

## Aromatic Thiocyanation using Supported Copper(I) Thiocyanate

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Charcoal supported copper(I) thiocyanate can be used to convert bromo- and iodo-benzenes into phenyl thiocyanates with no contamination from phenyl isothiocyanates.

Aromatic thiocyanates may be prepared by several different methods, the most common of which is conversion of the diazotised primary aromatic amines with metal thiocyanates<sup>1</sup> although the activating effect of the diazonium group may lead to displacement of another substituent in the molecule.<sup>2</sup> The major problem with thiocyanations is the production of the corresponding, thermodynamically more stable isothiocyanate, often in appreciable quantities.<sup>3</sup> It has been reported that aryl thallium(III) compounds can be converted to the corresponding thiocyanate,<sup>4</sup> although the starting thallium precursors are unreactive if substituted with electron withdrawing groups. They are also highly toxic.

We have recently described the preparation of solid copper(I) reagents, alumina-CuI, charcoal-CuI,<sup>5</sup> alumina-CuCN, and charcoal-CuCN,<sup>6</sup> which are believed to contain both Cu<sup>+</sup> and CuX<sub>2</sub><sup>-</sup> ions dispersed on the surface of the supports. The advantages of these materials is that they are reactive towards unactivated aromatic substrates in non-polar solvents. We now report the successful preparation of supported copper(I) thiocyanate, which is a remarkably selective and easy to use thiocyanating agent.

The supported reagent charcoal-CuSCN was prepared *via* KCu(SCN)<sub>2</sub>. CuSCN in aqueous KSCN was stirred with the required amount of charcoal. Water was added at a rate of 30

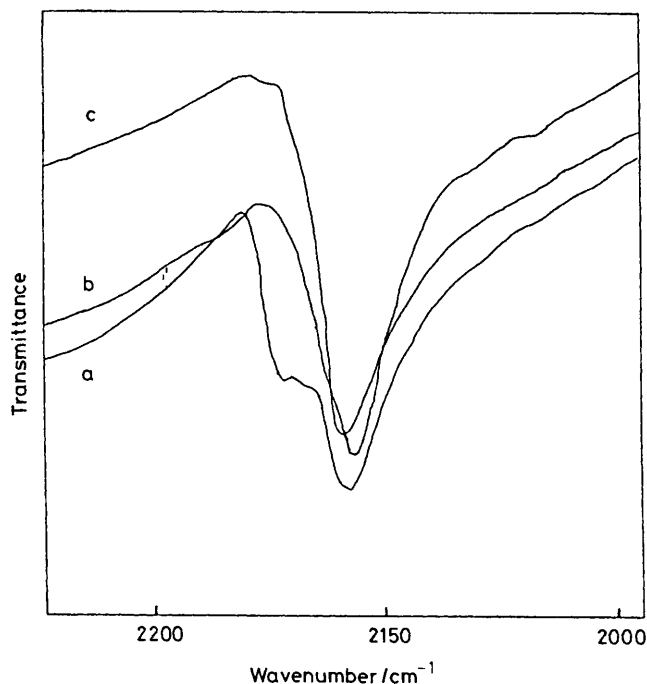
ml per h over a period of several hours to precipitate slowly the CuSCN onto the charcoal. The charcoal-CuSCN support was filtered, washed several times with water, ethanol, and ethoxyethane before being dried under vacuum at 120 °C for 24 h. In a typical reaction charcoal-CuSCN (3.3 mmol/g of support) was stirred vigorously with 1-iodo-2-nitrobenzene (4-CuSCN: aromatic substrate) in *t*-butylbenzene solvent at 150 °C for 7 h. Work-up of the reaction mixture (filtration and purification by column chromatography) gave an isolated yield of 68% of analytically pure 2-nitrophenylthiocyanate [mass spec. *m/z* 180 (*M*<sup>+</sup>), 134 (*M* - 46<sup>+</sup>), 122 (*M* - SCN<sup>+</sup>); i.r.  $\nu$  2162 (SCN), 733 (CS) cm<sup>-1</sup>; <sup>13</sup>C n.m.r.  $\delta$  137 (C-NO<sub>2</sub>) and 131 (C-SCN); negative chemical test for isothiocyanate].<sup>7</sup> Generally, infrared analysis was the most useful analytical technique, the  $\nu$ (SCN) asymmetric mode occurring as a sharp band of half-band width *ca.* 15 cm<sup>-1</sup>, easily distinguished from the  $\nu$ (SCN) mode of the isothiocyanate which is broad (half-band width *ca.* 100 cm<sup>-1</sup>).<sup>8</sup>

