from the titration of BuLi with 1.04 mmol of 1 indicated a mixture of BuTePh (0.06 mmol), BuTeBu (0.49 mmol), and PhTePh (0.45 mmol) together with 1 (0.54 mmol) derived from benzenetellurolate. The pale yellow endpoint color is attributable to these telluride species. The main formation of the symmetrical tellurides is against our prediction based on eq 1. These results indicate the reaction pathways as shown in Scheme I. Highly nucleophilic BuLi reacts rapidly not only with 1 but also with BuTePh formed initially. The latter transmetalation liberates BuTeBu and PhLi, and then PhLi again reacts with 1 to afford PhTePh and PhTeLi. The accumulation of the symmetrical tellurides indicates that the second reaction predominates the first one. On the other hand, the titration of BuMgBr with 0.92 mmol of 1 formed 1 (0.46 mmol) and BuTePh (0.89 mmol) together with trace amounts of BuTeBu (0.03 mmol) and PhTePh (0.03 mmol). The less nucleophilicity of BuMgBr seems to depress transmetalation reaction following eq 1.

Scheme I

$$\mathrm{PhTeTePh + BuLi \rightarrow BuTePh + PhTeLi}$$

$$\mathrm{BuTePh + BuLi \rightarrow BuTeBu + PhLi}$$

$$\mathrm{PhTeTePh + PhLi \rightarrow PhTePh + PhTeLi}$$

$$\mathrm{2PhTeTePh + 2BuLi \rightarrow BuTeBu + PhTePh + 2PhTeLi}$$

The present single-titration method using diphenyl ditelluride (1) as an indicator is simple to practice, and it is easy to observe the end point, like the colored dianion methods. In particular, this procedure is significantly useful in titrations of organomagnesium halides and weakly basic alkynyllithium reagents.

Experimental Section

Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Diethyl ether was distilled over calcium hydride and stored over sodium. Benzene was distilled over calcium hydride and stored in a Schlenck tube under argon. Organolithium and organomagnesium reagents were purchased from Aldrich Chemical Co. or Kanto Chemical Co. or prepared by using unexceptional procedures. Tellurium was purchased as a 300-mesh powder from Nacalai Tesque Inc.

Diphenyl Ditelluride (1). The synthesis of 1 was carried out by modification of the previously reported method[14] as follows. To a suspension of tellurium powder (63.8 g, 0.50 mol) in THF (400 mL) was added a solution of phenylmagnesium bromide, which was prepared from bromobenzene (70.7 g, 0.45 mol) and magnesium (11.2 g, 0.45 mol) in THF (600 mL), with a double-tipped transfer needle. The mixture was stirred under reflux for 4 h and then poured into ice–water. The mixture was acidified with HCl (10% aqueous solution) and extracted with benzene. The organic phase was washed with brine and dried over $MgSO_4$. Evaporation of the solvent and recrystallization from benzene–hexane afforded 1 as orange–red crystals (80.6 g, 88%), mp 65–66 °C (lit.[14] mp 66 °C).

General Procedure for the Titration Using Diphenyl Ditelluride (1) in THF. A 50-mL round-bottom flask containing a magnetic stirring bar was baked out with a heat gun under reduced pressure and cooled to room temperature under argon pressure. The dry flask was charged with accurately weighed diphenyl ditelluride (1, ~1.0 mmol), fitted with a rubber septum cap, and flushed with argon. Anhydrous THF (10 mL) was then added, and stirring was started. After 1 was completely dissolved, the flask was cooled to 0 °C in an ice bath, and the organometallic reagent was added dropwise via a 1.00-mL syringe graduated by 0.01 mL until the red solution faded to pale yellow. The amount consumed contains 1 equiv of organometallic reagent relative to 1.

Diphenyl ditelluride is a low volatile stable compound. Waste solutions from titrations should be, however, handled in a hood, because some alkylphenyl tellurides have a peculiarly bad odor and toxicity data on organotellurium compounds are sparse.

Registry No. 1, 32294-60-3.

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Regioselective 1,2-Reduction of Conjugated Enones and Enals with Sodium Monoacetoxyborohydride: Preparation of Allylic Alcohols

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The need to effect a regioselective reduction of an α,β-unsaturated aldehyde or ketone is frequently encountered in organic synthesis. Reduction of these systems with sodium borohydride, one of the most widely utilized reducing agents, is highly solvent dependent and generally does not result in useful regioselectivity (Table I).

