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SYNTHESES OF FUNCTIONALLY SUBSTITUTED DIVINYLMERCURY COMPOUNDS

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Summary

Reductive disproportionation of vinylmercuric chlorides by alkaline sodium stannite produces divinylmercurials in high yields. The reaction conditions are optimized to obtain functionally substituted divinylmercurials in pure form, free from undesirable side products.

Organomercurials [1,2] have received renewed attention in recent years due to their ability to accommodate a variety of functional groups and the ease with which they undergo transmetallation reactions. As part of our program of incorporating radioisotopes into physiologically active compounds [3,4], we decided to investigate the potential use of organomercury reagents in radiopharmaceutical research. We were particularly interested in the syntheses of functionally substituted divinylmercury compounds due to their possible utility in the preparation of radiolabeled vinyl halides [4].

Diorganomercurials are generally prepared by symmetrization (eq. 1) or reductive disproportionation (eq. 2) of the corresponding organomercuric salts [5]. They may also be prepared via transmetallation reactions utilizing organic derivatives of

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

$$2RHgX + 2M \rightleftharpoons R_2Hg + 2MX + Hg^0 \quad (2)$$

lithium, magnesium, aluminum, and other metals [5]. The scope of these transmetallation reactions is often limited by the availability and stability of the necessary organometallic starting material. We chose to synthesize the desired divinylmercurials via the reductive disproportionation of the corresponding vinylmercuric chlorides because the desired mercuric chlorides could be readily obtained from functionally substituted borane reagents (eq. 3) [6]. Interestingly, only a few simple divinylmercurials have been reported. They were prepared via transmetallation reactions

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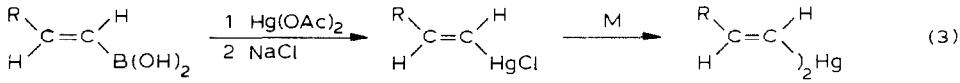
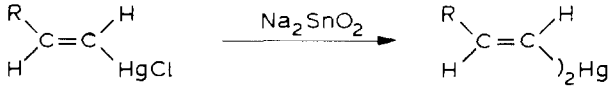


(3)

involving boron [7], lithium [8], magnesium [9]; and copper [10] reagents or via reaction of vinylmercuric salts with ammonia [11], sodium stannite [12], sodium iodide [13], and triphenylphosphine [14]. The sodium stannite method appeared to be the method of choice (eq. 4).

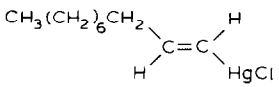
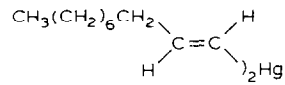
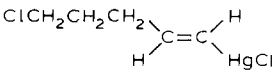
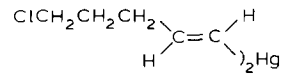
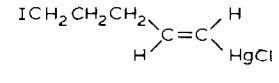
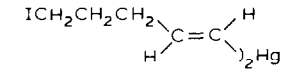
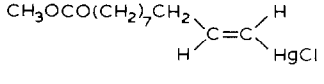
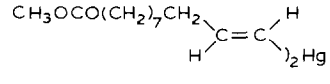
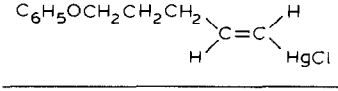
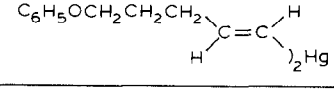


(4)

In our hands, the reductive disproportionation of vinylmercuric chlorides by sodium stannite generally produced good yields (> 90%) of the desired products but significant quantities of undesirable side products were formed and isolation of the desired products was difficult. After carrying out a solvent/temperature study, the origin of the side products was traced to the use of acetone as the reaction solvent. The side products were, in fact, condensation products of acetone. The use of tetrahydrofuran as reaction solvent leads to essentially quantitative yields of the desired products and obviates the formation of undesirable side products. Our results are summarized in Table 1.

