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TEMPERATURE-DEPENDENT NUCLEAR MAGNETIC RESONANCE SPECTRUM OF OCTAMETHYLSEMIBULLVALENE

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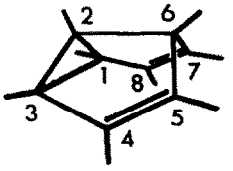
Several systems are now known containing a 3,4-homotropilidene moiety.[1-4] Of these, the bullvalene,[1] dihydrobullvalene[1c,d] and barbaralane[1f,2] systems as well as homotropilidene itself[3] have been shown to exhibit temperature-dependent nmr spectra. For semibullvalenes, however, temperature-independent nmr spectra have been reported down to -110° (semibullvalene)[4a] and -100° (octamethylsemibullvalene).[4b] We now wish to report the temperature-dependence of a semibullvalene nmr spectrum.



I

In its high temperature spectrum (Fig. 1, -60°), octamethylsemibullvalene[5] (I) (2% I in vinylchloride/pyridine = 5:1, 100 MHz) exhibits the 1:2:1 pattern expected of a semibullvalene undergoing a rapid Cope rearrangement. The resonances of methyls 1,3,5 and 7 are averaged to give a single peak B of relative intensity 2 at τ 8.59. Methyls 2 and 6 average to a single peak C of intensity 1 at τ 9.13, and methyls 4 and 8 appear as a single peak A of intensity 1 at τ 8.55.

Upon cooling peaks B and C widen much more rapidly than A, and at -141° B begins to split into two peaks. At -151° peaks B and C are split into B_1, B_2 and C_1, C_2 respectively, intensity ratios B_1 : A : B_2 : C_1 : C_2 being about 2:2:2:1:1 as expected for a semibullvalene undergoing the Cope rearrangement slowly on the nmr time scale.

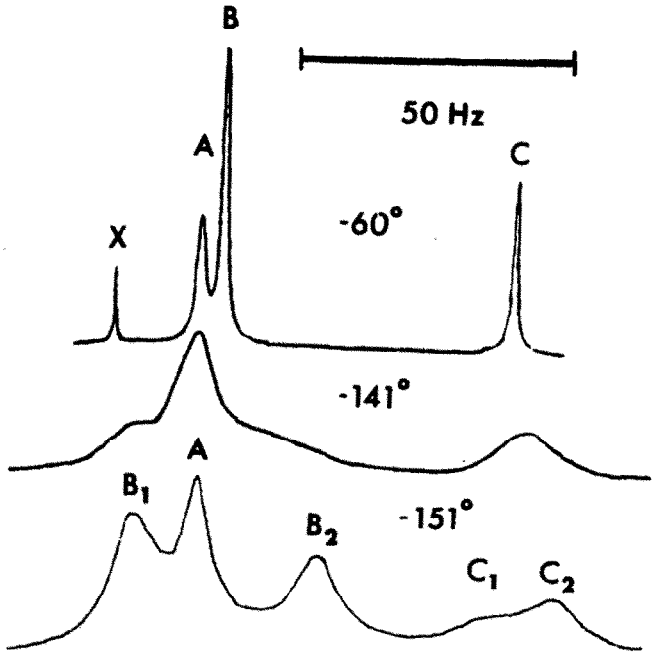


Figure I. 100 MHz nmr spectra of octamethylsemibullvalene at various temperatures. X = octamethylcyclooctatetraene impurity.

At -151° the lines are rather broad with B_1, B_2, C_1 and C_2 being wider than A, and A in turn wider than the TMS reference line (half-width 2 Hz at -151°). This is partly due to the non-averaging at low temperatures of long range couplings (about 1 Hz in similar systems), but mainly to chemical exchange still occurring at an appreciable rate at -151°. The dissymmetric appearance of C_1, C_2 is ascribed to different relaxation times T_2^o for the two methyl groups.

Peak B_1 ($\simeq \tau$ 8.42) is assigned to methyls 5 and 7 for its closeness to the chemical shift of octamethylcyclooctatetraene (τ 8.40). Peak B_2 (τ 8.75) therefore originates from methyls 1 and 3. On the basis of the shielding effect[6] of cyclopropyl groups on cyclopropyl methyls, C_2 (τ 9.18) is assigned to methyl 2 and C_1 correspondingly to methyl 6.

From the coalescence temperature and the chemical shift difference between B_1 and B_2 the free energy of activation for the Cope rearrangement in octamethylsemibullvalene is calculated to be

$$\Delta F^{\dagger} = 6.4 \pm 0.2 \text{ kcal/mole at } -141°.$$

Free energies of activation are now available for all types of homotropilidene systems undergoing rapidly reversible degenerate Cope rearrangements (Table 1).[7]

Table 1

Free Energy Barriers $\Delta F^{\dagger}$ in Homotropilidenes

Compound	$\Delta F^{\dagger}$[a], kcal/mole	Temp. °C	Ref.
1,3,5,7-tetramethylhomotropilidene[b]	13.6	0	3b
bullvalene	12.8	100	1e
dihydrobullvalene	9.5	-40	1d
barbaralone	9.6	-55	2a
barbaralane	7.8	-77	1f
octamethylsemibullvalene	6.4	-141	this work

[a] Calculated from rate constants given in references.

[b] Numbering as in semibullvalene.

The trend is somewhat obscured by the $\Delta F^{\dagger}$'s for the Cope rearrangements in bullvalene and barbaralone which certainly reflect not only the effect of strain but also electronic effects such as bicycloconjugation.[8,9] Shortening the bridge between the 2 and 6 positions narrows the energy gap between the symmetrical bishomobenzene-like transition state and the less symmetrical ground state, but not enough to make octamethylsemibullvalene a symmetrical bishomobenzene.[10]

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(5) Obtained by a modification of Criegee's procedure.[4b]

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(7) The free energies of activation are considered a good guideline for comparison though measured at different temperatures, since the entropies of activation are probably similar and close to zero in degenerate Cope rearrangements.[9,1e]

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(9) P. Ahlberg, J. B. Grutzner, D. L. Harris, S. Winstein, J. Amer. Chem. Soc., in press, have found a barrier of >13.8 kcal/mole in protonated barbaralone.

(10) Zimmerman and Grunewald[4a] have favored the classical structure on the basis of room temperature nmr and the similarity of uv spectra between semibullvalene and dihydrobullvalene.