177–178 °C; IR (Nujol) 1595, 1605, 1705, and 3150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–7.5 (m, protons of benzoyl, phenyl, tolyl, and H-3), 16.19 (s, 1, OH); ^{13}C NMR ($CDCl_3$) δ 127.0–130.0 (complex spectrum of 7 closely spaced doublets,[45] J = 160–165 Hz), 138.8 and 142.3 (both s, benzoyl and phenyl), 180.1 and 181.5 (both s, CO of benzoyl and C-7); MS, M^+ calcd at m/e 486, found m/e 331 (M^+ – tosyl). Anal. Calcd for $C_{28}H_{22}O_4S_2$: C, 69.11; H, 4.56; S, 13.18. Found: C, 68.95; H, 4.51; S, 13.22.

6-Benzoyl-7-hydroxy-5-phenylbenzo[*b*]thiophene (9d). (Typical Example of Formation of Benzo[*b*]thiophenes from Thiophenecarboxylate 2b (Section B, Table III)). To a mixture of **2b** (588 mg, 2 mmol) and chalcone (417 mg, 2 mmol) in Me_2SO (10 mL) was added MeONa (300 mg, 5.5 mmol), and the mxiture was stirred for 25 h at room temperature, poured out in water, and acidified (0.5 N HCl) to about pH 6. The yellow precipitate was washed (H_2O), dissolved in CH_2Cl_2, and combined with a CH_2Cl_2 extract of the filtrate. The CH_2Cl_2 solution was washed (H_2O), dried (Na_2SO_4), and concentrated to give crude **9d**. Crystallization (EtOH/Et_2O) afforded **9d** (334 mg, 50%): mp 141–142 °C; IR (Nujol) 1590, 1600, and 3050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–7.5 (m, protons of benzoyl, phenyl, and half AB q of thiophene), 11.15 (s, 1, OH); ^{13}C NMR ($CDCl_3$) δ 126.7, 127.2, 127.8, 129.1, 129.6, 131.5 (six d, J = 160–161 Hz, CH of benzoyl and phenyl), 139.5 (s, CCO of benzoyl), 141.1 (s, phenyl), 201.4 (s, CO). Anal. Calcd for $C_{21}H_{14}O_2S$: C, 76.36; H, 4.24; S, 9.70. Found: C, 76.20; H, 4.27; S, 9.48.

Methyl 7-Hydroxy-5-phenyl-4-tosyl-4,5-dihydrobenzo-[*c*]thiophene-6-carboxylate (12c). (Typical Example of Formation of a Dihydrobenzo[*c*]thiophene (Section D, Table V)). A mixture of **4a** (310 mg, 1.0 mmol) and methyl cinnamate (165 mg, 1.0 mmol) in DME (5 mL) was stirred with *t*-BuOK (280 mg, 2.5 mmol) for 24 h at 20 °C and then for 3 h at 60 °C. The mixture was cooled and poured in a mixture of 60 mL of water plus 10 mL of 0.5 N HCl. The precipitate was collected, washed with water (200 mL), and dissolved in Et_2O, and this solution was washed with brine and dried ($MgSO_4$). Concentration gave crude **12c** which was washed with Et_2O/pentane to give **12c** (231 mg, 53%): mp 149–151 °C; IR (Nujol) 1620, 1640, and 3115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.62 (s, 3, MeO), 6.75–7.50 (m, 10, Ar protons), 12.03 (s, 1, OH); ^{13}C NMR ($CDCl_3$) δ 51.9 (q, J = 149 Hz, MeO), 124.7, 127.0, and 127.1 (all d, J = 160–168 Hz, CH of phenyl), 132.3 (s, phenyl), 162.0 (s, C-7), 171.8 (s, CO_2R). Anal. Calcd for $C_{23}H_{20}O_5S_2$: C, 62.70; H, 4.58; S, 14.56. Found: C, 62.72; H, 4.70; S, 14.56.

