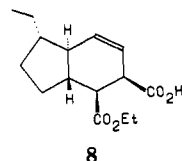


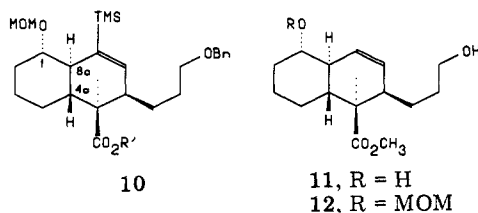
assigned the stereostructure **7** in 85% yield.^{19,22} Examination of the crude reaction mixture by high field (300 MHz) NMR indicated that the mixture contained less than 1% of stereoisomeric adducts. We were unable to isolate any minor cycloadducts if they were present. Thus, the stereoselectivity for the cyclization of **6** is $\geq 100:1$, a 20-fold enhancement over **1**. We confirmed the stereostructure of **7** by conversion to acid **8**. Removal of the Me₃Si group occurred smoothly, concomitant with cleavage of the *tert*-butyl ester, upon treatment of **7** with anhydrous HF(g) in CH₂Cl₂ (room temperature/15 min), affording **8** in 92% yield, identical with that prepared by cyclization of **1**.^{19,23}



Encouraged by this result, we prepared triene **9**, a much more demanding test, by the route outlined in Scheme II.¹⁹ Introduction of the Me₃Si group and development of the required olefin geometry at an early stage were important elements of this successful approach.²⁴

As expected, **9** proved to be significantly less reactive than the system **4** studied by Roush. Thermolysis of **9** at 180 °C for 24 h (concentration $\sim 10^{-4}$ M) afforded cleanly a single cycloadduct ($>100:1$) in 89% yield. If the reaction is conducted at higher concentrations (e.g. $\sim 10^{-2}$ M), significant amounts of bimolecular dimer form. The stereostructure of the adduct was tentatively assigned as **10** on the basis of difference decoupling experiments which established that the coupling constants $J_{1,8a} = 10.4$ Hz and $J_{4a,8a} = 10.5$ Hz were consistent with a *trans* diaxial relationship between H_{8a} and both H₁ and H_{4a}.¹⁹ Therefore in the cyclization of **9**, a very demanding case, stereocontrol resulting from introduction of the Me₃Si group provided an ~ 600 -fold increase in stereoselectivity over **4**.

To confirm the structural assignments unequivocally, we converted **10** to diol ester **11**, previously prepared and



correlated with a degradation product of chlorothricolide by Roush.¹³ Treatment of **10** with BF₃-Et₂O (6 equiv/EtSH (12 equiv) for 24 h at room temperature resulted in concomitant cleavage of the benzyl and methoxymethyl ethers, as well as cleavage of the trimethylsilyl group to

afford **11** in 84% yield.^{19,25} This material was identical in all respects with a sample of **11** prepared from acid **12** by esterification (CH₂N₂/Et₂O) and cleavage of the methoxymethyl ether (BF₃-Et₂O/PhSH).^{13,26}

Thus, use of strategically positioned stereochemical control elements constitutes a powerful protocol applicable to the preparation of hydrindene and octalin systems with essentially complete stereocontrol ($\geq 100:1$). The only apparent restriction is the currently limited number of general synthetic methods which permit ready introduction of the required trimethylsilyl group with high geometrical control.

Further studies extending this concept to other substitution patterns and to applications to natural products synthesis are currently in progress.

Acknowledgment. We gratefully acknowledge financial support for this investigation through grants from the National Science Foundation (CHE-81-19823) and the National Institute for General Medical Sciences of the NIH (GM-29290).

(25) Kieczkowski, G. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 782.

(26) We thank Professor Roush for providing a generous sample of authentic acid **12** to permit the structural correlation.

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Alkylation of Pyridine in Free Radical Chain Reactions Utilizing Alkylmercurials¹

Summary: Pyridines or *N,N,N',N'*-tetramethyl-*p*-phenylenediamine will undergo a photostimulated free radical chain reaction with alkylmercury halides or carboxylates, yielding ring alkylated substitution products. Alkene mercuriation products (R¹CH(Y)CH(R²)HgX with Y = HO, RO, CH₃CONH; X = Cl, CH₃CO₂, CF₃CO₂) can be used without isolation for the alkylation reaction.

