NEIGHBORING GROUP PARTICIPATION BY PYRIDINE RINGS AND N-OXIDES. SYNTHESIS AND REACTIONS OF 5,8-DIHYDRO-5,8-METHANOISOQUINOLINE DERIVATIVES

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Aromatic ring substituents have been found to exert a linear $\rho\sigma^+$ relationship ($\rho = -3.09$ on hydrolysis in 50% aqueous t-butanol at 50°C) on solvolyses of benzonorbornen-6(exo)-yl arenesulfonates and to cause stereochemical variation in the product (retention or inversion). This kind of research was extended to a pyridine system, 5,8-dihydro-5,8-methanoisoquinoline and N-oxide derivatives. When the rate of benzonorbornen-6(exo)-yl arenesulfonate in 50% aqueous t-butanol is assigned as 1, substituent effects at 3 position on the relative rates of 5,8-methano-5,6,7,8-tetrahydroisoquinolin-7(exo)-yl arenesulfonates are shown as 1.5 for CH_3O, 4.4×10^{-2} for CH_3, 5.9×10^{-3} for H, and 8.9×10^{-4} for Cl. The $\rho\sigma^+$ treatment gave a straight line with ρ value of -3.45 at 50°C. With the unsubstituted 5,8-methano-5,6,7,8-tetrahydroisoquinolin-exo-yl arenesulfonates and their N-oxides, relative rates are summarized as 1.8×10^{-5} for 6(exo), 5.1×10^{-4} for 6(exo) N-oxide, 5.9×10^{-3} for 7(exo), and 5.1×10^{-6} for 7(exo) N-oxide. Addition of hypochlorous acid for 5,8-dihydro-5,8-methanoisoquinoline yielded mainly 5,8-methano-5,6,7,8-tetrahydro-9(anti)-chloroisoquinoline-7(exo)-ol and the reaction for the corresponding N-oxide yielded mainly the corresponding 6(exo)-ol. The solvolyses and additions give evidence for an electron-supplying character of the N-oxide function for the homopara transition state and an electron-withdrawing character of that for the homometa state.