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ORGANOBORANES

XIV. REACTION OF ORGANOBORANES WITH MERCURIC ACETATE. A CONVENIENT PREPARATION OF DIALKYLMERCURIALS VIA HYDROBORATION–MERCURATION

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SUMMARY

Organoboranes derived from terminal olefins react with mercuric acetate in tetrahydrofuran (THF) giving rise to dialkylmercury compounds. The first two alkyl groups react rapidly at room temperature while the third is more sluggish. Organoboranes derived from internal olefins are unreactive to various mercury(II) salts under these conditions. Dicyclohexylalkylboranes give rise to quantitative yields of dialkylmercurials when reacted with mercuric acetate. Alkylmercuric acetates are converted in high yields to dialkylmercury compounds when treated with zinc dust at room temperature in the presence of Lewis acid catalysts.

INTRODUCTION

Organoboranes derived from the hydroboration of terminal olefins react rapidly and quantitatively with mercuric acetate in THF at room temperature to give the corresponding alkylmercuric acetates[1,2] [eqn. (1)].

$$3\,\mathrm{RCH{=}CH_2} + \mathrm{BH_3} \xrightarrow{\mathrm{THF}} \mathrm{(RCH_2CH_2)_3B} \xrightarrow[\mathrm{THF}]{3\,\mathrm{Hg(OAc)_2}} 3\,\mathrm{RCH_2CH_2HgOAc} + \mathrm{B(OAc)_3} \qquad (1)$$

These acetates are readily converted to various alkylmercuric salts [eqn (2)].

$$\mathrm{RCH_2CH_2HgOAc} + \mathrm{MX} \rightarrow \mathrm{RCH_2CH_2HgX} + \mathrm{MOAc} \qquad (2)$$

Organoboranes derived from internal olefins generally require much harsher conditions and give lower yields of products[2,3]. The ability of organoboranes to alkylate mercury salts completely to the dialkylmercury compounds has been shown in limited examples[4,5], but the utility or scope of the reaction was not investigated.

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We wish to report here the results of our study of the synthetic utility of the mercuri-deboronation of trialkylboranes with mercuric acetate in the preparation of dialkylmercurials. These results make readily available in high yield a wide range of simple and substituted dialkylmercurials, many of which would be difficult or impossible to obtain by other means.

RESULTS AND DISCUSSION

Mercuri-deboronation of primary trialkylboranes

It has been shown that all three alkyl groups in trialkylboranes are transferred quantitatively to mercury in less than 5 min at 0° when added to a suspension of three equivalents of mercuric acetate in THF[1] [eqn. (1)]. In order to determine the rate of further alkylation to R_2Hg, tri-n-butylborane was treated with n-butylmercuric acetate in THF in B/Hg ratios of 1/1 (1 alkyl group transferred corresponds to 100% n-Bu_2Hg), 1/2 (2 alkyl groups), and 1/3 (all three alkyl groups transferrable) [eqn. (3)].

$$\text{n-Bu}_3\text{B} + \text{n-BuHgOAc} \xrightarrow{\text{THF}} \text{n-Bu}_2\text{Hg} + \text{n-Bu}_2\text{BOAc} \quad (3)$$

The amount of n-Bu_2Hg formed was determined by GLC analysis. These experiments showed that two of the three alkyl groups are transferred completely within 15 min at room temperature, while the third group requires about 4 h in refluxing THF for complete reaction. Thus, when one mole of n-Bu_3B was reacted with 1.5 moles $Hg(OAc)_2$ in THF, a 48% yield of n-Bu_2Hg was obtained after 30 min at room temperature and a 76% yield after 4 h at reflux. (The transfer of two alkyl groups from boron would correspond to a 33% yield.)* [Eqn. (4)].

$$\begin{array}{lllll} R_3B + 1.5\ Hg(OAc)_2 & \rightarrow RB(OAc)_2 & + RHgOAc & + 0.5\ R_2Hg & (4) \\ 100 \quad 150 & \quad 100 & \quad 100 & \quad 50(33\%) & \end{array}$$

Since secondary groups on boron have been found to be unreactive (see later) and since hydroboration of a terminal olefin gives 6% secondary B–alkyl bonds[6], transfer of only the reactive primary groups would give rise to an 88% maximum yield [eqn. (5)].

$$\begin{array}{llllll} R_3B + 1.5\ Hg(OAc)_2 & \rightarrow RB(OAc)_2 & + R_2Hg & + RHgOAc & + B(OAc)_3 & (5) \\ 100 \quad 150 & \quad 18 & \quad 132(88\%) & \quad 18 & \quad 82 & \end{array}$$

In order to overcome this problem, various amounts of excess borane were used. Table 1 shows the results of using excess trialkylborane.

