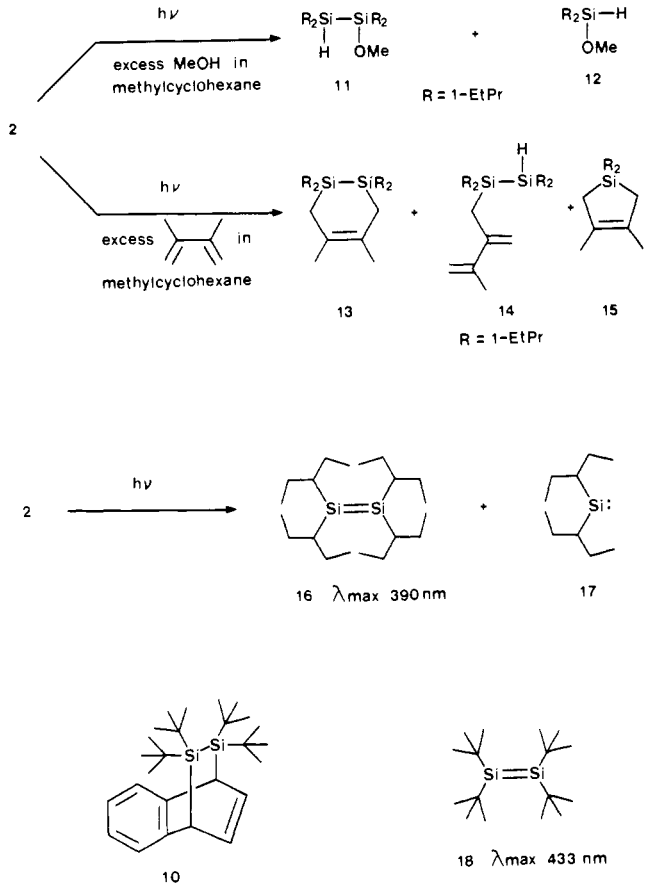
Scheme II



Thus, complete disappearance of **2** (60 mg in 4 mL of methylcyclohexane, 2×10^{-2} M) requires several hours of irradiation with a spiral low-pressure mercury lamp (125-watt output) at 4 °C. In the presence of methanol (1 M), this photolysis of **2** provides 1,1,2,2-tetrakis(1-ethylpropyl)methoxydisilane (**11**) (97% yield)[5] and bis(1-ethylpropyl)methoxysilane (**12**) (82%),[5] while the use of 2,3-dimethylbutadiene as a trapping agent leads to the formation of compounds **13**[5] (19% yield), **14**[5] (29%), and **15**[5] (56%) (see Scheme II). These experiments clearly demonstrate that the primary photoproducts are the disilene **16** and silylene **17**, as earlier observed for **1**.[1,8] In the absence of a trapping agent, the photolysate develops yellow coloration (λ_{max} at 390 nm) which is almost certainly ascribed to **16**, as the color disappears instantly upon addition of methanol. That this absorption appears at a wavelength shorter than that (433 nm) of tetra-*tert*-butyldisilene (**18**)[8] is of great interest.[9] We plan to present elsewhere an interpretation of this fact as well as an account of both the ground and excited states of alkylcyclotrisilanes, which are now readily available.[10]

Acknowledgment. We thank the National Science Foundation and Yoshitomi Pharmaceutical Industries, Ltd., Japan, for financial support. High-resolution mass spectra were provided by the facility, supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann), from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: A listing of physical properties of new compounds (4 pages). Ordering information is given on any current masthead page.

(8) Masamune, S.; Murakami, S.; Tobita, H., unpublished results.
(9) Also note that tetrakis(2,6-dimethylphenyl)disilene has a UV absorption maximum at 422 nm. (a) Reference 1 and (b) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343.
(10) **Note Added in Proof**: After the submission of this communication a report on the synthesis of another cyclotrisilane appeared. Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781.

