# Photochemical Rearrangement of Diallylic Compounds: Lack of Inversion of the Migrating Allyl Group demonstrated by Deuterium Labelling

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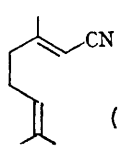
IN none of the examples of photochemical 1,3-allylic shifts in derivatives of hexa-1,5-diene recently reported[1] did both allyl groups undergo inversion: for example, geranonitrile (I, *cis* or *trans*) yielded the products from migration of either allyl group separately, but not the isomer (II) arising from a Cope rearrangement. The behaviour of a simple allyl derivative now shows that this is a necessary feature of the reaction, not just a trivial result of the pattern of substitution in the compounds studied.

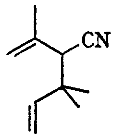
The specifically deuteriated compounds (III) and (IV) were made by hydrogenation of 3-deuteriopropargyl precursors at a convenient point in the synthetic sequence. The expected exclusive *cis*-configuration of hydrogen on the double bonds in (III) and (IV) was shown by infrared and $^1$H n.m.r. spectroscopy. Irradiation of (III) in ethanol through silica with light from a bank of low-pressure mercury lamps (mainly 254 nm.) caused rearrangement to the unconjugated isomer, accompanied by some polymer. The infrared and $^1$H n.m.r. spectra of the product showed that it was a 1 : 1 mixture of 3-*cis*- and 3-*trans*-isomers (IV) and (V), free from any detectable amount of the 1-deuterioallyl compound (*i.e.*, $< 3\%$). Thermal Cope rearrangement of the mixture of (IV) and (V) or of pure synthetic (IV) gave (VI).

These results rule out the following possible mechanisms for the rearrangement: (1) Cope rearrangement through the vibrationally excited electronic ground-state—which would require inversion of the allyl group; (2) crossing of the excited singlet to the triplet, cleavage into a pair of radicals† and recombination—it would be a remarkably narrow solvent cage that allowed enough movement for the migration and *cis–trans*-isomerisation, but not for inversion of the allyl group. Only a concerted reaction of an electronically excited state provides a simple explanation.‡

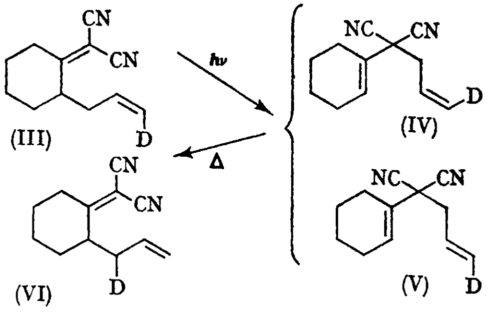
Woodward and Hoffmann's rules[2] allow a 1,3-shift in the lowest $\pi,\pi^*$ excited state. The *cis–trans*-equilibration of the migrating allyl group seems to be an integral part of the rearrangement, because the conjugated isomer recovered from incomplete rearrangement was unchanged (III) and the *cis*-unconjugated isomer (IV) was stable to irradiation even in the presence of cyclohexylidene-malononitrile [simulating possible photosensitised *cis–trans*-isomerisation of (IV) by unreacted (III)]. This suggests that isomerisation of the product occurs before it falls to the electronic and vibrational ground-state, or, more likely, that the rearrangement proceeds through a transition state with the axes of the *p* orbitals of C-2 and C-3 of the allyl group at right angles.



(I)



(II)



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† The trace of propene produced in the reaction may arise from such a process.

‡ In agreement, Dr. N. A. Mirza finds that triplet photosensitisers such as acetone divert the reaction of geranonitrile (I) from allylic rearrangement (ref. 1) entirely to cyclobutane formation, giving the two epimers of 1,6,6-trimethylbicyclo[2,1,1]hexane-5-carbonitrile. Irradiation through Pyrex of unlabelled (III) in acetone gives the tricyclic cyclobutane isomer in high yield.

[1] R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Letters*, 1965, 3955.
[2] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511.