 1967 published two studies concerning molecules which undergo fast and reversible valence isomerization. By valence isomerization, we understand a reorganization of the π and σ bonds with simultaneous modifications of certain interatomic distances and bond angles. The valence isomerization obeys the first-order kinetic laws; it is an intramolecular rearrangement whose rate of reaction is influenced merely by the temperature. It belongs to the group of reactions that have been termed 'no mechanism' [3].

Homotropylidene (= bicyclo[5.1.0]octa-2,5-diene) undergoes a fast and reversible valence isomerization. The molecule homotropylidene has two conformers, one *transoid* and the other *cisoid*.



cisoid

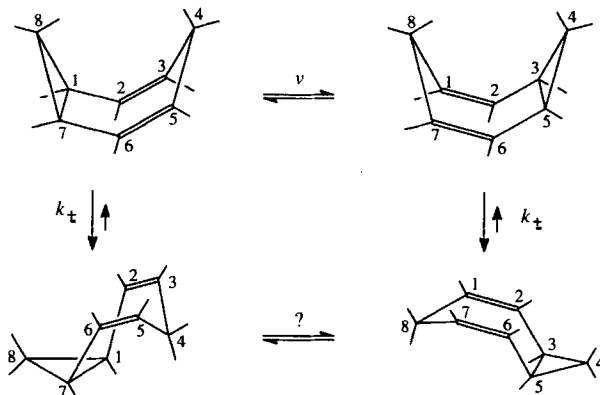


transoid

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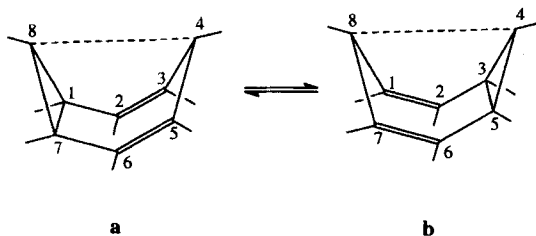
Doering and Roth [4–6] were the first authors who described the valence isomerization of homotropylidene. In Scheme 1 the conformational mobility k and the valence isomerization v of the Cope [7] rearrangement are shown.

Scheme 1. Conformational Mobility k and Valence Isomerization v of Homotropylidene



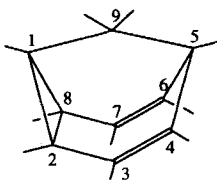
The energy of the *transoid*-conformation is lower than the one of the *cisoid*, but the valence isomerization takes place between two *cisoid*-structures. The isomerization between two *transoid*-structures has never been observed. The valence isomerization in the homotropylidene moiety is shown in Scheme 2. At temperatures above 300°, the homotropylidene is transformed irreversibly into bicyclo[3.3.0]octa-2,6-diene.

Scheme 2. Valence Isomerization of Homotropylidene



In Scheme 2, the structures **a** and **b** are identical as long as the C- and H-atoms are not marked. If we compare the structures **a** and **b** after we have labeled them, we observe that in structure **a** C(1) and C(7) belong to the cyclopropyl moiety, whereas in **b** they have olefinic character. The two structures are in a dynamic equilibrium.

The fast and reversible valence isomerizations in the bridged homotropylidenes, such as barbaralane, are particularly interesting from the mechanistic point of view, because they are degenerate.



In barbaralane, the conformation of the homotropyliene moiety is locked into the *cisoid*-form by the presence of a bridge. It was found that the augmentation of the number of C-atoms between the bridgeheads of the homotropyliene resulted in an increase in the activation energy of the reversible isomerization process. The aim of this work is to compare *ab initio* calculations of the reaction pathway of the sterically fixed barbaralane with those of *boat*- and *chair*-hexa-1,5-diene. The consistency of the experimental and theoretical results encourages us to investigate other interesting unsolved questions of similar bridged compounds.

Synthesis. – The synthesis of barbaralane was realized in four steps: *a*) Synthesis of ethyl cycloheptatriene-carboxylate, of cycloheptatriene-carboxylic acid, as well as of cycloheptatriene-carbonyl chloride according to *Dewar* and *Pettit* [8]. *b*) Synthesis of CH_2N_2 by the method of *Boer* and *Backer* [9]. *c*) Synthesis of the diazomethylacetone of cycloheptatriene and of barbaralane [10]. *d*) Reduction of barbaralane to barbaralane by the *Wolff-Kishner* method [11]. The synthesis is described in detail in the thesis of *Voellinger* [12].

