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MERCURY IN ORGANIC CHEMISTRY

IV*. AN IMPROVED PROCEDURE FOR THE CONVERSION OF INTERNAL OLEFINS INTO sec-ALKYLMERCURIC SALTS

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Summary

Tri-sec-alkylboranes, readily available from internal olefins via hydroboration, undergo a facile reaction with mercury(I) alkoxides in alcohol to transfer two of the three alkyl groups from boron to mercury. Mercury(I) tert-butoxide in tert-butanol appears to be the reagent of choice for these reactions. The alkoxide and solvent employed are critical and exhibit effects exactly opposite to those observed previously with mercury(II) alkoxides.

Introduction

We recently reported that tri-sec-alkylboranes, readily available from internal olefins via hydroboration [1], undergo a rapid reaction at room temperature in tetrahydrofuran (THF) with mercury(II) methoxide to give the corresponding sec-alkylmercuric salts (eqn. 1) [2]. The reaction does not proceed well in methanol unless brought to reflux. These reactions appeared to be further examples of free radical chain reactions of organoboranes [3, 4].

$$R_3B + Hg(OCH_3)_2 \rightarrow RHgOCH_3 + R_2BOCH_3 \qquad (1)$$

Although this reaction provided the first general procedure for the conversion of these organoboranes into organomercurials, only one of the three alkyl groups of the organoborane was utilized. We now wish to report that the corresponding reaction of mercury(I) alkoxides in alcohol also proceeds smoothly at room temperature and readily converts two of the three alkyl groups of the organoborane into the corresponding sec-alkylmercuric salts (eqn. 2). Furthermore, the extent of reaction varies markedly with the alkoxide and solvent em-

$$R_3B + 2\,Hg_2(OR')_2 \rightarrow 2\,RHgOR' + 2\,Hg^0 + RB(OR')_2 \qquad (2)$$

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* For part III see ref. 6.

TABLE 1

THE REACTION OF MERCURY(I) ALKOXIDES AND TRI-sec-ALKYLBORANES

$R_3B + n\,Hg_2(OR')_2 \xrightarrow{HCl} 2\,RHgCl$

Tri-sec-alkylborane	Mercury(I) alkoxide	Equiv. [a] n =	Solvent	Isolated yield of RHgCl [b] (%)
Tricyclohexylborane	Methoxide	1	THF	7-37
		2		17-53
		3		60-70 [c]
		1	Methanol	11-16
		2		63
		3		78
		3	Pentane	5-14
Tricyclopentylborane	Methoxide	3	Methanol	59
Tri-*exo*-2-norbornylborane	Methoxide	3	Methanol	59
Tricyclohexylborane	tert-Butoxide	3	THF	26-36
Tricyclohexylborane	tert-Butoxide	3	tert-Butanol	83
Tricyclopentylborane	tert-Butoxide	3	tert-Butanol	91
Tri-*exo*-2-norbornylborane	tert-Butoxide	3	tert-Butanol	82

[a] Equiv. of mercury(I) alkoxide. [b] Yield based on reaction of two alkyl groups. [c] Wildly exothermic reaction.

ployed, and exhibits *exactly opposite effects* to those observed in the mercury(II) alkoxide reactions [2]. However, a free radical chain reaction again appears to best explain the results.

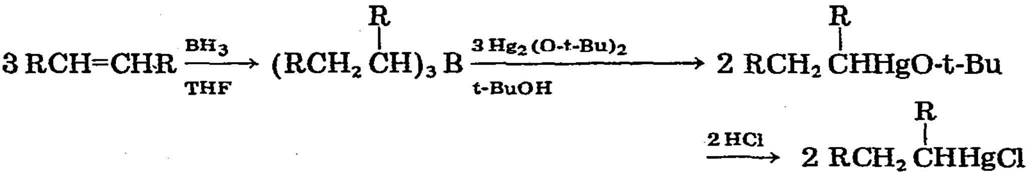
Results and discussion

We have chosen tricyclohexylborane as a representative tri-sec-alkylborane and examined its reaction with mercury(I) alkoxides. Particular attention was paid to the effect of each of the following reaction parameters upon the yield: stoichiometry, solvent and alkoxide. The results are summarized in Table 1.

