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THE REACTION OF VINYLBORONIC ACIDS WITH VINYLMERCURIC ACETATES; A NEW SYNTHESIS OF DIVINYLMERCURIALS *

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Summary

The reaction of vinylboronic acids with vinylmercuric acetates produces symmetrical divinylmercurials in high yield. The reaction can be utilized to prepare functionally substituted mercurials. Attempts to prepare unsymmetrical divinylmercurials resulted in redistribution products yielding symmetrical and unsymmetrical divinylmercury compounds.

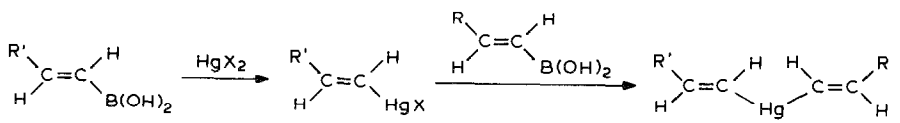
Organomercurials [1–3] are useful synthetic intermediates due to their ability to accommodate a variety of functional groups and the ease with which they undergo transmetallation reactions. We have been investigating the potential utility of divinylmercurials as intermediates in radiopharmaceutical syntheses [4]. Divinylmercury compounds have been prepared via symmetrization (eq. 1) and reductive disproportionation (eq. 2) of the corresponding vinylmercuric salts [1]. They have also been prepared by transmetallation reactions (eq. 3) [1].

$$2RHgX \rightarrow R_2Hg + HgX_2 \quad (1)$$

$$2RHgX + 2e^- \rightarrow R_2Hg + Hg^0 + 2X^- \quad (2)$$

$$2RM + HgX_2 \rightarrow R_2Hg + MX_2 \quad (3)$$

Since the available syntheses are limited to the preparation of symmetrical molecules, we decided to investigate the syntheses of unsymmetrical divinylmercurials via transmetallation reactions involving the reaction of organoborane reagents with vinylmercuric halides (eq. 4)



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Results and discussion

Since organoboranes are known to react with mercury salts to generate a mixture of the corresponding mono- and di-organylmercurials (eq. 5) [5], we felt that the

$$R_3B + 1.5\ HgX_2 \rightarrow RBX_2 + RHgX + 0.5\ R_2Hg \quad (5)$$

addition of a vinylboronic acid to a vinylmercuric salt offered the most reasonable opportunity for synthesizing unsymmetrical divinylmercurials.

We first investigated the reaction of a series of (*E*)-1-decenylmercuric salts with (*E*)-1-decenylboronic acid (eq. 6). We found that the reaction occurred only when

(6)

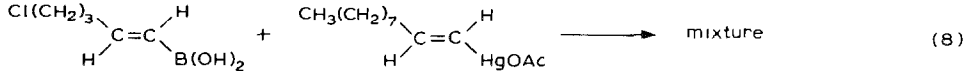
(X = Cl, Br, OAc)

the anion was acetate [6]. The corresponding mercuric bromides and chlorides were unreactive. The reaction is readily monitored by ^{13}C NMR because the vinylic carbons in the product (δ 158.3 and 150.3 ppm) are readily differentiated from the vinylic carbons in the vinylmercuric acetate (δ 151.4 and 125.8 ppm) and the vinylboronic acid (δ 151.6 ppm). Interestingly, no evidence for the formation of *Z*-alkenyl isomers could be ascertained (^{13}C NMR and ^{1}H NMR) for either the vinylmercuric acetates or the divinylmercurials even though such isomerizations had been noted in earlier structures [5d]. Although, the equilibration of dialkyl and diarylmercury reagents is well known (eq. 7) [7], we felt that the mild reaction

$$R_2Hg + R'_2Hg \rightleftarrows 2\ R\text{-}Hg\text{-}R' \quad (7)$$

conditions (room temperature or lower, various solvents) would permit us to synthesize unsymmetrical divinylmercurial derivatives. The data from our initial experiments were encouraging. We prepared (*E*)-1-decenylmercuric acetate and then added methyl (*E*)-10-carbomethoxy-1-decenylboronic acid to it under a variety of conditions (solvents and temperature were varied). The ^{13}C NMR of the resultant reaction mixtures exhibited two resonances in the vinyl region as expected (δ 158.3 and 150.2 ppm). These resonances were different from those observed in the ^{13}C NMR of the starting vinylmercuric acetate (δ 151.4 and 125.8 ppm) and vinylboronic acid (δ 151.6 ppm) but, unfortunately, were identical to those of authentic samples of the corresponding di[(*E*)-1-decenyl]mercury and bis[(*E*)-10-carbomethoxy-1-decenyl]mercury. Consequently, the NMR data were inconclusive.

