# Self-immolative Asymmetric Synthesis in the Allylic Rearrangement of an Optically Active Amine Oxide

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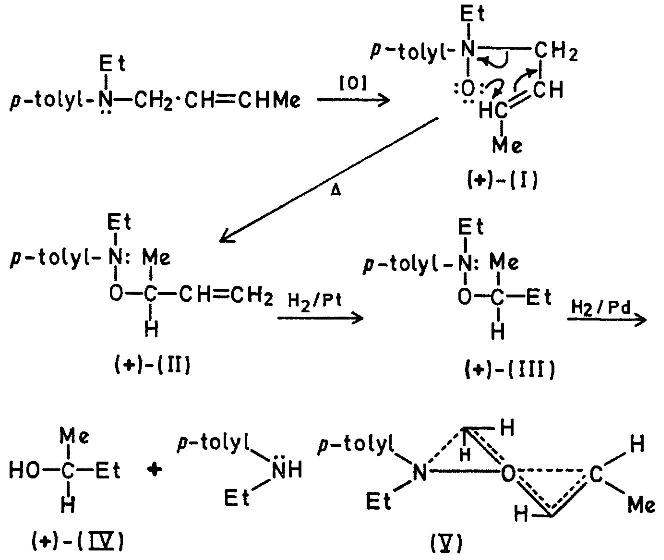
*Summary* Transfer of chirality of tetraco-ordinate nitrogen to carbon atom occurred in the thermal sigmatropic rearrangement of (+)-*N*-*trans*-but-2-enyl-*N*-ethyl-*p*-toluidine oxide to (+)-*O*-1-methylprop-2-enyl-*N*-ethyl-*p*-tolylhydroxylamine, whose absolute configuration was correlated with (*S*)-(+)-butan-2-ol.

TRANSFER of asymmetry from tetraco-ordinate nitrogen to a dissymmetric carbon atom being newly created at the expense of the former has recently been achieved by Hill[1] in an elegant Stevens rearrangement of (*R*)-(+)-allylbenzylmethylammonium cation into (*S*)-(—)-3-(*N*-methylanilino)-4-phenylbut-1-ene. This study, together with other self-immolative asymmetric syntheses in Claisen and Cope rearrangements,[2] has shed light on the transition-state topology and the "no-mechanism" pathways of the reactions. The concerted cyclic mechanism has been confirmed by the surprisingly high stereoselectivity as shown by nearly complete conservation of optical purity.

Amine oxides with dissimilar substituents are examples of configurationally stable tetraco-ordinate hetero-atom compounds capable of existing in enantiomeric forms (*e.g.* methylethylallylamine oxide[3]). Therefore, the sigmatropic rearrangement of optically active *N*-*trans*-but-2-enyl-*N*-ethyl-*p*-toluidine oxide (I) into *O*-1-methylprop-2-enyl-*N*-ethyl-*p*-tolylhydroxylamine (II) should proceed with transfer of chirality of tetraco-ordinate nitrogen to the trigonal carbon atom. A non-dissymmetric rearrangement of this type has already been described[4] in an analogous system, but-2-enylmethylaniline oxide. A more recent example of self-immolative asymmetric synthesis[5] is the rearrangement of

(*S*)-(−)-α-methylallyl *p*-toluenesulphenate to (*S*)-(−)-*trans*-but-2-enyl*p*-tolyl sulphoxide, which suggests that the present reaction is feasible because of close similarity in mechanism.†

Partial asymmetric oxidation of *N*-*trans*-but-2-enyl-*N*-ethyl-*p*-toluidine with (−)-*OO*-dibenzoyl-D-pertartaric acid in chilled methylene dichloride afforded (+)-*N*-*trans*-but-2-enyl-*N*-ethyl-*p*-toluidine oxide‡ [(I) $n_D^{25}$ 1·5088; $[\alpha]_D^{25}$ + 5·5° (*c*, 9·65, MeOH); picrate m.p. 105—106° (decomp.); 92% yield]. Boiling of (+)-(I) under reflux in 10%-NaOH (50 ml) for 30 min. gave (+)-*O*-1-methylprop-2-enyl-*N*-ethyl-*p*-tolylhydroxylamine [(II); b.p. 99—100°/3 mm; $n_D^{25}$ 1·5047; $[\alpha]_D^{25}$ + 1·1° (*c*, 3·46, MeOH); 9·8 g. 90% yield].



This is believed to constitute the second example of transfer of chirality of a tetraco-ordinate nitrogen to carbon. Since neither the absolute configuration nor the maximum rotation of (I) has been known, it is difficult to assess the degree of stereoselectivity and to deduce the transition-state topology. However, configurational correlation of (+)-(II) with (*S*)-(+)-butan-2-ol (IV) permits some positive statements to be made on the steric course. Catalytic hydrogenation of (+)-(II) (5 g 0·025 mole) over platinum oxide yielded (+)-*O*-2-butyl-*N*-ethyl-*p*-tolylhydroxylamine [(III); b.p. 82—84°/3 mm; $n_D^{25}$ 1·4953; $[\alpha]_D^{25}$ +1·8° (*c*, 9·85, MeOH); 5 g, 93% yield], an equivalent amount of hydrogen (570 ml at 25°; 0·025 mole) having been absorbed. Hydrogenolysis of (+)-(III) (2 g, 0·01 mole) over palladium-charcoal yielded (+)-butan-2-ol [(IV); b.p. 100°; $n_D^{25}$ 1·3980; $[\alpha]_D^{25}$ +1·0°(*c*, 10·8, EtOH), optical purity 7·7% based on $[\alpha]_D^{25}$ +13° (EtOH);[6] 0·32 g, 40% yield], together with *N*-ethyl-*p*-toluidine.

Since the *S*-configuration of (+)-(IV) has been unequivocally established,[7] the same *S*-configuration can be assigned to (+)-(III) and (+)-(II). Accepting the cyclic concerted mechanism as a reasonable one and with the knowledge of the configuration of (+)-(II), one may conclude that the starting amine oxide (+)-(I) possesses the *R*-configuration. This is based on the assumption that *a priori* the non-bonded repulsive interactions should be minimized in the transition state by a staggered disposition of all the substituents in a half-chair conformation, with tolyl and methyl groups oriented *trans* to each other, as in (V).

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† The Woodward–Hoffmann orbital symmetry rule shows (A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.) that five-centred rearrangements of allyl sulphenates (ref. 5) and phosphinates (A. W. Herriot and K. Mislow, *Tetrahedron Letters*, 1968, 3013) to the respective oxides, the reverse processes of the present system, can be viewed as a [2,3]sigmatropic rearrangement with six electrons participating in the transition state: it is therefore thermally allowed.

‡ Correct elemental analyses, i.r., and n.m.r. spectroscopic support were obtained for all the compounds reported herein.

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