available criteria. First, it avoids the need for an arbitrary or hypothetical external reference structure; instead, we employ the planar geometry of the actual system being studied as an internal reference. Second, our computational approach enables us to consider systems that are experimentally inaccessible, providing a means to evaluate the degree of aromaticity or antiaromaticity of experimentally unobservable species. Third, the computations can provide a quantitative measure of the degree of aromaticity or antiaromaticity. Work aimed at broadening the scope and applicability of this method is currently underway in our laboratory.

Acknowledgment. We thank Dr. Kendall N. Houk and Dr. John Yates (University of California at Los Angeles; University of Pennsylvania) for providing us with a copy of the Harris-800 version of GAUSSIAN 80. The IBM version of that program was generously provided by Dr. Sid E. Topiol (Berlex Laboratories, Inc.; Mt. Sinai School of Medicine).

Registry No. 1, 53249-01-7; 2, 3026-16-2; 3, 113811-17-9; 4, 113811-18-0; 5, 290-67-5; 6, 290-79-9; 7, 71-43-2; 8, 110-86-1; 9, 290-37-9.

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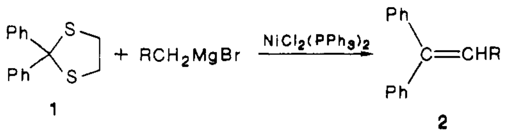
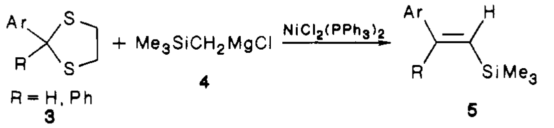
Nickel-Catalyzed Silylolefination of Dithioacetals. A Stereoselective Way to Vinylsilanes[1]

Summary: (*E*)-Vinylsilanes are synthesized stereoselectively in good yields from dithioacetals and Me_3SiCH_2MgCl in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$.

Sir: Vinylsilanes demonstrate an enormous variety of fascinating applications in organic synthesis.[2,3] A number of procedures have been available for their preparations and most of them use alkynes as starting materials.[4] It is noted that the reaction of (silylmethyl)magnesium halide reagent with carbonyl compounds affords exclusively the corresponding desilylated olefins.[5] Some modified silyl reagents have been employed for the synthesis of vinylsilanes;[6] none of them, however, are easily accessible. The transition-metal-catalyzed coupling reaction of aryl or vinyl thioethers with Grignard reagents is well-documented.[7] Recently we found that benzophenone dithioacetal can couple with Grignard reagents in the presence of a nickel catalyst to give the alkylated olefin (eq 1).[8] We felt that this reaction could be exploited in the synthesis of vinylsilanes. As part of our continuing interest in the transition-metal-mediated C–S bond cleavage reactions[8-10] and, in particular, the synthetic applications of dithioacetals,[8,10] we present here a convenient method for the stereoselective synthesis of vinylsilanes (eq 2).



(1)



(2)

In a typical procedure, a mixture of dithioacetal, 3 equiv of Me_3SiCH_2MgCl (4), and 5 mol % of $NiCl_2(PPh_3)_2$ in ether–benzene or ether–THF was heated under reflux overnight. After the usual workup, the corresponding vinylsilane was obtained. The results are tabulated in Table 1.[11]

As can be seen from Table I, a variety of (*E*)-vinylsilanes were synthesized in good yields. The presence of electron-donating substituents (entries 2–5) has no effect on the yields of the reactions. It is particularly noteworthy that the ethereal linkages in **3d** and **3e** are stable under the reaction conditions.[12] Substrates containing two dithioacetal functions behaved similarly. Thus, both *o*- and *p*-phthalaldehyde dithioacetals (**3f**, **3g**) afforded the bissilylolefination products in satisfactory yields (entries 6 and 7).

Aryl halides are known to couple with the Grignard reagent in the presence of a nickel catalyst.[13] Accordingly,

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(1) Transition Metal Promoted Reactions, 22.

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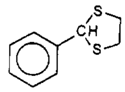
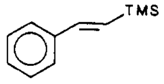
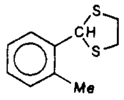
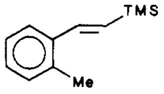
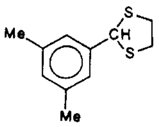
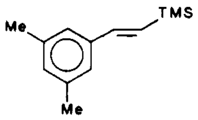
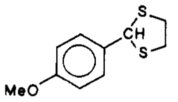
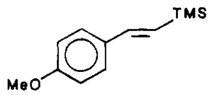
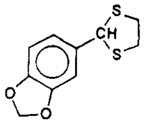
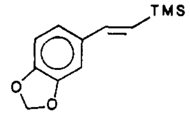
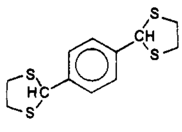
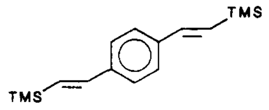
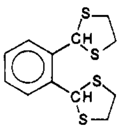
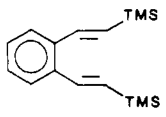
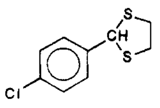
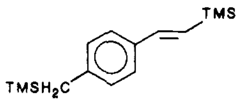
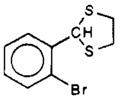
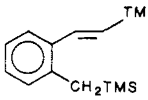
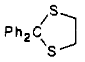
(10) Wong, C. S.; Leung, W. S.; Yeung, L. L.; Luh, T.-Y. *J. Organomet. Chem.* **1986**, *307*, C49. (b) Yeung, L. L.; Yip, Y. C.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 981.

