11,14,32,35-Tetrathia[3.6.3.6.0^{1,22}](1,3)benzenophane-2,23-diene (5A) and 11,14,32,35-Tetrathia[3.6.3.6.0^{1,24}](1,3)-benzenophane-2,22-diene (5B). Benzene (1.7 L) and 0.8 L of ethanol were refluxed in a 4-L 2C-VP apparatus. The solutions of 1.50 g (1.97 mmol) of freshly purified *meso*- or *d,l*-1,3,4,6-tetrakis[3-(bromomethyl)phenyl]-1,5-hexadiene (**15**), respectively, in 250 mL of benzene and 0.46 g (5.00 mmol) of 1,2-ethanedithiol or 1.12 g (0.02 mol) of potassium hydroxide in 250 mL of ethanol were added dropwise simultaneously during 8 h. After complete addition the mixture was heated under reflux for additional 2 h. The mixture was evaporated to dryness, the residue taken up in chloroform, and the solution filtered from the insoluble residue. The solvent was removed and the raw product purified by column chromatography (SiO_2; chloroform/cyclohexane, 1:1): yield, 15–20% of **5A** or **5B**, respectively; ^{1}H NMR (*meso*-**5**, $CDCl_3$/TMS_{int}) δ 2.46, 2.48 (2 s, 2 × 4 H, SCH_2CH_2S), 3.60–3.68 (2 s, 2 × 4 H, SCH_2–aryl), 3.72 (m, 2 CH), 6.04 (m, 4 =CH), 6.8–7.48 (m, 16 aryl H); ^{1}H NMR (*d,l*-**5**, $CDCl_3$/TMS_{int}) δ 2.24, 2.63 (2 s, 2 × 4 H, SCH_2CH_2S), 3.57, 3.62 (2 s, 2 × 4 H, SCH_2–aryl), 3.74 (m, 2 CH), 6.44 (m, 4 =CH), 6.93–7.55 (m, 16 aryl H); MS, *m/z* 622 (M^+) (*meso*-**5** and *d,l*-**5**); high-resolution MS, $C_{38}H_{34}S_4$, 622.1859 (*d,l*-**5**), $C_{38}H_{34}S_4$, 622.1648 (*meso*-**5**).

***d,l*-[3.2.3.2.0^{1,18}](1,3)Benzeneophane-2,19-diene (6B) through Cyclization of *d,l*-1,3,4,6-Tetrakis[3-(bromomethyl)phenyl]-1,5-hexadiene (15) with Phenyllithium.**[5] In a 500-mL, three-necked flask previously heated and filled with argon, fitted with a septum cap, gas inlet tube, reflux condenser with bubble counter, and magnetic stirrer, *d,l*-1,3,4,6-tetrakis-[3-(bromomethyl)phenyl]-1,5-hexadiene (**15**; 1.30 g, 1.715 mmol) was heated to boiling in benzene and phenyllithium (1.8 M in benzene/ether, 70:30, 2.30 mL, 4.28 mmol) was added slowly by means of a syringe, whereupon a color change from yellow to orange and dark red was observed. Stirring under reflux was continued for 2 h. The solvent was removed and the residue taken up in chloroform. The solution was washed with water and the organic phase separated and dried over $MgSO_4$. The chloroform was evaporated to dryness. The byproduct biphenyl was distilled off in sufficient high vacuo. The remaining red residue was purified by column chromatography (SiO_2; chloroform/cyclohexane, 1:5): 12.4 mg (1.7%), yield of pure substance with mp 210 °C; R_f 0.55 (SiO_2; chloroform/cyclohexane, 1:5); ^{1}H NMR ($CDCl_3$/TMS_{int}, 200 MHz) δ 2.17 (d of t, J = 12.6 and 3.6 Hz, 2 H), 2.48 (d of t, J = 12.6 and 3.6 Hz, 2 H), 3.01 (t of d, J = 12.6 and 3.6 Hz, 2 H), 3.17 (t of d, J = 11 Hz) [AA'BB' system], 3.42 (d, 2 CH, J = 11 Hz), 4.9 (s, 2 H_i), 5.9 (s, 2 H_i), 6.12 (t, 2 =CH, J = 11 Hz), 6.65 (m, 2 aryl H), 6.78 (d, 2 =CH, J = 11 Hz), 6.93–7.4 (m, 14 aryl H); MS, *m/z* 438 (M^+); high-resolution MS, $C_{34}H_{30}$, 438.2351. Calcd: C, 93.11; H, 6.89. Found: C, 93.24; H, 7.04.

X-ray Structure Analysis of 6B. Colorless flat needles were obtained by crystallization from chloroform/methanol. Crystal data: $C_{34}H_{30}$; M_r 438.6; crystal dimensions, 0.3 × 0.3 × 1.25 mm^3 orthorhombic, space group $P2_12_12$ (No. 18); a = 1450.2 (2) pm, b = 1403.7 (2) pm, c = 594.4 (6) pm; α = 90.15 (8)°, β = 89.98 (5)°, γ = 89.97 (2)°; U = 1.209 nm^3; Z = 2; d = 1.21 g cm^{-3}; μ = 0.34 cm^{-1}. Final R = 0.101 for 1762 unique reflexions [θ < 28°, $\sigma(I)$ < 0.67(I)], using unit weights. Due to low crystal quality a smaller R value could not be obtained. Intensity data were obtained at 293 K on a four-circle diffractometer CAD4 (Enraf-Nonius) using Mo Kα radiation with graphite monochromator. The structure was solved by direct methods (MULTAN 80[9]). All H atoms could be localized in a difference Fourier map. The refinement was carried out by least-squares methods (170 parameters, SHELX 76[10]) with anisotropic temperature factors for all carbon atoms. H atoms were included with constraints (C–H, 108 ppm) and a common isotropic temperature factor.

Registry No. **5A**, 110044-16-1; **5B**, 103953-96-4; **6A**, 109997-27-5; **6B**, 109997-26-4; **7**, 2142-63-4; **8**, 3132-99-8; **9**, 103953-98-6; (±)-**10**, 109997-24-2; (±)-**11**, 109997-25-3; *meso*-**12**, 103958-69-6; *d,l*-**12**, 103954-01-4; *meso*-**13**, 103954-02-5; *d,l*-**13**, 103954-03-6; *meso*-**14**, 103954-04-7; *d,l*-**14**, 103954-05-8; *meso*-**15**, 103972-41-4; *d,l*-**15**, 103954-06-9.

Supplementary Material Available: Figure of unit cell of **6B** (1 page). Ordering information is given on any current masthead page.

(9) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. "MULTAN 80: A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data"; University of York, 1980.

