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REACTIONS OF COPPER (I) THIOLATES WITH HALOAROMATICS

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Chemical reaction scheme showing the synthesis of various tetrafluorobenzene derivatives from 1,2-dibromo-4,5-difluorobenzene.

Starting material: 1,2-dibromo-4,5-difluorobenzene.

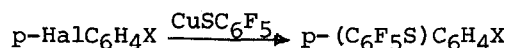
Reactions:

- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSMes}}$ 1,2-dimethoxy-4,5-difluorobenzene
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSC}_6\text{F}_5}$ *o*-(C₆F₅)₂C₆F₄
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSMes}}$ 1,2-dimethoxy-4,5-difluorobenzene
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSC}_6\text{F}_5}$ *m*-(C₆F₅)₂C₆F₄
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSMes}}$ *p*-(MeS)₂C₆F₄ (ref. 1)
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSC}_6\text{F}_5}$ *p*-(C₆F₅)₂C₆F₄ (ref. 2)
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSMes}}$ *p*-(MeS)₂C₆F₄
- 1,2-dibromo-4,5-difluorobenzene $\xrightarrow{\text{CuSC}_6\text{F}_5}$ *p*-(C₆F₅)₂C₆F₄

The scheme also shows the conversion of 1,2-dibromo-4,5-difluorobenzene to 1,2-dibromo-4,5-difluoro-3-methoxybenzene via a series of steps involving MeS⁻ and CuSMes.

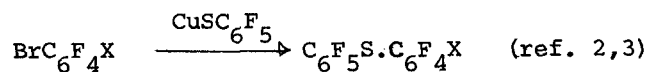
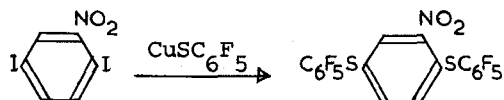
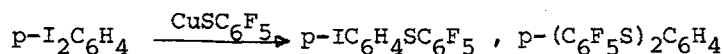
All the new compounds isolated have been characterized fully by chemical analysis, mass and infrared spectroscopy and their structures deduced from their proton and fluorine NMR spectra.

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



Hal = I, X = Me, Cl

Hal = Br, X = $CO_2C_6F_5$, OMe, $p\text{-C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$



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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