responding experimental DISPA plot (left) for sodium ion in a laurate/lauric acid sample. The spectrum was phased by minimizing rotation of the DISPA plot.[8] A series of theoretical DISPA plots were then constructed for various choices of τ_c. The DISPA curve at lower right in Figure 2b gave the closest theoretical match to the experimental case and corresponds to $\omega_0\tau_c = 5.6$, for which the two component peak widths have a ratio of 13.71:1.

It is of course conceivable that the frequency difference demonstrated in Figure 2 could be due to two *chemically* different ^{23}Na environments, each represented by a single Lorentzian line. Three facts argue very strongly against that interpretation. First, a least-squares fit of the absorption signal of Figure 2b, in which the two peak positions, widths, and intensities were allowed to vary *independently*, gave two peaks of relative area 1.46:1 $\simeq$ 1.5:1, and relative widths of 13.72:1 (both exactly the same as from the DISPA simulation). It is highly improbable that two different chemical environments would happen to have relative populations (3:2) exactly the same as for the two components of a dynamic frequency-shifted pair of lines. Second, a 180°-τ-10° inversion–recovery experiment (not shown) clearly resolved the longitudinal relaxation of the broad and narrow component peaks, with a T_1 difference consistent with the line width and frequency shift differences predicted by the DISPA simulation. Finally, the close match between the experimental DISPA data and the DISPA curve simulated for a dynamic frequency-shifted system further supports the present interpretation.

In conclusion, dynamic frequency shifts have been predicted[9,10] and observed[11,12] in ESR and predicted in NMR.[1-4] The present paper provides the first convincing expermental demonstration of multiple peak positions and widths for quadrupolar nuclei in NMR. A useful result of the present analysis is that the rotational correlation time, τ_c, can be determined from a *single* experimental spectrum. It is suggested that future NMR studies using quadrupolar nuclei to probe chemical and motional environment at slowly tumbling sites (e.g., micelles, membrane vesicles, polymers, biological macromolecules) should employ DISPA analysis to detect any dynamic frequency shifts and use them to determine rotational correlation times. Full details of the data reduction[14] and theoretical simulations for DISPA analysis of NMR spectra of spin $^3/_2$ nuclei will be published elsewhere.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Na, 7440-23-5; sodium laurate, 629-25-4; lauric acid, 143-07-7.

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Silicon-Induced Fragmentations: Stereoselective Preparation of (*Z*,*E*)- and (*Z*,*Z*)-1,4-Dienamine Derivatives. Synthesis of (9*Z*,12*E*)-Tetradecadien-1-yl Acetate, Pheromone of Various Lepidoptera[1]

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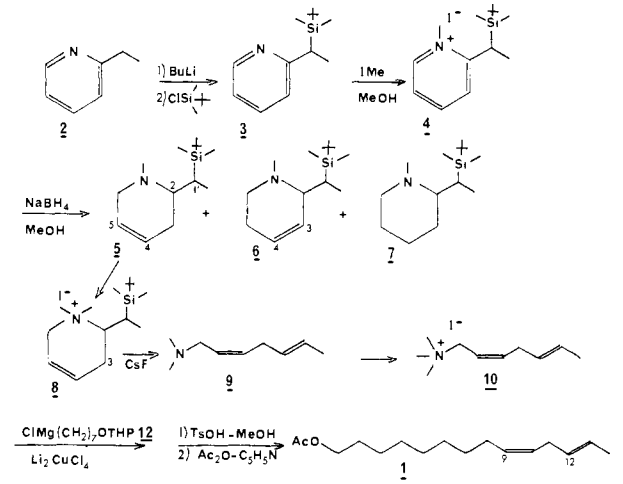
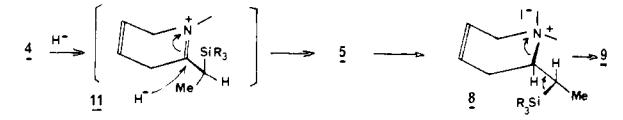
During the past decade, the synthesis of pheromones of Lepidoptera, which are generally found as straight chain mono- or polyolefinic acetates, alcohols, or aldehydes, attracted increasing attention.[2,3] Highly stereoselective methods were developed for the synthesis of these chemical messengers which are often active as a mixture of components in accurate proportions. Our approach to the synthesis of conjugated dienes using 2-alkylpyridines as starting material gave access to various *Z*,*E*, *E*,*E*,[4] and *E*,*Z*[5] pheromones.

