REACTIONS OF SOME NITROFLUOROAROMATICS WITH THE METHANETHIOLATE ANION

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Previous studies on the reactions of simple fluoroaromatics, ${^C6F_x}{^H}_{6-x}$, with sodium methanethiolate in an ethylene glycol/pyridine solvent mixture have shown that at least two fluorine atoms remained

$$C_6F_5H + SMe^- \rightarrow C_6F_2H(SMe)_2$$

on the aromatic ring. When the reactions of simple nitrofluoro-aromatics, $C_6F_xH_yNO_2$ were studied under the same conditions stepwise replacement of all the aromatic fluorines was observed. This clearly demonstrates the activating effect of the nitro group in these reactions, and is in marked contrast to the deactivating effect of the amino group observed previously in analogous reactions of the fluoroaniline. Details of these reactions will be discussed. In one case the expected substitution was not observed and an azoxybenzene was formed.

The methylthio group can readily be oxidized, but

$$\sum_{\text{SMe}}^{\text{NO}_2} \longrightarrow \sum_{\text{FO}_2^{\text{Me}}}^{\text{NO}_2}$$

simple reduction of the nitrogroup to an amino group was not feasible.

All the new compounds isolated have been characterized by chemical analysis and mass spectroscopy. The structures have been determined by NMR spectroscopy usually proton and/or fluorine, but in cases of ambiguity the carbon-13 spectra have also been examined.