(10) Sheldrick, G. M. "SHELX76: Program for crystal structure determination"; Cambridge University, 1976. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Reaction of Potassium Triphenylborohydride with Selected Organic Compounds Containing Representative Functional Groups

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Potassium triphenylborohydride (KTPBH) is a very mild reducing agent. With the exception of aldehyde, ketone, quinone, phenyl isocyanate, *n*-alkyl iodide, and aromatic disulfide, most functional groups studied react slowly or are inert toward KTPBH. KTPBH exhibits a remarkable stereoselectivity in the reduction of cyclic ketones. The reductions of epoxides are very slow, but the presence of the Lewis acid Ph_3B dramatically accelerates the rates and changes the regioselectivity in the case of trisubstituted epoxides.

Among the common alkali-metal hydrides LiH, NaH, and KH, potassium hydride has been established as possessing an exceptional ability to transfer hydride to trialkylboranes, producing the corresponding trialkylborohydrides,[1] which are powerful reducing agents,[2] to trialkoxyboranes,[3] which form the corresponding trialkoxyborohydrides,[4] and to dialkylalkoxyborane, producing the corresponding dialkylalkoxyborohydrides,[5] which are very mild but highly selective reducing agents.

Although the preparation of alkali-metal triarylborohydride from the reaction of common alkali-metal hydride and triarylboranes has been reported,[6] application of these

(1) (a) Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100. (b) Brown, C. A.; Krishnamurthy, S. *J. Organomet. Chem.* **1978**, *156*, 111.

(2) (a) Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55. (b) Brown, H. C.; Kim, S. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 1.

(3) (a) Brown, H. C.; Nazer, B.; Sikorski, J. A. *Organometallics* **1983**, *2*, 634. (b) Brown, H. C.; Cha, J. S.; Nazer, B. *Inorg. Chem.* **1984**, *23*, 2929.

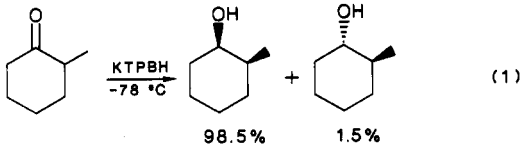
(4) (a) Brown, H. C.; Cha, J. S.; Nazer, B.; Kim, S. C.; Krishnamurthy, S.; Brown, C. A. *J. Org. Chem.* **1984**, *49*, 885. (b) Brown, H. C.; Cha, J. S.; Nazer, B. *Synthesis* **1984**, 494.

(5) (a) Brown, H. C.; Cha, J. S.; Nazer, B. *J. Org. Chem.* **1984**, *49*, 2073. (b) Brown, H. C.; Cha, J. S.; Nazer, B. *J. Org. Chem.* **1985**, *50*, 498.

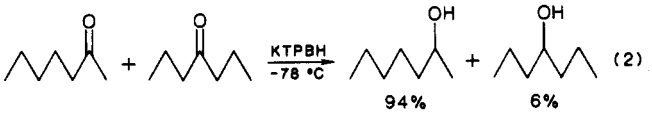
(6) (a) Hooz, J.; Akiyama, S.; Cedar, F. J.; Bennett, M. J.; Tuggle, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 274. (b) Wittig, G.; Keicher, G.; Ruckert, A.; Raff, P. *Justus Liebigs Ann. Chem.* **1949**, *563*, 110.

0022-3263/87/1952-5564$01.50/0

reagents to the reduction of organic compounds has been investigated only with lithium dimesitylborohydride–bis(dimethoxyethane) ($LDMBH_2 \cdot 2DME$).[6a] In 1949, potassium triphenylborohydride(KTPBH) was first reported by Wittig and co-workers.[6b] They prepared this reagent from triphenylborane and 1,4-dipotassio-1,1,4,4-tetraphenylbutane, instead of potassium hydride. Recently, we prepared KTPBH from triphenylborane and potassium hydride in tetrahydrofuran (THF) and showed that it is a highly chemo- and stereoselective reducing agent[7] (eq 1 and 2).



(1)



(2)

In order to better understand the reducing characteristics of KTPBH, we undertook a detailed study of the rate, stoichiometry, and products of the reaction of KTPBH with a standard list of organic compounds containing representative functional groups.

Results and Discussion

Preparation of Standard Solution of Potassium Triphenylborohydride (KTPBH). A standard solution of KTPBH was prepared by the addition of triphenylborane to a 50% excess of potassium hydride in THF with vigorous stirring for 6 h at 25 °C to provide a quantitative yield of potassium triphenylborohydride (eq 3).

$$\underset{(300\ \text{mmol})}{KH} + \underset{(200\ \text{mmol})}{Ph_3B} \xrightarrow[98.7\%,\ 6\ \text{h}]{\text{THF, 25 °C}} \underset{(197\ \text{mmol})}{KPh_3BH} \quad (3)$$

The course of the reaction was monitored by withdrawing aliquots of the clear reaction mixture at appropriate intervals and analyzing its hydride concentration. Potassium hydride reacts with triphenylborane somewhat slower than with tri-*sec*-butylborane but much faster than with trisiamylborane.[1b] The rate difference may be attributed to the steric and electronic effects.

Triphenylborane appears to undergo a simple Lewis acid–base reaction in 1/1 ratio to form a molecular addition compound. On the basis of this stoichiometry, the ratio of K/B/H in solution should be 1/1/1, and analysis[1b] confirmed this ratio. The concentration of potassium was determined by hydrolysis of a known aliquot of the solution with water and titrating the base formed. Boron was determined by GLC analysis of the phenol produced by oxidation of KTPBH. Hydride concentration was measured by hydrogen evolution on hydrolysis.

The solution of KTPBH in THF displayed a characteristic IR absorption at 2200 cm^{-1} (strong, broad), attributed to the B–H stretching vibration.[8] Also ^{11}B NMR showed a clean sharp doublet (J_{B-H} = 78.7 Hz) centered at δ −7.96 relative to $BF_3 \cdot OEt_2$. Similar values have been reported for the tetraethylammonium triphenylborohydride (2198 cm^{-1}; J_{B-H} = 79 ± 1 Hz).[8]

Maintained under dry nitrogen, at room temperature, the hydride concentration of KTPBH remained constant as shown by periodic checking over 2 months.

(7) Yoon, N. M.; Kim K. E.; Kang, J. *J. Org. Chem.* **1986**, *51*, 226.
(8) Burlitch, J. M.; Burk, J. H.; Leonowicz, M. E.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1702.

Table I. Reaction of Potassium Triphenylborohydride with Representative Active Hydrogen Compounds in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
1-hexanol	12.0	0.00	0.00	0.00
benzyl alcohol	6.0	0.00	0.00	0.00
3-hexanol	6.0	0.00	0.00	0.00
3-ethyl-3-pentanol	6.0	0.00	0.00	0.00
phenol	1.0	0.87	0.87	0.00
	3.0	1.00	1.00	0.00
2,6-di-*tert*-butylphenol	24.0	0.12	0.12	0.00
n-hexylamine	6.0	0.00	0.00	0.00
1-hexanethiol	24.0	0.16	0.1[c]	0.00
benzenethiol	1.0	0.91	0.91	0.00
	6.0	1.00	1.00	0.00

[a] Four mmoles of compound was added to 16.0 mmol of KTPBH (16.0 mmol of hydride) in 32 mL of solution; 0.125 M in compound and 0.5 M in hydride. [b] In mmol/mmol of compound.

