

## Optically Active (2 + 2) Cycloadducts from *R*-(-)-1,3-Dimethylallene and Acrylonitrile

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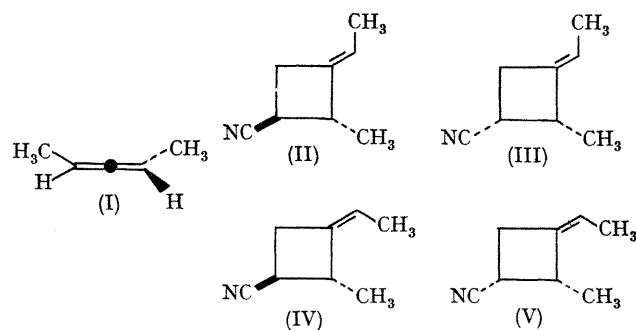
**Summary** The four isomeric ethylidene-cyclobutanes from *R*-(-)-1,3-dimethylallene and acrylonitrile are all optically active, a result excluding non-dissymmetric reactive intermediates in the cycloadditions.

assuming the olefin takes the least hindered approach toward the allene, and the methylene group of the allene which rotates to overlap with the adjacent double bond does

CYCLOADDITIONS of 1,1-dimethylallene with dimethyl maleate and fumarate are highly stereoselective with respect to the olefinic component.<sup>1</sup> We have found a complementary stereoselectivity in the cycloadditions of *R*-(-)-1,3-dimethylallene<sup>2-4</sup> (I) with acrylonitrile: four isomers (II, III, IV, V) are formed in approximately equal proportions, and each shows a negative plain optical rotatory dispersion curve to 220 nm in methanol.

Ozonization of the adducts (II, III, IV, V) gave *trans*- and *cis*-2-methyl-3-cyanocyclobutanone having a negative circular dichroism maximum at 302 nm,<sup>5</sup> confirming the assignments of absolute stereochemistry, *R* at C(2) of the 1-ethylidene-cyclobutanes.

These results require that the intermediate<sup>6</sup> in allene-olefin cycloadditions be dissymmetric; "diracids" such as (VI), for instance, having a symmetry plane cutting every carbon atom and bisecting the H-C(4)-H angle, are inadequate formulations. A new model for the intermediate in allene-olefin (2 + 2) cycloadditions may be developed by

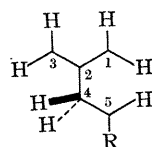


so only in the sense specified by orbital symmetry requirements.<sup>7</sup> The two intermediates so generated (VII, VIII), having C(1), C(3), their substituents, C(2), and C(4) in one plane; C(2), C(4), and C(5) in a perpendicular plane; and C(4), C(5), X, and Y in a third plane, could each give two products through formation of a bond between C(1) or C(3)

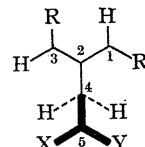
and C(5). The formation of (II, III, IV, V) all in the same and experimentally observed stereochemical family follows at once.

The intermediate (IX) is quite unlike the species appropriate to the halfway point in a concerted 1,3-sigmatropic shift mechanism<sup>8</sup> for the methylenecyclobutane rearrangement;<sup>9</sup> calculations<sup>10</sup> using extended Hückel and CNDO-II methods suggest it is considerably lower in energy than the planar diradical (X).<sup>9</sup>

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(VI) R=CN  
(X) R=H



(VII) X=H, Y=CN, R=CH<sub>3</sub>  
(VIII) X=CN, Y=H, R=CH<sub>3</sub>.  
(IX) X=H, Y=H, R=H

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