The solvent effects in these mercuration reactions are remarkable. Whereas the reaction of tricyclohexylborane and mercury(II) methoxide (3 equiv.) in THF proceeds smoothly at room temperature to give a 47% conversion of two of the alkyl groups into cyclohexylmercurial (94% of one group), the corresponding reaction with mercury(I) methoxide in THF is very erratic. With small amounts of mercury(I) methoxide the reaction in THF often fails completely. At other times the reaction is exothermic and the yields of organomercurial are modest. With three equiv. of mercury(I) methoxide an induction period of up to 30 min is observed, followed by a rather violent reaction which causes the THF to reflux out of the condenser. Work-up gives 60-70% yields of cyclohexylmercuric chloride based on reaction of 2 alkyl groups of the organoborane. In methanol, the reaction of mercury(II) methoxide with tricyclohexylborane exhibits an induction period [2], but the reaction with mercury(I) methoxide proceeds smoothly to give a 78% isolated yield of cyclohexylmercuric chloride upon work-up. Neither reaction proceeds readily in pentane.

The effect of the alkoxide also is rather amazing. Although mercury(II) methoxide gives good yields of cyclohexylmercurial, based on one alkyl group of the organoborane in both THF and refluxing methanol, mercury(II) tert-butoxide gives extremely poor yields in the analogous reaction in both THF and tert-butanol. Similarly, mercury(I) methoxide gives high yields of cyclohexylmercuric chloride in both methanol and THF, but mercury(I) tert-butoxide gives only a 26-36% yield of this product in THF. However, an excellent 83% yield of cyclohexylmercuric chloride can be obtained in tert-butanol when mercury(I) tert-butoxide is used.

Thus, mercury(I) methoxide in methanol and mercury(I) tert-butoxide in tert-butanol appear to be useful reagents for the conversion of internal olefins into sec-alkylmercuric salts via hydroboration—mercuration. Examination of the yields of alkylmercuric chloride obtained from tricyclopentylborane and tri-*exo*-2-norbornylborane (Table 1) indicates that mercury(I) tert-butoxide is the superior reagent (eqn. 3). Isolated yields of sec-alkylmercuric chlorides of 82-91% have been obtained using this reagent.



$$3\,RCH{=}CHR \xrightarrow[THF]{BH_3} (RCH_2\overset{R}{\overset{|}{C}}H)_3B \xrightarrow[t\text{-}BuOH]{3\,Hg_2(O\text{-}t\text{-}Bu)_2} 2\,RCH_2\overset{R}{\overset{|}{C}}HHgO\text{-}t\text{-}Bu \xrightarrow{2\,HCl} 2\,RCH_2\overset{R}{\overset{|}{C}}HHgCl \quad (3)$$

We have again obtained some evidence for a free radical pathway in these reactions. First, the induction period evident in THF is reminiscent of many free radical reactions. Secondly, bromination of the 2-norbornylmercuric chloride in pyridine at —40° indicated some loss of configuration during the mercuration reaction [2]. NMR analysis indicated that the 2-norbornyl bromide obtained was only $\approx$ 80-85% *exo*, whereas the trialkylborane is $>$ 99% *exo*. A similar 85/15 *exo* to *endo* ratio has been obtained in the mercuration of tri-*exo*-2-norbornylborane by mercury(II) alkoxides [2]. Many reactions in which the 2-norbornyl radical is an intermediate show a similar loss of stereochemistry.

