

## Letters to the Editor

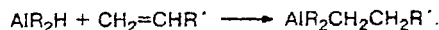
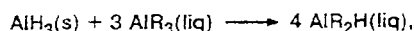
### Synthesis of trialkylaluminum by the reaction of nonsolvated aluminum hydride with $\alpha$ -olefins

V. V. Gavrilenko

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
28 ul. Vavilova, 117813 Moscow, Russian Federation.  
Fax: 007 (095) 135 5085

Hydroalumination of olefins is one of the most important reactions in the synthesis of alkylaluminum compounds. Solid aluminum hydride obtained from an ether solution<sup>1</sup> has a composition of  $(\text{AlH}_3)_3 \cdot \text{OEt}_2$ , and its reaction with  $\alpha$ -olefins at 120 °C results in the formation of a mixture of  $\text{AlR}_3$  (yield 60%) and  $\text{AlR}_3 \cdot \text{OEt}_2$  (40%).<sup>2</sup> Nonsolvated crystalline  $\text{AlH}_3$  has also been obtained.<sup>3</sup>

This work studied the reaction of nonsolvated  $\text{AlH}_3$  with  $\alpha$ -olefins. This hydride is inert to olefins; however, the reaction occurs vigorously in the presence of a catalytic quantity of  $\text{AlR}_3$ , for example,  $\text{AlEt}_3$  and  $\text{AlBu}^i_3$  (2–10 mol.% of the amount of  $\text{AlH}_3$ ). The role of these additives is their interaction with  $\text{AlH}_3$  resulting in the formation of dialkylaluminum hydrides  $\text{AlR}_2\text{H}$ , which, as is known, react readily with olefins at 60–80 °C to form trialkylaluminum:



The  $\text{AlR}_2\text{CH}_2\text{CH}_2\text{R}'$  obtained again enters the reaction cycle, and the process is completed by the "dissolution" of  $\text{AlH}_3$  and the formation of trialkylaluminum. The reactions of  $\text{AlH}_3$  with olefins are substantially accelerated under the conditions of mechanochemical activation, for example, in a ball or in a cavitational mill.

**Triisobutylaluminum.** Nonsolvated  $\text{AlH}_3$  (6.3 g, 0.21 mol) obtained by a known procedure,<sup>3</sup> hexane (100 mL),  $\text{AlBu}^i_3$  (2 g), and isobutylene (56 g, 1 mol) were placed in an atmosphere of nitrogen in an autoclave (0.5 L) cooled to –30 °C, and steel balls 3–5 mm in diameter (100 mL) were added. The autoclave was heated to 100 °C with rotation and kept at 140 °C for 3 h. The reaction was stopped at 80–90 °C. The suspension obtained was filtered off through a No. 4 glass filter, and the excess isobutylene and hexane was removed *in vacuo*. The residue was distilled at 50–52 °C (1 Torr).  $\text{AlBu}^i_3$  (31.1 g, 74.8%) was obtained. Found (%): Al, 13.91.  $\text{C}_{12}\text{H}_{27}\text{Al}$ . Calculated (%): Al, 13.60.

**Trihexylaluminum.** Similarly to the procedure described above,  $\text{AlH}_3$  (6.3 g), hexene (84 g, 1.0 mol),  $\text{AlBu}^i_3$  (3 g, 0.015 mol), and hexane (120 mL) were placed in an autoclave. The autoclave was heated to 140 °C with rotation (1 h), the temperature was decreased to 120 °C, and the autoclave was left for 8 h. The suspension that formed was filtered off, and the volatile products were removed *in vacuo* at 60 °C (1 Torr).  $\text{AlHex}_3$  (55.6 g, yield 89.1% calculated per  $\text{AlH}_3$ ) was obtained. Found (%): Al, 9.02.  $\text{C}_{18}\text{H}_{39}\text{Al}$ . Calculated (%): Al, 9.51. Then this product (28.3 g) in heptane (100 mL) was oxidized by dry air at 0–50 °C. After hydrolysis, extraction with ether, drying over  $\text{Na}_2\text{SO}_4$ , and distillation, hexanol (24.8 g, 81%) was isolated, b.p. 156–157 °C,  $n_D^{20}$  1.4128 (cf. Ref. 5: b.p. 155.2 °C,  $n_D^{20}$  1.41326).

**Tridecylaluminum.**  $\text{AlH}_3$  (2.1 g), dec-1-ene (86.4 g), and  $\text{AlEt}_3$  (2 g) were placed in an atmosphere of argon in a vertical-type ball mill (see Ref. 4). The contents was stirred at 20 °C for 2 h and heated to 140 °C (30 min). The reaction was continued at 110 °C for 6 h. The product was filtered off, and the excess decene was distilled off at 70–80 °C (1 Torr).

