

The Cope Rearrangement in Substituted Semibullvalenes as Studied by Dynamic ^{13}C NMR

C. Schnieders and K. Müllen*

Institut für Organische Chemie der Universität Köln,
Greinstr. 4, D-5000 Köln (West-Germany)

C. Braig, H. Schuster and J. Sauer*

Institut für Organische Chemie der Universität Regensburg,
Universitätsstr. 31, D-8400 Regensburg (West-Germany)

Summary: NMR-data for some substituted semibullvalenes are reported and the Cope rearrangement is analysed kinetically. Substituent effects on the activation barriers are discussed.

The great interest in neutral bishomoconjugated molecules ^[1] has initiated thorough investigations of substituent effects on the activation barrier of the Cope rearrangement in semibullvalene 1 ^[2]. While a true bishomoconjugated species has not been achieved there is firm evidence that electron attracting groups in positions 2, 4, 6 and 8 and electron donating groups in positions 1 and 5 tend to accelerate the valence isomerisation ^{[3]-[7]}. The influence of substituents attached to centres 3 and 7 has attracted much less attention ^{[8]-[10]}. The inclusion of such semibullvalenes might be revealing, however, since it is known from acyclic 1,5-hexadienes that appropriate phenyl substitution (e. g. compound 5) significantly affects the mechanism of the Cope rearrangement ^[11]. Not surprisingly in view of the very low activation energies involved exact determinations of the relevant kinetic data via dynamic NMR spectroscopy have been rare ^[12]. The present work describes the synthesis of the semibullvalene derivatives 2, 3 and 4 as well as the kinetic analysis of their Cope rearrangement.

All semibullvalenes were obtained according to the new one-pot synthesis reported earlier ^[8]; this method proved also to be successful for the synthesis of the highly labile monophenyl derivative 3. The ^1H NMR spectrum of compound 3 could be calculated for the rapid equilibrium case (24°C , 250 MHz, CDCl_3). The best fit between experimental and calculated spectra was obtained for the AA'BB'X-type with the following set of δ - and J-values:

$$\begin{array}{lll} \nu_7 = & 5.22 \text{ [ppm]} & J_{2,4} = 2.53 \pm 0.3 \text{ [Hz]} & J_{2,8} = J_{4,6} = 3.85 \pm 0.1 \text{ [Hz]} \\ \nu_2 = \nu_4 = & 4.39 \text{ [ppm]} & J_{6,8} = 0.76 \pm 0.1 \text{ [Hz]} & J_{2,6} = J_{4,8} = 0.30 \pm 0.1 \text{ [Hz]} \\ \nu_6 = \nu_8 = & 4.20 \text{ [ppm]} & & J_{6,7} = J_{7,8} = 3.90 \pm 0.05 \text{ [Hz]} \\ & & \text{or vice versa} & J_{2,7} = J_{4,7} = 0.00 \pm 0.05 \text{ [Hz]} \end{array}$$

The number of resonances in the ^{13}C -NMR spectra (75 MHz) of 2, 3 and 4 at moderately low temperatures ($> -40^\circ\text{C}$) indicates that the degenerate Cope rearrangement is rapid on the NMR time scale. Except for the case of 3 signal assignments follow immediately from inspection of the relevant chemical shifts and from off-resonance decoupling. Particularly significant in the spectra of 2, 3 and 4 are the resonances of C-2, C-4, C-6, C-8 at 89.0, 89.4 (92.5) and 97.7 respectively, representing the average value of olefinic and cyclopropanic chemical shifts. The occurrence of

