

CESIUM FLUORIDE PROMOTED FORMATION OF N-CHLORO AND N-BROMO AMINES AND IMINES

D. D. DesMarteau*, B. A. O'Brien, Q.-C. Mir and Y. Y. Zheng

Clemson University, Clemson, SC 29631 (U.S.A.)

Cesium fluoride is a very effective reagent for the fluoride promoted oxidation of nitriles and imines by Cl_2 , Br_2 and BrCl . Previous work by us had demonstrated that CsF fluoride was effective in promoting the oxidation of $\text{R}_f\text{CF}=\text{NF}$ by Cl_2 and Br_2 to $\text{R}_f\text{CF}_2\text{NFCl}$ and $\text{R}_f\text{CF}_2\text{NBr}$, the oxidation of R_fCN to $\text{R}_f\text{CF}_2\text{NCl}_2$ by Cl_2 and the apparent oxidation of R_fCN to $\text{R}_f\text{CF}=\text{NBr}$ by Br_2 (S.C. Chang and D. D. DesMarteau, Inorg. Chem. 1983, 48, 771).

We have now made a detailed investigation of the CsF promoted oxidation of R_fCN , $\text{NCCF}=\text{NF}$, $\text{CF}_2=\text{NCl}$, $(\text{CN})_2$ and $\text{CF}_3\text{N}=\text{CFR}_x$ by Cl_2 , Br_2 and BrCl . Significant results to be discussed will include the general high yield syntheses of $\text{R}_f\text{CF}=\text{NBr}$, $\text{CF}_3\text{N}(\text{Cl})\text{CF}_2\text{R}_x$, a comparison of the reactivity of $-\text{C}\equiv\text{N}$ vs $-\text{CF}=\text{NF}$ in $\text{NCCF}=\text{NF}$, the stepwise halogenation of $(\text{CN})_2$ by Cl_2 and Br_2 , the novel compounds CF_3NBrCl and CF_3NBr_2 from $\text{CF}_2=\text{NCl}$ and the unique CsF promoted conversion of R_fNCl_2 by Br_2 to R_fNBrCl and R_fNBr_2 . Furthermore, the utility of BrCl -vs- Cl_2 in the formation of certain N-chloro compounds will be shown.