Sir: Alkylmercury halides are convenient sources of free alkyl radicals in chain reactions.²⁻⁴ Among the reactions which will regenerate R· from RHgX (Scheme I) are S_H2 attack at X (X = PhCH₂, H),^{3,5} electron transfer (X = halogen, carboxylate),² and S_H2 substitution at Hg (X = alkyl, halogen).^{3,4} Chain reactions involving electron transfer (S_{RN}1) have been observed in which primary, secondary, or tertiary alkyl radicals have been added to anions such as NO₂⁻, N₃⁻, R¹R²C=NO₂⁻, R¹R²C=C(O⁻)Ph, Ph₂C=C=N⁻, PhC(CO₂Et)₂⁻, or phthalimide⁻ to generate RA· of Scheme I.² Neutral radicalphiles (πH) which can generate an easily oxidized adduct (RπH), or an adduct readily converted to Rπ⁻, can also participate in chain reactions of the S_{RN}1 type (Scheme II). Pyridines, quin-

(20) For examples of the use of bis TMS esters in the Peterson reaction and the effects of counterion on geometry, see: Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737. Larcheveque, M.; Debal, A. *J. Chem. Soc., Chem. Commun.* **1981**, 877.

(21) The results of our studies on the origin of the observed geometric selectivity in the process will be reported elsewhere: Boeckman, R. K., Jr.; Chinn, R. L. *Tetrahedron Lett.*, in press.

(22) The rate of cyclization of **6** is $\sim 10\times$ slower than **1** ($t_{1/2} \approx 3$ h (165 °C) vs. ≈ 0.33 h (150 °C)).

(23) Comparison was made with acid **8** obtained by cleavage of the *tert*-butyl ester of the major cycloadduct derived from **1** (150 °C, 3 h) with trifluoroacetic acid in CH₂Cl₂ at room temperature (0.5 h).

(24) The nature of the substrates in this case prevents introduction of the TMS group at a late stage by silylation of a carbanion. A kinetic method must be utilized to access the required trisubstituted TMS olefin since the *Z* isomer is much less stable than the related *E* isomer.

(1) Electron Transfer Processes. 38. This work was supported by grants from the National Science Foundation (CHE-8119343) and Petroleum Research Fund (14784-AC4).

(2) Russell, G. A.; Hershberger, J.; Owens, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312; *J. Organomet. Chem.* **1982**, *224*, 43. Russell, G. A.; Khanna, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 1450.

(3) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.

(4) Russell, G. A.; Tashtoush, H.; Ngovivatchai, P. *J. Am. Chem. Soc.* **1984**, *106*, 4622.

(5) Whitesides, G. M.; San Filippo, J. *J. Am. Chem. Soc.* **1970**, *92*, 6611. Hill, C. L.; Whitesides, G. M. *Ibid.* **1974**, *96*, 980. Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239.

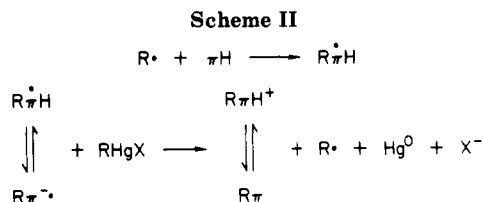
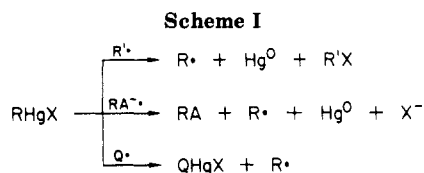


Table I. Photostimulated Reactions of RHgCl with Pyridine^a

| R | % Hg | % RC ₅ H ₄ N ^b | <i>o/p</i> |
|---|------|---|------------|
| <i>n</i> -C ₂ H ₅ | 66 | 64 (N) | 2.0 |
| <i>n</i> -C ₄ H ₉ | 82 | 66 (I), 73 (GC) | 2.4 |
| <i>n</i> -C ₄ H ₉ ^c | | 85 (GC) | 1.9 |
| <i>n</i> -C ₆ H ₁₃ | 83 | 50 (N) | |
| Me ₃ CCH ₂ CH ₂ | | 64 (N) | 2.5 |
| Me ₃ CCH ₂ | | 54 (N) | 1.9 |
| <i>c</i> -C ₅ H ₉ CH ₂ | 93 | 77 (N) | 1.9 |
| <i>i</i> -C ₃ H ₇ | | 72 (N) | 1.6 |
| <i>i</i> -C ₃ H ₇ ^c | | 89 (GC) | 3.1 |
| <i>c</i> -C ₆ H ₁₁ | 90 | 69 (I) | 3.1 |
| 2-norbornyl | 95 | 90 (I) | 4.1 |
| Me ₃ C | 98 | 94 (N) | 1.4 |
| Me ₃ C ^d | | 98 (GC) | 6.0 |

