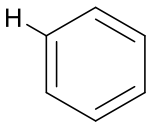
Organic chemistry practical course

Protodecarboxylation of benzoic acids
(Synthesis of benzene)
(C_6H_6)



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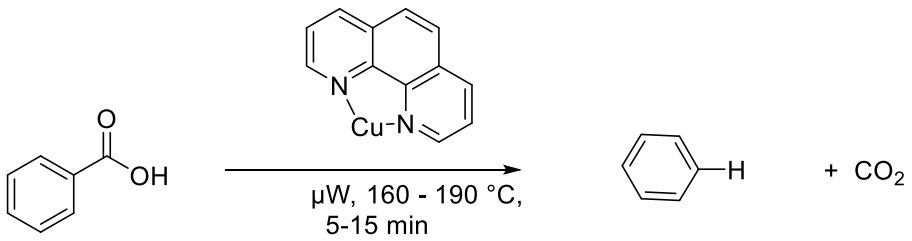
I. Reaction: [1]



$M(C_7H_6O)$ = 122.12 g/mol

$D(C_7H_6O)$ = 1.26 g/cm^3

$M(C_6H_6)$ = 78.11 g/mol

$D(C_6H_6)$ =0.8787 g/cm^3

II. Theory: [1]

This experimental session involves the catalytic removal of the carboxyl functional group of benzoic acid, followed by a protonation, hence the name protodecarboxylation. This carboxyl group is released in the form of carbon dioxide. The catalyst (metal – ligand complex) used for this purpose was generated *in situ* from copper(I) oxide and 1,10-phenanthroline.

According to literature,[1] even in the absence of catalysts, such reactions can readily take place for highly activated carboxylic acids like -oxo acids, diphenylacetic acids, or polyfluorinated as compared to simple aromatic benzoic acids.[2]

Heavy metals are not used due to their possible environmental impact.

In this synthetic process, high temperature of around 170° C is applied and the released CO_2 contains some of the volatile products. However, the loss of these volatile product is easily controlled by retarding the CO_2 release and cooling the reaction medium to room temperature.

Furthermore, it is a small-scale reaction. As such, a laboratory microwave is used which have beneficial aspects like effective heating and high pressure, which can be easily achieved since microwave reaction vials are used.

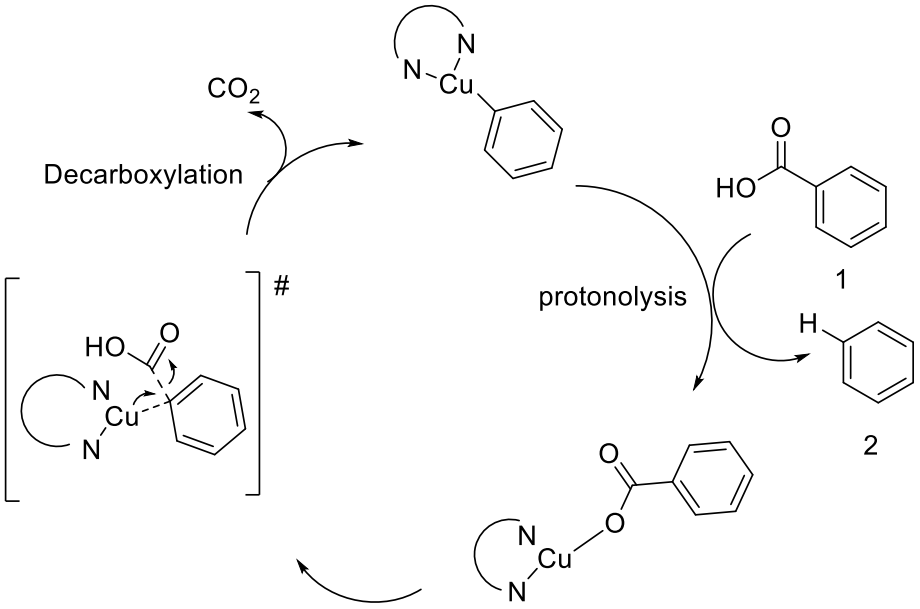
The choice of the solvent mixture for this reaction is very critical as some would absorb microwave radiation during the reaction resulting in a temperature rise of the reaction medium.

This reaction is called cross-coupling reactions because it involves the combination of an organometallic reagent with an organic electrophile to obtain a C–C, C–H, C–N, C–O, C–S, C–P, or C–M bonding. In addition, cross-coupling reactions are very important in organic synthesis such as polymerisation, synthesis of liquid crystals, pharmaceuticals and natural products.

These reactions occur mechanistically in three major steps: Oxidative addition, transmetallation and reductive elimination [3]

III. Mechanism:[4]

The mechanism for this reaction is represented as a cycle.



First, the metal complex catalyst undergoes an oxidative addition to benzoic acid, followed by transmetalation of the ligand onto the benzoic acid, thereby removing the carboxyl group (decarboxylation). This then undergoes reductive elimination in which the catalyst is removed from the aromatic substrate where protonolysis occurs and the product is formed.

IV. Procedure: [1]

First, a 10 mL microwave vial was dried in an oven. Then, benzoic acid (0,122 mg, 1.0 mmol), Cu_2O (7.2 mg, 0.05 mmol), and 1,10-phenanthroline (18 mg, 0.10 mmol) were poured into the vial. Using a syringe, a mixture of 1.5 mL of NMP (N-methyl-2-pyrrolidon) and 0.5 mL of quinoline was added to the above reaction mixture. The resulting mixture was placed in a microwave and irradiated under the following conditions: 190 °C, 15 min , 150 W and pressure of 5.5 bar. The mixture was diluted with 10 mL of 5N aqueous HCl, then extracted several times with 2 ml portions of diethylether, respectively. The obtained organic layer was washed with water and brine, dried over $MgSO_4$ and then filtered. The solvents were removed *via* fractional distillation over a vigreux column, and the was product obtained.

V. Results and Analysis:

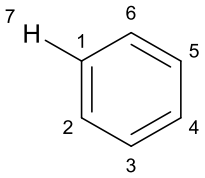
$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoritical yield}} * 100$$

Mass of Product = Actual yield = 6.25 g

Theoritical yield = 7.79 g

Percentage yield = 80.21 %

- **Proton NMR Analysis**



^{1}H NMR (300 MHz, DMSO-d_6): δ= 7.34 (s, 2H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H) ppm.

Thus, the ^{1}H-NMR spectrum is consistent with the products structure. Furthermore, all six protons of the structure are equivalent, which is why only one singlet is observed on the spectrum.

VI. References:

[1] Goossen L. J., Manjolinho F., Khan B. A., Rodriguez N., *J. Org. Chem.* **2009**, *74*, 2620 - 2623.

[2] Snow R. A., Degenhardt, C. D., Paquette L. A., *Tetrahedron Lett.* **1976**, 4447 - 4450.

[3] Nolan S. P., Navarro O., *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, **2013.**

[4] Goossen L. J., Thiel, W. R. Rodriguez, Linder, N. C., Melzer B., *Adv. Synth. Catal*. **2007**, *349*, 2241 - 2246.