

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

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Summary The retention of configuration of the migrating benzylic group in a photochemical 1,3-allylic shift is demonstrated in the rearrangement of 3-methyl-5-phenyldicyanomethylenecyclohexane to 2,2-dicyano-5-methyl-3-phenylmethylenecyclohexane.

In the photochemical 1,3-carbon shift that converts a bicyclo[3,2,0]hept-3-en-2-one (I) into a bicyclo[2,2,1]hept-2-en-7-one (II) the stereochemistry of the migrating carbon is lost when it carries a phenyl group ($R = Ar$), indicating the diradical as an intermediate.¹ It has recently been reported that configuration is also lost even in the parent system ($R = D$), where the migrating radical centre is secondary rather than benzylic² [although interpretation was complicated by competing epimerisation of the original ketone (I)].

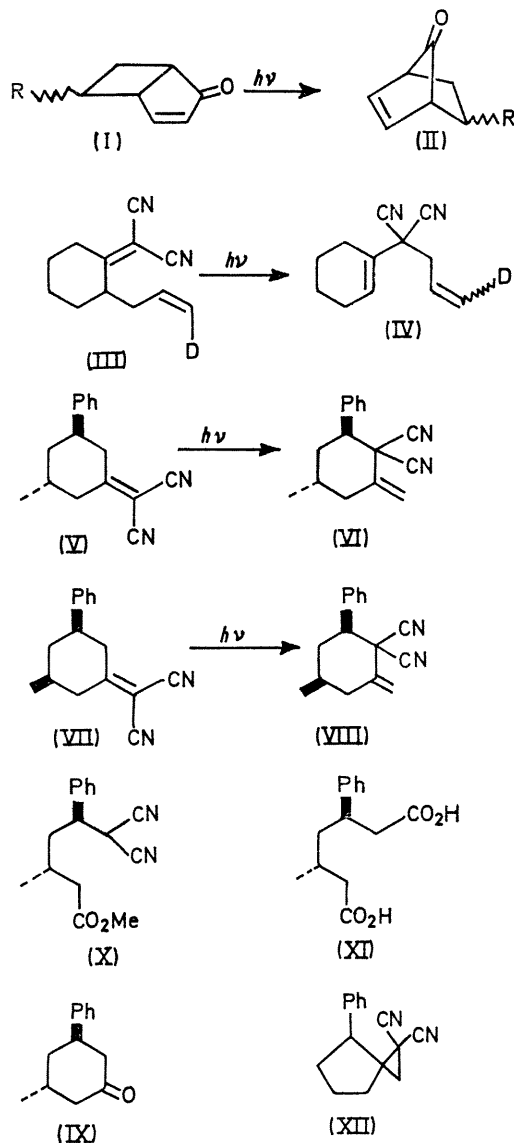
On the other hand, the photochemical 1,3-shift of the deuterio-allyl group in the dinitrile (III) to give (IV) was shown to be concerted and to involve the excited singlet state by the lack of inversion of the allyl group and by diversion of the rearrangement to intramolecular cyclobutane formation in presence of triplet sensitizers.³ We now demonstrate the retention of configuration of the migrating group in this system, predicted by the Woodward-Hoffmann rules for the first excited state.

After investigation of several other systems we selected *cis*- and *trans*-3-methyl-5-phenyldicyanomethylenecyclohexane (V) and (VII), made by condensation of the respective ketones with malonitrile. *trans*-3-Methyl-5-phenylcyclohexanone (IX) (semicarbazone, m.p. 179–180°) was made by addition of methylmagnesium iodide to 5-phenylcyclohex-2-enone in presence of cuprous chloride, or by similar addition of phenylmagnesium bromide to 5-methylcyclohex-2-enone. Reaction of 3-ethoxy-5-methylcyclohex-2-enone with phenyl-lithium gave 5-methyl-3-phenylcyclohex-2-enone, reduced by hydrogen over palladium (10%) on charcoal to a 1:1 mixture of the *cis*- and *trans*-ketones. Since the *cis*-ketone was difficult to obtain pure, the mixture was condensed with malonitrile and the *cis*-isomer (VII) was separated by fractional crystallisation from methanol.

Irradiation through silica (mainly 254 nm) of a solution in ethanol of the *trans*-isomer (V), m.p. 90–91°, produced the *trans*-photoisomer (VI), m.p. 71–72° [9% yield of (VI) isolated, 24% of (V) recovered; the rest polymer]. Similar irradiation of the *cis*-isomer (VII), m.p. 74–75°, produced the *cis*-photoisomer (VIII), m.p. 95° [12% (VIII), 24% (VII), plus polymer]. No trace of *cis*-photoisomer (VIII) was formed from the *trans*-compound (V), nor of *trans*-photoisomer (VI) from the *cis*-compound (VII), so that the rearrangement is completely stereospecific. It remained to prove the stereochemical relationship of the initial dinitriles to the photoproducts (*i.e.* to distinguish complete retention from complete inversion of configuration).

Ozonolysis of the *trans*-photoisomer (VI) in methanol-chloroform followed by reductive hydrolysis gave the methyl ester (X), m.p. 88°, which was hydrolysed by acid

to the dicarboxylic acid (XI), m.p. 180°. This same acid (XI) was made by acylation of the *trans*-ketone (IX) with ethyl chloroformate and hydrolysis (the same product is



formed on hydrolysis whichever side of the carbonyl group is acylated). The configuration is therefore unchanged by photoisomerisation. Ozonolysis and hydrolysis of the *cis*-photoisomer (VIII) produced a different dicarboxylic acid, m.p. 115°.

Although this proof of the retention of configuration of the migrating benzylic centre in the photoisomerisation does not require knowledge of which series is *cis* and which

trans, the actual configurations follow from the methods of preparation of the ketones⁴ and, more conclusively, from the n.m.r. spectra, which clearly show that the methyl group is axial in the compounds drawn *trans* [(V) and (VI)] and equatorial in those drawn *cis* [(VII) and (VIII)]. The structures of all the new compounds were confirmed by microanalysis, i.r., u.v., n.m.r., and mass spectra.

Irradiation of the parent 3-phenylcyclohexylidenemalononitrile, m.p. 69–70°, in ethanol gave the corresponding

photoisomer, m.p. 79–80°, but it was quite stable to prolonged irradiation in acetone. There was no sign of the product (XII) of 1,2-shift.⁵ The rearrangement seems, therefore, again to occur from an excited singlet state, although there is yet no clear evidence of whether it is (as implicitly assumed) the π, π^* state of the methylenemalononitrile chromophore, the n, π^* , or the π, π^* of the phenyl group: in any case, the two chromophores are likely to be strongly coupled.

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⁵ E. C. Sanford and G. S. Hammond, *J. Amer. Chem. Soc.*, 1970, **92**, 3497.