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A STUDY OF SOME CYCLOHEXYL TIN COMPOUNDS

A thesis, presented to the Department of
Chemistry of Union College, in partial fulfillment
of the requirements for the Degree of Bachelor of
Science in Chemistry, by

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Approved by

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Introduction

Although a large number of organotin compounds have been prepared (Dr. Garzuly¹ lists over one hundred and fifty), comparatively little is known about them. It was the purpose of this investigation to study some of the cyclohexyl tin compounds with a view toward finding out more about their preparation and properties, and to prepare some that had not been prepared before. Unfortunately time and circumstances prevented the latter.

Historical

Gruttner² obtained tetracyclohexyl tin from cyclohexyl bromide, converted in the usual way in ether into the Grignard compound, and tin tetrachloride. These compounds were brought together at 0°C., then heated one hour and allowed to stand overnight. On crystallization from benzene he obtained white, microscopic granules m. 248°.

Krause and Pohland³, following essentially the same procedure but using tin tetrabromide and refluxing for three hours, report the formation of a mixture of tetracyclohexyl tin and hexacyclohexyldistannane. From this mixture pure tetracyclohexyl tin was obtained by conversion, with bromine in cold chloroform, into tricyclohexyltin bromide and subsequent treatment with the Grignard compound. They report as the melting point 263-4°.

This result is in disagreement with Gruttner's by 16° , and indicates a probable difference in compounds.

Gruttner² prepared tricyclohexyltin monochloride by heating tetracyclohexyltin and tin tetrachloride in benzene solution for two hours. On crystallization from benzene this gave white needles m. 264° . It is interesting and possibly relevant to note here that this is the temperature reported by Krause and Pohland for the melting point of tetracyclohexyltin.

From tricyclohexyltin hydroxide and dilute hydrochloric acid, Krause and Pohland³ obtained a compound which they report as tricyclohexyltin monochloride m. $129-30^{\circ}$. Here again we see a large discrepancy in the melting points of the compounds prepared by the two investigators. This is obviously a case of misidentification on the part of one of them.

Gruttner did not prepare any of the other monohalogen compounds, so we have no comparison here. Krause and Pohland³, however, give the following results: Tricyclohexyltin bromide, from the mixture of tetracyclohexyltin and hexacyclohexyldistannane by adding the calculated amount of bromine in cold chloroform or carbon tetrachloride, m. 77° and decomposing about 280° ; Tricyclohexyltin iodide, from the mixture and the calculated amount of iodine

in benzene at room temperature, m. 65° and decomposing about 290° ; Tricyclohexyltin fluoride, from the bromide and potassium fluoride in boiling alcohol, decomposes about 305° .

The dicyclohexyltin dibromide compound was obtained by Gruttner² from tetracyclohexyltin and bromine in carbon disulfide after 48 hours. On crystallization from alcohol it gave needles m. 58° . Iodine in benzene at 110° gave the diiodide, red needles from benzene m. 145° , soluble in alcohol without color and in petroleum ether with red color.

Similarly Krause and Pohland³ prepared the dicyclohexyltin dibromide from the same compounds in chloroform and obtained the same melting point. However they report the diiodide as m. 42° , the melt assuming a yellowish turbidity at about 253° , then gradually becoming dark red and finally black above 300° . They prepared it by the same method as Gruttner, and also by warming the oxide with moderately dilute hydriodic acid. The dichloride, m. $88-9^{\circ}$, was obtained from the oxide warmed a long time with concentrated hydrochloric acid. On heating the clear melt becomes turbid about 220° and decomposes at a slightly higher temperature. It is stable towards moist air, but is hydrolyzed by much water. The difluoride, from the dichloride or dibromide and the calculated amount of potassium fluoride in aqueous

alcohol, m. 273°.

The tricyclohexyltin hydroxide was prepared from the bromide in ether with excess of 15% KOH. Melting about 220-2°, on heating in the vacuum of a water pump over phosphorous pentoxide it loses an amount of water corresponding to the formation of di-tricyclohexylstannic oxide. If dicyclohexyltin bromide is shaken for a long time in ether with several fresh portions of water, or more rapidly when dissolved in 5% KOH, it gives the dihydroxide (or oxide). An amorphous solid, it becomes yellowish about 280°, sinters at 287°, melts 291°.

Krause and Pohland³ also prepared dicyclohexyltin, the bivalent tin compound. From the Grignard in ether diluted with benzene, and treated in a nitrogen atmosphere with powdered stannous chloride, then heated on a water bath they obtained an intensely yellow, odorless, tasteless powder. It is stable for months in the dark in nitrogen, and is much more stable in air than in solution. Heated in the absence of air, it becomes dark orange-yellow about 130°, m. 176-8°, begins to deposit tin about 285°.

Other compounds prepared by Krause and Pohland³ include: hexacyclohexyldistannane from tricyclohexyltin bromide refluxed three hours with about ten times the calculated amount of sodium in xylene; tricyclohexylmethyl tin from the bromide and a large excess

of methyl grignard; and similarly tricyclohexyl tin ethyl, phenyl, and tolyl.

