

## NOTE

STERICALLY HINDERED GROUP IVA ORGANOMETALLICS  
VIII\*. PREPARATION AND SOME PROPERTIES OF NEOHEXYLTIN  
COMPOUNDS

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In continuation of our studies of the preparation and chemical properties of Group IVA organometals, we have prepared several organotin compounds containing the 3,3-dimethylbutyl (neoheptyl) group. In these compounds the "neo" structure is one carbon further removed from the tin atom than in the neopentyl compounds previously made. This shifting of the bulky "neo" structure away from the tin decreases the steric hindrance at the tin-carbon bond and allows reactions at that site which occur sluggishly or not at all with the corresponding neopentyl tin compounds<sup>2</sup>.

This is readily demonstrated in the preparation of the tetrasubstituted tin compounds from the reaction of stannic chloride with excess Grignard reagent. Using the neoheptyl Grignard reagent an eighty percent yield of tetraneohexyltin (**1**) was obtained. In contrast to this reaction, with neopentyl Grignard reagent the major product was trineopentyltin chloride<sup>2</sup>, indicating that the three neopentyl groups already present prevent reaction with a fourth equivalent of the Grignard reagent.

Likewise, whereas **1** reacted readily with bromine in carbon tetrachloride at room temperature to form trineohexyltin bromide, the corresponding reaction with tetraneopentyltin (**2**) required refluxing.

On heating together a mixture of stannic chloride and **1**, a Kocheshkov reaction occurs and dineohexyltin dichloride is formed. It was found that this reaction does not occur with **2**, again showing the difference in steric hindrance imposed by these two groups.

A PMR spectrum of **1** taken on a Varian A-60 instrument was unable to show any long-range coupling between <sup>117</sup>Sn or <sup>119</sup>Sn with the protons of the CH<sub>3</sub> groups<sup>3</sup>.

## EXPERIMENTAL

Melting points were taken on a Mel-Temp apparatus and are uncorrected. In all of the following procedures R is the neoheptyl group.

*Tetraneohexyltin (1)*

A Grignard solution was prepared in the usual way from 24.1 g (0.20 mole)

\* For Part VII see ref. 1.

of neohexyl chloride in 300 ml of anhydrous tetrahydrofuran (THF). To this was added over a 10 min period a solution of 11.5 g (0.044 mole) of  $\text{SnCl}_4$  in 40 ml of benzene. The reaction was well stirred and cooled in an ice bath during addition. The ice bath was removed and the stirred suspension was heated in an  $80^\circ$  oil bath for one day. All of the above procedure was carried out under  $\text{N}_2$ . After completion the reaction mixture was poured into water and extracted with ether. The ether extract was washed several times with water and dried with anhydrous  $\text{Na}_2\text{SO}_4$ .

Through previous experience it was known that the crude product contains a small amount of  $\text{R}_3\text{SnSnR}_3$  which is difficult to remove from the  $\text{R}_4\text{Sn}$  by recrystallization. For this reason the ether solution was treated at room temperature with a dilute solution of iodine in  $\text{CCl}_4$  until the iodine color persisted for a minute. A saturated solution of KF in methanol was then added to react with the  $\text{R}_3\text{SnI}$  which had been formed by cleavage of the  $\text{R}_3\text{SnSnR}_3$ . The resulting precipitate of  $\text{R}_3\text{SnF}$  was filtered off and the filtrate was washed, dried, and evaporated to dryness. The residue was recrystallized twice from acetone to yield 5.0 g of **1** as long, flat prisms, m.p.  $76\text{--}77^\circ$ . Further crops of somewhat lower melting points brought the yield to 16 g (80%). (Found: C, 63.04; H, 11.19.  $\text{C}_{24}\text{H}_{52}\text{Sn}$  calcd.: C, 62.75; H, 11.41 %.)

#### *Trineohexyltin bromide*

A solution of 4.00 g (0.0087 mole) of  $\text{R}_4\text{Sn}$  in 15 ml of  $\text{CCl}_4$  was protected from light with aluminum foil. To this was added a solution of 1.39 g (0.0087 mole) of bromine in  $\text{CCl}_4$ . After 10 to 15 min the bromine color had disappeared. Concentrating and cooling the solution yielded 1.88 g (48%) of needles, m.p.  $122\text{--}127^\circ$ . Part of this was recrystallized from acetone to give an analytical sample, m.p.  $128\text{--}130^\circ$ . (Found: Br, 17.64.  $\text{C}_{18}\text{H}_{39}\text{BrSn}$  calcd.: Br, 17.60 %.)

#### *Trineohexyltin fluoride*

Solutions of  $\text{R}_3\text{SnBr}$  in ethyl ether and KF in ethanol were mixed together. The resulting precipitate was filtered off and rinsed with water and with ether. It was easily purified by sublimation at  $200^\circ$  and 0.1 mm Hg to yield a solid melting at  $333\text{--}336^\circ$ . (Found: C, 55.26; H, 10.06.  $\text{C}_{18}\text{H}_{39}\text{FSn}$  calcd.: C, 54.98; H, 9.98 %.)

#### *Hexaneohexylditin*

A solution of 5.1 g (0.011 mole) of  $\text{R}_3\text{SnBr}$  in 20 ml of anhydrous THF was magnetically stirred at  $65^\circ$  under Ar with 0.08 g (0.011 g-atom) of lithium shot for 7 h. At that time the lithium had completely disappeared. The reaction was poured into water and extracted with ether. The extract was washed, dried, and evaporated to dryness. Three recrystallizations from acetone yielded plates of  $\text{R}_3\text{SnSnR}_3$ , m.p.  $93\text{--}94.5^\circ$ . (Found: C, 58.04; H, 10.43; mol. wt. Rast, 817.  $\text{C}_{36}\text{H}_{78}\text{Sn}_2$  calcd.: C, 57.77; H, 10.51 %; mol. wt., 848.4.)

#### *Dineohexyltin dichloride*

A mixture of 4.95 g (0.010 mole) of  $\text{R}_4\text{Sn}$  and 2.60 g (0.010 mole) of  $\text{SnCl}_4$  was placed in a small flask fitted with a reflux condenser which was fitted with a drying tube. The flask was heated to  $200^\circ$  in an oil bath overnight. On recrystallizing twice from hexane,  $\text{R}_2\text{SnCl}_2$  was obtained, m.p.  $162\text{--}163^\circ$ . (Found: C, 40.10; H, 7.25.  $\text{C}_{12}\text{H}_{26}\text{Cl}_2\text{Sn}$  calcd.: C, 40.04; H, 7.28 %.)

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