CARBONYLATION REACTION

COMMUNICATION 13. REACTION OF CARBON MONOXIDE WITH TRIALKYLBORANES

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The use of organoboranes as organometallic reagents in organic synthesis is constantly increasing [1]. The trialkylcarbinols were obtained previously from CO and certain trialkylboranes at 500-900 atm in aqueous medium [2], or directly from olefins at atmospheric pressure in diglyme medium by successively running the reactions of hydroborination, carbonylation in the presence of ethylene glycol, and oxidation without isolating the intermediate products [3]. We ran the reaction of CO with the tricyclohexylborane that was isolated after hydroborination at atmospheric pressure [4].

In the present paper we studied the reaction of CO with some other trialkylboranes: the tri-n-propyl-, tri-n-hexyl-, tri-n-heptyl-, and tricyclopentylboranes, at atmospheric pressure and 100° in diglyme medium, in the presence of excess ethylene glycol. The experiments were run by two methods: with the isolation of the carbonylation products from the reaction mixture (Table 1), and without their isolation and subsequent oxidation with alkaline H_2O_2 solution (Table 2). The isolation of the carbonylation products made it possible to obtain the cyclic esters of ethylene glycol and the corresponding trialkylcarbinylboric acids in 60-67% yields. From tripropylborane, besides the glycol ester of tri-n-propylcarbinylboric acid, the cyclic trimer of the anhydride of this acid was obtained in 19% yield. The obtained esters were oxidized in quantitative yield to the trialkylcarbinols. The carbonylation of the trialkylboranes and subsequent oxidation with alkaline H_2O_2 solution, without isolating the carbonylation products, gave the trialkylcarbinols, which had one more carbon atom than the starting organoborane, in 65-74% yields.

The change in the direction of the reaction when small amounts of sodium metal are added to the reaction medium deserves attention: the carbonylation of tri-n-propylborane after oxidation gave di-n-propylcarbinol in 39% yield; this is similar to the situation where dicyclohexylcarbinol was obtained from tricyclohexylborane when sodium was added [4]. We will mention that the reaction of CO with trialkylboranes in diglyme medium, in the absence of ethylene glycol, usually gave highly polymeric products.

A stepwise scheme for the reaction of CO with trialkylboranes was proposed previously [2, 3], and was cited in [4]. The important steps of the reaction are intramolecular rearrangements, with the successive migration from the boron atom to the carbon atom in the adduct $R_3\overset{-}{B}:\overset{+}{C}O$, formed from CO and the organoborane, of one, two, and three alkyl groups. It was found [2, 3] that the number of alkyl groups, migrating from the boron atom to the carbon atom, is determined by the reaction conditions, and especially by the temperature, pressure, and nature of the reaction medium. When the reaction is run in diglyme or THF at 45°, in the presence of $NaBH_4$ or $LiBH_4$, only one alkyl group migrates, which makes it possible to synthesize either primary alcohols or aldehydes. Two alkyl groups migrate in water–diglyme medium at ordinary pressure (synthesis of either secondary alcohols or ketones); three alkyl groups migrate in aqueous medium at 500-900 atm and 150° (synthesis of tertiary alcohols). The data obtained by us show that the addition of small amounts of Na to the reaction medium makes it possible to stop the process at the step of the migration of two alkyl groups, with the formation, after oxidation, of secondary alcohols instead of

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TABLE 1. Carbonylation of Trialkylboranes

Starting trialkylborane, M	Ethylene glycol, M/M of trialkylborane	Diglyme, ml	Cyclic ester of trialkylcarbinol acid and ethylene glycol					$\frac{\text{Found}}{\text{Calculated}}$			
			compound	yield, in % (based on starting borane)	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	mol. wt.	C, %	H, %	B, %
Tri-n-propylborane, 0.177	2,5	100	Ester of tri-n-propylcarbinylboric acid	60,2	236—237	1,4442	0,9017	$\frac{212}{212}$	$\frac{68{,}00}{67{,}93}$	$\frac{11{,}82}{11{,}87}$	$\frac{5{,}21}{5{,}10}$
			Tris-tri-n-propylcarbinylboroxine	19,3	211—215 (7)	1,4472	0,8714	$\frac{504}{504}$	$\frac{71{,}50}{71{,}43}$	$\frac{12{,}63}{12{,}60}$	$\frac{6{,}38}{6{,}44}$
Tricyclopentylborane, 0.510	2,0	300	Ester of tricyclopentylcarbinylboric acid	65,7	192—194 (5) Mp 94			$\frac{290}{290}$	$\frac{74{,}41}{74{,}42}$	$\frac{10{,}62}{10{,}69}$	$\frac{3{,}97}{3{,}80}$
Tri-n-hexylborane, 0.620	2,5	400	Ester of tri-n-hexylcarbinylboric acid [2]	62,5	220—223 (17)	1,4490	0,9062	$\frac{338}{338}$	$\frac{74{,}45}{74{,}55}$	$\frac{12{,}79}{12{,}72}$	$\frac{3{,}21}{3{,}26}$
Tri-n-propylborane,* 0.177	2,5	100	Ester of tri-n-propylcarbinylboric acid	58,2	236—237	1,4445	0,9079				
			Tris-tri-n-propylcarbinylboroxine	17,3	211—215 (7)	1,4462	0,8710				

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*At the end of carbonylation, the reaction mixture was heated at 150° for 1 h.

