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Asymmetric Allylboration of Acylsilanes

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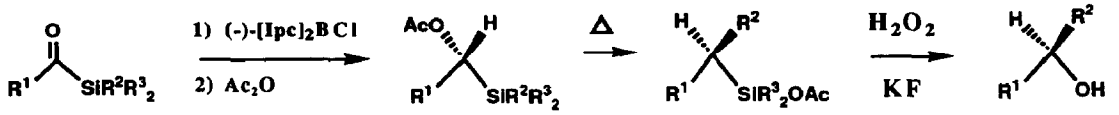
Summary: Asymmetric allylboration of acylsilanes with *B*-allyldiisopinocampheylborane [(+)-Ipc$_2$BAll] is highly substrate dependent, resulting in variable amounts of asymmetric induction. The determination of enantiomeric excess of the resulting highly hindered tertiary silylcarbinols was accomplished by reaction with diazaphospholidine **6** in the presence of a catalytic amount of methoxyacetic acid.

We recently reported a unique approach to the preparation of chiral secondary alcohols.[1] The methodology, shown below, involves the initial preparation of chiral secondary silylcarbinols through the asymmetric reduction of an acylsilane.[2] These resultant silyl carbinols are then acylated and thermolized as shown, leading to the migration of one alkyl (or aryl) substituent from silicon to carbon with the simultaneous transfer of the acyloxy group from carbon to silicon (sometimes referred to as a dyeotropic shift). A potential advantage of this methodology (over the direct chiral reduction of ketones) is the ability to prepare chiral alcohols in which R^1 and R^2 are very similar (ex. R^1 = Ph, R^2 = *p*-Tol).

Scheme 1



1 2 3 4

The potential application of this methodology to the preparation of chiral *tertiary* alcohols requires the following: 1) Acylsilanes must be shown to react with an asymmetric reductive-alkylating reagent to achieve a reasonably high enantiomeric excess; 2) The resulting tertiary silylcarbinols must rearrange in their acylated form to produce tertiary silafunctional compounds analogous to **3**; 3) Oxidative cleavage of these materials must proceed in reasonable yield. We would now like to report our progress toward the first of these objectives.

Chiral allylboration of aldehydes is a well-established method for the production of chiral homoallyl secondary alcohols from aldehydes.[3] While an initial paper[3a] included allylboration of four methyl ketones, the enantiomeric excess in these cases was modest and no further studies on the allylboration of ketones have appeared.

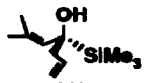
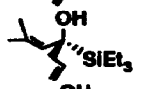
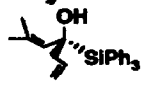
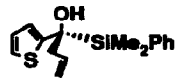
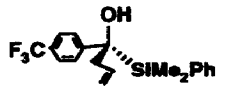
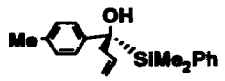
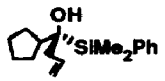
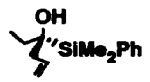
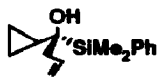
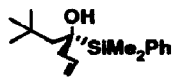
Experimentally, we discovered that most acylsilanes are substantially less reactive toward Ipc_2BAll than are aldehydes. The reaction[4] was performed in ethyl ether at temperatures from -78 °C to room temperature. To proceed to completion, the reactions typically required from several hours to several days (for very hindered acylsilanes) at room temperature. By contrast, most aldehydes are allylborated in a few hours at -78 °C.

A key difficulty encountered in our study was the accurate measurement of the enantiomeric excess of these extremely hindered tertiary alcohols.[5] We were unable to form Mosher esters under a variety of conditions. Chiral shift reagents did not provide the necessary resolution. The tertiary silylcarbinols are thermally sensitive, precluding the use of gas chromatography on a chiral stationary phase.

