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CYCLOBUTANE FORMATION IN THE $2\pi + 2\pi$ CYCLOADDITION OF ALLYL AND RELATED CATIONS TO UNACTIVATED OLEFINS. EVIDENCE FOR THE SECOND STEP IN THE PROPOSED MECHANISM OF THE IONIC DIELS-ALDER REACTION.

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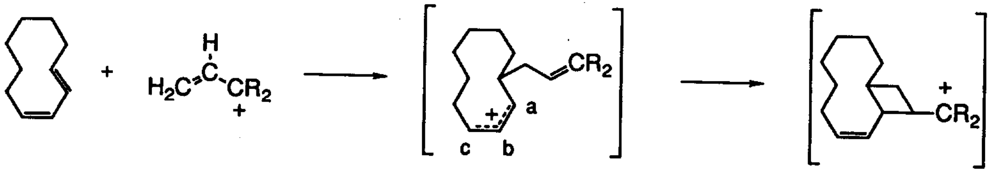
Abstract: A variety of carbocation activated olefins have been shown to add to unactivated olefins in a $2\pi + 2\pi$ cycloaddition to yield cyclobutanes.

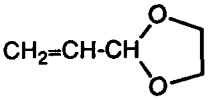
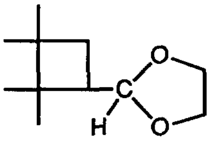
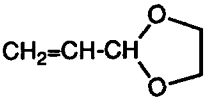
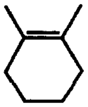
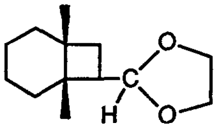
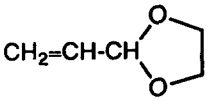
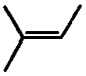
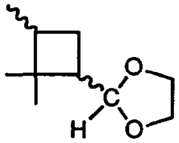
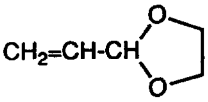
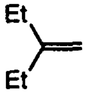
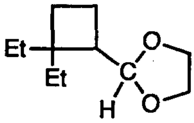
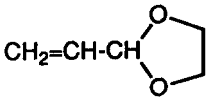
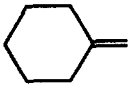
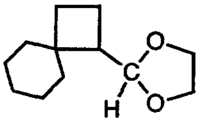
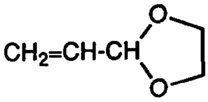
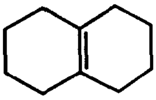
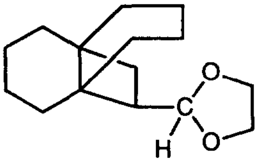
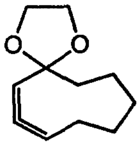
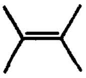
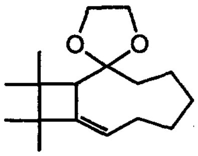
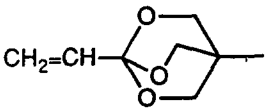
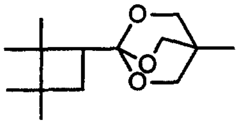
The $2\pi + 4\pi$ cycloaddition of allyl cations to 1,3-dienes in a formal Diels-Alder reaction has been shown to be a synthetically useful reaction.[1] However, in the case of strained (1Z,3E)-cyclodienes, allyl cation addition gave $2\pi + 2\pi$ cycloadducts, instead of $2\pi + 4\pi$ cycloadducts.[2-5] This cyclobutane formation would appear to have occurred through the stepwise addition of 1 to 2 to produce 3, followed by ring closure of 3 to give 4. The second step of this process, which involved the intramolecular addition of position C_a of the allyl cation 3 to an isolated olefin, differed from the proposed stepwise mechanism for the $2\pi + 4\pi$ cycloaddition[6] only in that cyclization occurred at C_a rather than at C_c. This suggested to us that allyl cations might be added to isolated olefins in an intramolecular stepwise process, which would provide strong evidence for the proposed second cyclization step of the ionic Diels-Alder reaction. We now wish to report that stepwise $2\pi + 2\pi$ cycloaddition of allyl cations to isolated olefins occurs.



