The analysis reported above for (Chl a·H_2O)$_2$ evidently applies also to that of closely analogous fluorescence lifetime measurements described for the monomer–dimer system involving covalently linked Chl a pairs.[16]

The research reported in this paper was supported by the Basic Research Division of the Gas Research Institute.

(16) Wasielewski, M. R., ref 11, Chapter 7, pp 242–246.

Application of Allenylsilanes in [3 + 2] Annulation Approaches to Oxygen and Nitrogen Heterocycles

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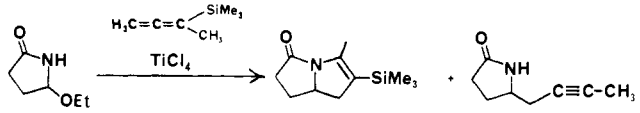
The reaction of allenylsilanes with electron-deficient olefins and acetylenes constitutes a powerful method for the regio- and stereocontrolled synthesis of highly substituted cyclopentenes (eq 1).[2] In this paper we report that carbonyl and N-acyl imine derivatives can participate as "heteroallenophiles" in a related [3 + 2] annulation approach to five-membered heterocyclic compounds (Scheme I).

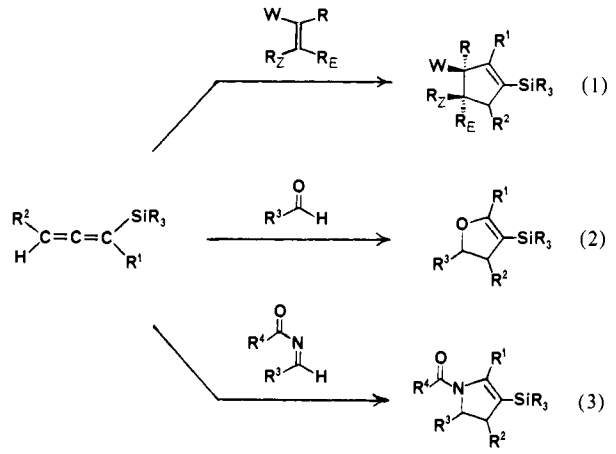
Initial attempts to extend our [3 + 2] annulation strategy to the synthesis of heterocyclic systems met with limited success. As we have previously noted,[3] the $TiCl_4$-promoted addition of allenyltrimethylsilanes to ketones and aldehydes leads predominantly to the formation of homopropargylic alcohols. More promising results were obtained, however, when we examined the reaction of allenylsilanes with N-acyl iminium ions.[4] For example, addition of 1-methyl-1-(trimethylsilyl)allene to 5-ethoxy-2-pyrrolidinone (**1**) in the presence of titanium tetrachloride (0 → 25 °C, CH_2Cl_2) produced the desired pyrrolizinone **2** in 28% yield, in addition to the acetylenic lactam **3** (59% yield).



1 2 3

In this reaction we considered it likely that the lactam products **2** and **3** were being generated via a pathway analogous to that involved in our earlier [3 + 2] cyclopentene annulation.[2b] Thus, regiospecific electrophilic substitution of the N-acyl iminium ion derived from **1** at C-3 of the allenylsilane produces a vinyl cation stabilized by hyperconjugative interaction with the adjacent carbon–silicon σ bond. A 1,2-cationic trimethylsilyl shift then occurs affording an isomeric vinyl cation, which is intercepted by the nucleophilic nitrogen atom to generate the new heterocyclic ring. Alternatively, either intermediate carbocation may undergo chloride-initiated desilylation and thus produce the acetylenic product **3**.

