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THESIS

THE SYNTHESIS OF 1,2,3,TRIPHENYLPROPANE

by

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THE SYNTHESIS OF 1,2,3,TRIPHENYLPROPANE.

The preparation of symmetrical triphenylpropane has been carried out by several different methods, principally by German chemists. Altho there is very little in the chemical literature on this compound, the method most frequently used was from tribromhydrin by the Friedel-Craft reaction. Cohn¹(Paul) obtained a hydrocarbon of the composition $C_{21}H_{20}$ which was probably symmetrical triphenylpropane, when 10² gms. of cyclophenylenebenzylidene oxide, or 10 gms. of orthohydroxybenzhydrilamine was heated at 140-150°C. with 40-50 cc. of fuming hydriodic acid and 10 gms. of red phosphorus. The liquid after shaking with ether, was made alkaline, distilled with steam, and after shaking with ether again, the ethereal solution was evaporated. A thick, heavy oil was obtained.

Claus and Mecklin², Meyer and Jacobson³, and others obtained the hydrocarbon by the reaction of benzene and anhydrous aluminum chloride on tribrom- or trichlorhydrin. Their product was a thick yellow oily liquid which boiled above 340°C., and could only be distilled under reduced pressure without decomposition.

It was thought best to first prepare this compound by the last mentioned method, and then prepare it by use of the Grignard reaction, first preparing the carbinol and reduction to the hydrocarbon. Nothing can be found in the literature where triphenylpropane has been formed by the use of magnesium alkyl halid condensation, so the method used in the formation of tertiary alcohols was followed.

PREPARATION: BY FRIEDEL-CRAFT REACTION.

The method of Claus and Mecklin was followed. In order that the tribromhydrin might be pure, it was prepared. When allyl iodide is acted upon by bromine, the double bond is broken by the addition of bromine⁴, and the iodine is also replaced by bromine, forming tribromhydrin. In this manner the tribromhydrin was prepared after first obtaining the allyl iodide. The allyl iodide was prepared by two different methods:-

(a) Reaction of Phosphorus and Iodine on Allyl Alcohol.

(b) Reaction of Phosphorus and Iodine on Glycerol.

(1) Jour. Chem. Soc., 1899, Vol.1, p295.

(2) Jour. Chem. Soc., 1886, Vol.1, pl43.
Ber., 18, 2935 (1885)

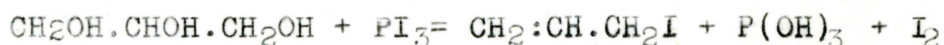
(3) Lehrbuch der Organischen Chemie, Vol. 2, Zweiter Theil, Erste Abtheilung. S.256.

(4) Fisher: Lab. Man. of Organic Chem., on Preparation of Ethyl Iodide. (Harry L. Fisher)

(a) 30 grams of allyl alcohol and 8 grams of red phosphorus were mixed in a flask, and 65 grams of iodine added in small portions, with cooling after each addition. When all the iodine had been added the mixture was allowed to stand for 24 hours, after which it was refluxed over a water bath heated gently. When the reaction had subsided somewhat (20 minutes), the mixture was distilled under reduced pressure. A reddish liquid was caught the boiling point being approximately 102°C. This was washed with water in a separatory funnel, and dried in fused calcium chloride. An accident while handling cut the yield down to 50% of the theoretical.

(b) In this method glycerol and yellow phosphorus replaced the allyl alcohol and red phosphorus used in the above reaction. This method by Rasik Lal Datta¹ is a modification of the methods of Claus², and Kemonikoff and Saytzeff. Lal Datta found that the operation may be quickly and smoothly carried out, and states that the yield is very satisfactory. Unfortunately, in this run, too strong an alkali was used for washing and the product decomposed.

The apparatus consisted of a retort with a glass stopper in the top, placed over a water bath for heating. A condenser and receiver were connected to the retort. 100 gms. of glycerol was added to the retort, followed by 137 gms. of iodine. The water bath was heated to boiling, and a small piece of yellow phosphorus was added, quickly replacing the stopper. When this came in contact with the iodine in the hot glycerol it reacted at once. Then more phosphorus was added piece by piece, and the formation of allyl iodide continues.



