propylsilane did not give isolable nitropropane but only propene indicative of ready HNO_2 elimination. When trimethylpropylsilane was reacted similar results were obtained together with 10% of nitromethane, indicating competing nitrodesilylation at the methyl carbon.

Subsequently the desilylative nitration of expected more reactive allylsilanes was studied with NO_2BF_4. In fact, allylsilanes are known to be very reactive toward electrophiles but give the corresponding products of allylic rearrangements.[5,6,12]

The reaction of allylsilane with NO_2BF_4 in dichloromethane solution was found to give 80% yield of the corresponding 3-nitroprop-1-ene (eq 5).

$$CH_2{=}CHCH_2SiMe_3 + NO_2^+BF_4^- \xrightarrow{CH_2Cl_2} CH_2{=}CHCH_2NO_2 + Me_3SiF + BF_3 \quad (5)$$

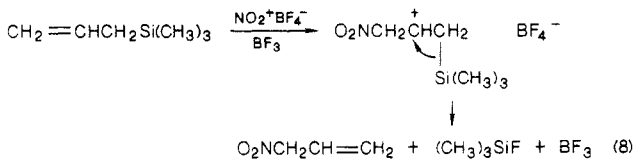
Representative is the reaction of allyltrimethylsilane with $NO_2^+BF_4^-$. In a 50-mL three-necked flask was added 0.001 mol of allyltrimethylsilane to 10 mL of dry dichloromethane. The system was cooled to −78 °C. $NO_2^+BF_4^-$ (0.001 mol, 1.33 g) was slowly added during a period of 20 min. A slow stream of dry nitrogen was passed through the system to purge trimethylfluorosilane and boron trifluoride formed in the reaction. After 30 min all the nitronium salt had disappeared. The mixture was then allowed to warm to room temperature, dichloromethane distilled off at atmospheric pressure, and the product distilled under vacuum: bp 62 °C/(25 mm); yield, 80%; ^{13}C NMR δ 77.75 (C_3), 123.86 (C_2), 126.62 (C_3); ^1H NMR δ 4.95 (CH_2NO_2, 2 H, d), 5.40 (CH, 1 H, m), 5.75–6.00 ($CH_2{=}$, 2 H, m).

Other allylsilanes such as 2-methyl-3-(trimethylsilyl)-propene and 1-(trimethylsilyl)but-2-ene were also reacted under similar conditions and gave the corresponding 2-methyl-3-nitropropene and 3-nitro-but-1-ene in 65% and 75% yields, respectively (eq 6 and 7).

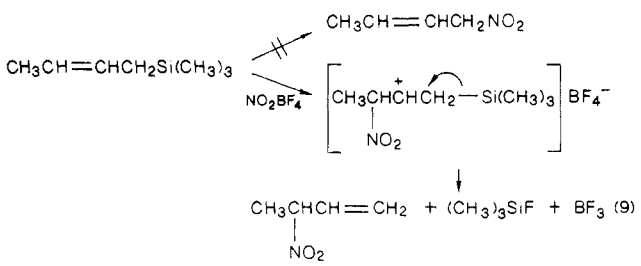
$$CH_2{=}C(CH_3)CH_2Si(CH_3)_3 + NO_2^+BF_4^- \rightarrow CH_2{=}C(CH_3)CH_2NO_2 + (CH_3)_3SiF + BF_3 \quad (6)$$

$$CH_3CH{=}CHCH_2Si(CH_3)_3 + NO_2^+BF_4^- \rightarrow CH_3CH(NO_2)CH{=}CH_2 + (CH_3)_3SiF + BF_3 \quad (7)$$

The desilylative nitration of allylsilanes is considered to proceed through initial electrophilic attack of NO_2^+ on the allyl system followed by desilylative elimination (eq 8).



This is clearly borne out in the reaction of 1-(trimethylsilyl)but-2-ene, where the product is not 1-nitrobut-2-ene (the direct desilylative nitration product) but only secondary 3-nitrobut-1-ene (eq 9).



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The desilylative nitration of alkylsilanes such as tetramethylsilane with nitronium tetrafluoroborate proceeds readily. This is the first example of desilylative nitration at saturated carbon and extends the scope and knowledge of electrophilic reactions at saturated Si–C bonds. As boron trifluoride is also formed as byproduct in the reactions it can facilitate in case of secondary and tertiary systems HNO_2 elimination and formation of olefins. 2-Nitropropane and 2-methyl-2-nitropropane when treated with BF_3 indeed were found readily eliminate HNO_2 to the corresponding olefins with subsequent polymerization. Allylsilanes in contrast give generally high yields of nitroalkenes. Their reactions, however, proceed via initial NO_2^+ attack on the π-system followed by desilylative elimination. Our work is continuing to overcome limitations and to make the desilylative nitration of aliphatic silanes a general method for the preparation of nitroaliphatics.