Scheme I



Upon considering this mechanism, it appeared evident to us that by simply increasing the steric shielding about silicon we might effectively suppress the unwelcome desilylation pathway and thereby direct the course of these reactions to afford exclusively the desired heterocyclic products. This simple stratagem proved eminently successful: in contrast to the reactions of allenyltrimethylsilanes, (*tert-butyldimethylsilyl)allenes*[5] smoothly combine with aldehydes and N-acyl imine derivatives to afford five-membered heterocycles (Table I and II). In a typical reaction, 1.1 equiv of $TiCl_4$ is added to a 0.2 M solution of the aldehyde in CH_2Cl_2 at −78 °C. After 10 min, 1.2 equiv of allenylsilane is added, and the resulting solution is stirred at −78 °C for 15–45 min. The reaction mixture is quenched by rapid addition of 7 equiv of Et_3N,[7] and then transferred into a mixture of ether and water. Ether extraction followed by chromatographic purification (or distillation) furnishes the desired 2,3-dihydrofurans.[8] For the synthesis of nitrogen heterocycles, a similar procedure is employed except that the reaction is carried out at 0–25 °C rather than at −78 °C.

A variety of aldehydes[9] function as heteroallenophiles in this [3 + 2] annulation (Table I). Reactions of the C-3 substituted allenylsilane **7** with achiral aldehydes (entries 3–5) afforded predominantly *cis-substituted* dihydrofurans,[10] as predicted based on the well-documented stereochemical course of Lewis acid promoted additions of 3-substituted allylsilanes to aldehydes.[11,12] Addition of the achiral allene **4** to the chiral α-alkoxy aldehyde **13** also proceeds as expected to produce exclusively **14** via che-

(1) Fellow of the Alfred P. Sloan Foundation, 1981–1985.

(2) (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (b) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. (c) Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513.

(3) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925.

(4) For examples of the addition of *allylsilanes* to N-acyl iminium ions, see: (a) Hart, D. J.; Tsai, Y.-M. *Tetrahedron Lett.* **1981**, *22*, 1567. (b) Kraus, G. A.; Neuenschwander, K. *J. Chem. Soc., Chem. Commun.* **1982**, 134. (c) Aratani, M.; Sawada, K.; Hashimoto, M. *Tetrahedron Lett.* **1982**, *23*, 3921. (d) Prasad, K.; Adlgasser, K.; Sharma, R.; Stutz, P. *Heterocycles* **1982**, *19*, 2099. (e) Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett.* **1983**, *24*, 1407. (f) Hiemstra, H.; Fortgens, H. P.; Speckamp, W. N. *Ibid.* **1984**, *25*, 3115. (g) Hiemstra, H.; Klaver, W. J.; Moolenaar, M. J.; Speckamp, W. N. *Ibid.* **1984**, *25*, 5453. (h) Hiemstra, H.; Klaver, W. J.; Speckamp, W. N. *J. Org. Chem.* **1984**, *49*, 1149. (i) Kozikowski, A. P.; Park, P. *Ibid.* **1984**, *49*, 1674. (j) Gramain, J. C.; Remuson, R. *Tetrahedron Lett.* **1985**, *26*, 327.

(5) 1-Methyl-1-(*tert*-butyldimethylsilyl)allene (**4**) was prepared in 63% overall yield (35-g scale) from propargyl alcohol by a procedure analogous to that previously used to prepare 1-methyl-1-(trimethylsilyl)allene.[2b,6] 1,3-Dimethyl-1-(*tert*-butyldimethylsilyl)allene (**7**) [bp 78–80 °C (20 mmHg)] was prepared from **4** by sequential treatment with 1.2 equiv of n-BuLi (−78 °C, 0.5 h) and then 4 equiv of CH_3I (−78 → 0 °C) in THF.

(6) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390.

(7) Partial hydrolysis of the products occurred when aqueous quenching procedures were employed.

(8) Recently 3,4-dihydrofurans have been isolated as byproducts from the reaction of propargyltrimethylsilanes with acetals: Pornet, J.; Miginiac, L.; Jaworski, K.; Randrianoelina, B. *Organometallics* **1985**, *4*, 333.

(9) Thus far annulations employing ketones as heteroallenophiles have been less successful. For example, reaction of the allenylsilane **4** with cyclohexanone produces the expected 2,3-dihydrofuran in only 20–25% yield.