Kinetic NMR Studies. – ^{13}C -NMR Spectroscopy (with ^1H decoupling) is an excellent tool to study the intramolecular dynamic processes of molecules in solution for two reasons: *a*) The absence of spin-spin decoupling simplifies the spectral analysis of complex exchanges, and *b*) compared to ^1H -NMR spectroscopy, ^{13}C -NMR involves chemical shifts which are useful over a range of temperatures in which the dynamics of the exchange may be studied. On the other hand, the *Overhauser* effect, which results from the ^1H , ^{13}C decoupling, may affect the observed intensity, which will no longer be perfectly proportional to the nuclear population. Furthermore, the weak signal/noise relation in the ^{13}C -NMR spectrum may lead to a broadening of the signals.

The simulation of the experimental NMR spectra was realized with the aid of program NMREX3 developed by *Heinzer et al.* [13]. This program allows a quantitative analysis of the exchange processes which result from internal isodynamic or non-isodynamic transformations. The simulation of an experimental spectrum is realized iteratively; the program allows variation of the following parameters: *a*) the population of the nuclei on the different sites (by taking in account the signal-intensity effects which result from the different times of relaxation spin-lattice and/or the *Overhauser* effect), *b*) the chemical shifts, *c*) the broadness of the signals which are characteristic for the sites, *d*) the molar fraction of the different structures implied in an asymmetric exchange, *e*) the rate constant(s) of the exchange(s), *f*) the position of the base line, *g*) the inclination of the base line (for further details of the computational methods, *cf.* [13]).

The NMR spectra were recorded on a *Varian XL-300* spectrometer. The cavity of the spectrometer containing the probe can be cooled by N_2 stream which passes through liquid N_2 . The temperature in the probe is held constant by a regulation device and measured by a thermocouple. The spectra were determined on solutions containing 20 mg of substance in 1 ml of solvent: *a*) 20 mg of barbaralane in $\text{CS}_2 + \text{TMSD}_{12}$, *b*) 5 mg of barbaralane in 1 ml of $\text{CS}_2 + \text{COS}$ (1:1 v/v) + TMSD_{12} for the measurements at low temperature (the tube was kept at -80° in MeOH/dry ice). The solutions were degassed and sealed under vacuum. The exper. results for barbaralane are summarized together with earlier results for this molecule in *Table 1*. It is noteworthy that the entropy of activation

determined by $^1\text{H-NMR}$ in 1967 [2] and the actual $^{13}\text{C-NMR}$ value differ strongly from each other (11.5 vs. 0.49 e.u.). The older results had only preliminary character, and, therefore, the experiment was repeated in the thesis of one of the authors (*A.V.*).

Table 1. *Experimental Kinetic Parameters for the Cope Rearrangement of Barbaralane* (energies in kcal mol $^{-1}$)

Ref.	$\log_{10}A$	E_a	k [s $^{-1}$]	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger [e.u.]	T [°C]
[11]	13.6 ± 0.3	8.6 ± 0.2	$173 \cdot 10^5$				
[2]	5.7 ± 0.3	10.4 ± 0.3	$26 \cdot 10^6$ $99 \cdot 10^4$	–	9.8 ± 0.3	11.5 ± 0.3	0 –40
[14]	12.90	7.71	–	7.60	7.32	–0.73	
[12]	13.19 ± 0.03	8.22 ± 0.02	$148 \cdot 10^5$	7.67 ± 0.06	7.81 ± 0.02	0.49 ± 0.14	25

Theoretical Studies of the Cope Rearrangement. – *Dewar* and *Jie* have already [15] offered a short review of the theoretical discussion of the *Cope* rearrangement. This rearrangement was recognized as one of the showpieces of a synchronous, pericyclic reaction; the symmetry rules of *Woodward* and *Hoffmann* [16] were applied to this type of reaction.

According to these rules, the *Cope* rearrangement is a thermally allowed pericyclic reaction which passes through an aromatic transition state (TS). *Doering* and *Roth* [17] showed that the TS with *chair*- is favored above the *boat*-form.

