

Retention of Configuration at the Migrating Centre in both Photochemical and Thermal [1,3]-Sigmatropic Shift of a Benzyl Group. Relaxation of Orbital Symmetry Control in an Unsymmetrical Allyl System

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Summary Photoisomerisation of (+)-1,1-dicyano-2-methyl-4-phenylpent-1-ene (VII) to 3,3-dicyano-2-methyl-4-phenylpent-1-ene (VIII) took place with *ca.* 85% retention of configuration at the migrating carbon atom and 15% inversion; thermal reversal of the rearrangement occurred with >90% retention and <10% inversion, rather than with the complete inversion expected for a concerted [1,3]-sigmatropic shift in the ground state: this apparent violation of orbital symmetry is attributed to the very unsymmetrical nature of the (dicyano) allyl group across which the α -phenylethyl group migrates.

THE required¹ inversion of configuration at the migrating carbon atom during a thermal [1,3]-sigmatropic shift has been demonstrated by Berson and Nelson² in the cases (Ia, b) \rightarrow (IIa, b). Similar concerted rearrangement of the *endo*-methyl derivative (Ic) with inversion would have to

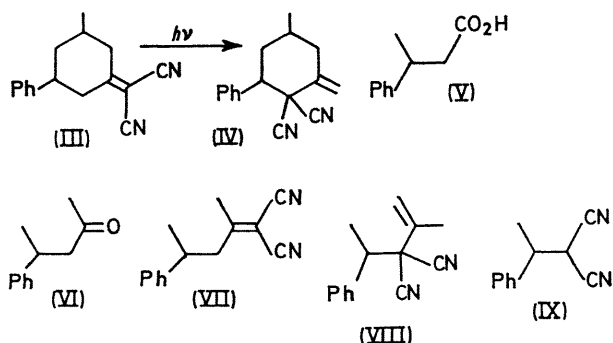
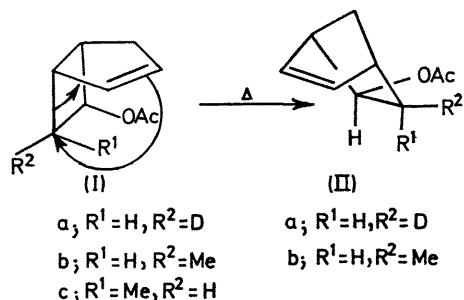
proceed through an extremely congested transition-state where the methyl group is forced into the allyl system across which migration is occurring. In fact, this compound (Ic) rearranged with predominant retention to (IIb), almost certainly through the diradical. We now draw attention to a concerted 1,3-shift that takes place with retention of configuration at the migrating centre, in apparent violation of orbital symmetry.

The photochemical 1,3-allylic shift of a benzylic centre across a 3,3-dicyano-allyl group was recently shown³ to occur with complete retention of configuration at the benzylic carbon atom, by stereospecific rearrangement of (III) to (IV) (*cis* \rightarrow *cis*, and *trans* \rightarrow *trans*). In this cyclic system the reverse thermal reaction (IV) \rightarrow (III) could not be realised. We have now found an acyclic system in which the stereochemistry of the reaction can be studied in both directions.

The optically pure acid (V) ($[\alpha]_D^{25} -60.0^\circ$, methyl ester $[\alpha]_D^{25} -44.3^\circ$) was converted through the acid chloride

† All rotations are given for solutions (*ca.* 10 mg per ml) in benzene at the sodium D line, measured on a Bendix-Ericson polarimeter.

(-23.5°) and methyl ketone (VI) (-74.5°) into the dinitrile (VII) (-3.6°). Irradiation of (VII) in cyclohexane solution with a medium-pressure mercury arc through silica until no unchanged dinitrile remained caused migration of the α -phenylethyl group to give the isomeric dinitrile (VIII) ($+22.4^\circ$) in a yield of 60% after distillation. The optical purity of the photoisomer (VIII) was determined by its treatment with ozonised oxygen at -78° , followed by zinc



dust and hot water, yielding the dinitrile (IX), hydrolysis of which produced the carboxylic acid (V) (-47.2° on crude product). The derived methyl ester (diazomethane) had $[\alpha]_D -29.6^\circ$. The optical purity of the acid was then apparently $47.2/60.0 = 78.7\%$, and that of the methyl ester $29.6/44.3 = 66.8\%$. Since none of the reactions used to convert the optically pure acid (V) into the dinitrile (VII) or the photoisomer (VIII) back into the ketone (VI) is likely to have touched the configuration of the α -phenylethyl group, the photoisomerisation must have occurred with 89% retention of configuration and 11% inversion, based on the $[\alpha]_D$ of the crude acid, or 83% retention and 17% inversion based on that of the pure methyl ester.

The photoisomer (VIII) was heated in a sealed tube under nitrogen: at 200° for 0.5 h it was hardly changed, but after 15–20 min at 250° the product consisted of unchanged (VIII) (14%), the conjugated dinitrile (VII) (36%), and decomposition products (51%) (analysed by g.l.c.). The mixture was boiled with ammonium acetate in aqueous acetone (1:1) for 18 h, when the conjugated isomer (VII) was hydrolysed to the ketone (VI), isolated by preparative g.l.c. (-45.2°). The optical purity of the ketone (VI) was thus $45.2/74.5 = 61\%$. The thermal rearrangement, therefore, happened with 95.5% retention of configuration and 4.5% inversion, based on the $[\alpha]_D$ of the methyl ester (or 89% retention and 11% inversion, based, presumably less reliably, on that of the crude acid).

The predominant retention of configuration in the photochemical rearrangement is to be expected, being an example of the $[\sigma 2_s + \pi 2_s]$ process, allowed in the π^* state of the allyl group.¹ The *ca.* 15% inversion might have come from that proportion of competing $[\sigma 2_a + \pi 2_s]$ reaction, in violation of orbital symmetry, or from *ca.* 30% recombination of radical pairs with racemisation. (The formally allowed antarafacial migration with inversion is probably geometrically impossible, and reaction through a vibrationally excited ground-state is not only unlikely in solution, but in any case thermal reaction in fact proceeds with retention.)

The predominant retention of configuration in the thermal rearrangement is notable, because a suprafacial 1,3-shift across an allyl group in the ground-state with retention at the migrating atom is forbidden¹ (again, the antarafacial shift is probably impossible,[‡] and recombination of unracemised singlet radical pairs⁴ in a fluid medium at 250° seems equally unlikely). The forbiddenness holds strictly, however, only when the allyl group is symmetrical, and a mirror plane passes through its middle carbon atom normal to the plane of the carbon skeleton. In the present case, though, the allyl group is strongly polarised by the two cyano-groups and very unsymmetrical, so that, *inter alia*, the node in the highest occupied π -orbital will no longer pass through C-2. The concerted suprafacial 1,3-shift with retention must thereby have become sufficiently allowed to permit it to compete successfully with the sterically more strained route with inversion.

These results serve as a warning against uncritical extension of orbital symmetry rules, from the parent systems to which they apply, to strongly perturbed derivatives. In this example even the reversal of stereochemistry expected for the thermal and photochemical processes does not occur.

All new compounds had analytical and spectroscopic properties consistent with the structures assigned.

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‡ A formal possibility in accordance with direct application of orbital symmetry rules to the present system would be a suprafacial [1,3]sigmatropic shift of the α -phenylethyl group of (VIII) in the opposite direction, to nitrogen, with inversion, followed by antarafacial [1,5]-shift in the intermediate ketenimine also with inversion. The net result would be the observed retention of configuration.

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