(11) ^1H NMR data (δ, $CDCl_3$, Me_4Si as internal standard in **5a–g**, as external standard otherwise). **5a**: 0.18 (s, 9 H), 6.40 (d, *J* = 20 Hz, 1 H), 6.80 (d, *J* = 20 Hz, 1 H), 7.12–7.51 (m, 5 H). **5b**: 0.15 (s, 9 H), 2.35 (s, 3 H), 6.34 (d, *J* = 20 Hz, 1 H), 7.10 (d, *J* = 20 Hz, 1 H), 7.00–7.36 (m, 4 H). **5c**: 0.15 (s, 9 H), 2.32 (s, 6 H), 6.45 (d, *J* = 20 Hz, 1 H), 6.82 (d, *J* = 20 Hz, 1 H), 6.88 (br s, 1 H), 7.05 (br s, 2 H). **5d**: 0.13 (s, 9 H), 3.78 (s, 3 H), 6.28 (d, *J* = 19 Hz, 1 H), 6.81 (d, *J* = 19 Hz, 1 H), 6.84 (d, *J* = 8 Hz, 2 H), 7.34 (d, *J* = 8 Hz, 2 H). **5e**: 0.15 (s, 9 H), 5.90 (s, 2 H), 6.22 (d, *J* = 19 Hz, 1 H), 6.73 (d, *J* = 19 Hz, 1 H), 6.70–7.23 (m, 3 H). **5f**: 0.15 (s, 18 H), 6.54 (d, *J* = 19 Hz, 2 H), 6.93 (d, *J* = 19 Hz, 2 H), 7.47 (s, 4 H). **5g**: 0.16 (s, 18 H), 6.32 (d, *J* = 19 Hz, 2 H), 7.20 (d, *J* = 19 Hz, 2 H), 7.13–7.53 (m, 4 H). **5h**: –0.02 (s, 9 H), 0.15 (s, 9 H), 2.05 (s, 2 H), 6.41 (d, *J* = 20 Hz, 1 H), 6.86 (d, *J* = 20 Hz, 1 H), 6.99 (d, *J* = 8 Hz, 2 H), 7.34 (d, *J* = 8 Hz, 2 H). **5i**: –0.03 (s, 9 H), 0.15 (s, 9 H), 2.18 (s, 2 H), 6.30 (d, *J* = 19 Hz, 1 H), 7.08 (d, *J* = 19 Hz, 1 H), 6.91–7.58 (m, 4 H). **5j**: –0.1 (s, 9 H), 6.28 (s, 1 H), 7.22 (s, 10 H). All new compounds give satisfactory analytical data and/or exact mass molecular weights.

(12) Aryl methyl ethers have been found to be reactive under similar conditions. Cf. Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246.

0022-3263/88/1953-2129$01.50/0

Table I. Nickel-Catalyzed Coupling of Dithioacetals with TMSCH$_2$MgCl[a,b]

entry	substrate	solvent[c]	product	% yield[d]
1	 **3a**	A	 **5a**	76
2	 **3b**	B	 **5b**	71
3	 **3c**	B	 **5c**	71
4	 **3d**	B	 **5d**	73
5	 **3e**	A	 **5e**	76
6	 **3f**	A	 **5f**	69[e]
7	 **3g**	B	 **5g**	80[e]
8	 **3h**	B	 **5h**	50[f]
9	 **3i**	B	 **5i**	82[f]
10	 **3j**	A	Ph$_2$C=CHTMS **5j**	79

[a] TMS = Me$_3$Si. [b] Unless otherwise stated, the reaction was carried out under the following conditions: A mixture of the substrate (1 mmol), TMSCH$_2$MgCl (3 mmol, ether solution, 1 M), and NiCl$_2$(PPh$_3$)$_2$ (0.05 mmol) in mixed solvent (ca. 5 mL) was refluxed overnight. [c] A = benzene–ether; B = THF–ether. [d] Isolated yield. [e] 6 mmol of Grignard reagent in 10 mL of solvent. [f] 5 mmol of Grignard reagent in 10 mL of THF.

reactants containing such functionality would be expected to react with **4** under the reaction conditions. Thus, dithioacetals of *o*-bromobenzaldehyde (**3h**) and *p*-chlorobenzaldehyde (**3i**) underwent a double coupling reaction to introduce both vinylsilane and benzylsilane functions in one step. The product **5i** would be very useful in the annelation reactions and, indeed, related compounds have been employed in natural product syntheses.[14]