Methods for Indole Alkaloid Synthesis: An Exceptionally Mild Procedure for Introducing the 6,7 Double Bond into Aspidosperma Alkaloids via Thiolactams†

Philip Magnus* and Paul Pappalardo

Department of Chemistry, Indiana University Bloomington, Indiana 47405

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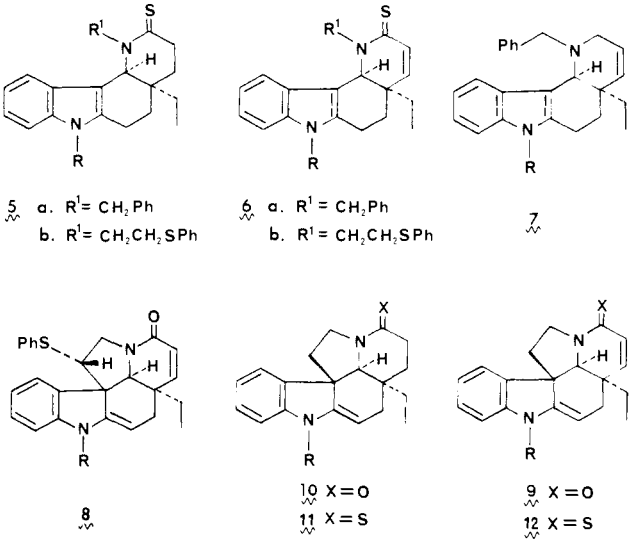
During recent years many new and versatile methods have been developed to introduce a double bond in conjugation with a carbonyl group. Only phenylselenylation of an amide enolate has been applied to the general problem of making the 6,7 double bond in Aspidosperma type alkaloids, but this procedure did not work for the systems described here.[1]

Here we describe a mild new method specifically designed to introduce the 6,7 double bond into alkaloid precursors (Scheme I). Such a transformation (**3** → **4**) is essential if the more highly functionalized indole alkaloids such as tabersonine or vindoline are to be synthesized by the indole-2,3-quinodimethane strategy.[2]

Treatment of the imine **1a** with the mixed carbonic anhydride **2**, (from 4-ethyl-4-pentenoic acid/Et_3N/vinyl chloroformate) in chlorobenzene at 140 °C for 18 h gave the tetracyclic lactam **3a** (50%; mp 204–205 °C).[2] Attempts to convert **3a** into the α,β-unsaturated amide **4a** using a variety of procedures (LDA/PhSeBr, LDA/$PhSO_2SPh$, $LiN(SiMe_3)_2/PhSO_2SPh$) only gave the starting lactam **3a** and intractable decomposition products.

Since protons adjacent to a thiolactam (ca. pK_a = 12–16) are considerably more acidic than those adjacent to a lactam (ca. pK_a = 32–36), we reasoned that a thiolactam should be readily dehydrogenated by treatment with a sulfinylating agent under mild conditions. Treatment of **3a** with the Lawesson reagent[3] (HMPA/85 °C/20 h) gave the thiolactam **5a** in 61% yield, (mp 201–202 °C). The thiolactam **5a** was treated with *p*-toluene-



sulfinyl chloride (CH_2Cl_2/N-*i*-Pr_2Et/0 °C/30 min) followed by aqueous acetic acid workup to give the α,β-unsaturated thiolactam **6a** in 75% yield (mp 221–225 °C). Subsequent desulfurization

† Dedicated to Professor Sir Derek Barton, on the occasion of his 65th birthday.

(1) Lévy, J.; Laronze, J.-Y.; Laronze, J.; LeMen, J. *Tetrahedron Lett.* **1978**, 1579. For syntheses of tabersonine that involve specific methods of introducing the C-6,C-7 double bond, see: Ziegler, F. E.; Bennett, G. B. *J. Am. Chem. Soc.* **1973**, *95*, 7458. Kutney, J. P.; Badger, R. A.; Beck, J. F.; Bosshardt, H.; Matough, F. S.; Ridaura-Sanz, V. E.; So, Y. H.; Sood, R. S.; Worth, B. R. *Can. J. Chem.* **1979**, *57*, 289. Ando, M.; Büchi, G.; Ohnuma, T. *J. Am. Chem. Soc.* **1975**, *97*, 6880.
(2) Gallagher, T.; Magnus, P. *J. Am. Chem. Soc.* **1982**, *104*, 1140; **1983**, *105*, 2086.
(3) Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.