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Asymmetric Reduction of Phosphinyl Imines with Hydride Reagents. Enantioselective Synthesis of Chiral Primary Amines

Summary: Prochiral diphenylphosphinyl imines are asymmetrically reduced by chiral hydride reagents to chiral diphenylphosphinylamines. For dialkyl examples, the enantioselectivities obtained are the highest thus far for hydride reductions of imine derivatives.

Sir: In contrast to the considerable successful attention devoted to the asymmetric reduction of prochiral ketones to chiral alcohols[1] with hydride reagents, corresponding studies and identification of useful enantioselective conversions of imine derivatives to amines have been sparse, and only very limited success has been obtained.[2]

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Table I. Reductions of Methyl Aryl Phosphinyl Imines

entry	imine 1	R_1	R_2	reagent	T, °C	t, h	% yield[a]	config	% ee[b]	% ee, ket
1	**1a**	CH_3	C_6H_5	(*S*)-(−)-**3**	−78	0.5	84	*S*-(−)	13	95, *S*[f]
2	**1a**			(*R*)-(+)-**3**	−78	48	20	*R*-(+)	100	95, *S*[f]
3	**1a**			(*S*)-(−)-**3**	25	24	35	*S*-(−)	77	95, *S*[f]
4	**1a**			**4**	0	0.7	66	*S*-(−)	41	75, *S*[g]
5	**1a**			**5**	−78	1	54	*R*-(+)	15	78, *S*[h]
6	**1b**	CH_3CH_2	C_6H_5	(*S*)-(−)-**3**	−78	0.7	93	*S*-(−)	14	98, *S*[f]
7	**1b**			(*S*)-(−)-**3**	25	66	14	*S*-(−)	80	98, *S*[f]
8	**1b**			**4**	0	0.5	61	*S*-(−)	17	
9	**1b**			**5**	−78	2	54	*S*-(−)	28	92, *R*[h]
10	**1c**	$(CH_3)_2CH$	C_6H_5	(*S*)-(−)-**3**	−78	0.5	73	(−)	2[c,d]	71, *S*[f]
11	**1c**			**4**	0	0.5	76	(+)	13[c,e]	20, *S*[g]
12	**1c**			**5**	−78	0.5	74	(−)	57[c,d]	87, *R*[h]
13	**1d**	CH_3	β-naphthyl	(*S*)-(−)-**3**	−78	0.5	66	*S*-(−)	7	
14	**1d**			(*S*)-(−)-**3**	25	70	16	*S*-(−)	98	
15	**1d**			**4**	0	0.5	84	*S*-(−)	22	
16	**1d**			**5**	−78	2	70	*R*-(+)	33	
17	**1e**	CH_3	α-naphthyl	(*R*)-(+)-**3**	−78	0.5	66	*R*-(−)	52	
18	**1e**			**4**	0	0.5	58	*S*-(+)	1	
19	**1e**			**5**	−100	0.5	82	*R*-(−)	77	

[a] Isolated products, purified by chromatography; all new products gave satisfactory elemental analyses. [b] Enantiomeric purities determined by comparison of rotations with authentic samples prepared from the optically active amines, unless otherwise indicated. [c] Determined via GLC analysis of the MTPA amide diastereomers (ref 17). [d] Configuration unknown, probably *S*. [e] Configuration unknown, probably *R*. [f] Reference 14. [g] Reference 15. [h] Reference 1f.

Table II. Reductions of Methyl Alkyl Phosphinyl Imines

entry	imine 1	R_1	R_2	reagent	T, °C	t, h	% yield[a]	config	% ee[b]	% ee, ket
1	**1f**	CH_3	CH_3CH_2	(*S*)-(−)-**3**	−40	0.67	63	*S*-(+)	40	
2	**1f**			(*S*)-(−)-**3**	25	70	38	*S*-(+)	93	
3	**1f**			**4**	0	0.5	87	*S*-(+)	17	
4	**1f**			**5**	−78	2	58	*R*-(−)	61	3, *R*[d]
5	**1f**			**5**	−100	0.5	56	*R*-(−)	64	3, *R*[d]
6	**1g**	CH_3	$CH_3(CH_2)_4$	(*S*)-(−)-**3**	−40	0.5	83	*S*-(+)	64	24, *R*[e]
7	**1g**			**4**	25	0.5	55	*S*-(+)	10	
8	**1g**			**5**	−78	0.5	71	*R*-(−)	50	
9	**1h**	CH_3	$(CH_3)_2CHCH_2$	**5**	−78	0.5	64	*R*-(−)	80[c]	
10	**1i**	CH_3	$C_6H_5CH_2$	**5**	−78	0.5	82	*R*-(−)	64[g]	
11	**1j**	CH_3	*c*-C_6H_{11}	(*S*)-(−)-**3**	0	0.5	80	*S*-(+)	42	
12	**1j**			(*R*)-(+)-**3**	−78	16	56	*R*-(−)	67	
13	**1j**			**4**	0	0.67	100	*S*-(+)	34	
14	**1j**			**5**	−78	0.5	95	*R*-(−)	84	
15	**1k**	CH_3	$(CH_3)_2CH$	**5**	−78	0.5	66	(−)[f]	68[c]	36, *R*[d]