After a considerable quantity of phosphorus has been added, the allyl iodide formed distilled off, due to the heat of the water bath and the heat of the reaction. 33.6 gms. of phosphorus was added, larger pieces being used as the reaction proceeded. The last traces were distilled by heating with a constantly moving flame. Some isopropyl iodide was formed with the allyl iodide as was shown when the distillate was washed with sodium hydroxide solution; the allyl iodide decomposed, leaving the more stable isopropyl iodide unaffected.

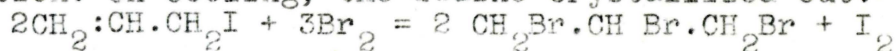
(1) Jour. Am. Chem. Soc., Vol 36-1, p1005.

(2) Ann. 131, 58(1864)

With the allyl iodide thus formed, the next step was the preparation of the tribromhydrin². According to Roscoe and Scharlemmer², propenyl tribrom, or tribromhydrin, $C_3H_5Br_3$, is formed together with the mono- and dibromhydrin by the action of phosphorus bromide on glycerine (Bertholet and de Luca). It is best prepared by treating allyl iodide with bromine (Wurtz, Ann. Chem. Phys. (3) 11.91.).

Kronstein³ heated equivalent quantities of trimethylene bromide⁴ and bromine in a sealed tube at 120 C. for nine hours and from the product washed and thrice fractionated obtained tribromhydrin as a colorless oil of specific gravity 2.44 at 25°, boiling at 219-220°C., and solidifying to a colorless mass on cooling to 0°. If the bromination is carried on in the presence of iron wire at 100 C., the yield of tribromhydrin is almost quantitative.

It was decided that the method of Wurtz should be followed: Bromine was added drop by drop thru a pipette to 44 gms. of allyl iodide in an Erlenmeyer flask. The reaction was very vigorous and required constant cooling. 62.5 gms. of bromine were added, the addition being slow and tedious on account of the active nature of the reaction. On cooling, the iodine crystallized out.



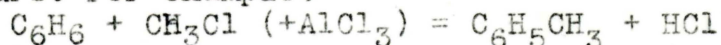
The product was slightly warmed (30-35°) and filtered from the iodine. the filtrate was then distilled under reduced pressure, and after the iodine had distilled over, the receivers changed, and the tribromhydrin caught. This was washed with dilute sodium carbonate solution, removing the iodine, and a colorless oil was obtained. This however assumed a reddish color on standing. Yield, 19.4 gms.

PREPARATION OF TRIPHENYLPROPANE.

The reaction discovered by Friedel and Crafts⁵, in which only anhydrous aluminum chloride is the active reducing agent, has had an extraordinary wide and varied application in organic syntheses. It is by this reaction that a union is effected between an aromatic

- (1) Chemisches Central-Blatt, 1896-2, p963; 1912-1, 887.
- (X) Chemical News, Vol. 21, Pgs. 154, 287, 298;
" " Vol. 22, Pgs. 21, 84.
- (3) Jour. Chem. Soc., 1892, p577.
- (2) Roscoe and Schorlenmer, Vol. 3, p347.
- (4) Erlenmeyer, A., 197, 180.
- (5) Cohen, Organic Chemistry, Vol.1, p195.
Comp. rend., 1877, 84, 1392.
Ann. Chem. Phys., 1884,(6), 1, 506.

hydrocarbon and its derivatives with a variety of other organic compounds, such as alkyl halides, acid chlorides, etc. A hydrocarbon can be obtained by combining an alkyl halid with benzene in the presence of anhydrous aluminum chloride, where a vigorous evolution of halogen acid occurs. For example:



It was by the use of this reaction that Claus and Muchlin, and Meyer and Jacobson prepared triphenylpropane.

In this preparation the tribromhydrin and benzene had been dried over anhydrous calcium chloride for several days. A slight excess of benzene was used. 19.2 gms. of benzene and 6 gms. of anhydrous aluminum chloride were mixed in a round bottom flask, and condenser attached for refluxing. 19.5 gms. of tribromhydrin was slowly added, but no reaction was perceptible for sometime. Then suddenly there was a rapid evolution of hydrobromic acid, which continued for 40-50 minutes. The flask was kept at 50° after the reaction had become less vigorous. The reaction mixture was poured into 100cc. of ice water, a dark, heavy, oily substance separating. Part of the water was decanted and then the hydrocarbon was separated by solution in ether (also-soluble-in-benzene), and washed in dilute sodium carbonate solution. The ether was distilled off, and the mixture distilled under reduced pressure. At 190°C. and #48mm. pressure, a yellow oil came over and was collected. The residue in the flask consisted of a black, tar-like solid. The oil obtained, when cooled to 0°, became very thick but did not solidify. This oil was found to be soluble in benzene.

