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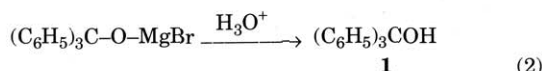
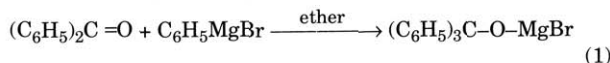
A Serendipitous Two-Step Synthesis from a Grignard Reaction

1-Ethoxy-1,1,1-triphenylmethane from the Reaction of Phenylmagnesium Bromide with Benzophenone

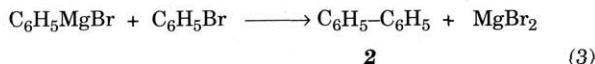
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In a second-year organic laboratory experiment to illustrate the potential products of a Grignard reaction, students prepared phenylmagnesium bromide in the usual manner from bromobenzene and magnesium turnings in diethyl ether. The Grignard reagent was then allowed to react with benzophenone (eqs 1–2)



While recognizing the complexity of Grignard reactions (1), including the variation in reagent–ether structure with concentration (2) and the recent accumulation of evidence for the presence of free-radical intermediates along the reaction pathway (1), triphenylmethanol, **1**, was accounted for in the Experimental Preface by the traditional “disguised carbanion” mechanism (3) (eqs 1–2). Biphenyl, **2**, appears as a side-product as a result of Fittig–Wurtz coupling (4) between the Grignard reagent and unmodified bromobenzene (eq 3).



These two products, **1** and **2**, were identified by the students by thin layer chromatography (TLC); comparison was made among authentic samples, the crude mixture, and **1**, purified by recrystallization from ethanol by the students.

In up to 10% of the cases an excess of ethanol was used in the recrystallization. To reduce the volume and obtain **1**, these solutions were boiled. After this treatment the product oiled out! Once isolated the product was found to melt at 70–78 °C (differences due to impurities, entrained solvent, etc.) rather than close to 165 °C (m.p. of pure **1**). The product had an r_f value intermediate between those of **1** and **2**. The ^1H NMR spectrum of the anomalous product was consistent with it being 1-ethoxy-1,1,1-triphenylmethane, **3** (CDCl_3 : 7.3 ppm (m, ca. 15 H, Ar), 3.1 ppm (q, 2H, CH_2 , $J = 6.0$ Hz), 1.2 ppm (t, 3H, CH_3 , $J = 6.0$ Hz)). The

slight inaccuracy in the integral for the aromatic region is likely due to traces of **1** and/or **2** in the sample. The hydroxyl peak of **1**, which exchanges upon treatment with D_2O , was found at 2.1–2.7 ppm in the NMR spectrum. Careful recrystallization of the product from ethanol yielded **3** with a m.p. of 80.5–82.5 °C, uncorrected (lit. 82.5–83.5 °C) (5).

The origin of **3** appears to lie in the extended period of boiling of the ethanol solution and the presence of traces of acid that were not neutralized in the Grignard workup procedure. A plausible mechanism for the formation of **3** involves protonation of **1**, formation of the triphenylmethyl cation after loss of water, followed by facile reaction with ethanol to yield **3**. This acid-catalyzed $\text{S}_{\text{N}}1$ mechanism is familiar to our students, although none of them suggested either the mechanism or the probable identity of the unknown product.

In support of the suggested mechanism we brought an ethanolic solution of **1** to reflux in the presence of a little strong acid (2 drops of H_2SO_4). After workup, the crude reaction product was found to consist of 39% **3** on the basis of comparison of the NMR signals for the methylene of **3** with the hydroxyl singlet of **1**. Moreover, while one suggested preparation for **3** from **1** involves dissolving **1** in 100% sulfuric acid in order to ensure the formation of the triphenylmethyl cation, followed by addition of the acidic solution to an excess of cold ethanol (6), a more recent reference reports preparation of **3** and related ethers of **1** using only traces of acid (7).

Our experience illustrates that serendipity plays a role even in a well-documented undergraduate organic experiment.

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