

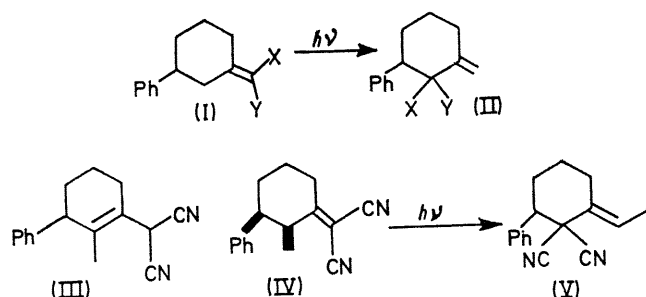
Retention of Configuration at C-1 of the Allyl Group in a Photochemical 1,3-Allylic Shift of a Benzyl Group

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Summary On direct u.v. irradiation *cis*-2-methyl-3-phenyl-dicyanomethylenecyclohexane (IV) rearranges to 2,2-dicyano-3-phenylethylidenecyclohexane (V), in which the methyl group is *trans* to the *gem*-dicyano-group; this constitutes a 1,3-shift of the benzylic centre with retention of configuration at C-1 of the dicyano-allyl group.

HAVING established that the configuration of the migrating benzyl group was retained in the photochemical 1,3-allylic shift,¹ we wished to test whether there was also retention of configuration at both ends of the allyl group.



Condensation of methyl cyanoacetate with 3-phenylcyclohexanone gave a mixture of the two geometrical isomers (I; X and Y = CN and CO₂Me) with about 20% of the $\beta\gamma$ -unsaturated isomer, from which one of the pure isomers (I), m.p. 84—85°, was isolated. Irradiation of this pure isomer (I) in ethanol through silica produced an oily photoproduct, shown by its n.m.r. spectrum to consist of a mixture of the two epimers of the expected structure (II). However, the recovered material (I) was also a *cis*-*trans*-mixture, so that no conclusion could be reached about the stereochemistry of the 1,3-shift at C-3.

trans-2-Methyl-3-phenylcyclohexanone(2,4-dinitrophenylhydrazone, m.p. 220—221°), made by cuprous iodide-catalysed addition of phenylmagnesium bromide to 2-methylcyclohex-2-enone or by hydrogenation of 2-methyl-3-phenylcyclohex-2-enone, condensed with malononitrile to form the *cis*-product (IV), m.p. 90—91°, and the unconjugated isomer (III). The absence of the *trans*-isomer no doubt results from the congestion that would arise from eclipsing an equatorial methyl group with the adjacent cyano-group.

Irradiation of the dinitrile (IV) caused the usual 1,3-shift, with production of a single photoisomer (V), m.p. 101—102° (25% isolated yield). The configuration of the conjugated isomer (IV) rests on the coupling constant between the two tertiary protons, *ca.* 4 Hz, characteristic of *cis* (*ax,eq*) protons. That of the photoisomer can be assigned from the chemical shifts of the ethylidene protons. The olefinic methylene protons in the photo-compound (II; X = Y = CN) appear as two singlets at δ 5.18 and 5.50 p.p.m. (CDCl₃), the one at lower field being assigned to the proton *cis* to the *gem*-dicyanide, where it is unshielded by the equatorial cyano-group. After allowance of an increment of +0.44 in chemical shift of the olefinic protons for substitution of the methyl group,² a *cis*-proton [as in (V)] is expected at δ 5.94 and a *trans* one at 5.62 p.p.m. The former agrees better with the experimental value of 6.12 p.p.m. This configuration (V) is also consistent with the normal chemical shift of the allylic methyl group (1.71 p.p.m.), whereas the methyl *cis* to the *gem*-dicyanide would be thrust right against the centre of the equatorial nitrile's triple bond, resulting in a shift to lower field.

The 1,3-rearrangement of (IV) to (V) therefore takes place with retention of configuration at C-1. Admittedly, both the reactant and the photoproduct are the more stable of the two possible geometrical isomers, but the lack of any trace of the geometrical isomer of (V) inclines one to believe that the reaction is intrinsically stereospecific.

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¹ Preceding communication.

² C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.