It has been previously demonstrated that treatment of borohydride with a controlled amount of acetic acid affords a reducing agent which is weaker and thereby more selective than the traditional sodium borohydride/ethanol reduction system. For example, Nutaitis and Gribble[2] have shown that tetra-*n*-butylammonium triacetoxyborohydride effectively reduces aldehydes in the presence of ketones, even with excess hydride present in the reaction medium. This selectivity is not possible with unmodified borohydride. Thus, we felt that utilization of an (acyloxy)borohydride species to reduce α,β-unsaturated carbonyl compounds would result in enhanced regioselectivity.

Our initial studies utilized 2-cyclohexen-1-one and 3-methyl-2-cyclohexen-1-one. These substrates were subjected to reduction with sodium mono-, di-, and triacetoxyborohydride, which were generated by addition of the requisite amount of glacial acetic acid to a suspension of sodium borohydride in dry THF. A fourth reaction, which consisted of addition of sodium borohydride pellets to a solution of the substrate in neat acetic acid, was also performed. The results of these experiments are shown in Table II.

As can be seen, the greatest regioselectivity was realized with either sodium monoacetoxyborohydride or sodium triacetoxyborohydride. Lower selectivity was exhibited by sodium diacetoxyborohydride as well as by the sodium borohydride/acetic acid system. The latter result is not unreasonable; as the pellet slowly dissolves, there will be a finite concentration of unmodified (more highly reactive) borohydride coexisting with the substrate in the reaction system for a period of time. As discussed above, unmodified borohydride does not exhibit high regioselectivity with regard to conjugated enone and enal reduction. The less efficient regioselectivity of sodium diacetoxyborohydride, however, was not expected. The reactivity of (acyloxy)borohydride species is generally believed to decrease as more electron withdrawing ligands become bonded to the central boron atom.[3] Thus, one would expect the re-

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Table I. Reduction of Unsaturated Carbonyls with Sodium Borohydride Reducing Systems

compound	reagent	product ratio 1,2/1,4
2-cyclohexen-1-one	$NaBH_4$/50% EtOH	59/41[1a]
	$NaBH_4$/THF	71/29[1b]
3-methyl-2-cyclohexen-1-one	$NaBH_4$/50% EtOH	70/30[1a]
	$NaBH_4$/2-propanol	55/45[1c]
	$NaBH_4$/pyridine	0/100[1c]
	$NaBH_4$/THF	67/33[1b]
4-phenyl-3-buten-2-one	$NaBH_4$/2-propanol	77/23[1d]
	$NaBH_4$/diglyme	58/42[1d]
	$NaBH_4$/pyridine	72/28[1d]
cinnamaldehyde	$NaBH_4$/THF	95/5[1b]
citral	$NaBH_4$/THF	99/1[1b]

Table II. Reduction of Unsaturated Carbonyls with Sodium Acetoxyborohydride Reagents

compound	reagent	product ratio[a] 1,2/1,4
2-cyclohexen-1-one	$NaBH_3(OAc)$	97/3
	$NaBH_2(OAc)_2$	88/12
	$NaBH(OAc)_3$	97/3
	$NaBH_4$/HOAc	97/3
3-methyl-2-cyclohexen-1-one	$NaBH_3(OAc)$	96/4
	$NaBH_2(OAc)_2$	90/10
	$NaBH(OAc)_3$	98/2
	$NaBH_4$/HOAc	69/31

[a] Determined by vapor-phase chromatography and compared to authentic material.

gioselectivity of diacetoxyborohydride to resemble the monoacetoxy and triacetoxy species. It may be that sodium diacetoxyborohydride is not as stable as the mono- and triacetoxy species and may undergo disproportionation reactions to generate the parent borohydride anion, which would not exhibit high regioselectivity. However, at the present time this explanation is only speculative.

Thus, it appeared that either sodium monoacetoxyborohydride or sodium triacetoxyborohydride could serve as an efficient regioselective reagent for the reduction of α,β-unsaturated aldehydes and ketones. We chose to further develop sodium monoacetoxyborohydride as a regioselective reducing agent; as alluded to earlier, the triacetoxyborohydride anion is not an efficient reagent for the reduction of ketones. The results of these investigations are listed in Table III.

