

PENTAFLUOROPHENYL COMPOUNDS OF POLYVALENT IODINE

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The oxidation of  $C_6F_5I$  by oxidizers containing positive chlorine was investigated with the intention to prepare pentafluorophenyl iodine (III) compounds:  $C_6F_5IX_2$ , where X are halides or oxoderivatives. Using  $ClF$ ,  $ClOCF_3$ ,  $Cl_2/AlCl_3$  or  $Cl_2O$  as oxidizers  $C_6F_5IF_2$ ,  $C_6F_5I$  and  $C_6F_5I(OCl)_2$  - all thermally unstable - could be prepared and characterized.

In contrast to these compounds the perfluoroaromatic carboxylates:  $C_6F_5I [O(O)C R_F]_2$  are crystalline solids thermally stable up to 200 °C. Single crystal investigations show T-coordinated iodine with significant secondary bonding between iodine and the keto oxygens.

$C_6F_5IO$  - formed by hydrolysis of  $C_6F_5IX_2$  - changes if stored at RT forming  $(C_6F_5)_2I^+ IO_3^-$ .

$(C_6F_5)_2I^+$  - formation is also observed when  $C_6F_5IO$  is heated in inert ( $C_6F_5I$ ,  $C_6H_6$ ,  $CCl_4$  ...), protic ( $H_2O$ ,  $CH_3OH$ , ...) and strong acidic ( $FSO_3H$  ...) dilution medium.

$C_6F_5IO$  reacts with acids, acid anhydrides and acid halides as could be shown by the preparation of  $C_6F_5ICl_2$  and  $C_6F_5ICl(NO_3)$ .

Starting with  $C_6F_5IX_2$  different preparative ways for  $(C_6F_5)_2I^+$  - compounds were successful. Principally  $(C_6F_5)_2IX$  - compounds decompose thermally forming  $C_6F_5I + C_6F_5X$ .

$C_6F_5IX_4$  - compounds can be obtained from  $C_6F_5IF_4$  which is the specific displacement product of  $IF_5$  with  $Si(C_6F_5)_4$ .

By nucleophilic displacement it is possible to prepare  $C_6F_5IF_2O$ ,  $C_6F_5IO_2$ ,  $C_6F_5IO(OAc)_2$  and  $C_6F_5I [OC(CH_3)_2 - C(CH_3)_2O]_2$ , which are all white, thermally stable solids.

For the fluorine-ligand-exchange we used silyl compounds as reagents. If the ligand is oxidable by  $C_6F_5I(V)$  a stepwise reduction via  $C_6F_5I(III)$  to  $C_6F_5I$  could be shown by NMR-measurements.