I36

IMIDOTETRAFLUOROSULFUR DERIVATIVES – SYNTHESIS, STEREOCHEMICAL RIGIDITY AND *AB INITIO* RESULTS

Matthew Clark, Jon B. Nielsen, Annmarie A. Mauerman and Joseph S. Thrasher*
Department of Chemistry, University of Alabama, P.O. Box H, Tuscaloosa, AL 35487-9671 (U.S.A.)

Imidotetrafluorosulfur derivatives of the type $SF_4NC(O)NR_2$ (1) [where R = CH_3, C_2H_5 (Clifford, A.; Howell, J. J. Fluorine Chem. **1977**, 10, 431)] can be prepared from the reaction of pentafluorosulfanyl isocyanate with dialkylaminotrimethylsilanes. These compounds are formed by the loss of trimethylfluorosilane from the intermediate silylamides $SF_5N(SiMe_3)C(O)NR_2$ (2). Further reaction of 1 with an additional equivalent of nucleophile leads to substitution at the sulfur, i.e. $R_2NSF_3{=}NC(O)NR_2$ (3). Variable temperature NMR studies have been undertaken in order to elucidate the dynamic intramolecular rearrangements possible in compounds 1 and 3. Th results of this study as well as an ab initio study of the relationship between the orientation of the S=Nπ bond and structural rigidity in $SF_4{=}NX$ derivatives [X=F, Cl, CF_3, SF_5, $C(O)NH_2$, CH_3, H (Günter, H.; Oberhammer, H.; Mews, R.; Stahl, I. Inorg. Chem. **1982**, 21, 1872), CH_3] will be presented.

Attempts to prepare derivatives related to 1 from the reaction of SF_5NCO with alkoxytrimethylsilanes gave instead the novel isocyanates cis-$ROSF_4NCO$ (4) (where R = CH_3, C_2H_5, n-C_3H_7, and $CH_2CH_2OSiMe_3$). The fact that only the cis-products are observed suggests that an intramolecular alkoxy group migration takes place following the loss of trimethylfluorosilane from the intermediate $SF_5N(SiMe_3)C(O)OR$ (5). The reaction of 5 with CsF gives the salts $Cs^+[N(SF_5)C(O)OR]^-$ (6).