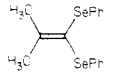
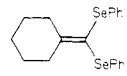
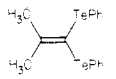
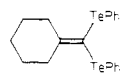
Table I. Spectral Properties and Yields of Products

compound	yield,[a] %	IR,[b] ν_{max}, cm^{-1}	^{1}H NMR,[c] δ (mult., H)	mass spectra,[d] %
 4	47	3050 (m), 2900 (s), 1725 (w), 1570 (s), 730 (s), 690 (s)	2.2 (s, 3), 7.1-7.3 (m, 5)	368 (18), 211 (22), 196 (21), 157 (34), 130 (100), 119 (100), 77 (42)
 5	61	3060 (m), 2920, 2860 (s), 1730 (w), 735 (s), 690 (s)	1.6 (m, 6), 2.75 (m, 4), 7.1-7.3 (m, 10)	406 (8), 251 (25), 169 (64), 141 (30), 115 (24), 91 (100), 77 (81)
 6	26	3060 (m), 2900 (m), 1740 (vw), 1670 (s), 740 (s), 700 (s)	2.3 (s, 3), 7.0-7.6 (m, 5)	466 (3), 261 (8), 207 (35), 129 (100), 77 (78)
 7	30	3060 (m), 2940, 2850 (s), 1730 (w), 1570 (s), 740 (s), 700 (s)	1.5 (m, 6), 2.6 (m, 4), 7.1-7.7 (m, 10)	504 (8), 410 (3), 301 (8), 207 (27), 170 (37), 77 (100)

[a] Isolated yields. [b] Neat. [c] $CDCl_3$, Me_4Si internal standard. [d] Most abundant isotope; 70 eV.

There is a marked difference in stabilities between the selenium and the tellurium products although both are isolable and easily handled. The selenium adduct is stable for weeks as an oil or in solution on the benchtop. Both tellurium products, however, decompose in solution to an insoluble white powder in a matter of days. The decomposition is much more rapid from chlorinated solvents (24 h) than with hexanes (~1 week). When left as a purified oil, decomposition of the tellurium compounds takes far longer. All four products, when stored as neat oils at 0 °C or less under argon, are stable for a month or more.

In summary, we have developed a new pathway for the synthesis of phenylseleno and phenyltelluro ketals. While yields of these compounds are moderate, the reaction is straightforward and purification simple. Studies of these compounds as to reactivities and possible synthetic applications are currently underway.

Experimental Section

Proton NMR spectra were recorded on a Varian EM-390 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Mass spectra were recorded on a VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG Data System 2000.

Triflates were prepared by published procedures.[10,11] Diphenyl diselenide (Aldrich) and diphenyl ditelluride (Strem) were recrystallized from hexanes prior to use. DME was distilled from potassium/benzophenone directly into the reaction vessel. Hexanes were washed with concentrated H_2SO_4 and saturated $NaHCO_3$, dried over $MgSO_4$, and then distilled from CaH_2.

General Procedure for the Insertion of Alkylidenecarbenes into Se–Se and Te–Te Bonds. Reaction of Triflate 2 with Diphenyl Diselenide. To a flame-dried, three-necked, 250-mL round-bottomed flask equipped with argon inlet, addition funnel, and gas bubbler was added 100 mL of dry DME along with 1.5 g (4.8 mmol) of diphenyl diselenide and 0.6 g (2.9 mmol) of triflate **2**. The reaction mixture was cooled to −50 °C, and a solution of 0.4 g (3.6 mmol) of potassium *tert*-butoxide in 50 mL of dry DME was added dropwise via the addition funnel. After the addition, stirring was continued for 15 min at −50 °C; then the reaction was allowed to warm to room temperature. DME was then removed on a rotary evaporator and the residue taken up in hexanes and filtered. The resulting colored solution was chromatographed on activated silica gel by using hexanes as eluant. The product band is then stripped of solvent at reduced pressure to yield 0.5 g (47%) of diselenide **4** as a viscous yellow oil. Anal. Calcd for $C_{16}H_{16}Se_2$: C, 52.47; H, 4.41; Se, 43.12. Found: C, 52.99; H, 4.69; Se, 41.47.

