

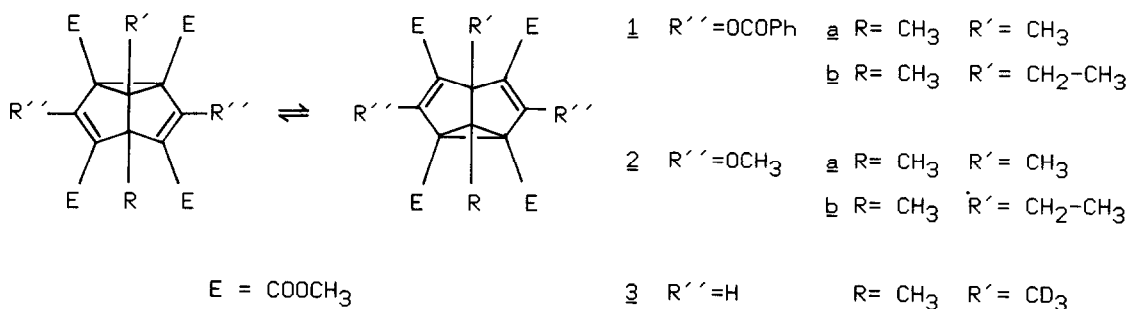
NON-ISOTOPIC PERTURBATION OF FAST EQUILIBRATING SYSTEMS.
 VALENCE TAUTOMERISM IN DONOR-ACCEPTOR-SUBSTITUTED SEMIBULLVALENES.

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Abstract: Substitution by different alkyl groups is used to perturb the rapid Cope rearrangement of donor-acceptor-substituted semibullvalenes.

Saunders' method of isotopic perturbation^{1,2} of degenerate valence tautomeric systems has proven to be a very powerful tool to analyze molecules and ions for which the energy barrier for the isomerization is very low. The acceptor substituted semibullvalenes **1** and **2** are candidates for very fast valence tautomerizations. Askani et al.³ used Saunders' method for **3** (R=CH₃, R'=CD₃). They found in the ¹³C NMR two signals for C-2/4/6/8 with a temperature dependent distance of 1.34 ppm at 29 °C. In order to synthesize **3** they had to develop a new synthetic route.



Our efforts to analyze semibullvalenes^{4,5} in which the degenerate Cope rearrangement may be so fast that the transition state becomes the ground state led us to the idea of perturbing the degenerate equilibrium not by using deuterium but by substituting with two different alkyl groups (cf. **1a/1b** or **2a/2b**).

The effect of slightly perturbing the symmetry of a molecule by groups which have not too severe effects on the internal structure of the molecule is the main feature of Saunders' method. If the perturbation is too strong we can only see one form in the NMR spectrum of the possibly fast equilibrating system. For 1 we hoped that a substitution with two different alkyl groups should give only small energy differences between the two valence isomeric forms.

Using Saunders' method the intrinsic effect of the perturbing group on the chemical shift has to be small^{1,2}. Judged from the increment tables given by Kalinowski⁶ it is expected for 1b and 2b that the intrinsic shift differences for the atoms C2/4/6/8 are small, too. The precursors 4 to 6 for the semibullvalenes 1 and 2 confirm this expectation as can be seen from the ¹³C NMR shift values in table 1⁵.

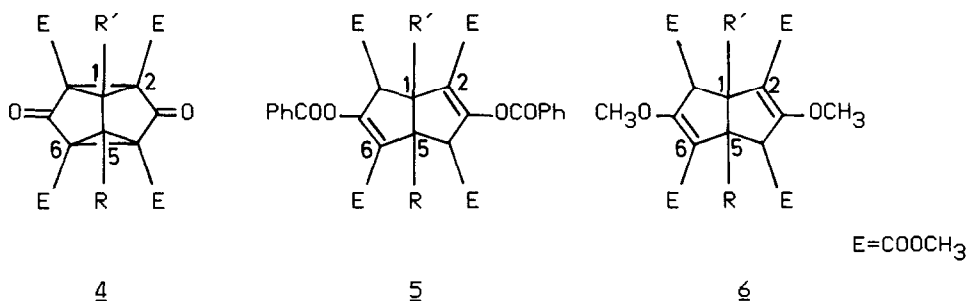


Table 1 ¹³C NMR data for 4 to 6 (ppm in CDCl₃ rel. to TMS).

