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1957

SovietRxiv

Abstract

Full Text

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The Use of Aluminum Trialkyls for the Synthesis of Organoelement Compounds

(Presented by Academician A. N. Nesmeyanov on 8 V 1957)

Chemistry

In connection with the fact that organoaluminum compounds have recently become readily accessible owing to the investigations of Ziegler and co-workers ([1]), the question naturally arises of the possibility of using them for the synthesis of other organoelement compounds.

The patent literature describes methods for obtaining zinc-, cadmium-, and mercury-organic compounds of the type RMeX ([2]), as well as trialkylborines ([3]), from halide compounds of these elements and the mixture of alkylaluminum halides formed by the action on aluminum of the corresponding alkyl halides:

$$3\mathrm{RX} + 2\mathrm{Al} \rightarrow \mathrm{RAlX_2} + \mathrm{R_2AlX}.$$

Since the latter reaction proceeds only with lower alkyls (R not higher than C_3H_7), this method cannot be sufficiently general; in combination with the necessity of using alkyl halides for the synthesis, this does not make the method more preferable than, for example, organomagnesium synthesis.

Recently Kester pointed out the possibility of obtaining alkyl derivatives of boron and silicon from aluminum trialkyls and boron trifluoride etherate or silicon tetrachloride ([4]). In the present work we have studied the interaction of the halides of boron, antimony, arsenic, phosphorus, tin, and mercury with triethylaluminum and triisobutylaluminum.

In all the cases studied, an exchange reaction takes place with formation of aluminum halide and alkyl derivatives of the elements taken.

On addition to triisobutylaluminum (27.1 g) of boron trifluoride etherate (19.0 g) at a temperature of 60-65° (due to the heat of reaction), triisobutylboron is formed, which can be distilled directly from the reaction mixture; yield 13.0 g (~60% of theoretical), b.p. 174-176°/745 mm; 57-58°/5 mm, $n_D^{22.8}$ 1.4188. Literature data ([5]): b.p. 86°/20 mm, $n_D^{22.8}$ 1.4188.

On passing gaseous boron trifluoride into a solution of triethylaluminum in decalin, triethylboron is formed, b.p. 95-96°. Literature data: b.p. 90-96° ([6]).

The reaction of triisobutylaluminum etherate (from 20.0 g of Al (iso-$C_4H_9)_3$) with a suspension of antimony trifluoride (17.9 g) in ether proceeds just as readily; by distillation of the reaction mixture, triisobutylstibine was obtained as a colorless liquid, yield 22.2 g (77% of theoretical), b.p. 101.5°/8 mm, $n_D^{19.5}$ 1.4955; d_4^{20} 1.124. Literature data (^{7}): b.p. 135°/31 mm, d_4^{23} 1.323.

Found, %: C 48.48; 48.56; H 9.08; 9.06
$C_{12}H_{27}Sb$. Calculated, %: C 49.17; H 9.28

The dibromide, obtained by bromination of triisobutylstibine in carbon tetrachloride, had a melting point of 95° (from ether) and showed no depression of the melting point in a mixed sample with the dibromide (m.p. 94°) from triisobutylstibine (b.p. 64-66°/1 mm, n_D^{20} 1.4957), synthesized by us from $SbCl_3$ and *iso*-C_4H_9MgBr.

It should be noted that the interaction of equivalent amounts of isobutylmagnesium bromide and $SbCl_3$ gives triisobutylstibine in only 22–23% yield, and the product obtained is colored (^{7}).

The interaction of triisobutylaluminum (36.7 g, 1 mole) with arsenic trichloride (33.0 g, 1 mole) in ether does not lead to trialkylarsine; the main reaction products are isobutyldichloroarsine and diisobutylchloroarsine. After completion of the reaction, the reaction mixture was treated with 200 ml of hydrochloric acid (1 : 1), and the mixture of chloroarsines was extracted with ether. Fractionation of the mixture gave:

a. Isobutyldichloroarsine, yield 12 g, b.p. 57-58°/8 mm, $n_D^{20.5}$ 1.5108, d_4^{20} 1.4126. Literature data (^{8}): b.p. 95.8°/50 mm, d_4^{20} 1.4465.

Found %:	As 37.19, 37.11
$C_4H_9AsCl_2$. Calculated %:	As 36.91

b. Diisobutylchloroarsine, yield 20 g, b.p. 76-77°/8 mm, $n_D^{20.5}$ 1.4862, d_4^{20} 1.1265.