Thus, using a stoichiometric ratio of reagents an 80% yield of R_2Hg can be obtained by refluxing for 4 h, or in the case of trialkylboranes derived from inexpensive olefins, a 50% excess of trialkylborane gives rise to a quantitative yield of R_2Hg merely by stirring the reagents for 30 min at room temperature. Table 2 shows the results of the preparation of various dialkylmercury compounds using trialkylboranes as alkylating agents. Tables 5 and 6 give the physical properties and elemental analyses of all mercurials prepared.

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* The equilibrium $2\ RHgOAc \rightleftharpoons R_2Hg + Hg(OAc)_2$ lies very far to the left.

TABLE 1

$n\text{-}Bu_3B + 1.5\ Hg(OAc)_2 \rightarrow 1.5\ n\text{-}Bu_2Hg + B(OAc)_3$

Excess n-Bu_3B (%)	*Yield n-Bu_2Hg^a (%)*	
	30 *min (R.T.)*	4 *h* (67°)
0	48	76
10	64	80
30	87	100
50	100	100

[a] By GLC analysis.

TABLE 2

PREPARATION OF R_2Hg FROM R_3B

Olefin hydroborated	*(mmole)*	*$Hg(OAc)_2$ (mmole)*	*Excess R_3B (%)*	*Yield R_2Hg^a (%)*
1-Butene	(260)	100	30	71
Isobutylene	(130)	50	30	73
1-Dodecene	(250)	100	25	83^b
3,3-Dimethyl-1-butene	(250)	100	25	85
2-Methyl-1-pentene	(250)	100	25	87
β-Pinene	(216)	100	8	86^b
1,1-Diphenylethylene	(125)	50	25	83

[a] Isolated yields. [b] Crude yield before recrystallization from pentane.

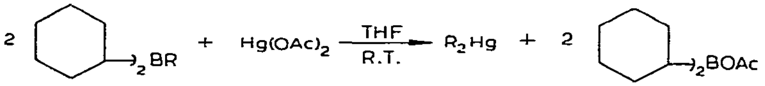
Mercuri-deboronation of secondary trialkylboranes

Previous work showed secondary trialkylboranes to be much more sluggish than primary ones[3]. Our work certainly confirms the reluctance of secondary trialkylboranes to undergo mercuration. When two moles of tri-sec-butylborane were reacted with one mole of various mercury salts in refluxing THF for periods up to 24 h, no significant amount of s-Bu_2Hg could be detected by GLC analysis. The mercury salts used were mercuric acetate, trifluoroacetate, nitrate, and methanesulfonate.

Mercuri-deboronation of mixed trialkylboranes

With the remarkable difference in reactivity between primary and secondary trialkylboranes, the use of mixed trialkylboranes which are readily available via hydroboration[6] appeared promising. However, previous workers[1] showed that appreciable ring-opening occurs when *B*-alkyl-9-borabicyclo[3.3.1]nonane was treated with mercuric acetate in THF, thus making it unsuitable. Other mixed boranes were tried with more success.

Thexyldi-n-butylborane(2,3-dimethyl-2-butyldi-n-butylborane) and thexyldi-iso-butylborane, upon treatment with an equimolar quantity of mercuric acetate in THF at room temperature, reacted slowly to give a 68% and 34% yield of di-n-butylmercury and di-iso-butylmercury respectively after 24 h. Also very slow was the reaction of disiamyl-n-butylborane[bis(1,2-dimethylpropyl)-n-butylborane] and disiamyl-iso-butylborane with 0.5 mole of mercuric acetate. These boranes yielded in 24 h at room temperature a 45% and 22% formation of the corresponding mercurials. However, dicyclohexyl-n-butylborane gave rise to a 94% yield of di-n-butylmercury in only 1 h, while dicyclohexyl-iso-butylborane yielded 95% di-iso-butylmercury in 1 h also. Thus, dicyclohexylboranes provide a convenient and efficient synthetic route to dialkylmercurials [eqn. (6)].