Nevertheless in 1971, *Doering et al.* [18] suggested an asynchronous mechanism where bond formation preceded bond cleavage, giving a biradical intermediate (IS_1). This hypothesis was supported by experimental and theoretical work on the *Cope* rearrangement of hexa-1,5-diene by *Dewar et al.* [19] [20], and *Komornicki* and *McIver* [21]. *Dewar* [22], in 1984, like *Doering*, proposed a non-synchronous mechanism, and subsequently, computed, with AM1 under C_2 symmetry, the energies of TS and IS_1 on the two possible reaction pathways [23]. The relative stability of IS_1 and TS was further studied by the introduction of different substituents [15] [24]. These studies showed that the mechanism could correspond as well to a one-step reaction *via* TS as to a two-step one *via* IS_1 . RHF, MP2, MP3, and MP4 studies by *Dewar* and *Healy* [25] showed that the energy difference between TS and IS_1 diminished as the basis set was extended from 3-21G to 6-31G*. Lastly, CASSCF/6-31G* computations [26] favor IS_1 over TS by 1.9 kcal mol $^{-1}$. Because the computed transition state is still by 12 kcal mol $^{-1}$ above the experimental value (33.5 kcal mol $^{-1}$) [18], it seems that the correlation energy is of crucial importance for the determination of the transition state. On the other hand, *Morokuma* and coworkers [27–29], on the basis of *ab initio* calculations, pleaded for an intermediate (IS_2) with two long bonds of 2.316 Å for the *boat*-form, and the TS with two shorter bonds of 2.086 Å for the *chair*-form. *Yamaguchi* and coworkers [30] performed simulations of the *Cope* reaction by a H_6 model. The UHF-based methods provide proper dissociation curves in the whole region, although spin-contamination errors were remarkable. They claim that the diradical character of the *Cope* reaction TS is not negligible for these symmetry-allowed concerted reactions in accord with the triplet instability of the RHF solution for cyclic transition structures.

More recent CASPT2N studies by *Borden* and coworkers [31] on the influence of the correlation energy indicate a concerted *Cope* reaction with synchronous breaking and forming of the bonds *via* TS.

Density functional theory computations of the *Becke* 3-LYP/6-31G* type by *Houk* and coworkers [32] confirmed this result. The energies for the *chair*- and *boat*-form transition states are in excellent agreement with the experimental results.

Jiao and *Schleyer* [33] also confirmed the experimental data with one-determinantal methods with inclusion of electron correlation (e.g., MP4SDTQ/6-31G*). According to them, the prototype of the *Cope* rearrangement is not a biradical but an aromatic mechanism.

More recently, *Davidson* and coworkers [34] developed MP2 methods for multireference wave functions which correct the overestimation of the diradical character of the CASSCF wave function. When this error is corrected, the *Dewar*-type diradical intermediate no longer occurs as a minimum on the potential-energy surface, and the aromatic transition state moves to shorter bond length. Some of these *ab initio* calculations were summarized by *Borden* and *Davidson* [35] and in *Table 2*.

Table 2. Recent *ab initio* Results for boat- and chair-Hexa-1,5-diene (energies in kcal mol⁻¹, bond length in Å)

Ref.	Method	<i>chair</i> R	TS ΔH^\ddagger	<i>boat</i> R	TS ^{a)} ΔH^\ddagger
[31]	CASPT2N/6-31G*	1.745	30.8	2.139	42.2
	CASPT2N/6-311 G**	1.775	32.3	2.139	41.0
	CASPT2N/6-311G(2d,2p)	1.885	32.2	2.204	41.2
[32]	SVWN/6-31G*	1.753	19.8	1.966	33.2
	BLYP/6-31G*	2.034	29.7	2.289	36.0
	BLYP/6-311G**	2.145	30.0	2.376	35.0
	B3LYP/6-31G*	1.971	34.2	2.208	42.0
	B3LYP/6-311G**	2.043	34.8	2.279	41.2
[33]	MP4SDTQ/6-31G*	1.784	32.7	2.055	44.9
	//MP2(fc)/6-31G*				
	QCISD(T)/6-31G*		35.3		47.2
	//MP2(fc)/6-31G*				
[34]	MROPT1	1.85	31	2.615	47
	MROPT2		31		46
	Exp.		33.5 ± 0.5		44.7 ± 2.0

^{a)} The *boat*-TS does not correspond to the one found in this work.

