

phenyl ester, 76359-02-9; 2-[(phenylthio)methyl]cyclohexanecarbo-selenoic acid *Se*-phenyl ester, 76359-03-0; 5-deoxy-3-*O*-methyl-1,2-*O*-(1-methylethylidene)- α -D-xylo-hexofuranuronoselenoic acid *Se*-phenyl ester, 76359-04-1; 2-propanamine, 75-31-0; *N*-ethylethan-amine, 109-89-7; benzenemethanamine, 100-46-9; *N*-(1-methylethyl)benzeneacetamide, 5215-54-3; *N,N*-diethylbenzeneacetamide, 2431-96-1; *N*-(phenylmethyl)benzeneacetamide, 7500-45-0; 4-methoxy-*N*-(1-methylethyl)benzamide, 7464-44-0; *N,N*-diethyl-4-methoxybenzamide, 7465-86-3; 4-chloro-*N*-(1-methylethyl)benzamide, 7464-41-8; 4-chloro-*N,N*-diethylbenzamide, 7461-38-3; *N*-(1-methylethyl)octanamide, 76359-05-2; *N*-(1-methylethyl)cyclohexanecarboxamide, 6335-52-0; *N,N*-diethylcyclohexanecarboxamide, 5461-52-9; α -methyl-*N*-(1-methylethyl)cyclohexaneacetamide, 76359-06-3.

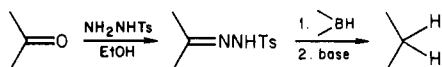
A Mild and Convenient Conversion of Ketones to the Corresponding Methylene Derivatives via Reduction of Tosylhydrazones by Bis(benzoyloxy)borane

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Received October 22, 1980

The conversion of carbonyl compounds to the corresponding methylene derivatives is one of the key transformations in organic synthesis. Not surprisingly, a great deal of literature exists concerning this transformation.¹ The classical reduction procedures utilize strong acids (Clemmensen) or bases (Wolff-Kishner) which preclude the presence of sensitive functional groups. However, the reduction of tosylhydrazones with boron hydride reagents offers a mild and convenient alternative to the classical methods.²⁻⁵



One of the most versatile of these procedures involves the use of catecholborane as the reducing agent.² The catecholborane-tosylhydrazone procedure offers a number of advantages over methods utilizing sodium borohydride^{3,5} and sodium cyanoborohydride.⁴ These advantages include (a) efficient use of hydride (only 1 equiv is necessary compared to the large excesses required in the other procedures), (b) mild reaction conditions (room temperature, neutral pH, and the use of common aprotic solvents), (c) the inertness of most functional groups toward catecholborane (only aldehydes are reduced faster than tosylhydrazones), and (d) formation of only a single hydrocarbon product. The catecholborane procedures reduce a variety of saturated⁶ and unsaturated carbonyl compounds.^{7,8} Regiospecific isomerizations occur during the reduction of α,β -unsaturated carbonyl derivatives often leading to unique alkenes^{7,8} and allenes (from the reduction of acetylenic reagents).⁹ The reaction can also be used

Table I. Conversion of Carbonyl Reagents into the Corresponding Methylene Derivatives^a

carbonyl reagent ^a	product ^b	% yield ^c
$\text{CH}_3(\text{CH}_2)_8\text{CHO}$	$\text{CH}_3(\text{CH}_2)_8\text{CH}_2$	91 (99) ^d
$\text{CH}_3(\text{CH}_2)_5\text{C(=O)CH}_3$	$\text{CH}_3(\text{CH}_2)_5\text{CH}_2$	78
		82
		82 (92) ^d
		68
$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C(=O)CH}_2\text{CO}_2\text{H}$	$\text{CH}_2=\text{CH}(\text{CH}_2)_{13}\text{CO}_2\text{H}$	96

^a The carbonyl reagents were first converted into the corresponding tosylhydrazone derivatives. ^b Products exhibited physical and spectral parameters in agreement with literature reports. ^c Isolated yields. ^d GLC analysis.

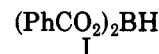
Table II. Conversion of α,β -Unsaturated Carbonyl Reagents into the Corresponding Methylene Derivatives^a

carbonyl reagent ^a	product ^b	% yield ^c
		85 (95) ^d
		83 (90) ^d
		21

^a The carbonyl reagents were first converted into the corresponding tosylhydrazone derivatives. ^b Products exhibited physical and spectral parameters in agreement with literature reports. ^c Isolated yields. ^d GLC analysis.

to incorporate deuterium regiospecifically by using deuterium oxide as the source of deuterium.¹⁰

The purpose of this study was to investigate reducing agents which are as versatile as catecholborane but which can be more readily prepared. We report that bis(benzoyloxy)borane, I,^{11,12} effectively reduces tosylhydrazones to



the corresponding methylene derivatives. The results parallel those obtained using catecholborane.

