

# **Acid-Catalyzed Aldol Condensation of Acetone**

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<Semester> <Year>, <course>**

## ABSTRACT

This synthesis was a repetition of previously reported acid catalyzed aldol condensation of acetone to produce mesityl oxide and phorone. The acid catalyzed aldol condensation of acetone, via treatment with anhydrous hydrogen chloride gas at room temperature resulted in the production of mesityl oxide at a yield of approximately 15.3%. Little intended phorone was produced. The Lewis acid, anhydrous aluminum chloride, was used to increase the yield of phorone. No reagent grade reagents were available to perform this synthesis, which could be the reason yields didn't approach those of the previously reported syntheses.

## 1.0 INTRODUCTION

An aldol condensation is a fundamental organic reaction where two carbonyl compounds (aldehydes or ketones) join to form a larger molecule (a  $\beta$ -hydroxy carbonyl) and then often eliminate water to create a conjugated  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound, forming a new carbon-carbon bond, typically catalyzed by acid or base. It involves an enolate ion attacking another carbonyl group, followed by dehydration, making it crucial for building complex carbon structures in synthesis. Aldol condensations, at least one of the carbonyls requires an  $\alpha$  hydrogen to form the enol or enolate.

Carbonyl compounds are usually found in an equilibrium condition referred to as keto/enol tautomerization. The keto tautomer (carbonyl) is in equilibrium with the enol tautomer, with the enol tautomers, typically, found only in very small amounts

Acid-catalyzed aldol condensation forms  $\alpha$ ,  $\beta$ -unsaturated carbonyls (enones/enal) from aldehydes/ketones via an enol intermediate (not enolate), involving carbonyl protonation, enol attack, and acid-catalyzed dehydration, generally favoring thermodynamic products and forming a stable conjugated system. The mechanism involves activating the carbonyl, creating a nucleophilic enol, nucleophilic attack, and water elimination, resulting in a conjugated product. Acid-catalyzed aldol condensations often do not stop at the first reaction, given there is a carbonyl remaining and, with an  $\alpha$  hydrogen present, can start the cycle again and attack another carbonyl.<sup>1</sup>

Phorone was initially synthesized in 1876 by Claisen who saturated acetone with anhydrous hydrogen chloride, letting it stand for three weeks at room temperature, with a subsequent treatment with alcoholic KOH<sup>2,3,4,5</sup>. This produced both mesityl oxide and phorone. Further research into this procedure demonstrated that the formation of mesityl oxide and phorone was a two-step process. An intermediate compound, mesityl oxide chloride and phorone dichloride, is formed then converted to the final products after treatment with alcoholic hydroxide<sup>6</sup>. This research aimed to repeat that paper's procedure for forming mesityl oxide and phorone.

## 2.0 EXPERIMENTAL

### 2.1 Chemicals

The chemicals used were anhydrous aluminum chloride, reagent grade, 99+%, GTI Laboratory Supplies, EBay.com (CAS# 7446-70-0), acetone, technical grade, Home Depot, Decatur, GA (CAS# 67-64-1), sodium chloride (kosher salt), technical grade, Kroger, inc., Decatur, GA (CAS# 7647-14-5), sulfuric acid, reagent grade, 99+%, ebay.com (CAS# 7664-93-9), argon gas, technical grade, Airgas Store, Chamblee, GA (CAS# 7440-37-1), calcium chloride (anhydrous), technical grade, Ebay.com (CAS# 10043-52-4), and 3 Å molecular sieve, ebay.com.

### 2.2 Equipment

The equipment used was an organic glassware set, (all the following have 24/40 ground glass fittings: 1 Liter Erlenmeyer flask; 300 mL addition funnel; vacuum adapter; thermometer adapter; two-necked boiling flask, 500 mL; 2-way distillation head (male-male) adapter, bent, 75 degree; vacuum take-off adapter, 50 mL single-neck boiling flask, and a glass stopper), Erlenmeyer flask, 250 mL, separatory funnel, 240 mL, polypropylene tubing, Buchner funnel, 250 ml filtering flask, 4 mm OD glass tubing, aluminum lattice lab frame, and Parafilm PM996 M Wrap, from eBay.com. Also used was a small 2-liter plastic bucket and a rubber stopper (2-hole).