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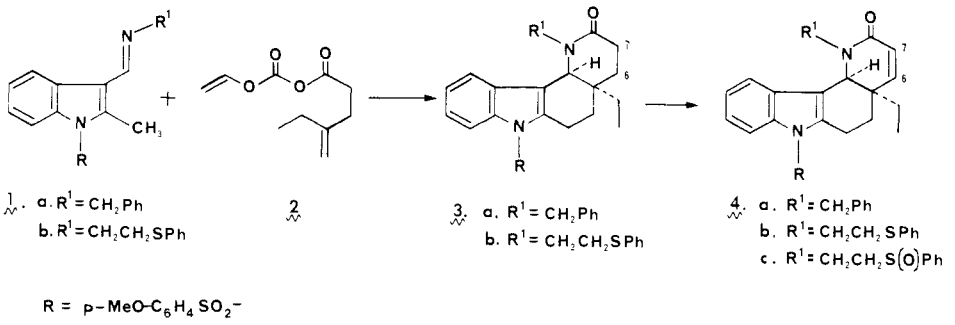
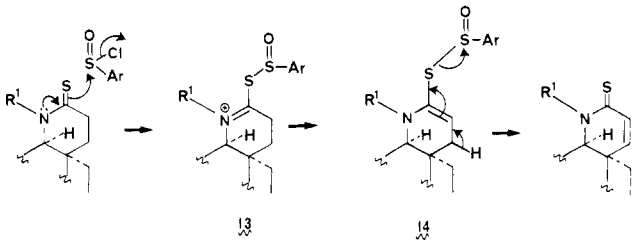
Scheme I



Scheme II



(MeI/THF/50 °C/4 h; $NaBH_4$/MeOH/25 °C)[4] gave the allylic amine **7** (52%, mp 72–76 °C).

The thiolactam **5b** was readily dehydrogenated (*p*-TolS(O)Cl/CH_2Cl_2/0 °C to room temperature/6 h) to give **6b** (81%, mp 183–185 °C). The α,β-unsaturated thiolactam was converted into the α,β-unsaturated lactam **4b** under nonoxidative conditions by treatment with $Et_3O^+BF_4^-$ (CH_2Cl_2/25 °C) and subsequent hydrolysis (KOH/H_2O/THF/25 °C). Conversion of **4b** into **4c** (*m*-CPBA/CH_2Cl_2/H_2O/$NaHCO_3$) followed by intramolecular Pummerer reaction (TFAA/PhCl/135 °C) gave the pentacyclic system **8** (65%, mp 203–207 °C). We were unable to desulfurize **8** (in attempts to prepare **9**) using a variety of Raney nickel catalysts without hydrogenating the enone double bond. We therefore changed the order of the reactions above.

Extension of the thiolactam dehydrogenation to the pentacyclic system **10** was readily achieved. Conversion of **10** into the thiolactam **11** was carried out using the Lawesson reagent (toluene/90 °C/2.5 h; 73%, mp 189–190 °C). When the thiolactam **11** was treated with *p*-TolS(O)Cl (CH_2Cl_2/N-*i*-Pr_2Et/65 °C; HOAc/H_2O/25 °C) it was cleanly converted into the α,β-unsaturated thiolactam **12** (92%, mp 166–168 °C). Treatment of **12** with Meerwein's salt ($Et_3O^+BF_4^-$/CH_2Cl_2/25 °C) followed by hydrolysis (KOH/H_2O/THF/25 °C) gave the pentacyclic unsaturated lactam **9** (80%, mp 168–171 °C).