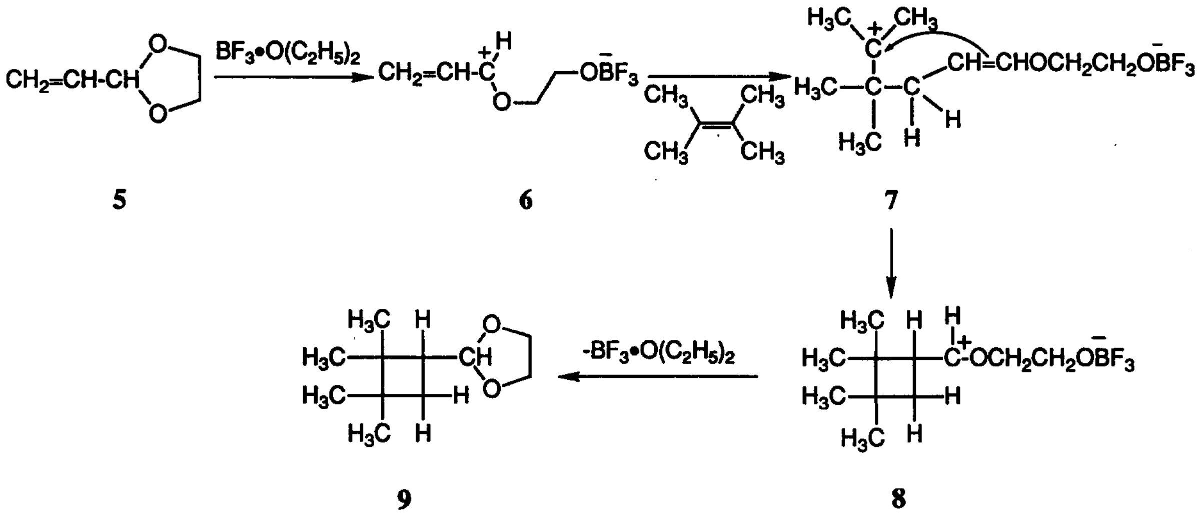
2 1 3 4

As shown in Table 1, a variety of oxo-stabilized allyl cations can be added to di-, tri-, and tetrasubstituted olefins to generate cyclobutanes. Examples 1-6 utilized the ethylene glycol acetal of acrolein (5)

Table 1. 2π + 2π Intermolecular Cycloadditions of Allyl Cations to Olefins Catalyzed by Boron Trifluoride Etherate in Methylene Chloride

Example	Allyl Cation Precursor	Olefin	Conditions	Products	% Yield Isolated
1			25 mol % cat. -60 to -40 °C 2 h		71
2			25 mol % cat. -78 to -10 °C 2 h		70
3			10 mol % cat. -78 to 0 °C 3.5 h		47
4			5 mol % cat. -78 to -10 °C 2.5 h		22
5			5 mol % cat. 0 to 25 °C 1.5 h, 2.5 h at 25 °C		20
6			20 mol % cat. -78 to -10 °C 2.5 h		40
7			50 mol % cat. -78 to -30 °C 2.5 h		52
8			50 mol % cat. -78 to 25 °C 1.5 h, 3 h at 25 °C		20

as the allyl cation precursor. Treatment of **5** with boron trifluoride etherate should yield **6**, which we believe would be a powerful electrophile. As illustrated, olefins such as 2,3-dimethyl-2-butene should be attacked



by **6** to yield tertiary carbocations such as **7**. Cyclization of **7** would be expected to produce **8**, which on reformation of the acetal moiety would give **9**.[7] The tetrasubstituted olefins used in examples 1 and 2 gave yields of cyclobutanes which are synthetically useful. The trisubstituted olefin used in example 3 gave a lower yield, while the disubstituted olefins used in examples 4 and 5 gave relatively low yields. Although the olefin used in example 6 was tetrasubstituted, the yield of 2π + 2π adduct was considerably less than those observed for examples 1 and 2. Examples 7 and 8 illustrate the use of other allyl cation precursors for cyclobutane formation.

In summary, allyl cations add intermolecularly to olefins which are electron rich and which will yield tertiary carbocations. This can only occur through a stepwise process. These results add support to the mechanism proposed for the formation of the second carbon-carbon bond in the stepwise 2π + 4π cycloaddition of allyl cations to 1,3-dienes in a formal Diels-Alder reaction.

Acknowledgement. We are indebted to the National Institute of General Medical Sciences of the National Institutes of Health for a grant which supported this investigation.

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7. Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds. All compounds gave spectral data consistent with the assigned structures.

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