Reaction of Triflate 3 with Diphenyl Diselenide. The reaction was performed according to the general procedure using 0.50 g (2.2 mmol) of triflate **3**, 1.5 g (4.8 mmol) of diphenyl diselenide, and 0.40 g (3.6 mmol) of potassium *tert*-butoxide. Isolated yield was 0.52 g (61%) of **5** as a yellow oil. Anal. Calcd for $C_{19}H_{20}Se_2$: C, 56.16; H, 4.97; Se, 38.87. Found: C, 56.23, H, 4.93, Se, 38.64.

Reaction of Triflate 2 with Diphenyl Ditelluride. The reaction was performed according to the general procedure using 0.20 g (0.98 mmol) of triflate **2**, 0.50 g (1.2 mmol) of diphenyl ditelluride, and 0.15 g (1.3 mmol) of potassium *tert*-butoxide. Isolated yield was 0.12 g (26%) of **6** as an orange oil.

Reaction of Triflate 3 with Diphenyl Ditelluride. The reaction was performed according to the general procedure using 0.25 g (1.1 mmol) of triflate **3**, 0.60 g (1.5 mmol) of diphenyl ditelluride, and 0.16 g (1.4 mmol) of potassium *tert*-butoxide. Isolated yield was 0.15 g (30%) of **7** as an orange oil.

Acknowledgment. Financial support for this work was provided by the NSF (CHE 81-03596). Funds for the mass spectrometer were provided by the NSF (CHE 81-00424) and the University of Utah Institutional Funds Committee. We are also grateful to the E.I. duPont deNemours Co. for glassware.

Registry No. **2**, 53282-30-7; **3**, 53282-32-9; **4**, 89438-15-3; **5**, 89438-16-4; **6**, 89438-17-5; **7**, 89438-18-6; diphenyl diselenide, 1666-13-3; diphenyl ditelluride, 32294-60-3.

A Mild Reductive Conversion of Oximes to Ketones

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A large number of ketone functional group equivalents are routinely employed in organic synthesis. Readily prepared and highly stable ketoximes (and oxime ethers) are useful in this regard both as protecting groups and selective activating groups. Notably, alkylation of dianions of oximes provides an excellent indirect method for highly regioselective monofunctionalization of ketones.[2] The utility of oximes as ketone equivalents is limited by methods employed for ketone regeneration. Thus, due to the relative hydrolytic stability of oximes,[3] a wide variety

(1) Recipient of a Camille and Henry Dreyfus Grant for Young Faculty in Chemistry.

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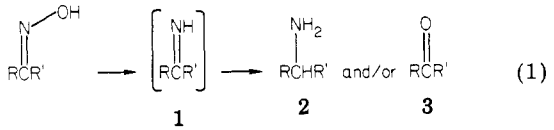
Table I

entry	oxime	cndns	time (at 25 °C), h	yield of 2,4-dinitrophenylhydrazone, %
1a	4-*tert*-butylcyclohexanone	*a*	2	81[c]
1b	methyl ether	*b*	24 (65 °C)	81
1c	benzyl ether	*b*	20 (60 °C)	71
2	cyclohexanone	*b*	4	80
3	acetophenone	*a*	8	72
4	norcamphor	*a*	18	56
5	cyclododecanone	*a*	36	82
6	cycloheptanone	*a*	18	69
7	2-octanone	*a*	8	52
8	3-octanone	*a*	8	76
9	androstanolone	*b*	24	100[c]

[a] 5:1 methanol/water. [b] 7:7:1 tetrahydrofuran:methanol:water. [c] Yield of solid ketone.

of oxidative[4] and reductive methods[5] have been developed. Unfortunately, many of these conditions are quite nonselective. We now report an exceedingly mild hydrogenolysis–hydrolysis method promoted by Raney nickel.

Interestingly, prior to the development of boron hydrides, a very common method for reductive amination of ketones involved oxime formation and reduction to the amine with a variety of standard metal catalysts including Raney nickel. Mechanistically, this was determined to proceed via initial N–O bond cleavage to produce imine 1 followed by further hydrogenation to amine 2 (eq 1).[6]



1 2 3 (1)

On occasion, ketones 3 were obtained as side products and reaction conditions were designed to minimize this pathway.[6,7] We have now discovered that under the proper conditions, ketones become the major to exclusive products.