Fortunately, a recent report[6] lead us to try derivatization with chiral diazaphospholidine **6** and observation of the ^{31}P NMR. Direct derivatization with this reagent succeeded for the less hindered tertiary silylalcohols, but in many cases, the derivatization reaction was still too slow. We discovered that this reaction could be catalyzed by strong acids, which unfortunately also caused concurrent decomposition of the substrate tertiary silylcarbinols. After extensive experimentation, methoxyacetic acid (pka=3.57) was found to be a suitable, nondestructive catalyst for this reaction.[7] The reaction probably proceeds via an intermediate, **7**, which is more reactive toward the alcohols than **6** (**Scheme 2**).

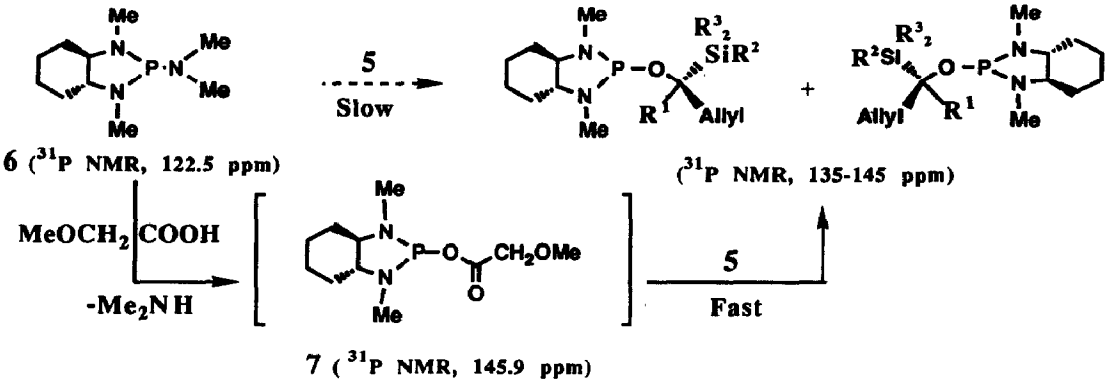
The results in **Table 1** illustrate that the asymmetric allylboration of acylsilanes proceeds with highly variable enantioselectivity. The highest values for the enantiomeric excess were obtained with α,β-unsaturated acylsilanes as substrates (entries 1-5). Only low values of asymmetric induction could be obtained with other substituents, including both aryl and alkyl-substituted acyl silanes. Attempts to increase the enantiomeric excess by changing to other solvents and/or using methoxydiisopinocampheylborane as the allylborane precursor were unsuccessful. We believe that the low yields observed in several cases are the result of at least three factors: a) Several of these tertiary silylcarbinols are unstable, leading to partial decomposition during column chromatography; b) Steric hindrance makes cleavage of the oxygen-boron bond of the initially formed boronates extremely slow; c) The allylboration reaction itself was often extremely slow even at room temperature. In attempts to improve the yields, most of these reactions were repeated using variable reaction and workup conditions. In each case, the enantiomeric excess was virtually unchanged, eliminating the possiblity of an undesired kinetic resolution due to these factors. The absolute configuration of the products were assigned by analogy with previously reported results on ketones and aldehydes, assuming that the (unsaturated) alkyl group is sterically the smallest. Especially in the case of entry 9, it is possible that the opposite stereoisomer has been produced.

Table 1. Allyboration of Acylsilanes

Entry	Product	$[\alpha]_D$[b]	e.e. (%)	^{31}P, $\Delta\delta$ (ppm)	Yield (%)[c]
1		34.1	89	1.03	72
2		37.0	59	1.99	32
3		11.9	92	2.99	61
4		53.9	81	1.19	53
5		62.4	79	1.25	44
6		3.3	17	0.95	81
7		21.3	36	2.60	81
8		11.2	26	2.44	65
9		-1.6	42	1.08	70
10		0.7	6	0.27	66
11		0.1	2	1.00	65
12[d]		-2.5	29	1.52	34

a) This reagent is derived from (+)-$[Ipc]_2BCl$ (which is, itself, derived from (-)-pinene)
b) in $CHCl_3$ at r.t. c) Isolated yields of pure products. d) Using (+)-$[Ipc]_2BAll$ from (+)-$[Ipc]_2BOMe$

