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Abstract

Full Text

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INTERACTION OF DIALKYLTIN OXIDES WITH IOCHICH’ S REAGENT

The interaction of Iochich’ s reagent with aldehydes and ketones is a classical method for the synthesis of acetylenic alcohols (^{1}). We ($^{2–5}$) were the first to apply this reaction to the preparation of acetylenic silanols by the interaction of magnesium bromoacetylenic compounds with polydiorganosiloxanes; the high reactivity of the latter was established and the chemistry of this reaction was determined.

$$n\mathrm{RC} \equiv \mathrm{CMgBr} + (\mathrm{R}'_2\mathrm{SO})_n \rightarrow n(\mathrm{RC} \equiv \mathrm{C})\mathrm{R}'_2\mathrm{SiOH},$$

where R $-$H, $CH_2 = CH$, C_6H_5, etc.; R$'$ $-H_3CH_3$, C_2H_5, C_3H_7, C_6H_5, etc.

Extending this reaction to other elements of Group IV of the periodic system, we considered it of interest, from both theoretical and practical points of view, to study the interaction of dialkyltin oxides with Iochich’ s reagent and to compare its course with analogous reactions of ketones and polydiorganosiloxanes. Solving the problem posed presents considerable difficulty. To date there are still no firmly established views even on the structure of dialkyltin oxides ($^{6–8}$). We are inclined to believe that these compounds, and many other derivatives of stannous chloride, are polymeric substances and, like polydiorganosiloxanes, should be represented by the formulas $(R_2SnO)_n$ and $HO(R_2SnO)_nH$.

In view of the foregoing, in the interaction of dialkyltin oxides with Iochich’ s reagent, by analogy with the reactions indicated, one might have expected the formation of acetylenic stannanols

$$n\mathrm{RC} \equiv \mathrm{CMgBr} + (\mathrm{R}'_2\mathrm{SnO})_n \rightarrow n(\mathrm{RC} \equiv \mathrm{C})\mathrm{R}'_2\mathrm{SnOH}.$$

However, this interaction proceeds in a fundamentally different manner from the corresponding reactions of carbon and silicon compounds. If ketones give acetylenic alcohols, and polydiorganosiloxanes give acetylenic silanols, then the reaction of dialkyltin oxides with Iochich’ s reagent leads to the production of diacetylenic stannanes

$$2RC \equiv CMgBr + (R'_2SnO)_n \rightarrow (RC \equiv C)_2SnR'_2 + (MgBr)_2O,$$

where R –H, CH_3, $CH = CH_2$, C_6H_5, etc.; R′ –C_2H_5, C_3H_7, C_4H_9, etc.

The interaction of ketones and polydiorganosiloxanes with Iochich’ s reagent is characterized by preservation of the C–O and Si–O bonds, whereas in the case of dialkyltin oxides the SnO bond is destroyed and oxygen is exchanged for acetylenic groups. The reason for this difference in the reactivity of dialkyltin oxides in reactions with organomagnesium compounds is due to the peculiarity of their structure and to the nature of the bond between the tin and oxygen atoms.

Apparently, the interaction of dialkyltin oxides not only with the Iotsich reagent, but also with the Grignard reagent proceeds through the stage of formation of the corresponding active complexes, which influence the final course of the reaction associated with depolymerization of dialkyltin oxides and formation of magnesium bromostannanolates according to the scheme

$$RC{\equiv}CMgBr + (R'_2SnO)_n \rightleftarrows [mRC{\equiv}CMgBr \cdot (R'_2SnO)_n] \rightleftarrows$$

$$\rightleftarrows [RC{\equiv}CMgBr \cdot R'_2SnO] \rightarrow (RC{\equiv}C)R'_2SnOMgBr.$$

The presence of the latter in one of the intermediate stages of the reaction was demonstrated on the example of the interaction of diethyltin oxide with ethylmagnesium bromide, as a result of which, along with tetraethylstannane, a certain amount (~6%) of triethylstannanol was isolated.

Taking into account the foregoing and bearing in mind the fact previously established by us (9,10) of exchange of the hydroxyl group of stannanols for organic radicals in reactions with organomagnesium compounds, we believe that the OMgBr residue is exchanged for an acetylene radical and leads to the formation of diacetylenic stannanes and unstable magnesium bromide oxide:

$$(RC{\equiv}C)R'_2SnOMgBr + RC{\equiv}CMgBr \rightarrow (RC{\equiv}C)_2SnR'_2 + (MgBr)_2O.$$

On decomposition of the latter, magnesium bromide is formed, which causes the side reaction of cleavage of the diacetylenic stannanes formed and bromination of dialkyltin oxides.

$$(RC{\equiv}C)_2SnR'_2 + MgBr_2 \rightarrow R'_2SnBr_2 + 2RC{\equiv}CMgBr,$$

$$(R'_2SnO)_n + nMgBr_2 \rightarrow R'_2SnBr_2 + MgO.$$

The side processes somewhat complicate the main reaction and lead to the fact that the highest yields of diacetylenic stannanes are obtained in an excess of the Iotsich reagent. Evidently, organotin oxides react in a similar way with vinylmagnesium chloride (11).

