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CONFORMATIONAL FEATURES OF FLUORINATED MONO- AND DIACYL-HYDRAZINES

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The structure and conformational features of N-Me, N-i-Pr, N-Ph-perfluoroacyl- and bis(perfluoroacyl)hydrazines prepared by the scheme

$R_FCOX + NH_2NHR \longrightarrow R_FCONHNHR$ (I)

$R_FCONRNHCOR_f$(II) with R_F = CF_3, C_2F_5, C_3F_7, C_4F_9, C_6F_{13}; X = OMe, $OCOR_F$, NH_2, Cl; R = H, Me, i-Pr, Ph have been studied by ^1H, ^{13}C, ^{19}F NMR spectroscopy. The data obtained have been compared with the results for nonfluorinated analogs and 1,2-diacyldimethylhydrazines (III). Restricted N-CO bond rotation accounts for the existence of monoacylhydrazines as two (E and Z) and diacylhydrazines as four conformations (EE, ZE, EZ and ZZ). Conformations conditioned by the restricted rotation about the N-N bond are not detected in the NMR spectra. Compounds I are in exclusively the Z-form. For II with R = H, the ZZ-conformation is typical, for those with R = Me, i-Pr, Ph, of the two forms observed the EE rotamer is predominant over the ZE.

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THE SYNTHESIS AND CHEMISTRY OF N-HALOALKYL-1,1-DIFLUOROMETHYL-AMINES

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The synthesis andchemistry of N-haloalkyl-1,1-difluoromethylenimines will be presented. At high temperature, CF_2=NCl reacts with olefins, by a free radical process, to provide RN=CF_2 (R = CF_2CF_2Cl, CF_2CFCl_2, CF_2CH_2Cl, $CF_2CFClBr$) in high yields. The reactions of these compounds with CF_3OOH result in the formation of CF_3OOCF_2HNR by addition across the C-N double bond. These amines yield the corresponding oxaziridines, $RNCF_2O$, upon reaction with KHF_2 at 22°C. The compounds CF_2=NR are isomerized by CsF to CF_3N=CFR' (R' = CF_2Cl, $CFCl_2$, CFClBr, CH_2Cl) at room temperature in excellent yields. All of the new compounds were characterized by their IR, NMR, and mass spectra, and their physical properties were determined.