

**SUPPORTING INFORMATION**

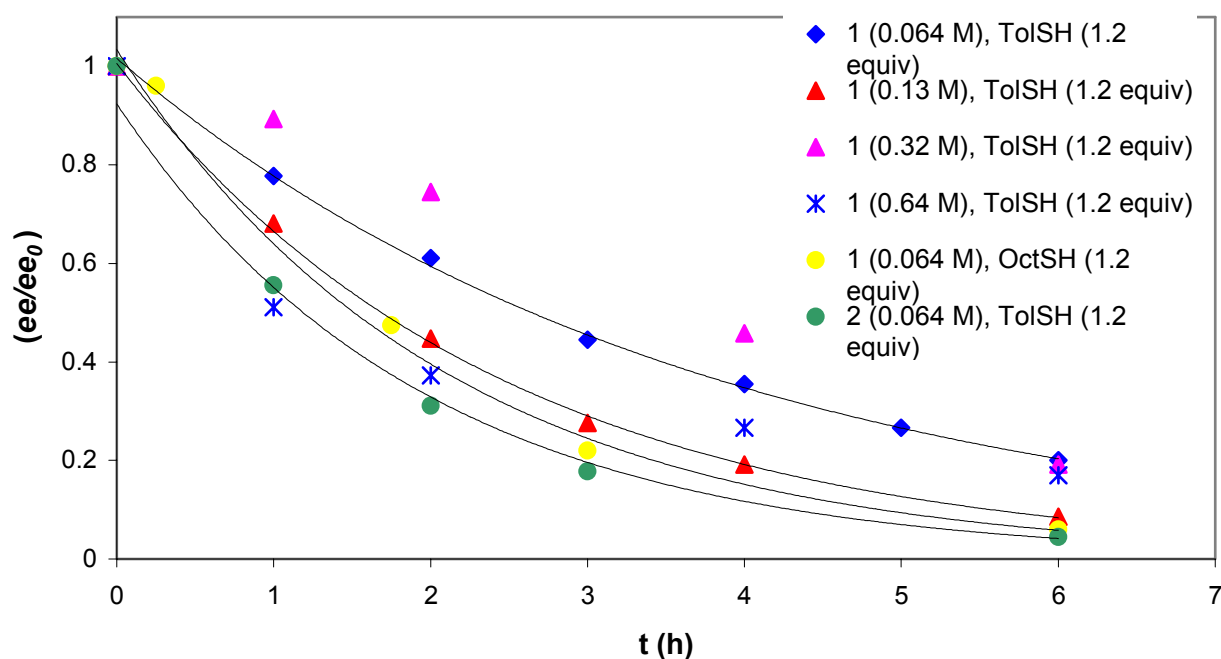
**Title:** Thiyl Radical Mediated Racemization of Benzylic Amines

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**Ref. No.:** O200600120

The variation of  $ee$  versus time was monitored (Figure 1). In spite of the portionwise addition of AIBN, ( $\sim 7$  mol% at 0, 2 and 4h, respectively), a linear relationship was found between  $\ln(ee/ee_0)$  and time at 0.064 and at 0.13 M concentration (Figure 2).

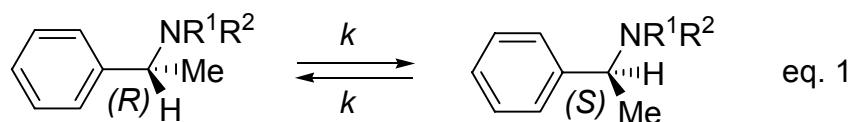
At higher concentrations (0.32 M and 0.64 M) there was no linear relationship. This could be due to the increased consumption of the thiol through the formation disulfide in the reaction medium at these concentrations.<sup>[1]</sup>



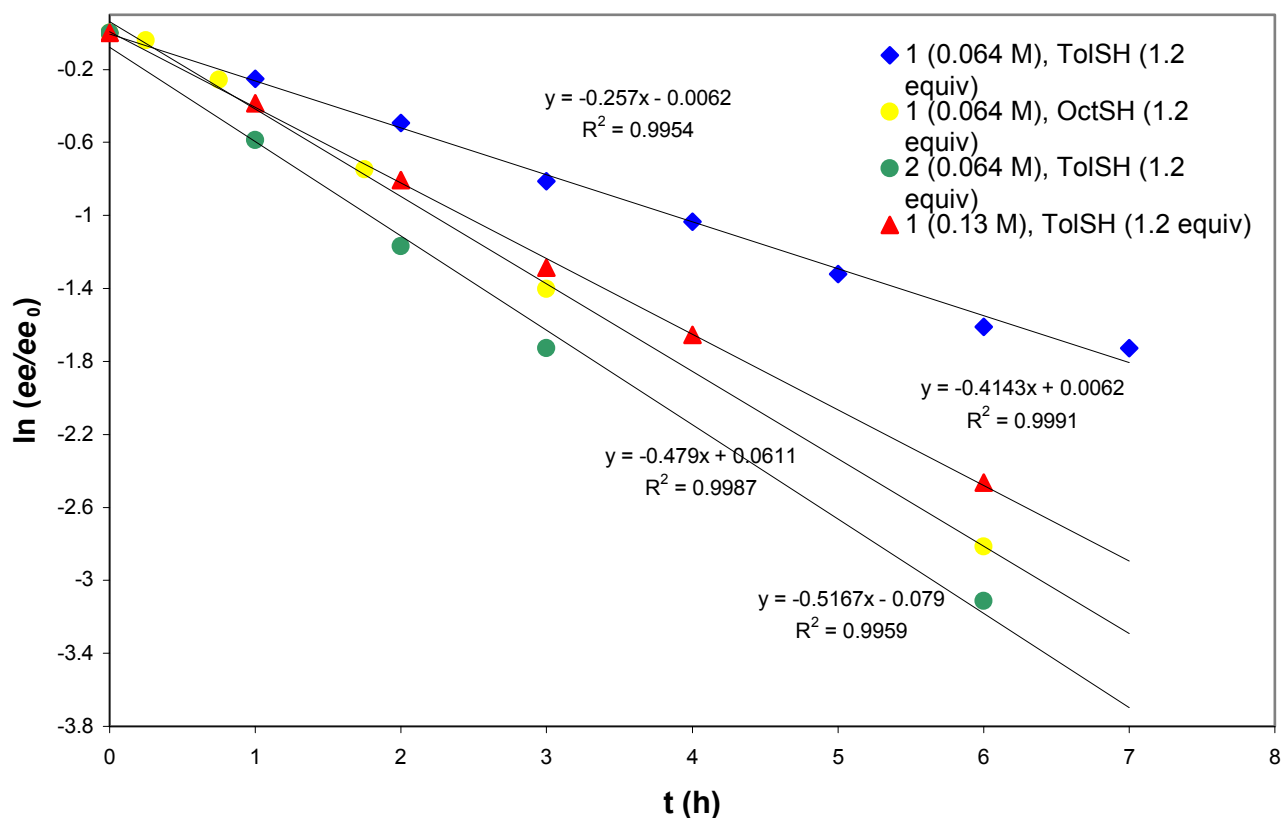
**Figure 1.** Plot of  $ee/ee_0$  at different concentrations for amines **1** and **2**

