Thermolysis of Cyclopropyl Azides: Stereochemistry of the Olefin Forming Process

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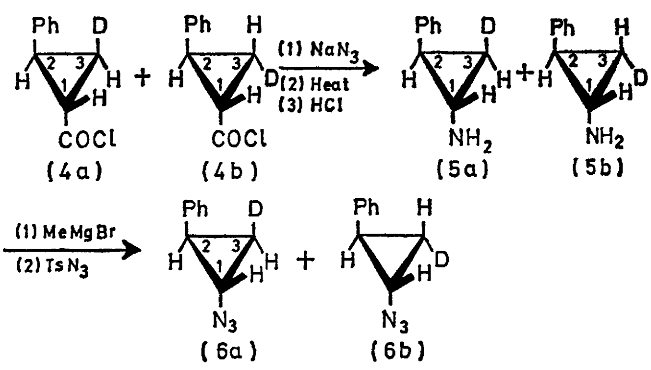
Summary From the thermal decomposition of *trans*-3-deuterio-2-phenylcyclopropyl azide it is concluded that the styrene formation follows a stereospecific *cis* route to at least 97%.

Thermal removal of nitrogen from cyclopropyl azides leads to 1-azetines, nitriles, and olefins.[1–3] We report the results of a study of the stereochemistry of the olefin forming reaction. As a model compound, *trans*-3-deuterio-2-phenylcyclopropyl azide was synthesized as shown in the Scheme. Compound (**1**) was obtained from its lithium salt with D_2O–DOAc and found by n.m.r. integration to contain 99·5 ± 0·5% deuterium. The addition of bis-(1,2-dimethylpropyl)borane to (**1**) followed by treatment with acetic acid yielded [β-^{2}H]styrene as a (98·5 : 1·5) ± 1·0 mixture of (**2a**) and (**2b**). No information on the steric purity of the ethyl 3-deuterio-2-phenylcycloproponecarboxylates† (**3**) and the *trans*-3-deuterio-2-phenylcycloproponecarboxylic acid chlorides (**4**) could be deduced from the n.m.r. spectra. N.m.r. analysis of *trans*-3-deuterio-2-phenylcyclopropylamine in the presence of $Eu(dpm)_3$ revealed that it consisted of a (90·1 : 9·9) ± 1·1 mixture of (**5a**) and (**5b**).‡ We assume that no change in the arrangement of deuterium occurs during the nitrogen transfer reaction of the amine mixture (**5a**)—(**5b**) to the azides (**6a**)—(**6b**).



Scheme

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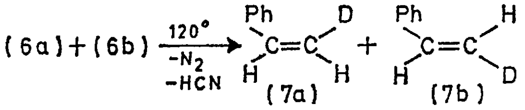
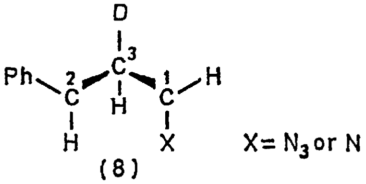
† Reisolated styrene after ethoxycarbonylcarbene addition showed the same (**2a**)–(**2b**) mixture as the starting material.

‡ We can only speculate at which stage of the reaction sequence partial loss of steric purity occurred. As the copper catalysed addition of ethoxycarbonylcarbene to olefins follows a stereospecific *cis*-route,[4] improper handling of the isomerisation procedure of the acid chloride (**4**)[5] might have caused the increase in (**4b**): rupture of the C-1–C-2 bond in (**4a**), rotation around the C-2–C-3 axis of the intermediate trimethylene species, reclosure of the centres C-1 and C-2, and isomerisation at C-1 of the *cis*-3-deuterio-2-phenylcyclopropanecarbonyl chloride to (**4b**) could account for the rise in (**4b**).

Thermal decomposition of the (**6a**)—(**6b**) mixture in triglyme at 120° gave as the main product[3] a styrene mixture (**7a**) : (**7b**) of (90·3 : 9·7) ± 1·0.





From this result we conclude that the formation of styrene from (**6**) follows a stereospecific *cis* course to at least 97%. This implies that no reaction mechanism in cyclopropyl azide thermolysis can be operating where cyclopropyl bond cleavage occurs in two separate steps with a trimethylene intermediate (**8**) capable of rotation around the bond C-2–C-3, but that the breaking of the cyclopropyl bonds follows a concerted pathway.

The thermolysis of cyclopropyl azides thus parallels the decomposition of cyclopropyldiazoalkanes,[6] where fragmentation of the intermediate cyclopropylcarbene to an olefin and an alkyne occurs. For the photochemical reaction this fragmentation has been shown to follow a stereospecific *cis* route.[7]

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