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ON THE SUBSTITUTION-REACTION OF IF_5 BY OXO-COMPOUNDS

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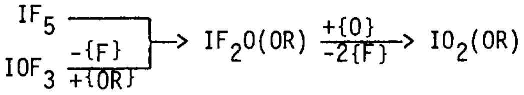
Fluorine in IF_5 can be replaced by oxogroups using silylated alcoholes, carboxylates or siloxane itself. Systematic investigations of the fluorine-monoalcoholate-exchange in solution [1] show that $IF_4(OR)$ is the only stable exchange-product at room temperature. Higher substitution products are unstable and undergo bismutation- and elimination-reactions:

$$IF_3(OR)_2 \longrightarrow IF_4(OR) + IF_2(OR)_3 \qquad IF_2(OR)_3 \xrightarrow{-ROR} IF_2O(OR)$$

IO_2OR as the final product of nucleophilic exchange results on different routes:



$$\begin{array}{l} IF_5 \\ IOF_3 \end{array} \xrightarrow[+\{OR\}]{-\{F\}} IF_2O(OR) \xrightarrow[-2\{F\}]{+\{O\}} IO_2(OR)$$

α-Branching in the aliphatic alcoholic group results in higher instability (alkylfluoride-elimination) of the iodine(V)fluoride alcoholates.

No stable iodine(V)fluoride phenolates can be prepared.

Using di- and trialcoholates two competing reaction products can be observed: $IF_4O(CRR')_nOIF_4$ and $IF_3[O(CRR')_nO]$

In addition higher exchange products are formed: $IF[O(CRR')_nO]_2$

Expanding our exchange-concept to the IF_5-carboxylate-system it was possible to synthesize $IO(O_2C\text{-}R)_3$, $IO_2(O_2C\text{-}R)$, and in the case of the oxalate-group: $IF_3(O_2CCO_2)$ and $IFO(O_2CCO_2)$.

1 H.J., Frohn, W.Pahlmann
J. Fluorine Chem., in press