

Synthesis and Characterization of some Dicarboxylic Acid Monomers

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Abstract: Cyclohexane-1,4-diacetic acid chloride; 2,6-Dimethyl-1,8-octyldicarboxylic acid chloride; and 2,5-dimethyl-1,7-heptyldicarboxylic acid chloride were synthesized starting with 1,4-cyclohexanedione, 2,5-hexanedione and 2,4-pentanedione. Diethyl-1,4-cyclohexylenediacetate and 1,4-cyclohexanediacetic acid as representative diesters and diacids were identified by proton NMR spectroscopy. The Nuclear magnetic resonance spectra were determined using Bruker WH-400. Elemental analysis data of 1,4-cyclohexanediacetic acid was provided by Galbraith Laboratories.

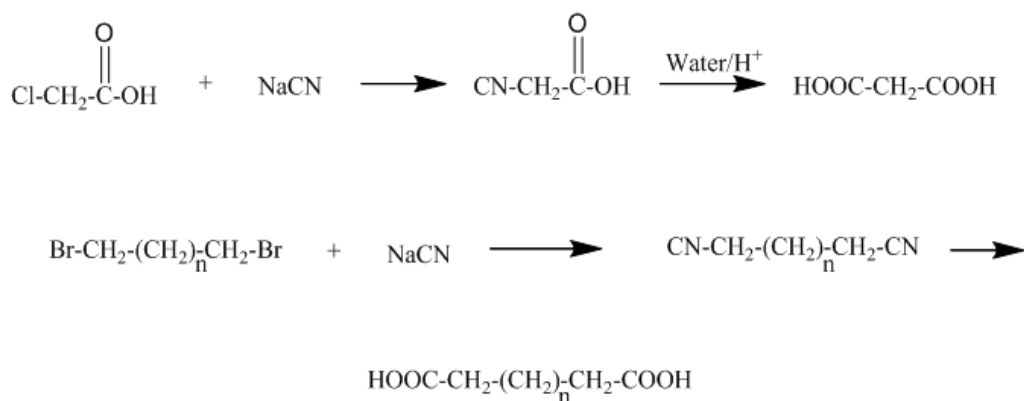
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I. Introduction

There are many industrial and laboratory ways of producing carboxylic acid functional group. Among the methods are: oxidation of alcohols and aldehydes, oxidative cleavage of alkene and alkynes, side chain oxidation of alkyl benzenes. Primary alcohols and aldehydes are oxidized to carboxylic acids by chromic acid, which is produced by the reaction of sodium chromate and sulfuric acid¹⁻⁴. Other methods of producing carboxylic acid include, hydrolysis of nitriles⁵⁻⁹, carboxylation of Grignard reagents, malonic ester synthesis¹⁰⁻¹⁵, halogenations of alpha-methyl ketones, hydroboration of terminal alkenes followed by chromium vi oxidation. These methods work for the production of both monofunctional and difunctional dicarboxylic acids as long as the functional groups being converted are difunctional. Most common dicarboxylic acids used in polyester or polyamide synthesis are adipic, sebacic, and azelaic acids. The common methods used in industries are oxidation of cyclic ketones¹⁶, malonic ester synthesis and cyanide synthesis. The nitrile synthetic approach produces a wide range of dicarboxylic acids starting from alpha-halogenated acid or polymethylenedihalide.



Over the years, researchers have been finding simpler and cost effective ways of synthesizing molecules useful to the polymer industry. In this regard, we synthesized 1,4-cyclohexane diacetyl chloride, 3,5-dimethyl-1,7-diheptanoyl chloride and 3,6-dimethyl-1,8-dioctanoyl chloride for making polyesters and polyamides. From these compounds, 1,4-cyclohexane diethanol, 3,5-dimethyl-1,7-heptanediol and 3,6-dimethyl-1,8-octanediol could be produced by simple reduction of carboxylic acid. These materials could be combined with diisocyanates and diamines to produce a variety of polyurethanes, polyesters and polyamides. In this work, we are going to describe the synthesis of the diacids. Cyclohexane-1,4-diacetic acid has been used, in combination with aromatic diols to produce linear polyesters. It has also been used to provide flexibility in rigid polyesters which helped to lower their melting points for ease in thermal processability¹⁷.