^a Reaction of 1 mmol of RHgCl in 10 mL of pyridine for 20 h at 40 °C; irradiation by a 275-W sunlamp ~20 cm from Pyrex reaction flask. ^b N, by ¹H NMR; I, isolate, GC by GLC. ^c In the presence of 0.2–0.5 M Dabco, 12 h irradiation. ^d In the presence of 0.1–0.5 M Dabco, 5 h irradiation.

olines, benzothiazole, pyrazine, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPDA), or *N,N*-dialkylanilines will undergo photostimulated ring substitution with a variety of alkylmercury halides (reaction 1). As summarized in Table I, yields in the presence of excess C₅H₅N decrease from R = *t*-Bu to secondary alkyl to primary alkyl.⁶



Reactions of RHgCl with C₅H₅N in a 1:1 or 1:4 molar ratio in Me₂SO were complicated by the formation of dialkylated pyridines, a product not observed using C₅H₅N as solvent. The reactions do not occur in the dark at 25–40 °C although a thermally initiated chain reaction of Me₃CHgCl occurred at 60–80 °C. The photostimulated reactions are initially inhibited by 10 mol % of (*t*-Bu)₂NO· or *m*-dinitrobenzene (1–2 h) and are severely retarded by radical traps such as anthracene. The alkylation reactions did not occur in the presence of O₂ or when R₂Hg was used instead of RHgCl.⁷ Reaction of 5-hexenylmercury chloride with C₅H₅N produced essentially all cyclized product (*o*- and *p*-cyclopentylcarbonylpyridines) as expected for a chain reaction involving R·. The high ortho/para ratios observed (Table I) are consistent with attack of R· mainly upon

(6) By competitive reactions we have found that the rate of electron transfer to RHgCl or S_{1/2} substitution at Hg by PhS· or PhSe· increases from R = *n*-Bu to R = *i*-Pr to R = *t*-Bu. Electrophilic cleavage reactions of RHgX by PyH⁺ (formed in reaction 1) would be more important for R = primary alkyl.

(7) Bass and Nababsing [Bass, K. C.; Nababsing, P. *J. Chem. Soc. C* 1969, 388] have observed that a large acceleration in the rate of the thermal reaction between (PhCH₂)₂Hg and quinoline occurs upon the addition of HOAc and attributed the rate increase to an increase in reactivity of quinoline upon protonation. Although this may be a factor,⁸ it appears as if the primary effect of HOAc is to electrophilically cleave (PhCH₂)₂Hg to PhCH₂HgOAc which can now participate in the chain sequence of Scheme II.

Table II. Alkylpyridines Formed by the Reaction of an Alkene with Hg(O₂CCF₃)₂/MeOH Followed by Reaction with C₅H₅N with Sunlamp Irradiation^a

| Alkene | % Hg | R | % RC ₅ H ₄ N | <i>o/p</i> |
|---|------|---|------------------------------------|------------|
| C ₂ H ₄ | 92 | CH ₂ CH ₂ OCH ₃ | 73 | 2.0 |
| CH ₃ C ₂ H ₃ | 87 | CH ₂ CH(CH ₃)OCH ₃ | 76 | 2.5 |
| C ₂ H ₅ C ₂ H ₃ | 92 | CH ₂ CH(C ₂ H ₅)OCH ₃ | 78 | 2.5 |
| <i>n</i> -C ₄ H ₉ C ₂ H ₃ | 91 | CH ₂ CH(<i>n</i> -C ₄ H ₉)OCH ₃ | 80 | 2.7 |
| <i>t</i> -C ₄ H ₉ C ₂ H ₃ | 80 | CH ₂ CH(<i>t</i> -C ₄ H ₉)OCH ₃ | 67 | 2.8 |
| CH ₃ CH=C- HCH ₃ | 90 | CH(CH ₃)CH(CH ₃)OCH ₃ | 81 | 1.9 |
| <i>c</i> -C ₆ H ₁₀ | 97 | 2-methoxycyclohexyl | 86 | 2.2 |
| norbornene | 91 | <i>exo</i> -3-methoxy-2-norbornyl | 78 | 3.0 |

