

Portland Community College

Grignard Synthesis Lab Report

Synthesis, Recrystallization & Spectroscopy

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Abstract:

Two phenyl groups were successfully added to an aryl ester (methyl benzoate) using reduction-oxidation via Grignard Synthesis to form an alcohol. Liquid GC/MS demonstrated 100% purity of the triphenylmethanol product, at 44% yield, with 5% loss after a competing biphenyl byproduct was removed via recrystallization. The anhydrous reaction produced exclusively triphenyl products, demonstrating successful exclusion of water vapor and avoiding premature protonation of the benzenide intermediate. Infrared spectroscopy (FTIR) data demonstrated aromatic and alcohol nature of the product, whereas melting point data corroborated purity of the recovered products, with 43.9% final yield, adjusted.

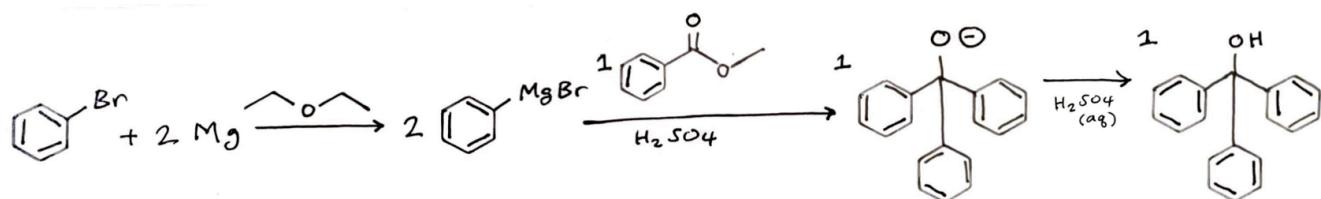


Figure 1: Triphenyl methanol formation by Grignard reagent

Introduction:

Producing carbon-carbon bonds is an essential goal in organic chemistry, yet carbon itself is relatively less reactive than many of the functional substituents it carries. The most popular mechanism for adding carbon groups directly is an organometallic reduction-oxidation agent, *Grignard reagent*. This ionic compound is often compounded from an alkyl halide with Magnesium metal [1]. Grignard effects kinetically-favored 1,2 addition on carbonyls. Remarkably, in alkenes it is mostly precluded from thermodynamically-favored 1,4 addition due to the irreversibly steep activation energy needed to break

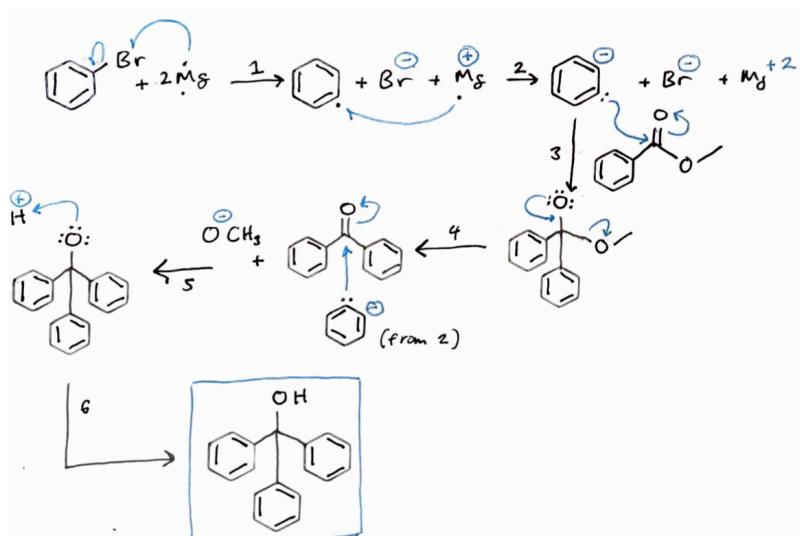


Figure 2: Mechanism of TrOH formation

the strong, newly-formed C-C bond. [2]

The addition of benzene to methyl benzoate (**Figure 1**) demonstrates how this “hard nucleophile” can create an irreversible addition. Indeed, the reaction is favorable enough to continue with a second addition, forming a triphenyl product by oxidation to the carbonyl, as in the mechanism of **Figure 2**.

Two competing mechanisms must be avoided during reagent prep, however. First when forming the benzenide anion from bromobenzene, the benzene may react with itself and form biphenyl in competition with the desired phenylmagnesium halide, viz. side product *(a)* of **Figure 3**.

