

NEW FLUORINE-CONTAINING PENTACOORDINATE SILICON COMPOUNDS

M. G. Voronkov, L. I. Gubanova, V. A. Pestunovich and Yu. L. Frolov

Institute of Organic Chemistry, Siberian Division, Ac. Sci. USSR, 1 Favorsky Street, 664033 Irkutsk (U.S.S.R.)

Dimethyl(trifluoroacetoxymethyl)acyloxysilanes, $F_3CCOOCH_2Me_2SiOCOR$ ($R = Me, CF_3$) with a pentacoordinate Si atom (according to ^{29}Si NMR data) have been synthesized. A new type of pentacoordinate silicon derivatives, organyltetraacyloxysilicates, $M^+[XCH_2Si(OCOF_3)_4]^-$ and dimethyltris(trifluoroacyloxy)silicates, $M^+[Me_2Si(OCOCF_3)_3]^-$ were revealed for the first time by ^{29}Si NMR spectroscopic titration of $XCH_2Me_{3-n}Si(OCOF_3)_n$ ($X = H, Cl, Br, I; n = 2, 3$) with trifluoroacetic and acetic salts, $RCOOM$ ($M = NH(C_2H_5)_3, N(C_2H_5)_4, Na$). The reaction of $XC_6H_4COOCH_2SiMe_{3-n}(OR)_n$ ($n = 1-3$) with SF_4, HF, BF_3 affords $XC_6H_4COOCH_2SiMe_{3-n}F_n$. These compounds can also be prepared by the reaction of $ClCH_2SiMe_{3-n}F_n$ ($n = 1-3$) with XC_6H_4K . Judging by X-ray diffraction, the silicon atom in $XC_6H_4COOCH_2SiMe_{3-n}F_n$ ($n = 2, 3$) is pentacoordinate. The presence of intramolecular coordinate $Si \leftarrow O$ bond is clearly manifested in the IR and $^{13}C, ^{17}O, ^{19}F$ and ^{29}Si NMR spectra of these compounds. In non-polar solvents $C_6H_5COOCH_2SiF_3$ forms 1:1 complexes with organic bases such as pyridine, triethylamine, 2,2'-bipyridine, 2-phenanthroline, N,N,N',N'-tetramethylethylenediamine. The reaction of (aroyloxymethyl)trifluorosilanes with KF, CsF and NH_4F gives the corresponding (aroyloxymethyl)tetra- and pentafluorosilicates, $M_n^+[XC_6H_4COOCH_2SiF_{3+n}]^{n-}$ ($M = K, CsF, NH_4; n = 1, 2$). The IR and UV spectra suggest the silicon atom in (aroyloxymethyl)-pentafluorosilicates to be heptacoordinate.