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비에테르성 용매중에서 에테르촉매를 사용한 그리냐르반응에 의한 유기스탄닐화합물의 합성

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The Syntheses of Organostannyl Compounds by Grignard Reaction Catalyzed by Ether in Non-ethereal Media

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요 약. 몇가지 유기할로겐화물, 즉 브롬화에틸, 염화부틸, 브롬화페닐 및 염화벤질등을 탄화수소중에서 그리냐르법으로 무수사염화주석과 반응시켰다.

이때 소량의 에테르를 그리냐르반응단계에서 계내에 투입하였을 때 보다 용이하게 반응이 진행되어 좋은 수율로 유기주석화합물들을 얻을 수 있었다.

ABSTRACT. Some alkyl or aryl halides, such as ethyl bromide, butyl chloride, phenyl bromide and benzyl chloride, were reacted by Grignard's method with anhydrous tin tetrachloride in hydrocarbon media.

When small amounts of ether were added into the Grignard reaction step, the reaction proceeded rather smoothly and gave good yields of corresponding organotin compounds.

Since 1900, when Grignard successfully synthesized organomagnesium compounds, organic chemistry has been progressed rapidly. Furthermore, the study for the new bonding of metals involving organic groups was introduced. The research for the organometallic compounds of group IV metals also was developed promptly through Grignard reaction.

But the halides of group IV metals, especially tin, form stable complex with ether which is a good solvent for Grignard reagents and produce various byproducts[1].

Therefore, numerous new methods have been devised. Zakharkin, *et al.*[2,3] synthesized tetra-alkyl(-aryl)tin without solvent or, in hydrocarbon media and Neumann[4] and Ziegler[5] reported

that they had got tetraalkyltin quantitatively from tin tetrachloride with a little excess of trialkylaluminum and complexing agent for aluminum halide such as alkali halide or tertiary amine.

$$4R_3Al+3SnCl_4+4NaCl\longrightarrow 3R_4Sn+4NaAlCl_4$$
$$4R_3Al+3SnCl_4+4R'_3N\longrightarrow 3R_4Sn+4R'_3N\cdot AlCl_3$$

And also, there is a report that the complexing agent was not needed when tin alkoxide, instead of tin halide, was used.[6]

$$4R_3Al+3Sn(OR')_4\longrightarrow 3R_4Sn+4Al(OR')_3$$

For alkylaluminum is very hard to handle, classical methods are still in use. Especially, Grignard reaction is preferred to various other good methods.[1,7~9]

We report here some new fact discovered during the preparation of tetraethyltin by Zakharkin's method.

Magnesium was heated with ethyl bromide in *n*-hexane, while in Zakharkin's method ethyl iodide and magnesium were heated in isooctane for 4 hours. Inspite of refluxing the *n*-hexane mixture for several hours no detectable change occurred. So we attempted to add small amounts of diethylether, then the mixture was reacted smoothly to give whitish grey suspension. This was turned out to be Grignard reagent by the means of colour reaction[10] of it's ethereal extract.

$$Et\text{-}Br+Mg\xrightarrow[\text{in } n\text{-hexane}]{Et_2O,\ I_2}Et\text{-}MgBr$$

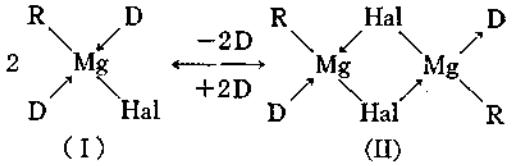
When the similar operations were carried out for methyl iodide, phenyl chloride, phenyl bromide, butyl chloride and benzyl chloride, satisfactory results were obtained except for methyl iodide and phenyl chloride. But they needed continuous heating till the reaction terminated, for they were not so exothermic as Zakharkin's description.[2]

In Zakharkin's results, the reaction initiated when the temperature was above 100 °C. But here, it was done at rather low temperature. It means that ether diminished the activation energy, that is, ether contributed to the reaction.