Scheme 2



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References and Notes:

1a) Buynak, J. D.; Strickland, J. B.; Hurd, T.; Phan, A. *J. Chem. Soc., Chem. Commun.*. **1989**, 89. b) Buynak, J. D.; Strickland, J. B.; Lamb, G. W.; Khasnis, D.; Modi, S.; Williams, D.; Zhang, H. *J. Org. Chem.* **1991**, *56*, 7076.

2 Soderquist, J.A.; Anderson, C. L.; Miranda, E. I.; Rivera, I.; Kabalka, G. W. *Tetrahedron Lett.* **1990**, *31*, 4677.

3 a) Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.*. **1986**, *51*, 432. b)Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1987**, *52*, 3701. c) Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1988**, *110* , 1535. d) Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 401. e) Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, *55*, 1868. f) Brown, H. C.; Randad, R. S. *Tetrahedron Lett.* **1990**, *31*, 455. g) Brown, H. C.; Racherla, U.S.; Liao, Y.; Khanna, V. V. *J. Org. Chem.* **1992**, *57*, 6608. *ibid*, 6614.

4 A solution of 3-Methyl-1-trimethylsilyl-2-buten-1-one (0.99g, 6.35 mmol) in 10mL ethyl ether was added dropwise to a solution of allyboration reagent prepared according reference 3a at -78°C. Stirring was continued at -78°C for 2h and then the reaction was allowed to warm to room temperature for 1 h. The reaction mixture was treated by ethanolamine for 12h, then partitioned between the saturated aqueous ammonium chloride and a mixture of pentane/ether (1/1). (An alternative to the ethanolamine was treatment with 30% H_2O_2/sat. $NaHCO_3$/MeOH (45 mL, 1/1/1) for 4 hr.) The organic layer was separated,washed with water and brine, and dried over Na_2SO_4. After concentration in vacuum, the crude tertiary silylcarbinol was purified by flash chromatography (1%ether/ 99%pentane) afford 0.91g of colorless oil (72%). (6-Methyl-4-trimethylsilyl-1,5-hexadien-4-ol).[α]=34.1°; e.e.%=89%; ^{1}H NMR($CDCl_3$) δ 0.06 (9H, s), 1.72(3H, d, J=1.0Hz), 1.84(3H, d, J=1.0Hz), 2.25(2H, m), 5.17(3H, m), 5.86(1H, m); ^{13}C NMR($CDCl_3$) δ -3.99, 18.61, 27.60, 43.04, 70.34, 118.87, 127.23, 131.54, 133.49; IR(CCl_4) 3605, 3030, 1660, 1275, 875cm^{-1}; HRMS calcd for $C_{11}H_{21}OSi$(M-H) 197.1362, found 197.1359.

5 Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, **1983**; Vol. 1.

6 Alexakis, A.; Mutti, S.; Mangeney, P. *J. Org. Chem.* **1992**, *57*, 1224. To verify that no kinetic resolution occured during the derivatizing process, a racemic sample of each tertiary silylalcohol was synthesized by the direct reaction of corresponding acyl silane with allyl magnesium bromide. In each case, after reaction with the organophosphorus reagent, two ^{31}P NMR signals were observed in a one to one ratio with chemical shift differences identicle to those reported above.

7 Typically, in a 5 mm NMR tube were placed the alcohol (0.2 mmol, 1.0 eq) and $CDCl_3$ (0.5 mL). **6** (1.3 eq) was then added, followed by methoxyacetic acid (0.2 eq). The ^{31}P NMR spectrum was recorded after allowing the reaction to stand for several hours at room temperature.

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