Rearrangements of Bicyclic Cyclopropylcarbenes. Stereochemistry of the Fragmentation Reaction

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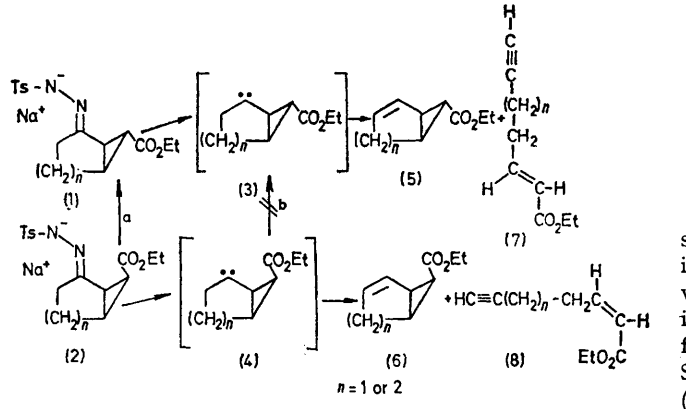
Summary The stereospecific fragmentation of a series of four cyclopropylcarbenes argues for a concerted cleavage of the two cyclopropyl bonds.

The stereochemistry of the fragmentation of cyclopropylcarbene to acetylene and ethylene has been a matter of some dispute in the recent literature.[1–4]

We report here the first stereochemical study of the fragmentation of a series of bicyclic cyclopropylcarbenes [(**3**) and (**4**)] (Scheme) and discuss the mechanistic implications.

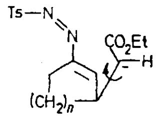


Scheme

The carbenes were generated by thermolysis of the appropriate dry tosylhydrazone sodium salts (**1**) and (**2**) in diglyme, triglyme, or tetraglyme. Products, all of which are stable under the reaction conditions and do not interconvert, were identified from spectral data and by comparison with independently synthesized samples. Product ratios were determined (± 1%) by g.l.p.c. after ether–water workup and were found to vary somewhat with thermolysis temperature.

The *exo* salts (**1**) gave only two products, (**5**) (hydrogen migration) and (**7**) (fragmentation).[5] Ratios [(**5**)/(**7**)] for $n = 1$ range from 85/15 at 200°C to 91/9 at 90°C and for $n = 2$ from 55/45 at 200°C to 69/31 at 90°C.

Thermolysis of the *endo*-salts (**2**) at 150—225°, however, gave a mixture of all four products, (**5**)—(**8**). From (**2**; $n = 1$), the ratio [(**5**) + (**7**)]/[(**6**) + (**8**)] ranged from *ca.* 28/59 at 200°C to 35/52 at 150°C.† From (**2**; $n = 2$), this ratio was *ca.* 74/26 at 225°C and 91/9 at 150°C. Thus, at first glance it would appear that the *endo*-carbenes (**4**) isomerize to the corresponding *exo*-carbenes (**3**) (path b) at rates competitive with hydrogen migration [→ (**6**)] and fragmentation [→ (**8**)].



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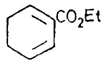

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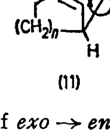
Further experiments suggest that the stereochemical scrambling occurs at an earlier stage. Aqueous quench of incomplete thermolyses of (**2**), followed by ether–water workup, yields a *mixture* of *exo* and *endo* tosylhydrazones in both [3,1,0] and [4,1,0] cases. [Aqueous quench of (**2**) before heating gives only unisomerized *endo*-tosylhydrazone.]‡ So formation of "*exo*-products" (**5**) and (**7**) from *endo* salt (**2**) can be attributed to *endo* → *exo* isomerization at the tosylhydrazone salt stage, (path a) probably *via* an intermediate such as (**9**), and path b is not required.§



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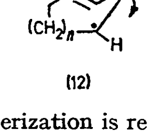

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The lack of *exo* → *endo* isomerization is reasonable, since the thermodynamic mixture of (**5**) and (**6**) ($n = 1$) at 260° is apparently at least 95% *exo*.[6]

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† A fifth product (*ca.* 13%), unique to the *endo*-[3,1,0] thermolyses, was identified by spectra and independent synthesis as (**10**). Experiments to distinguish between the interesting alternative mechanisms for its formation are in progress.

‡ The *endo*-tosylhydrazone itself ($n = 1$) is stable at 150° in triglyme.

§ The possibility that (**5**) [(**6**)] is formed from (**3**)[(**4**)], while (**7**)[(**8**)] is formed from the appropriate rotamer of (**9**) cannot be strictly ruled out. However, we consider it unlikely in view of the similar ease of fragmentation when -CO$_2$Et is replaced by -H.[5]

The **(5)**/**(7)** ratio is observed to be the same from the *endo*- as from the *exo*-tosylhydrazone salt at a given temperature (200°, 170°, 150°). This provides strong evidence that the immediate precursor to **(5)** and **(7)** [presumably **(3)**] is the same in the thermolysis of **(2)** as in the thermolysis of **(1)**.

We have reported previously[5] that the fragmentation of **(3)** [from **(1)**] is completely stereospecific [*i.e.*, **(3)** $-/-/\rightarrow$ **(8)**]. We suggest here that the fragmentation of **(4)** is also stereospecific [**(4)** $-/-/\rightarrow$ **(7)**], since any **(7)** contributed by **(4)** to the product mixture from *endo*-salt thermolysis would reduce the **(5)**/**(7)** ratio (relative to that from *exo*-salt thermolysis).

Faced with these four examples of stereospecific cyclopropylcarbene fragmentations, we conclude that the reaction is concerted,[7] at least in these bicyclic systems where geometric constraints favour a singlet ground state.[8] The alternative is a two-step process, where cleavage of the second bond in the intermediate 1,4-diradical [**(11)** or **(12)**] would have to be at least 50 times faster than the torsional motions indicated. Although slow rotations in 1,4-diradicals are currently of considerable theoretical interest, the few experimental examples are at lower temperatures and do not involve rotations to significantly more stable conformations.[9]

Stereochemical scrambling in the fragmentation of the unconstrained 2,3-dimethylcyclopropylcarbene has been attributed to a triplet ground state[2] or excess vibrational energy,[3] but recent work[4] suggests that it too fragments in a concerted reaction from singlet ground state.

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