Scheme I



Scheme II



We report herein a new methodology leading to (*Z*,*E*)- and (*Z*,*Z*)-1,4-dienamine derivatives **9** and **15** by a fluoride ion induced silicon fragmentation or by a "sila-Cope" elimination. The dienamine **9** is a direct synthetic precursor of the (9*Z*,12*E*)-tetradecadien-1-yl acetate (**1**) pheromone of various Lepidoptera.[6]

Thus the carbanion of 2-ethylpyridine formed with *n*-butyllithium (1.1 equiv) in tetrahydrofuran at −70 °C reacts readily with tert-butyldimethylchlorosilane (1.1 equiv, −70 to 0 °C) and led to the pyridine derivative **3** (83%). This compound after treatment with an excess of methyl iodide gave rise to the corresponding pyridinium salt **4**, which when reduced with sodium borohydride in methanol, afforded products **5**–**7** in 76%, 8%, and 5% yield, respectively. The spectral characteristics and in particular 400-MHz ^{1}H NMR decoupling experiments were consistent with the proposed structure for those compounds.

Alkylation of the 1,2,3,6-tetrahydropyridine **5** with methyl

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(7) NMR (400 MHz, Me_4Si = 0 ppm, $CDCl_3$) δ (**5**) 0.03 and 0.10 (3 H × 2, 2 s, CH_3Si), 0.89 (9 H, s, *t*-BuSi), 1.08 (3 H, d, $J_{2'-1'}$ = 7 Hz, $C_{2'}H_3$), 1.18 (1 H, m, $C_{1'}H$), 2.03 (2 H, m, C_3H_2), 2.29 (3 H, s, NCH_3), 2.62 (1 H, m, C_2H), 3.09 and 3.21 (2 H, dd, $J_{HH'}$ = 18 Hz, C_6-H and C_6-H'), 5.63 (1 H, d, J_{4-5} = 10 Hz, C_5H), 5.75 (1 H, d, J_{4-5} = 10 Hz, C_4H); (**6**) −0.04 and 0.08 (3 H × 2, 2 s, CH_3Si), 0.92 (9 H, s, *t*-BuSi), 1.07 (3 H, d, $J_{2'-1'}$ = 7 Hz, $C_{2'}H_3$), 1.45 (1 H, m, $C_{1'}H$), 1.93 and 1.98 (2 H, 2 m, C_5H and C_5H'), 2.33 (3 H, s, NCH_3), 2.60 (1 H, m, C_2H), 2.83 (2 H, m, C_6H_2), 5.65 (1 H, br d, J_{3-4} = 10 Hz, C_3H), 5.73 (1 H, m, C_4H); (**10**) 1.65 (3 H, d, J_{7-6} = 6.3 Hz, C_7H_3), 3.05 (2 H, t, C_4H_2), 3.45 (6 H, s, $N(CH_3)_2$), 4.36 (2 H, d, J_{1-2} = 8.5 Hz, C_1H_2), 5.40 and 5.44 (1 H, 2 t, J_{5-6} = 15.2 Hz, J_{4-5} = 6.3 Hz, C_5H), 5.61 (1 H, m, C_6H), 5.64 and 5.67 (1 H, 2t, J_{2-3} = 11 Hz, J_{1-2} = 8.5 Hz, C_2-H), 6.20 and 6.22 (1 H, 2 t, J_{2-3} = 11 Hz, J_{3-4} = 7.6 Hz, C_3H); (**1**) 1.30 (12 H, m, C_2–C_7), 1.60 and 1.65 (m and d, J_{13-14} = 6 Hz, C_8H_2 and $C_{14}H_3$), 2.05 (3 H, s, $OCOCH_3$), 2.73 (2 H, m, $C_{11}H_2$), 4.07 (2 H, t, J_{1-2} = 7 Hz, C_1H_2), 5.34–5.51 (4 H, 2 m, C_9H, $C_{10}H$, $C_{12}H$, and $C_{13}H$); (**16**, $CDCl_3$ + CF_3CO_2H) 1.15 (9 H, s, *t*-BuSi), 1.6 (3 H, dd, J_{7-6} = 7 Hz, J_{7-5} = 1.6 Hz, C_7H_3), 2.8 (2 H, m, C_4H_2), 3.06 (3 H, s, NCH_3), 4.06 (2 H, m, C_1H_2), 5.21 (1 H, m, J_{5-6} = 10.5 Hz, J_{4-5} = 7 Hz, J_{7-5} = 1.6 Hz, C_5H), 5.53 (2 H, m, C_2H and C_6H), 6.05 (1 H, 2 t, J_{2-3} = 11 Hz, J_{3-4} = 7 Hz, C_3-H), 7.5–8 (10 H, m, ArH).