(6)

The use of dicyclohexylboranes is advantageous in that dicyclohexylborane is a more selective hydroborating agent than BH_3[6], and a wide range of functional groups can be tolerated (an advantage which is not enjoyed in the normal Grignard preparation of dialkylmercurials).

Attempts at the direct removal of the by-product, $(C_6H_{11})_2BO_2CCH_3$, proved to be unsuccessful by various simple means. However, many high molecular weight mercurials can be frozen out of the reaction mixture in high yield and high purity (Method A). Thus, reaction of two moles of dicyclohexylalkylborane with a mole of mercuric acetate in THF at room temperature for 2 h, followed by precipitation of the product at −78° represents an extremely simple procedure for the preparation of a wide variety of dialkylmercurials. For those mercury compounds which will not crystallize from THF at −78°, simple oxidation of the borane with NaOH and H_2O_2 followed by distillation of the resulting cyclohexanol from the mercurial gives good yields of mercury compounds (Method B). Table 3 gives the results of the preparation of organomercurials via dicyclohexylalkylboranes.

Dialkylmercurials via symmetrization of RHgOAc

In the past, many diorganomercurials have been prepared from various organomercuric salts via the so-called symmetrization reaction[15] [eqn. (7)].

$$2\,RHgX \rightarrow R_2Hg + HgX_2 \tag{7}$$

A wide variety of reagents have been used for this transformation. With the ready availability of alkylmercuric acetates[1], we investigated the symmetrization of n-

TABLE 3

PREPARATION OF R_2Hg FROM $(C_6H_{11})_2BR$

Olefin hydroborated	*(mmole)*	*Hg(OAc)$_2$ (mmole)*	*Yield R$_2$Hg^a (%)*	*Method*
1-Dodecene	(200)	100	86	A
Methyl 10-undecenoate	(100)	50	89	A
5-Bromo-1-pentene	(100)	50	94^b	A
2-Vinylnaphthalene	(100)	50	71	A
3,3-Dimethyl-1-butene	(100)	50	41^c	B
2-Methyl-1-pentene	(100)	50	73	B

^{a} Isolated yields. ^{b} Isolated as Br–$(CH_2)_5$–HgBr since the dialkyl compound melted below room temperature. ^{c} Low yield due to the slow reaction of the hindered borane even after 6 h reaction time.

BuHgOAc directly to di-n-butylmercury. Since alkylmercuric bromides had been successfully converted to dialkylmercurials in high yield by metallic magnesium[16], various metals (including Zn, Mg, Li, Na, Al, Cu and Fe) were tried in the attempted symmetrization of n-butylmercuric acetate. While Li, Mg, Al and Zn were successful with n-BuHgCl, very poor yields were obtained in all cases with the acetate, even in refluxing THF. Various other symmetrization agents were then tried on n-BuHgOAc (*e.g.*, NaI, NaCN, LiI, $Na_2S_2O_3$, Bu_3P, $H_2NNH_2 \cdot H_2O$), again without success.

Satisfied that the direct symmetrization of RHgOAc was not feasible, the conversion of RHgOAc to RHgX (X = halogen) was then investigated. It was hoped that treatment of the resulting RHgX with metallic Mg would give rise to R_2Hg in high yields without isolation of the intermediate mercury compounds [eqn. (8)].

$$R_3B + 3\ Hg(OAc)_2 \rightarrow 3\ RHgOAc \rightarrow 3\ RHgX \rightarrow 1.5\ R_2Hg \tag{8}$$

In THF at room temperature, NaCl, NaBr, LiCl and Me_4NBr were found completely ineffective in the acetate to halide conversion. While excess NaI, LiBr, and LiI gave quantitative yields of RHgX, very viscous solutions resulted which were difficult to handle. $MgCl_2$ also gave quantitative yields but required 8 h at room temperature. However, 0.5 mole $ZnCl_2$ gave 100% n-BuHgCl from n-BuHgOAc within 5 min at room temperature.