There are commercial methods of producing Cyclohexane-1,4-diacetic acid however, these methods require sophistication in equipment design. These equipments can withstand high temperature and pressure. Where such equipments were not available, a simple laboratory process was used in the synthesis. By high temperature and pressure, selective hydrogenation of 1,4-diacetyl methyl ester substituted benzene ring, 1,4-cyclohexyl diacetylesther derivatives was produced.

II. Materials and Method

Cyclohexane 1,4-dione, 2,5-hexanedione, 2,4-hexanedione, triethylphosphite and ethylbromoacetate were obtained from Sigma-Aldrich and used without further purification. Thionyl chloride, Sodium hydroxide, Sodium hydride, Tetrahydrofuran (THF) and Chloroform were also purchased from Sigma-Aldrich. THF was dried over anhydrous sodium sulfate.

Preparation of Diethyl(carboethoxymethyl) phosphonate

This compound was prepared using the Michelis-Arbuzov method¹⁸. Equimolar amounts of triethylphosphite and alpha-bromoethylacetate were mixed in a three necked round bottom flask, equipped with magnetic stirrer, thermometer and a condenser. After mixing for 10 minutes, exothermic reaction started and ethylbromide began to condense. The reaction was heated with refluxing for additional two hours. Ethylbromide was removed by distillation. Diethyl(carboethoxymethyl) phosphonate was collected for the next phase of the reaction.

Preparation of 1,4-Cyclohexylidene diethylacetate

12.0 g (0.0535 mol) of diethyl(carboethoxymethyl) phosphonate was added drop wise over a period of 1 hour to a stirring mixture of 2.13 g (0.0535 mol) of 60% sodium hydride and dry THF. When the evolution of hydrogen gas had stopped, 3.00 g (0.0267 mol) of 1,4-cyclohexanedione in 15cm³ THF was added drop wise to the flask at 30⁰ C. The mixture was stirred for 6 hours. THF was removed at reduced pressure and the residue was poured into a large excess of water. Chloroform was added into the water mixture to extract the compound. It was dried over anhydrous sodium sulfate. After evaporating the chloroform, about 6 g of the compound was recovered. This represented a yield of 89%.

Hydrogenation of Diethyl-1,4-cyclohexylidenediacetate

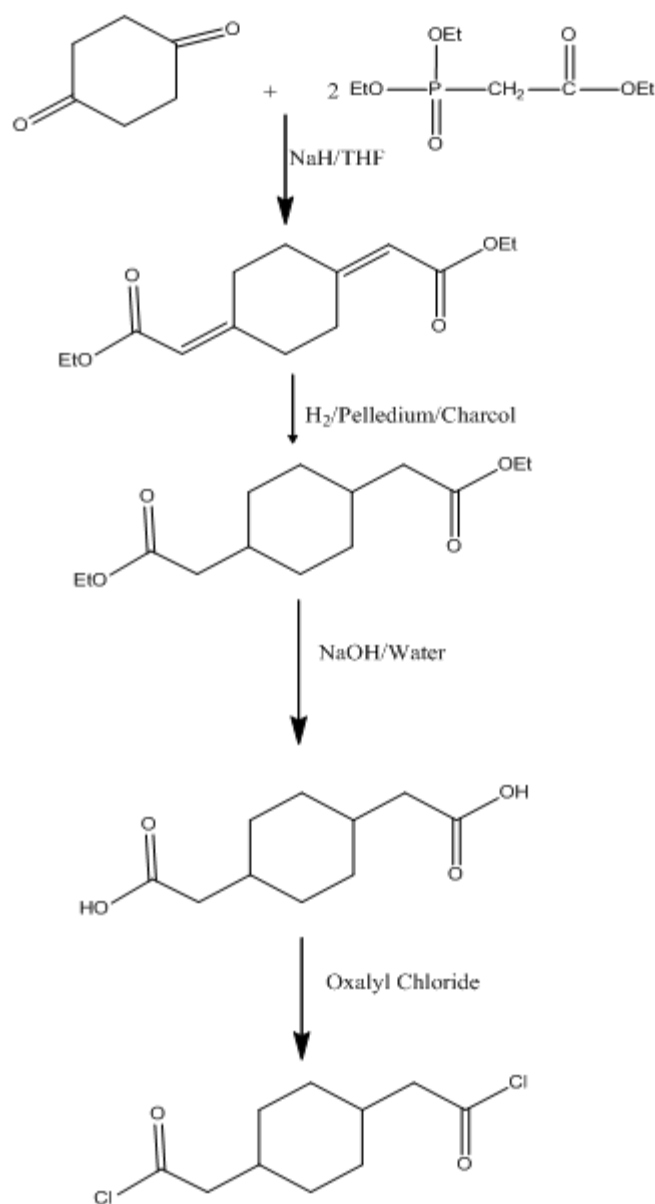
This compound was charged into a hydrogenation chamber at room temperature. 10% by weight palladium on charcoal was also added to the chamber. About 50 psi hydrogen gas was maintained while the chamber was oscillating. After work-up, 98% of Diethyl-1,4-cyclohexanediacetate was recovered