Table II. Reaction of Potassium Triphenylborohydride with Representative Aldehydes and Ketones in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
n-hexanal	5 min	0.02	1.01	0.99
benzaldehyde	5 min	0.01	1.02	1.01
2-heptanone	0.5	0.00	0.86	0.86
	3.0	0.00	1.00	1.00
norcamphor	0.5	0.00	0.75	0.75
	3.0	0.00	1.00	1.00
acetophenone	0.5	0.00	0.82	0.82
	1.0	0.00	1.01	1.01
benzophenone	0.5	0.00	0.78	0.78
	1.0	0.00	1.00	1.00
cinnamaldehyde	0.5	0.02	0.97	0.95
	1.0	0.02	0.99	0.97
	3.0[c]	0.02	1.01	0.99
3-penten-2-one	0.5	0.00	1.55	1.55
	3.0	0.00	2.03	2.03
2-cyclohexenone	0.5	0.00	1.78	1.78
	3.0[d]	0.00	1.99	1.99
chalcone	1.0	0.01	0.63	0.62
	3.0[e]	0.01	0.99	0.98

[a,b] See the corresponding footnotes in Table I. [c] A 97% yield of cinnamyl alcohol. [d] A 98% yield of cyclohexanol in 4 h (H^-/compound = 3). [e] A 98% yield of 1,3-diphenyl-2-propen-1-ol.

Procedure for Rate and Stoichiometry Studies. In order to define the reducing characteristics of KTPBH, we undertook a systematic study of the KTPBH with selected organic compounds containing representative functional groups under standardized conditions (THF, 0 °C). The general procedure adopted was to add 4.0 mmol of the organic compounds to 16.0 mmol of KTPBH in THF. The initial concentrations were 0.50 M in KTPBH and 0.125 M in the compound under examination. Hydrogen evolution was measured. A blank reaction was also run under identical conditions but without addition of the compound. The reaction mixtures were maintained at 0 °C, and aliquots were removed at appropriate intervals and analyzed for residual hydride by hydrolysis with a mixture of 4 N H_2SO_4–THF (1:1). From the difference in the residual hydrides in the two cases, the hydride used by the compound for reduction was determined.

Alcohols, Phenols, Amines, and Thiols (Table I). Of the active hydrogen compounds studied, alcohols were inert to the reagent. Phenol evolved 1 equiv of hydrogen over a period of 3 h, but 2,6-di-*tert*-butylphenol evolved hydrogen only sluggishly. *n*-Butylamine was inert to the

Table III. Stereoselective Reduction of Cyclic and Bicyclic Ketones with Potassium Triphenylborohydride (KTPBH) in THF[a,b]

ketone	temp, °C	less stable isomer	% of less stable isomer		
			KTPBH	$LDMBH_2$·2DME[e]	Li-*sec*-Bu_3BH[f]
2-methylcyclohexanone	0	cis	95.4	99.0	99.3(99.0)[g]
	−78		98.5		
3-methylcyclohexanone	0	trans	82.0	99	85
	−78		94.2		95
4-methylcyclohexanone	0	cis	78.1	94	80.5(88.0)[g]
	−78		92.3		90.0
3,3,5-trimethylcyclohexanone	0	trans	99.0		99.8
4-*tert*-butylcyclohexanone	0	cis	78.5	94.0	93.0
	−78		92.8		
norcamphor	0	endo	91.2		99.6
	−78		98.1		
d-camphor	0	exo			99.6
	25		*c*	99.8	
	65		96.5[d]		

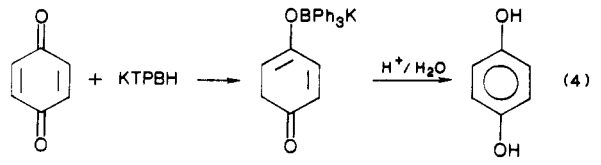
[a] Reaction mixtures were 0.25 M in ketone at 0 °C, and those at −78 °C were 0.125 M. Ratio for reagent–ketone was 1.1:1. Reactions at 0 °C were run for 1 h and those at −78 °C for 3 h. [b] The yields of alcohols (GLC) were quantitative. [c] A 25% reduction to the corresponding alcohol in 24 h at 25 °C. [d] A 91% reduction to the corresponding alcohol in 6 h. [e] Lithium dimesitylborohydride–bis(dimethoxyethane): Hooz, J.; Akiyama, F. J.; Cedar, M. T.; Tuggl, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 274. [f] L-Selectride: Krishnamurthy, S.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 7159. [g] K-Selectride: Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100.

reagent under these conditions. 1-Hexanethiol evolved hydrogen sluggishly, but benzenethiol evolved 1 equiv of hydrogen at a moderate rate (3 h).

Aldehydes and Ketones (Table II). All of the aldehydes and ketones examined took up 1 equiv of hydride rapidly, indicating clean reduction to the corresponding alcohol stage. Hydrolysis of the reaction products provided the corresponding alcohols in quantitative yields. Cinnamaldehyde took up 1 equiv of hydride rapidly, with no sign of further reduction. This suggested the reduction to cinnamyl alcohol, and indeed we obtained this allylic alcohol in 97% yield. Similar results were also observed with chalcone. On the other hand, 3-penten-2-one and 2-cyclohexenone both took up 2 equiv of hydride rapidly, to give the corresponding saturated alcohols. Interestingly, only the saturated ketones were obtained exclusively from these α,β-unsaturated ketones with 1 equiv of KTPBH. A more extensive study of the reduction of α,β-unsaturated ketones with KTPBH will be reported shortly.

The stereoselectivity (Table III) of the reagent toward cyclic ketones was also studied. Generally, potassium triphenylborohydride exhibited very good stereoselectivity,[7] comparable to other stereoselective hydride reducing agents, such as Li-*sec*-Bu_3BH, K-*sec*-Bu_3BH,[1a] and $LDMBH_2$–2DME.[6a] The reduction of *d*-camphor was very slow, giving only 25% reduction in 24 h at 25 °C. Therefore the reduction was carried out at reflux (65 °C); good stereoselectivity (96.5% exo) was realized at this temperature.

Quinones (Table IV). *p*-Benzoquinone consumed 1 equiv of hydride rapidly with an accompanying color change to dark green and formation of a precipitate. The color changed to violet on standing. The one hydride uptake with no hydrogen evolution, and the color changes suggest that 1,4-addition of the reagent occur to give an enolate, which would form hydroquinone upon acid hydrolysis as shown below. Indeed, hydroquinone was isolated in 75% yield after hydrolysis (eq 4).



