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THE ABSOLUTE CONFIGURATION OF 1,3-DIMETHYLALLENE

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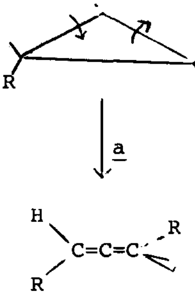
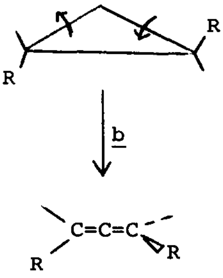
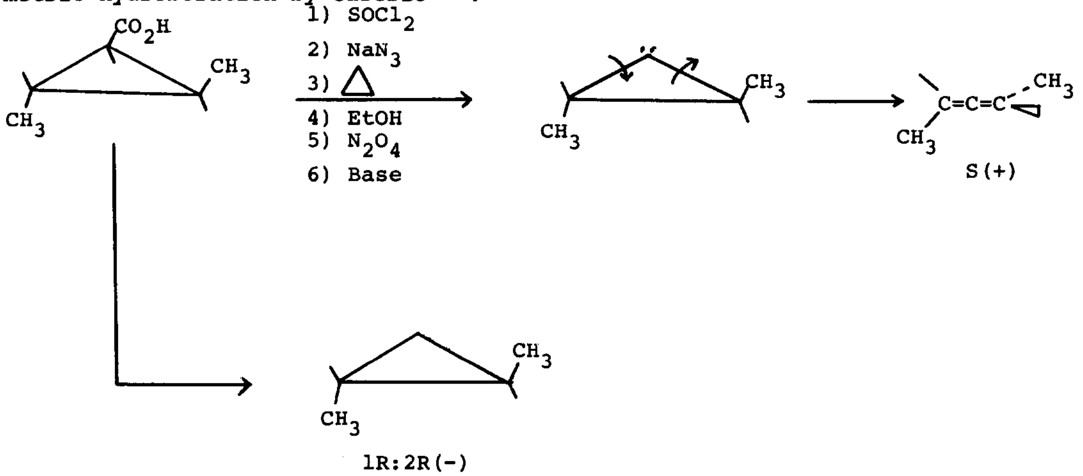
It has been reported(1) that (+)-2,3-dimethylcyclopropane carboxylic acid gives, by way of the carbene, (+)-1,3-dimethylallene. Since the stereochemistry of this type of ring opening is apparently controlled by steric repulsion of the trans-groups(2) (path a favored over b) knowledge of the absolute configuration of trans-2,3-dimethylcyclopropylidene (or its acid precursor) would allow absolute configuration assignment to the allene. We now report our finding that decarboxylation of (+)-trans-2,3-dimethylcyclopropanecarboxylic acid gives (-)-1,2-dimethylcyclopropane, a compound whose absolute configuration has been firmly established(3) as 1R.2R. This leads to the 2S:3S configuration for the carboxylic acid and the S configuration for (+)-dimethylallene, a configuration which has been predicted by Brewster(4) and independently assigned by asym-





metric hydroboration by Caserio(5).



The decarboxylation was effected in the following way. In a round-bottom flask equipped with a thermostated (35°) reflux condensor surmounted with a connecting tube to a cold trap cooled in a Dry-Ice acetone bath was placed a mixture of 20 ml quinoline, 1.5 g (+)trans-2,3-dimethylcyclopropane carboxylic acid and 0.2 g of copper chromite catalyst(6). The mixture was refluxed for 7 days. The volatile material which had collected in the trap was transferred on the vacuum line to a receiver containing silica gel. From this it was transferred to a gas cell for infrared. The gas phase infrared spectrum of trans-1,2-dimethylcyclopropane has been reported(7) and is quite distinctive showing 26 resolvable absorptions. The material resulting from the decarboxylation showed all 26 absorptions. In addition, the spectrum showed a small amount of foreign material whose spectrum indicated olefin. The vpc of the product showed the dimethylcyclopropane peak with a slight shoulder. Treatment of the product with permanganate removed the shoulder to give 15 mg of a gas chromatographically pure product. From acid with $(\alpha)_D^{25} = +6.15^\circ$ (c 15.3, 95% ethanol) was obtained cyclopropane with $(\alpha)_D^{25} = -5.5^\circ$ (c 15, diglyme). In another experiment where the decarboxylation was conducted slightly below the boiling point of quinoline, the dimethylcyclopropane showed no olefin although it did contain a small amount of an unidentified carbonyl compound. In this case, acid with $(\alpha)_D^{25} = -10.4^\circ$ gave dimethylcyclopropane with $(\alpha)_D^{25} = +9.63^\circ$.

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