Certainly, in the polar solvents which act as Lowis base such as ether, such rigorous conditions were not necessary and the amounts of ether introduced here not sufficient as solvent. Therefore we might say that the ether in Grignard reaction acted not only as solvent but also as a catalyst.

There are some cases using isopropyl alcohol[11] or aluminun alkoxide[12] as catalyst, among the reports for the Grignard reaction in hydrocarbon media or without solvent.

Even if Grignard type reaction mechanism has not yet been reported, it is well known that Grignard reagents equilbrated with Lewis base as follow:



(I) (II)

D: Ether, Amine, etc.

II is stable even though heated for several hours at 150 °C under reduced pressure,[13] and when pure *n*-propylmagnesium iodide was mixed with ether, it makes mono ether complex with heat evolution of 6.63 kcal/mole and diether complex (12.30 kcal/mole).[14] These facts offer some evidences that ether takes a role in Grignard reaction.

However, these Grignard reagents reacted with tin tetrachloride exothermally and chilling by cold water bath was needed. After the one half equivalent of tin tetrachloride was dropped

Table 1. The yields of products compared with Zakharkin's method.

Method	Reactant	Time	Media	Product	Yield(%)
Zakharkin's	Et-I	5.5 hrs	Isooctane	Et_4Sn	30
	Bu-Cl	1 hr	None	Bu_4Sn	90
			Isooctane	Bu_2SnO	65
	Ph-Br	3 hrs	Decahydro-naphthalene	Ph_4Sn	74
Ours	Et-Br	3.5 hrs	*n*-Hexane	Et_4Sn	70
	Bu-Cl	3.5 hrs	*n*-Hexane	Bu_4Sn	85
	Ph-Br	3.5 hrs	Benzene	Ph_4Sn	70
	Bz-Cl	3.5 hrs	Benzene	Bz_4Sn	75

in, the mixture was refluxed for an hour. The yields of organotin compounds are summerized in *Table* 1.

As shown in *Table* 1, the yields of tetraalkyltin by Zakharkin's method in hydrocarbon media were very low, but we relatively good yields in spite of using hydrocarbon media.

In conclusion, it might be acceptable that adequate amount of ether in hydrocarbon media reforms the reaction condition and we may get a best condition if these are revised.

EXPERIMENTAL

All the reactions were carried out in dry nitrogen stream with dried materials and the mole-ratios of reactants were, organic halides: 1 mole, magnesium: 1 mole and tin tetra chloride: 1/8 mole.

The identification of Grignard reagents was performed by the Gilman's method[10]; 1 % Michler ketone was used for the qualitative detection of the reagent.

Preparation of Tetraethyltin. During the powdered magnesium (24 g) and iodine(0.01 g) in a 1 *l*-threenecked flask (Without solvent) was agitated, *n*-hexane solution (150 m*l*) of ethyl bromide (10 g) and ether (6 m*l*) was added dropwise in an hour with mild heating and then tin tetrachloride (32 g) with cooling. After refluxing of an hour, the reaction mixture was chilled, poured into an iced 1*N* HCl solution. The hydrocarbon layer was separated and dried over anhydrous calsium chloride. Fractional distillation gave 20 g of tetraethyltin (b; 178~9) which was 70 % (based on tin tetrachloride) of theoretical yield.

Preparation of Tetrabutyltin. Similar to those of tetraethyltin, except that butyl chloride (92 g) instead of ethyl bromide was used. Thirty seven grams of tetrabutyltin (b_{11}; 144~5, 85%) was obtained.

Preparation of Tetraphenyltin. Benzene(150 m*l*) was used for solvent and phenyl bromide used was 157 g. The purification was carried out by the means of Chamber's.[15] The recrystallization from benzene gave 37 g (70 %) of tetraphenyltin.

Preparation of Tetrabenzyltin. Similar to the method for phenyltin compound, but for 126 g of benzyl chloride instead of phenyl bromide.

For the purification of the product, the method proposed by Smith[16] was used. The yield

was 75 % (45 g).

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