(10) The major isomers produced in these annulations were identified as the cis-substituted dihydrofurans by ^1H NMR spectroscopic analysis. These assignments are consistent with the stereochemical course of the reactions of the corresponding (trimethylsilyl)allenes.[12]

(11) (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107. (b) Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. *Tetrahedron Lett.* **1983**, *28*, 2865. (c) Denmark, S.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655.

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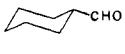
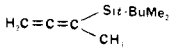
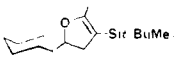
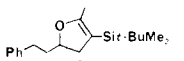
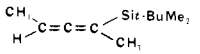
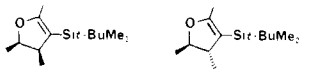
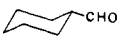
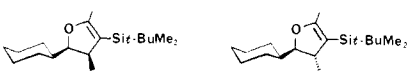
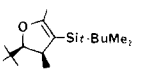
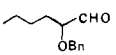
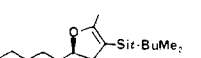
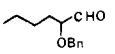
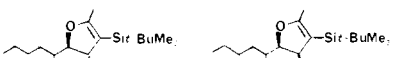
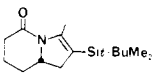
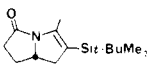
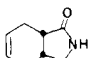
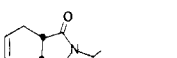
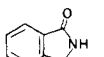
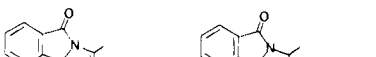
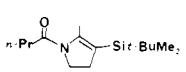
Table I. Synthesis of Oxygen Heterocycles via [3 + 2] Annulation

entry	allenophile	allene	annulation product(s)	yield, %[a]
1		 4	 5	76
2	$PhCH_2CH_2CHO$	4	 6	70
3	CH_3CHO	 7	 8 9	78 (1.4:1)
4		7	 10 11	97 (7:1)
5	*t*-BuCHO	7	 12	92
6	 13[b]	4	 14	88
7	 13	7	 15a,b 16	86 (3.5:1)

[a] Isolated yiel s of products purified by distillation or preparative radial thin layer chromatography on Et_3N-treated SiO_2. IR, ^1H NMR, ^{13}C NMR, and mass spectral data were fully consistent with the assigned structures. High-resoluiion mass spectra and/or elemental analyses were obtained for all new compounds. Isomer ratios were determined by ^1H NMR analysis of unpurified reaction products. [b] Prepared in 67% yield from valeraldehyde via the sequence (1) H_2C=CHMgBr, THF, (2) NaH, BnBr, catalytic *n*-Bu_4NI, THF, and (3) O_3, MeOH, Me_2S.

Table II. Synthesis of Nitrogen Heterocycles via [3 + 2] Annulation

entry	allenophile	allene	annulation product(s)	yield, %[a]
1	17	4	 18	67
2	19	4	 19	63
3	 20	4	 21	76[d]
4	 22	4	 23 24	64 (2.8:1)
5	1	7	25 26	60 (1.2:1)[f]
6	*n*-PrCONHCH$_2$O*t*-Bu 27[g]	4	 28	25

[a] Isolated yields of products purified by chromatography. Yields are calculated on the basis of either the alkoxy lactam (entry 3) or the corresponding imide (entries 1,2, 4,5) or amide precursors (entry 6). IR, ^1H NMR, ^{13}C NMR, and mass spectral data were fully consistent with the assigned structures. High-resolution mass spectra and/or elemental analyses were obtained for all new compounds. [b] Prepared by $NaBH_4$ reduction (HCl, EtOH) of the corresponding imide according to the method of: Hubert, J. C.; Wijnberg, J. B. P. A., Speckamp, W. N. *Tetrahedron* 1975, *31*, 1437. [c] Reference 4f. [d] The diastereomeric product was isolated in 0.6% yield. [e] Matoba, K.; Yamazaki, T. *Chem. Pharm. Bull.* 1974, *22*, 2999. [f] The major isomer was tentatively assigned as **25** by ^1H and ^{13}C NMR analysis. [g] Prepared from *N*-(hydroxymethyl)butyramide (Einhorn, A.; Hamburger, A. *Justus Liebigs Ann. Chem.* 1908, *361*, 122) by treatment with *t*-BuOH in the presence of catalytic HCl (25 °C, 2 h) according to the procedure of: Chwala, v. A. *Monatsh. Chem.* 1948, *78*, 172.