Dimethyl 4-Hydroxybenzo[*c*]thiophene-5,6-dicarboxylate (14a). (Typical Example of Annulations of 3,4-Disubstituted Thiophene 4a (Section D, Table V)). To a solution of **4a** (310 mg, 1 mmol) and dimethyl maleate (212 mg, 1.5 mmol) in DME (5 mL) was added *t*-BuOK (280 mg, 2.5 mmol). The mixture was stirred for 5 h at 60–70 °C, then kept at 20 °C overnight, and subsequently poured in water. Acidification (0.5 N HCl) to about pH 6 gave a precipitate that was collected, washed (H_2O), and dissolved in Et_2O. The solution was dried ($MgSO_4$) and concentrated to give crude **14a** as a brown-yellow solid. This crude product was filtered with Et_2O over a layer (1 cm) of silica gel and crystallized (CH_2Cl_2, heptane, Et_2O) to yield **14a** (185 mg, 70%): mp 114–116 °C; IR (Nujol) 1655, 1725, 3095, and 3115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 and 3.87 (two s, 3, MeO), 12.04 (s, 1, OH); ^{13}C NMR ($CDCl_3$) δ 52.3 (q, J = 147 Hz, MeO), 52.5 (q, J = 148 Hz, MeO), 169.6 and 170.6 (s, and s, two ester carbonyls). Anal. Calcd for $C_{12}H_{10}O_5S$: C, 54.13; H, 3.79; S, 12.04. Found: C, 53.86; H, 3.89; S, 11.90.

Registry No. **1a**, 99708-86-8; **1b**, 99708-87-9; **2a**, 81452-50-8; **2b**, 81458-99-3; **2c**, 99708-82-4; **3a**, 99708-83-5; **3b**, 99708-84-6; **3c**, 99708-85-7; **4a**, 99708-93-7; **4b**, 99708-94-8; **4c**, 99708-95-9; **5**, 99708-96-0; **6a**, 81459-01-0; **6b**, 99708-98-2; **6c**, 99708-99-3; **7a**, 81452-61-1; **7b**, 98449-83-3; **7c**, 81452-62-2; **7d**, 81452-53-1; **7e**, 81452-63-3; **7f**, 99708-97-1; **8a**, 81452-64-4; **8b**, 81452-65-5; **8c**, 81452-51-9; **8d**, 99709-01-0; **9a**, 81452-59-7; **9b**, 81452-49-5; **9c**, 99709-00-9; **9d**, 81452-46-2; **9e**, 99709-02-1; **10**, 99709-04-3; **11**, 99709-03-2; **12a**, 99709-06-5; **12b**, 99709-07-6; **12c**, 99709-09-8; **13**, 99709-13-4; **14a**, 99709-05-4; **14b**, 99709-08-7; **14c**, 99709-10-1; **14d**, 99709-11-2; **15**, 99709-12-3; **21**, 16494-40-9; **22a**, 81452-54-2; **22b**, 59961-15-8; **22c**, 55406-13-8; **22d**, 99708-88-0; **23a**, 99708-89-1; **23b**, 99708-90-4; **24**, 30318-99-1; **25a**, 73229-39-7; **25b**, 99708-91-5; **25c**, 61755-84-8; **25d**, 99708-92-6; (E)-4-$O_2NC_6H_4CH$=CHCOPh, 2960-55-6; (E)-PhCOCH=CHCOPh, 959-28-4; (E)-PhCOCH=CHPh, 614-47-1; (E)-PhCH=CHCOOMe, 1754-62-7; dimethyl fumarate, 624-49-7; methyl crotonate, 18707-60-3; 6,6-dimethylcyclohex-2-enone, 6553-64-6; sodium *p*-toluenesulfinate, 824-79-3; sodium *p*-thiocresolate, 10486-08-5.

Supplementary Material Available: Table VI with NMR data (^1H and ^{13}C chemical shifts and coupling constants) of the benzothiophene skeleton of compounds **6–9**, **12**, **14**, **26**, and **27** (3 pages). Ordering information is given on any current masthead page.

(45) Two lines probably fall together in this spectrum. However, the coupled spectrum is too complex to decide which ones.

Notes

Interfacial Superbase Chemistry. The Catalyzed Reaction of Potassium Hydride with Trisiamylborane. A New Convenient Synthesis of Potassium Trisiamylborohydride[1a]

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Potassium hydride is a highly reactive reagent for the metalation of highly hindered alcohols, amines, phenols, ketones, sulfoxides, etc.[2] The reactivity exhibited by this hydride is far superior to the other, more commonly used, alkali metal hydrides. In addition, potassium hydride is exceptionally reactive toward weak Lewis acids, such as trialkylboranes and trialkoxyboranes.[3] Unlike lithium and sodium hydrides, potassium hydride reacts with hindered organoboranes, such as tri-*sec*-butylborane, rapidly and quantitatively, even at room temperature. The corre-

(1) (a) Quaternary Boron. 8. Part 7; Brown, C. A.; Desai, M. C.; Jadhav, P. K. submitted for publication. Part 6, see ref 5b. (b) Joint Study Fellow at IBM, Spring 1977.

(2) (a) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913 and references therein. (b) Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 982. (c) Brown, C. A. *Synthesis* **1974**, 427. (d) Fieser, L. F.; Fieser, M. F. "Reagents for Organic Synthesis"; Wiley: New York, 1967–82; Vol. 1–10, and references therein.