At present we believe that the mechanism of this extremely mild thiolactam dehydrogenation involves phenylsulfinylation on sulfur to give the thioiminium ion **13** (Scheme II). Proton loss to give **14**, followed by 1,4-elimination leads to the α,β-unsaturated thiolactam.[5] We discount the usual α-phenyl sulfoxide followed by syn elimination since the conditions for such a process are not compatible with the mild reaction conditions. It should be noted that the application of this new procedure has not yet been extended to other systems, and our present evidence indicates that the steric and electronic environment of the nitrogen atom plays an important part in determining whether or not the dehydrogenation works.[6] Despite these present, general limitations, this mild new method provides a high yielding way to introduce the 6,7-double bond into Aspidosperma type alkaloids.[7]

Acknowledgment. The National Institutes of Health (GM 29802) are thanked for their financial support. The National Science Foundation (CHE 81-05004) is thanked for funds to purchase a 360-MHz NMR spectrometer.

(4) Raucher, S.; Klein, P. *Tetrahedron Lett.* **1980**, 4061. Sundberg, R. J.; Walters, C. P.; Bloom, J. D. *J. Org. Chem.* **1981**, *46*, 3730.

(5) For reaction of *sec*-thioamides with sulfinylating agents, see: Walter, W.; Hell, P.-M. *Liebigs Ann. Chem.* **1969**, *727*, 50. Chabrier, P.; Renard, S. H. *Bull. Soc. Chim. Fr.* **1949**, 272. Hurd, R. N.; De La Mater, G. *Chem. Rev.* **1961**, *61*, 45. Walter, W.; Hell, P.-M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 696.

(6) The chemistry of the RSS(O)R functional group has been studied: Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *J. Org. Chem.* **1982**, **47**, 3403. Pyrolysis of dibenzyl thiosulfinate gave thiobenzaldehyde and phenylmethanesulfenic acid. Baldwin, J. E.; Lopez, R. C. G. *J. Chem. Soc. Chem. Commun.* **1982**, 1029.

(7) All new compounds described here gave microanalytical data (C, H, N), IR, and ^1H NMR (360 MHz) consistent with the assigned structure and elemental composition.

Hydrogen Atom Transfer Reactions: The Nature of the Transition State As Delineated from the Temperature Dependence of the Primary KIE[1]

Henry L. Strong, Marilyn L. Brownawell, and Joseph San Filippo, Jr.*

Department of Chemistry, Rutgers University New Brunswick, New Jersey 08903

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Because hydrogen atom transfer reactions are among the simplest of all bond-making–bond-breaking processes, their study has been and remains a matter of theoretical as well as general interest. Johnston and co-workers,[2] for example, have studied extensively the gas-phase reaction

$$F_3C\cdot + CH_4 \rightarrow F_3CH + H_3C\cdot$$

and find that a substantial correction for tunneling is required ($k_H/k_D > 15$ at 80 °C). Investigations of similar processes in solution have been less extensive. Thus, both Pryor[3] and Lewis[4] studied the reaction

$$R\cdot + R'SH \rightarrow RH + R'S\cdot$$

and found a rough correlation between the magnitude of the kinetic isotope effect and the heat of reaction, $\Delta H°$; however, no single internally consistent plot of KIE vs. $\Delta H°$ was observed. Two opposing factors were suggested to account for this failure: (1) steric repulsion in the transition state resulting in an increase in activation energy and (2) the reduction in activation energy caused by polar contributions to the structure of the transition state. In a related study,[5] the attack of a variety of carbon radicals on tri-*n*-butyltin hydride was examined, but few meaningful conclusions were drawn.

(1) Supported by the NSF, Grant CHE 80-17045.

(2) Johnston, H. S. "Gas Phase Reaction Rate Theory"; Ronald Press: New York, 1966.

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(4) Lewis, E. S.; Ogino, K. *J. Am. Chem. Soc.* **1976**, *98*, 2260.

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