A dense liquid (34.3 g) was obtained. Found (%): Al, 5.57.  $C_{30}H_{63}Al$ . Calculated (%): Al, 5.98. After this product (22.6 g) in heptane was oxidized by air oxygen, decanol (18.6 g) was obtained, b.p. 108–109 °C (7 Torr),  $n_D^{20}$  1.4352 (cf. Ref. 5: b.p. 107–108 °C (7 Torr),  $n_D^{20}$  1.43719).

### References

1. A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1947, **69**, 1199.

2. K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Anal.*, 1954, **589**, 91; 115.
3. F. M. Brower, N. E. Matzek, P. F. Reigel, H. W. Rinn, Ch. B. Roberts, D. L. Schmidt, J. A. Snover, and K. Terada, *J. Am. Chem. Soc.*, 1976, **98**, 2450.
4. H. Clasen, *Angew. Chem.*, 1961, **73**, 322.
5. *Dictionary of Organic Compounds*, Eds. I. Heilborn and H. M. Bunbury, London, 1946.

Received May 14, 1997

## Palladium-catalyzed reactions of organoboron compounds with acyl chlorides

V. V. Bykov, D. N. Korolev, and N. A. Bumagin\*

Department of Chemistry, M. V. Lomonosov Moscow State University,  
Vorob'evy Gory, 119899 Moscow, Russian Federation.  
Fax: 007 (095) 939 0126. E-mail: bna@bumagin.chem.msu.su

We have shown previously<sup>1–3</sup> that the reaction of organoboron compounds (OBC) with organic halides, which is an important method for the formation of a new C—C bond,<sup>4</sup> occurs readily in an aqueous organic solvent or in water when catalyzed by "ligand-free" palladium<sup>5</sup> in the presence of a base. However, the interactions of OBC with acyl chlorides under similar conditions remain almost unstudied. It has only been reported<sup>6</sup> that the  $Pd(Ph_3P)_4$ -catalyzed reaction of  $Ph_4BNa$  with  $RCOCl$  involves only one phenyl group of borate and results in the corresponding ketones  $RCOPh$ .

In this work, we have established for the first time that chloroanhydrides of carboxylic acids react with arylboric acids in the presence of "ligand-free" palladium to form the corresponding diaryl ketones in high yields (Scheme 1). It also was found that ketones are formed under similar conditions from chloroanhydrides of carboxylic acids and  $Ph_4BNa$ , and all four phenyl groups of OBC participate in the reaction.

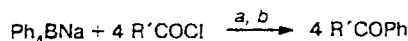
The  $PdCl_2$ -catalyzed reaction of benzoyl chloride with  $ArB(OH)_2$  or  $Ph_4BNa$  in the presence of  $Na_2CO_3$  in aqueous acetone is completed in 1 h at room temperature. Easily hydrolyzed acyl chlorides (*m*-nitrobenzoyl chloride and cinnamoyl chloride) react smoothly with OBC catalyzed by  $Pd(OAc)_2$  in anhydrous acetone in the presence of  $Na_2CO_3$ .

***m*-Methylbenzophenone.** *m*-Tolylboric acid (0.697 g, 0.5 mmol) was dissolved in a mixture of acetone (2 mL) and an aqueous 1.63 *M* solution of  $Na_2CO_3$  (1 mL) in an atmo-

Scheme 1



Ar = *o*-MeC<sub>6</sub>H<sub>4</sub>, *m*-MeC<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>-4-MeC<sub>6</sub>H<sub>3</sub>; R = Ph



R' = *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, (E)-PhCH=CH, Ph

**Reagents and conditions:** a. 1 mol.%  $PdCl_2$ ,  $Na_2CO_3$ , acetone, water, 20 °C; b. 1 mol.%  $Pd(OAc)_2$ ,  $Na_2CO_3$ , acetone, 20 °C.

sphere of argon, and  $PhCOCl$  (0.06 mL, 0.5 mmol) and an aqueous 0.1 *M* solution of  $PdCl_2$  (0.05 mL, 0.005 mmol) were added. After stirring at 20 °C for 15 min, Pd black precipitated from the reaction mixture. Then an aqueous 0.1 *M* solution of  $PdCl_2$  (0.05 mL, 0.005 mmol) was added, and the mixture was stirred for 30 min. The reaction mixture was diluted with water (10 mL), saturated with NaCl, and extracted with ether (5×5 mL). The ether extract was dried by  $MgSO_4$ . After evaporation of the ether, *m*-methylbenzophenone (0.0804 g, 82%) was obtained, m.p. 220–222 °C (cf. Ref. 7: m.p. 221–222 °C).

3-Nitro-4-methylbenzophenone (yield 96%), *o*-methylbenzophenone (80%), and benzophenone (96%) were obtained similarly from  $Ar(OH)_2$  or  $Ph_4BNa$  and  $PhCOCl$ .