The Biscyclopropylidene–Methylenespiropentane Interconversion. A Non-planar Trimethylenemethane Intermediate

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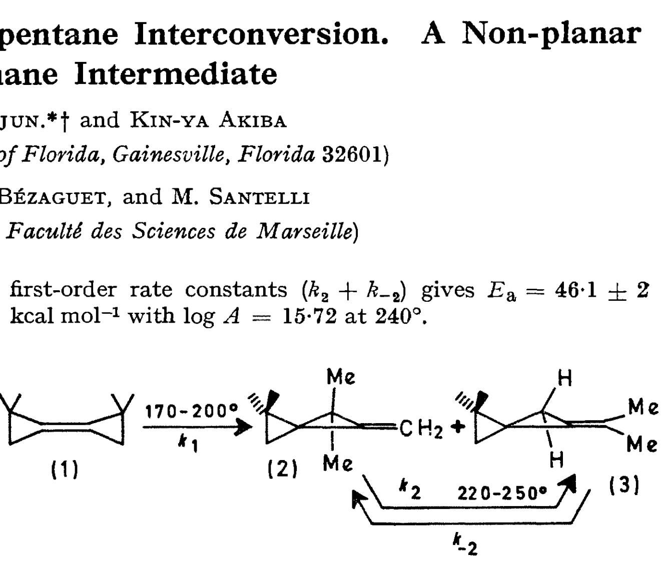
Summary The thermal reorganization of *cis*- and *trans*-2,2,2′,2′-tetramethylbiscyclopropylidene to a mixture of 2,2,4,4-tetramethylmethylenespiropentane and 4,4-dimethylisopropylidenespiropentane is best rationalized in terms of a non-planar trimethylenemethane intermediate.

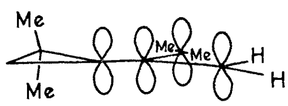
THE trimethylenemethane diradical, commonly invoked as an intermediate in methylenecyclopropane rearrangements, is the centre of much controversy. While theoretical and experimental work has indicated the parent species with a planar geometry to be most stable,[1] evidence has recently been obtained by Gajewski[2] and Gilbert and Butler[3] which precludes the existence of such planar intermediates in the rearrangements of *trans*-2,3-dimethylmethylenecyclo-propane and 2,2-diphenylmethylenecyclopropane, respectively. We report further evidence that planar intermediates should not be generally invoked in thermal rearrangements of methylenecyclopropane systems.

When *cis*-2,2,2′,2′-tetramethylbiscyclopropylidene (**1**)[4] is heated to 170—200° in the gas phase, a clean unimolecular rearrangement to a 3·4 ± 0·1 : 1 mixture of 2,2,4,4-tetramethylmethylenespiropentane (**2**) and 4,4-dimethylisopropylidenespiropentane (**3**) occurs. An Arrhenius plot gives $E_a = 38{\cdot}9 \pm 2$ kcal mol^{-1} and log $A = 14{\cdot}81$ at 190°, from which values of $\Delta H^\ddagger = 38{\cdot}0 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = 6{\cdot}4 \pm 4$ cal degree^{-1} can be calculated. No detectable biscyclopropylidene (**1**) is present in equilibrium with products (**2**) and (**3**). When heated to 220—250°, the product mixture undergoes a first-order equilibration in which (**3**) proves thermodynamically more stable with the ratio of (**3**) : (**2**) = 3·0 ± 0·1 : 1. An Arrhenius plot of the two first-order rate constants ($k_2 + k_{-2}$) gives $E_a = 46{\cdot}1 \pm 2$ kcal mol^{-1} with log $A = 15{\cdot}72$ at 240°.



At even higher temperatures (>300°) further rearrangements occur which appear similar to those reported by Crandall for the similar hexamethyl system.[5]

That a planar diradical such as (**4**) cannot be involved in the reaction is indicated by the clear kinetic preference for the less stable methylenespiropentane product (**2**). It has been shown, for instance, that the primary site of the 1-methylallyl radical is twice as reactive as the secondary site in trapping methyl radicals.[6] In coupling processes believed to proceed *via* substituted allyl radicals, the less substituted site was always the most reactive.[7] Thus, if such a diradical as (**4**) were to exist, the primary site would be expected to be substantially more reactive than



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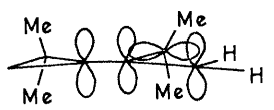

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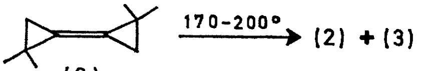
the tertiary site in the ring-closure step. Since this is clearly not observed, the status of (**4**) as the intermediate formed upon initial bond-cleavage is in serious doubt.

As in Gajewski's case, however, the results can be explained satisfactorily by invoking a diradical species such as (**5**) as the initially formed intermediate. This species, with the *p*-orbital of the tertiary radical orthogonal to the planar allyl radical would be formed by a 90° rotation of only the methylene group upon bond cleavage. (Models indicate that total planarity would cause serious van der Waals interactions with the isopropylidene group.) This diradical would be expected to lead directly to the methylenespiropentane product (**2**) upon a 90° rotation of the cyclopropyl radical, while product (**3**) could be obtained only by higher energy processes, *i.e.*, (i) *via* the planar diradical (**4**), (ii) with a more complicated series of rotations of (**5**), or (iii) *via* the diradical with the isopropylidene group planar and the methylene group orthogonal.



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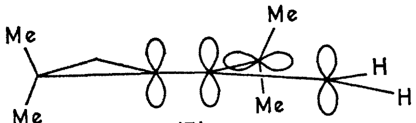

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trans-2,2,2′,2′-Tetramethylbiscyclopropylidene (**6**)[4] undergoes a similar rearrangement, with almost identical activation parameters, resulting, however, in a significantly different ratio of products [*i.e.* (**2**) : (**3**) *ca.* 13 : 1]. This difference can be satisfactorily rationalized by the fact that the transition state for ring closure to product (**2**) from intermediate (**7**), would have substantially less van der Waals repulsion between the four methyl groups than that from intermediate (**5**).

In Crandall's study,[5] no product analogous to (**2**) was observed. Possibly in his system the steric repulsion of the tetramethylcyclopropyl group made this ring closure occur at a prohibitively slow rate.

While the exact source of the thermodynamically-preferred product (**3**) cannot be definitively ascertained from these experiments, it seems clear that a planar diradical intermediate such as (**4**) cannot satisfactorily explain the experimental results. It may be that planar trimethylenemethanes should not be generally invoked, except in the case of the parent system. It is probable that van der Waals repulsions are substantial enough to overcome the slight preference of the totally planar species in most other systems. Our data cannot entirely rule out a completely fluid transformation of (**1**) to (**2**) and (**3**) without passing through any actual intermediate.

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