^a Reaction of 10 mmol of alkene and 10 mmol of Hg(O₂CCF₃)₂ in 10 mL of MeOH. After 10 min, 8 mL of C₅H₅N was added and the mixture irradiated with a sunlamp for 8 h. Yields by GLC.

pyridine and not PyH⁺ since radical attack upon PyH⁺ is known to occur mainly at the para position.⁸ However, the reactions may involve significant attack of R· at PyH⁺ or Py---Hg(R)Cl as well as C₅H₅N. The reactions were thus examined in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco) and Me₂C=NO₂⁻ to avoid reactions of PyH⁺ including the electrophilic cleavage of RHgCl by PyH⁺. It was also expected that Dabco would preferentially complex RHgCl and significantly reduce the concentration of δ⁺-Py---Hg^{δ+}(R)Cl. The presence of Dabco increased the yield of the *n*-butylation reaction without an increase in the ortho/para ratio indicating that for *n*-Bu· alkylation of PyH⁺ was not occurring. Competitive reaction of Me₂C=NO₂⁻ (0.10 M) and C₅H₅N (12 M) with *n*-BuHgCl gave the same relative reactivity with 0.01 or 0.03 M *n*-BuHgCl.⁹ In the presence of 0.1 M Dabco, Me₂C=NO₂⁻ was 2500 times more reactive than C₅H₅N. Since the observed relative reactivity is independent of [*n*-BuHgCl], it appears that the reacting species is mainly C₅H₅N and not C₅H₅N---Hg(R)Cl. Addition of 5-hexenyl radical to Me₂C=NO₂⁻ has a rate constant of 2.5 × 10⁵ M⁻¹ s⁻¹ (Me₂SO, 40 °C)⁵ which leads to a rate constant for the attack of *n*-Bu· upon C₅H₅N of 100 M⁻¹ s⁻¹.¹⁰ Reaction of 0.1 M Me₃CHgCl with 12 M C₅H₅N gave an ortho/para ratio of 1.4 which in the presence of 0.1–0.5 M Dabco or 0.3 M Me₂NH increased to 6 (Table I). With the more nucleophilic *tert*-butyl radical, competition between attack upon PyH⁺ or Py---Hg(R)Cl and C₅H₅N is a more serious problem than for *n*-Bu·. The relative reactivity of C₅H₅N/Me₂C=NO₂⁻ determined in the presence of Dabco was 6.6 × 10⁻⁵ toward Me₃C·.⁹

TMPDA was much more reactive than Py toward *n*-Bu· and in competition with Me₂C=NO₂⁻ gave a relative reactivity of 0.11, i.e., *k*_{add} = 2.8 × 10⁴ M⁻¹ s⁻¹. With Me₃CHgCl substituted pyridines gave the following products (substituent, product, %); 4-Me, 2-*t*-Bu, 87; 3-Me,

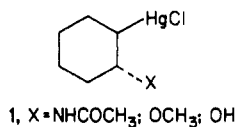
(8) Minisci, F.; Bernadi, R.; Bertini, F.; Galli, R.; Perchinommo, M. *Tetrahedron* 1971, 27, 3575.

(9) In the presence of Me₂C=NO₂⁻, the ortho/para ratios were higher than those listed in Table I and decreased with a decrease in [Me₂C=NO₂⁻]. We interpret this result as indicative of a competition between the radical attack of Scheme I and a photochemical reaction yielding only *o*-RC₅H₄N (e.g., Py---RHgCl $\xrightarrow{h\nu}$ *o*-RC₅H₄NH⁺Cl⁻ + Hg⁰). Unusually high ortho/para ratios were also observed in reactions retarded by the presence of (*t*-Bu)₂NO·, *m*-dinitrobenzene, or anthracene. Competitive reactions of Me₂C=NO₂⁻ and C₅H₅N with RHgCl in the presence of Dabco gave the ortho/para ratios of Table I.

