SUBSTITUTION REACTIONS OF IF_5

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Using silyl protected organic hydroxo compounds substitution of fluorine in IF_5 is successful.

Reacting IF_5 with $Si(OCH_3)_4$ in CH_3CN or SO_2 using different molar ratios it was shown that in the series $IF_{5-n}(OCH_3)_n$ only the first member $IF_4(OCH_3)$ (n=1) is stable enough to be isolated. The product in solution with n=2 bismutates to products with n=1 and n=3 if isolated as solids. The last one decomposes to the new oxo compound $IF_2O(OCH_3)$ under elimination of CH_3OCH_3. With n=4,5 only redox reaction products could be isolated.

$IF_2O(OCH_3)$ can also be obtained by treating $IF_4(OCH_3)$ with $(CH_3)_6Si_2O$. Similarly reaction of IF_5 with the disiloxane represents a new method to win IOF_3. Excess of the oxygen transfer reagent leads to formation of IO_2F and I_2O_5. An other oxo compound, $IO(CH_3COO)_3$, can be prepared by disolving IF_5, IOF_3 or IO_2F in acetic acid anhydride.

Reactions of IF_5 with trimethylsilyl protected fluorinated benzoic acids $R_fCOOSi(CH_3)_3$ ($R_f = C_6F_5$, 4-H-C_6F_4) appeared to be independent of the educts' molar ratios because the only products are $IF(R_fCOO)_4$.

In order to stabilize iodine (V) derivates with bifunctional chelating oxo ligands we applicated bis(trimethylsilyl)pinacolate, and in smooth reactions we yielded $IF_3[OC(CH_3)_2{-}C(CH_3)_2O]$ and $IF[OC(CH_3)_2-C(CH_3)_2O]_2$, in which iodine is part of five membered heterocyclic rings. The ^{19}F-nmr-spectra are consistent with the diolate occupying the axiale and equatorial positions.

An extension of the silyl method is the new synthesis of $C_6F_5IF_4$ which could be obtained in the smooth reaction of IF_5 with stochiometric amounts of $Si(C_6F_5)_4$.