[a] Isolated products, purified by chromatography; all new products gave satisfactory elemental analyses. [b] Enantiomeric purities determined by comparison of rotations with authentic samples prepared from the optically active amines, unless otherwise indicated. [c] Detemined via ^{31}P NMR of diastereomeric amides prepared from (2*R*,4*R*,5*S*)-(+)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulfide (Johnson's Reagent, ref 18). [d] Reference 1f. [e] Reference 14a, for 2-octanone. [f] Configuration unknown, presumably *R*. [g] Determined by comparison with the maximum rotation reported for **2i** (ref 7b).

This paper describes preliminary results for the asymmetric reduction of prochiral *N*-diphenylphosphinyl imines **1**[7] to chiral *N*-(diphenylphosphinyl)amines **2** with chiral aluminum and boron derived hydride reagents. The derivatives **1** provide readily prepared,[7] stable, but highly reactive[8] alternatives to normally unviable ammonia imines, which, upon reduction, gave protected versions of primary amines that are readily cleaved under acidic conditions to the free amine salts.[9]

(2) Thus, certain cyclic imines are enantioselectively reduced to chiral cyclic amines by lithium alkyldipinan-3α-ylborates (4–25% ee, ref 3) and sodium (acyloxy)borohydrides (0–86% ee, ref 4). Ketoximes are reduced by glucofuranose/$LiAlH_4$ complexes with variable (9.5–56%) ee but usually mediocre inductions (most ca. 10–25% ee, ref 5a). Similarly, achiral acetophenone oxime ethers are reduced with a chiral polymer-supported borane complex to the amine in 18–67% ee (ref 5b) while chiral examples of the same oxime ethers are reduced with borane in 4–44% ee (ref 5c). Chiral *N*-alkylidene sulfonimides are reduced to the corresponding sulfonamides by $LiAlH_4$ with good (57–80% ee) asymmetric control but the preparation of the chiral substrates is tedious, and the chiral auxiliary reagent is racemized by the vigorous acidic cleavage procedure used to obtain the free amines (ref 6). *N*-Phosphinyl imines have been reduced by a chiral quinine/$LiAlH_4$ reagent to chiral *N*-phosphinyl amides in a pioneering investigation by Stec (ref 7b), but the enantiomeric inductions were low to moderate (8–36% ee).

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(8) The highly electron-withdrawing diphenylphosphinyl group greatly enhances the electrophilicity of the imine carbon so that nucleophilic attack by most boron- and aluminum-based hydride reagents, including hindered, chiral examples, is rapid (i.e., complete reduction in 1–30 min, most <5 min) even at low temperatures (i.e., −40 to −100 °C). Indeed, diphenylphosphinyl imines are more reactive than ketones toward hydride reagents.

After considerable experimental probes,[10] the three most promising reagents identified for exploration were (*R*)- or (*S*)-bi-2-naphthol/$LiAlH_4$ (**3**, Binal-H, Noyori's reagent[14]), 1,2(*S*)-diphenyl-3(*R*)-methyl-4-(dimethylamino)-2-butanol/$LiAlH_4$ (**4**, Chirald/LAH, Mosher's reagent[15]), and potassium 9-*O*-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane (**5**, K 9-*O*-DIPGF-9-BBNH, Brown's reagent[1f]). The requisite imines **1**, chosen to incorporate a variety of structural features, were synthesized from the corresponding ketoximes and chlorodiphenylphosphine (eq 1).[7] In general, the reaction

$$R_1R_2C{=}NOH \xrightarrow[-40\ °C]{(C_6H_5)_2PCl} [R_1R_2C{=}NOP(C_6H_5)_2] \rightarrow \underset{\mathbf{1}}{R_1R_2C{=}NP(O)(C_6H_5)_2} \xrightarrow{\text{reduction}} \underset{\mathbf{2}}{R_1R_2CHNHP(O)(C_6H_5)_2} \quad (1)$$

conditions for reductions were initially chosen to mimic those found most successful for corresponding studies with ketones,[1f,14,15] except that shorter reaction times were found sufficient[8] (Tables I and II).