TABLE 1

PREPARATION OF DIVINYLMERCURY COMPOUNDS

Starting material[a]	Product	Yield (%)[b]
		94
		97
		93
		96
		95

[a] Prepared from the corresponding vinylboronic acid. [b] Isolated yield

Experimental

Melting points and boiling points are uncorrected. Routine NMR spectra were run on a JEOL FX-90Q spectrometer and referenced to $(H_3C)_4Si$. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

Commercially available samples of 1-decyne (Farchan), 10-undecynoic acid (Farchan), 5-chloro-1-pentyne (Farchan) were purified prior to use. Methyl 10-undecynoate and 5-iodo-1-pentyne were prepared according to published procedures [4e,15]. 5-Phenoxy-1-pentyne, was prepared via the reaction of 5-chloro-1-pentyne with potassium phenoxide [16,17].

General procedure for preparation of the (E)-vinylboronic acids. The appropriate alkyne (50 mmol) was hydroborated with catecholborane (50 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 [4e,15].

General procedure for preparation of the (E)-vinylmercuric chlorides. The appropriate vinyl boronic acid (20 mmol) was dissolved in 40 ml of THF in an Erlenmeyer flask. Mercury(II) acetate (20 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 and then added to a well-stirred aqueous sodium chloride solution (0.4 *M*, 50 ml); a white precipitate formed immediately. The mixture was stirred for 30 min, filtered and the solid product washed with water (50 ml). The product was then dissolved in chloroform, dried ($MgSO_4$) and concentrated to yield the product vinylmercuric chloride which was recrystallized from diethyl ether. All of the mercuric chlorides were characterized by ^{13}C NMR and ^1H NMR.

General procedures for preparation of the divinylmercurials. Alkaline sodium stannite (prepared from NaOH (1 g, 25 mmol) in 10 ml water and hydrated stannous chloride, (0.56 g, 2.5 mmol) in 15 ml water) was added to a well stirred solution of the appropriate vinylmercuric chloride (4 mmol) dissolved in THF (30 ml) at room temperature (formation of two layers was observed). The reaction mixture was stirred at 0 °C for 2 h and then kept at 10 °C overnight.

The reaction mixture (containing two layers) was then transferred to a separatory funnel and the mixture 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 analytical samples were obtained by column chromatography on silica gel using petroleum ether/ether (90/10) as eluent and recrystallized from diethyl ether. The samples were characterized by NMR and elemental analyses.

Preparation of (E)-di-1-decenylmercury. (*E*)-1-Decenylboronic acid (3.68 g; 20 mmol) was treated with mercury(II) acetate and then with sodium chloride as described in the general procedure to yield (*E*)-1-decenylmercuric chloride, 7.3 g (97%); m.p. 104–105 °C (lit. [6d] 102.5–103 °C); ^1H NMR ($CDCl_3$)δ 0.88 (t, 3H, CH_3), 1.28 (bs, 12H, alkane), 2.19 (m, 2H, CH_2–CH=), 5.7–6.0 ppm (m, 2H, CH=CH). ^{13}C NMR ($CDCl_3$)δ 151.35 (CH=CHHg), 132.6 ppm (CH=CHHg).

The reduction of (*E*)-1-decenylmercuric chloride (1.87 g, 5 mmol) was carried out as described in the general procedure to yield (*E*)-di-1-decenylmercury, 1.12 g (94%) as a colorless oil; ^1H NMR ($CDCl_3$)δ 0.88 (t, 6H, CH_3), 1.28 (bs, 14H, alkane);

1.9–2.2 (m, 4H, CH_2–CH=), 5.6–6.3 ppm (m, 4H, CH=CH); ^{13}C NMR ($CDCl_3$)δ 158.3 (CH=CHHg), 150.4 ppm (CH=CHHg); Anal. Found: C, 50.04; H, 7.75; Hg, 41.83. $C_{20}H_{38}Hg$ calcd.: C, 50.15; H, 7.94; Hg, 41.91%.

