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Preliminary communication

AN EFFICIENT ELECTROCHEMICAL SYNTHESIS OF PHENYLETHYNYL-COPPER(I), $C_6H_5C{\equiv}CCu$

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Summary

Phenylethynylcopper(I) can be prepared in high yield by the oxidation of a copper anode in a solution of phenylacetylene in acetone or acetonitrile. This synthesis represents a significant improvement over existing methods.

Copper compounds have been widely used in organic synthesis, and acetylenic derivatives are especially useful in the Castro and Glaser coupling reactions [1,2]. Phenylethynyl-copper(I), or copper(I) phenylacetylide, has been much studied in this respect; the compound is also a photo-semiconductor [3]. The properties and methods of synthesis have been reviewed by Sladkov and Golding [4]. The recommended preparative routes involve transmetallation ($CuX + C_6H_5CCLi$), or the reaction of phenylacetylene with copper(I) species such as C_4H_9OCu, C_6H_5SCu, $[Cu(NH_3)_2]^+$, copper(I) ketenide, etc.

We now report the first direct synthesis of C_6H_5CCCu by the electrochemical oxidation of the metal, using the simple apparatus and techniques described in previous papers from this laboratory [5—7]. The cell consists of a platinum cathode and a sacrifical copper foil anode suspended in a solution of phenylacetylene (2 ml, 1.8 g) in either dry acetone or dry acetonitrile (50 ml) containing 25 mg tetraethylammonium perchlorate. In a typical experiment, an applied voltage of 20 V gave an initial current of 20 mA. A yellow solid began to precipitate at the anode as soon as current flowed, and continued to form throughout the experiment; hydrogen gas was evolved at the cathode. After approximately 1 h, the product was collected, washed (solvent, and then petroleum ether) and dried. The free-flowing powder was identified as C_6H_5CCCu by copper analysis (Calc'd. Cu 38.6%; found (atomic absorption) Cu 39.1%), and by the identity of the infrared spectrum (KBr disc) with that reported by Garbusova et al. [8]. The chemical yield (0.13 g) was essentially quantitative, based on the loss of copper from the anode; larger quantities of product can obviously be obtained by running the experiment for longer periods.

The electrochemical efficiency, defined as moles of copper dissolved per Faraday of electricity, was 1.06 mol F^{-1}, corresponding to the electrode reactions:

cathode; $C_6H_5CCH + e \rightarrow C_6H_5CC^- + \frac{1}{2} H_2(g)$

anode; $C_6H_5CC^- + Cu \rightarrow C_6H_5CCCu + e$

The method appears to be a general one for the preparation of phenylacetylides of other metals, since we have obtained similar results with silver, zinc, cadmium and indium. It has also been possible to synthesise adducts of C_6H_5CCCu with 2,2′-bipyridine or 1,10-phenanthroline by adding the neutral ligand to the cell prior to the electrolysis. In the latter case, electrochemical oxidation yielded a dark red solution, which on cooling and slow evaporation deposited a red-brown solid identified as $(C_6H_5CCCu)_2$phen (Calc'd. Cu 24.9%; found Cu 25.5%. Infrared spectroscopy confirms the presence of $C_6H_5C{\equiv}C$ and 1,10-phenanthroline). The electrochemical efficiency is again close to unity.

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