Preparation of 1,4-Cyclohexanediacetic acid

A solution of 6.00 g (0.0234 mol) of Diethyl-1,4-cyclohexanediacetate in 100 cm³ of 6N Hydrochloric acid was refluxed for 12 hours. After cooling, the diacid was collected by filtration. It was washed several times with cold water and dried in vacuum oven to yield 3.4 grams of product

Preparation of 1,4-Cyclohexanediacetyl chloride

The acid chloride was prepared according to the method of Miyano, M. and Dorn, C



1,4-Cyclohexanediactoyl chloride

Preparation of non-cyclic analogs of cyclohexanediactetic acid

non-cyclic analogs of diactoyl chloride monomers were also prepared using the same method.

Preparation of Diethyl-3,6-dimethyl-2,6-octadieneoate

About 25.0 g (0.107m) of diethyl(carboethoxymethyl) phosphonate was added drop wise over a period of 1 hour to a stirring mixture of 2.57 g (0.107 m) of 60% sodium hydride and dry THF. When the evolution of hydrogen gas had stopped, 6.10 g (0.0535m) of Hexane-3,5-dione in 15 cm³ THF was added drop wise to the flask at 30⁰ C. The mixture was stirred for 6 hours. THF was removed at reduced pressure and the residue was poured into a large excess of water. Chloroform was added into the water mixture to extract the compound. It was dried over anhydrous sodium sulfate and chloroform was evaporated, leaving a viscous liquid.

Hydrogenation of Diethyl-3,6-dimethyl-2,6-octadieneoate

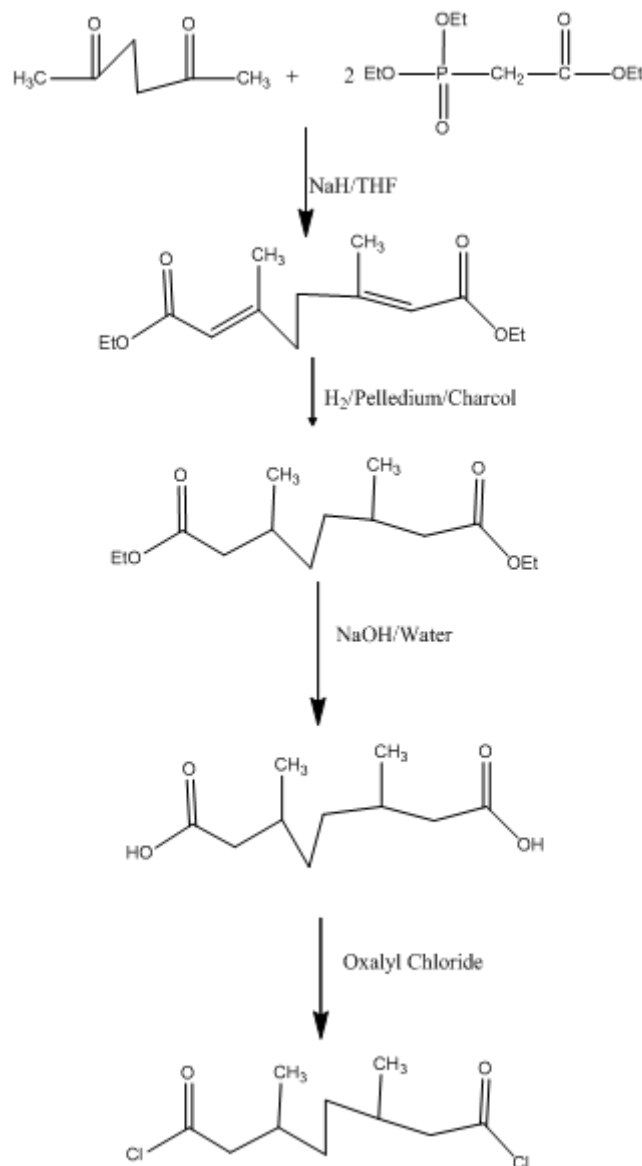
This compound was charged into a hydrogenation chamber at room temperature. About 10% by weight palladium on charcoal was also added to the chamber. About 50 psi hydrogen gas was maintained while the chamber was oscillating. After work-up, 98% of 3,6-dimethyloctane-1,8-diethylidioate was recovered.

