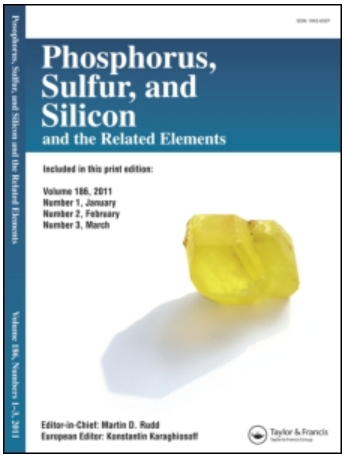

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REACTIONS OF COPPER (I) THIOLATES WITH HALOAROMATICS

W. James Frazee[a]; Linda J. Johnston[a]; Michael E. Peach[a]
[a] Department of Chemistry, Acadia University, Wolfville, Canada

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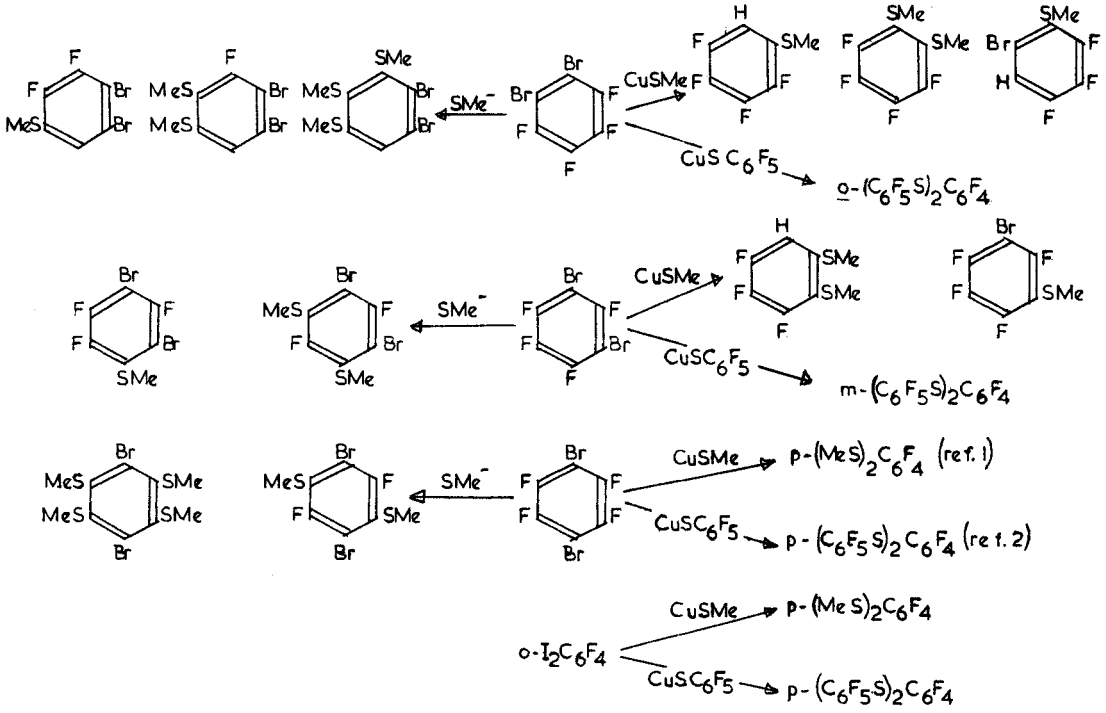
REACTIONS OF COPPER (I) THIOLATES WITH HALOAROMATICS

W. James Frazee, Linda J. Johnston and Michael E. Peach

Department of Chemistry, Acadia University, Wolfville, Nova Scotia, Canada

Recent studies have shown that replacement of I or Br and not Cl or F in haloaromatic compounds occurred when copper (I) thiolates, CuSR, were used as nucleophiles. Some proto debromination was also observed. Conversely using the free thiolate anion, SR^-, in solution, replacement of F or Cl rather than I or Br in haloaromatic compounds was observed. These general observations have been confirmed in the reactions of the isomeric dibromotetrafluorobenzenes with copper (I) methanethiolate, copper (I) pentafluorothiophenolate, and the methanethiolate anion.



All the new compounds isolated have been characterized fully by chemical analysis, mass and infrared spectroscopy and their structures deduced from their proton and fluorine NMR spectra.

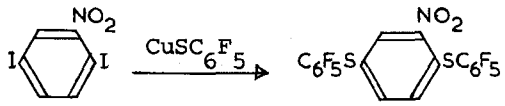
Copper (I) pentafluorothiophenolate has been studied as a nucleophilic reagent for introducing the C_6F_5S group into aromatic compounds by replacement of Br or I. The pentafluorothiophenolate anion, $C_6F_5S^-$, cannot readily be used as a nucleophile due to its polymerization in basic solution. The reactions studied of $CuSC_6F_5$ include those with dibromo and diiodotetrafluorobenzene and those listed below

$$p\text{-}HalC_6H_4X \xrightarrow{CuSC_6F_5} p\text{-}(C_6F_5S)C_6H_4X$$

Hal = I, X = Me, Cl

Hal = Br, X = CO_2C_6F, OMe, $p\text{-}C_6H_4.C_6H_5$

$$p\text{-}I_2C_6H_4 \xrightarrow{CuSC_6F_5} p\text{-}IC_6H_4SC_6F_5 \ , \ p\text{-}(C_6F_5S)_2C_6H_4$$



$$BrC_6F_4X \xrightarrow{CuSC_6F_5} C_6F_5S.C_6F_4X \quad \text{(ref. 2,3)}$$

X= NO_2, NH_2, F

Copper (I) pentafluorothiophenolate is readily prepared and is obviously an excellent reagent for introducing the C_6F_5S group into aromatic compounds. Details of the experimental conditions, identification of the products, etc., will be given.

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