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REACTIONS OF TIN(II) AND LEAD(II) THIOLATES WITH SOME FLUOROAROMATICS

Rosemary C. Hynes, Michael E. Peach* and Kevin C. Smith

Department of Chemistry, Acadia University, Wolfville, N.S. (Canada)

The aromatic thiolates of tin(II) and lead(II), $M(SAr)_2$ (M = Sn, Pb) are readily prepared, and are stable at room temperature. The reactions of these thiolates $Sn(SAr)_2$ (Ar = Ph, $\underline{p}$-$CH_3C_6H_4$) and $Pb(SPh)_2$ with various fluoroaromatics have been studied in DMF. The $Pb(SPh)_2$ was reasonably soluble in DMF, but $Sn(SAr)_2$ was not very soluble, forming a suspension.

Although the reactions do not give complete fluorine substitution, as occurs with sodium thiolates

$$C_6F_6 + NaSR \xrightarrow{DMF} \underline{p}\text{-}(RS)C_6F_4;\ \underline{p}\text{-}F_2C_6(SR)_4;\ C_6(SR)_6$$

$$C_6F_6 + Pb(SPh)_2 \longrightarrow \underline{p}\text{-}(PhS)_2C_6F_4;\ \underline{p}\text{-}F_2C_6(SPh)_4$$

$$C_6F_6 + Sn(SAr)_2 \longrightarrow \underline{p}\text{-}(ArS)_2C_6F_4$$

in DMF, there are several advantages. The extent of the reaction can be followed visually as the yellow colour of the metal thiolate is replaced by that of the colourless fluoride. The generation of the free thiol is eliminated at the quenching stage, as no acid is required. The disadvantages are that the displacement does not occur to the same extent and the reactions are not as rapid, when compared with those of sodium thiolates. The aliphatic thiolates of the heavy metals do not appear to be sufficiently stable to be used in this type of reaction.

The new products have been fully characterized by elemental analysis; mass infrared and nuclear magnetic resonance (H-1 and F-19) spectroscopy. A possible mechanism of the reaction will be discussed.