

ASYMMETRIC INDUCTION ON THE SCHIFF BASES

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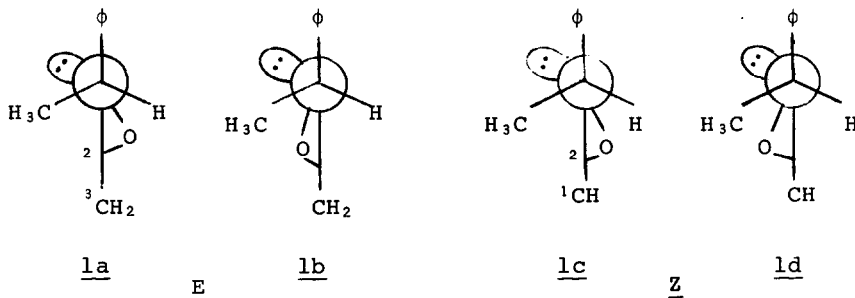
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Summary

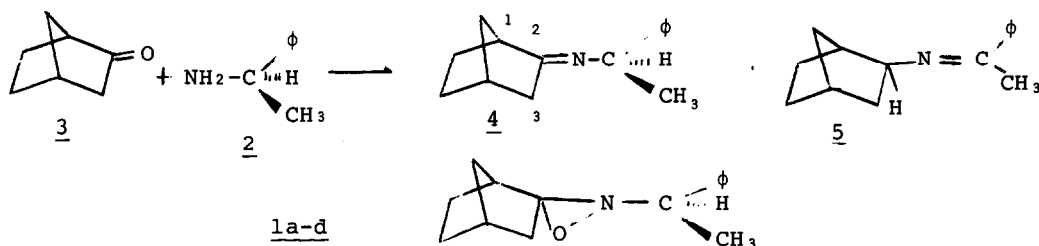
Oxidation of chiral Schiff bases leads to nonracemic diastereometric oxaziridines with a preferential formation of an E isomer.

The chiral Schiff bases offer an interesting synthetic potential - they could be stereospecifically transformed into oxaziridines with a reasonably high optical yield (1-3). The condensation of chiral R- α -phenylethylamine (2) and alicyclic ketone 2-norbornanone (3), followed by oxidation of the resulting N-2-norbornylidene- α -phenylethylamine (4), leads to 2-[α -phenylethyl]3,3-norbornanylene oxaziranes (1a-d). The excess of one isomer (1a) in the mixture clearly indicates the asymmetric induction during oxidation. The same reaction carried out on racemic amine (R,S) 2 results in a lack of this specificity.

The condensation of 2 and 3 (4,5) produced only one compound 4 (Rt 4 min; ^1H NMR: 4.40 ppm (q, 3, $\overline{\text{CH}}-\text{CH}_3$), 1.47 (d, 1, $\text{CH}-\text{CH}_3$), 7.4 (m, 0.5, ϕ), m/e 213 (M^+ , 21%), 105 (100%)). The oxidation of 4 with m-chloroperbenzoic acid (CH_2Cl_2 , 0-5 $^\circ$, 5 hrs) has produced four compounds: the two major ones, 1a (39%) and 1b (40%) with the E configuration and the two minor, 1c (21%) and 1d (16%) with the Z configuration. The total induction ratio E/Z (63:37) is smaller than previously observed for other compounds. However, the C-1 and C-3 sides of the bicyclo[2:2:1]heptane skeleton are quite similar and according to experiment in other cases do not show a pronounced stereoselectivity. The major oxidation compound of each pair, 1a and 1c, is formed according to Cram's rule. This observation is useful for predicting the direction of asymmetric induction during oxidation of the Schiff base.



The structure assignment has been done after separating the compounds by GC and by comparing them to available chiral model compounds (1). The spectroscopic characteristics of the compounds are: 1a Rt 7.2 min; $^1\text{H NMR}$: 3.57 (q, 1, $\text{CH}-\text{CH}_3$), 1.55 (d, 3, $\text{CH}-\text{CH}_3$), 7.2 - 7.4 (m, 5, ϕ), ^{13}C : 66.6 (d, $\text{CH}-\text{CH}_3$), 23.2 (q, $\text{CH}-\text{CH}_3$), 126-8 (ϕ), 94.9 (s, C-3); m/e 229 (M^+ , 32), 163 (35), 105 (100); 1b (same order) Rt 8.3 min; $^1\text{H NMR}$: 3.27, 1.42, 7.2 - 7.4; ^{13}C : 65.1, 22.7, 126-7, 94.9; m/e 229 (61), 214 (37), 138 (36), 105 (100); 1c Rt 6 min; $^1\text{H NMR}$: 3.20, 1.50, 7.2 - 7.4, ^{13}C : 64.4, 24.1, 126-8, 45.2; m/e 229 (56), 214 (62), 120 (35), 105 (100); 1d Rt 5.5 min; $^1\text{H NMR}$: 3.25, 1.40, 7.2 - 7.4, ^{13}C : 63.9, 22.0, 126-8, 95.2; m/e 229 (33), 214 (40), 105 (100). All NMR spectra have been recorded in CDCl_3 on a Varian FT 80 spectrometer and the mass spectra on a GC-MS on Hitachi RM-50 (OV 101 column).



In order to verify the possibility of the isomerisation of imine 4 to imine 5 (7) we have condensed acetophenone with 2-amino norbornane (6). Only one imine 5 has been obtained (Rt 2.5 min; NMR 1.9 (s, 3, CH_3), 3.7 (m, 1, $\text{CH}-\text{N}$), 7.4 - 7.8 (m, 5, ϕ); m/e 213 (M^+)).

This verification, ignored in previous studies, is necessary where the imine could easily undergo such an isomerisation (8).

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8. The technical assistance of R. Luce is acknowledged.

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