(4)

On the other hand, anthraquinone consumed 2 equiv of hydride without hydrogen evolution, suggesting a clean reduction to 9,10-dihydro-9,10-anthracenediol.[2b]

Table IV. Reaction of Potassium Triphenylborohydride with Representative Quinones in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
p-benzoquinone[c,d]	0.5	0.04	1.02	0.98
	3.0[e]	0.04	1.06	1.02
	24.0	0.04	1.16	1.12
anthraquinone[c,f]	1.0	0.00	1.43	1.43
	6.0	0.00	1.69	1.69
	24.0	0.00	2.03	2.03

[a,b] See the corresponding footnotes in Table I. [c] Each measurement was done separately. [d] Color changed to dark green immediately, a precipitate was obtained, and then color changed to violet. [e] A 75% yield of hydroquinone was obtained by isolation. [f] Reverse addition; KTPBH was added to a suspension of anthraquinone. Color changed to dark green immediately.

Table V. Reaction of Potassium Triphenylborohydride with Representative Acids and Acyl Derivatives in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
hexanoic acid[c]	1.0	0.73	0.73	0.00
	3.0	0.98	0.98	0.00
benzoic acid	3.0	0.36	0.36	0.00
	12.0	0.57	0.57	0.00
acetic anhydride	1.0	0.00	0.86	0.86
	6.0	0.00	1.64	1.64
	24.0	0.00	1.88	1.88
succinic anhydride	1.0	0.00	1.04	1.04
	6.0	0.00	1.55	1.55
	24.0	0.00	1.64	1.64
phthalic anhydride	1.0	0.00	1.39	1.39
	6.0	0.00	1.81	1.81
	24.0	0.00	1.96	1.96
hexanoyl chloride	0.25	0.00	2.03	2.03
benzoyl chloride	0.25	0.00	1.98	1.98
	0.5[d]	0.00	1.98	1.98

[a,b] See the corresponding footnotes in Table I. [c] The solution turned milky and got thicker with time. [d] Product study was performed utilizing 1.0 equiv of KTPBH at −78 °C, and benzyl alcohol was obtained in 48% yield.

Carboxylic Acids and Acyl Derivatives (Table V). Carboxylic acids react with evolution of 1 equiv of hydrogen immediately by the reaction with other borohydrides such as $LiEt_3BH$[2b] and $LiBH_4$.[9] However, with

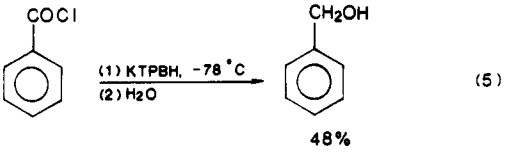
Table VI. Reaction of Potassium Triphenylborohydride with Representative Esters and Lactones in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
ethyl hexanoate	4.0	0.00	0.00	0.00
ethyl benzoate	24.0	0.00	0.52	0.52
phenyl acetate	6.0	0.00	0.71	0.71
	24.0	0.00	1.18	1.18
γ-butyrolactone	24.0	0.00	0.24	0.24
phthalide	6.0	0.00	0.83	0.83
	24.0	0.00	1.01	1.01
isopropenyl acetate	6.0	0.00	1.90	1.90
	24.0	0.00	1.94	1.94
	48.0	0.00	1.94	1.94

[a,b] See the corresponding footnotes in Table I.

KTPBH, hexanoic acid gave 1 equiv of hydrogen over 3 h, and benzoic acid evolved only 0.57 equiv in 12 h at 0 °C. Acid chlorides were rapidly reduced to the corresponding alcohols, whereas cyclic anhydrides were slowly reduced to the lactones. Thus, KTPBH is considerably milder than $LiBH_4$[9] but distinctly stronger than $K(i\text{-}PrO)_3BH$.[4a]

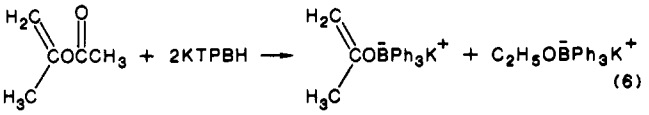
In order to test for aldehyde formation, one equiv of KTPBH was added to benzoyl chloride at −78 °C. However, only benzyl alcohol was obtained in a yield of 48% (eq 5).



(5)

Esters and Lactones (Table VI). Ethyl hexanoate is inert to KTPBH, whereas ethyl benzoate is reduced very slowly, showing a 26% reduction in 24 h. The same tendency was also observed in the reduction of lactones, phthalide being reduced faster than γ-butyrolactone. On the other hand, isopropenyl acetate was rapidly reduced, consuming 2 equiv of hydrides in 1 h.

A simple explanation would be the reduction of acetate group (require two hydrides), leaving boron enolate intact as shown in eq 6. However this is unlikely, since the



(6)

enolate should be reduced readily in the presence of excess hydride as we have seen in the reduction of α,β-unsaturated ketones. This suggests an alternative scheme[10] for the rapid reaction observed. $LiEt_3BH$[2b] was previously reported to utilize 3 equiv of hydride, the acetate group being reduced to ethanol stage (two hydrides) and isopropenyl group to isopropyl alcohol (one hydride).

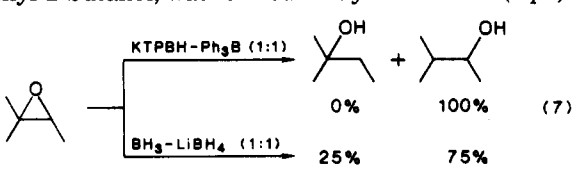
Epoxides (Table VII). 1,2-Butene oxide and styrene oxide were reduced in 48 h at 0 °C and 12 h at room temperature. Cyclohexene oxide was reduced slowly over 48 h at room temperature, and *trans*-2-butene oxide reacted only sluggishly, giving only 17% reduction in 48 h. Trisubstituted and tetrasubstituted epoxides, 2-methyl-2-butene oxide, 1-methylcyclohexene oxide, and 2,3-dimethyl-2-butene oxide also reacted very sluggishly at room temperature. However, the addition of Ph_3B dramatically