(3) (a) Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100. (b) Brown, H. C.; Nazer, B.; Sikorski, J. A. *Organometallics* **1983**, *2*, 634.

0022-3263/86/1951-0238$01.50/0

Table I. Reaction of Potassium Hydride with Trisiamylborane in Tetrahydrofuran at 25 °C[a]

catalyst (mol %)	hydride concentration, M						
	1.0 h	2.0 h	3.0 h	6.0 h	12.0 h	18.0 h	24.0 h
none	0.02		0.04			0.09	0.09
$(MeO)_3B$ (5)	0.39		0.41		0.45		0.45
$(i\text{-PrO})_3B$ (5)[b]	0.31		0.51		0.86		1.03
$(i\text{-PrO})_3B$ (20)[b]		1.24					

[a] The reaction mixtures were 1.0 M in trisiamylborane; excess (~50%) potassium hydride was utilized. [b] Hydride concentration measured is due to both potassium trisiamylborohydride and potassium triisopropoxyborohydride (5–20%).

sponding potassium trialkylborohydrides are formed in quantitative yield under such mild conditions.[4]

During the course of our investigation of the rates of reaction of potassium hydride with representative trialkylboranes of increasing steric requirements,[4] we discovered that two highly hindered trialkylboranes—tris(*trans*-2-methylcyclopentyl)borane and trisiamylborane—react only sluggishly. Thus, the reaction of potassium hydride with a 1.0 M solution in THF of trisiamylborane at 25 °C proceeded to about 10% conversion (by hydride activity in solution) (eq 1a). Recent studies[5] have shown

$$KH + Sia_3B \xrightarrow[24\ h]{THF,\ 25\ ^\circ C} \underset{10\%}{KSia_3BH} \qquad (1a)$$

that trialkoxyborohydride **1a** is a very mild reducing agent compared to alkali metal trialkylborohydrides **1b**.[2a,5] This is in direct opposition to prior suggestions[7] that hydride donation ability is inversely related to the strength of the boron Lewis acid **2** toward hydride transfer to electrophiles (eq 1b). However, triisopropoxyborohydride is capable

$$\underset{\substack{\mathbf{1a},\ X = OR\\ \mathbf{b},\ X = \text{alkyl}}}{[X_3BH]^-} + E \rightarrow \underset{\mathbf{2}}{X_3B} + [HE]^- \qquad (1b)$$

of transferring hydride rapidly and quantitatively to trialkylboranes (eq 2).[8] Hindered trialkylborohydrides such

$$\underset{\mathbf{3}}{[(i\text{-PrO})_3BH]^-K^+} + Br_3 \rightarrow \underset{\substack{\mathbf{4a},\ R = \text{alkyl}\\ \mathbf{4b},\ R = \text{siamyl}}}{(i\text{-PrO})_3B} + \underset{\mathbf{5}}{[HBR_3]^-K^+} \qquad (2)$$

as trisiamylborohydride (siamyl = *sec*-isoamyl, 3-methyl-2-butyl) are remarkably stereoselective reducing agents toward cyclic ketones,[5] and we sought a simple direct route to catalyze the reaction of potassium hydride with hindered trialkylboranes **4a**.

We now report that the reaction of potassium hydride with trisiamylborane is readily catalyzed by a small quantity of triisopropoxyborane (**5**). Thus it is unnecessary to prepare **3** and to react this with **4** in a separate step. The rate of the reaction was dependent upon the catalyst concentration. The addition of 20 mol % of triisopropoxyborane to a mixture of a 1.0 M solution of trisiamylborane and excess (~50%) potassium hydride (suspended)

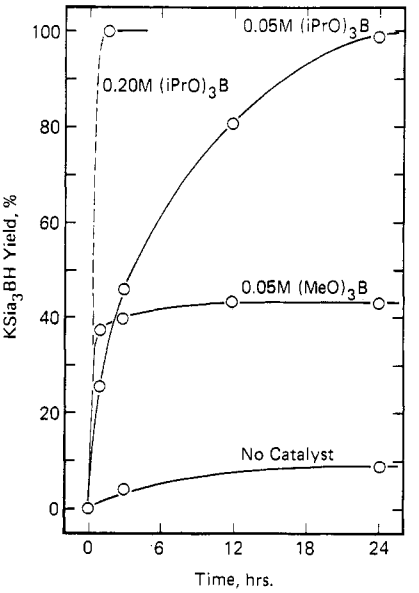

Figure 1. Reaction of trisiamylborane (1 M) with potassium hydride in tetrahydrofuran at 25 °C.