Experimental Part

1. Interaction of diethyltin oxide with ethylmagnesium bromide. Into a 1-liter synthesis apparatus are placed 60 g of diethyltin oxide in 300 ml of absolute ether, and with stirring the Grignard reagent, prepared from 14.8 g of magnesium and 65.4 g of ethyl bromide, is gradually added. The contents of the flask are heated on a water bath for 5-6 hr, and then decomposed with 5% hydrochloric acid. The ether layer is separated, dried over Na_2SO_4, and after the usual work-up 47.4 g (65%) of tetraethylstannane is isolated, b.p. 48°/5 mm, n_D^{20} 1.4720. Lit. (12): b.p. 178.5°/760 mm, n_D^{20} 1.4719; and 4.5 g (6%) of triethylstannanol, m.p. 44°. Lit. (12): m.p. 44–45°.

2. Dipropyldiethynylstannane. To ethylmagnesium bromide, prepared from 4.8 g of magnesium and 21.8 g of ethyl bromide in 300 ml of tetrahydrofuran, with stirring 11 g of dipropyltin oxide is added in small portions. The reaction mixture is heated with stirring for 5 hr and then centrifuged. The organic layer is separated; the precipitate is mixed with ether and again centrifuged. This operation is repeated another 2-3 times. The ether is removed, and the main substance is distilled in vacuum. 4.2 g (34.5%) of dipropyldiethynylstannane is isolated, b.p. 70°/2 mm, n_D^{20} 1.4785, d_4^{20} 1.1819, *MR* found 61.10, calculated 61.48.

Found, %:	C 47.67;	Sn 46.55
$C_{10}H_{16}Sn$. Calculated, %:	C 47.12;	Sn 46.57

In addition, 9.5 g (53%) of dipropyldibromostannane is isolated, m.p. 49° and b.p. 86°/15 mm. Lit. (12): m.p. 49°, b.p. 263–265°/760 mm.

Analogously, in the interaction of diethyltin oxide with ethynylmagnesium bromide, 12 g (71%) of diethyldibromostannane is formed, b.p. 84–85°/2 mm and m.p. 65°. Lit. (12): b.p. 239°/760 mm, m.p. 63°.

3. **Bis-(methylethynyl)-diethylstannane** was synthesized analogously to that described above from 4.8 g of magnesium, 21.8 g of ethyl bromide, 8 g of methylacetylene, and 9 g of diethyltin oxide in 100 ml of abs. ether. This gave 5.1 g (66%) of a substance with b.p. 62°/1 mm, n_D^{20} 1.4977, d_4^{20} 1.2332, *MR* found 60.50, calculated 61.48.

Found, %: C 47.30; H 6.40; Sn 46.83
$C_{10}H_{16}Sn$. Calculated, %: C 47.1; H 6.27; Sn 46.63

4. **Bis-(vinylethynyl)-diethylstannane** was obtained in an analogous manner from 3.6 g of magnesium, 16.6 g of ethyl bromide, 14 g of

vinylacetylene, and 10 g of diethyltin oxide. Yield 10.6 g (70%), b.p. 96°/1 mm, n_D^{20} 1.5428, d_4^{20} 1.2267, MR found 71.59, calculated 69.80.

Found, %: C 51.79; H 5.62; Sn 49.9
$C_{12}H_{16}Sn$. Calculated, %: C 52.1; H 5.7; Sn 42.2

5. **Bis-(vinylethynyl)-dipropylstannane** was prepared from 3.26 g of magnesium, 14.9 g of ethyl bromide, 13 g of vinylacetylene, and 15 g of dipropyltin oxide. Yield 12.3 g (58%), b.p. 102°/1 mm, n_D^{20} 1.5343, d_4^{20} 1.1840, MR found 80.60, calculated 79.06.

Found, %: C 54.3; H 6.68; Sn 37.9
$C_{14}H_{20}Sn$. Calculated, %: C 54.8; H 6.52; Sn 38.6

6. **Bis-(vinylethynyl)-dibutylstannane** was synthesized from 2.88 g of magnesium, 13.2 g of ethyl bromide, 12.5 g of vinylacetylene, and 15 g of dibutyltin oxide. Yield 13.4 g (65%), b.p. 108°/1 mm, n_D^{20} 1.5188, d_4^{20} 1.1352, MR found 89.50, calculated 88.22.

Found, %: C 57.6; H 7.21; Sn 35.20
$C_{16}H_{24}Sn$. Calculated, %: C 57.3; H 7.17; Sn 35.61

7. **Bis-(phenylethynyl)-dipropylstannane** was obtained from 6.25 g of magnesium, 28.4 g of ethyl bromide, 26.5 g of phenylacetylene, and 15 g of dipropyltin oxide. Fifteen grams of crude product were isolated; on distillation in vacuum at 135°/0.9 mm it polymerizes. The IR spectrum of this substance showed the presence of $C\equiv C$ and of a benzene ring.

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Note: Figure translations are in progress. See original paper for figures.