ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE ETHYL CORPORATION]

Triorganoboranes as Alkylating Agents[1]

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Triethyl-, tri-*n*-hexyl- and triphenylborane are capable of alkylating mercuric salts to form the corresponding dialkyl- or diarylmercury compounds. The reaction has been carried out in ethers and in aqueous solution. Tetraethyllead has also been prepared from triethylborane and divalent lead compounds. Tri-*n*-hexylborane similarly reacts with lead salts to give an R_4Pb derivative.

Jones and Gilman[2] have pointed out that the most widely used synthesis of organometallic compounds is by the reaction of an organometallic derivative with a metal salt

$$RM + M'X \longrightarrow RM' + MX$$

Most often, X is a halide ion, although it can be hydride or alkoxide. The Grignard and organolithium reagents are the usual alkylating agents and their use is well known.[2] More recently, organoaluminum derivatives have been found to undergo this reaction. With the aluminum reagents, organic derivatives of boron,[3,4] silicon,[5] titanium,[6] arsenic,[7] cadmium,[5] tin,[7,8] antimony,[5,7] mercury[7] and lead[5,9-11] have been prepared.

We have found that trialkyl- and triarylboranes can also be used to prepare organometallic derivatives of certain elements. The formation of diethylmercury from triethylborane in aqueous and organic media was reported by us in a preliminary Communication.[12] The reaction now has been extended to tri-*n*-hexylborane and triphenylborane, both of which yield organic derivatives of mercury. The results are summarized in Table I. As with the ethyl analog, the above-mentioned boranes react with the mercuric salt in an aqueous solution or in an ether. In addition to alkylating mercuric compounds, triethylborane and tri-*n*-hexylborane are capable of reacting with lead salts in aqueous systems. The same two boranes also yield the corresponding tetraalkyllead compounds in ether solution.

Three-quarters of a century ago, the formation of phenylmercuric chloride from mercuric chloride and benzeneboronic acid, $C_6H_5B(OH)_2$, was reported.[13] The reaction was carried out in water under mild conditions. Other reports of similar preparations with arylboronic acids have since appeared.[14-17] It was claimed that *n*-propaneboronic acid behaved similarly with mercuric chloride,[18] but the report has been disputed.[19] To our knowledge, this ability of the Ar–B groups, and possibly R–B groups, to effect arylation or alkylation has not previously been extended to the triorganoboranes.

Based upon this background, our observation of the reactivity of triorganoboranes with mercuric chloride, and the assumption that the alkylation proceeded stepwise, it was thought that possibly

$$R_3B + HgCl_2 + 2NaOH \longrightarrow R_2BONa + RHgCl + NaCl + H_2O$$

$$\underline{R_2BONa + RHgCl + 2NaOH \longrightarrow RB(ONa)_2 + R_2Hg + NaCl + H_2O}$$

$$R_3B + HgCl_2 + 4NaOH \longrightarrow RB(ONa)_2 + R_2Hg + 2NaCl + 2H_2O$$

all three organic groups from the R_3B might be utilized. While we have not yet conclusively

$$2R_3B + 3HgCl_2 + 12NaOH \longrightarrow 3R_2Hg + 2B(ONa)_3 + 6NaCl + 6H_2O$$

shown that such is the case, the very high yield of diethylmercury obtained in alkaline solution leads us to the belief that it is possible. Under these conditions essentially all of the available mercury reagent was fully ethylated. This point will be explored further in future work.

An interesting aspect of the reaction with mercuric compounds is the relationship of our synthesis of mercury compounds to an earlier preparation of organoboron derivatives. Michaelis[20-21] used diarylmercury reagents and boron trihalides to form $ArBX_2$ or Ar_2BX depending upon the quantity of mercury compound employed. The direction and extent of alkyl or aryl group transfer probably depends upon the particular organic and anionic groups involved. Thus, with proper choice of reagents, it should be possible to form organo-

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[1] Presented at the Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., December 3-5, 1959.

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TABLE I

R of R_3B	Mole R_3B	Metal compound	Mole	Solvent	Product	Yield, %
C_2H_5	0.05	$HgCl_2$	0.05	H_2O-NaOH	$(C_2H_5)_2Hg$	95[a]
C_2H_5	.05	HgO	.05	H_2O–NaOH	$(C_2H_5)_2Hg$	65
C_2H_5	.02	$Hg(OCOCH_3)_2$	.04	$(CH_3OCH_2)_2$	$(C_2H_5)_2Hg$	66[a]
C_2H_5	.07	$Hg(OCOCH_3)_2$	.035	THF[c]	$(C_2H_5)_2Hg$	54
C_2H_5	.07	$Pb(ONp)_2$[b]	.03	THF	$(C_2H_5)_4Pb$	27
C_2H_5	.13	PbO	.06	H_2O–NaOH	$(C_2H_5)_4Pb$	42
C_2H_5	.07	PbO	.035	H_2O	$(C_2H_5)_4Pb$	19
n-C_6H_{13}	.055	$HgCl_2$	.055	H_2O–NaOH	$(n\text{-}C_6H_{13})_2Hg$	55
n-C_6H_{13}	.028	$Hg(OCOCH_3)_2$	.02	THF	$(n\text{-}C_6H_{13})_2Hg$	50
n-C_6H_{13}	.028	$Hg(OCOCH_3)_2$	.02	$(CH_3OCH_2)_2$	$(n\text{-}C_6H_{13})_2Hg$	52
n-C_6H_{13}	.02	$Pb(ONp)_2$	.01	$(CH_3OCH_2)_2$	$(n\text{-}C_6H_{13})_4Pb$	18
C_6H_5	.05	$HgCl_2$	.05	H_2O–NaOH	$(C_6H_5)_2Hg$	52
C_6H_5	.13	$Hg(OCOCH_3)_2$	.13	$(CH_3OCH_2)_2$	$(C_6H_5)_2Hg$	47

[a] Reference 12. [b] Lead naphthenate; see Experimental section. [c] Tetrahydrofuran.

mercury compounds from organoboranes or alternatively to proceed in the opposite direction.