In summary, reduction of α,β-unsaturated aldehydes and ketones with sodium acetoxyborohydride reagents is highly regioselective, resulting in formation of the corresponding allylic alcohols. Sodium monoacetoxyborohydride is the most efficient reagent studied and should prove to be an attractive alternative to existing regioselective borohydride methods, which include $NaBH_4/CeCl_3$,[4a,b] $LiBH_3$(*n*-butyl),[4c] borohydride exchange resin,[4d] and $NaBH_4$/MeOH/THF.[4e]

Experimental Section

General Methods. Tetrahydrofuran was distilled from sodium benzophenone. Commercial sodium borohydride powder and glacial acetic acid were used directly. Vapor-phase chromatography was performed on a Hewlett-Packard HP5890A gas chromatograph equipped with a Supelco, Inc., SPB-1 capillary column, FID detector, and a Hewlett-Packard 3392A integrator. ^1H NMR spectra were recorded on a Varian EM360A spectrometer as solutions in $CDCl_3$ using tetramethylsilane as an internal standard.

Table III. Reduction of Unsaturated Carbonyls with Sodium Monoacetoxyborohydride

compound	yield,[a,b] %	product ratio[c] 1,2/1,4
2-cyclohexen-1-one	32	97/3
3-methyl-2-cyclohexen-1-one	49	96/4
trans-4-phenyl-3-buten-2-one	70	96/4
trans-cinnamaldehyde	70	99/1
citral	86	99/1

[a] Refers to chromatographed material. [b] Compounds exhibited satisfactory ^1H NMR spectra. [c] Determined by vapor-phase chromatography and compared to authentic material.

Preparation of *trans*-4-Phenyl-3-buten-2-ol (General Procedure). To a magnetically stirred suspension of sodium borohydride powder (0.43 g, 11.4 mmol) in dry THF (25 mL) at 25 °C was added over 2 min glacial acetic acid (0.65 mL, 11.4 mmol). After 0.5 h, *trans*-4-phenyl-3-buten-2-one (1.0 g, 6.8 mmol) was added, and the resulting mixture was stirred for 20 h at 25 °C. The mixture was poured into 10% aqueous NaOH (25 mL), stirred for 0.5 h, and extracted with ether (2 × 50 mL). The combined extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to afford a colorless oil (1.05 g). Flash chromatography (2:1 hexanes/ether) gave a colorless oil (0.71 g, 70%), which was homogeneous by TLC: ^1H NMR ($CDCl_3$) 7.3–7.0 (m, 5 H), 6.6–5.9 (m, 2 H), 4.5–4.1 (m, 1 H), 3.1 (broad s, 1 H), 1.3 (d, 3 H) ppm; GC (oven 125 °C, injection 270 °C, detector 270 °C, 1-μL injection) showed 96% 1,2-reduction and 4% 1,4-reduction (t_R: 2.75 and 1.95 min, respectively).

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Registry No. $NaBH_3(OAc)$, 71604-09-6; $NaBH_2(OAc)_2$, 123183-64-2; $NaBH(OAc)_3$, 56553-60-7; $NaBH_4$, 16940-66-2; (*E*)-PhCH=CHCH$_2$OH, 4407-36-7; $(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OH$, 624-15-7; 2-cyclohexen-1-one, 930-68-7; 2-cyclohexen-1-ol, 822-67-3; cyclohexanone, 108-94-1; 3-methyl-2-cyclohexen-1-one, 1193-18-6; 3-methyl-2-cyclohexen-1-ol, 21378-21-2; 3-methylcyclohexanone, 591-24-2; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; *trans*-4-phenyl-3-buten-2-ol, 36004-04-3; 4-phenyl-2-butanone, 2550-26-7; *trans*-cinnamaldehyde, 14371-10-9; citral, 5392-40-5.

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Ultrasound-Promoted Synthesis of α-Difluoromethylated Carboxylic Acids

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Numerous studies have shown that difluoromethyl substitution confers very interesting properties to important organic materials such as bioactive compounds.[1-3] However, except for the difluoromethyl compounds made from chlorodifluoromethane and nucleophiles,[4,5] no other

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