lation-controlled addition to the carbonyl group.[13,14] However, reaction of the chiral allene **7** with the chiral α-alkoxy aldehyde **13** yielded three diastereomeric products in a 2.7:1:0.8 ratio. ^{1}H NMR analysis identified the major and minor isomers (**15a** and **15b**) as *trans*-substituted dihydrofurans; the configuration of the benzyloxy group could not be established with certainty. The mechanistic basis for this interesting reversal from syn to anti diasteroselectivity is under further investigation.

The examples presented in Table II illustrate the application of our [3 + 2] annulation strategy to the synthesis of nitrogen heterocycles. Two limitations of the method have been identified. Annulations employing acyclic *N*-acyl iminium ions (e.g., entry 6) produce the desired 2-pyrroline derivatives in relatively low yield.[15] Interestingly, reaction of **4** with the iminium ion derived from phthalimide (entry 4) leads to a mixture of **24** and the aromatized product **23**.

The heterocyclic systems generated in our new [3 + 2] annulation strategy are incorporated as key structural features in several important classes of natural products, including the pyrrolizidine alkaloids and the carbapenem and ionophore antibiotics. Further studies are planned in our laboratory to demonstrate the utility of this methodology in the synthesis of these biologically significant compounds.

Acknowledgment. We thank the National Science Foundation, Firmenich SA, and Eli Lilly and Co. for generous financial support. We are grateful to Dr. John C. Dewan for the X-ray structure determination of the dihydro-1,3-oxazine ii.

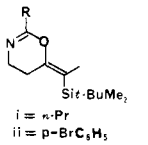
Supplementary Material Available: Full characterization (250-MHz ^{1}H NMR, ^{13}C NMR, IR, and high-resolution mass spectral data and/or elemental analyses) for all annulation products and details of the X-ray diffraction analysis of the dihydro-1,3-oxazine ii (21 pages). Ordering information is given on any current masthead page.

(12) We have found that the $TiCl_4$-promoted addition of 3-substituted allenyltrimethylsilanes to aldehydes produces (mainly) *syn*-homopropargylic alcohols; the stereochemistry of these products was established by conversion to known compounds: Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A., unpublished results.

(13) The stereochemical identity of **14** was established by its conversion to *d,l*-5,6-decanediol via the sequence (a) anhydrous HCl, MeOH, (b) $HSCH_2CH_2CH_2SH$, BF_3·Et_2O, CH_2Cl_2, and (c) Li, $EtNH_2$.

(14) For examples of the related addition of *allylsilanes* to chiral α-alkoxy aldehydes, see: (a) Reetz, M. T.; Kesseler, K.; Schmidtberger, S.; Wenderoth, B.; Steinbach, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 989. (b) Heathcock, C. H.; Kiyooka, S.-I.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214. (c) Reetz, M. T.; Kesseler, K.; Jung, A. *Tetrahedron Lett.* **1984**, *25*, 729. (d) For a general review of addition reactions of chiral α- and β-alkoxy carbonyl compounds, see: Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556.

(15) A second product identified as the dihydro-1,3-oxazine i was also generated in this reaction (41%). The structure of this side product was



i = *n*-Pr
ii = p-BrC_6H_5

established by an X-ray diffraction analysis of the analogous annulation byproduct ii (see Supplementary Material).