With n-BuHgCl in hand, only the final symmetrization remained to be tried. However, when one mole of n-Bu_3B was treated with 3 moles mercuric acetate followed by 1.5 moles $ZnCl_2$ and the resulting solution was treated with Mg, a disappointing 32% yield of n-Bu_2Hg was obtained after 2 h at room temperature [eqns. (9), (10), (11)].

$$\text{n-}Bu_3B + 3\ Hg(OAc)_2 \rightarrow 3\ \text{n-}BuHgOAc + B(OAc)_3 \tag{9}$$

$$2\ \text{n-}BuHgOAc + ZnCl_2 \rightarrow 2\ \text{n-}BuHgCl + Zn(OAc)_2 \tag{10}$$

$$2\ \text{n-}BuHgCl + Mg \rightarrow \text{n-}Bu_2Hg + Hg + MgCl_2 \tag{11}$$

Surprisingly, the yield of n-Bu_2Hg increased as the amount of $ZnCl_2$ used was decreased. With no $ZnCl_2$ present, 85% n-Bu_2Hg was obtained after 5 h, while with Zn dust in place of Mg, a 90% yield was obtained in 30 min. When pure n-BuHgOAc was treated with these metals in earlier symmetrization attempts, a 50% and 52% yield of n-Bu_2Hg was obtained with Mg and Zn respectively. The increased reactivity of the n-BuHgOAc in the reaction mixture must then be due to the presumed $B(OAc)_3$ present [eqn. (9)].

To test this hypothesis, another Lewis acid, $BF_3 \cdot OEt_2$, was examined. It proved to be an effective catalyst also. Thus, when n-BuHgOAc (0.83 *M*) was treated with Zn in THF at room temperature, a 52% yield of n-Bu_2Hg was obtained in 1 h. However, when 25 mole % of $BF_3 \cdot OEt_2$ was added, a 92% yield was obtained under the same conditions. Thus, conveniently, the by-product of the mercuri-deboronation reaction [$B(OAc)_3$] serves as the catalyst for the Zn symmetrization reaction. In conclusion, reaction of R_3B with 3 moles of $Hg(OAc)_2$ followed by treatment with Zn dust gives rise to 90% yields of R_2Hg. Filtration of the reaction mixture to remove excess Zn and Hg followed by washing with 3 *N* NaOH [to remove $Zn(OAc)_2$ and $B(OAc)_3$] and drying gives rise to solutions of pure R_2Hg. Table 4 shows the results of preparations of dialkylmercury compounds by this procedure.

TABLE 4

PREPARATION OF R_2Hg VIA SYMMETRIZATION OF RHgOAc

Olefin hydroborated	*(mmole)*	*$Hg(OAc)_2$ (mmole)*	*Yield R_2Hg*[a] *(%)*
1-Butene[b]	(192)[c]	180	88
Isobutylene	(180)	180	90
1-Dodecene	(90)	90	70[c]
1,1-Diphenylethylene	(90)	90	65

[a] Isolated yields. [b] Distilled commercial n-Bu_3B from Callery Chemical Co. was used. [c] 6–7% unreacted secondary groups on boron assumed.

TABLE 5

PROPERTIES OF DIALKYLMERCURIALS

R_2Hg	*B.p. (°C/mmHg)*	*M.p. (°C) (lit. value)*	*n_D^{20} (lit. value)*	*Derivative, m.p. (°C) (lit. value)*
Di-n-butylmercury	64/1.2		1.5072 (1.5081)[7]	BuHgCl, 126–127 (125)[8] (129)[7]
Di-isobutylmercury	64/5.0		1.4948 (1.4966)[7]	BuHgI, 71–73 (72)[9]
Di-n-dodecylmercury		44.5–45 (44.0–44.5)[10]		n-$C_{12}H_{25}HgCl$, 115–115.5 (114–114.5)[10]
Bis(3,3-dimethylbutyl)-mercury	70–72/0.05		1.4955	$C_6H_{13}HgCl$, 134–134.5 (133–133.5)[11]
Bis(2-methylpentyl)-mercury	78–80/0.15		1.4975 (1.4907)[12]	
Di-*cis*-myrtanylmercury		43.5–45		*cis*-Myrtanyl bromide[a]
Bis(2,2-diphenylethyl)-mercury		99.2–100		2,2-Diphenylethyl bromide, 54.5–55 (63)[13]
Bis[10-(methoxycarbonyl)-decyl]mercury		52.9–53.5		$C_{12}H_{23}O_2HgCl$, 97–97.5 (97.5–98)[1]
Bis[(2-naphthyl)ethyl]-mercury		137.5–137.8		$C_{12}H_{11}HgCl$, 194–195
Bis(5-bromopentyl)-mercury				$Br(CH_2)_5HgBr$, 86.1–86.6 (84)[14]

[a] Shown to be identical to an authentic sample by IR spectroscopy.