The numbering corresponds to the semibullvalenes 1 and 2.

Comp.	R	R'	C1 or C5	C2 or C6	C2/C6 (averaged)
<u>4a</u>	CH ₃	CH ₃	48.00	49.83	49.83
<u>4b</u>	CH ₃	C ₂ H ₅	47.58 49.87	50.16 53.55	51.86
<u>5a</u>	CH ₃	CH ₃	55.79	125.31	125.31
<u>5b</u>	CH ₃	C ₂ H ₅	56.49 60.12	123.09 126.27	124.68
<u>6a</u>	CH ₃	CH ₃	55.37	113.09	113.09
<u>6b</u>	CH ₃	C ₂ H ₅	56.34 56.55	110.52 113.83	112.10

The synthesis of 1b and 2b followed exactly the lines which were used to get the semibullvalenes 1a and 2a ^{4,5}. The ¹³C NMR spectrum of 1b and 2b showed for the atoms involved in the Cope rearrangement (C-2/4/6/8) two signals whose shift difference increased as the temperature decreased (see table 2). The mean value of these two signals corresponds nicely to the value of the averaged signal found for the rapidly equilibrating Cope system in 1a ($\delta=94.38$ ppm) and 2a ($\delta=89.59$ ppm).

Table 2 ¹³C NMR data (ppm in CDCl₃ rel. to TMS)

Temp.(K)	Comp.	C2/C4/C6/C8 (averaged)	C2/C8	or	C4/C6	C4/C6-C2/C8
306	<u>1a</u>	94.38	-		-	-
306	<u>1b</u>	94.43	88.11		100.74	12.63
273	"	94.32	86.75		101.89	15.14
252	"	94.24	85.72		102.77	17.05
233	"	94.10	84.60		103.80	19.20
306	<u>2a</u>	89.59	-		-	-
306	<u>2b</u>	89.52	83.81		95.23	11.42
252	"	88.57	79.89		97.24	17.35
233	"	88.40	78.40		98.39	19.99

In order to use Saunders' formulae^{1,2} we have to know the chemical shift values for the frozen non-equilibrating semibullvalenes 1 and 2. Since it was not possible to get the ¹³C NMR spectra of 1 and 2 at lower temperatures than that of coalescence of the signals for C2/4/6/8 we chose as model compounds for non-rearranging semibullvalenes the precursors 4 to 6. The averaged ¹³C NMR shift values are given in table 1.

With these values we estimate using Saunders' symbols^{1,2} $\Delta=73\pm 3$ ppm for 1b and $\Delta=60\pm 3$ ppm for 2b. We get for the slightly perturbed equilibrium the following small energy differences corresponding to a double-minimum energy potential:

<u>1b</u> : $\Delta G = 0.21\pm 0.01$ kcal/mole at 306 K	<u>2b</u> : $\Delta G = 0.23\pm 0.01$ kcal/mole at 306 K
$\Delta H = 0.37\pm 0.04$ kcal/mole	$\Delta H = 0.60\pm 0.04$ kcal/mole
$\Delta S = 0.5 \pm 0.1$ e.u.	$\Delta S = 1.2 \pm 0.1$ e.u.

The energy differences ΔH for 1b and 2b are about 40-60 times greater than those for the deuterium perturbed semibullvalene 3³. But both experiments show clearly

the acceptor substituted semibullvalenes 1 and 2 to be fast equilibrating tautomeric systems with double-minima in the reaction energy profile.

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