We have recently developed a smooth reductive transformation of Δ^2-isoxazolines to β-hydroxy ketones via Raney nickel catalyzed hydrogenolysis to the β-hydroxy imine followed by rapid imine hydrolysis.[8] Central to the success of this reaction was the employment of boric acid to promote hydrolysis of the β-hydroxy imine prior to undesired side reactions including overreduction, epimerization, and retro-Aldol reaction.[8a,b] Subjection of acetophenone oxime to these conditions (Ra-Ni, $B(OH)_3$; $MeOH/H_2O$, H_2 gas) produced acetophenone as the major product. Somewhat to our surprise, substantial amounts (up to 25%) of 1-phenylethylamine and also some 1-phenylethanol were isolated. Similar results were obtained with 4-*tert*-butylcyclohexanone oxime. We have discovered that these side products can be suppressed or eliminated entirely by a simple modification of introducing 2–5 equiv of acetone to the reduction mixture.[11] Typically, acetone and boric acid (3–10 equiv) were added to a suspension of W-2 Raney nickel in aqueous methanol. On occasion, THF was used as cosolvent to enhance substrate solubility. After stirring the mixture 1 h at room temperature, the substrate was added and the reaction was placed under hydrogen atmosphere and stirred for the indicated time. According to this procedure, a wide variety of oximes were transformed to their parent ketones in good yield as indicated in Table I. In several cases, some material losses may have been incurred due to the volatility of the ketones.

Several points are worthy of note. As expected, in the absence of Ra-Ni no ketone is formed. Under the standard conditions, the formation of alcohol products was not observed and the amines were typically formed in yields <5%. Oxime ethers required substantially longer reduction times and reflux temperatures. In the case of the benzyl oximes, benzyl alcohol can be identified. This indicates the expected initial N–O bond cleavage in this case.[9] Finally, it is expected that reduction of aldoximes to aldehydes may not be viable since attempted reduction of *p*-anisaldoxime produced a mixture of amines (major) and *p*-methoxylbenzyl alcohol (minor) with no aldehyde being present.

This method for reductive transformation of oximes to ketones is especially mild and selective. Any functional group stable to Ra-Ni at near neutral pH is expected to survive. It is anticipated that common functional groups such as ketones, esters, amides, alcohols, amines, etc., can be retained unprotected. In addition, the near neutrality (pH ~5.5–6) insures the survival of common acid-sensitive protecting groups including acetals, tetrahydropyranyl

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(9) Pd-C produces C–O bond hydrogenolysis. Corey, E. J.; Petrzilka, M.; Ueda, Y. *Helv. Chim. Acta* **1977**, *60*, 2294.

ethers, and *tert*-butyldimethylsilyl ethers.[8b] The major limitation is that sterically accessible olefins are likely to be saturated under these conditions.

Experimental Section

General Methods. W-2 Raney nickel was prepared according to the standard procedure.[10] The catalyst was stored at −20 °C under methanol. In several cases, freshly prepared (i.e., less than 24-h old) catalyst was found to be too active and caused overreduction. To avoid this, the catalyst was routinely stored for 2 weeks at −20 °C prior to first use. Activity was maintained up to 4–6 months. Overreduction was also effected by excess amounts of catalyst.

General Reduction Procedure. A spatula tip of Raney nickel under methanol (estimated 50–100 mg) was added to a mixture of boric acid (359 mg, 5.8 mmol) and acetone[11] (156 mg, 2.7 mmol) in THF:MeOH:H_2O (7:7:1; 4 mL) or MeOH:H_2O (5:1). After stirring for 1 h at room temperature, the oxime (1 mmol) was added and the reaction was placed under an atmosphere of hydrogen (balloon) by repeated evacuation and flushing (~5 times). The reaction mixture was vigorously stirred for the indicated time (monitored by TLC), filtered through Celite, and diluted with water (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was washed with water (2 × 25 mL) and brine (1 × 25 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude ketone (>90%) was usually obtained in a good state of purity. Occasionally, trace amounts of amine (<5%) were detected. Isolated yields were determined by 2,4-dinitrophenylhydrazone formation.

Acknowledgment is made to the National Institutes of Health (GM-31678) and the Health Research and Services Foundation for partial support of this work.

