SYNTHESIS, STEREOCHEMISTRY, AND REARRANGEMENT OF 9-ALKYL- AND $9-PHENYL-THIOXANTHENE\ N-p-TOLUENESULFONYLSULFILIMINES$

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cis- and trans-9-Methyl (la), cis- and trans-9-ethyl- (lb), trans-9-isopropyl- (lc), and cis- and trans-9-phenyl-thioxanthene N-p-toluenesulfonylsulfilimines (ld) were prepared by two methods; (A) tosylation of 10-aminothioxanthenium mesitylenesulfonates which were obtained by the reaction of the corresponding thioxanthenes with 0-mesityl-enesulfonylhydroxylamine, and (B) reaction of the thioxanthenes with chloramine-T. The stereochemistry of the sulfilimines la-d was ascertained by an examination of the NMR spectra of la-d and by the thermal equilibration of la-d. Upon treatment with base in benzene, la-d rearranged to the corresponding 9-substituted 9-(N-p-toluene-sulfonamido)thioxanthenes (2a-d). The rates of the rearrangement of la-d decreased in the order trans-la,ld>trans-lb>cis-ld>cis-la>cis-lb>trans-lc.

a, R=Me; b, R=Et; c, R=i-Pr; d, R=Ph