CONCLUSIONS

As these results show, trialkylboranes derived from terminal olefins function as efficient alkylating agents in the preparation of dialkylmercurials from mercuric acetate under very mild conditions. Not only does this make a wide range of dialkylmercurials very readily available, but also a large number of functional groups can be tolerated in the hydroboration, mercuri-deboronation and symmetrization reactions (particularly when dicyclohexylborane is used as the hydroborating agent).

TABLE 6

ANALYSES OF DIALKYLMERCURIALS

R_2Hg	*Analysis found (calcd.) (%)*		
	C	*H*	*Hg*
Di-n-butylmercury	30.81 (30.52)	5.83 (5.76)	63.52 (63.72)
Di-iso-butylmercury	30.70 (30.52)	5.82 (5.76)	63.47 (63.72)
Bi(3,3-dimethylbutyl)mercury	38.77 (38.86)	7.21 (7.07)	54.21 (54.08)
Bis(2-methylpentyl)mercury	38.85 (38.86)	7.07 (7.07)	54.12 (54.08)
Di-*cis*-myrtanylmercury	50.49 (50.56)	7.13 (7.21)	42.13 (42.22)
Bis(2,2-diphenylethyl)mercury	59.42 (59.72)	4.70 (4.65)	35.88 (35.62)
Bis[10-(methoxycarbonyl)decyl]-mercury	48.33 (48.11)	8.01 (7.74)	33.42 (33.47)
Bis[2-(2-naphthyl)ethyl]mercury	56.26 (56.41)	4.52 (4.34)	39.12 (39.24)
5-Bromopentylmercuric bromide	14.19 (13.95)	2.49 (2.34)	46.74 (46.59)

Mercurials containing these functional groups could not possibly be prepared directly by the usual Grignard procedures [eqn. (12)].

$$2\,RMgX + HgX_2 \rightarrow R_2Hg + 2\,MgX_2 \qquad (12)$$

Thus, terminal olefins can be converted directly into dialkylmercurials in a one-pot synthesis without isolation of any intermediates.

EXPERIMENTAL

Materials

All glassware was dried in an oven, assembled hot, and cooled by flushing with dry nitrogen. THF was dried over lithium aluminum hydride before distillation and storage under nitrogen. Standard borane–THF was prepared by the procedure of Brown and Sharp[19] and stored without hydride loss at 0°. Olefins used in hydroboration were used directly as obtained commercially, and in most cases were $\geqslant 99\%$ pure. Organoboranes were prepared using standard hydroboration procedures[6]. All melting points are uncorrected.

Mercuric acetate was a reagent grade commercial product (Mallinckrodt and Baker) and was stored in a desiccator after opening. Mercuric nitrate was also obtained commercially (Mallinckrodt). Mercuric trifluoroacetate was prepared by literature procedures[17,20], m.p. 166–167.5 (lit.[17] m.p. 167–169°). Mercuric methanesulfonate was prepared by dissolving HgO in methanesulfonic acid and distilling off the water and excess acid, m.p. 265–270°.

n-Butylmercuric acetate was prepared by two means. First, equimolar amounts of n-Bu_2Hg and $Hg(OAc)_2$ were stirred together at room temperature, after which the THF was distilled off. The resulting white solid was recrystallized from pentane at −10°, m.p. 57.8–58.3° (lit.[18] m.p. 54–56°). Alternatively, n-Bu_3B was reacted with 3 moles of $Hg(OAc)_2$ in THF at room temperature, the reaction mixture washed with nearly saturated aqueous NaOAc, dried with anhydrous $MgSO_4$, and the THF distilled off.

All other reagents were obtained commercially.

