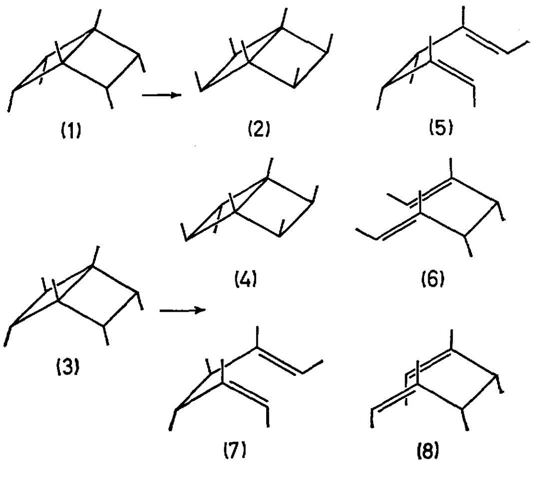
Inversion and Ring Opening of Hexamethylbicyclo[2,2,0]hexanes

By Anton Sinnema, Fred van Rantwijk,* Adrianus J. de Koning, Augustinus M. van Wijk, and Herman van Bekkum

(*Laboratory of Organic Chemistry, Delft Technological University, Julianalaan* 136, *Delft*-2208, *The Netherlands*)

Summary Hexamethylbicyclo[2,2,0]hexanes exhibit thermally induced skeletal inversion and stereospecific cleavage; the reaction mechanism is discussed.

In view of recent interest in bicyclo[2,2,0]hexane cleavage[1] and inversion,[1k,2] we report our latest results. Thermolysis of the all-*endo*-hexamethylbicyclo[2,2,0]hexane (**1**) at 137—177° provided the all-*exo*-isomer (**2**) (see Scheme). Similarly, thermal skeletal inversion of the 2-*exo*-isomer (**3**) at 196—216° gave the invertomer (**4**). Thermolysis of (**1**) also produced *erythro*-3,4,5,6-tetramethylocta-2*Z*,6*E*-diene (**5**), whereas with (**3**) ring opening predominated: *erythro*-3,4,5,6-tetramethylocta-2*E*,6*E*-diene (**6**) and *threo*-3,4,5,6-tetramethylocta-2*Z*,6*E*-diene (**7**) were formed, together with a minor amount of the *erythro*-2*Z*,6*Z*-isomer (**8**). Thermolysis of (**2**) and (**4**) required higher temperatures and provided only ring-opening products. Further data are given in the Table.



Scheme

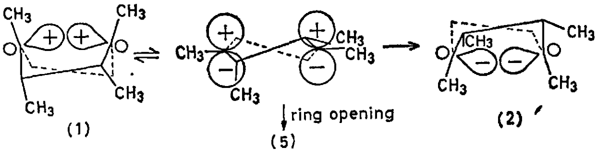
TABLE. *Inversion and ring opening of hexamethylbicyclo*[2,2,0]-*hexanes*[a]

	Temp. (t/°C)	$t_{\frac{1}{2}}$/h	Products (%)					
			(2)	(4)	(5)	(6)	(7)	(8)
(**1**)	153	3·5	73		27			
(**2**)	231	3·6			95	5		
(**3**)	200	2·0		22		46	26	6
(**4**)	231	1·4				50	36	14

[a] Reactions in sealed glass, n-heptane solution or neat.

First-order kinetics for conversion of (**1**) and (**3**) were observed. The activation parameters [(**1**): $\Delta H^{\ddagger}$ 140 ± 7 kJ mol^{-1}, $\Delta S^{\ddagger}$ + 1 ± 15 J mol^{-1} K^{-1}; (**3**): $\Delta H^{\ddagger}$ 137 ± 6 kJ mol^{-1}, $\Delta S^{\ddagger}$ − 33 ± 10 J mol^{-1} K^{-1}†], the inversion phenomenon, and the stereospecificity of the ring opening reaction exclude, in our opinion, the intermediate formation of a strainless biradical.‡

To account for the results, two processes have been considered that satisfy the Woodward–Hoffmann selection rules: a synchronous ${}_{\sigma}2_{\text{s}} + {}_{\sigma}2_{\text{a}}$ process, involving the C(1)–C(4) and C(2)–C(3) bonds, and a two-step process, *i.e.* conversion of the C(1)–C(4) σ-bond into a π-bond followed by conrotatory opening of the C(2)–C(3) bond.



FIGURE

The former process requires severe twisting of the bicyclic system and has therefore been rejected.[1e,g]§ The latter offers an elegant way to combine both inversion and ring opening mechanisms. The C(1)–C(4) π-bonded intermediate (see Figure) is common to both.

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† Calories = Joules × 0·239.

‡ A higher activation energy and a positive activation entropy are expected for a radical reaction; *cf. cis-* and *trans*-1,2-dimethyl cyclobutane:[3] E_{a} 254, 259 kJ mol^{-1}; $\Delta S^{\ddagger}$ + 39·7, +39·7 J mol^{-1} K^{-1}, respectively.

§ Considering the possibility of puckering[4] of the bicyclic system the synchronous process cannot *a priori* be discounted.

Added in proof: Puckering of bicyclo[2,2,0]hexane has recently been reported (B. Anderson and R. Srinivasan, *Acta. Chem. Scand.* 1972, **26**, 3468).

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