resulted in the rapid dissolution of potassium hydride. After 2 h, hydride analysis of the clear solution indicated a hydride concentration of 1.24 M, which corresponds to completion of the reaction of potassium hydride with trisiamylborane (plus reaction with the triisopropoxyborane). In the presence of only 5 mol % of triisopropoxyborane, the reaction required 24 h for completion (Figure 1) (eq 3). These results are summarized in Figure 1 and Table I.

$$KH + Sia_3B \xrightarrow[25\ ^\circ C,\ 24\ h]{THF,\ 5\ mol\ \%\ (i\text{-PrO})_3B} \underset{100\%}{KSia_3BH} + \underset{5\%}{K(i\text{-PrO})_3BH} \qquad (3)$$

The reaction presumably proceeds through the formation of soluble potassium triisopropoxyborohydride, which rapidly transfers the hydride to trisiamylborane (eq 4 and 5), regenerating triisopropoxyborane. While both reac-

$$\underset{\text{solid}}{KH} + \underset{\text{catalytic}}{(i\text{-PrO})_3B} \xrightarrow{THF} \underset{\text{solution}}{K(i\text{-PrO})_3BH} \qquad (4)$$

$$\underset{\text{solution}}{K(i\text{-PrO})_3BH} + \underset{\text{solution}}{Sia_3B} \rightarrow \underset{\text{solution}}{KSia_3BH} + \underset{\text{recycles}}{(i\text{-PrO})_3B} \qquad (5)$$

tions can be separately demonstrated, the existence of this cycle cannot be definitively proven. Washing KH with tetrahydrofuran containing triisopropoxyborane does not appear to activate the KH. However, the exact mechanism by which catalysis occurs is only peripheral to utility of the method.

After the reaction is over, the mixture is filtered to remove excess potassium hydride. The crystal clear solution thus obtained can be stored under nitrogen. Hydrolysis of a known aliquot of the reaction mixture with measurement of the hydrogen evolved indicated the solution to be 1.03 M in hydride. Consequently, we have an essentially quantitative yield of trisiamylborohydride, in addition to the probable presence of a small quantity (~5%) of potassium triisopropoxyborohydride. The sluggish reaction of **4** with most organic substrates[9] compared to **6** indicates that the small residual quantity of **4** can be

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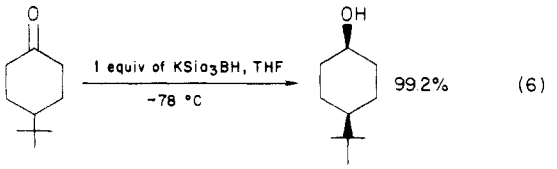
(9) (a) Brown, H. C.; Mead, E. J.; Tierney, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 5400. (b) Brown, H. C.; Mead, E. J.; Shoaf, C. J. *Ibid.* **1956**, *78*, 3613.

regarded as an inert component; however, it may be readily removed by addition of an equivalent amount of trisiamylborane (eq 2) or another hydride acceptor such as *n*-octyl chloride. The analysis of the solution for K^+:B:H^- indicated it to be essentially 1:1:1. The reagent appears to be quite stable and appears to reduce cyclic ketones with exceptional stereoselectivity, comparable to that of the lithium analogue[5] (eq 6).



(6)

Attempts were made to catalyze the reaction with trimethoxyborane as well. Initially (see Figure 1 and Table I) the reaction appeared to proceed even more readily than with **4** as the catalyst; however, reaction ceased with only 40% of **4** converted to **6**. This apparently reflects destruction of the intermediate **1a** (R = Me) via disproportionation to potassium tetramethoxyborate (stable to KH) and potassium borohydride (insoluble in THF, not observed to transfer hydride to trialkylboranes). Such disproportionation has been reported to be facile and is the basis of the usual preparation of sodium borohydride from trimethoxyborane and sodium hydride.[9]

The curves for triisopropoxyborane catalysis in Figure 1 present a puzzle. The shape of the curve in the figure for 5 mol % triisopropoxyborane clearly shows a marked decrease in rate as the reaction proceeds. Transfer of hydride from **3** to **4** is very fast and quantitative under these conditions. Consequently, we would expect that the observed curve reflects the rate of reaction of **5** with KH(s). However, the latter is present in 50% excess; thus the reaction curve must reflect either a marked decrease in surface area as smaller particles are consumed or some progressive "poisoning" of the KH surface as the reaction proceeds. Moreover, the ratio of observed reaction times (ca. 25:1) with 5 mol % and 20 mol % triisopropoxyborane is much longer than would be expected a priori from the relative amounts of catalyst. This suggests the presence of an impurity which reacts with a fixed amount of the **5** (or **3**), thereby increasing the actual ratio of active catalyst in the two experiments. This is consistent with the possibility that the trialkoxyborane functions to remove a surface contaminant from the KH (as well as serving as a hydride carrier); the reaction with the suggested surface contaminant, if irreversible, would provide the mechanism for loss of catalyst. The importance of this explanation lies in the possibility that, with careful control of reagents, it may be possible to effect the catalysis with only traces of the trialkoxyborane.