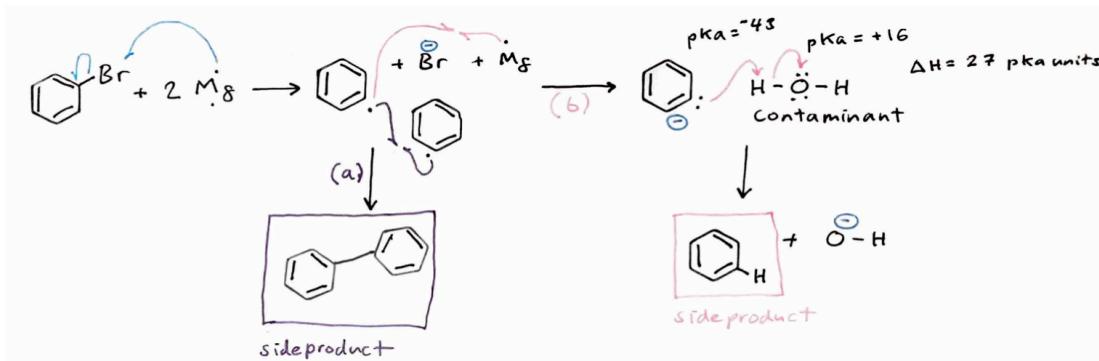


Figure 3: Competing Reactions

Alternatively, the presence of moisture could prematurely protonate the benzenide ion before it can react with the ester, also shown in **Figure 3**, side product *(b)*. An experiment was configured to demonstrate the predicted reduction-oxidation (“redox”) abilities of Grignard reagent, using bromobenzene on methyl benzoate as an example. Triphenylmethanol (TrOH) was predicted.

Results

Liquid bromobenzene (4.60mL, 0.0437mol) and diethyl ether (12.50mL, 0.120mol) were sourced from PCC laboratory stock and combined in a reflux apparatus voided of water vapor. Magnesium metal (1.0245g, 0.04214mol) was combined in the solution with iodine (~0.1g) as activator and the mixture heated. Upon evidence of bubbling, additional diethyl ether (12.2mL, 0.117mol) was added and the oily, plum-hued solution was refluxed for 60 minutes, producing an oily condensate.

The solution was gently heated to invigorate bubbling and refluxed for an additional 10 minutes, yielding a brownish-yellow slurry of approximately one-half the initial volume, and consuming approximately 80% of visible magnesium. This phenylmagnesium bromide reagent was gradually cooled to 0°C via ice-bath, forming a reddish solution, with a dark sediment of residual alkaline metal.

Ester Reaction

Methyl benzoate (2.315mL, 0.0184mol) was introduced into anhydrous diethyl ether (7.5mL) by syringe. This ester reagent was gradually drained into the phenylmagnesium halide, causing a moderately vigorous bubbling reaction with a foamy white top layer. The stable anion intermediate was cooled to 0°C, forming a brown fluid with muddy sediment and white top layer. Storage for 7 days evolved the product into a yellow, oily solution with a beige, clayey sediment of “gum drops” and orange crust (**Figure 4**).



Protonation

Residual magnesium was neutralized with an acid-ice mixture of 1M H₂SO₄ (25.0mL, 0.0250mol) and ice (12.4125g, 0.6888mol) at 0°C. Evolved hydrogen gas was vented and white sediment broken up and mixed back into the effervescent acidic mixture, simultaneously protonating the triphenyl methoxide intermediate.

Figure 4: TrO- solution (Week 1)

A yellow organic layer was partitioned from a whitish aqueous layer of magnesium salts (**Figure 5**). This organic layer was again washed with 1M H₂SO₄ (10.1mL, 0.0114mol) and left to desiccate with sodium sulfate (2.5249g, 0.01777mol) for 5 minutes. Desiccant was removed via a glass wool filter and rinsed with ether, then purified of ether through rotovap to yield 10.1188g of yellow fluid (**Figure 6**).



Crude product was triturated with ligroin (petroleum ether) over a stir plate to drive beige precipitate and solids back into solution. The ligroin was removed through vacuum filtration and discarded as a dark filtrate. This crude product was recovered as 2.3278g of sugary crystals and subject to further analysis.

Recrystallization

Purification was effected by recrystallizing the clumpy solid after dissolution in boiling aqueous 2-propanol (99%, ~5mL). Precipitation was achieved by cooling the solution for 10 minutes, yielding a cloudy, yellowish fluid with a surface layer of white oil and whitish sediment. The precipitate was recovered via vacuum filtration, rinsed with deionized water, and recovered as 2.0986g of cuboid crystals, tending to form thin sheets. (**Figure 7**).

Product was analyzed for functional groups using Fourier Transform

Figure 5: TrOH Extraction



Figure 6: TrOH Rotovap

Infrared Spectroscopy (FTIR) with Diamond ATR on an Agilent Cary 630, at 64 sample scans within the range 4000-650cm⁻¹ over 32 background scans. Peaks were identified manually using the Agilent MicroLab software and provided graphically in **Appendix 2**. Peaks were predicted according to Mohrig [3], compared to K:Br reference spectra [4] and reported in **Table 1**.

