

The barrier to enantiomerization of *N*-Boc-2-lithopyrrolidine: the effect of chiral and achiral diamines

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Electronic Supplementary Information

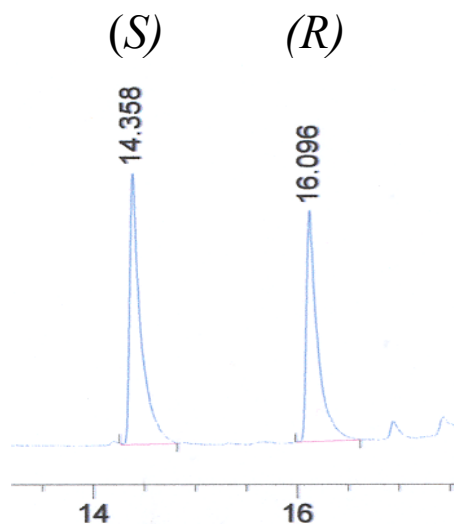


Figure 1. Chromatogram of (N)-Boc-2-trimethylsilylpyrrolidine run on a β -Cyclodextrin capillary column. The column temperature was programmed as follows:- Initial Temperature $T = 70\text{ }^{\circ}\text{C}$ for 5 mins, followed by a gradient of $5\text{ }^{\circ}\text{C}/\text{min}$ until $T = 200\text{ }^{\circ}\text{C}$, maintained for 10 mins β -cyclodextrin column. The regulator pressures were: $\text{H}_2 = 6\text{ psi}$; $\text{N}_2 = 52\text{ psi}$; Air = 50 psi.

Kinetic data were fitted to Equation 1, the integrated rate equation for a 1st order process relaxing to equilibrium:-

$$0.5 \ln [T - 2R] = -kt \quad \dots\dots\dots \text{Equation 1}$$

T = total initial concentration of stannane

R = concentration of 4-(*R*)- at time, t .

k = rate constant for enantiomerization

Graphs plotting equation 1 for the racemisation of 4-(*S*) to 4-(*R*) with each of three ligands at four different temperatures are given below:-

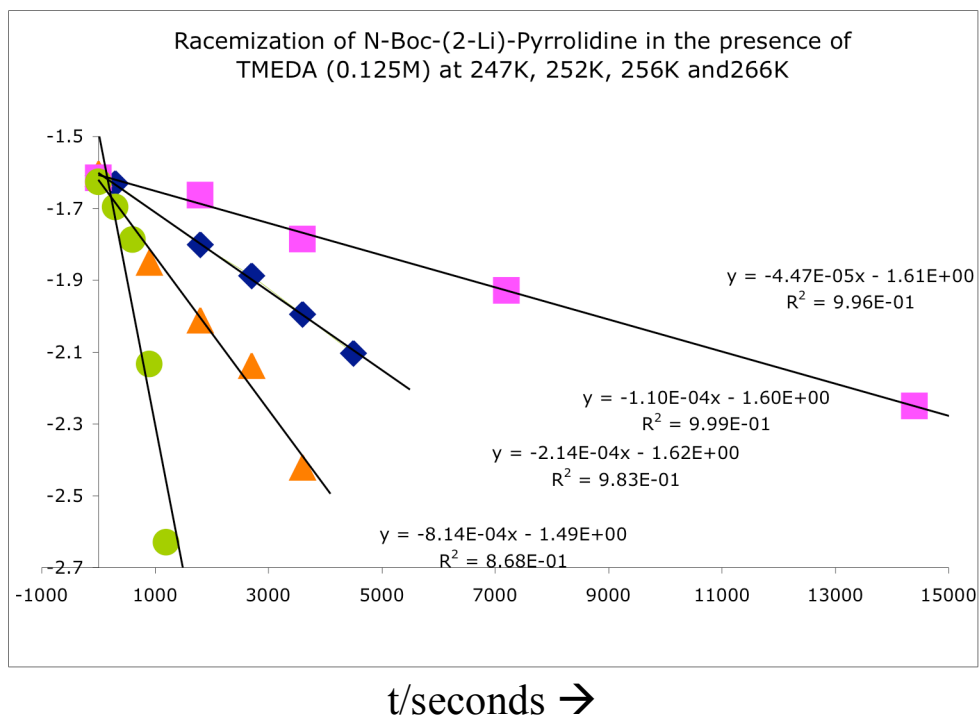


Figure 2. 1st order rate plots for the racemization of *N*-Boc-2-Li-pyrrolidine in the presence of TMEDA.