In an attempt to elucidate the nature of the active thiocyanating species, F.t.i.r. spectra were run before and after the reaction with iodobenzene, along with that of an unreactive version of the supported reagent (prepared by fast precipitation of the salt onto the charcoal surface). The support before reaction shows a pronounced shoulder at 2173

**Table 1.** Results of exchange reactions between aryl iodides and bromides and charcoal-CuSCN.

Substrate <sup>a</sup>	Time/h	Conversion to thiocyanate <sup>b</sup>	% Conversion to monosulphide	% Conversion to disulphide
Iodobenzene	14	72	6	13
Bromobenzene	25	43	15	28
2-Iodotoluene	25	69	8	10
4-Iodotoluene	27	72	6	13
2-Bromotoluene	24	32	9	16
4-Bromotoluene	24	37	7	18
1-Iodo-2-nitrobenzene	7	84	0	0
1-Iodo-4-nitrobenzene	24	0	0	0
1-Bromo-2-nitrobenzene	9	71	0	0
1-Bromo-4-nitrobenzene	24	0	0	0
2-Bromobenzonitrile	12	78	0	0
3-Bromobenzonitrile	12	74	0	0
4-Bromobenzonitrile	12	81	0	0

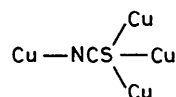
<sup>a</sup> Reactions carried out at 150°C in *t*-butylbenzene solvent; Cu:Substrate 4:1. <sup>b</sup> Reactions monitored by g.c. and yields are quoted as g.c. yields, products confirmed by g.c.-mass spectrometry, F.t.i.r. spectroscopy, and <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy.



**Figure 1.** Infrared spectra of the active form of supported CuSCN (a) before reaction, (b) after reaction, and (c) of an unreactive form.

$\text{cm}^{-1}$  [Figure (1a)] which is absent after reaction [Figure (1b)] and is not present in the unreactive material [Figure (1c)]. The frequency of this shoulder is characteristic of a bridged species in which the sulphur of thiocyanate group is interacting with neighbouring  $\text{Cu}^{\text{I}}$  centres [Figure (2)].<sup>9</sup> The band at  $2156 \text{ cm}^{-1}$  is due to the parent salt.

The system we have described can be reasonably compared to conventional copper(I) nucleophilic substitution reactions,<sup>10</sup> where unactivated aromatic halides are activated in the presence of copper(I). Our reagent has the unique advantage of being effective in non-polar solvents, and is highly selective towards thiocyanate formation. The unactivated substrates produce mono and disulphides which is believed to be due to a base catalysed reaction.<sup>3</sup> 4-Iodo- and bromo-nitrobenzenes show no reactivity towards charcoal-



**Figure 2.** Structure of active thiocyanate species.

CuSCN, which is presumably due to the nitro group having a high affinity for the surface causing the molecules to sit with their halogen centres distant from the surface bound copper species.

We have shown that CuSCN is activated for nucleophilic substitution by adsorption on charcoal, and that this supported reagent can be used for the conversion of unactivated and some activated aryl iodides or bromides to the corresponding thiocyanates. F.t.i.r. analysis of the charcoal-CuSCN has revealed an active bridged complex on the surface of the support. The reactivity can be attributed to good surface dispersion of reactive species. We believe this material represents a further breakthrough in the development of new and useful reagents for the synthetic chemist.

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