*Book Reviews**

Principles of Adsorption and Absorption Processes. By D. M. Ruthven (University of New Brunswick, Fredericton). John Wiley & Sons: New York. 1984. xxiv + 433 pp. $49.50 ISBN 0-471-86606-7.

This book is aimed at the chemical engineering of physisorption processes (separations and removal of impurities) with particular emphasis on molecular sieve adsorbents. However, the book starts with a rather detailed, general treatment of the physical chemical background of adsorption processes, the structure and nature of silica gel, alumina, adsorbent carbons, and zeolites, the experimental and theoretical characteristics of physisorption, the thermodynamics of physisorption, isotherms, and diffusion in porous media. It then proceeds through the chemical engineering aspects of adsorption processes and closes with chapters on chromatographic separation processes and adsorption separation processes in cyclic batch systems and then in continuous countercurrent systems. The details of the design of units for adsorption processes are treated in detail. A number of specific commercial processes are described, but the removal of water from solvents and the purification of waste water are specifically excluded from consideration.

The book is well organized and should be very useful to those concerned with the area.

Robert L. Burwell, Jr., *Northwestern University*

Determination of Organic Reaction Mechanisms. By Barry K. Carpenter (Cornell University). John Wiley and Sons: New York. 1984. IX + 247 pp. $34.95. ISBN 0471-89369-2

This book is based on a one-semester course offered by the author at Cornell. The author states "it is intended for students who have already had substantial exposure to organic chemistry, probably including a graduate-level course". The reviewer agrees with this evaluation.

The techniques considered in this text include isotopic labeling, chirality and stereochemistry, kinetics, isotope effects, methods in acid–base chemistry, interpretation of activation parameters, and direct detection of reactive intermediates. The approach to these topics is to use literature examples, which is of course the best and most interesting way. Each example is fully referenced, which is good, because beginners may well wish to read the original papers for further amplification of the nuances of the work. The author's style is terse. Nothing is left out, but certainly in some cases further readings will be of value. The choice of examples reflects the author's interests. Those readers who have lived through physical organic chemistry's finest hours will be subject to waves of nostalgia as they study the various examples. Finally there is a rather extensive discussion of kinetic analysis by linear algebra techniques.

This book will be of interest to all mechanistically inclined organic chemists.

Donald A. Denney, *Rutgers, The State University of New Jersey*

The Science and Technology of Coal Utilization. By B. R. Cooper (West Virginia University) and W. A. Ellingson (Argonna National Laboratory). Plenum Press: New York and London. 1984. 666 pp. $85.00. ISBN 0-306-414368.

This book, as stated by the editors, is intended to review the current status of coal utilization and technology. The book is written for scientists wishing to acquaint themselves with the characterization and uses for this fossil fuel resource.

Chapter 1, with the same title as the book itself, is a review of following chapters along with the editors' opinions on energy policy and research funding. The second chapter, Coal Characterization, gives a broad review of this subject, with particular emphasis on coal petrography and the porosity/surface area characteristics of coal. The third chapter concerns itself with Coal Preparation and Cleaning, and a good treatment of present preparation practices as well as more advanced pilot-plant scale technologies and chemical cleaning approaches is given. Chapter 4 (ambiguously titled Role of Impurities) is a discussion of mineral matter effects operative during coal utilization and draws extensively on the chapter authors' research on pyrite decomposition and catalysis during coal liquefaction. Chapter 5 treats the subjects of Gasification and Indirect Liquefaction, while Chapter 6 reviews Direct Liquefaction. The former chapter is process and technology oriented while the latter provides a more fundamental chemical and mechanistic treatment. Chapters 7 through 9 cover Fluidized-Bed Combustion, Coal-Fired Open-Cycle MHD Plants, and Fuel Cell Power Plant Systems, respectively. Chapter 10 provides a comprehensive review of Catalysis and Catalytic Deacti-

*Unsigned book reviews are by the Book Review Editor.