Preparation of di-1-[(E)-5-chloro-1-pentenyl]mercury. (*E*)-5-Chloro-1-pentenylboronic acid (2.97 g, 20 mmol) was treated with mercury(II) acetate and then with sodium chloride as described in the general procedure to yield (*E*)-5-chloro-1-pentenylmercuric chloride 5.67 g, (84%); m.p. 94°C (lit [6c] 94.5–95.6°C); ^1H NMR ($CDCl_3$) δ 1.89 (m, 2H, $CH_2CH_2CH_2$), 2.38 (m, 2H, CH_2–CH=), 3.56 (t, 2H, CH_2Cl), 5.89 ppm (bs, 2H, CH=CH); ^{13}C NMR ($CDCl_3$)δ 148.58 (CH=CHHg), 134.66 ppm (CH=CHHg).

The reduction of (*E*)-5-chloro-1-pentenylmercuric chloride (1.35 g, 4 mmol) was carried out as described in the general procedure to yield di-1-[(*E*)-5-chloro-1-pentenyl]mercury, 0.79 g (97%) as a colorless oil; ^1H NMR ($CDCl_3$)δ 1.86 (m, 4H, $CH_2CH_2CH_2$); 2.27 (m, 4H, CH_2–CH=), 3.54 (t, 4H, CH_2Cl), 5.5–6.4 ppm (m, 4H, CH=CH); ^{13}C NMR ($CDCl_3$)δ 159.7 (CH=CHHg), 147.8 ppm (CH=CH–Hg); Anal. Found: C, 29.75; H, 4.19; Hg, 48.53. $C_{10}H_{16}Cl_2Hg$ calcd.: C, 29.46; H, 3.96; Hg, 49.19%.

Preparation of di-1-[(E)-5-iodo-1-pentenyl]mercury. (*E*)-5-Iodo-1-pentenylboronic acid (2.4 g, 10 mmol) was treated with mercury(II) acetate and then with sodium chloride as described in the general procedure to yield (*E*)-5-iodo-1-pentenylmercuric chloride, 4.1 g (96%); m.p. 62–63°C; ^1H NMR ($CDCl_3$)δ 1.95 (m, 2H, $CH_2CH_2CH_2$), 2.29 (m, 2H, CH_2CH=), 3.24 (t, 2H, CH_2I), 5.93 ppm (bs, 2H, CH=CH); ^{13}C NMR ($CDCl_3$)δ 147.39 (CH=CHHg), 135.99 ppm (CH=CHHg).

The reaction of (*E*)-5-iodo-1-pentenylmercuric chloride (1.72 g, 4 mmol) was carried out as desribed in the general procedure to yield di-1-[(*E*)-5-iodo-1-pentenyl]mercury, 1.1 g (93%) as a colorless liquid; ^1H NMR ($CDCl_3$)δ 1.91 (m, 4H, $CH_2CH_2CH_2$) 2.22 (m, 4H, CH_2–CH=), 3.19 (t, 4H, CH_2I), 5.5–6.5 ppm (m, 4H, CH=CH); ^{13}C NMR ($CDCl_3$) δ 159.88 (CH=CHHg), 147.20 ppm (CH=CHHg). Anal. Found: C, 20.53; H, 2.88; Hg, 33.45. $C_{10}H_{16}I_2Hg$ calcd.: C, 20.32; H, 2.71; Hg, 33.98%.

Preparation of di-1-[(E)-10-carbomethoxy-1-decenyl]mercury. (*E*)-Methyl-10-undecenylboronic acid (4.84 g, 20 mmol) was treated with mercury(II) acetate and then with sodium chloride as described in the general procedure to yield (*E*)-methyl-10-undecenylmercuric chloride, 7.8 g (90%); m.p. 74–75°C; (lit. [6d] 54-?°C). ^1H NMR ($CDCl_3$) δ 1.29 (bs, 12H, alkane), 2.26 (m, 4H, CH_2COO and CH_2–CH=); 3.65 (s, 3H, CH_3O), 5.82 ppm (bs, 2H, CH=CH); ^{13}C NMR ($CDCl_3$) δ 150.94 (CH=CHHg), 132.82 ppm (CH=CHHg).