Experimental

Tin tetrabromide

Made by a direct combination of the two elements. Liquid bromine was dropped slowly on tin granules in a round bottom flask. The reaction should be carried out under a hood as the bromine fumes are poisonous. The heat of reaction is largely exothermic, and therefore care must be taken not to break the flask. A slight excess of bromine is added over the calculated amount as some of it is lost in vaporization. After all the bromine is added, it is let stand a short time, and then heated to drive off the excess bromine. The pure tin tetrabromide is then distilled over at 202° in over 90% yield.

Cyclohexylchloride

Prepared from our commercial supply of cyclohexanol and concentrated hydrochloric acid refluxed together for several hours. The first time the reaction was carried out with anhydrous calcium chloride crystals in the bottom of the reaction flask. This proved very unsatisfactory as the calcium chloride absorbed the cyclohexanol thereby decreasing the yield, and also giving a product which distilled over as a mixture having a variable boiling point. Half saturating the hydrochloric acid with calcium chloride

was also tried, and proved unsatisfactory. It was found that the best method was to reflux the two reactants together without using the calcium chloride at all. This gave a much more satisfactory product distilling over at $141-3^{\circ}$, in about 70% yield.

Cyclohexyl magnesium chloride

The Grignard was prepared in the usual way. The magnesium strips were put in the bottom of the Grignard flask which was then heated gently while a stream of nitrogen flowed through the system. This drove off any water vapor which may have been present in the system and left an inert atmosphere free of oxygen. A small amount of a mixture of previously dried ether and cyclohexylchloride was then added. The mechanical stirrer was started, several crystals of iodine added, and the flask heated gently at the point where the iodine crystals were. This started the reaction which then proceeded spontaneously. It was found that the reaction started quite readily and ran better if the entire system and reacting products were thoroughly dry. After starting the reaction the remainder of the cyclohexylchloride was dropped slowly in, together with dry ether from time to time. The whole was refluxed for about one hour and then allowed to cool.

Tetracyclohexyltin

Tin tetrabromide in benzene solution was added

to the Grignard in amount slightly less than necessary (calculated on the basis of a 80% yield of the Grignard) for the reaction



The amount of tin tetrabromide added was purposely made smaller to assure enough Grignard for the formation of the tetracyclohexyltin rather than the tri or di compound. The mixture of the grignard and tin tetrabromide was refluxed for several hours, the excess ether then driven off and benzene substituted as a solvent. The solution was filtered and tetracyclohexyltin, m. 246-50°, was crystallized from the benzene solution in a yield of 55%. On recrystallization the product had a much sharper melting point 247-9°.

The following is the data of a typical run:

Cyclohexylchloride	180 g.
Magnesium	37 g.
Stannic bromide	120 g.
Theoretical yield	123 g.
Actual yield	67 g.
Percentage yield	55%

Analysis for tin by oxidizing the compound with fuming nitric acid to stannic oxide showed the following:

	(1)	(2)
Weight of sample	.6971 g.	.3510 g.
Weight of SnO ₂	.2471 g.	.1239 g.

Percentage tin found	27.9%	27.8%
Average percentage	27.85%	
Calculated percentage	26.30%	

While the observed and calculated values for the percentage tin in the compound tetracyclohexyltin vary slightly, they are sufficiently close to warrant the assumption that the prepared compound is actually tetracyclohexyltin. The melting point on this compound is $247-9^{\circ}$, a result in agreement with Gruttner's of 248° , but in disagreement with Krause and Pohland's of 264° .

Reduction of tetracyclohexyltin

An attempt to reduce tetracyclohexyltin by sodium in liquid ammonia to tricyclohexyltin sodium was made. While the tetracyclohexyltin compound dissolved rather easily, there was no observable reaction. On evaporation of the ammonia the original tetra compound was recovered.

Tetracyclohexyltin and tin tetrabromide

These two compounds were refluxed together in benzene for several hours in amounts sufficient to produce the tricyclohexyltin bromide. A light tan powdery substance was precipitated which burns but does not melt even in the heat of the bunsen flame. After evaporating some of the benzene, the remainder was allowed to cool. A white solid crystallized out which has a variable melting point of $238-44^{\circ}$, and

probably is a mixture of the original tetra compound and the tricyclohexyltin bromide since both are crystallized from benzene. Time prevented the purification and subsequent identification of the compounds. On evaporation of all the benzene another white crystalline substance remained. This compound has a melting point of $57-60^{\circ}$, and is undoubtedly dicyclohexyltin dibromide.

Tetracyclohexyltin and bromine

An attempt to make dicyclohexyltin dibromide from solid tetracyclohexyltin by dropping bromine slowly onto it failed. The heat of the reaction was so great, even when bromine was added slowly, as to decompose the tetracyclohexyltin with the evolution of hydrogen bromide fumes and the formation of a residue of carbon.

Summary

1. A substance, which is undoubtedly tetracyclohexyltin, was prepared in 55% yield. The melting point on this compound was $247-9^{\circ}$, in agreement with Gruttner.

2. An attempt to reduce this compound with sodium in liquid ammonia failed.

3. A reaction between this compound and tin tetrabromide gave a small amount of a compound m. $57-60^{\circ}$, which is undoubtedly dicyclohexyltin dibromide.

Bibliography

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