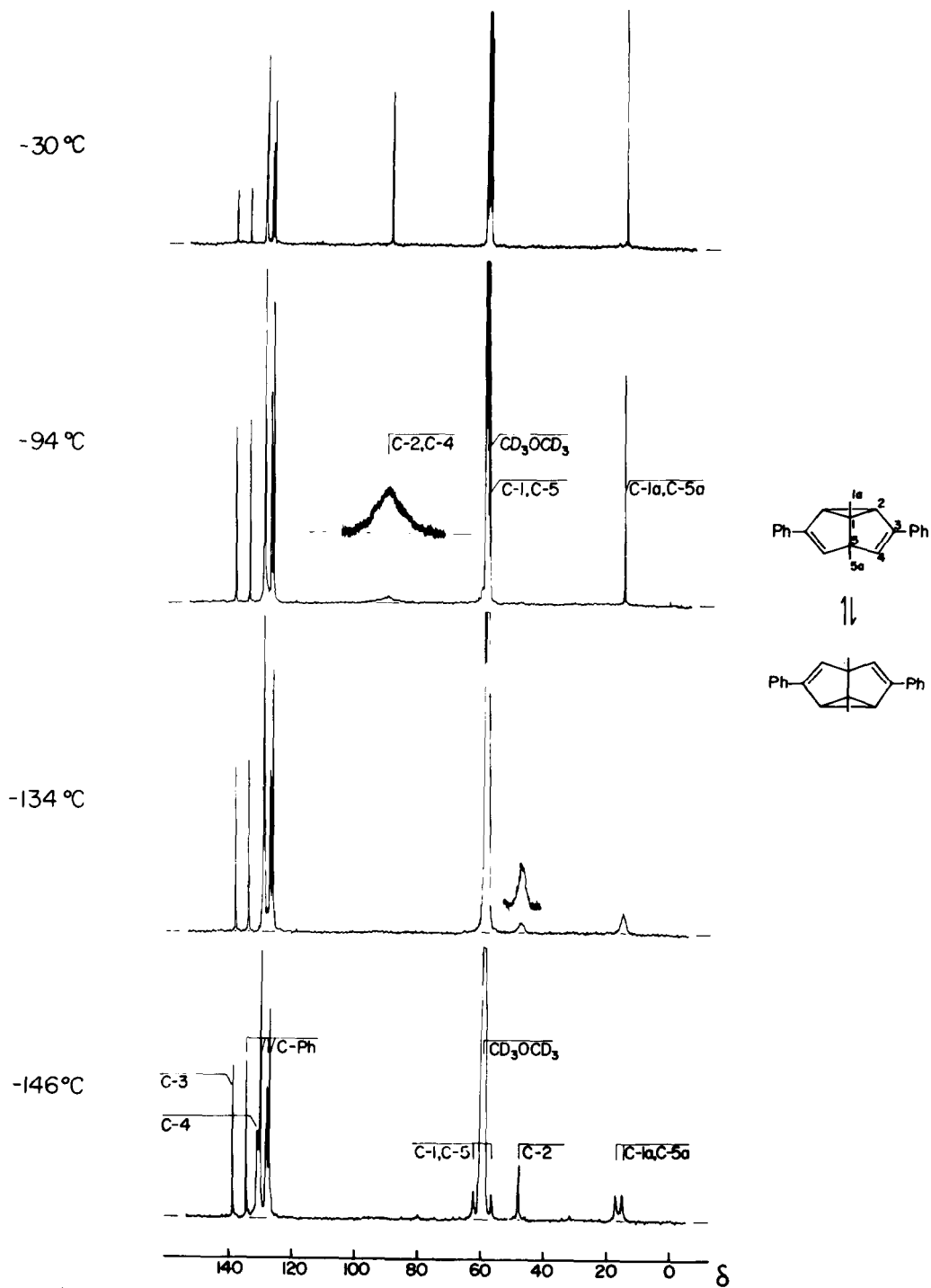


Fig. ^{13}C NMR spectra (75.5 MHz, dimethylether- d_6) of compound 2 at different temperatures