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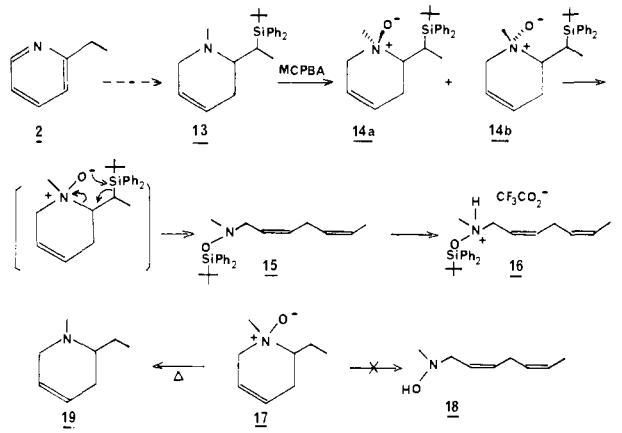
Scheme III



iodide in methanol gave rise to the tetrahydropyridinium salt **8**. With the requisite substrate in hand, its fragmentation was examined. Treatment of **8** with CsF (10 equiv) in refluxing acetonitrile for 4 h led smoothly by a stereoselective fragmentation[8] to the (2*Z*,5*E*)-1-(dimethylamino)heptadiene **9** (77%; Scheme I). It is noteworthy that the silicon-induced fragmentation was the sole reaction observed excluding Hoffmann elimination of the allylic proton on C_3.[4]

The geometry of the two double bonds was established by a careful double-irradiation experiment at 400 MHz[7] of the corresponding ammonium salt **10**. The stereoselectivity of the fragmentation led to the assignment of the 2*R*,1′*S* relative configurations to the tetrahydropyridine **5**, if an antielimination could be assumed by analogy with other desilicohalogenation reactions.[9] Furthermore, examination of the molecular model of the 3,6 dihydropyridinium intermediate **11** and consideration of the steric interactions could account for the stereospecific attack of hydride ion during the reduction step affording compound **5** (Scheme II). In addition, hydrogenation of the tetrahydropyridines **5** and **6** led to the same piperidine, **7**, showing that these three products presented the same relative configurations at C_2 and $C_{1'}$.

With the desired diene ammonium salt **10** in hand, the synthesis of the (9*Z*,12*E*)-tetradecadien-1-yl acetate (**1**) was achieved in three steps: alkylation with the Grignard reagent **12** in the presence of lithium tetrachlorocuprate[10] (THF, −30 °C, 4 h), deprotection of the alcohol (TsOH, MeOH, reflux), and acetylation (Ac_2O, pyridine) afforded the acetate **1** (74%) after purification (preparative TLC, SiO_2–NO_3Ag (15%), 90:10 hexane–AcOEt; Scheme I). This compound was identical with an authentic sample of (9*Z*,12*E*)-tetradecadien-1-yl acetate.

The behavior of the *N*-oxide **14** has been examined in order to make a comparison with the results obtained from the previous fragmentation process. By analogy with 1,3-silicon migration,[11] a "sila-Cope" elimination was expected to occur by a syn elimination which could afford the (*Z*,*Z*)-1,4-dienamine derivative **15**.

