SYNTHESIS AND ASYMMETRIC INDUCTION OF AZIRIDINOKETONES

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The reaction of diphenyl free sulfilimine with cis- and trans-dibenzoylethylene in benzene gave trans-2,3-dibenzoylaziridine(1)(~50%) and trans-1-amino-2,3-dibenzoylethylene(2)(~50%). Dimethyl fumarate and dimethyl maleate also gave the corresponding trans-aziridine(~40%) and trans-enamine(~20%). Trans-benzalacetophenone gave aziridine in good yield. However, phenyl vinyl sulfone or acrylonitrile afforded not the corresponding aziridine but N-alkylsulfilimine. The configuration of 2,3-dibenzoylaziridine was assigned as trans form by observation of NMR methine signals of the corresponding N-chloroaziridine prepared by treating it with t-butyl hypochlorite.

Kinetic experiments and examination of the solvent effects were carried out in the reaction of dibenzoylethylene. The solvent effect on the rate is rather small but product ratio of the aziridine to the enamine (1:2) was substantially varied by changing the solvent. In the case of the reaction in benzene solution, very small activation energy (5.81 kcal/mole) and large negative activation entropy (-50.1 e.u.) were obtained. From the temperature dependency of the product ratio, it was found that activation energy and entropy in the formation of aziridine is 14.9 kcal/mole, and 48.9 e.u. larger than those for the formation of enamine. The product ratios also depend on the concentration, namely, the higher the concentration, the lower the yield of aziridine.

Optically active 2-acylaziridines were synthesized in one step by treating optically active o-methoxyphenyl phenyl sulfilimine with cis- and trans-dibenzoylethylene, benzalacetophenone, and benzalacetone in various solvents. Optical purity of 2-benzoyl-3-phenylaziridine(3) was found to be ca. 30%. CD spectrum of (3) and comparison with that of (-)-(1R,2R)-trans-1-benzoyl-2-phenylcyclopropane suggested that the aziridine (3) should have (2R,3R)-configuration.