On the inconsistency between *ab initio* and the semiempirical results, *Dewar* and *Jie* stated that UHF-AM1 computations heavily overestimate the stability of IS₁ and, therefore, should be used only with care [36]. Based on newest results [34], quantum-chemical computations exclude with certainty the first of three possible mechanisms, namely *a)* via the biradical-like intermediate state (IS₁), *b)* via the aromatic six-electron transition state (TS), or *c)* via two more or less separated allyl radicals (IS₂).

The *Cope* Rearrangement of Barbaralane. – The bridged homotropylienes (= bicyclo[5.1.0]octa-2,5-dienes) are particularly interesting from the theoretical point of view, because the *Cope* rearrangement is forced to proceed *via* the *boat*-form all along the reaction pathway. Furthermore, some computational problems are relieved, because the rearrangement is degenerate.

Attempts of a theoretical interpretation of the experimental results for this type of reaction by semiempirical methods have a long history. MINDO/2 Computations [37] [38] for bullvalene, semibullvalene, and barbaralane were already performed in 1971. According to these computations, the reaction passes through a biradical TS, geometrically very similar to the initial products. The results of the two publications differ only insofar as there is a full geometry optimization in [37] (*Table 3*).

Table 3. Activation Enthalpies of Bullvalene, Semibullvalene, and Barbaralane Computed by Different Semiempirical Methods

Molecule	ΔH^\ddagger			
	AM1 ^{a)}	MINDO/2	UHF-MINDO/3 + Spin projection	exp.
Bullvalene	29.1	11.3 ^{b)} , 25.4 ^{c)}	8.0 ^{d)}	12.3 ^{f)} , 12.6 ^{g)}
Semibullvalene	19.7	2.3 ^{b)} , 18.3 ^{c)}	5.7 ^{d)}	4.8 ^{h)}
Barbaralane	23.9	5.9 ^{b)} , 18.3 ^{c)}	7.0 ^{e)}	7.81 ^{e)}

^{a)} [15]. ^{b)} [37]. ^{c)} [38]. ^{d)} [39]. ^{e)} [12]. ^{f)} [40]. ^{g)} [41]. ^{h)} [42].

These results were brought into question by unpublished MNDO computations as mentioned in [15] which showed far too high enthalpies of activation. *Miller et al.* [43] found by MNDO-half electron (2×2)CI computations for semibullvalene, a TS with biradical character and an activation energy of 5.7 kcal/mol, which fits well with the experimental value of 4.8 kcal mol⁻¹ [42]. *Dewar and Jie* [15] pointed to the fact that 'open shell' versions of MNDO normally overestimate the stabilities of biradicals and, therefore, repeated the computations with the AM1 method. In *Table 3*, their results are summarized together with our preliminary computations using UHF-MINDO/3 with subsequent spin projection. As the activation energies in *Table 3* demonstrate, the AM1 computations deviate by *ca.* 15 kcal mol⁻¹ from the experimental values.

The Potential-Energy Surfaces of boat- and chair-Hexa-1,5-diene and Barbaralane. – In this work, the potential-energy surfaces of the *Cope* rearrangements of the three structures are computed using UMP2/3-21G geometries. Single-point UMP2/6-31G** computations were performed to generate the NOs, and subsequently UNO-CASSCF/6-31G** calculations furnished the energies. The calculations were performed with Gaussian94 [44], and the structures drawn with Molden [45].

This method of using UHF NOs goes back to *Yamaguchi* [46] and was later discussed in detail by *Pulay et al.* [47]. The MCSCF wave function is used for the correct description of the zeroth-order correlation, and not for describing dynamical correlation. Configuration selection based on fractional occupation appears to be the basis for a reliable automated procedure. The active space should include NOs with significant fractional occupation, between 0.02 and 1.98. According to *Pulay*, it is unlikely that CASSCF can be competitive with UNO-CASSCF, but the latter collapses to the closed-shell RHF wave function, if the wave function becomes triplet stable. This seems to be only a minor disadvantage, unless, the transition state is very close to the instability point.