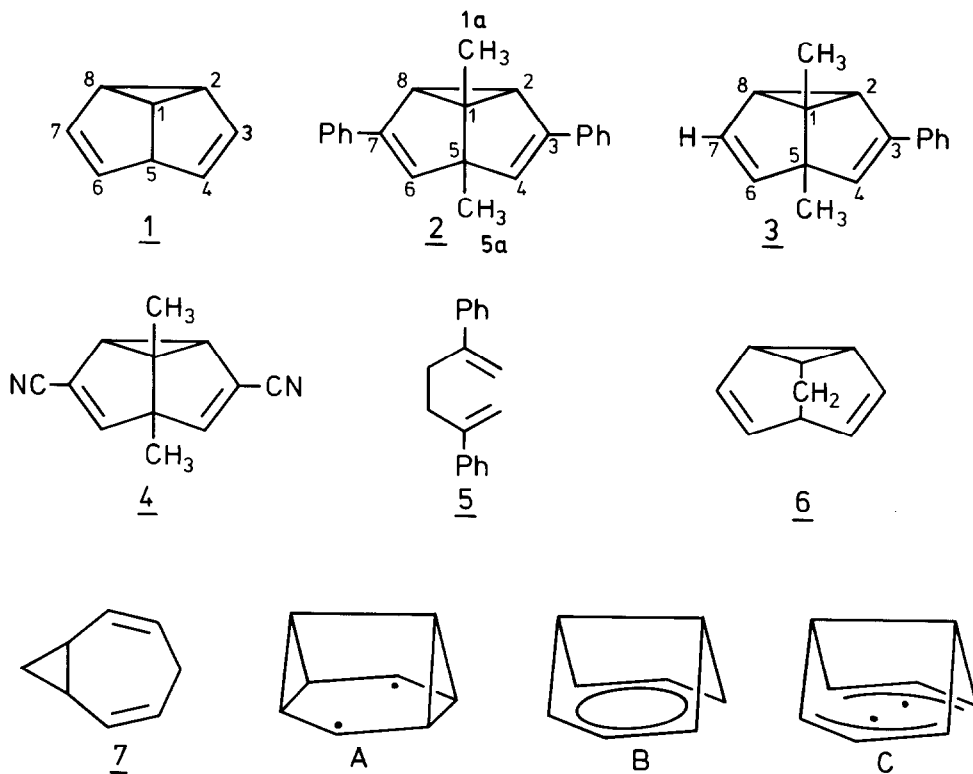


Table: Activation parameters for the Cope-rearrangement of semibullvalenes 1 - 4.

Compound	E_A [kcal/mol]	ΔH^\ddagger 25°C [kcal/mol]	ΔG^\ddagger 25°C [kcal/mol]	ΔS^\ddagger [e.u.]
<u>1</u> [12]	5.1	4.8	5.5	-5.4
<u>2</u> a)	6.7 ± 0.2	6.1 ± 0.2	6.1 ± 0.1	-0.2 ± 0.3
<u>3</u> a)	4.7 ± 0.5	4.1 ± 0.5	5.5 ± 0.1	-4.9 ± 5
<u>4</u> b)	6.2 ± 0.2	5.6 ± 0.2	6.0 ± 0.1	-1.2 ± 3

a) Dimethylether- d_6 .

b) Difluorochloromethane/dichloromethane- d_2 (4:1).

an exchange process in 2, 3 and 4 is evidenced by the line broadening of the above resonances at temperatures below -50°C . The slow exchange domain for 2 and 4 is achieved below -145°C , where the carbon atoms C-2/ C-8 and C-4/ C-6, C-1 and C-5 as well as C-1a and C-5a, respectively are detected by separate sharp signals (see Figure). The same result is found for compound 3 although its analysis is complicated by the fact that the signals of C-2 and C-8 (with some residual broadening at -147°C) overlap. Line shape analysis of the exchange broadened signals both above and below coalescence have been performed by the program DNMRIT [13] whereby rate constants at 14 (2) and 11 (4) different temperatures between -140 and -76°C as well as -145 and -76°C respectively have been included in the Arrhenius plots. The errors quoted in the table have been determined according to ref. 13. The somewhat larger errors for 3 are due to the uncertainty of the chemical shifts of C-2 and C-8 (see above) and due to the smaller temperature range covered.

The resulting kinetic data are given in the table ($k[\text{s}^{-1}]$ at -133°C : 7100 (1), 600 (2), 1920 (4)). The following conclusions are obvious:

