CONFIGURATIONAL STABILITY OF NITROGEN IN 1-TOSYLOXY-2,2-bis(TRIFLUOROMETHYL)AZIRIDINE

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A new class of thermally stable compounds with frozen inversion of the asymmetrical nitrogen, viz., $R-NCH_2C(CF_3)_2$ ($R=p-X-C_6H_4SO_3$), was found in the 2,2-bis(trifluoromethyl)aziridine series [1]. The NMR

spectrum of the protons of the Y ring of the AB type with additional splitting in the ^{19}F nuclei does not change on heating to 190° in nitrobenzene. The introduction into R of suitable functional groups opens up the possibility for separation into enantiomers. Aziridines with other electronegative N-substituents (R = MeO and Me₂N) cannot be obtained: II and III do not react with diazomethane because of weakening of the polarization of the C=N bond due to the positive mesomeric effect of R

$$\begin{aligned} &(\mathrm{CF_3})_2\,\mathrm{C}\!=\!\mathrm{NOMe}\,\,(\mathrm{II}) \underbrace{\overset{\mathrm{CH_2N_2}}{(\mathrm{C_4H_5})_2\,\mathrm{O}}}_{(\mathrm{CF_3})_2\,\mathrm{C}}\,(\mathrm{CF_3})_2\,\mathrm{C}\!=\!\mathrm{NOH}(\mathrm{I}) \underbrace{\overset{\mathrm{TsCl}}{\mathrm{C_5H_5N}}}_{\mathrm{C_5H_5N}}\,(\mathrm{CF_3})_2\,\mathrm{C}\!=\!\mathrm{NOTs}\,\,(\mathrm{III}) \\ &(\mathrm{CF_3})_2\,\mathrm{CCH_2N}\,\mathrm{OTs}(\mathrm{V}) \underbrace{\overset{\mathrm{CH_2N_2}}{(\mathrm{C_2H_5})_2\,\mathrm{O}}}_{(\mathrm{C_2H_5})_2\,\mathrm{O}}\,\,(\mathrm{III}) \xrightarrow{\mathrm{Me_2NH}}_{\mathrm{CF_3}}\,\,(\mathrm{CF_3})_2\,\mathrm{C}\!=\!\mathrm{NNMe_2}\,\,\,(\mathrm{IV}) \end{aligned}$$

Compound I was obtained by the method in [2]. II was obtained in 37% yield and had bp 43-46°, n_D^{20} 1.2985, δ_{Me} 4.22 ppm (in CCl₄ with tetramethylsilane as the internal standard), and M⁺ m/e 195 (66%). III was obtained in 85% yield and had mp 86-88° (from heptane). IV was obtained in 48% yield and had bp 130°, n_D^{20} 1.3714, δ_{Me} 3.28 ppm, a multiplet (in CCl₄ relative to tetramethylsilane), and M⁺ m/e 208 (75%). V was obtained in 25% yield and had mp 65-67° [from heptane and sublimation at 60° (1 mm)], and M⁺ m/e 349 (7.5%). PMR spectrum (in CCl₄ relative to tetramethylsilane): ring protons at δ_{Ha} 2.73 and δ_{Hg} 3.13 ppm, J_{AB} = 5.2, $J_{\text{Ha}\text{CF}_3}$ = 2.1, $J_{\text{Hg}\text{CF}_3}$ = 0.75 Hz, δ_{Me} 2.45 ppm, phenyl protons at 7.34 and 7.8 ppm, J_{AB} = 8.5 Hz; ¹⁹F NMR (in CCl₄ with C₆F₆ as the internal standard): δ_{CF_3} -93.5 and -101.5 ppm, $J_{\text{CF}_3\text{CF}_3}$ = 7.3 Hz.

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