

Short Communications

Cyclopentadienylcopper Reactions with Organic Halides in the Presence of Dimethyl Sulfide

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Cyclopentadienylcopper forms complexes with various soft ligands such as phosphines, phosphites, isonitriles and carbon monoxide.¹ Cyclopentadienyl(tributylphosphine)copper (CpCuPBu₃) is rather stable and still reactive towards different organic halides. It gives cyclopentadienylarenes,^{2,3} acyloxyfulvenes⁴ and dicyclopentadienylphenylmethane⁵ from iodoarenes, acid halides and dibromodiphenylmethane, respectively.

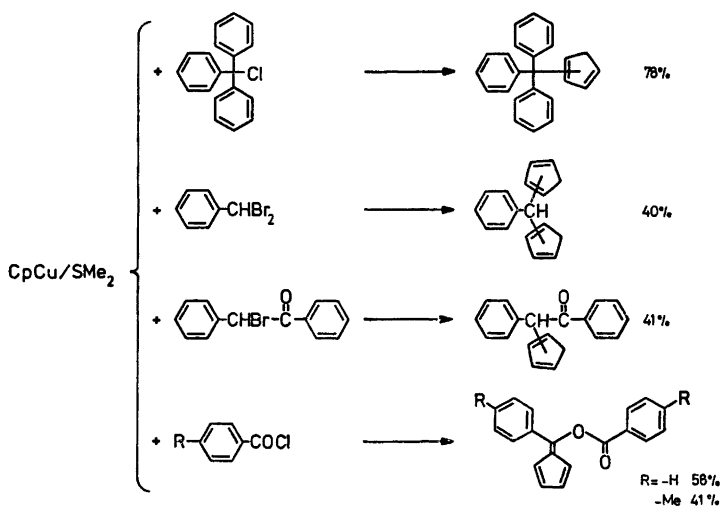
Phosphines stabilize organocopper(I) complexes such as *sec*- and *tert*-alkylcuprates.⁶ However, phosphines are avoided in organocuprate reactions due to their interference in product isolation.¹¹ Such difficulties often arise in reactions performed with CpCuPBu₃, too. This paper reports one method to circumvent these problems.

If alkali-free cyclopentadienylthallium is reacted with copper(I) iodide dimethyl sulfide (CuISMe₂)⁸ in a dimethyl sulfide/ether solution, a reagent is obtained which has been reacted with a number of organic halides. The exchange of tributylphosphine for the more volatile dimethyl sulfide in cyclopentadienylcopper reactions makes it possible to obtain almost ligand-free product mixtures. Accordingly, the separation and isolation of products are simplified.

The cyclopentadienyl(dimethyl sulfide)copper reagent (CpCu/SMe₂) was reacted with halides known to react with CpCuPBu₃ (Scheme 1).

The yields of cyclopentadienyl-substituted products were comparable to or higher than those of reactions performed with CpCuPBu₃. Preliminary studies on the reaction between CpCu/SMe₂ and 2-bromoacetophenone, which gives 2-cyclopentadienylacetophenone (NMR evidence, 20% after 7 h), have indicated a possibility of obtaining cyclopentadienyl compounds, where the CpCuPBu₃ reaction fails.

By-products are also formed in the above reactions: *e.g.* *trans*-stilbene from the reaction with dibromodiphenylmethane and 1,2,3,4-tetraphenylbutan-1,4-dione from 2-bromo-2-phenylacetophenone. CpCu/SMe₂ and CpCuPBu₃ give identical product patterns, which indicates



Scheme 1.

a close resemblance in reaction mechanism(s). The mechanism of CpCuPBu₃ reactions has been discussed previously.^{5,12}

Experimental. All cyclopentadienylcopper reactions were performed in a dry apparatus with dry solvents and under dry, oxygen-free nitrogen. Each reaction was carried out at room temperature.

General procedure. The CpCu/SMe₂ reagent was prepared by analogy with the preparation of CpCuPBu₃, as previously described²⁻⁵ by replacing CuIPBu₃ with CuISMe₂. Thus, copper(I) iodide (10 mmol) was stirred with an excess of dimethyl sulfide (10 ml) for 10 min. Then the solution was filtered into ether (10 ml).^{7,8} The resulting solution of CuISMe₂ was added dropwise to alkali-free cyclopentadienylthallium (10 mmol) in ether (80 ml). The color slowly changed from greyish-white to greenish-yellow on addition of CuISMe₂. The reaction mixture was stirred for an additional 15 min.

An ethereal solution of the organic halide was added dropwise to the reaction mixture without removal of the thallium iodide formed. When the reaction was completed, the mixture was filtered to remove TII. The residue was repeatedly washed with concentrated aqueous ammonia until the aqueous phase no longer was colored blue. After drying and evaporation of the organic solvent, an almost dimethyl sulfide-free product mixture was obtained. Oily residues were chromatographed on silica gel (Merck, Kieselgel 60, 70–230 mesh ASTM).

All products were identified by spectral comparison (NMR, MS and/or UV) with authentic samples. No reactions were observed if copper(I) iodide was omitted in the above reactions even after heating or prolonged reaction times.

Cyclopentadienyltriphenylmethane. Cyclopentadienylcopper dimethyl sulfide, CpCu/SMe₂, (10 mmol) in ether/dimethyl sulfide (100 ml) and chlorotriphenylmethane (5 mmol) in ether (50 ml) gave after 18 h cyclopentadienyltriphenylmethane (1.17 g, 78 %, m.p. 200–201 °C, lit.^{5,9} 199–200 °C) as white crystals.

6-Phenyl-6-benzoyloxyfulvene. CpCu/SMe₂ (20 mmol) in ether/dimethyl sulfide (100 ml) and benzoyl chloride (10 mmol) in ether (50 ml) gave after 16 h and chromatographic work-up 6-phenyl-6-benzoyloxyfulvene (1.80 g, 65 %, m.p. 96–100 °C, lit.⁴ 95–101 °C) as orange-red crystals.

6-p-Tolyl-6-p-tolyloxyfulvene.¹³ By analogy with the previous reaction CpCu/SMe₂ (10 mmol) and *p*-methylbenzoyl chloride (5 mmol) gave 6-*p*-tolyl-6-*p*-tolyloxyfulvene (0.62 g, 41 %, m.p. 83–84 °C) as orange red-crystals after 18 h and chromatographic work-up.

Dicyclopentadienylphenylmethane. CpCu/SMe₂ (40 mmol) in ether/dimethyl sulfide (270 ml) and dibromodiphenylmethane (25 mmol) in ether (75 ml) gave after 15 h and chromatographic work-up dicyclopentadienylphenylmethane (1.80 g, 40 %) as a yellow oil.¹¹

2-Cyclopentadienyl-2-phenylacetophenone. CpCu/SMe₂ (20 mmol) in ether/dimethyl sulfide (115 ml) and 2-bromo-2-phenylacetophenone (10 mmol) in ether (75 ml) gave after 15 h faint yellow crystals of 2-cyclopentadienyl-2-phenylacetophenone (1.07 g, 41 %, 87–88 °C, lit.⁶ 73–76 °C).

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