Table VII. Reaction of Potassium Triphenylborohydride with Representative Epoxides in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
1-butene oxide	6.0	0.00	0.65	0.65
	24.0	0.00	0.95	0.95
	48.0	0.00	1.00	1.00
	0.5[c]	0.00	1.00	1.00
	6.0[d]	0.00	0.89	0.89
	12.0[d,f]	0.00	1.00	1.00
	0.25[c,d]	0.00	1.00	1.00
styrene oxide	6.0	0.00	0.63	0.63
	24.0	0.00	0.96	0.96
	48.0	0.00	1.00	1.00
	0.5[c]	0.00	1.00	1.00
	3.0[d]	0.00	0.62	0.62
	12.0[d,g]	0.00	1.00	1.00
	0.25[c,d]	0.00	1.00	1.00
cyclohexene oxide	24.0	0.00	0.68	0.68
	48.0	0.00	1.00	1.00
	0.5[c,h]	0.00	1.00	1.00
	6.0[d]	0.00	0.42	0.42
	24.0[d]	0.00	0.73	0.73
	48.0[d]	0.00	1.00	1.00
trans-2-butene oxide	24.0[d,i]	0.00	0.10	0.10
	48.0[d]	0.00	0.17	0.17
	24.0[c,d]	0.00	0.10	0.10
	1.0[e,j]	0.00	1.00	1.00
2-methyl-2-butene oxide	24.0[c]	0.00	0.09	0.09
	1.0[e,k]	0.00	1.00	1.00
	48.0[d]	0.00	0.09	0.09
	72.0[d,l]	0.00	0.14	0.14
1-methylcyclohexene oxide	1.0[e,m]	0.00	1.00	1.00
	48.0[d,n]	0.00	0.20	0.20
	72.0[d]	0.00	0.25	0.25
2,3-dimethyl-2-butene oxide	48.0[d]	0.00	0.00	0.00
	24.0[d,e]	0.00	0.05	0.05

[a,b] See the corresponding footnotes in Table I. [c] In the presence of 0.1 mmol of Ph_3B per mmol of epoxide. [d] At 25 °C. [e] In the presence of 1.0 mmol of Ph_3B per mmol of epoxide. [f] Product studies denoted by *f–k* were performed by utilizing 1.1 equiv of KTPBH at 25 °C and the corresponding alcohols were estimated by GLC. A 98% yield of 2-butanol in 24 h. [g] A 95% yield of phenylethanols, the ratio of 1- and 2-phenylethanol being 97.5/2.5. [h] A 99.5% yield of cyclohexanol. [i] A 8% yield of 2-butanol. [j] A 99% yield of 2-butanol. [k] A 99% yield of 3-methyl-2-butanol. [l] A 8% yield of 2-methyl-2-butanol. [m] A 94.7% yield of *cis*-2-methylcyclohexanol. [n] A 11.1% yield of 1-methylcyclohexanol.

changed the situation. The presence of 0.1 equiv of Ph_3B made the reductions of the terminal epoxides and cyclohexene oxide complete in 0.5 h at 0 °C. The reductions of *trans*-2-butene oxide and the two trisubstituted epoxides were also complete in 0.5–1 h in the presence of 1 equiv of Ph_3B. Conversely 2,3-dimethyl-2-butene oxide was not reduced even in the presence of Ph_3B. With trisubstituted epoxides, Ph_3B not only accelerated the rates but also changed the products drastically. Thus the reduction of 2-methyl-2-butene oxide with KTPBH was very slow (8% in 72 h) and gave the more substituted 2-methyl-2-butanol, as a sole product, however, in the presence of Ph_3B only 3-methyl-2-butanol, was formed in a yield of 99% (eq 7).



(7)

A similar trend has been observed with BH_3-$LiBH_4$ (1:1).[11] Similary the reduction of 1-methylcyclohexene oxide gave *cis*-2-methylcyclohexanol as a sole product in 90% isolated

(9) Yoon, N. M.; Cha, J. S. *J. Korean Chem. Soc.* **1977**, *21*, 108.
(10) Warwell, S.; Schmitt, G.; Asinger, F. *J. Organomet. Chem.* **1972**, *36*, 243.
(11) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1968**, *90*, 2686.

Table VIII. Reaction of Potassium Triphenylborohydride with Representative Amides and Nitriles in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
hexanamide	3.0	0.02	0.02	0.00
	24.0	0.08	0.08	0.00
benzamide	3.0	0.04	0.04	0.00
	24.0	0.35	0.35	0.00
N,N-dimethylhexanamide	24.0	0.00	0.00	0.00
N,N-dimethylbenzamide	24.0	0.00	0.00	0.00
hexanenitrile	24.0	0.00	0.00	0.00
benzonitrile	6.0	0.00	0.35	0.35
	24.0	0.00	0.43	0.43

[a,b] See the corresponding footnotes in Table I.

Table IX. Reaction of Potassium Triphenylborohydride with Representative Nitro Compounds and Their Derivatives in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
1-nitropropane	6.0	0.00	0.83	0.83
	24.0	0.00	0.95	0.95
nitrobenzene[c]	3.0	0.00	0.61	0.61
	24.0	0.00	1.57	1.57
azobenzene	24.0	0.00	0.00	0.00
azoxybenzene[d]	24.0	0.00	0.00	0.00

[a,b] See the corresponding footnotes in Table I. [c] A white precipitate formed immediately. [d] The color changed to dark brown immediately.

yield. Several years ago, $NaBH_3CN$–BF_3 was reported to give similar ring opening,[12] but we believe KTPBH–Ph_3B system to be the reagent of choice for this kind of opening of trisubstituted epoxide.

Amides and Nitriles (Table VIII). Primary amides, hexanamide, and benzamide are not reduced by KTPBH. Hydrogen evolution was also sluggish. Tertiary amides, such as *N,N*-dimethylhexanamide and *N,N*-dimethylbenzamide, do not react with KTPBH under these conditions. Hexanenitrile is also inert to the reagent, whereas benzonitrile was reduced very slowly showing a 20% reduction in 24 h at 0 °C.

Nitro Compounds and Their Derivatives (Table IX). $LiEt_3BH$[2b] evolves 1 equiv of hydrogen from 1-nitropropane due to the acidic hydrogen. However, the slow reduction with KTPBH proceeds without hydrogen evolution. Nitrobenzene formed a white precipitate immediately, but reduction proceeded slowly, and with hydrogen evolution. Azobenzene and azoxybenzene did not consume hydride in spite of the dark brown color which appeared immediately in the latter reaction mixture.

Other Nitrogen Compounds (Table X). Cyclohexanone oxime was not reduced with KTPBH under these conditions. Unlike $LiBH_4$ which liberates 1 equiv of hydrogen readily, almost no hydrogen evolution was observed with KTPBH. Phenyl isocyanate was rapidly reduced to the amide stage. Pyridine and pyridine *N*-oxide are inert to the reagent under the standard conditions.

Halides and Tosylates (Table XI). 1-Iodooctane was reduced within 1 h, whereas 1-bromooctane and *n*-octyl tosylate were reduced at moderate rate (24 h), and 1-chlorooctane was reduced very slowly. Secondary halides and tosylate (2-bromooctane, cyclohexyl bromide, and cyclohexyl tosylate) were all inert to the reagent under these conditions. These results suggest that *n*-alkyl iodide, bromide, and tosylate can be selectively reduced in the presence of *sec*-alkyl halide or tosylate.