boat-Hexa-1,5-diene. The results of the computations of *boat*-hexa-1,5-diene are represented in *Fig. 1* and summarized in *Table 4*. We find a result which, curiously,

has never been discussed before. The most probable transition state has the bond lengths $R1 = 2.1 \text{ \AA}$ and $R2 = 1.55 \text{ \AA}$, and leads to an intermediate, namely the stable bicyclic molecule *cis*-bicyclo[2.2.0]hexane with the bond length $R1 = R2 = 1.587 \text{ \AA}$. Hexa-1,5-diene has an enthalpy of formation of $20.4 \pm 0.4 \text{ kcal mol}^{-1}$ [48], and *cis*-bicyclo[2.2.0]hexane $29.9 \text{ kcal mol}^{-1}$ [49]. The $\Delta\Delta H_f$ (exp.) accordingly is, therefore, $9.5 \text{ kcal mol}^{-1}$ which compares favorably with our computed value of $8.7 \text{ kcal mol}^{-1}$. Moreover, the experimental enthalpy of activation is (from Goldstein and Benzon [50]) $44.7 \pm 2 \text{ kcal mol}^{-1}$, compared to our calculations with $42.1 \text{ kcal mol}^{-1}$.

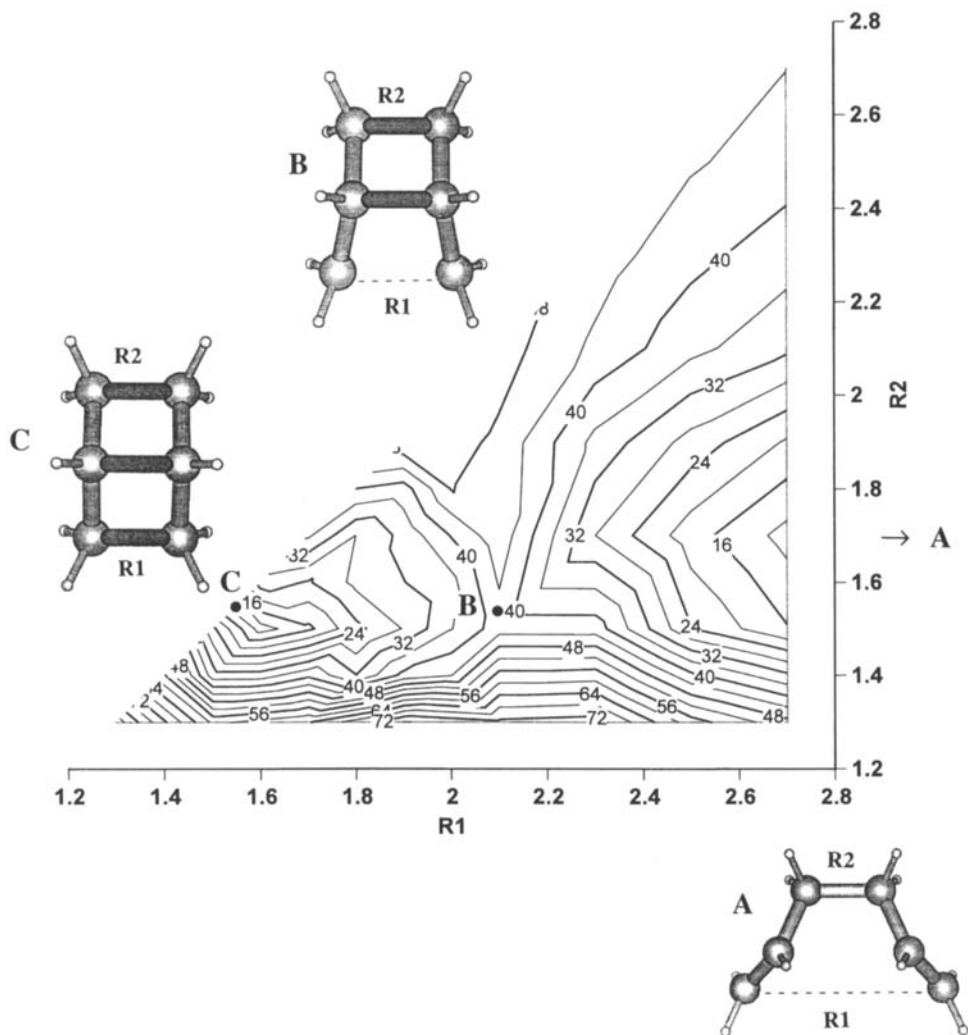


Fig. 1. Cope rearrangement of boat-hexa-1,5-diene. UNO-CASSCF-6-31G** Computations. Equipotential: 4 kcal mol^{-1} . R in \AA . **A**: Initial/final product, $R1 = 4.293 \text{ \AA}$, $R2 = 1.587 \text{ \AA}$; **B**: TS, $R1 = 2.1 \text{ \AA}$, $R2 = 1.55 \text{ \AA}$; **C**: Intermediate, $R1 = R2 = 1.587 \text{ \AA}$ (PES interpolated from 59 computed energies).