PREPARATION OF PHENYL-DIBENZYL CARBINOL; GRIGNARD'S SYNTHESIS.

The great value of magnesium as a synthetic reagent was indicated in 1900 when Grignard showed how various hydrocarbon and alcohols could be prepared from the compounds obtained by allowing the metal to react with an alkyl halid in the presence of dry ether. The metal has to a great extent replaced zinc, which was used in 1849 by Frankland in the preparation of paraffin hydrocarbons and zinc alkyls. Since the discovery by Grignard², research by the use of magnesium compounds has made it possible to prepare secondary alcohols from aldehydes; tertiary alcohols from ketones, acid chlorides, esters, and carbonyl chloride; ketones from acid chlorides,

(1) Compt. rend., 1900, 130, 1322.

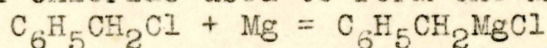
(2) Cohen, Vol.1, pg. 213.

(3) Hale, Synthetic Use of Metals, pgs.45-49.

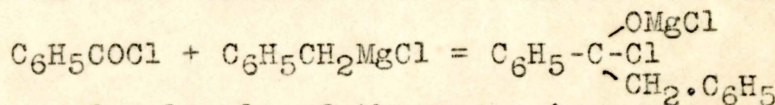
cyanogen, nitriles², and amides; aldehyde from formic and ortho-formic acids; hydroxylamine derivatives from amyl nitrite; anilides from amyl carbimide; diazo compounds from azoimides; and many other preparations².

Altho the behavior of the magnesium alkyl compounds greatly resembles in many respects that of zinc alkyls, their greater activity, due to the more electro-positive character of the metal, as well as the convenience of preparation, offer greater advantages over the use of zinc compounds. Moreover, aromatic halogen compounds, such as brom- and iodo-benzene and toluene, may be used in addition to the alkyl halids².

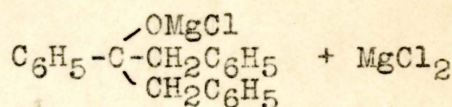
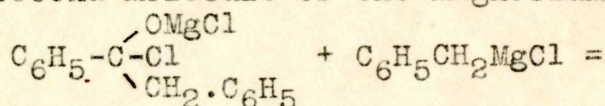
In this synthesis, benzyl chloride was the aryl chloride used to form the magnesium compound:



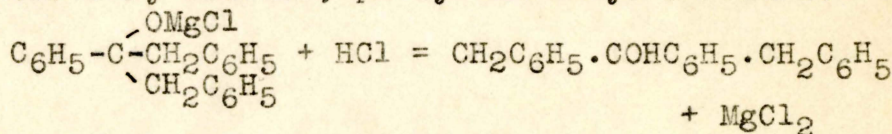
The compound when treated with a molecule of benzoyl chloride:



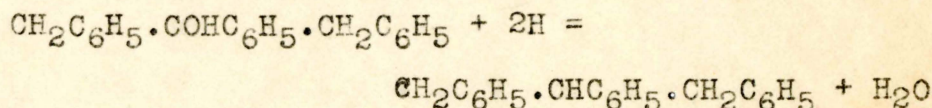
With a second molecule of the magnesium compound:



This compound when treated with dilute hydrochloric acid gives a tertiary alcohol, phenyl-dibenzyl carbinol:



The reduction of this alcohol ^{should} gives the hydrocarbon:



Hunter and Winslow³ prepared phenyl-dibenzyl carbinol from dibenzylketone and phenyl magnesium chloride in anhydrous ether. Davies and Kipping⁴ prepared the carbinol from ethyl benzoate and benzyl chloride in the presence of magnesium, the reaction proceeding without

- (1) Hale, Synthetic Use Of Metals, pgs.45-49.
- (2) Cohen, Organic Chemistry, Vol.1, pg. 209.
- (3) Unpublished Notes.
- (4) Jour. Chem. Soc., Vol.99-1, 1911.

difficulty. The product was distilled under diminished pressure, and the distillate readily solidified to a hard, pale yellow cake. On recrystallization from light petroleum, the carbinol was obtained as colorless needles, the yield was 60% of the theoretical. Klages² describes the compound as small, colorless needle crystals, melting at 86-87°.