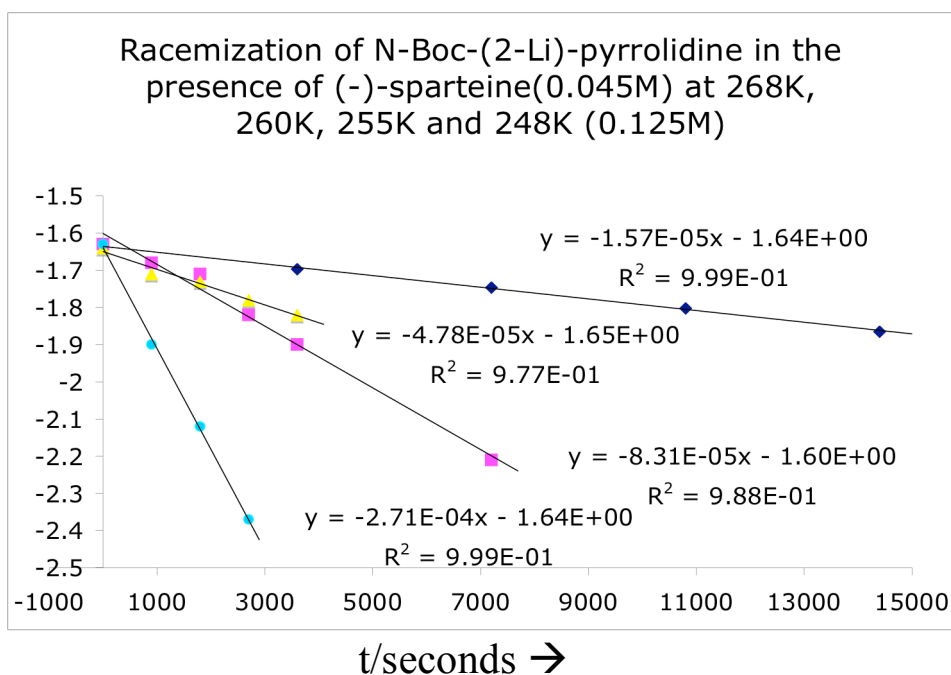


Figure 3. 1st order rate plots for the racemization of *N*-Boc-2-Li-pyrrolidine in the presence of sparteine.

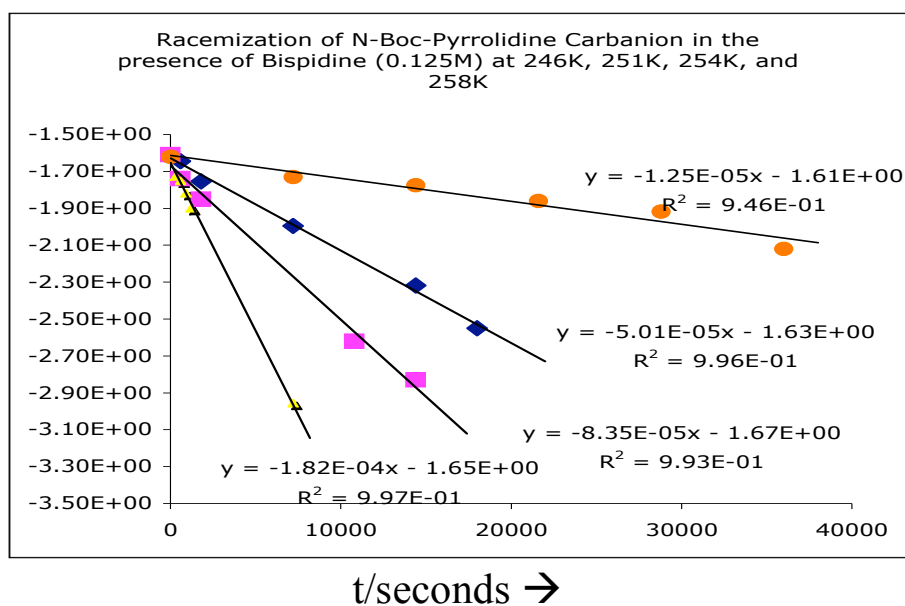


Figure 4. 1st order rate plots for the racemization of *N*-Boc-2-Li-pyrrolidine in the presence of bispidine.

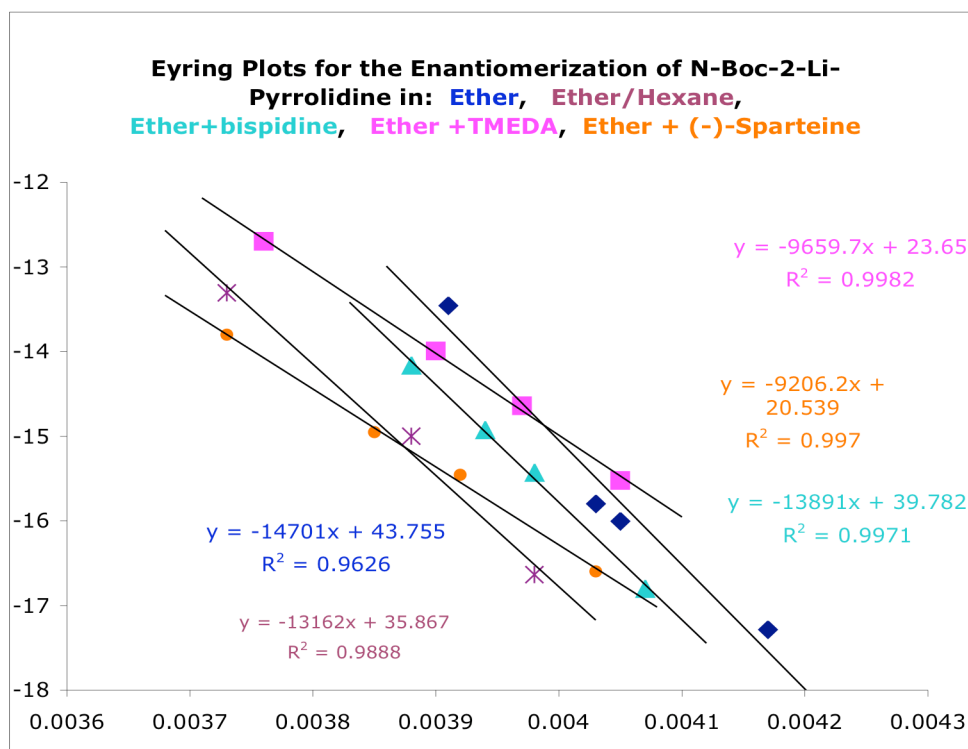


Figure 5. Eyring plots for the enantiomerization of *N*-Boc-2-Li-pyrrolidine in the presence and absence of diamines. Data for ether and ether/hexane are duplicated from ref. 8 for comparison, with one extra data point in the ether plot to assure continuity between experimentalists.