We then decided to treat (*E*)-5-chloro-1-pentenylboronic acid with (*E*)-1-decenylmercuric acetate (eq. 8). The ^{13}C NMR of the vinyl region contained eight lines! Four of the resonances corresponded, exactly, to the vinyl carbons of di[(*E*)-



(8)

1-decenyl]mercury (δ 158.3 and 150.2 ppm) and bis[(*E*)-5-chloro-1-pentenyl]mercury (δ 159.7 and 147.8 ppm). The other four resonances presumably correspond to the four vinyl carbons in the desired unsymmetrical divinylmercury compound (δ 160.4, 157.5, 150.5 and 147.6 ppm). The vinyl regions of the pertinent ^{13}C NMR are

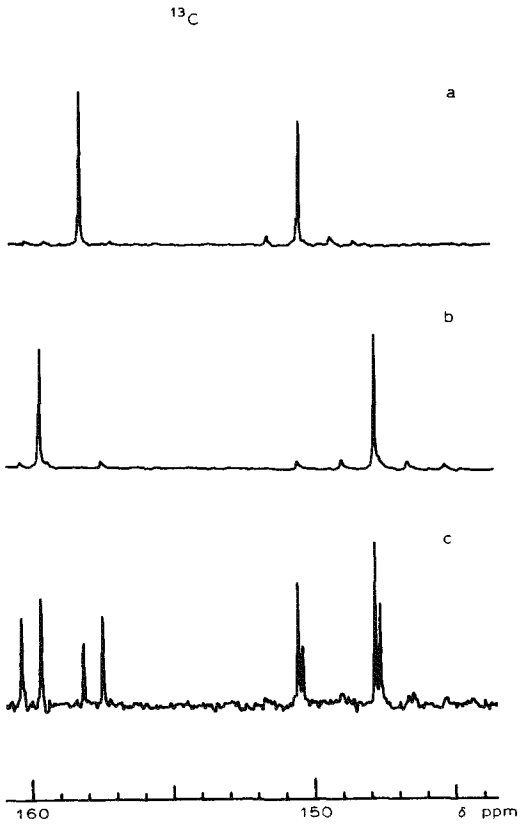
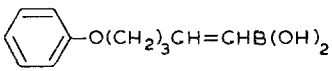
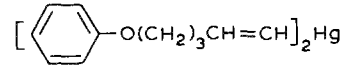


Fig. 1. Carbon-13 NMR spectra of the vinyl region of related divinylmercury compounds: (a) di[(*E*)-1-decenyl]mercury (δ 158.3 and 150.2 ppm); (b) bis[(*E*)-5-chloro-1-phentenyl]mercury (δ 159.7 and 147.8 ppm); (c) reaction products obtained via addition of (*E*)-5-chloro-1-pentenylboronic acid to (*E*)-1-decenylmercuric acetate (δ 160.4, 159.7, 158.3, 157.5, 150.5, 150.2, 147.8, and 147.6 ppm) which corresponds to the unsymmetrical divinylmercury reagent and the two symmetrical, divinylmercury equilibration products.

TABLE 1

PREPARATION OF DIVINYLMERCURY COMPOUNDS

Boronic acid	Product [a,b]	Yield (%)
$H_3C(CH_2)_7CH{=}CHB(OH)_2$	$[H_3C(CH_2)_7CH{=}CH]_2Hg$	96
$Cl(CH_2)_3CH{=}CHB(OH)_2$	$[Cl(CH_2)_3CH{=}CH]_2Hg$	83
$I(CH_2)_3CH{=}CHB(OH)_2$	$[I(CH_2)_3CH{=}CH]_2Hg$	76
$H_3COOC(CH_2)_8CH{=}CHB(OH)_2$	$[H_3COOC(CH_2)_8CH{=}CH]_2Hg$	88
		92