Reductive results with reagents **3**, **4**, and **5** for arylalkyl and methylalkyl derivatives of **1** are displayed in Tables I and II, respectively, along with comparisons (where known) with results for reductions of the corresponding ketones. Several significant features of the conversions are evident from the tables. Thus, in general, enantioselectivities obtained with dialkyl cases match or exceed the selectivities with arylalkyl examples, in contrast to results generally observed with ketones when these reagents are used.[1f,14,15] Furthermore, with all examples, control of the chiral sense displayed appears to depend roughly on the relative bulk of the groups flanking the imine and not on electronic interactions as postulated for some ketones.[14] This is particularly evident with reagent **5**. Thus, with **1a** (Table I, entry 5), very little distinction between phenyl and methyl is observed (15% ee). However, as the alkyl size increases, the chiral sense obtained changes (*R* to *S*) and the magnitude of enantioselectivity is enhanced (compare entries 5, 9 and 12, Table I). Likewise, increasing the effective bulk of the aryl group affords increased discrimination of constant chiral sense[16] (*R*, compare entries 5, 16, and 17, Table I). Apparently, aromatic rings (except α-naphthyl[16]) behave as relatively small groups that project an unencumbered flat orientation toward the encroaching reagent, and therefore the sense and degree of chiral recognition is controlled by the comparative size of the alkyl group.

With dialkyl groups, reagent **5** consistantly affords the *R* enantiomer predominately (as is obtained with ketones[1f]), and the magnitude of enantioselectivity is again controlled mostly by relative group sizes. *Significantly, the reductions of dialkyl derivatives of* **1** *with* **5** *represent the highest enantioselectivities (50–84% ee) obtained to date for the conversion of prochiral imine derivatives to chiral amines with hydride reagents.*

A further interesting feature of reductions of arylalkyl derivatives was observed with reagent **3** upon extended reaction times. Thus, with **1a**, **1b**, and **1d**, allowing the reactions to proceed for 24–70 h resulted in much lower chemical yields but concomitant dramatic relative enrichments of the major enantiomers (compare entries 1 vs. 2 and 3, 6 vs. 7, 13 vs 14; Table I). Evidently, kinetic asymmetric distruction selectively depletes the minor enantiomer. This curious and potentially useful kinetic resolution is currently under further investigation.

As mentioned, the procedures utilized were those found to proceed successfully for the reduction of ketones.[1f,14,15] The following procedure for the reduction of 1-cyclohexyl-*N*-(diphenylphosphinyl)ethanimine **1j** with reagent **5** is illustrative. To the *N*-diphenylphosphinyl imine **1j** (1.01 g, 3.1 mmol) in dry THF (10 mL) cooled to −78 °C under N_2 was added a solution of K 9-*O*-DIPGF-9-BBNH (**5**)[1f] (3.8 mmol). The mixture was stirred at −78 °C for 30 min and then quenched with 5% aqueous HCl. The mixture was extracted with ether which was dried ($MgSO_4$) and evaporated to obtain an oily residue (2.2 g). Flash column chromatography[19] on silica gel (CH_2Cl_2 followed by 5% THF/CH_2Cl_2) afforded the phosphinylamine **2j** (0.98 g, 95%; $[\alpha]^{25}_D$ −13.5° (*c* 10, CH_2Cl_2)) which represents an 84% ee based on comparison of a rotation of $[\alpha]^{25}_D$ −15.93° (*c* 10, C_2Cl_2) for an authentic sample prepared from a sample of the optically pure amine.

Further investigations including the preparation of chiral α-amino acids are currently under way.

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(10) Ineffective reagents investigated include the trisubstituted boranes *B*-(3-pinanyl)-9-borabicyclo[3.3.1]nonane (ref 1d), nopol-9-BBN (ref 11), and diisopinocampheylchloroborane (ref 1e), which did not afford reduced products, the corresponding borohydrides from the former two reagents (ref 1a, 12, 13), and the chiral sulfamide/$LiAlH_4$ reagent (ref 1g), which gave good chemical yields but poor enantioselectivity (i.e., <10%).

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Novel Photochemical–Diradical Cyclization Methods for Protoberberine Alkaloid Synthesis. Preparation of (±)-Xylopinine and (±)-Stylopine

Summary: A new synthetic approach to members of the protoberberine alkaloid family based upon a photochemical–diradical cyclization methodology is described.

Sir: In recent years, a host of new approaches for carbocyclic and heterocyclic ring construction have grown out of mechanistic studies in the areas of radical and excited-state chemistry.[1,2] Our efforts in this area have focused

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