CARBONYLATION REACTIONS

COMMUNICATION 3. REACTION OF CARBON MONOXIDE WITH TRICYCLOHEXYLBORANE AT ATMOSPHERIC PRESSURE

K. V. Puzitskii, S. D. Pirozhkov,
K. G. Ryabova, I. V. Pastukhova,
and Ya. T. Éidus

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The reaction of carbon monoxide with organomagnesium and organomercury compounds was studied by us previously [1, 2]. The reactions of CO with organoboron compounds are of great interest, and they have found extensive use in organic synthesis [3]. A characteristic trait of the reaction of CO with trialkylboranes consists in the migration of alkyl groups from the boron atom to the carbon atom, in which connection varying the nature of the solvent, pressure, and reaction temperature makes it possible to regulate the number of migrating alkyl groups and obtain, after the appropriate treatment, trialkylcarbinols [4, 5], dialkylcarbinols [4], dialkyl ketones, or methylol derivatives of olefins [5]. The trialkylcarbinols were obtained from CO and trialkylboranes in aqueous medium at 500-900 atm [4]. These same carbinols were synthesized in good yield directly from the olefins at atmospheric pressure in diglyme medium by successively running the reactions of hydroboration with diborane, carbonylation with CO in the presence of ethylene glycol, and oxidation with H_2O_2 [5].

The reaction of CO with tricyclohexylborane at atmospheric pressure in diglyme medium was studied in the present paper. Here we studied the effect of adding ethylene glycol, metallic Na, $NaBH_4$, or $LiAlBH_4$ on the reaction, and we also ascertained the nature of the intermediate compounds.

Of special interest are the data obtained by us in the experiments with Na, the addition of which led, after oxidation, to the formation not of tricyclohexylcarbinol, but of dicyclohexylcarbinol. As a result, despite the fact that the reaction of CO with tricyclohexylborane went in diglyme medium and the reaction product, prior to oxidation, was heated at 160°C, only two of the cyclohexyl groups migrated from the boron atom to the carbon atom. In contrast to Na, the addition of either $NaBH_4$ or $LiAlH_4$ failed to affect the course of the reaction. It is interesting that Brown observed the catalytic action of both $NaBH_4$ and $LiBH_4$ on the carbonylation reaction of trialkylboranes at 45° in either diglyme or THF with the formation, after oxidation, of primary alcohols [5], and on the reaction of CO with diborane in THF with the formation of trimethylboroxin [6]. According to [4], in the carbonylation of trialkylboranes in aqueous medium at 500-900 atm and 25-27° the reaction product, after alkaline hydrolysis or oxidation with H_2O_2 in alkaline medium, was converted to the dialkylcarbinol containing traces of the dialkyl ketone, whereas when it was heated to 150-160° it gave the trialkylcarbinol after oxidation.

According to the data given in [5], the character of the end product was determined not only by the temperature of the carbonylation of trialkylboranes with CO or the type of treatment to which the reaction product was subjected, but also by the nature of the solvent: in diglyme medium they obtained trialkylcarbinols, the addition of water to the diglyme gave dialkyl ketones, while the methylol derivatives of olefins were obtained in ether medium, which are formed as the result of only one alkyl group migrating from the boron atom to the carbon atom.

The role of added ethylene glycol was established in our experiments. A repetition of the reaction for the carbonylation of tricyclohexylborane with CO in diglyme medium, but in the absence of ethylene

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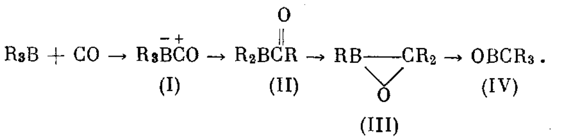
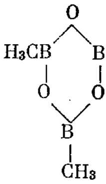
glycol, followed by oxidation or without it, led only to the formation of high-molecular products. The addition of 1-3 M of ethylene glycol per mole of tricyclohexylborane gave the cyclic glycol ester of tricyclohexylcarbinylboric acid in 73-80% yield, with a quantitative absorption of CO. From this it follows that the formation of this ester is the route by which the ethylene glycol prevents the polymerization of the intermediate carbonylation products. This cyclic ester is oxidized in quantitative yield to tricyclohexylcarbinol. Tricyclohexylcarbinol was obtained in 80% yield when the carbonylation reaction was run in diglyme medium in the presence of ethylene glycol and subsequent oxidation.

The migration of alkyl groups from the boron atom to the carbon atom during the carbonylation of trialkylboranes can be depicted as a stepwise process, which begins with the formation of adduct (I). This is followed by a number of rearrangements with the formation of acyl organoboron compound (II), boron epoxide (III), and then the anhydride of the trialkylcarbinylboric acid (IV) [4, 5]



The formation of trialkylboranecarbonyl (I), with a coordination bond between the boron and carbon atoms, finds substantiation in the analogy with the reaction of CO with diborane in sealed tubes at 100° and 20 atm, with the formation of boranecarbonyl H_3BCO [7]. Trimethylboroxin (V) was obtained under these conditions in the presence of 0.3-2 mole % of $NaBH_4$ from CO and diborane in THF medium [6]



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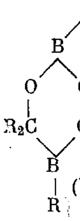

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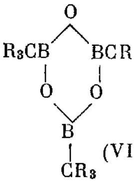

(VII)

The formation of (V) is accompanied by the migration of three hydrogen atoms from the boron atom to the carbon atom.

The dimers and trimers of trialkylboranecarbonyls $(R_3BCO)_n$, where n = 2-3, were obtained from CO and trialkylboranes at 100-200 atm and 10-18° in THF [8]. However, the carbonyl nature of these compounds was not proved. Apparently, the dimers have the structure of boradioxanes (VI).