TABLE 2. Reaction of Carbon Monoxide with Trialkylboranes and Subsequent Oxidation of Carbonylation Products

Starting trialkylborane, mole	Ethylene glycol, mole /mole of trialkylborane	Diglyme, ml	Reaction product (after oxidation)					Found / Calculated		
			compound	yield (%) based on starting bor·	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	mol. wt.	C, %	H, %
Tri-n-propylborane, 0.734	2	300	Tri-n-propylcarbinol	74,2	194—195 *	1,4370	0,8365	$\frac{158}{158}$	$\frac{76,06}{75,95}$	$\frac{13,87}{13,95}$
Tri-n-propylborane, 0.177	2,5	100 +1 g Na	Di-n-propylcarbinol	39,2	154—155,5 †	1,4208	0,8177	$\frac{116}{116}$	$\frac{72,25}{72,35}$	$\frac{13,85}{13,87}$
Tricyclopentylborane, 1.6	1,5	300	Tricyclopentylcarbinol	65,3	166 (5) Mp 21	1,5125 ‡	1,0213	$\frac{236}{236}$	$\frac{81,25}{81,35}$	$\frac{11,76}{11,85}$
Tri-n-hexylborane, 0.174	3	260	Tri-n-hexylcarbinol	68,2	182—185 (18) ** Mp 43			$\frac{284}{284}$	$\frac{80,28}{80,28}$	$\frac{14,04}{14,09}$
Tri-n-heptylborane, 0.180	2	300	Tri-n-heptylcarbinol	67,4	193—195 (16) Mp 52			$\frac{326}{326}$	$\frac{80,72}{80,88}$	$\frac{14,20}{14,22}$

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*From [5]: 193-195°; [6]: n_D^{20} 1.4355; d_4^{20} 0.8340.

† From [6]:155,4°; n_D^{20} 1,4205; d_4^{20} 0.8183.

‡From [4]:n_D^{20} 1,5128.

**From [2]:121-123° (0.2mm).

tertiary alcohols. Under the adopted conditions, contrary to the data given in [2, 3], additional heating of the reaction mixture at 150° is not required for migration of all three alkyl groups (without adding the Na). Migration of the three alkyl groups occurs even during the reaction process when the reaction is run in diglyme medium at 100-110° and, after oxidation, the tertiary alcohols are obtained.

EXPERIMENTAL METHOD

The starting trialkylboranes were synthesized as described in [7], by the passage of diborane into an ether solution of the olefin. The mixture of isomeric trialkylboranes obtained in the hydroborination of the olefins was carbonylated by the passage of a CO stream for 5-6 h at atmospheric pressure and 100° in the presence of 1.5-3 mole of ethylene glycol per mole of trialkylborane and 100-400 ml of diglyme. This method of running the reaction differed from that cited in [4] in that, on conclusion of reaction at 100°, the mixture was not heated at 150-160° (see above). In the experiments, given in Table 1, after carbonylation the reaction product was isolated by the addition of 600 ml of water and 20 ml of hydrochloric acid, with cooling in ice water. The method for the oxidation of the carbonylation products with alkaline H_2O_2 solution is given in [4]. In the experiments with added Na the reaction components were loaded in the following order: diglyme, 1 g Na, and ethylene glycol. The stirred mixture was heated at 100° until the sodium glycolate was formed. Then the organoborane was added and the CO stream was passed through. At the end of CO absorption the carbonylation product was oxidized with H_2O_2.

Di-n-propylcarbinol was formed when the reaction with tri-n-propylborane was run in the presence of Na, which was isolated by fractional distillation through a column with an efficiency of 90 theoretical plates (see Table 2).

The synthesized aliphatic tertiary alcohols, which were obtained by starting with a mixture of isomeric trialkylboranes, evidently also represent a mixture of tertiary alcohols, which contain isomeric aliphatic radicals. We were able to obtain tri-n-propylcarbinol and di-n-propylcarbinol in a fairly pure state by fractional distillation (see Table 2). Tri-n-hexylcarbinol and tri-n-heptylcarbinol are solids. Several recrystallizations from various solvents (hexane, benzene, ethanol) failed to change the melting point, which indicates that they are quite pure. The molecular weights, determined by the mass spectroscopy method, as well as the elemental analyses of the obtained products, are given in Tables 1 and 2.

CONCLUSIONS

1. Cyclic glycol esters of trialkylcarbinylboric acids were synthesized from trialkylboranes and carbon monoxide in 60-70% yield, while tertiary alcohols were obtained by their oxidation.

2. The addition of small amounts of sodium metal changed the direction of the reaction, which made it possible to obtain secondary alcohols.

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