Sulfur Derivatives (Table XII). Di-*n*-butyl disulfide was reduced very slowly, whereas diphenyl disulfide was readily reduced to the corresponding thiol in 1 h at 0 °C, with rapid evolution of 1 equiv of hydrogen. These results suggest the possibility of selective reduction of aromatic disulfides with KTPBH in the presence of aliphatic disulfides.[13] Sulfides, sulfoxides, and sulfones are all inert to the reagent under these conditions. It is interesting to note that KTPBH evolves only 2 equiv of hydrogen with *p*-toluenesulfonic acid monohydrate, similar to $LiEt_3BH$[2b]

Table X. Reaction of Potassium Triphenylborohydride with Other Representative Nitrogen Compounds in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
cyclohexanone oxime	12.0	0.06	0.06	0.00
phenyl isocyanate	1.0	0.00	0.82	0.82
	3.0	0.00	1.01	1.01
pyridine	24.0	0.00	0.00	0.00
pyridine *N*-oxide	24.0	0.00	0.00	0.00

[a,b] See corresponding footnotes in Table I.

Table XI. Reaction of Potassium Triphenylborohydride with Representative Halides and Tosylates in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
1-chlorooctane	3.0	0.00	0.06	0.06
	24.0	0.00	0.22	0.22
1-bromooctane[c]	3.0	0.00	0.43	0.43
	24.0[d]	0.00	0.95	0.95
1-iodooctane[c]	0.5	0.00	0.94	0.94
	1.0	0.00	1.06	1.06
2-bromooctane	24.0	0.00	0.00	0.00
cyclohexyl bromide	24.0	0.00	0.00	0.00
n-octyl tosylate	6.0	0.00	0.28	0.28
	24.0	0.00	1.07	1.07
cyclohexyl tosylate	24.0	0.00	0.00	0.00

[a,b] See the corresponding footnotes in Table I. [c] A white gel-like precipitate formed gradually. [d] 6.4% 1-bromooctane remained.

Table XII. Reaction of Potassium Triphenylborohydride with Representative Sulfur Derivatives in Tetrahydrofuran at 0 °C

compound[a]	time, h	hydrogen evolved[b]	hydride used[b]	hydride used for redn[b]
di-*n*-butyl disulfide	6.0	0.03	0.11	0.08
	24.0	0.05	0.21	0.16
diphenyl disulfide	0.5	0.88	1.75	0.87
	1.0	1.01	1.99	0.98
	3.0	1.03	2.02	0.99
	6.0	1.03	2.02	0.99
methyl *p*-tolyl sulfide	24.0	0.00	0.00	0.00
dimethyl sulfoxide	24.0	0.00	0.00	0.00
diphenyl sulfone	24.0	0.00	0.00	0.00
p-toluenesulfonic acid monohydrate	0.5	1.76	1.76	0.00
	3.0	2.06	2.06	0.00
	6.0	2.06	2.06	0.00

[a,b] See the corresponding footnotes in Table I.

(12) Hutchins, R. O.; Taffer, I. M.; Burgoyne, W. *J. Org. Chem.* **1981**, *46*, 5214. They reported that 84% *cis*-2-methylcyclohexanol and 2.6% 1-methylcyclohexanol could be obtained from the reduction of 1-methylcyclohexene oxide.

(13) Brown, H. C.; Nazer, J. S.; Cha, J. S. *Synth. Commun.* **1984**, 498.

and in contrast to $LiBH_4$,[9] which evolves 3 equiv of hydrogen.

Simplified Product Isolation. KTPBH possesses a practical advantage in facilitating the recovery of alcohol product. Thus it was found that the procedure[14] developed for K-9-OThx-9-BBNH could also be applied to KTPBH. Controled addition of water to the reaction mixture converts the triphenylborane moiety to an "ate" complex (eq 8). When the THF solvent is removed and pentane is

$$[Ph_3BOR]^-K^+ + H_2O \xrightarrow{\text{pentane}} [Ph_3BOH]^-K^+ + ROH \quad (8)$$

added, the "ate" complex precipitates. The isolation of a 95% yield of 2-methylcyclohexanol following removal of Ph_3B moiety from the reaction of 2-methylcyclohexanone with KTPBH illustrates the utility of this procedure.

Experimental Section

General. The reaction flasks and other glassware required for the experiments were oven dried at 140 °C for several hours, assembled hot, and cooled under a stream of dry nitrogen. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered side arms, by using standard techniques for handling air-sensitive materials.[15] Hypodermic syringes were used to transfer the solutions.

Materials. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl and stored under dry nitrogen. Triphenylborane (8–10% sodium hydroxide adduct solution) was obtained from Du Pont and was separated from the sodium hydroxide adduct prior to use.[16] Potassium hydride was used as received from Fluka. Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary.[17]

Instruments. A Varian 3700 chromatograph equipped with a thermal conductivity detector was used. All of the yields of products were determined by utilizing suitable internal standards and authentic mixtures. Refractive indexes were measured on a Bausch and Lomb Abbe-3L refractometer. Melting point was measured on an Electrochemical melting point apparatus. NMR spectrometers used were a Varian Model E-M 360A (60 MHz) for ^1H NMR spectrum and a Varian FT-80A for ^{11}B NMR spectrum. IR spectra were taken with a Shimadzu IR-440 spectrometer.

Preparation of Potassium Triphenylborohydride (KTPBH). An oven-dried, 100-mL, round-bottom flask with a side arm, a condenser, and an adaptor was connected to a mercury bubbler. The flask was flushed with dry nitrogen and maintained under a slight pressure of nitrogen. To this was added 12.0 g of potassium hydride (300 mmol, 50% excess) as an oil suspension by using a double-ended needle. The mineral oil was removed by washing with *n*-pentane (3 × 60 mL). To this was added 250 mL of 0.80 M solution of triphenylborane in THF (200 mmol), with stirring at room temperature. After 6 h, the reaction mixture was centrifuged and the total volume of clear solution increased from 250 to 260 mL. In another run an aliquot was removed at intervals, excess KH was removed by a centrifugation and the sample was injected into a hydrolysis solution consisting of a 1:1 mixture of 4 N H_2SO_4 and THF. The hydride concentration was determined from the corrected volume of hydrogen evolved and was found to be 0.52 (135 mmol, 67.6%, 1 h), 0.68 (177 mmol, 88.4%, 3 h), 0.76 (197 mmol, 98.7%, 6 h), and 0.76 M (197 mmol, 98.7%, 12 h). The KTPBH solutions were routinely prepared in 150–200-mmol scale as above (6 h). The ^{11}B NMR spectrum of the resulting clear solution showed only a double centered at δ −7.96 (J_{B-H} = 78.7 Hz), and the IR spectrum showed a strong absorption at 2200 cm^{-1}. This KTPBH solution (0.76 M in hydride) was analyzed for boron and potassium. The boron concentration was estimated to be 0.76 M from the amount of phenol produced by oxidation of an aliquot of the solution with $NaOH-H_2O_2$. The potassium content was measured as potassium hydroxide, by quenching with water and titration with standard acid. This solution of KTPBH in THF was maintained under dry nitrogen at room temperature and analyzed for the hydride concentration periodically by hydrolysis of aliquots. The hydride concentration of KTPBH remained constant (0.76 M) over 2 months at room temperature.