### 2.3 Experimental Conditions

<experimental conditions, like temp, gas flow, et. al.>

### 2.4 Procedures

Acetone was purified via fractional distillation using technical grade acetone. The distillation product was then dried over a 3 Å molecular sieve for 24 hours. Before starting HCl production,

the system was flushed with argon gas. The apparatus was set up so that 200 grams of salt (sodium chloride) in an Erlenmeyer flask would have concentrated sulfuric acid dripped into it, and the resulting HCl gas flow through a second Erlenmeyer flask with anhydrous calcium chloride, to dry it, on the way to being bubbled through dry acetone in a round-bottom flask. Excess HCl was to be bubbled through water containing calcium carbonate. The connections were set to protect against liquid being drawn back into the system (backflow preventer) or sulfuric acid having a path into the acetone.

Once the apparatus was set up, 179 g (3 mol) of sodium chloride was added to the gas generation flask, sulfuric acid was added to the dehydration flask, and the system was flushed with argon. One hundred grams of anhydrous acetone was added to the 500 mL, two-necked, round-bottom flask with 1 gram of anhydrous  $\text{AlCl}_3$  and the flask sealed. The system was again flushed with argon.

Concentrated sulfuric acid was added to the addition funnel and it was adjusted to let one drop of sulfuric acid drop approximately every second. Once the generation of HCl had begun, ice was added to the plastic bucket had ice and some water added to keep the round-bottom acetone reaction mixture cool. See Figure 1.



Figure 1. Apparatus setup during operation

This proceeded for an hour, then more salt was added to the gas generation flask, and sulfuric acid restarted. It was allowed to continue for another hour to ensure the acetone was fully saturated with HCl gas.

The acetone started turning light yellow during the saturation process, proceeding to an orange color. The HCl gas was allowed 15 more minutes of bubbling through the acetone, then the sulfuric acid drip was stopped, and the acetone reaction flask sealed with two glass stoppers. The stopper seals were then covered by parafilm.

After 24 hours, the reaction mixture was a deep purple color. The sealed reaction solution was allowed to react for three weeks, at room temperature. At the end of the reaction period, diethyl ether was washed with NaOH solution until the mixture ceased testing acidic. To the ether solution saturated ethanolic KOH was added and mixed until KCl ceased precipitating. The ether fraction was separated with a separatory funnel and washed with 10 batches, 50 mL each, of distilled water until the water portion tested neutral. The ethereal portion was dried over anhydrous MgSO<sub>4</sub> and filtered by vacuum filtration.

The ether was removed via fractional distillation. Mesityl oxide was distilled off via fractional distillation, collecting 15 milliliters. The remaining residue was a mixture of materials. It appeared to contain less than a gram of material. Its smell indicated the presence of phorone.

### 3.0 RESULTS AND DISCUSSION

This reaction caused acetone to react in an aldol reaction, forming mesityl oxide chloride, phorone chloride, and presumably other condensation products. Treating with ethanolic KOH converted the mesityl oxide chloride to mesityl oxide and phorone chloride to phorone, the former of which was separated via fractional distillation.

Fifteen milliliters of mesityl oxide was obtained after distillation. Given 100 grams (~1.7 mols) of acetone were the starting reactant, the product obtained was 15 mL (12.87 g/0.13 mols) with acetone requiring 2 moles for every 1 mole of mesityl oxide, computes to a 15.3% yield. This is a great deal below the Konieczny and Sosnovsky paper's reported mesityl oxide yield (52%) and with negligible phorone produced, nothing like their 39% yield of phorone.

The failure to reach the yields of the Konieczny and Sosnovsky paper are likely due to poor reagents. The only reagent that was ACS grade was the sulfuric acid used to generate the HCl gas.

The AlCl<sub>3</sub> was from Ebay, therefore possibly not anhydrous and the acetone, though distilled, was from Home Depot, so containing possible contaminants.

## 4.0 CONCLUSIONS

This research was a repetition of the Konieczny and Sosnovsky paper, with regards to the acid-catalyzed aldol condensation. It used HCl gas saturating acetone and allowed it to react for 21 days, then neutralized and treated with ethanolic KOH. After purification and distillation, mesityl oxide product was produced at a 15.3% yield. There was an odor of phorone present, but with no significant yield of phorone separated from the remaining residue.

## 5.0 REFERENCES

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