Further extension of the work reported here is planned. With organoboranes more readily obtainable than in the past, another convenient synthesis of various organometallic compounds is available. This is particularly true for the formation of organomercury derivatives in aqueous media.

Experimental[22]

Triorganoboranes with Mercuric Oxide in Water.—As briefly described earlier,[12] to a stirred solution of 13.5 g. (0.05 mole) of mercuric chloride in 100 ml. of water was added 6.0 g. (0.15 mole) of sodium hydroxide in about 25 ml. of water. The resulting yellow mercuric oxide, without isolation, was heated to 70–80° and then 4.9 g. (0.05 mole) of triethylborane was added from a dropping funnel. The addition of the borane required 15 minutes. Stirring was stopped after an additional 10 minutes, and two colorless liquid phases separated. The lower layer was washed with 100 ml. of 2 *N* aqueous sodium hydroxide and with water. The remaining oil was distilled to yield 9.5 g. (95%) of diethylmercury, b.p. 67–68° (19 mm.).[23]

A suspension of 10.8 g. (0.05 mole) of commercial yellow mercuric oxide in 100 ml. of water containing 6.0 g. (0.15 mole) of sodium hydroxide was stirred and heated to about 75°. Slowly, 4.9 g. (0.05 mole) of triethylborane was added dropwise. After about 15 minutes the mixture was worked up as described above to give a 65% yield of diethylmercury.

Using mercuric oxide generated *in situ* from the chloride as described above, the alkylation was repeated using tri-*n*-hexylborane[24] and triphenylborane.[25] The yields of di-*n*-hexylmercury,[26] b.p. 155–157° (10 mm.), and diphenylmercury,[27] m.p. 120–121°, were 55 and 52%, respectively.

Triorganoboranes with Mercuric Acetate in 1,2-Dimethoxyethane.—With shaking, 3.9 g. (0.04 mole) of triethylborane was added slowly to a mixture of 6.4 g. (0.02 mole) of mercuric acetate and 25 ml. of 1,2-dimethoxyethane.[12] (This addition was accomplished with a hypodermic syringe, the needle of which was inserted through the rubber stopper of the reaction flask.) The mercuric acetate slowly dissolved and the mixture became warm. The solution was refluxed for about 2 hours. A small amount of a light gray solid appeared during this operation. After cooling, 5 g. (0.12 mole) of sodium hydroxide in 15 ml. of water was added with shaking. Two clear layers separated. Continued addition of 20% aqueous sodium hydroxide and then water gave a small amount of a heavy oil which on distillation yielded 66.7% of diethylmercury.

In a similar fashion, mercuric acetate was allowed to react with tri-*n*-hexylborane and with triphenylborane. The di-*n*-hexyl- and diphenylmercury were obtained in yields of 52 and 47%, respectively. Using tetrahydrofuran as the solvent, a 50% yield of di-*n*-hexylmercury was realized.

Triorganoboranes with Lead Oxide in Water.—A stirred mixture of 13.4 g. (0.06 mole) of lead(II) oxide, 14.8 g. (0.37 mole) of sodium hydroxide and 250 ml. of water was heated to 80°. Over a 6-minute period, 12.7 g. (0.13 mole) of triethylborane was added. A black solid began to form almost immediately. After 30 minutes the mixture was allowed to cool and treated with 100 ml. of hexane to extract the tetraethyllead. The resulting partial emulsion was allowed to stand for 3 days to effect complete separation of the layers. Analysis of the hexane phase[28] showed that a 42% yield of tetraethyllead had been formed. A similar experiment, in which the alkali was omitted, gave a 19% yield of product.

Triorganoboranes with Lead Naphthenate[29] in Ethers.—A solution of 6.9 g. (0.07 mole) of triethylborane, 25.9 g. (0.03 mole) of lead naphthenate and 100 ml. of THF was refluxed for 6–7 hours. A black solid slowly separated and the yellow-brown color of the solution faded to a pale yellow. After cooling, the mixture was diluted with 200 ml. of toluene and hydrolyzed with 50 ml. of 10% aqueous sodium hydroxide solution. The two layers were separated and the organic layer was washed with several portions of sodium hydroxide solution, then with water. Analysis[28] of the dried toluene layer showed a 27% yield of tetraethyllead.

Using 1,2-dimethoxyethane as the solvent and a reflux time of 6.5 hours, tri-*n*-hexylborane was similarly treated with lead naphthenate. The yield of tetraalkyllead compound was 18%.

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[22] The air-sensitive reagents were handled and the reactions carried out under nitrogen or in an inert atmosphere box. All melting and boiling points are uncorrected. Product identification was made by the use of infrared comparison and physical constants.

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[29] Purchased from Advance Solvents and Chemical Division of Carlisle Chemical Works, Inc. The material is a yellow-brown liquid containing 24% lead according to the supplier.