Procedure for Study of Rate and Stoichiometry. All reactions were carried out under dry nitrogen. The reduction of *n*-hexanal is described to examplify the reduction procedure. The KTPBH solution, (21.0 mL of a 0.76 M, solution 16 mmol), and 7.0 mL of THF were introduced into a dried 50-mL flask fitted with a rubber syringe cap on a inlet port, a magnetic stirring bar, and a reflux condenser connected to a gas buret. The flask was immersed in an ice bath, and 4.0 mL of 1.0 M solution of *n*-hexanal (4.0 mL) in THF was injected rapidly. Hydrogen evolution was monitored. In this way, a solution was obtained which was 0.5 M in KTPBH and 0.125 M in *n*-hexanal. Upon addition of the compound, 1.5 mL of hydrogen was evolved, corresponding to 0.02 mmol/mmol of compound. No more hydrogen evolution was observed throughout the reaction. After 5 min, a 8.0-mL aliquot of the reaction mixture was removed and injected into a hydrolyzing mixture of 4 N H_2SO_4–THF (1:1). The hydrogen evolved was 2.99 mmol, indicating that 1.0 mmol of *n*-hexanal had used 1.01 mmol of hydride, of which 0.99 mmol (1.01 − 0.02 = 0.99) of hydride was used for reduction. Aliquot was also analyzed after 1 h. The amount of hydrogen evolved was also 2.99 mmol, indicating the reaction was complete within 5 min.

Procedure for Product Analysis by GLC. The reduction of cinnamaldehyde to cinnamyl alcohol is representative. In a 50-mL flask, fitted with a rubber syringe cap on an inlet, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, were placed 10.5 mL (8.0 mmol) of a 0.76 M solution of KTPBH and 3.5 mL of dry THF. With stirring, 2 mL (2.0 mmol) of 1.0 M solution of cinnamaldehyde was added at 0 °C. After stirring for 3 h, the excess hydride was hydrolyzed with 1.0 mL of 2 M HCl. Then the reaction mixture was oxidized by the addition of 2.0 mL of 2 N NaOH, followed by 0.8 mL of 30% H_2O_2 and heating at 30–35 °C for 2 h. After addition of 2.0 mmol of *n*-octyl alcohol as an internal standard, the aqueous layer was saturated with anhydrous K_2CO_3, and GLC analysis of the dry THF layer indicated the presence of cinnamyl alcohol in 97% yield.

Preparative Procedure for the Reduction of 1-Methylcyclohexene Oxide. In a large-scale reaction, the simplified isolation procedure was followed.[7] In a 100-mL flask was placed 14.5 mL (11 mmol) of a 0.76 M solution of KTPBH and 13.0 mL (10 mmol) of 0.76 M solution of Ph_3B–THF. The mixture was stirred at 0 °C, and 10.0 mmol (10 mL) of precooled 1-methylcyclohexene oxide was introduced. After being stirred for 0.5 h, the reaction mixture was hydrolyzed with 0.3 mL of water for 0.5 h at room temperature. The THF solvent was removed by an aspirator, and pentane (20 mL) was added to the residue. A white solid precipitated as the mixture was stirred for 1 h. The precipitate was filtered and the pentane was pumped off by aspirator. This gave 1.0 g (90%) of essentially pure *cis*-2-methylcyclohexanol. GLC examination showed that the product was 100% *cis*-2-methylcyclohexanol, and the identity of the product was further confirmed by NMR.

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Registry No. Hydroquinone, 123-31-9; 9,10-dihydro-9,10-anthracenediol, 4981-66-2; benzyl alcohol, 100-51-6; potassium triphenylborohydride, 99747-36-1; potassium hydride, 7693-26-7; 1-hexanol, 111-27-3; 3-hexanol, 623-37-0; 3-ethyl-3-pentanol,

(14) Brown, H. C.; Cha, J. S.; Nazer, B. *J. Org. Chem.* **1985**, *50*, 549.
(15) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.
(16) Isolation of triphenylborane (Ph_3B) from the adduct solution (ca. 8% Ph_3B as Ph_3B·NaOH) involves neutralization with concentrated HCl and then drying the isolated triphenylborane in a vacuum oven.
(17) Perrin, D. D.; Armarego, W. L. F.; Perrin D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, England, 1980.

597-49-9; phenol, 108-95-2; 2,6-di-*tert*-butylphenol, 128-39-2; *n*-hexylamine, 111-26-2; 1-hexanethiol, 111-31-9; benzenethiol, 108-98-5; *n*-hexanol, 66-25-1; benzaldehyde, 100-52-7; 2-heptanone, 110-43-0; norcamphor, 497-38-1; acetophenone, 98-86-2; benzophenone, 119-61-9; cinnamaldehyde, 104-55-2; 3-penten-2-one, 625-33-2; 2-cyclohexenone, 930-68-7; chalcone, 94-41-7; cinnamyl alcohol, 104-54-1; cyclohexanol, 108-93-0; 1,3-diphenyl-2-propen-1-ol, 4663-33-6; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 3,3,5-trimethylcyclohexanone, 873-94-9; 4-*tert*-butylcyclohexanone, 98-53-3; *d*-camphor, 464-49-3; *cis*-2-methylcyclohexan-1-ol, 7443-70-1; *trans*-3-methylcyclohexan-1-ol, 7443-55-2; *cis*-4-methylcyclohexan-1-ol, 7731-28-4; *trans*-3,3,5-trimethylcyclohexan-1-ol, 767-54-4; *cis*-4-*tert*-butylcyclohexan-1-ol, 98-52-2; *endo*-norcamphor-2-ol, 497-36-9; (1*R*)-*exo*-camphor-2-ol, 10334-13-1; *p*-benzoquinone, 106-51-4; anthraquinone, 84-65-1; hexanoic acid, 142-62-1; benzoic acid, 65-85-0; acetic anhydride, 108-24-7; succinic anhydride, 108-30-5; phthalic anhydride, 85-44-9; hexanoyl chloride, 142-61-0; benzoyl chloride, 98-88-4; ethyl hexanoate, 123-66-0; ethyl benzoate, 93-89-0; phenyl acetate, 122-79-2; γ-butyrolactone, 96-48-0; phthalide, 87-41-2; isopropenyl acetate, 108-22-5; 1-butene oxide, 106-88-7; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; *trans*-2-butene oxide, 21490-63-1; 2-methyl-2-butene oxide, 5076-19-7; 1-methylcyclohexene oxide, 1713-33-3; 2,3-dimethyl-2-butene oxide, 5076-20-0; 2-butanol, 78-92-2; 1-phenylethanol, 98-85-1; 3-methyl-2-butanol, 598-75-4; 2-methyl-2-butanol, 75-85-4; 1-methylcyclohexanol, 590-67-0; hexanamide, 628-02-4; benzamide, 55-21-0; *N,N*-dimethylhexanamide, 5830-30-8; *N,N*-dimethylbenzamide, 611-74-5; hexanenitrile, 628-73-9; benzonitrile, 100-47-0; 1-nitropropane, 108-03-2; nitrobenzene, 98-95-3; azobenzene, 103-33-3; azoxybenzene, 495-48-7; cyclohexanone oxime, 100-64-1; phenyl isocyanate, 103-71-9; pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7; 1-chlorooctane, 111-85-3; 1-bromooctane, 111-83-1; 1-iodooctane, 629-27-6; 2-bromooctane, 557-35-7; cyclohexyl bromide, 108-85-0; *N*-octyl tosylate, 3386-35-4; cyclohexyl tosylate, 953-91-3; di-*n*-butyl disulfide, 629-45-8; dipheny disulfide, 882-33-7; methyl *p*-tolyl sulfide, 623-13-2; dimethyl sulfoxide, 67-68-5; diphenyl sulfone, 127-63-9; *p*-toluenesulfonic acid, 104-15-4; triphenylborane, 960-71-4.