- It appears from the ΔG^{\ddagger} -values as well as from the rate constants that the Cope rearrangement in the substituted semibullvalene derivatives 2, 3 and 4 is slower than in the parent compound 1 [12]. As expected 3 behaves more similarly to 1 than 2. A related, although more pronounced rate decreasing effect of phenyl substitution has been observed by Kessler [14] for the case of barbaralane 6 and homotropilidene 7.
- In the latter compounds this feature has been rationalized by assuming a destabilisation of the transition state (with increased electron density) by the electron donating substituents [2],[14]. This is in disagreement with the observed increase of the activation energy in 4.
- One has also invoked the steric destabilisation exerted by the phenyl groups on the boat-shaped transition state of 7 [14]. The smaller influence of the substituents in 2 with respect to the diphenyl substituted barbaralane and homotropilidene species might, indeed, point out the role of steric substituent effects which are less significant in the highly strained semibullvalene.
- There is no need from the relatively weak retarding influence of the substituents in 2 and 3 to assume a biradicaloid transition state (A) instead of a cyclic 6π (B)- or bisallyl-type (C) situation [15].
- The observation of a degenerate Cope rearrangement with "ordinary" kinetic parameters for 4 is particularly important since 4 is known from X-ray data to exhibit a surprisingly long C-2/C-8 cyclopropane bond and a short non-bonding distance of C-4 and C-6 [16]. Consequently, the latter findings are specific of the crystal lattice and cannot be taken as indicating a tendency toward a bishomoconjugated ground state.
- Semibullvalene 4 shows a higher activation energy for the Cope rearrangement than the isomeric 2,6-dinitrile, which was obtained by Quast and coworkers [17] quite recently in accordance with theoretical predictions [2].

Work directed toward an incorporation of a greater variety of substituents into the semibullvalene moiety is in progress.

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R E F E R E N C E S

- [1] K.N. Houk, R.W. Gandour, R.W. Strozier, N.G. Rondan, L.A. Paquette, *J. Am. Chem. Soc.* **101**, 6797 (1979); [2] R. Hoffmann, W.-D. Stohrer, *J. Am. Chem. Soc.* **93**, 6941 (1971); M.J.S. Dewar, D.M. Lo, *J. Am. Chem. Soc.* **93**, 7201 (1971); M.J.S. Dewar, Z. Nahlovská, B.D. Nahlovsky, *Chem. Commun.* 1971, 1377; [3] L.S. Müller, K. Grohmann, J.J. Dannenberg, L. Todaro, *J. Am. Chem. Soc.* **103**, 6249 (1981); [4] R. Gompper, M.-L. Schwarzensteiner, *Angew. Chem., Int. Ed. Engl.* **21**, 438 (1982); [5] R. Askani, M. Littmann, *Tetrahedron Lett.* **1982**, 3651; [6] H. Quast, J. Christ, Y. Görlach, W. van der Saal, *Tetrahedron Lett.* **1982**, 3653; [7] C. Schnieders, H.-J. Altenbach, K. Müllen, *Angew. Chem., Int. Ed. Engl.* **21**, 637 (1982); [8] D. Paske, R. Ringshandl, I. Sellner, H. Sichert, J. Sauer, *Angew. Chem., Int. Ed. Engl.* **19**, 456 (1980); [9] H. Schuster, H. Sichert, J. Sauer, *Tetrahedron Lett.* **1983**, 1481; [10] H. Schuster, J. Sauer, *Tetrahedron Lett.* **1983**, 4087; [11] M.J.S. Dewar, L.E. Wade, *J. Am. Chem. Soc.* **95**, 290 (1973); [12] F.A.L. Anet, G.E. Schenk, *Tetrahedron Lett.* **1970**, 4237; A.K. Cheng, F.A.L. Anet, J. Mioduski, J. Meinwald, *J. Am. Chem. Soc.* **96**, 2887 (1974); [13] J. Heinzer, J.F.M. Oth, *Helv. Chim. Acta* **64**, 258 (1981); [14] H. Kessler, W. Ott, *J. Am. Chem. Soc.* **98**, 5015 (1976); [15] A comparison of 1 and 2 will also have to consider the -potentially- rate accelerating effect of the methyl; [16] I. Sellner, H. Schuster, H. Sichert, J. Sauer, H. Nöth, *Chem. Ber.*, in press; [17] We are grateful for information prior to publication: H. Quast, Y. Görlach, J. Christ, E.M. Peters, K. Peters, H.G. von Schnering, L.M. Jackman, G. Ibar, A.J. Freyer, *Tetrahedron Lett.*, in press. H. Quast, Y. Görlach, *Tetrahedron Lett.*, in press.

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