Analyses

n-Bu_2Hg analyses were performed by removing aliquots from the reaction mixtures, subjecting them to reduction with excess 1 *M* $NaBH_4$ in 3 *M* aqueous NaOH, saturating the aqueous layer with NaCl, and analyzing by GLC, the resulting organic layer. It was determined separately that $Hg(OAc)_2$ and n-BuHgOAc are reduced quantitatively to Hg^0 with no formation of n-Bu_2Hg under these conditions, while n-Bu_2Hg was unaffected. GLC analyses were performed on a $4\frac{1}{2}' \times \frac{1}{4}''$ stainless steel column packed with 5% Dow Corning Silicon 200 (or D.C. Silicone 550) on Chromosorb W. Analyses were performed at 105° with dodecane as internal standard.

Preparation of R_2Hg from R_3B

The trialkylboranes were prepared as usual in THF (20–50% excess R_3B normally used). To the solution was added in small portions at 0° the dry mercuric acetate (via a large diameter rubber tube). If 50% excess borane was used, the mixture was stirred 30 min at room temperature, otherwise, 4 h of refluxing was required. The reaction mixture was then washed twice with 6 *N* NaOH and twice with aqueous K_2CO_3. Drying with anhydrous $MgSO_4$ gave a THF solution of R_2Hg which could be reacted further or isolated by distillation of the THF followed by vacuum distillation of the liquid mercurials or recrystallization of the solid products from pentane at −20° (see Table 2).

Preparation of R_2Hg from dicyclohexylalkylboranes

The stoichiometric amount of $Hg(OAc)_2$ was added to the dicyclohexylalkylborane as above and stirred for 2 h. The reaction mixture was then cooled to −78°. If a precipitate formed (Method A), it was collected by filtration, the filtrate reduced in volume by distillation, and a second crop of crystals obtained by recooling. The resulting white solids were recrystallized from pentane at −20°. If no precipitate formed upon cooling (Method B), 3 *N* NaOH was added (2 moles NaOH per mole boron) followed by the dropwise addition of 30% H_2O_2 (2 moles H_2O_2 per mole boron plus 20% excess). The oxidation was performed in a water bath to control heat evolution. After saturating the aqueous layer with K_2CO_3 the organic layer was separated, dried with anhydrous $MgSO_4$, and the R_2Hg isolated from the cyclohexanol by fractional distillation. (see Table 3).

Attempted symmetrization of n-BuHgOAc by metals

3.16 g (10.0 mmoles) n-BuHgOAc dissolved in 15 ml THF and either 5.0 or 10.0 mmoles of the appropriate metal were stirred together at room temperature (or at reflux). Aliquots were removed periodically for n-Bu_2Hg analysis. Technical grades of Li wire, Na Lumps, 8 mesh Al, Ca turnings, Fe filings and Zn dust were used along with reagent 40 mesh Mg and Cu purified powder.

Attempted symmetrization of n-BuHgOAc by other symmetrization agents

3.16 g (10.0 mmoles) n-BuHgOAc in 10 ml THF was stirred with various reagents (10.0 or 20.0 moles) at room temperature. Samples were removed for n-Bu_2Hg analysis periodically. Reagents used were NaI, LiI, NaCN, NaSCN, $Na_2S \cdot 9\,H_2O$, di-n-propylsulfide, thiourea, thioacetamide, $Na_2S_2O_3$, EDTA (disodium salt), Ph_3P, Bu_3P, ethylenediamine, hydrazine hydrate, and Dow PEI-6 (polyethyleneimine).

Conversion of n-BuHgOAc to n-BuHgX

To 1.58 g (5.0 mmole) n-BuHgOAc in 7 ml THF was added 5.0 mmoles of the halide and stirred at room temperature. Small aliquots were analyzed by IR spectroscopy (Perkin–Elmer Model 700 Spectrometer) in 0.05 mm NaCl cells. The spectra obtained were compared with known mixtures of n-BuHgOAc and n-BuHgX.

Preparation of R_2Hg from RHgOAc

To the appropriate trialkylborane prepared in the usual manner[6] was added 3 moles $Hg(OAc)_2$ at 0°. After stirring 30 min at room temperature 3 moles of Zn dust (tech.) was added and the suspension stirred 2–3 h at room temperature. After filtration of the reaction mixture followed by washing with 6 *N* NaOH and drying with anhydrous $MgSO_4$ the mercurial was isolated by distillation or crystallization from THF at −78°. (see Table 4).

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