Functional Group	Typical Range (cm-1) [1]	K:Br Reference (cm-1) [2]	Observed Crude (cm-1)	Observed Final (cm-1)
-OH	3500-3100	3474	3459	3462
C-sp2-H	3100-3000	3087-3034	3026, 3056	3026, 3060
C-sp3-H	2990-2850	—	—	—
C=O (conjugated)	1730-1715	—	—	—
C=C (aromatic)	1620-1440	1598, 1491	1599, 1494	1595, 1490
Fingerprint (C-C)	1500-1000	1446, 1331, 1206, 1158	1442, 1326, 1293, 1151	1442, 1326, 1293, 1155
C-O stretch (speculative)	1300-1000	1011	1010	1010
CH Bend	880-680	760	753	757

Table 1: FTIR Peaks of Triphenylmethanol

Purity of both crude and final samples was assessed by capillation of <1mg product into a Vernier Melt Station with LoggerPro and visual inspection of melting point as described in Mohrig [3]. Product compared favorably to that expected in range and value for TrOH (**Table 2**).

Product	Melting Point (°C)	Range (±C°)	Relative Error (δ)
Crude	162.3 - 164.3	2.0	0.0%
Purified	163.0 - 163.7	0.7	0.0%
Accepted TrOH [2]	160 - 163	3.0	N/A

Table 2: Observed and Expected Melting Points of TrOH

Product was finally analyzed via GC/MS, reported in **Table 3**. As with prior experiments, GC/MS was conducted with smoothing and filtering enabled and monitoring 3-7 minutes of elution time. Labeled GC/MS waveforms provided in **Appendix 3**.

Fragment ID	Crude		Final		Structure
	Retention Time (min)	Peak Area (%)	Retention Time (min)	Peak Area (%)	
Triphenylmethanol	13.823	100.00	13.814	100.00	

Table 3: Gas Column Chromatography and Mass Spectrometry Results

Product was weighed in a digital balance before after recrystallization, and respective ratios computed using the physical characteristics reported in literature [5] per **Table 5**, with calculations included in **Appendix 1**. Overall the initial synthesis yielded 2.3278g of crude product, of which 2.0986g was recovered after recrystallization. This made for an initial crude recovery of 48.69%, and yielded 43.90% of final product, including any needed adjustments for GC/MS peak areas, reported in **Table 4**.

TrOH	Mass (g)	Moles (mol)	% Yield	% Yield, adjusted by GC/MS
Theoretical Yield	4.7806	0.018364	100%	100%
Actual Crude	2.3278	0.008942	48.69%	48.69%
Actual Final	2.0986	0.008061	43.90%	43.90%

Table 4: Actual and Theoretical Yield

	Empirical Volume (mL)	Density (g/mL) [3]	Actual Mass (g)	Molar Mass (g/mol)	Actual Moles (mol)	Molar Ratio	Effective Moles (mol)
PhCO ₂ Me* (limiting)	2.315	1.08	2.50	136.15	0.01836	1:1	0.01836
PhBr	4.60	1.51	6.95	157.02	0.04424	2:1	0.02212
Mg ⁰	—	—	1.02	24.305	0.04215	2:1	0.02108
1M H ₂ SO ₄	25	—	—	—	0.02500	1:1	0.02500

Table 5: Effective Ratio of Reagents

Discussion

First it must be proven the product was a pure aromatic alcohol. This is demonstrated by the homogenous white crystalline structure and yellow coloration in the acidic stage - a known characteristic of triaryl compounds which are popular as yellow dyes [7]. Both crude and final product were sugary and crystalline, suggesting relatively little biphenyl side-product. The product also exhibited itself as a solid, without the acute odor of typical of esters or phenols. This suggests the product was more substantial than the initial monophenyl liquid reagent, since most triaryl compounds are solids at room temperature and have a higher ability to pack into crystals [2].

I. Melting Point

Melting point also corroborates a triphenyl methanol isomer, with the final product melting at 163-164°C (Table 3), within the range reported in literature [4].

The crude product was also within the accepted range, though it exhibited a slightly lower melting point and wider range by 1°C. This suggests the initial synthesis only contained minor quantity of biphenyl impurities, with most successfully removed earlier by the non-polar ligroin solvent.



Figure 7: Purified TrOH Crystals

II. Spectroscopy

Infrared spectroscopy also seems to confirm an aromatic alcohol was recovered, with a distinct hydroxy peak at 3462cm⁻¹ which

matches the broad peak predicted in Mohrig for an alcohol [3], and corroborated further by a large peak at 1011cm^{-1} potentially matching its corresponding C-O stretch. Whereas the product exhibited $C_{sp^2}\text{-H}$ peaks at 3026 and 3060 cm^{-1} , no $C_{sp^3}\text{-H}$ peaks were observed, demonstrating the successful evaporation of aliphatic reagents such as diethyl ether and 1-propanol. Spectroscopy also confirms aromatic rings are present, via the C-H bend ($\sim 760\text{cm}^{-1}$) and C=C peaks in **Table 1** and presented in **Appendix 2**.