Table 4. *Experimental, UNO-CASSCF-, and B3LYP-Computed Activation Enthalpies of the Cope Rearrangement of Barbaralane, boat-, and chair-Hexa-1,5-diene*

Molecule	ΔH^\ddagger		
	UNO-CASSCF	B3LYP	exp.
Barbaralane	12.6	7.5	7.81–9.8
<i>boat</i> -Hexa-1,5-diene	42.1	42.0 ^{a)}	44.7 ± 2
<i>chair</i> -Hexa-1,5-diene	38.3	34.2 ^{a)}	33.5 ± 0.5

^{a)} [32].

As we shall see later, we cannot directly transfer this situation to barbaralane. *boat*-Hexa-1,5-diene is not a prototype for all *boat*-form Cope rearrangements. Rather, it does provide a reality check on the methodology which we apply to barbaralane.

chair-Hexa-1,5-diene. The results of the computations of *chair*-hexa-1,5-diene are represented in Fig. 2 and summarized in Table 4. Our results are in good agreement with those of Morokuma and coworkers [27–29]. There exist two transition states TS₁ and TS₂ of symmetry C_{2h} with bond lengths R1 = R2 = 1.732 Å and R1 = R2 = 2.3 Å, respectively, which are separated by a small hill. As we have seen before, this result seems to have its origin in the neglect of the dynamical correlation energy [31–35]. Nevertheless, our energetic results are in good agreement with the experiment. The two transition states lie by 38.3 and 38.9 kcal mol⁻¹ above the initial product. This value is rather close to the experimental value found by Doering *et al.* [18] to be 33.5 ± 0.5 kcal mol⁻¹. For both TSs, our calculations predict very small biradical character. Fractional occupation numbers of the NOs are 1.96, 1.94, 1.81, 0.19, 0.06, 0.04, and 1.95, 1.89, 1.84, 0.16, 0.11, 0.5, respectively.

Barbaralane. The results of the computations of barbaralane are represented in Fig. 3 and Table 4. The values are also in good agreement with the experimental results. The TS of C_{2v} symmetry is by 12.6 kcal mol⁻¹ above the energy of the initial product. By inspection of Table 1, we find experimental values between 7.81 and 9.8 kcal mol⁻¹. The large energy difference between hexa-1,5-diene and barbaralane is excellently reproduced. The TS has bond lengths of R1 = R2 = 2.2 Å. The biradical character is somewhat higher than for *chair*-hexa-1,5-diene (1.95, 1.91, 1.78, 0.22, 0.09, 0.05). The transition state resembles two weakly coupled allyl radicals.

The geometries of TSs were found by inspection of the two-dimensional energy surfaces, because for the applied procedure, the method proposed by McIver and Komornicki [51] to characterize a pass on the potential-energy surface cannot be used. Our single-point computations with the UNO-CASSCF/(6,6)-6-31G** method are only approximations to the exact TSs, because the geometries were computed at a lower level. For barbaralane, however, we performed a B3LYP/6-31G* full-geometry optimization for the initial product and the TS. The TS geometry found by this method has somewhat shorter bond length (R1 = R2 = 2.083 Å). The force constant matrix was diagonalized, and only one negative eigenvalue was found in agreement with the method of McIver and Komornicki [51]. The B3LYP/6-31G* enthalpy of activation for barbaralane is in agreement with our experimental results for this molecule (see Table 4), and the entropy of activation of -1.9 e.u. is close to the newer measured values given in Table 1.