Molybdenum(0)-Catalyzed Reductive Dehalogenation of α-Halo Ketones with Phenylsilane

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Reductive dehalogenation of α-halo ketones and esters is effectively achieved by using a novel reducing system comprised of phenylsilane and catalytic amounts of molybdenum hexacarbonyl and triphenylphosphine. Reactions are carried out at 60–80 °C in variety of solvents, including THF, benzene, toluene, and diglyme. With respect to α-halo carbonyl reduction, this combination of Mo(0) and phenylsilane is superior to our previously described palladium(0)/diphenylsilane system and produces higher yields and cleaner products.

Introduction

Methods for selective removal of halogen substituents adjacent to a carbonyl functionality yielding the parent carbonyl compound have recently received considerable attention. The various procedures and reagents that have been developed for reductive dehalogenation of α-halo carbonyl compounds include (a) reducing agents such as zinc in acetic acid,[1] sodium dithionate,[2] organotin hydrides,[3] borohydride,[4] and low-valent transition-metal salts (e.g. titanium(III),[5] vanadium(II),[6] and chromium(II)[7]); (b) strong nucleophiles that may act as reducing agents such as iodide ions,[8] phosphines,[9] iodophosphines,[10] iodotrimethylsilane,[11] thiols,[12] selenols,[13] tellurolates,[14] amines[15]; (c) stoichiometric amounts of zero-valent transition-metal carbonyls of iron,[16] cobalt,[17] and molybdenum[18]; and (d) heterogeneous hydrogenation catalysts involving transition-metal surfaces.[19]

In recent years we have developed an array of composite reducing systems based on new combinations of tin or silicon hydrides with transition-metal catalysts, including palladium,[20] ruthenium,[21] and molybdenum.[22] These represent a promising new family of reducing media, particularly useful for reductive cleavage of allylic heter-

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(1) (a) Sauers, R. R.; Hu, C. K. *J. Org. Chem.* **1971**, *36*, 1153. (b) Zimmerman, H. E.; Mais, A. *J. Am. Chem. Soc.* **1959**, *81*, 3644. (c) Evans, R. M.; Hamlet, J. C.; Hunt, J. S.; Jones, P. G.; Long, A. G.; Oughton, J. F.; Stephenson, L.; Walker, T.; Wilson, B. M. *J. Chem. Soc.* **1956**, 4356. (d) Schreiber, K.; Ronsch, H.; *Justus Liebigs Ann. Chem.* **1965**, *681*, 196. (e) Grieco, P. A. *J. Org. Chem.* **1972**, *37*, 2363.

(2) (a) Ho, T. L.; Wong, C. M. *J. Org. Chem.* **1974**, *39*, 562. (b) Chung, S. K.; Hu, Q. Y. *Synth. Commun.* **1982**, *12*, 261.

(3) Kuivila, H. G.; Menapace, L. W. *J. Org. Chem.* **1963**, *28*, 2165.

(4) Goto, T.; Kishi, Y. *Tetrahedron Lett.* **1961**, 513.

(5) (a) Ho, T.-L.; Wong, C. M. *Synth. Commun.* **1973**, *3*, 237. (b) McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281. (c) Conant, J. B.; Lutz, R. E. *J. Am. Chem. Soc.* **1925**, *47*, 881.

(6) Ho, T. L.; Olah, G. A. *Synthesis* **1976**, 807.

(7) (a) Castro, C. E.; Kray, W. C., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 2768.

(8) (a) Townsend, J. M.; Spencer, T. A. *Tetrahedron Lett.* **1971**, 137. (b) Olah, G. A.; Vankar, Y. D.; Fung, A. P. *Synthesis* **1979**, 59. (c) Gemel, A. L.; Luche, J. L. *Tetrahedron Lett.* **1980**, *21*, 3195. (d) Ho, T.-L. *Synth. Commun.* **1979**, *9*, 241. (e) Fleisker, G. A.; Kendall, E. C. *J. Org. Chem.* **1951**, *16*, 573. (f) Rosenkranz, G.; Djerassi, C.; Yashin, R.; Pataki, J. *Nature (London)* **1951**, *168*, 28.

(9) (a) Borowitz, I. J.; Parnes, H. *J. Org. Chem* **1967**, *32*, 3560. (b) Borowitz, I. J.; Virkhaus, R. *J. Am. Chem. Soc.* **1963**, *85*, 2183. (c) Borowitz, I. J.; Grossman, L. I. *Tetrahedron Lett.* **1962**, 471. (d) Borowitz, I. J.; Kirby, K. C., Jr.; Virkhaus, R. *J. Org. Chem.* **1966**, *31*, 4031. (e) Hoffmann, H.; Dier, H. J. *Tetrahedron Lett.* **1962**, 583. (f) Chopard, P. A.; Hudson, R. F.; Klopman, G. *J. Chem. Soc.* **1965**, 1379. (g) Borowitz I. J.; Kirby, K. C., Jr.; Rusek, P, E.; Lord, E. *J. Org. Chem.* **1969**, *34*, 2687.

(10) Denis, J. N.; Krief, A. *Tetrahedron. Lett.* **1981**, 22, 1431.

0022-3263/87/1952-5570$01.50/0