Preparation of 3,6-Dimethyl-1,8-octanedicarboxylic acid

A solution of 12.00 g (0.0392m) of 3,6-dimethyloctane-1,8-diethyldioate was mixed with 3.14 g (0.0784 m) of NaOH dissolved in 200cm³ of water, was refluxed for 12 hours. After cooling, the diacid was collected by filtration. It was washed several times with cold water and dried in vacuum oven.

Preparation of 3,6-Dimethyl-1,8-octanedicarboxylic acid chloride

The acid chloride was prepared according to the method of Miyano, M. and Dorn, C.



Preparation of Diethyl-3,5-dimethyl-2,5-heptadieneoate

About 25.0 g (0.107 mol) of diethyl(carboethoxymethyl) phosphonate was added drop wise over a period of 1 hour to a stirring mixture of 2.57 g (0.107 m) of 60% sodium hydride and dry THF. When the evolution of hydrogen gas had stopped, 5.35g (0.0535 m) of Pentane-2,4-dione in 15cm³ THF was added drop wise to the flask at 30⁰ C. The mixture was stirred for 6 hours. THF was removed at reduced pressure and the residue was poured into a large excess of water. Chloroform was added into the water mixture to extract the compound. It was dried over anhydrous sodium sulfate and chloroform was evaporated, leaving a viscous liquid.

Hydrogenation of Diethyl-3,5-dimethyl-2,5-heptyldieneoate

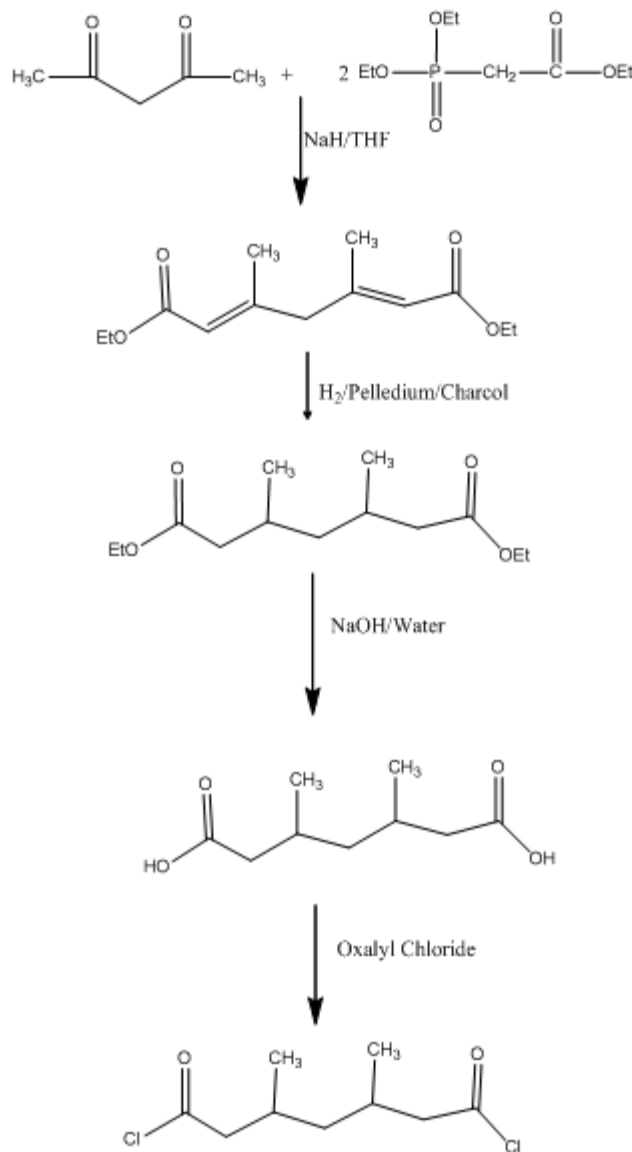
This compound was charged into a hydrogenation chamber at room temperature. About 10% by weight palladium on charcoal was also added to the chamber. About 50 psi hydrogen gas was maintained while the chamber was oscillating. After work-up, 90% of 3,5-dimethylheptyl-1,7-diethyldioate was recovered.

