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THE STEREOCHEMISTRY OF THE CYCLOPROPANE-ALLENE CONVERSION

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The recent finding[1] that (-)-trans-2,3-diphenylcyclopropanecarboxylic acid (I) can be converted (most likely *via* a combination of concerted collapse of the diazocyclopropane II and rearrangement of the cyclopropylidene III) to (+)-1,3-diphenylallene (IV) (Figure 1) suggested an attractive possible method for relating the absolute configurations of optically active allenes[2,3] to optically active cyclopropanes.

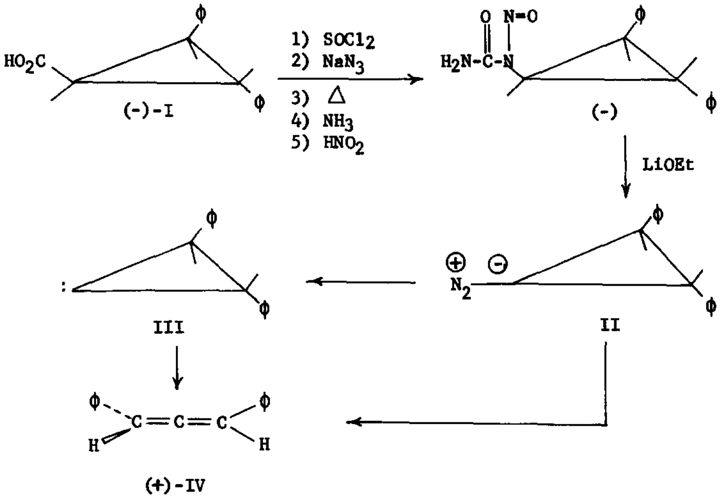


Figure 1

This method depended on a consideration of the various steric interactions[31] that would be expected to accompany ring opening. To review the arguments, the concerted decomposition of only the diazocyclopropane will be discussed. However, it should be kept in mind that the same arguments also hold for opening the cyclopropylidene (III) ring except that the leaving nitrogen would be replaced by a pair of electrons.

As the ring opens (Figure 2), a total of 90° of rotation must occur around bonds (a) and (b) as demanded by the geometry of the allenic product. Furthermore, the observed optical activity of the allene requires this rotation to proceed to at least some extent prior to the ultimate colinearity of the three cyclopropane carbons. For the sake of simplicity, assume that the groups on carbon 3 are held in place and let the

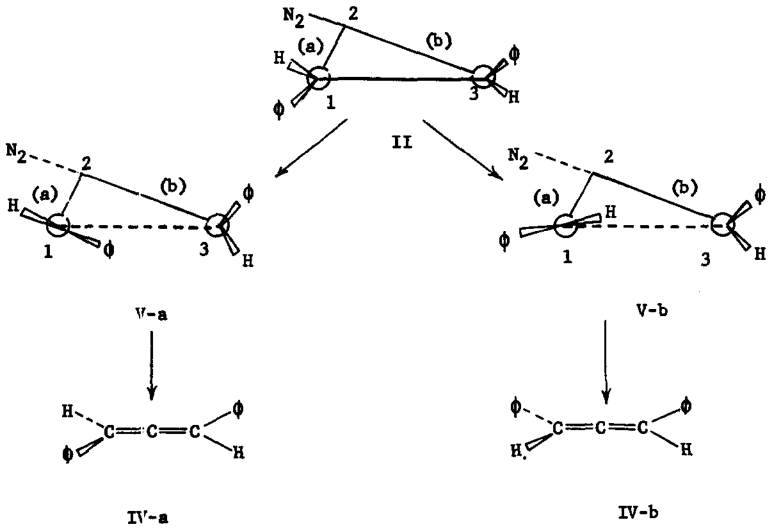
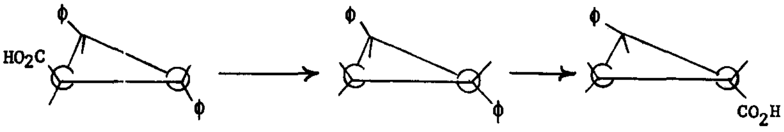


Figure 2

entire rotation occur around bond (a). It can be seen that counterclockwise rotation of the substituents on carbon 1 leads to the intermediate V-a in which the phenyl on carbon 1 experiences interactions with the phenyl and hydrogen on carbon 3 while the hydrogen on carbon 1 is opposed to the leaving nitrogen on carbon 2. The net result is formation of enantiomer IVa. Alternatively, if the substituents on carbon 1 are rotated in a clockwise manner around bond (a) to give intermediate V-b, the hydrogen on carbon 1 experiences interactions with the phenyl and hydrogen on carbon 3 and the phenyl is opposed to the leaving nitrogen and the net result is formation of the other enantiomer (IV-b). Clearly, then, if steric interactions with the leaving nitrogen are less important than with the phenyl and hydrogen on carbon 3, the clockwise rotation will be preferred and enantiomeric allene IV-b will be the predominant product. And, of course, the other enantiomer would obtain if the converse were true.