Most interesting is the selectivity of the reaction of mercury(I) alkoxides with n-hexyldicyclohexylborane. Mercury(II) methoxide (1 equiv.) in THF reacts exclusively with the n-hexyl group [2] as do all other mercury(II) salts examined [5]. Mercury(I) methoxide in methanol gives approximately a 3/2 ratio of n-hexyl/cyclohexyl products and mercury(I) tert-butoxide in tert-butanol gives approximately a 1/7 ratio of n-hexyl/cyclohexyl groups reacting. Mercury(II) methoxide evidently proceeds by a more rapid electrophilic cleavage reaction, while the mercury(I) alkoxides give results more consistent with a free radical reaction.

Once again it appears necessary that the mercury alkoxide be thermally unstable under the reaction conditions before the reaction will proceed. Thus, mercury(I) methoxide is moderately stable in THF, but rapidly decomposes in methanol. Mercury(I) tert-butoxide is also less stable in tert-butanol than in THF. Mercury(II) alkoxides show the same correlation between instability and reactivity. Thus, mercury(II) methoxide is stable in methanol, but smoothly decomposes in THF. On the other hand mercury(II) tert-butoxide appears to be quite stable in both solvents. Consistent with these observations is the fact that only mercury(I) methoxide or tert-butoxide in the corresponding alcohol and mercury(II) methoxide in THF give smooth reactions and good yields of organomercurial at room temperature.

The exact mechanism of these reactions remains a puzzle. It is obvious from the solvent effects that the mercury(I) alkoxides are not simply disproportionating into metallic mercury and mercury(II) alkoxides which then react further with the organoborane. We also have examined the opposite possibility, namely that the mercury(II) alkoxides are reacting with metallic mercury to give mercury(I) alkoxides which are the reactive species. However, the addition of metallic mercury to a mixture of tricyclohexylborane and mercury(II) tert-butoxide (which do not react under these conditions) in tert-butanol fails to bring about any significant reaction. The solvent effects further suggest that an initial decomposition of the mercury alkoxide is required. Although specific details of the mechanism are not presently known, the following scheme is a plausible representation of the overall reaction (eqns. 4—6).

$$Hg_2(OR)_2 \rightarrow 2\,Hg^0 + 2\,\cdot OR \qquad (4)$$

$$RO\cdot + R_3B \rightarrow ROBR_2 + R\cdot \qquad (5)$$

$$R\cdot + Hg_2(OR)_2 \rightarrow RHgOR + Hg^0 + \cdot OR \qquad (6)$$

Conclusive evidence regarding the free radical nature of these reactions has so far evaded us. We have not yet found a suitable free radical initiator or inhibitor for these reactions. Attempted photolysis of several of these reaction mixtures at 0° has provided only inconclusive results. Thus, photolysis of tricyclohexylborane and mercury(I) methoxide (3 equiv.) in pentane and mercury (II) methoxide (3 equiv.) in methanol both at 0° (conditions under which no significant reaction generally occurs) gave 40 and 32% isolated yields (based on two alkyl groups reacting) of cyclohexylmercuric chloride upon work-up. These modest yields may, however, be due to thermal initiation on the hot upper portions of the flask.

Experimental

All materials, chemicals and experimental procedures have been recently reported elsewhere [2]. The following general procedure for the synthesis of sec-alkylmercuric salts is representative. Fifty mmol of tri-sec-alkylborane was prepared in the usual manner [1]. After replacing the THF by 100 ml of tert-butanol, 0.30 mol of potassium tert-butoxide (33.66g) was added with cooling followed by 0.15 mol of mercury(I) chloride (70.8 g). This thick suspension was shaken by hand and occasionally cooled until the reaction mixture became sufficiently thin that a magnetic stirrer could be used. After it had been stirred at room temperature for 4 h the reaction mixture was worked up in the manner described previously [2]. Using this procedure the following isolated recrystallized yields were obtained: cyclohexylmercuric chloride, 83%; cyclopentylmercuric chloride, 91%; 2-norbornylmercuric chloride, 82%; with yields based on utilization of two of the three R groups of R_3B.

The techniques used to determine the stereochemistry of the 2-norbornyl bromide and the selectivity of the mercuration of n-hexyldicyclohexylborane have been reported previously [2].

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