The tetrahydropyridine **13** was prepared as previously in three steps from 2-ethylpyridine **2** (overall yield 71%). Oxidation with MCPBA led to diastereoisomeric *N*-oxides **14a** and **14b**, which could not be separated. Even with the more stable diphenyl *tert*-butylsilicon group,[12] these two *N*-oxides were found to be unstable and gave rise spontaneously to a sila Cope elimination leading to the diene hydroxylamine derivative **15** (65%;[13] Scheme III). The *Z*,*Z* configuration of the two double bonds was established after careful examination of the 400-MHz NMR spectrum of the corresponding ammonium salt **16**.[7] As far as we know, this is the first example of this type of elimination.

It is noteworthy that the related *N*-oxide **17** did not give rise to the corresponding diene hydroxylamine **18**, but under more drastic conditions (toluene reflux) led to the tetrahydropyridine **19** (40%). The formation of this product is clearly the result of an intermolecular oxidation–reduction process observed already in the piperidine series by Cope and Lebel.[14]

Further work directed toward the synthesis of pheromones and other natural products including a (*Z*,*Z*)-1,4-diene unit is in progress in our laboratory.

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Registry No. 1, 30507-70-1; **2**, 100-71-0; **3**, 83862-20-8; **4**, 83862-21-9; **5**, 83862-22-0; **6**, 83862-23-1; **7**, 83862-24-2; **8**, 83862-25-3; **9**, 83862-26-4; **10**, 83862-27-5; **13**, 83862-28-6; **14a**/**14b**, 83862-29-7; **15**, 838-30-0; **16**, 83862-31-1; **17**, 83862-32-2; **19**, 5126-34-0; *tert*-butyldimethylchlorosilane, 18162-48-6; 2-[(7-chloroheptyl)oxy]tetrahydro-2*H*-pyran, 55944-71-3.

(8) For a related fragmentation see: Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476.

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(12) Hanessian, S.; Lavallee, P. *Can. J. Chem.* **1975**, *53*, 2975.

(13) MCPBA (2.7 mmol) was added to a solution of amine **13** (1.07 mmol) in CH_2Cl_2 (30 mL) at −20 °C. After 5 min, the reaction mixture was poured into a 10% aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The residue obtained after evaporation of the organic layer was refluxed in CH_3CN (10 mL) for 30 min. After evaporation of the solvent, the resulting diene was purified by TLC (SiO_2, 90–10 hexane–AcOEt).

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Chiral Allenylboronic Esters: A Practical Reagent for Enantioselective Carbon–Carbon Bond Formation

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Condensations of aldehydes with chiral allenylboronic esters provide β-acetylenic alcohols with an exceptionally high degree of enantioselectivity (Scheme I.)[1,2]

The present investigation originates from the assumption that the chiral allenyl anion may react with aldehydes via a transition state of type **1**.[3] The structure **1** appears less sterically constrained than that of its diastereomer, in which the position of the H and R groups are interchanged. Thus, if the reaction is stereospecific it will result *in predictable transfer of chirality from chiral auxiliary ligand (easily obtainable from (+)- or (−)-dialkyl tartrate) to a newly formed carbon–carbon bond.*[4] Verification of this hypothesis has been obtained as illustrated in Table I.

The following experiment provides details of the new process: A 1-L round-bottomed flask, equipped with a magnetic stirring

(1) Recent applications of allenyl anions for organic synthesis: Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Org. Chem.* **1982**, *47*, 2225.

(2) Condensations of aldehydes with enantiomerically enriched allylboranes were shown to provide homoallylic alcohols with 50–85% ee: Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330. See also: Herold, T.; Schrott, U.; Hoffmann, R. W. *Chem. Ber.* **1981**, *114*, 359. Recently, reactions of allenic and propargylic boranes were reported: Pearson, N. R.; Hahn, G.; Zweifel, G. *J. Org. Chem.* **1982**, *47*, 3364.

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0002-7863/82/1504-7667$01.25/0