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PARTIAL RESOLUTION AND CORRELATION OF THE ABSOLUTE CONFIGURATION OF (-)-(R)-2-PHENYLISOBUTENYLIDENECYCLOPROPANE

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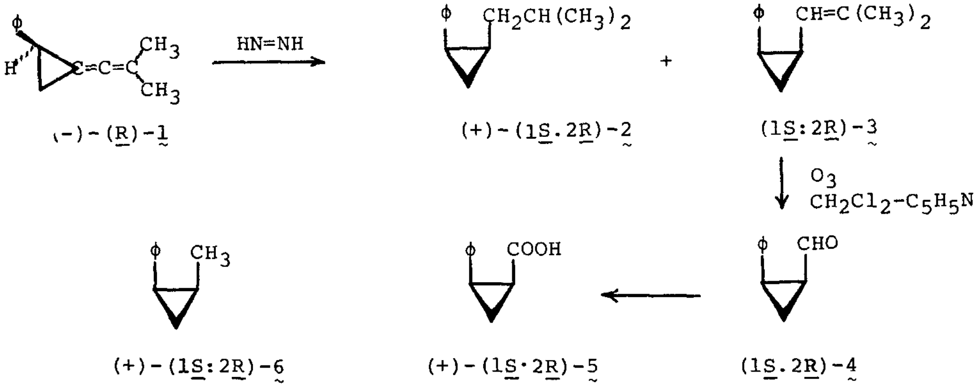
Previous stereochemical correlations of substituted cyclopropanes, methylenecyclopropanes and spiropentanes have shown that the introduction of the exocyclic double bond or the second three-membered ring has no effect on the sign of rotation in a series of compounds possessing the same absolute configuration.[1] In conjunction with a study of cycloaddition reactions of alkenylidenecyclopropanes[2] we have prepared a 2-phenylisobutenylidenecyclopropane (1) having the same sign of rotation and configuration as in the methylenecyclopropanes and spiropentanes thus extending a general observation that the attachment of a group possessing planes of symmetry to the three-membered ring does not have an effect on the sign of rotation.

Partial asymmetric hydroboration of 1 with (+)-diisopinocampheylborane (DIPCB) produces (-)-1 ($[\alpha]_D^{25}$ -19.0°) (no pinene is liberated during the course of the reaction). The absolute configuration of (-)-1 is predicted to be (R) on the basis of our recently proposed model transition state for asymmetric hydroboration[3] (based on a modified combination of the Brown[4] and Streitwieser[5] models). In various addition reactions 1 reacts nearly exclusively at the C_1-C_4 double bond at the face opposite the phenyl group (*vide infra*) with the electrophilic group becoming attached to C_4. Long range steric interactions in the hydroboration transition state are maximal with (R)-1.

The (R)-configuration of (-)-1 was confirmed by conversion to (+)-(1S.-2R)-2-phenylcyclopropane carboxylic acid (5). Reduction of (-)-1 with diimide (10-fold excess in 75% aqueous-ethanol generated from hydrazine and hydrogen peroxide[6]) produced a mixture of 2 and 3. Direct ozonolysis of the mixture of 2 and 3 in 2:1 methylene chloride-pyridine gave a mixture of 2 and **4**, which on chromic acid oxidation in 1:1 acetone-30% sulfuric acid produced a mixture of **2** and **5** which was separated by basic extraction techniques. The stereochemistry of **5** ($[\alpha]_D^{25}$ +3.8°)[7] was identified by comparison of its nmr spectrum with those of *cis*- and *trans*-2-phenylcyclopropane carboxylic acid[8] and by comparison of its sign of rotation with that of (+)-(1*S*:2*R*)-2-phenylcyclopropane carboxylic acid.[1] The stereochemistry of (+)-**2** ($[\alpha]_D^{25}$ +19.2°; based on 100% optical purity) is assigned on the basis of its anticipated formation only *via* **2**, and the similarity in sign of rotation of **2** as compared with (+)-(1*S*.2*R*)-1-methyl-2-phenylcyclopropane (**6**) (the *trans* isomer (1*R*·2*R*)-1-methyl-2-phenylcyclopropane possesses a negative rotation).[1] The stereochemistry of the intermediates involved in the conversion of **1** to **5** can thus be assigned as shown in the following reaction scheme.



Although the rotation of optically pure (+)-**5** is reported to be +30° it was not clearly indicated how the optically pure material was obtained.[1] Furthermore, as only milligram quantities of (+)-**5** were available in the present study and an accurate determination of its optical purity was critical to the related studies on the cycloaddition reactions of (+)-**5**, it was necessary to determine the optical purity of (+)-**5** in a more accurate manner. The optical purity of (+)-**5** was determined by conversion to the corresponding methyl ester with diazomethane and recording its nmr spectrum in the presence of the chiral shift reagent tris-(trifluoroacetylcamphorato)-europium (Eu(tfac)$_3$). The methoxyl hydrogens experience considerable paramagnetic deshielding and line broadending. At room temperature the line broadening precluded an accurate integration of the methoxyl hydrogens of the two optical antipodes. At 100°, however, the line broadening was significantly reduced such that the methoxyl resonances could be easily and accurately integrated. The nmr spectrum obtained at 100° with a 0.3:1.0 molar ratio of Eu(tfac)$_3$:ester indicated the optical purity of the ester, and the corresponding (-)-**1** from which it was formed, to be 64 2 ± 1.0%. The maximum rotation of optically pure (*R*)-**1** is thus -66.8° Attempted analysis of the optical purity of either the aldehyde **4** or the free acid (+)-**5** with Eu(tfac)$_3$ could not be accomplished because of the extreme line broadening and the overlapping of the resonance peaks

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