Registry No. Ra-Ni, 7440-02-0; $B(OH)_3$, 10043-35-3; 4-*tert*-butylcyclohexanone oxime, 4701-98-8; 4-*tert*-butylcyclohexanone oxime methyl ether, 61580-74-3; 4-*tert*-butylcyclohexanone oxime benzyl ether, 89231-89-0; 4-*tert*-butylcyclohexanone 2,4-dinitrophenylhydrazone, 54532-12-6; 4-*tert*-butylcyclohexanone, 98-53-3; cyclohexanone oxime, 100-64-1; cyclohexanone 2,4-dinitrophenylhydrazone, 1589-62-4; acetophenone oxime, 613-91-2; acetophenone 2,4-dinitrophenylhydrazone, 1677-87-8; norcamphor oxime, 4576-48-1; norcamphor 2,4-dinitrophenylhydrazone, 3281-03-6; cyclododecanone oxime, 946-89-4; cyclododecanone 2,4-dinitrophenylhydrazone, 907-99-3; cycloheptanone oxime, 2158-31-8; cycloheptanone 2,4-dinitrophenylhydrazone, 3349-73-3; 2-octanone oxime, 7207-49-0; 2-octanone 2,4-dinitrophenylhydrazone, 2074-06-8; 3-octanone oxime, 7207-50-3; 3-octanone 2,4-dinitrophenylhydrazone, 14129-50-1; androstanolone oxime, 2436-48-8; androstanolone, 521-18-6; acetone, 67-64-1.

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Synthesis of Dialkylamines via the Reaction of Organoboranes with *N*-Chloroalkylamines

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Organoboranes react with chloramine[1,2] and hydroxylamine-*O*-sulfonic acid[3,4] derivatives to produce the corresponding alkylamines in good yields.

$$R_3B + NH_2X \rightarrow RNH_2$$

where X = Cl or OSO_3H

The reaction has been extended to the preparation of alkyldimethylamines but is complicated by a free-radical side reaction that leads to the formation of chloroalkanes.[5,6]

$$R_3B + (CH_3)_2NCl \rightarrow RN(CH_3)_2 + RCl$$

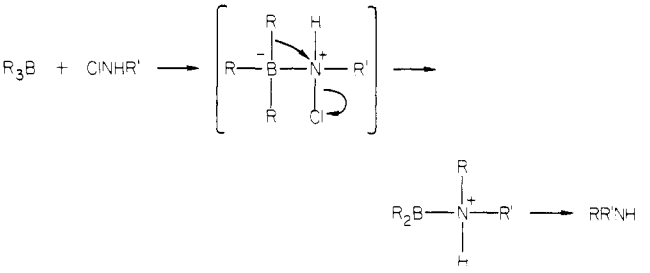
The successful reaction of *N*-chloroalkylamines with trialkylboranes has never been reported, but there are related reactions that would indicate that the reaction would be successful. For example, the reactions of trialkylboranes with *N*-chlorosulfonamides[7] and *N*-chloro-*O*-dinitrophenylhydroxylamine[8] are known.

$$R_3B + C_6H_6SO_2NHClNa \rightarrow RNHSO_2C_6H_5$$

We report that the reaction of trialkylboranes with *N*-chloroalkylamines can be utilized to synthesize a wide variety of functionally substituted dialkylamines in good yield. The reaction complements the synthesis of dialkylamines via the reaction of trialkylboranes with organic azides.[9] Our results are summarized in Tables I and II.

$$R_3B + R'NHCl \rightarrow RR'NH$$

The reaction is analogous to the reaction of chloramine with organoboranes and presumably occurs via an anionotropic migration of an alkyl group from boron to nitrogen.



The formation of alkyl chlorides as byproducts is often noted in the reactions, indicating that a competitive free-radical reaction can occur.[6] As an example, the reaction of tri-*n*-octylborane with *N*-chloro-1-octylamine yields both di-*n*-octylamine in 70% yield (isolated) and 1-chlorooctane in 20% yield. The yields of dialkylamines generally decrease as the steric bulk of either the *N*-chloroalkylamine or the organoborane increase. Thus, tricyclohexylborane reacts with *N*-chloro-1-octylamine to yield the corresponding dialkylamine in 60% yield, but the reaction of tricyclohexylborane with *N*-chloro-2-octylamine produces only trace amounts of the desired product. In an analogous fashion, *N*-chloro-*tert*-butylamine failed to produce the desired *tert*-butylalkylamines when it was allowed to react with a variety of trialkylboranes.[10]

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