[a] All products exhibited physical and spectral properties in accord with authentic samples [3]. [b] When the intermediate vinylmercuric acetate was isolated and treated with boronic acid, essentially quantitative yields of divinylmercurials were obtained.

summarized in Fig. 1. The shift in NMR resonance frequencies of the vinyl carbons in the unsymmetrical product is presumably due to the magnetic effects of the chlorine atom in proximity to the vinyl group. Our postulation that an equilibration was occurring was further supported by our observation that an equimolar mixture of di[(*E*)-1-decenyl]mercury and bis[(*E*)-5-chloro-1-pentenyl]mercury produced the same eight vinylic resonances in the ^{13}C NMR.

In spite of the fact that the unsymmetrical divinylmercurials cannot be isolated in a pure state, the reaction provides a new convenient route for the synthesis of isomerically pure, symmetrical divinylmercurials under very mild conditions. The reactions may be carried out in one-pot and good yields of a number of functionally substituted divinylmercurials have been obtained. Our results are summarized in Table 1.

Experimental

Commercially available samples of 1-decyne (Farchan), 10-undecynoic acid (Farchan), 5-chloro-1-pentyne (Farchan) were purified by distillation prior to use. Methyl 10-undecynoate and 5-iodo-1-pentyne were prepared according to published procedures [8,9]. 5-Phenoxy-1-pentyne, was prepared via the reaction of 5-chloro-1-pentyne with potassium phenoxide [10,11]. Routine NMR spectra were run on a JEOL FX-90Q spectrometer and referenced to $(CH_3)_4Si$.

General procedure for preparation of the (E)-vinylboronic acids [9]

The appropriate alkyne (10 mmol) was hydroborated with catecholborane (10 mmol) at 70 °C for 6 h. The product boronic ester was then hydrolyzed overnight with a large excess of water. The solid boronic acid was filtered and recrystallized from an acetone/petroleum ether mixture. All of the purified boronic acids exhibited spectral characteristics in accord with literature values [8,9].

General procedure for the preparation of vinylmercuric acetates

The vinylboronic acid (2 mmol) was dissolved in THF (4 ml) at room temperature. Mercury(II) acetate (0.64 g, 2 mmol) was gradually added to the above solution in small portions and then the solution was stirred for 30 min. The clear solution was then added to cooled aqueous sodium fluoride (20 ml of 0.1 *M* solution), a white solid precipitated [6]. The mixture was stirred for 30 min and then filtered. The precipitate was dissolved in chloroform, dried ($MgSO_4$), and the solvent removed to yield the vinylmercury acetates which exhibited physical and spectral characteristics in accord with literature values [6].

Attempted preparation of unsymmetrical divinylmercurials

(*E*)-5-Chloro-1-pentenylboronic acid (0.3 g, 2 mmol) was added to a solution of (*E*)-1-decenylmercuric acetate (0.8 g, 2 mmol) in THF (4 ml) at room temperature. The solution was stirred for 30 min and then analyzed by ^{13}C NMR ($CDCl_3$) δ 160.4, 159.7, 158.3, 157.5, 150.5, 150.3, 147.8 and 147.6 ppm (vinylic carbons).

General procedure for preparation of the divinylmercurials (one-pot method)

The appropriate vinylboronic acid (2 mmol) was dissolved in THF (4 ml). Mercury(II) acetate (2 mmol) was then added in small portions to the stirred

solutions of the boronic acid at room temperature. The clear solution was stirred for 15 min to form the vinylmercuric acetate.

A second equivalent of vinylboronic acid (2 mmol) was then added, the reaction mixture stirred for 1 h, and transferred to a separatory funnel. The mixture was extracted with diethyl ether (3 × 50 ml). The combined organic layers were washed with water, dried ($MgSO_4$), and the solvent removed under reduced pressure to yield the corresponding divinylmercurials. The products exhibited physical and spectral characteristics in accord with authentic samples [3].

Alternatively, the vinylmercuric acetates could be isolated by filtration and then treated with the vinylboronic acid. The yields of divinylmercury compounds are essentially quantitative utilizing the two step procedure.

Anknowledgement

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