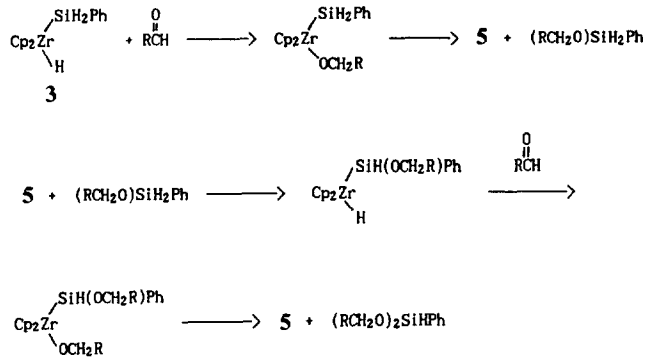

Scheme 2.

silation to produce the dialkoxyphenylsilane and **5** with dialkoxyphenylsilane to produce the trialkoxysilane. When **5** reacts with **2** to produce **3**, the catalytic cycle begins again.

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7. In a typical procedure, dimethylzirconocene (0.11 mmole), for an example, was added to a mixture of allylalcohol (4.1 mmole) and phenylsilane (1.1 mmole) in benzene. The mixture was kept at room temperature under argon for more than 24h. All manipulations were carried out under argon (or nitrogen) by using standard inert-atmosphere techniques. All solvents, phenylsilane, alcohols, aldehydes were saturated with argon (or nitrogen) before use.
8. The GC analyses were performed on a Varian 3300 chromatograph using 50 cm×1/8 inch column packed with 50% OV-101 Chrom G.H.P. 100/120. GC/MS analyses were carried out on a JEOL-JMX-DX 303, with HP 5890 capillary column. [compd, fragment, m/e (% base): $(C_3H_5O)_3SiPH$, M-H, 275 (7); M-C_3H_5, 235 (39); M-C_3H_5O, 219 (39); M-$C_6H_9O_2$, 163 (100); M-PhC_6H_{10}, 117 (39); M-$PHC_6H_{10}O$, 101 (39): $(C_3H_7O)_2SiHPh$, M-H, 223 (100); M-C_3H_7, 181 (11), M-C_3H_7O, 165 (57); M-PhH, 146 (78); M-$C_6H_{13}O$, 123 (73); M-$C_6H_{15}O_2$, 105 (26): $(C_3H_7O)_3SiPh$, M, 282 (19); M-C_2H_5, 253 (34); M-C_3H_7O, 223 (100); M-PhH, 204 (72); M-C_6H_{15}, 195 (53); M-$C_6H_{15}O_2$, 163 (15); M-$C_9H_{21}O_3$, 105 (9): $(C_4H_7O)_2SiHPh$, M, 248 (27); M-CH_3 233 (21); M-C_4H_7, 193 (51); M-C_4H_7O, 177 (48); M-C_8H_{13}, 139 (83); M-$C_8H_{13}O$, 123 (100): $(C_4H_7O)_3SiPh$, M, 318 (22); M-CH_3, 303 (11), M-C_4H_7, 263 (69); M-C_4H_7O, 247 (11); M-$C_8H_{13}O$, 193 (28); M-$C_8H_{13}O_2$, 177 (22); M-$C_{12}H_{19}O$, 139 (100).]
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10. In the case of aldehyde reactions, equimoles (3.5 mmole) of the aldehyde and phenysilane were reacted to find whether the hydrogenation of C=C or C=O groups occures preferably. No hydrogenation products to C=C group of crotonaldehyde were detected. However, the amount of alcohol detected was less than 1%, which could stem from the hydrogenation of C=O group.
11. About 48h after the begining of the reaction, ^{1}H-NMR peak (δ *ca* 9) of carbonyl CH of the aldehyde usually disappears and the pattern of ^{1}H-NMR turns completely to that of corresponding alkoxy group.

Bifunctional Diaziridine: Synthesis of Vinylic Diaziridylcarbamate[1]

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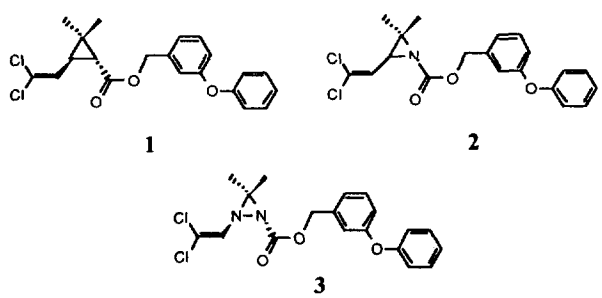
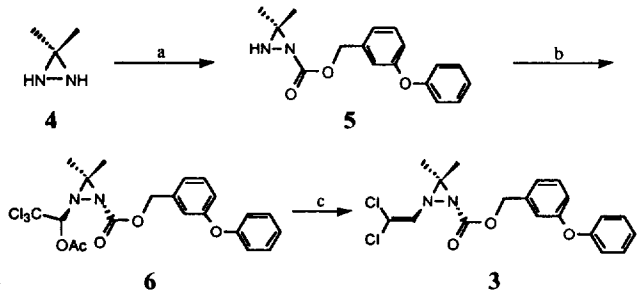
Diaziridines, structurally simple three membered heterocycles with two nitrogen atoms, are fairly new class of compounds not only for their structural inertness but also for the unique chemical reactivities.[3] With regard to the unique structural aspects, diaziridines exhibit several characteristics, namely i) trans isomer favority over *cis* isomer so that the preparation of chiral diaziridines is possible by asymmetric induction[4] ii) relatively low basicity due to the trans orientation of nonbonding electrons on nitrogen atoms[5] iii) and good stabilities toward high temperature and acidic or basic media compared to their close analogue, oxaziridines.[3] Given those attractive features of diaziridines, we have been interested in designing biologically active substances especially new





