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Cross-nucleophilic Addition of Carbide Ion to Two Different Ketones

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Abstract: The study dealt with the synthesis of asymmetric acetylenic diols by cross – nucleophilic addition of calcium carbide using two different ketones; acetophenone and cyclohexanone. It aimed to develop a methodology for the said synthesis that is safe and efficient. The reaction mixture consisted of calcium carbide and KOH with acetophenone and cyclohexanone added differently on each synthesis. The three mode of additions are alternate dropwise, dropwise and one-shot addition. Crystals that were formed were purified and subjected to Gas Chromatography and FT – IR Spectrophotometer. The reaction optimized by different mode of additions yielded 10 -12% of acetylenic diols. Purity of the products were also tested by melting point determination and thin layer chromatography. Alternate Dropwise addition gave a peak between two reference products in gas chromatogram, these references are theoretically assumed to be the product from previous studies¹. The ratio of the peak between the reference standards was one 1-(3-Hydroxy-3-phenyl-but-ynyl)-cyclohexanol in 46.85 of bis(1-hydroxycyclohexyl)ethyne. Major functional groups that are present in IR spectra were identified based on the proposed structure [i.e. -OH, -CH₂, -CH (sp³ stretch)]. Further characterization is needed to confirm the structure of the reference standards at products.

Key Words: asymmetric acetylenic diols; calcium carbide; cross-nucleophilic addition

1. INTRODUCTION

Acetylenic diols are used as precursors in the synthesis of natural products and vitamins.^[9] It is also used as surfactants by lowering the surface tension and interfacial tension of liquids.^[10] The common synthesis of acetylenic diols is by reacting acetylide Grignard reagent with ketones. This procedure requires inert atmosphere and high pressure

acetylene gas, which need careful handling. Also, the reaction consists of tedious steps, and several purification processes, especially when adding the acetylide ion to two different ketones. This type of reaction is called cross-nucleophilic addition.

In contrast to the use of Grignard reagent that involves several steps, acetylenic diols can also be prepared from one-pot reaction of



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calcium carbide (or calcium acetylide) and two equivalent ketones in the presence of a strong base (e. g. KOH, NaOH, MeOK, and *t*-BuOK). However, studies involving cross-nucleophilic addition of acetylide ion (carbide ion) to two different ketones to produce asymmetric acetylenic diol has not been reported in the literature.

Asymmetric acetylenic diols have various potential applications and properties. They are used as dienophiles in Diels-Alder reactions and as a precursor for synthesis of acetylenic diones for the natural product synthesis. Furthermore, chemical and physical properties of these asymmetric acetylenic diols are noteworthy to explore. Moreover, the surfactants derived from acetylenic diols lead to many uses (e.g. inks, paints/coatings, adhesives, dyes/pigments and pesticides). Also, the one-pot cross-nucleophilic addition of calcium carbide to two different ketones is an efficient method for the production of acetylenic diol.

2. METHODOLOGY

A reaction mixture that contains ratio of 62.40 mmol of CaC_2 (4 grams) and 93.61 mmol of KOH (5.25 grams) with a 50 ml of benzene was placed in a 250-ml, two-necked, round bottom flask fitted with magnetic stirrer and stirred at 28 °C (room temperature). Sixty two point forty mmol of cyclohexanone and acetophenone was added drop-wise, alternate drop-wise and one-shot addition (the different addition of ketones are for optimization) for about 30-60 minutes. The reaction was stirred at the next 48 hours. Then it will be acidified with 1 M HCl. The organic layer was separated and filtered. Finally, the yellow filtrate was allowed to cool until the crystals started to

form. The crude crystals were recrystallized in hexane.

The products obtained in the reaction were tested for purity by melting point determination, thin layer chromatography (hexane and ethyl acetate as a solvent system) and was subjected to Hewlett Packard 6890 Series II Gas Chromatography.

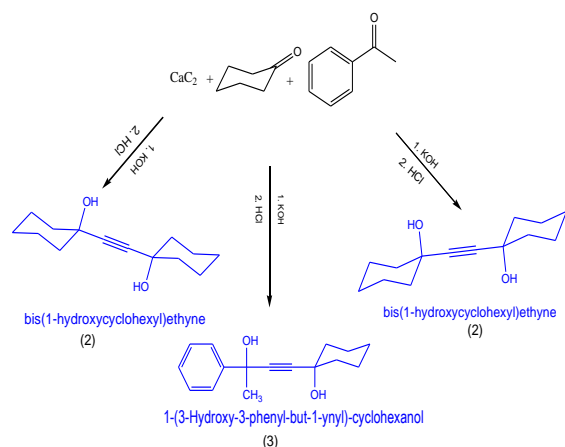
Functional groups that are present in the compound were determined by Thermo Scientific Fourier Transfer Infrared Spectrophotometer.

3. RESULTS AND DISCUSSION

Acetophenone and cyclohexanone was used in a reaction mixture in the presence of benzene and KOH as a base. The two different ketones was added (2) One-shot, (2) Dropwise and (3) Alternate dropwise. The reaction yielded 11.99%, 7.06% and 9.51% respectively. The products are soluble in diethyl ether and ethanol, but insoluble in water. To test the purity of the compounds, the product crystals undergone melting point determination, this obtained the following readings 90-95°C, 94-95°C, and 96-100°C. Thin layer chromatography was also done and showed that there were no tailing occurred. Hexane and ethyl acetate (50:50) was used as a solvent system. The reference products were tested for purity by Gas Chromatography as well as the products for the three mode of addition. Based from the method of previous studies, it was assumed that the reference products are the product obtained from latter.¹

The alternate dropwise mode of addition gave a small peak at the chromatogram in between the retention time of the references with area 1:47. The said peak was then assumed to be another compound or the asymmetric acetylenic diol(3) besides the reference products. The proposed scheme below

is fully theoretical since the products and reference products were not tested using GC-MS or NMR.



Scheme 1. Summary of Reaction of Calcium Carbide with Cyclohexanone and Acetophenone: *Conditions:* Stirred for 48 hours with benzene and KOH (93.61mmol) at 28°C.

4. CONCLUSIONS

Among the three mode of additions that were performed in reacting calcium carbide into two different ketones, alternate dropwise addition was the only one that yielded two different compounds [1-(3-Hydroxy-3-phenyl-but-ynyl)-cyclohexanol and bis(1-hydroxycyclohexyl)ethyne]. This were based on the peaks that gas chromatography spectrum gave. This mode of addition also had a total yield of 9.51%.

On the other hand, dropwise addition yielded a total of 7.06% and 11.99% for one-shot addition. These two modes of addition gave a same compound which is bis(1-hydroxycyclohexyl)ethyne.

However, the proposed compounds are only theoretical, because the product crystals were

only tested using Gas Chromatography and Fourier Transfer Infrared Spectrophotometer.

Moreover, it is suggested that the time of stirring the reaction mixture should be maximized to 63 hours for greater yields. Reacting calcium carbide in 0°C should also be done, since the aim of the reaction is to produce compounds. The product crystals must be tested using GC- MS and NMR for verification of molecular weight and structures.

5. ACKNOWLEDGMENTS

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