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EVIDENCE FOR A CARBENE INTERMEDIATE IN THE THERMAL REARRANGEMENT OF A CYCLOPROPENE

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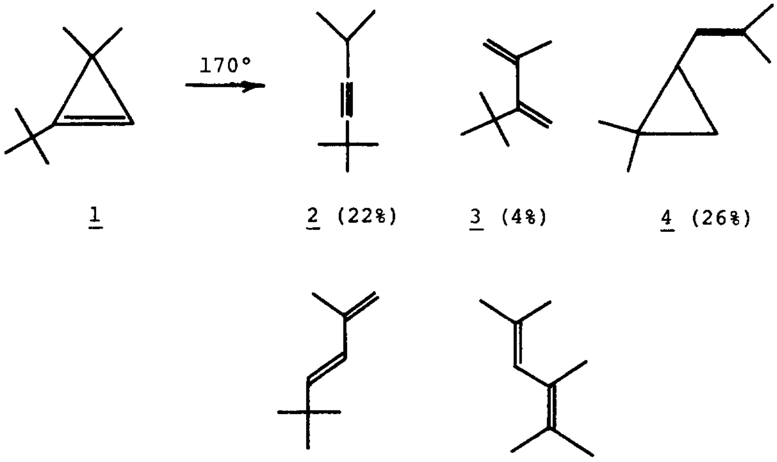
The thermal isomerization of variously substituted cyclopropenes has been studied kinetically and for product formation.[1-5] Products most often observed are alkynes and dienes which may be accounted for simplistically by ring-opening to a "diradical" (vinyl carbene) followed by intramolecular hydrogen abstraction Interestingly, none of the products reported point explicitly to a vinyl carbene intermediate. We describe here the first example of a cyclopropene thermolysis which clearly involves a carbene intermediate.

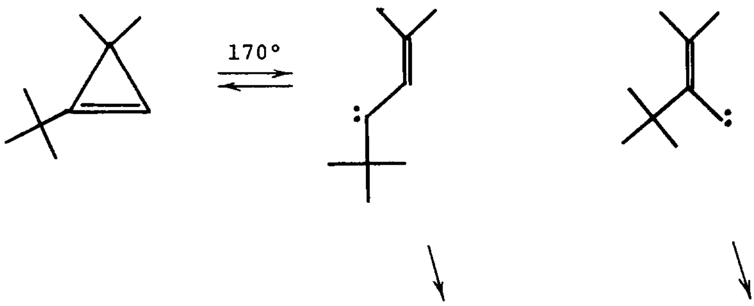
The thermal rearrangement of 1-t-butyl-3,3-dimethylcyclopropene (1) in benzene solution, with added $CaCO_3$ to ensure an acid-free system, followed first-order kinetics and gave 2-6 in yields shown.[6] Data on formation rates of individual products were not sufficiently good to permit the calculation of reliable parameters but they were good enough to confirm that all products are formed independently and are therefore primary. The disappearance of 1 gave a good first-order plot from which the activation energy was calculated to be 29.8 ± 1.1 Kcal mole $^{-1}$ and $\Delta S^{\ddagger}$ -17.8 e.u. Reactions were run at five temperatures between 150° and 195°. This E_a value is substantially lower than those reported for gas phase isomerization of cyclopropenes having varying degrees of methyl substitution.[1]



1 2 (22%) 3 (4%) 4 (26%)

5 (13%) 6 (35%)

These data are for the most part consistent with a sequence involving ring-opening to the two isomeric vinyl carbenes followed by intramolecular hydrogen abstraction to give 2,3, and 5, or by insertion at a methyl of the *t*-butyl group to give 4 or, finally, by methyl migration to produce 6.[7] Other mechanisms can be invoked to rationalize the formation of 2,3, and 5 but all are objectionable for various reasons. The production of 4 and 6, on the other hand, is rather good evidence for a carbene intermediate.[7-9] The question of whether or not some of the initially formed singlet carbene undergoes spin inversion to the lower energy triplet state[10] before reacting cannot be answered with certainty. Available data suggest that insertion can occur in either state and that hydrogen abstraction is more likely a triplet state process.



2,4,5,6 3

It should be noted that the initial step as written is simply the reverse of the well known formation of cyclopropenes from vinyl carbene precursors.

The rather large negative $\Delta S^{\ddagger}$ found here and for several other cyclopropenes[11] is inconsistent with the simple ring-opening shown. It is suggestive of either a bond cleavage which is concerted with migration or the formation of a more highly structured intermediate which rapidly rearranges to the two isomeric vinyl carbenes. Evidence for the latter is presently being sought.

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