Assuming the effective concentration of initiator and, as a consequence the concentration of thiyl radical, could be roughly considered as constant enabled us to estimate the rate constant for the racemization process at these concentrations and subsequently the order of magnitude of  $k_H$ .

In the presence of 1.2 equiv of thiol, the racemization rate constants could be estimated from the slopes by the equation  $-2kt = \ln(ee/ee_0)$ , where  $2k$  is the racemization constant. This equation is adapted from the usual expression for a reversible, first-order reaction where the equilibrium constant  $K$  is 1, since the racemization can be summarized by eq. 1.



In the presence of a stoichiometric amount of thiol, the racemization proceeded slightly faster for the secondary amine **2** than for the tertiary amine **1**. The linear plots of  $\ln (ee/ee_0)$  vs time for amine **1** at concentrations 0.064 M in the presence of thiocresol, and in the presence of octanethiol, led to  $2k = 2.6 \times 10^{-1} \text{ h}^{-1}$  ( $R^2 = 0.995$ ),  $2k = 4.8 \times 10^{-1} \text{ h}^{-1}$  ( $R^2 = 0.998$ ), respectively. The constant was  $2k = 5.2 \times 10^{-1} \text{ h}^{-1}$  ( $R^2 = 0.996$ ) for the thiocresol-mediated racemization of amine **2** at the same concentration.



**Figure 2:** Plots of  $\ln(ee/ee_0)$  versus time for amines **1** and **2**.

The variation of the concentration of TolS $\cdot$  with time according to the portionwise addition of AIBN was simulated, the values are given in the Table. <sup>[2]</sup> A  $1.4 \times 10^{-4} \text{ s}^{-1}$  value was calculated

for the rate constant for the unimolecular decomposition of AIBN at 353K according to Van Hook and Tobolsky.<sup>[2]</sup>

t	[TolS•]	[TolS•]/[TolS•] <sub>0</sub>
0	5.47E-09	1
1	4.25E-09	0.78
2	6.38E-09	1.17
3	4.96E-09	0.91
4	6.69E-09	1.22
5	8.61E-09	1.57
6	4.04E-09	0.74
	6.73E-09	1.23

**Table.** Estimated concentration of TolS• versus time

Taking the average value of [TolS•] led to a rough estimate  $k_H = k_t / [\text{TolS}\bullet]$ . The value is very close to  $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

It can be noted that when the initial concentration was doubled (0.13 M), the quantity of initiator was also doubled and a linear relationship between  $\ln(ee/ee_0)$  and time was still observed. The ratio of the corresponding estimated racemization constants ( $0.41/0.26 = 1.57$ ) is consistent, within the limits of experimental errors, with the estimated average values for [TolS•] ( $9.6 \times 10^{-9} / 6.7 \times 10^{-9} = 1.43 \sim \sqrt{2}$ ).

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[1] The formation of diphenyldisulfide could be monitored by <sup>1</sup>H NMR, whereas the formation of ditolyldisulfide could not. When amine **3** (0.64 M) was allowed to react with 1.2 equiv. of PhSH, in 6 h, 50% of the initial molar amount of thiol was consumed by the formation of (PhS)<sub>2</sub>, whereas less than 10% of disulfide were detected at 0.064 molar concentration.

[2] The average value of [TolS•] was estimated assuming the rate of initiation equal to the rate of termination, *i.e.*,  $[\text{TolS}\bullet] = (2 \times 0.5 \times k_d [\text{AIBN}] / 2k_t)^{1/2}$ . The rate of decomposition of AIBN at 353 K was determined from J. P. Van-Hook, S. Tobolsky, *J. Am. Chem. Soc.* **1958**, *80*, 779-782, a 50% efficiency was taken into account; and a  $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  value was assumed for  $2k_t$ , according to C. Chatgililoglu, A. Abdelouahid, M. Guerra, H. Fischer, *Chem. Phys. Chem.* **2005**, *6*, 286-291.