A slight trace of water is disastrous to the efficiency of this reaction between magnesium and aromatic halids, consequently all reagents had to be dried over calcium chloride (fused) and redistilled. The ether was dried over metallic sodium and distilled. According to Hale, in the use of brombenzene or benzyl chloride, to prevent secondary reaction such as the formation of diphenyl or dibenzyl, all the reagents should be mixed at once, thus omitting the first step (preparation of the RMgX compound).

Using benzyl chloride, an attempt was made with the simultaneous mixing of the reagents. 50gms. (2 mol) of benzyl chloride was dissolved in 60cc. of ether, and to this was added 27.7gms. (1 mol) of benzoyl chloride which had been dissolved in its own weight of ether. The mixture of benzyl and benzoyl chlorides was added to 9.6gms of magnesium turnings in a round bottom flask, the magnesium having been washed in ether to remove grease and impurities from the surface. A crystal of iodine was added to hasten the reaction. It was gently heated under a reflux, the top of which was closed by a calcium chloride drying tube. After several hours there was no evidence of a reaction, so it was concluded that with the use of these reagents, there is another exception to the generalization offered by Hale².

The second run, the procedure was varied in that the magnesium aryl halid was first formed, and this proved more successful. the same quantities of dried reagents were used. The benzyl chloride was dissolved in ether and added to the magnesium in a flask under a reflux. A crystal of iodine was added and the flask very gently heated. The reaction started with a slight bubbling, and with increasing speed until it was necessary to cool occasionally with a wet towel. The solution turned a slight greenish hue, and quite a bit of the magnesium remained undissolved. The benzoyl chloride was added thru the reflux, and the mixture well shaken and refluxed for an hour. After standing overnight, a little ether was added and the product poured off the undissolved magnesium as well as possible. To this was added 2N hydrochloric acid until the solid dissolved. The ethereal solution was separated from the aqueous, and washed twice with dilute sodium carbonate solution, then with water, and dried in fused calcium chloride. The ether

(1) Ber., 1904, 37, 1456.

(2) Hale, Synthetic Use Of Metals, pg.45.

was removed by distillation, and the residue distilled "in vacuo". The excess benzoyl chloride came over at 110-130°C. (40 mm.), the receivers changed, and the supposed carbinol boiling about 172° (48mm.) was collected. It solidified in the receiver as a white crystalline mass, the crystals being needle-shaped. Another fraction, 190-230°C. (48mm.) gave a yellow oil which was thought to be the hydrocarbon, triphenylpropane. 15 grams of the white crystals were obtained, the melting point of which was found to be 54°C.

Sachs and Loewy in attempting to prepare tribenzylcarbinol, obtained a substance with melting point of 55° and boiling point of 277-278°. This substance however was later recognized to be the impure dibenzyl compound.

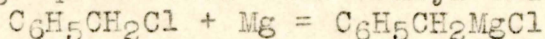
This white substance was treated with phosphorus trichloride, and after decomposing the excess with water, the oil remaining was dissolved in ether. Upon the evaporation of the ether, crystals of the same structure and melting point were obtained, showing that the phosphorus trichloride had had no effect upon the compound. The fact that this compound was a hydrocarbon and not a carbinol was further substantiated when an attempted reduction was made by heating with hydriodic acid and red phosphorus in a sealed tube at 180° for 24 hours. This treatment however had no effect on the compound, which was recovered undecomposed.

CONCLUSIONS

It is possible to prepare symmetrical triphenylpropane by the Friedel-Craft reaction, altho' the yield is small.

The reaction between benzal chloride, benzoyl chloride, and magnesium will not take place with the simultaneous mixing of these reagents using iodine as a catalytic agent.

The hydrocarbon, dibenzyl, is formed in large quantities when benzyl chloride acts upon magnesium:



$\text{C}_6\text{H}_5\text{CH}_2\text{MgCl} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 + \text{MgCl}_2$
It is the control of this reaction that will determine the formation of triphenylpropane. It is believed that the temperature was allowed to rise too high when this was carried out.

The selection of the proper catalytic agent to start the reaction when the reagents are mixed at one time is a possible solution to this particular scheme for the preparation of triphenylpropane.