Synthetic Applications of Organoboranes: A Simple Synthesis of Dihydrojasmone

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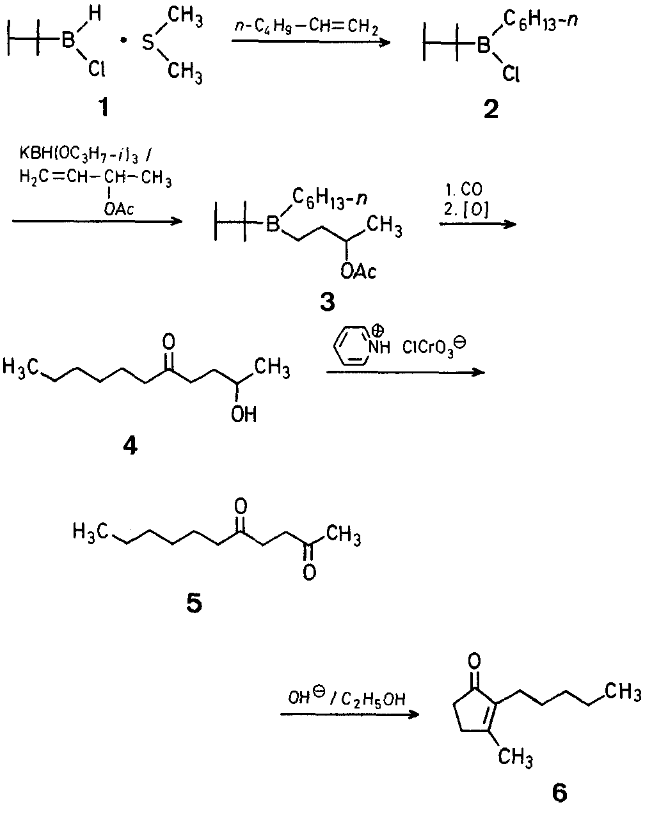
Dihydrojasmone (**6**) is an important perfume ingredient and is a constituent of bergamot oil. It has attracted attention from synthetic organic chemists[1,2] over the past two decades because of the interesting synthetic problem it offers as well as its commercial importance.

The importance of organoboranes, readily available by simple hydroboration, as versatile intermediates in organic synthesis is evident[3]. In addition, several new synthetic methodologies involving organoboranes as key intermediates have been published over the past decade, further enriching the synthetic scope of organoboranes[4].

In a continuation of our interest in the synthesis of pheromones[5-9] and other important natural products[10] via organoboranes, we report here a simple and highly efficient synthesis of dihydrojasmone (**6**) via the high pressure carbonylation of mixed trialkylboranes[3,11] - a method recently explored in detail in our laboratory for the synthesis of a wide variety of unsymmetrical ketones[12].

Hydroboration of 1-hexene with thexylchloroborane[13] (**1**) cleanly afforded *n*-hexylthexylchloroborane (**2**), which, upon hydridation by potassium triisopropoxyborohydride in the presence of 2-acetoxy-3-butene gave quantitatively (2-acetoxy-4-butyl)-*n*-hexylthexylborane (**3**). Subsequent high pressure carbonylation[12], followed by alkaline hydrogen peroxide oxidation, produced 2-hydroxy-5-undecanone (**4**), which, on pyridinium chlorochromate oxidation[14], furnished the desired 2,5-undecadione (**5**). Base-catalyzed cyclization[15] of the 1,4-diketone **5** afforded dihydrojasmone (**6**) in 75% overall yield, starting from 1-hexene.



Thus, the present synthesis of dihydrojasmone elegantly demonstrates the synthetic application of the high pressure carbonylation of organoboranes. Further applications of this procedure are currently underway in our laboratory.

Boiling points are uncorrected. The G.L.C. analysis were carried out on a Hewlett-Packard 5750 research chromatograph (column 6 ft × 0.25 in, packed with 10% SE-30 on Chromosorb W AW DMCS). 2-Acetoxy-3-butene (b.p. 57-58°C/100 torr; n_D^{20}: 1.4016) was prepared from the commercially available 3-buten-2-ol (Wiley Organics). I.R. spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrometer. ^{1}H-N.M.R. spectra of 2,5-undecadione (**5**) and dihydrojasmone (**6**) were recorded on a Perkin-Elmer R-32 (90 MHz) spectrometer and a Varian XL-200 (200 MHz) spectrometer, respectively. General procedures for the manipulation of air-sensitive materials have been described elsewhere[3].

2,5-Undecadione (5):

To a 1.95 molar solution of thexylchloroborane/dimethyl sulfide (**1**; 15.4 ml, 30 mmol) in dichloromethane is added 1-hexene (2.53 g, 30 mmol) at 0°C. The mixture is stirred at room temperature for 2 h. Then the mixture is again cooled to 0°C and a 1.10 molar solution of potassium triisopropoxyborohydride in tetrahydrofuran (27.3 ml, 30 mmol) is added, followed by a dropwise addition of 2-acetoxy-3-butene (3.42 g, 30 mmol). The thick precipitate of potassium chloride is formed instantly. After 2 h at 0°C, the mixture is diluted with tetrahydrofuran (20 ml), centrifuged, and the supernatant liquid is separated. The precipitate is washed with tetrahydrofuran (2 × 15 ml) and the washings combined. The tetrahydrofuran solution of **3** is then subjected to high-pressure carbonylation at 1000 psi and 50°C for 5 h and subsequently oxidized by the standard procedure[16]. Regular workup and distillation produces *2-hydroxy-5-undecanone* (**4**); yield: 4.65 g; b.p. 94°C/0.05 torr [Lit.[17], b.p. 95°C/0.05 torr].

The entire sample of **4** is then oxidized by pyridinium chlorochromate using the reported procedure[14] to obtain, after distillation, *2,5-undecadione* (**5**); yield: 4.37 g (79% based on 1-hexene); b.p. 70°C/0.2 torr [Lit.[18], b.p. 71°C/0.2 torr]; chemical purity ≥99% by G.L.C.

I.R. (neat): $\nu = 1715$ cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 0.87$ (distorted t, 3H); 1.1-1.85 (m, 8H); 2.15 (s, 3H); 2.43 (t, 2H); 2.65 ppm (s, 4H).

Dihydrojasmone (6):

To 2,5-undecadione (**5**; 3.68 g, 20 mmol) in ethanol (90 ml), 2% aqueous sodium hydroxide (340 ml) is added and the solution is refluxed for 5 h, according to the reported procedure[15]. Regular workup, followed by distillation, affords dihydrojasmone (**6**); yield: 3.18 g (96%); b.p. 62°C/0.2 torr [Lit.[18], b.p. 64°C/0.2 torr]; n_D^{20}: 1.4746 [Lit.[19], n_D^{25}: 1.4771]; chemical purity ~100% by G.L.C.

I.R. (neat): $\nu = 1695, 1645$ cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 0.9$ (distorted t, 3H); 1.1-1.6 (m, 6H); 2.01 (s, 3H); 2.14 (m, 2H); 2.34 (m, 2H); 2.45 ppm (m, 2H).

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