Experimental Procedures

Experiment: 5 **Date: 02/04/2020;**
Lab No: 4 **Time: 9:00a.m. to 1:00p.m.**

Alkyl Alcohol to Alkyl Bromide

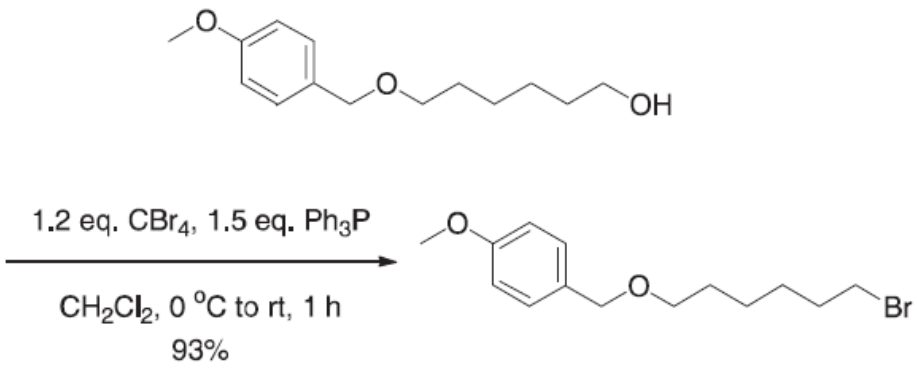

Figure 1 synthesis of Alkyl Bromide

Procedure:

To a mixture of the alcohol (0.800 g, 3.36 mmol) and carbon tetrabromide (1.337 g, 4.03 mmol) in CH_2Cl_2 at 0 ºC was added a solution of PPh_3 (1.319 g, 5.03 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at room temperature for 2 h, concentrated under reduced pressure, and purified by column chromatography to afford the bromide.

Reference: Hu, T.-S.; Yu, Q.; Wu,Y.-L.; Wu,Y. *J. Org. Chem.* **2001**, *66*, 853–861.

Yield: 0.941 g, 93% yield.

Experiment: 6 **Date: 06/04/2020;**
Lab No: 5 **Time: 9:00a.m. to 1:00p.m.**

Amide Formation through Acid Chloride by Thionyl Chloride

Thionyl chloride costs less and liberates less gas than oxalyl chloride.

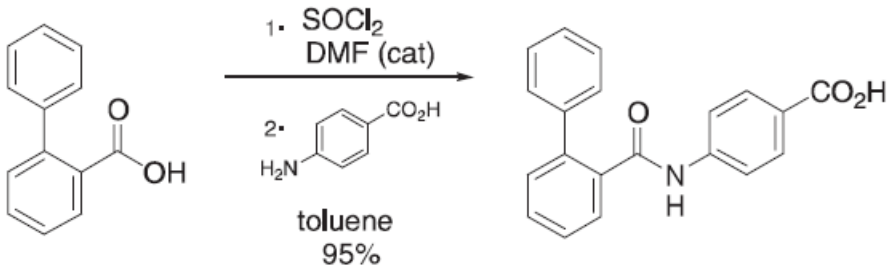

Figure 2 synthesis of amide derivatives

Procedure:

Thionyl chloride (10.4 g, 87.4 mmol) was added to a mixture of biphenyl-2-carboxylic acid (15.0 g, 75.7 mmol) and DMF (0.28 g, 3.83 mmol) in toluene (72 mL) at an internal temperature of 40 ºC. The mixture was stirred at this temperature for approximately 2 h. After completion of the reaction, the mixture was concentrated to dryness at 60 ºC. The resultant residue was then diluted with toluene (36 mL) and concentrated to dryness at 60 ºC, and the process was repeated again to give biphenyl-2-carbonyl chloride as an oil. Acetone (100 mL) was added to the oil, and 4-amino benzoic acid (10.4 g, 75.8 mmol) and *N*,*N*-dimethylaniline (10.1 g, 83.3 mmol) were added to the resultant solution at 25 ºC. The mixture was stirred at this temperature for approximately 2 h. Water (100 mL) was then poured into the mixture, and it was stirred at 25 ºC for more than 1 h. The resultant crystals were collected by filtration and dissolved in DMF (100 mL) at 25 ºC. The solution was then filtered to remove insoluble materials, water (100 mL) was poured into the filtrate, and it was stirred at 25 ºC for approximately 2 h. The resultant crystals were collected by filtration and dried at 40 ºC to give the amide as white crystals.