As shown in Table I, it is important to note that in all cases only (*E*)-vinylsilane was isolated and no detectable quantity of Z isomer was observed from the reactions. Furthermore, no trace amount of Peterson olefination[5] product was obtained at all in these reactions. The re-

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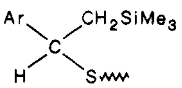
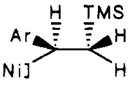
action may proceed via the first coupling reaction with **4** to give the intermediate **6** which may undergo an oxidative addition[15] with a Ni(0) species to afford **7**.[8] A β-elimination process may then occur to yield the corresponding vinylsilane. The requirement of cis coplanarity of Ni–C–C–H atoms for β-elimination and the steric effect of the silyl group determine the stereochemistry of product.[16]



6



7

In summary, we have depicted a convenient synthesis of vinylsilanes from dithioacetals. Thus, our method provides a short passage for the stereoselective transformation of aldehyde to vinylsilane via dithioacetal which is readily accessible.

Acknowledgment. We thank the Croucher Foundation for generous support. Z.J.N. thanks Beijing-Hong Kong Academic Exchange Centre for support and the Lee Hysan Foundation for a fellowship.

Registry No. **3a**, 5616-55-7; **3b**, 67810-92-8; **3c**, 113509-20-9; **3d**, 6712-20-5; **3e**, 5769-01-7; **3f**, 69922-37-8; **3g**, 113509-21-0; **3h**, 23229-32-5; **3i**, 113509-22-1; **3j**, 6317-10-8; **4**, 13170-43-9; **5a**, 19372-00-0; **5b**, 113509-23-2; **5c**, 113509-24-3; **5d**, 76711-42-7; **5e**, 113509-25-4; **5f**, 113509-26-5; **5g**, 113509-27-6; **5h**, 113509-28-7; **5i**, 113509-29-8; **5j**, 51318-07-1; $NiCl_2(PPh_3)_2$, 14264-16-5.

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(17) Lee Hysan Foundation Graduate Fellow, 1986–87.

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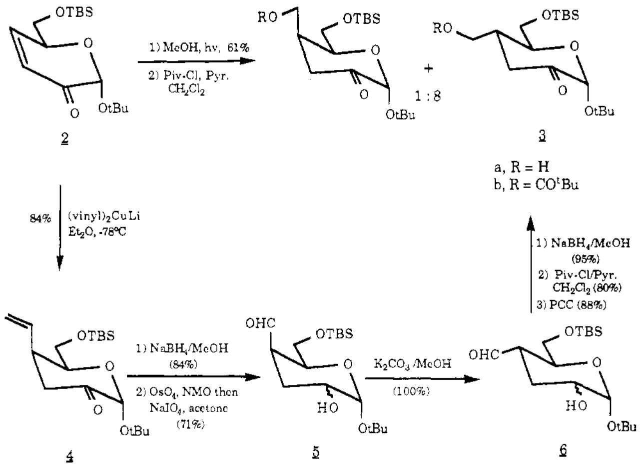
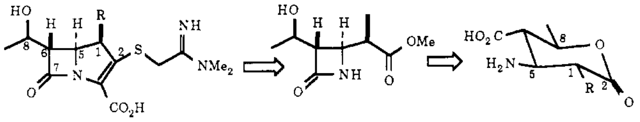
Electrophilic Amination as a Route to Deoxyamino Sugars: Synthesis of the Key Intermediate for 1β-Methylcarbapenem

Summary: The application of electrophilic amination of keto sugars as a route to deoxyamino sugars by the reaction of sugar enolates with dibenzyl azodicarboxylate has been explored. Although the success of the reaction is dependent on several factors, such as the location of the carbonyl group and the substitution pattern on the pyranosidulose ring, the process is synthetically promising. This has been demonstrated by preparation of the protected Melillo Lactone analogue **18**, a key intermediate for 1β-methylcarbapenem.

Scheme I



Sir: In most procedures for the preparation of deoxyamino sugars, the nitrogen is introduced as a nucleophile which displaces a leaving group[1] or reacts with an electrophilic site[2,3] in a pyranoside partner. Electrophilic amination[4,5] has been unexplored, in spite of the availability of a wide variety of ketonic sugars which conceivably could be suitable nucleophilic partners. In this manuscript, we report some of our work on electrophilic amination of sugars in the context of a formal total synthesis of 1β-methylcarbapenem (**1a**).[6,7]



1 Thienamycin
a, R = H
b, R = CH_3 1-β-methylcarbapenem

7
a, R = H (Melillo lactone)[13]
b, R = CH_3

Our interest in this project grew out of an unexpected observation in connection with our continuing interest in the mechanistic details of photochemically induced addition of methanol to α-enones.[8-10] In all the substrates we have examined the photoaddition and normal conjugate additions proceeded with the same stereoselectivity.[8] However, with enone **2**,[11] photoaddition gave primarily the equatorial adduct **3a** (Scheme I), while normal conjugate addition displayed the opposite stereoselectivity. This was confirmed by degradation of adduct **4** to the aldehyde **5** and epimerization to give **6**. The latter was then converted into the photoadduct, **3a**, by standard operations (Scheme I).

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