The purpose of this communication is to report our finding that the former of these two possibilities actually obtains. This conclusion is based on Mason's recent assignment of structure IV-b as the absolute configuration of (+)-1,3-diphenylallene by circular dichroism studies[4] and our chemical determination of the absolute configuration of (-)-*trans*-2,3-diphenylcyclopropanecarboxylic acid (I) which allows us to assign structure II in the absolute sense as the allene precursor. The correlation scheme used for assigning the absolute configuration to the cyclopropanecarboxylic acid (I) is depicted in Figure 3.



(-)-I (-)-VI (-)-VII

Figure 3

(-)-trans-2,3-Diphenylcyclopropanecarboxylic acid (I) (2.1 g., $[a]_D^{19}$ -10.9°, c = 2.86, absolute ethanol) was refluxed with 10 ml. of reagent grade quinoline and 0.2 g. of copper chromite catalyst under argon for six hours. The reaction mixture was taken up in ether, filtered, extracted with dilute hydrochloric acid, followed by extraction with 2N sodium hydroxide and finally washed with water. Removal of the solvent afforded 0.7 g. (43%) of (-)-trans-1,2-diphenylcyclopropane (VI), $[a]_D^{20}$ -30.9° (c = 1.0, absolute ethanol).[5] (-)-VI was degraded by ozonolysis for 2.5 hours at room temperature in 80 ml. of glacial acetic acid (gas flow = 0.35 cfm, Welsbach ozone generator). Oxidative workup of the reaction mixture with hydrogen peroxide[6] gave an oil which was dissolved in water. Extraction of the aqueous solution with 30-60° petroleum ether gave 0.1 g. of a white solid, m.p. 72-78°. One recrystallization from hot water gave (-)-VII, m.p. 87.5-90.0°, $[a]_D^{20}$ -5.7° (c = 1.9, absolute ethanol),[7,8] the absolute configuration of which has been shown to be 1R:2R.[6]

These results, then, support our initial suggestion regarding the dominant steric effects in this conversion and also support our suggestion that this may be a general method for assigning absolute configurations to allenes from the known configurations of cyclopropanes.

As a more rigorous test of these conclusions, we are presently working on an unequivocal correlation of a cyclopropane with an allene which is based entirely on chemical conversions.

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REFERENCES

1. W. M. Jones, J. W. Wilson, Jr., and F. B. Tutweiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963).

2. For allene configurational assignment based on mechanistic assumptions see E. Eliel, *Stereochemistry of Carbon Compounds*, Chapter II, McGraw-Hill Book Co., Inc., New York, N. Y. (1962).

3. W. C. Agosta, *J. Am. Chem. Soc.*, **86**, 2638 (1964).

3a. A referee of this note has suggested that the direction of ring opening of a cyclopropylidene or diazocyclopropane could be controlled by electronic effects rather than steric effects and points to the recent communication of Woodward and Hoffmann (*J. Am. Chem. Soc.*, **87**, 395 (1965).) in support of his suggestion. Since this is not the first time that we have encountered this same suggestion, we feel that we should include some comment on this matter.

    The calculations of Woodward and Hoffmann deal primarily with whether a ring will open in a conrotatory or disrotatory manner. These calculations cannot be applied to the direction of ring opening in our system since the geometry of the allene requires a conrotatory motion to give rise to the observed product. Furthermore, it is not possible to predict by the Woodward and Hoffmann method which direction of conrotatory opening would be preferred. We would like to express our appreciation to Dr. Hoffmann for his helpful correspondence on this matter.

4. S. F. Mason and G. W. Vane, *Tetrahedron Letters*, following communication.

5. Physical constants and the infrared spectrum of the optically active hydrocarbon were in agreement with those reported for the racemic material; D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961). This material was chromatographically homogenous on a thin layer of Merck silica gel using chloroform as developer and had an R_f value of 0.70. All rotations were taken in a 1 dc. tube.

6. Y. Inouye, T. Sigita and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964).

7. H. Nozaki, K. Kondo, O. Nakanisi and K. Sisido, *ibid.*, **19**, 1617 (1963) report m.p. 88-89° for (-)-VII of $[a]_D^{20}$ -5.7°.

8. Analysis by thin layer chromatography and infrared showed (-)-VII to be identical to authentic racemic VII.