Reference: Tsunoda, T.; Yamazaki, A.; Mase, T.; Sakamoto, S. *Org. Process Res. Dev.* **2005**, *9*, 593–598.

Yield: 22.7 g, 95%.

Experiment: 7 **Date: 09/04/2020;**
Lab No: 4 **Time: 9:00a.m. to 1:00p.m.**

5-methylene-6-heptenenitrile to 5-methylene-6-heptenoic acid

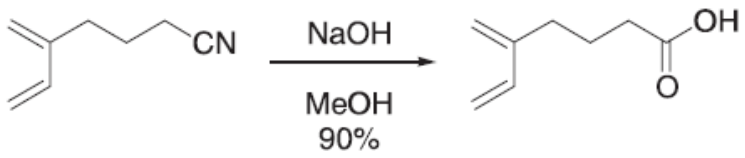

Figure 3 synthesis of 5-methylene-6-heptenoic acid

Procedure:

A solution of 5-methylene-6-heptenenitrile (2.0 g, 16.5 mmol) in 25% NaOH (95 mL) and MeOH (300 mL) was heated to reflux for 48 h. The solution was cooled, concentrated to half its original volume, and acidified with concentrated HCl to pH 1. The mixture was extracted with Et2O (2 × 30 mL), the combined extracts dried (MgSO4), and concentrated in vacuo to afford 2.10 g (90%) of 5-methylene-6-heptenoic acid as a pale yellow oil.

Reference: Sparks, S. M.; Chow, C. P.; Zhu, L.; Shea K. J. *J. Org. Chem*. **2004**, *69*, 3025–3035.

Yield: 2.10 g, 90%

Experiment: 8 **Date: 13/04/2020;**
Lab No: 5 **Time: 9:00a.m. to 1:00p.m.**

4-hydroxybenzyl alcohol to 4-hydroxybenzaldehyde

Most aliphatic alcohols react slowly if at all with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), allowing selective allylic or benzylic alcohol oxidation.

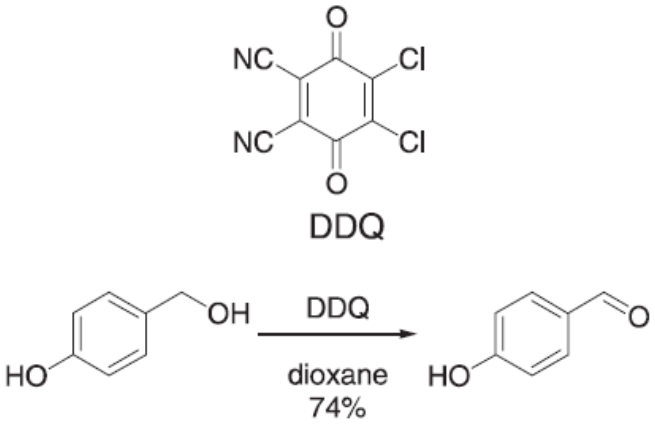

Figure 4 synthesis of 4-hydroxybenzaldehyde

Procedure:

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ 908 mg, 4 mmol) was added to a solution of 4-hydroxybenzyl alcohol (496 mg, 4 mmol) in dioxane (24 mL). The reaction mixture immediately turned deep green (exothermic reaction), and $DDQH_2$ started precipitating within 1 min. Thin layer chromatography (TLC) analysis indicated consumption of starting material after 15 min. The solvent was removed from the yellow reaction mixture in vacuo. Treatment of the residue with CH_2Cl_2 left $DDQH_2$ undissolved (quantitatively). Filtration followed by evaporation of CH_2Cl_2 gave 4-hydroxybenzaldehyde (74% yield) which was recrystallized from water.

Reference: Becker, H.-D.; Bjork, A.; Alder, E. *J. Org. Chem*. **1980**, *45*, 1596−1600.

Yield: 670 mg, 74%