Results and Discussions

Catecholborane exhibits a stability and reactivity which is greater than most boronic acid esters presumably due to delocalization of the nonbonding p electrons on oxygen into the benzene ring.¹³ Apparently, the carbonyl groups in the acyloxyboranes behave similarly since a number of bis(acyloxy)boranes are stable.¹¹

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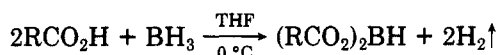
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R = alkyl or phenyl

We decided to investigate bis(benzoyloxy)borane as a reducing agent because of its ready preparation from benzoic acid.¹⁴ The reduction of tosylhydrazones leads to single hydrocarbon products in high yields. The reaction times vary, generally being from 0.5 to 2 h.¹⁵ Our results are summarized in Table I.

Unsaturated carbonyl derivatives are readily reduced by bis(benzoyloxy)borane. As with catecholborane a regio-specific and stereospecific rearrangement occurs. In previous studies, this rearrangement has permitted the syntheses of thermodynamically unstable materials.⁷⁻⁹ Our results are summarized in Table II.

In summary, the reduction of tosylhydrazones by bis(benzoyloxy)borane offers a convenient alternative to the Wolff-Kishner and Clemmensen reductions.

Experimental Section

Proton NMR spectra were recorded on a Varian T-60 spectrometer. All chemical shifts are reported in parts per million downfield from Me₄Si.

All carbonyl reagents were obtained commercially and distilled prior to use. The only exception was 6-oxo-15-hexadecenoic acid which was prepared according to a published procedure.¹⁶ Melting points are uncorrected.

Tosylhydrazone Preparation. The tosylhydrazones were prepared by reacting the appropriate ketone with *p*-toluenesulfonhydrazide in ethanol.⁸ The melting points of the tosylhydrazones are given in parenthesis following the name of the carbonyl reagent from which they were prepared: decanal (106–108 °C), 2-octanone (96.5–98 °C), 4-*tert*-butylcyclohexanone (149–150 °C), benzaldehyde (127–128 °C), acetophenone (145–146 °C), 6-oxo-15-hexadecenoic acid (82–84 °C), cinnamaldehyde (158–159 °C), (*E*)-4-phenyl-3-buten-2-one (174–175 °C), isophorone (137–138 °C), and 4-phenyl-3-buten-2-one (164–166 °C).

Reduction of Tosylhydrazones. General Procedure. The reduction of the tosylhydrazone of 6-oxo-15-hexadecenoic acid is representative. Benzoic acid (0.69 g, 5.67 mmol) was placed in a dried, nitrogen-flushed, 25-mL flask fitted with a septum inlet and magnetic stirring bar. Ethanol-free chloroform (5 mL) was added and the mixture cooled to 0 °C. BH₃·THF (1.2 mL of a 2.35 M solution, 2.82 mmol) was added dropwise. (Caution: hydrogen evolution.¹) The clear solution was stirred for 30 min and then the tosylhydrazone of 6-oxo-15-hexadecenoic acid (0.62, 1.42 mmol) was added. The reduction was allowed to proceed for 60 min¹⁵ and then NaOAc·3H₂O (0.46 g, 3.4 mmol) was added and the solution allowed to warm to room temperature.

Pentane (30 mL) was added and the organic layer was separated and washed with 50 mL of a 2% acetic acid solution and then 50-mL portions of warm water (50 °C) (for nonacidic materials, the pentane layer is washed with 5% Na₂CO₃ followed by water). The pentane layer was dried over anhydrous MgSO₄, the solvent removed under reduced pressure, and the product isolated by column chromatography (silica gel using 1:10 ethyl acetate–petroleum ether as eluant): yield 0.347 g (96%); mp 42–43 °C; NMR (CDCl₃) δ 1.21 (m, 22 H, =CHCH₂(CH₂)₁₁CH₂), 1.77–2.07 (m, 2 H, =CHCH₂CH₂), 2.13–2.33 (m, 2 H, CH₂CO₂H), 4.73 (s, 1 H, CH₂=CH), 4.9–5.07 (d, 2 H, CH₂=CH), 11.9 (s, 1 H, CO₂H).

Octane. The tosylhydrazone of 2-octanone (5.34 g, 18.0 mmol) was reduced by using bis(benzoyloxy)borane (36 mmol). Reduction time was 60 min and the yield was 1.89 g (91%) of octane, bp 125 °C (760 mmHg).

(14) The more expensive bis(trifluoroacetoxy)borane also appear to be effective in these reductions.

(15) As in all reductions of tosylhydrazones, the reaction should be quenched as soon as the hydrazone has been reduced to obtain maximum yields. Fortunately the reactions are easily monitored by NMR or TLC.

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Decane. The tosylhydrazone of decanal (1.34 g, 4.13 mmol) was reduced with bis(benzoyloxy)borane (8 mmol). Reduction time was 30 min and the yield was 0.46 g (78%), bp 174 °C (760 mmHg).

