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The preparation of (*Z*)-2-lithio-*ortho*-styryllithium *via* an *ortho*-directed lithiation

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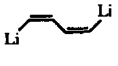
Abstract

Lithiation of (*Z*)-2-lithiostyrene with t-butyllithium/TMEDA pentane led directly to (*Z*)-2-lithio-*ortho*-styryllithium. Subsequent treatment of this dilithio compound with difunctional electrophiles allowed the preparation of a variety of benzo[*b*]heteroles.

1. Introduction

There is considerable current interest in 1,4-dilithio compounds since several derivatives adopt unusual structures involving double lithium bridging [1–7]. Calculations indicate that (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene (**1**) possesses a particularly favorable symmetrically bridged structure **2** [1,8–10]. It is also of interest that derivatives of **1** can serve as useful synthons for the preparation of five-membered ring heterocycles [11–13]. The recent report of the conversion of benzo[*b*]tellurophene (**3**) to (*Z*)-2-lithio-*ortho*-styryllithium (**4**) via tellurium-lithium exchange [14] prompts us to report on our independent preparation of **4** via an *ortho*-directed lithiation.



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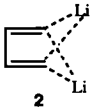

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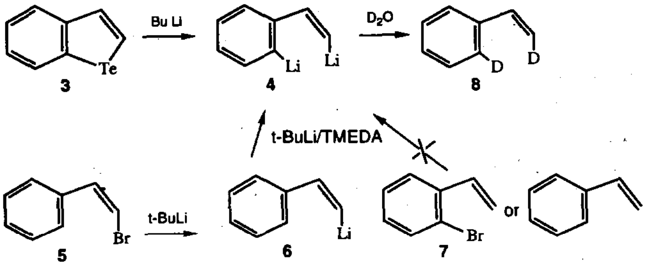
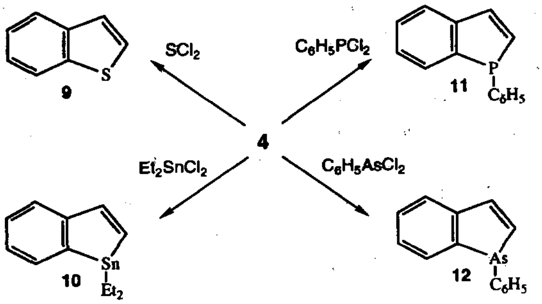


2. Results and discussion

Although several aromatic hydrocarbons can be dilithiated directly with butyllithium/TMEDA to give derivatives of **1** [15,16], application of this procedure to styrene gives only polystyrene. On the other hand, the readily available (*Z*)-2-bromostyrene (**5**) [17] may be lithiated with t-butyllithium to give **6**. Further lithiation of **6** with t-butyllithium/TMEDA is specifically directed to the *ortho* position affording **4**. However, the alternative dilithiation starting from *ortho*-bromostyrene (**7**) affords only intractable products. Quenching **4** with D_2O gives styrene-d_2 (**8**) exclusively. The ^1H NMR and ^{13}C NMR spectra of **4** show small solvent shifts but are otherwise identical to those reported for **4** prepared from **3** [14].



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Like other 1,4-dilithiocompounds, **4** is a useful precursor for the corresponding heteroles. For example, the reaction of **4** with SCl_2 in THF gave benzo[*b*]thiophene (**9**) in 50% yield. The reaction of **4** with diethyltin dichloride affords 54% of 1,1-diethylbenzo[*b*]stannole (**10**). Since similar stannoles undergo facile exchange reactions [11,18], this preparation offers an efficient method for the synthesis of other heterocycles.

Treating **4** with phenylphosphorus dichloride gives 52% of 1-phenylphosphindole (**11**). This procedure is considerably more convenient and efficient than the two literature preparations of **11** [19,20]. In a similar manner, the reaction of phenylarsenic dichloride with **4** gave 35% of 1-phenylarsindole (**12**). In conclusion, this procedure offers a simple, efficient method for the preparation of a variety of benzo[*b*]heteroles.

3. Experimental details

All reactions were carried out under an atmosphere of nitrogen. Solvents were dried using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained using either a Brucker WH-360 or AM-300 spectrometer. The ^1H NMR and ^{13}C NMR spectra were calibrated using signals from the solvents referenced to Me_4Si.

3.1. *(Z)-2-Lithio-ortho-lithiostyrene (4)*

A solution of 4 mmol of t-butyllithium in 7.5 ml of pentane at −100°C was added dropwise with vigorous stirring a solution of (*Z*)-2-bromostyrene (0.36 g, 2 mmol) in 5 ml of ether and 5 ml of pentane at −100°C. The resulting lemon-yellow suspension was stirred for 30 min at −100°C and then 2 mmol of t-butyllithium in 1.2 ml of pentane and 0.9 ml (6 mmol) TMEDA were added. The resulting mixture was allowed to warm to 25°C and then heated under reflux for 3 h, affording a purple-red suspension of **4**.

