Thermal Reorganisations of Some Cyclopropylidene-cycloalkanes. The Unique Character of the Biscycloproplidene–Methylenespiropentane System

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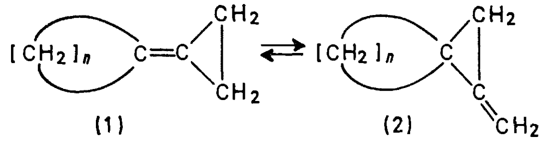
Summary A kinetic and thermodynamic investigation of the thermal reorganization of cyclopropylidene-cycloalkanes to methylenespiro[2,*n*]alkanes is presented: the exceptional behaviour of the biscyclopropylidene–methylenespiropentane system is discussed.

IT has been observed that biscyclopropylidene systems are substantially thermodynamically less stable than the isomeric methylenespiropentane systems.[1-3] No biscyclopropylidene has been able to be detected in thermal equilibrium with either the parent methylenespiropentane[1] or the tetramethyl[2] or hexamethylmethylene spiropentanes.[3]

Was this disparity of stabilities to be expected as indicated by the thermal behaviour of homologous cyclopropylidene cycloalkanes, or is it due to some unique properties of these molecules? We report kinetic and thermodynamic data which indicate that the latter explanation is correct.



(1) (2)

Since the rate-determining step in each rearrangement of (**1**) to (**2**) should be similar with the formation of some type of trimethylenemethane diradical,[2] the activation energies would be expected to be similar as long as there is no variable inherent strain in the cyclopropylidene-cycloalkanes, *i.e.* strain which cannot be approximated by

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summing the component strains (spiropentane contains a strain energy of 63·1 kcal mol^{-1}:[4] two cyclopropanes would have a total[5] of 2 × 27·2 or 54·4 cal mol^{-1} which means that spiropentane has an additional, inherent strain of 8·7 kcal mol^{-1}).

As can be seen from the Table, the E_a's do vary, with apparent inherent strain increasing as n decreases. The biscyclopropylidene system is not especially remarkable in this sense, although it is the most reactive. The methyl groups on the biscyclopropylidene system would certainly contribute substantially to the lower E_a for this system.

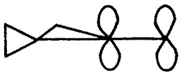
Activation and equilibrium parameters for **(1)** $\underset{k'}{\overset{k}{\rightleftharpoons}}$ **(2)**

n[a]	E_a	log A	$\Delta H^{\ddagger}$(220°)	$\Delta S^{\ddagger}$(220°)	K_{eqm}(220°)
5	45·6 ± 2	15·86	44·6 ± 2	11·0 ± 4	1·15
4	41·4 ± 2	14·92	40·5 ± 2	6·8 ± 4	0·312
3	39·7 ± 2	14·25	38·7 ± 2	3·7 ± 4	0·823
2[b]	38·9 ± 2	14·81[c]	38·0 ± 2[c]	6·4 ± 4[c]	>100

[a] M. Bertrand, *Bull. Soc. chim. France*, 1968, 3044.
[b] *cis*-2,2,2′,2′-Tetramethylbiscyclopropylidene
[c] At 190°.

The most remarkable aspect of this study is the variation of the equilibrium constants. From these data it is seen that there is no trend that can be used to rationalize the disparate stabilities of biscyclopropylidene and methylenespiropentane.

It seems from the data that this contrast in thermodynamic stabilities cannot be wholly attributed to an unusual inherent strain in the biscyclopropylidene and that to some extent an extra stabilization in the methylenespiropentane exists. Such a stabilization could arise from the overlap of the two C–C σ-bonds of the saturated cyclopropane ring, which are perfectly aligned geometrically for such overlap, with the π-bond of the methylenespiropentane (see Figure). Staley has attributed a stabilization of 1·09 kcal mol^{-1} to conjugation of a cyclopropane ring with a double bond.[6] It is conceivable that the more highly strained spiropentane system will be even more greatly stabilized.



FIGURE

While our estimates of strain energy and heats of formation of the various cyclopropylidene cycloalkanes and methylenespiro[2,n]alkanes tend to support the above hypothesis, such estimates are only approximate. Heats of combustion are needed for each component before a definitive answer can be found.

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[1] W. R. Dolbier, jun., *Tetrahedron Letters*, 1968, 393.
[2] W. R. Dolbier, jun., K. Akiba, M. Bertrand, A. Bézaguet, and M. Santelli, preceding Communication.
[3] J. K. Crandall, D. R. Paulson, and C. A. Bunnell, *Tetrahedron Letters*, 1969, 4217.
[4] F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stand.*, 1955, **54**, 143.
[5] J. W. Knowttan and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 113.
[6] S. W. Staley, *J. Amer. Chem. Soc.*, 1967, **89**, 1532.