The graph shown for trimethoxyborane catalysis in the figure, as the other graphs, was corrected for the maximum amount of trialkoxyborohydride which can be formed. Due to the probably disproportionation and precipitation of hydride derived from trimethoxyborane, this graph could be up to 5% low; this does not affect the conclusions.

In summary, triisopropoxyborane serves as an efficient catalyst for reaction of KH with trisiamylborane, providing the first route to potassium trisiamylborohydride nearly free of other boron species. The procedure is, in all probability, applicable to reaction of other highly hindered trialkyboranes.

Experimental Section

General Considerations. Procedures for the preparation of trialkyboranes, their reactions with KH, and relevant analysis have been published elsewhere in detail.[3,4,10,11] For the catalytic studies purified trialkoxyborane was added to a suspension of KH (50% excess) in THF with stirring under nitrogen. At intervals stirring was stopped and samples of the clear solution were removed with a hypodermic syringe and analyzed for active hydride content by hydrogen gas evolution upon hydrolysis.[10] This analysis gives the total soluble hydride in solution, from both **3** and **6**. The values in the table reflect total hydride found; the graphs in the figure have been corrected for the hydride due to the catalyst. In the case of trimethoxyborane, disproportionation of the trimethoxyborohydride and subsequent precipitation of the tetrahydridoborate (see text) removes from solution the hydride due to catalyst; therefore, in this case, the hydride analyses are assumed to be entirely due to trisiamylborohydride. The maximum discrepancy this could entail in 0.05/0.40 or 12.5%.

Reduction of 4-*tert*-butylcyclohexanone, and GLPC analysis of the products, was carried out according to procedures published for reductions with the lithium analogue.[5]

Potassium Trisiamylborohydride (6). A uniform oil dispersion of potassium hydride (3.0 g net KH, 75 mmol) was transferred under nitrogen to a dry 100-mL round-bottomed flask with the aid of a hypodermic syringe fitted with a 16-gauge needle. The flask was fitted with a poly-TFE covered magnetic stirring bar and an injection port closed by a small rubber septum. The oil carrier was removed by three successive washes of ca. 50 mL of pentane (dried overnight over molecular sieves); residual pentane was removed in a stream of nitrogen. The pure KH was dispersed a 1.0 M solution of trisiamylborane in the THF (50 mL, 50.0 mmol), previously prepared.[11] Triisopropoxyborane (0.58 mL, 2.5 mmol purified by distillation from sodium) was injected to the mixture with a syringe. At intervals stirring was stopped and a 2.0-mL sample of the clear supernatant liquid was withdrawn with an oven-dried syringe and analyzed by hydrolysis with a 1:1:1 mixture of THF:glycerine:aqueous HCl (0.10 N). Hydride content was determined by measurement of the evolved hydrogen. After 24 h the hydride content of the solution was constant at 1.03–1.05 M, indicating a quantitative conversion to **6** (+ca. 5% **4**): IR (THF) 2040 cm^{-1}, B–H stretch; ^{11}B NMR (THF, external BF_3:Et_2O = 0δ), δ = −11.6 and −13.8, J_{B-H} = 75 Hz, two pairs of doublets due to diasteriomers, partially superimposed.

Registry No. **2** (X = MeO), 121-43-7; **4b**, 32327-52-9; **5**, 5419-55-6; **6**, 67966-25-0; KH, 7693-26-7.

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Meerwein-Ponndorf-Verley Type Reduction of Ketones and Oppenauer Type Oxidation of Alcohols under the Influence of Cp_2ZrH_2

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A more direct synthesis of bis(cyclopentadienyl)zirconium dihydride, Cp_2ZrH_2 (**1**), has been reported relatively recently by Wailes et al.[1] They have also reported in their subsequent papers[2-4] that **1** reacts with acetone to give bis(cyclopentadienyl)zirconium diisopropoxide, $Cp_2Zr[OCH(CH_3)_2]_2$ (**2**), and with 2-propanol to give **2** and zirconium tetraisopropoxide, $Zr[OCH(CH_3)_2]_4$, in which the

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(4) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C32.

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