3.2. *D_2O quenching of the lithium compounds*

The solution of (*Z*)-2-lithiostyrene (**6**) prepared as above prior to the addition of the t-butyllithium/TMEDA was allowed to warm to −80°C. Then excess D_2O was added and the resulting mixture was allowed to warm to 25°C. The organic layer was separated, washed with water and dried over anhydrous $MgSO_4$. Removal of the solvent gave (*Z*)-2-deuterostyrene. MS: *m/z* (relative intensity): 105 (100, M^+ for (C_8H_7D). ^1H NMR ($CDCl_3$): δ 5.24 (d, $J = 11.1$ Hz, 1H, *Hβ*); 6.71 (dt, $^3J(HH) = 11.1$, $^3J(HD) = 2.7$ Hz, 1 H, *Hα*); 7.23–7.43 (m, 3H, *Hm, Hp*); 7.49 (dd, $J = 8.3$, 2.0 Hz, 2H, *Ho*).

Excess D_2O was added at −78°C to a suspension of **4** prepared as above. After warming to 25°C, the organic layer was separated, then washed with water and dried over anhydrous $MgSO_4$. Removal of solvent left **8** as a yellow oil. MS *m/z* (relative intensity): 106(100, M^+ for $C_8H_6D_2$). ^1H NMR ($CDCl_3$): δ 5.19 (d, $J =$ 10.9 Hz, 1H, *Hβ*); 6.68 (dt, $^3J(HH) = 11.0$, $^3J(HD) = 2.7$ Hz, 1H, *Hα*); 7.18–7.40 (m, 3H, *Hm, Hp*); 7.47 (m, 1H, *Ho*).

3.3. *Benzo[b]thiophene (9)*

A suspension of **4** prepared as above was cooled to −78°C and diluted by adding 15 ml of THF. A solution of SCl_2 (0.31 g, 3 mmol) in 10 ml of THF was then added dropwise with stirring. After warming to 25°C, the reaction mixture was stirred for 10 h at 25°C. An excess of water was added and the organic layer was separated and dried over anhydrous $MgSO_4$. Removal of solvent left 0.3 g of a brown oil, which was subject to flash chromatography (silica gel, hexane) to give 0.13 g (49%) of **9**, which was identical to an authentic sample.

3.4. *1,1-Diethyl-benzo[b]stannole (10)*

In the same manner as above, addition of diethyltin dichloride (0.74 g, 3 mmol) in 10 ml of THF to **4** afforded 0.45 g of brown oil on removal of the solvent. The crude product was purified by Kugelrohr distillation at 100°C (0.1 Torr) giving 0.32 g (54%) of **10** as a yellow oil. ^1H NMR ($CDCl_3$): δ 1.15–1.32 (m, 10H, *Et*); 6.74 (d, $J = 10.4$, $J(^{119}SnH) = 132.3$ Hz, 1H, H_2); 7.23 (dt, $J = 6.6$, 2.5 Hz, 1H); 7.27–7.31 (m, 2H); 7.56 (d, $J = 7.0$, 1H); 7.63 (d, $J = 10.4$, $J(^{119}SnH) = 137.7$ Hz, H_3). ^{13}C NMR (CCl_3): δ 3.4 ($J(^{119}SnC) = 363$ Hz), 11.3, 126.3, 127.1, 128.6($J^{119}SnC) = 385$ Hz); 132.3, 135.8, 139.1, 150.0, 150.2. MS: *m/z* (relative intensity) 280 (15, M^+ for $C_{12}H_{16}{}^{120}Sn$); 251 (100, $M^+ - C_2H_5$). MS exact mass (EI): Found: 280.0293. $C_{12}H_{16}{}^{120}Sn$ calc.: 280.0274.

3.5. *1-Phenylphosphindole (11)*

In the same manner as above, addition of phenylphosphorus dichloride (0.74 g, 3 mmol) in 10 ml of THF to **4** afforded 0.40 g of crude **11** as a brown oil. On standing, the oil crystallized to give 0.22 g (52%) of light yellow crystals, m.p. 63–64°C (lit. 65°C) [18,19]. The NMR and MS data were identical to those reported for **11**.

3.6. *1-Phenylarsindole (12)*

In the same manner as above, addition of phenylarsenic dichloride (0.67 g, 3 mmol) in 10 ml of THF to **4** gave 0.6 g of a brown oil on removal of the solvent. Pure **12** was obtained by Kugelrohr distillation at 150°C (0.005 Torr) giving 0.175 g (35%) of **12** as a yellow oil.

^1H NMR ($CDCl_3$): δ 7.16 (d, $J = 7.7$ Hz, 1H); 7.20–7.25 (m, 4H); 7.31 (m, 2H); 7.35 (dt, $J = 7.5$, 1.2 Hz, 1H); 7.49 (d, $J = 7.7$ Hz, 1H); 7.54 (d, $J = 7.2$ Hz, 1H); 7.65 (d, $J = 7.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 124.8, 126.5, 127.5, 128.2, 128.61, 128.63, 130.5, 132.7, 137.4, 139.0, 140.0, 147.2. MS: m/z (relative intensity) 254 (100, M^+ for $C_{14}H_{11}As$). MS exact mass (EI): Found: 254.0058. $C_{14}H_{11}As$ calc.: 254.0077.

Acknowledgements

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