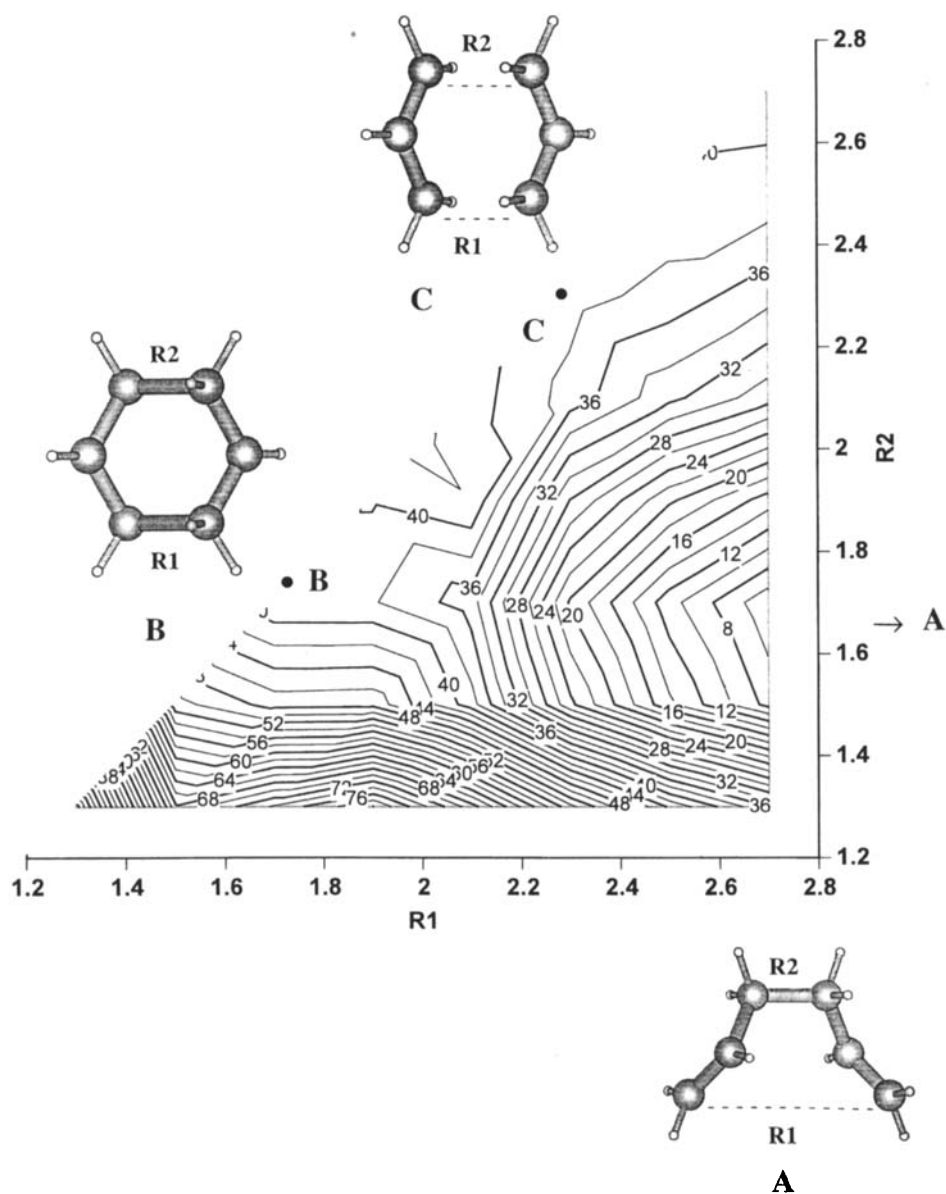


Fig. 2. Cope rearrangement of chair-hexa-1,5-diene. UNO-CASSCF-6-31G** Computations. Equipotential: 2 kcal mol⁻¹. R in Å. A: Initial/final product, $R_1 = 4.310$ Å, $R_2 = 1.562$ Å; B: TS₁, $R_1 = R_2 = 1.732$ Å; C: TS₂, $R_1 = R_2 = 2.3$ Å (PES interpolated from 37 computed energies).

Conclusions. – Our study shows that the Cope rearrangement of barbaralane cannot be explained by a reaction of the prototype *boat-hexa-1,5-diene*. For *boat-hexa-1,5-diene*, our computations predict the stable bicyclic molecule, *cis-bicyclo[2.2.0]hexane* of symme-