Preparation of 3,5-Dimethyl-1,7-heptyldicarboxylic acid

A solution of 12.00 g (0.0392 m) of 3,5-dimethylheptyl-1,7-diethyldioate was mixed with 3.14 g (0.0784 m) of NaOH dissolved in 200cm³ of water, was refluxed for 12 hours. After cooling, the diacid was collected by filtration. It was washed several times with cold water and dried in vacuum oven.

Preparation of 3,5-Dimethyl-1,7-heptyldicarboxylic acid chloride

The acid chloride was prepared according to the method of Miyano, M. and Dorn, C.



NMR ANALYSIS

The Nuclear magnetic resonance spectra were determined using Bruker WH-400. Elemental analysis data of 1,4-cyclohexanediactic acid was provided by Galbraith Laboratories.

III. Results And Discussion

The result obtained from the preparation and analysis of some dicarboxylic acid esters are stated below. Fig 1 below is the elucidated structure of Diethyl-1,4-cyclohexyldenediacetate. This structure was obtained from the proton NMR below fig 2 combined with elemental analysis.

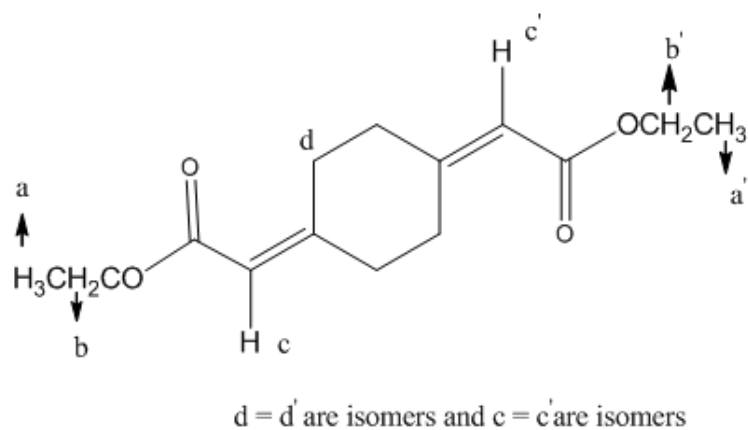


Fig 1

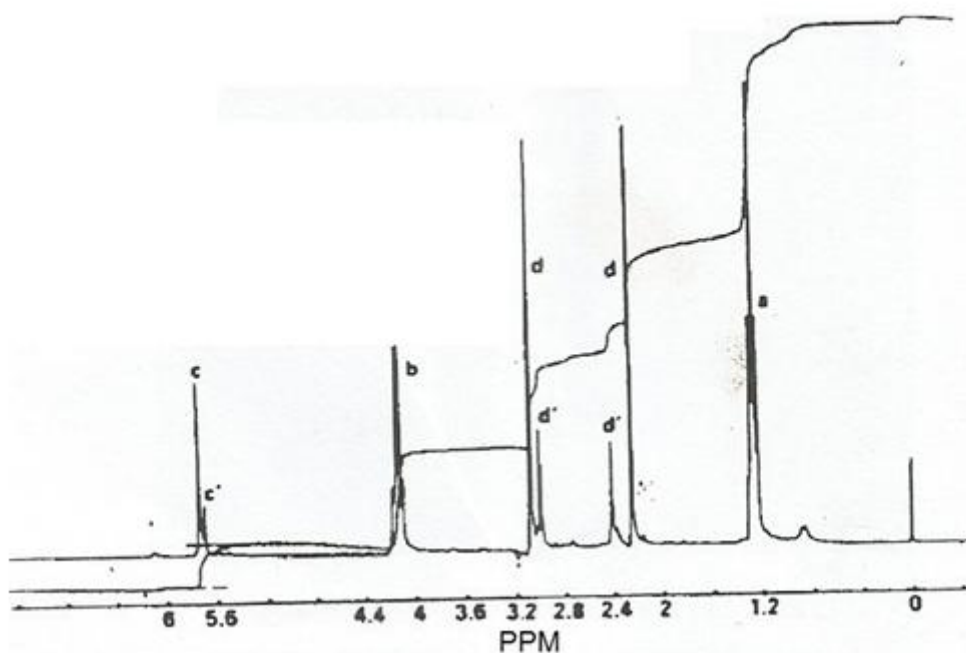


Figure 2: Proton NMR of Diethyl-1,4-cyclohexylidenediacetate

