
Attempted Phenylation of Several Organic Solvents by Phenylmagnesium Bromide in the Presence of Cuprous Salts[1]

K. DARRELL BERLIN and DON E. GIBBS[2]

Department of Chemistry, Oklahoma State University, Stillwater

Because phenylcopper is reported to decompose under mild conditions (Reich, 1923), it was anticipated that it might be used as a phenylating reagent. Mixtures of phenyl Grignard reagents and cuprous halides, which could possibly contain phenyl copper, were investigated for their phenylation aptitude. No phenylation was observed with cyclohexene or anisole at 5 C. The three phenylpyridines were obtained at 5 C and 3-phenylcyclohexene at 70 C.

The first evidence for the possible existence of phenylcopper (Turner, 1920), although not reported as such at the time, was provided by the formation of 2,2′-dimethylbiphenyl in 30% yield by adding cupric chloride to o-tolylmagnesium bromide. Biphenyl was likewise obtained in good yield from phenylmagnesium bromide. It is probable that cuprous chloride is first formed since Grignard reagents reduce cupric salts readily (Kharasch and Reinmuth, 1954).

Phenylcopper was first reported (Reich, 1923) as a grey powder obtained in 60% yield (assuming it to be C_6H_5Cu) by adding cuprous iodide to phenylmagnesium bromide at 0-5 C. The green solution which first formed deposited the grey solid which was filtered out under a nitrogen atmosphere. In boiling benzene, biphenyl (95%) was the reported product while with water, phenylcopper was decomposed to benzene and cuprous oxide. The next preparation (Gilman and Straley, 1936) used the method of Reich except that phenylmagnesium iodide was substituted for the bromide. The reaction gave a brown solid which was dissolved in the reaction vessel with ether. A white solid then precipitated in 86% yield and was assumed to be pure phenylcopper. A repetition of Reich's basic work has been published (Filler and Rao, 1962). Preparation from phenyllithium and cuprous iodide (Warf, 1952) was found to be preferable to using Grignard reagents.

The physical properties of phenylcopper given by Reich are as follows: it melts at 80 C with formation of copper and biphenyl and is soluble in pyridine, benzyl cyanide, and benzaldehyde, slightly soluble in chloroform, carbon tetrachloride, bromoethane, and bromobenzene, and insoluble in ether and carbon disulfide.

Phenylcopper was not isolated as a solid when the procedure of Gilman and Straley (1936) was used in this laboratory. When phenylmagnesium bromide was substituted for the iodide, the green heavy suspension, as previously reported by Reich (1923), was obtained. In each of

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our preparations, attempts to isolate a solid were unsuccessful because of rapid decomposition in the mixture. Thus the reagents (anisole, cyclohexene, or pyridine) were added directly to the original mixtures under nitrogen.

Treatment of cyclohexene or anisole at 5 C with phenylcopper (2:1 molar ratio) gave as the main products biphenyl and copper. Gas chromatography showed no evidence for phenylation of the original reactants. 3-Phenylcyclohexene was formed in low yield from cyclohexene at 70 C, although biphenyl was still the major product. There was no reaction with anisole at 73 C.

A study of the decomposition of phenylcopper in pyridine is complicated by the reaction between pyridine and unconverted phenylmagnesium bromide. A small amount of 2-phenylpyridine is reported (Bergstrom and McAllister, 1930) from boiling phenylmagnesium bromide and pyridine in ether. We have repeated this work and have found all three isomeric phenylpyridines in low yield as well as biphenyl. In the experiment with pyridine and phenylcopper prepared from cuprous iodide, the yield of biphenyl was increased and that of the phenylpyridines was greatly reduced (less than 5%). One possible reason for the reduction in yield of the latter may be that some of the pyridine was complexed with cuprous iodide, since quinoline is known to form complexes with cuprous salts (Mutchler and Bradley, 1958). The lower concentration of the Grignard reagent, which had presumably been partially converted to phenylcopper, would also contribute to this reduction. It should be pointed out that reaction of benzoyl peroxide and pyridine at 80 C has been found to yield *o-*, *m-*, and *p-* phenylpyridines in a ratio of 4:2:1 (Dannley and Gregg, 1954). In summary, phenylation of cyclohexene, anisole, or pyridine does not occur readily by thermal decomposition of phenyl Grignard reagents in the presence of cuprous salts.

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