The formation of acyl organoboron compounds (II) is analogous to the intermediate step of forming acyl organometallic compounds [1, 2]. The formation of the boron epoxide form (III) finds substantiation in the formation of its dimers as the 2,3,3,5,6,6-hexaalkyl-2,5-dibora-1,4-dioxanes (VI), which were isolated from the reaction products of CO with trialkylboranes in aqueous medium at 25-80° and 500-900 atm [4]. Tris-trialkylcarbinylboroxins (VII) were obtained when this reaction was run at a higher temperature (≥150°), which represent cyclic trimers of the anhydrides of trialkylcarbinylboric acids [4]. The formation of the monomeric form of the anhydride of tricyclohexylcarbinylboric acid is proved in the present paper by the preparation of the cyclic ester of ethylene glycol and this acid.

From what has been said it can be seen that the chemistry of the carbonylation of tricyclohexylborane in diglyme medium at atmospheric pressure, and in aqueous medium at pressures of 500-900 atm, has a variable character. Compounds (VI) and (VII) were not isolated by us; in place of them we obtained the cyclic glycol ester.

EXPERIMENTAL METHOD

Tricyclohexylborane was obtained from diborane and cyclohexene as described in [9]; yield 85-90%; mp 100°C; cf. [10].

Carbonylation of $(C_6H_{11})_3B$. The reaction of CO with $(C_6H_{11})_3B$ was run at 100-110° and atmospheric pressure, in diglyme medium (100 ml) containing ethylene glycol, and subsequent oxidation of the carbonylation product (without isolating it from the reaction mixture) with alkaline H_2O_2 solution. In the experiments, which were run for 0.3-3 h, we took 50-150 mM of $(C_6H_{11})_3B$, and for every mole of the latter we used 0.0-0.9 M of additive ($NaBH_4$, $LiAlH_4$, or Na) and 0.0-3.0 M of ethylene glycol. The reaction components were charged in the following order: diglyme, additive, ethylene glycol after stirring for 5 min, and finally the organoborane. Vigorous reaction with the evolution of H_2 occurred when the ethylene glycol was added. About 1/3 of the taken ethylene glycol was consumed for this. When Na was added the H_2 evolution occurred when the mixture was heated to 100°. After all of the organoborane had been added the stirring was continued for another 5 min, after which the mixture was heated to 100-110° and CO was passed in. The reaction without an additive was ended in 0.5-1 h, in 20 min when Na was added, while in the experiments using $LiAlH_4$ the reaction lasted as long as 3 h. At the end of reaction the mixture was heated for 1 h at 150-160° in a CO stream, cooled, and then it was oxidized by the addition of NaOH solution and excess H_2O_2, followed by heating at 80-90°. The oxidation product separated on subsequent dilution with water and cooling. One of the experiments is described below.

Into a mixture of 100 ml of dry diglyme, 1 g of $LiAlH_4$, 10 ml of ethylene glycol, and 25 g of molten $(C_6H_{11})_3B$ at 100-110° was passed CO for 2 h. The reaction mixture was heated in a CO stream for 2 h at 160°, after which it was cooled to 70° and a solution of 20 ml of 6 N NaOH solution and 40 ml of 30% H_2O_2 solution were added in 1 h. The mixture was heated at 80-90° for 1 h, after which 800 ml of water and 20 ml of HCl (to dissolve the glycolates) were added and the mixture was cooled in ice water. The obtained crystals were filtered, washed with water, and dried; yield 86%; mp 95° (from hexane); cf. [5].

In the experiments in which Na was used as the additive we obtained dicyclohexylcarbinol, mp 63° (from hexane); cf. [11].

In order to ascertain the character of the product of the carbonylation of $(C_6H_{11})_3B$ with CO we ran some carbonylation experiments in 100 ml of diglyme at 100-110°, where oxidation of the reaction mixture was omitted. At the end of the carbonylation reaction, followed by heating the reaction mixture at 150-160°, we added 800 ml of water and 20 ml of HCl, and cooled the mixture in ice water. The obtained fine white crystals of 2-tricyclohexylcarbinyl-2-borondioxalane were separated; yield 70-76%; mp 157°; bp 239-240° (9 mm). Found: C 75.71; H 11.19; B 3.43%; mol. wt. 333 (ebulliometrically). $C_{21}H_{37}O_2B$. Calculated: C 75.88; H 11.23; B 3.25%; mol. wt. 332. This cyclic ester does not polymerize when heated and is stable when stored under the conditions of steam-distillation and in vacuo. Similar esters were obtained previously by the reaction of CO with other trialkylboranes in ethylene glycol medium at 650 atm [4].

To a solution of the obtained cyclic ester (32 g in 200 ml of diglyme) were added 20 ml of 6 N NaOH solution and 100 ml of 30% H_2O_2 solution in 1 h at 50-60°, after which the mixture was heated at 70-90° for 1 h, diluted with water, and cooled. We obtained crystals with mp 95° (from hexane).

CONCLUSIONS

1. The reaction of CO with tricyclohexylborane in diglyme, in the presence of ethylene glycol, gives the cyclic glycol ester of tricyclohexylcarbinylboric acid, which when oxidized with H_2O_2 is quantitatively converted to tricyclohexylcarbinol.

2. The addition of Na leads to the formation of an adduct, the oxidation of which gives dicyclohexylcarbinol. The addition of either $NaBH_4$ or $LiAlH_4$ fails to affect the direction of the reaction.

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