Found %:	As 33.33; 33.49
$C_8H_{18}AsCl$. Calculated %:	As 33.35

The interaction of triisobutylaluminum with phosphorus trichloride proceeds in a more complex manner. As a result of a vigorous reaction, regardless of the solvent used (ether, *n*-heptane, or excess PCl_3), a complex of the reaction products with aluminum chloride is formed.

Isobutyldichlorophosphine can be distilled from the reaction mass in vacuo. From 32.5 g of triisobutylaluminum, on addition to excess PCl_3, 11.5 g of isobutyldichlorophosphine was obtained, b.p. 148-149°, n_D^{20} 1.4818, d_4^{20} 1.1268; MR_D 39.07. Calculated for $C_4H_9PCl_2$, MR_D 38.55. Literature data: b.p. 155-157°, d^{23} 1.1236 (^{9}), b.p. 48.5-49.5/12 mm, n_D^{20} 1.4719, d_0^{20} 1.172 (^{10}).

Found %: C 30.55; 30.67; H 5.75; 5.88; Cl 44.27; 44.72; P 18.91; 18.85
$C_4H_9PCl_2$. Calculated %: C 30.21; H 5.64; Cl 44.60; P 19.48

On further heating of the residue after distillation of isobutyldichlorophosphine in vacuo, deep decomposition occurs with formation of volatile products and elemental phosphorus.

The interaction of equimolecular amounts of triisobutyl- or triethylaluminum with mercuric bromide or corrosive sublimate in ether or hexane leads mainly to symmetrical dialkyl derivatives of mercury. Thus, upon addition to a suspension of $HgBr_2$ (28 g) in 100 ml of ether of triisobutylaluminum (15.5 g), after decomposition of the reaction mass with ice and sodium bicarbonate, the following were obtained: a) diisobutylmercury, yield 16.0 g (65.5% of theoretical), b.p. 123-123.5°/65 mm, n_D^{20} 1.4964, d_4^{20} 1.770; literature data ([11]): b.p. 108-109°/25 mm, n_D^{20} 1.4969, d_4^{20} 1.7670.

Found %: C 30.02; 30.24 H 5.78; 5.70
$C_8H_{18}Hg$. Calculated %: C 30.46; H 5.76

c. Isobutylmercuric bromide, m.p. 78° (from alcohol), showing no depression of the melting point in a mixed sample with a specimen obtained from $HgBr_2$ and *iso*-C_4H_9MgBr.

Found %: C 13.89; 13.96; H 2.68; 2.61
C_4H_9HgBr. Calculated %: C 14.22; H 2.68

From sulema (27.1 g) and triethylaluminum (11.4 g) in hexane (100 ml), diethylmercury was obtained, yield 15.0 g (58.6% of theoretical), b.p. 95-96°/90 mm, n_D^{22} 1.5400; d_4^{20} 1.4658. Literature data: b.p. 57°/16 mm, $n_D^{23.2}$ 1.5399 (12), d_4^{20} 1.4660 (13).

Tin tetrachloride (18.8 g), under the action of triisobutylaluminum (19.0 g) in heptane at 40-48°, gives (after decomposition with NaOH solution) tetraisobutyltin, yield 8.5 g (53.6% of theoretical), b.p. 128-129°/8 mm, $n_D^{19.5}$ 1.4751; d_4^{20} 1.0517. Literature data (14): b.p. 143°/16.5 mm, n_D^{20} 1.4760.

$C_{16}H_{36}Sn$. Found %: C 55.00; 55.14; H 10.37; 10.59; Sn 33.77; 34.11
Calculated %: C 55.35; H 10.43; Sn 34.18

In addition, on distillation of the residue over sodium, triisobutyltin oxide can be isolated, yield 7.4 g, b.p. 197-198°/12 mm, n_D^{21} 1.4850, d_4^{20} 1.1547, formed, apparently, by dehydration of the corresponding hydroxide.

$C_{24}H_{54}Sn_2O$.	Found %:	C 48.52; 48.71; Sn 39.90; 39.90; H 9.04; 9.31
	Calculated %:	C 48.36; Sn 39.83; H 9.14

Thus, in the case of the interaction of triisobutylaluminum and tin tetrachloride, (iso-$C_4H_9)_4$Sn and (iso-$C_4H_9)_3$SnCl are formed.

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Received
7 V 1957

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