Letters to the Editor

Synthesis of trialkylaluminum by the reaction of nonsolvated aluminum hydride with α-olefins

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Hydroalumination of olefins is one of the most important reactions in the synthesis of alkylaluminum compounds. Solid aluminum hydride obtained from an ether solution[1] has a composition of $(AlH_3)_3 \cdot OEt_2$, and its reaction with α-olefins at 120 °C results in the formation of a mixture of AlR_3 (yield 60%) and $AlR_3 \cdot OEt_2$ (40%).[2] Nonsolvated crystalline AlH_3 has also been obtained.[3]

This work studied the reaction of nonsolvated AlH_3 with α-olefins. This hydride is inert to olefins; however, the reaction occurs vigorously in the presence of a catalytic quantity of AlR_3, for example, $AlEt_3$ and $AlBu^i_3$ (2—10 mol.% of the amount of AlH_3). The role of these additives is their interaction with AlH_3 resulting in the formation of dialkylaluminum hydrides AlR_2H, which, as is known, react readily with olefins at 60—80 °C to form trialkylaluminum:

$$AlH_3(s) + 3\,AlR_3(liq) \longrightarrow 4\,AlR_2H(liq),$$

$$AlR_2H + CH_2{=}CHR' \longrightarrow AlR_2CH_2CH_2R'.$$

The $AlR_2CH_2CH_2R'$ obtained again enters the reaction cycle, and the process is completed by the "dissolution" of AlH_3 and the formation of trialkylaluminum. The reactions of 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 AlH_3 (6.3 g, 0.21 mol) obtained by a known procedure,[3] hexane (100 mL), $AlBu^i_3$ (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). $AlBu^i_3$ (31.1 g, 74.8%) was obtained. Found (%): Al, 13.91. $C_{12}H_{27}Al$. Calculated (%): Al, 13.60.

Trihexylaluminum. Similarly to the procedure described above, AlH_3 (6.3 g), hexene (84 g, 1.0 mol), $AlBu^i_3$ (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). $AlHex_3$ (55.6 g, yield 89.1% calculated per AlH_3) was obtained. Found (%): Al, 9.02. $C_{18}H_{39}Al$. 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 Na_2SO_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. AlH_3 (2.1 g), dec-1-ene (86.4 g), and $AlEt_3$ (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).

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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).

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Palladium-catalyzed reactions of organoboron compounds with acyl chlorides

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We have shown previously[1–3] that the reaction of organoboron compounds (OBC) with organic halides, which is an important method for the formation of a new C—C bond,[4] occurs readily in an aqueous organic solvent or in water when catalyzed by "ligand-free" palladium[5] 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[6] 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.

Scheme 1

$$ArB(OH)_2 + RCOCl \xrightarrow{a} RCOAr$$

Ar = *o*-MeC_6H_4, *m*-MeC_6H_4, 3-NO_2-4-MeC_6H_3; R = Ph

$$Ph_4BNa + 4\ R'COCl \xrightarrow{a,\ b} 4\ R'COPh$$

R' = *m*-$NO_2C_6H_4$, (*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.

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 atmosphere 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.

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