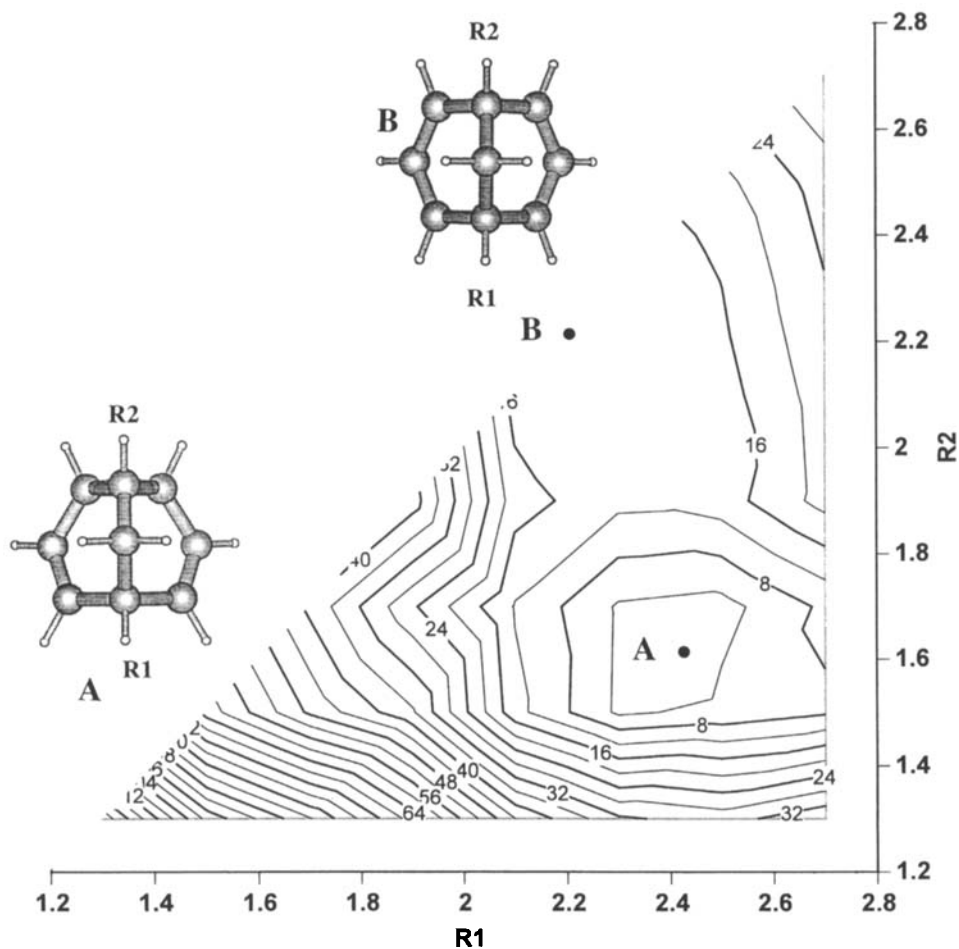


Fig. 3. Cope rearrangement of barbaralane. UNO-CASSCF-6-31G** Computations. Equipotential: 4 kcal mol⁻¹. R in Å. **A**: Initial/final product, $R_1 = 2.415$ Å, $R_2 = 1.61$ Å; **B**: TS, $R_1 = R_2 = 2.2$ Å (PES interpolated from 48 computed energies).

try C_{2v} , as an intermediate; for the *chair*-form there exist two TSs of symmetry C_{2h} . Several authors have shown that these two TSs fall together, when the dynamical correlation energy is included. For barbaralane, finally, we find a much lower lying transition state of symmetry C_{2v} than for the so-called prototype reaction (~ 28 kcal mol⁻¹) with somewhat higher biradical character¹ compared to the one of hexa-1,5-diene.

The aim of our calculations was to find a method which is at the same time sufficiently correct and computationally effective to be able to furnish two dimensional potential-energy surfaces. As *Minkin et al.* [52] state, the reaction coordinate method often employed in practical calculations has turned out to be incorrect in the general case. Only in case when the internal coordinate being varied is really sufficiently close to the genuine reaction coordinate does this method yield correct results regarding the localization of

the TSs. Possible transition states can be easily identified on two-dimensional potential-energy surfaces.

Our study shows that the *Cope* rearrangement of barbaralane, though belonging in the category of concerted reactions, is not synchronous [22]. First the σ bond opposite to the bridgehead in the cyclopropane ring is opened, while the distance between the two C-atoms at the other end of the molecule changes very little. When it reaches the length of *ca.* 2.2 Å, the other σ bond forms by a continuous reduction of the distance between the terminal allylic C-atoms, while the σ bond at the other end of the molecule remains practically unchanged. The region of the TS is very flat, and we cannot exclude that, in other cases, there may exist an intermediate biradical. This will be the subject of further studies.

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