The d protons on each carbon are not magnetically equivalent. The d' and c' signals represent the cis, trans isomer in lower abundance.

After hydrogenation and hydrolysis of Diethyl-1,4-cyclohexylidenediacetate, the proton NMR was taken which is shown in figure 2.

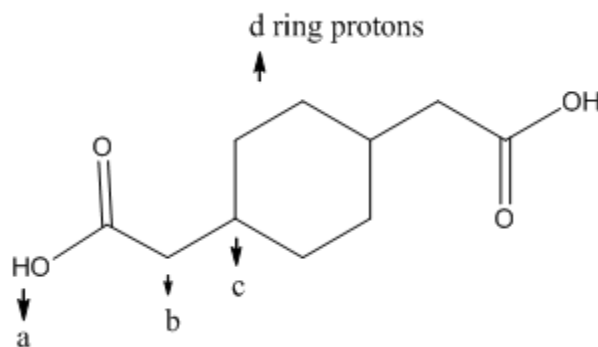


Fig 3

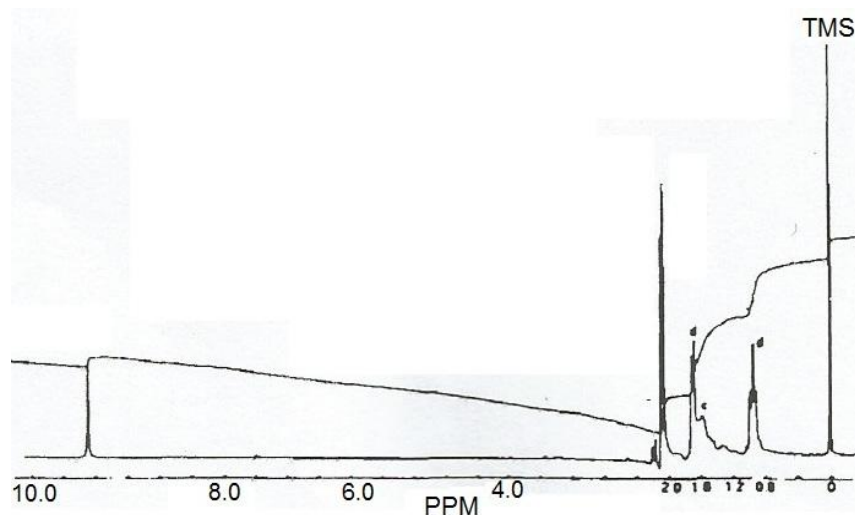


Figure 4. Proton NMR spectrum of 1,4-cyclohexanedicarboxylic acid

Elemental analysis of 1,4-cyclohexanedicarboxylic acid showed: calculated for $C_{10}H_{16}O_4$ as C, 60.00, H, 8.00; Found C, 63.01, H, 8.50

The proton NMR and Elemental analyses show clearly that we obtained 1,4-cyclohexanedicarboxylic acid. The difference between the calculated and found in the elemental analyses may be due to minor impurities. The cis and trans isomers found in the proton NMR of 1,4-cyclohexylidene diacetate, disappeared upon hydrogenation of the double bond. The proton signal between 9 and 10 ppm is indicative of the removal of the ethyl group from the ester and replacement with acidic proton upon hydrolysis.

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