Comparing the fingerprint region to a known TrOH reference [5], four distinctive peaks are visible in the fingerprint region at 1028 - 1010 , 1155 , 1326 , and 1442 cm^{-1} . Both crude and final product exhibited near-identical fingerprint peaks. Although the mechanism of how C-C bonds harmonize to create these fingerprint peaks is complex and unpredictable, the similar shape and location of these four peaks suggests identity with TrOH.

Finally, the absence of C=O peaks in Table 1 also proves the ester product - as limiting reagent - was completely consumed during the Grignard reaction. This also demonstrates the resulting alcohol was not oxidized inadvertently during treatment with sulfuric acid, which would also evolve unwanted carbonyl bonds. Whereas these spectra can prove the presence or absence of functional groups, fully proving the presence of three phenyl groups for TrOH requires GC/MS.

III. GC/MS Analysis

Remarkably, both crude and final products only exhibited GC/MS fragments consistent with triphenyl methanol (100% peak area) per **Table 3** above. These fragments are predicted based on ionization causing an M+ peak product as shown in **Figure 8**, with spectrum labeled in **A3**. The base peak is consistent with alpha-cleavage of TrOH to a biphenyl cation.

Both compounds eluted between 13.823 and 13.814 minutes, according to the Gas Column chromatogram (**A3**). This suggests

relatively few Grignard compound molecules self-reacted to form biphenyls in the first stage of the synthesis, or they were successfully removed by ligroin solvent. Recrystallization did seem to reduce the elution time very slightly, but this could be due to natural instrument variance.

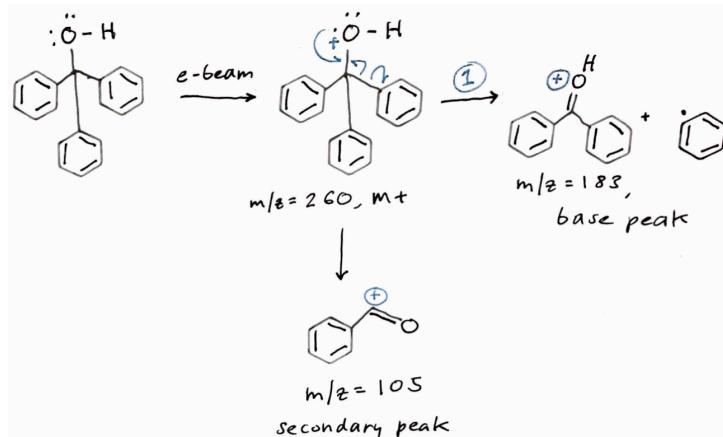


Figure 8: Formation of M+ and Base Peaks

Summary & Conclusion

The crisp melting point (range 2 C°) and well-formed crystals demonstrate purity of product. Meanwhile, the presence of all expected functional groups in FTIR show that Grignard addition was successful. Moreover, the spectrum shows the ester (C=O) and aliphatic (Csp_3 -H) reagents were fully consumed or filtered out during this redox reaction. Finally, the mass spectrometry peaks and retention times (**A3**) match known patterns for triphenylmethanol (TrOH), proving the experiment did not merely reduce methyl benzoate to a phenol.

Although the experiment warned about competing formation of biphenyls as a side-product (**Figure 3**), and consequently advised recrystallizing, our GC/MS results showed no fragments matching the biphenyl signature, even prior to recrystallization (**Table 3**). Clearly the Grignard reagent formed preferentially or the side-product was removed completely by petroleum ether. Possibly this recrystallization could be omitted in an expedited one-day synthesis.

The yield was favorable at 43.9%, with some loss likely attributable to unreacted ester product. Although 60 minutes was dedicated towards Grignard formation, the ester was only given 10 minutes to react and may need a longer induction period to achieve the full phenyl addition required here. If so, this limiting reagent was likely discarded as filtrate, perhaps reducing the overall yield by half. Transfer of crystalline product from the filter paper and flask also seemed to result in some loss of product. We further observed some groups decanted the TrO- intermediate at the start of week 2 - rather than blending in the solid beige precipitate - with a corresponding reduction in yield.

If doing the experiment again, yield could be improved perhaps by giving the ester more time to react with the Grignard product. This could be monitored by perhaps eluting the evolving products on silica TLC against a known TrOH standard, to better guess when the reaction was nearing completion. During recrystallization, more care could be exerted in applying the 2-propanol in smaller quantities until dissolution was achieved, ultimately yielding more precipitate during recrystallization. One could also investigate the time benefits of omitting the recrystallization step, given the apparent purity of the crude sample from predicted biphenyl or benzene side products.

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