(E)-Methyl-10-undecenylmercuric chloride (1.73 g, 4 mmol) was reduced with alkaline sodium stannite to yield di-1-[(*E*)-10-carbomethoxy-1-decenyl]mercury, 1.14 g (96%), m.p. 50–51°C; ^1H NMR ($CDCl_3$) δ 1.29 (bs, 24H, alkane), 2.2 (m, 4H, CH_2COO and CH_2–CH=), 3.65 (s, 6H, OCH_3), 5.5–6.4 ppm (m, 4H, CHCH=CH); ^{13}C NMR ($CDCl_3$) δ 173.91 (C=O), 158.25 (CH=CHHg), 149.86 ppm (CH=CHHg); Anal. Found: C, 48.39; H, 7.2; Hg, 33.49. $C_{24}H_{42}O_4Hg$ calcd.: C, 48.43; H, 7.06; Hg, 33.74%.

Preparation of (E)-5-phenoxy-1-pentenylboronic acid. 5-Phenoxy-1-pentyne (8.0 g, 50 mmol) was hydroborated with catecholborane (5.46 ml, 50 mmol) at 70°C for 6 h to yield (*E*)-5-phenoxy-1-pentenylboronic acid 7.4 g (72%); m.p. 95–96°C; ^1H NMR ($CDCl_3$) δ 1.91 (m, 2H, $CH_2CH_2CH_2$), 2.28 (m, 2H, CH_2–CH=), 3.17 (s,

OH), 3.99 (t, 2H, CH_2O), 5.5 (d, 1H, CH=C*H*B(OH)$_2$, *J* 17.5 Hz), 6.9–8.0 ppm (complex m, 6H, ArH and C*H*=CHB).

Preparation of di-1-[(E)-5-phenoxy-1-pentenyl]mercury. (*E*)-5-Phenoxy-1-pentenylboronic acid (2.06 g, 10 mmol) was treated with mercury(II) acetate and then with sodium chloride as described in the general procedure to yield (*E*)-5-phenoxy-1-pentenylmercuric chloride, 3.7 g (95%); m.p. 144–145 °C; ^{1}H NMR ($CDCl_3$) δ 1.90 (m, 2H, $CH_2CH_2CH_2$), 2.38 (m, 2H, CH_2–CH=), 3.97 (t, 2H, CH_2O), 5.8–6.0 (m, 2H, C*H*=C*H*), 6.8–7.4 ppm (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 149.88 (CH=*C*HHg), 133.82 (*C*H=CHHg), 158.9, 129.54, 120.79, 114.53 (aryl carbons), 66.8 ppm (OCH_2).

(*E*)-5-Phenoxy-1-pentenylmercuric chloride (1.59 g, 4 mmol) was reduced with alkaline sodium stannite to yield di-1-[(*E*)-5-phenoxy-1-pentenyl]mercury, 0.99 g (95%); m.p. 59–60 °C; ^{1}H NMR ($CDCl_3$) δ 1.83 (m, 4H, $CH_2CH_2CH_2$), 2.26 (m, 4H, CH_2–CH=), 3.89 (t, 4H, CH_2O), 5.5–6.4 (m, 4H, C*H*=C*H*), 6.7–7.4 ppm (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 159.1 (CH=*C*HHg), 148.4 (*C*H=CHHg), 158.9, 129.3, 120.4, 114.3 (aryl carbons), 67.02 ppm (OCH_2). Anal. Found: C, 50.96; H, 5.08; Hg 37.96. $C_{22}H_{26}O_2Hg$ calcd.: C, 50.52; H, 4.97; Hg, 38.38%.

Acknowledgement

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