Nitrogen inversion barriers in several acyclic dialkylhydroxylamines and their acetyl derivs. are detd. by 1H NMR band shape anal. A barrier range of 50.0-57.7 kJ/mol is obsd. The hydroxylamines with bulky substituents show a lower barrier. The smaller activation barrier for the acetyl derivs. reflects the dominance of π-repulsive character of oxygen lone pairs in the transition state during nitrogen inversion.