***tert*-Butylcyclohexane.** The tosylhydrazone of 4-*tert*-butylcyclohexanone (2.04 g, 6.34 mmol) was reduced with bis(benzoyloxy)borane (12.68 mmol). Reduction time was 30 min and the yield was 0.733 g (82%) of *tert*-butylcyclohexane: bp 171 °C (760 mmHg); NMR (CDCl₃) δ 0.83 (s, 9 H, C(CH₃)₃), 0.90–1.90 (m, 11 H, CH₂ and CH).

Toluene. The tosylhydrazone of benzaldehyde (5.49 g, 20 mmol) was reduced with bis(benzoyloxy)borane (40 mmol). The reduction time was 70 min and the yield was 1.51 g (82%) of toluene, bp 110 °C (760 mmHg).

Ethylbenzene. The tosylhydrazone of acetophenone (2.89 g, 10 mmol) was reduced with bis(benzoyloxy)borane (20 mmol). The reaction time was 2.5 h and the yield of ethylbenzene was 0.72 g (68%).

3-Phenyl-1-propene. The tosylhydrazone of cinnamaldehyde (5.64 g, 18.8 mmol) was reduced with bis(benzoyloxy)borane (37 mmol). The reduction time was 1 h and the yield of 3-phenyl-1-propene was 1.89 g (85%): bp 156 °C (760 mmHg); NMR (neat) δ 3.22 (d, 2 H, PhCH₂), 4.85 (m, 1 H, PhCH₂CH=CHH), 5.05 (m, 1 H, PhCH₂CH=CHH), 5.52–6.12 (m, 1 H, PhCH₂CH=CH₂), 7.05 (s, 5 H, PhCH₂).

3,5,5-Trimethylcyclohexene. The tosylhydrazone of isophorone (6.128 g, 20 mmol) was reduced with bis(benzoyloxy)borane (40 mmol). The reaction time was 30 min and the yield was 2.07 g (83%): bp 130 °C (760 mmHg); NMR (CDCl₃) δ 0.90–0.99 (m, 9 H, methyls), 1.0–1.8 (m, 4 H, ring CH₂), 2.17 (br m, 1 H, CHCH₃), 5.50 (s, 2 H, vinyl).

1-Phenyl-1,2-butadiene. The tosylhydrazone of 4-phenyl-3-buten-2-one (3.89 g, 12.5 mmol) was reduced with bis(benzoyloxy)borane (25 mmol). The reduction time was 66 h and the yield was 0.32 g (21%) of 1-phenyl-1,2-butadiene: bp 200 °C (760 mmHg); IR 1955 cm⁻¹ (C=C=C); NMR (CDCl₃) δ 1.7 (m, 3 H, C=CHCH₃), 5.4 (m, 1 H, C=CHCH₃), 5.95 (m, 1 H, C=CHPh), 7.13 (m, 5 H, C=CHPh).

Acknowledgment. We thank the Department of Energy (Contract No. DE-ASO5-80EV10363) for support of this work.

Registry No. Decanal, 112-31-2; 2-octanone, 111-13-7; 4-*tert*-butylcyclohexanone, 98-53-3; benzaldehyde, 100-52-7; acetophenone, 98-86-2; 6-oxo-15-hexadecenoic acid, 76402-73-8; cinnamaldehyde, 104-55-2; isophorone, 78-59-1; 4-phenyl-3-buten-2-one, 1817-57-8; decanal tosylhydrazone, 41780-50-1; 2-octanone tosylhydrazone, 54798-76-4; 4-*tert*-butylcyclohexanone tosylhydrazone, 41780-53-4; benzaldehyde tosylhydrazone, 1666-17-7; acetophenone tosylhydrazone, 4545-21-5; 6-oxo-15-hexadecenoic acid tosylhydrazone, 76421-16-4; cinnamaldehyde tosylhydrazone, 7318-33-4; isophorone tosylhydrazone, 4545-18-0; 4-phenyl-3-buten-2-one tosylhydrazone, 69180-02-5; decane, 124-18-5; octane, 111-65-9; *tert*-butylcyclohexane, 3178-22-1; toluene, 108-88-3; ethylbenzene, 100-41-4; 15-hexadecenoic acid, 4675-57-4; 3-phenyl-1-propene, 300-57-2; 3,5,5-trimethylcyclohexene, 933-12-0; 1-phenyl-1,2-butadiene, 2327-98-2; bis(benzoyloxy)borane, 76402-74-9; (*E*)-4-phenyl-3-buten-2-one tosylhydrazone, 53941-18-7.

Polyether-Based Triphase Catalysts. A Synthetic Comparison¹

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Received October 28, 1980

Cross-linked phosphonium and ammonium polymers are receiving considerable attention as triphase catalysts.³

(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).