reagents: a. 3-Phenoxybenzyl chloroformate, Et_3N, CH_2Cl_2
b. i. CCl_3CHO, cat. $Bu_2Sn(OAc)_2$ ii. CH_3COCl, Et_3N, CH_2Cl_2
c. Zn, AcOH, DMF

Scheme 1.

synthetic pyrethroids containing diaziridine moiety.

Since the advent of photochemically stable permethrin **1**,[6] numerous synthetic pyrethroids have been developed during last 20 years.[7] Among them, synthetic pyrethroid **2** containing aziridine moiety in lieu of cyclopropane ring have been found in the literature,[8] but there has been no report regarding diaziridine counterpart **3**. In principle, the synthesis of **3** consists of two major functionalization; acylation of one side nitrogen and vinylation on the other. Even though there are reports on alkylation of diaziridine, functionalization of N-acyldiaziridine has been reported not so trivial mainly because of occasional ring enlargement to five membered heterocycles particulary in acidic condition.[9] We wish to report herein the synthesis of bifunctional diaziridine **3** with conservation of the three membered ring.

As shown in Scheme 1, these studies began with 3,3-dimethyldiaziridine (**4**) prepared from acetone and hydroxylamine-O-sulfonic acid in aquous ammonia.[10] Treatment of 3,3-dimethyldiaziridine (**4**) with 3-phenoxybenzyl chloroformate in the presence of Et_3N in CH_2Cl_2 at 0℃ for 2 h afforded N-acylated compound **5** in 63% chromatographed yield with no incident.[11] Regarding this N-acylation procedure, it is noteworthy to recall the statement by Schmitz[12] that acylation of 3,3-dialkyldiaziridine proceeded without exception with fission of the three membered ring.

Of special interest is the reaction sequence leading to compound **3**. Our initial attempts to prepare **3** by condensing **5** with chloral in the presence of stannous chloride or tributyltin hydride in one pot operation were not successful. Attention was turned next to the two step sequence of trapping the condensation product followed by reductive cleavage. The condensation adduct between **5** and chloral in the presence of $Bu_2Sn(OAc)_2$ catalyst was trapped by acetyl chloride to give acetate **6** in 68% yield.[13] Upon treatment of **6** with Zn along with minimum amount of acetic acid in DMF at 25℃ for 1 h afforded desired compound **3** in 34% purified yield.[14] This unique diaziridine **3** has shown to be stable under normal condition; no evidence of decomposition at room temperature for several months.

In conclusion, our studies have demonstrated that the N-acylidiaziridine can be functionalized through reductive cleavage by zinc in acetic acid to afford bifunctional diaziridine and that the pyrethroid analogue containing the diaziridine can be prepared. Other properties of diaziridine in company with this work, mainly rearrangement of unsymmetric diaziridines to five membered heterocycles, will be reported in due course.

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11. Spectral data for **5**: mass spectra (EI) m/z 298 (M^+); IR (neat) 3337, 3205, 2991, 2870, 1725, 1549, 1488, 1205, 1032, 835 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.98 (s, 3H), 2.05 (s, 3H), 2.85 (br s, 1H), 5.24 (s, 2H), 6.91-7.67 (m, 9H).
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13. Spectral data for **6**: IR (Film) 1705, 1770 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.62 (s, 3H), 1.73 (s, 3H), 2.14 (s, 3H X 2/3), 2.18 (s, 3H X 1/3, diastereomer), 5.17 (s, 2H), 5.59 (s, 1H X 1/3, diastereomer), 5.61 (s, 1H X 2/3), 6.92-7.53 (m, 9H).
14. Spectral data for **3**: R_f 0.42 (hexane : EtOAc = 2 : 1); mass spectra (EI) m/z 395 ($M^+ + 2$), 393 (M^+); IR (film) 3042, 2932, 1726 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.10 (s, 3H), 1.20 (s, 3H), 4.85 (d, J = 7.5 Hz, 1H), 4.91 (d, J = 7.5 Hz, 1H), 6.07 (s, 1H), 6.81-7.18 (m, 9H).