(10) Addition of Me· to C₅H₅N at 65 °C (isooctane) has a rate constant of 150 M⁻¹ s⁻¹: Ingold, K. U. In "Free Radicals"; Kochi, J. Ed.; John Wiley and Sons: New York, 1973; Vol. 1, Chapter 2, p 93. Attack of *n*-Bu· and *t*-Bu· upon PyH⁺ at 57 °C occurs with rate constants of 4.4 × 10⁴ and 3.3 × 10⁴ M⁻¹ s⁻¹, respectively; Citterio, A.; Minisci, F.; Franchi, V. *J. Org. Chem.* 1980, 45, 4752. Toward *n*-Bu·, *p*-MeC₅H₄NH⁺ and *p*-MeC₅H₄N have *k*_{add} = 1.1 × 10⁵ and 1.6 × 10³ M⁻¹ s⁻¹, respectively; Citterio, A.; Minisci, F.; Porta, O.; Sesana, G. *J. Am. Chem. Soc.* 1977, 99, 7960.

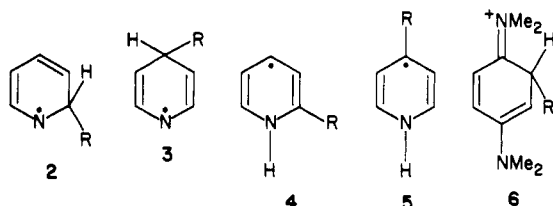
6-*t*-Bu, 90; 2-Me, mixture of 4 and 6-*t*-Bu, 90; 4-Ph, 2-*t*-Bu, 60; 3-Ph, 6-*t*-Bu, 60; 2-Ph, 2.2:1 mixture 6-*t*-Bu and 4-*t*-Bu, 69; 2-Cl, 1.3:1 mixture of 6-*t*-Bu and 4-*t*-Bu, 85; 3-MeO₂C, 6-*t*-Bu, 74; 3-MeNHCO, 6-*t*-Bu, 87; 4-methylquinoline, 2-*tert*-butyl-4-methylquinoline, 93; benzothiazole, 2-*tert*-butylbenzothiazole, 70. Reactions were not observed with 4-benzyl-, 4-acetyl-, 4-cyano-, 4-(dimethylamino)-, 2-methoxy-, or 2- or 3-fluoropyridines or with acridine, thiophene, furan, pyrrole, *N*-benzylpyrrole, or imidazole.

Olefin mercuration products such as 1 reacted with photostimulation to produce the expected mixtures or alkylated pyridines, e.g., X = NHCOCH₃, 69%, o/p = 2.3.



The olefin mercuration product need not be isolated and a one-pot reaction can be achieved by first reacting an olefin with Hg(O₂CCF₃)₂ in MeOH¹¹ followed by the addition of excess pyridine and sunlamp irradiation to initiate the chain process. Table II summarizes typical yields.

The initial attack of R· upon pyridine leads to the azacyclohexadienyl radicals 2 and 3. These may lose H⁺ to



pyridine to form the radical anion (Rπ⁻ in Scheme II) or undergo isomerization (presumably via reaction with PyH⁺ and Py) to yield the easily oxidized radicals 4 and 5 (RπH in Scheme II). There is a consistent trend in the ortho/para ratios (*n*-Bu = 1.9; *i*-Pr = 3.1; 2-norbornyl = 4.1; *t*-Bu = 6.0), indicating that radicals which are better electron donors yield a higher fraction of the ortho substitution product. In the case of TMPDA, the initially formed adduct can undergo electron transfer without hydrogen migration to form 6 which may aromatize in a subsequent step. Reaction of TMPDA failed with R = *t*-Bu but occurred readily with R = cyclohexyl or benzyl to give only the monoalkylated products.¹²

Typical Procedures. *exo*-2-Norbornylmercury chloride (3 g) in 10 mL of pyridine at 30–35 °C was deoxygenated by a helium stream and irradiated by a 275-W sunlamp ~20 cm from the Pyrex tube. Mercury metal precipitated from the solution after an induction period of 5–10 min. After 24 h, the pyridine solution was added to 10 mL 0.1 M KOH, and extracted with Et₂O, and the ether solution was washed twice with 10 mL of H₂O. The dried ether solution was evaporated and Kugelrohr distilled to give 1.40 g (90%) of a 4.1:1 mixture (by GLC) of 2- and 4-*exo*-2-norbornylpyridines, bp 125–145 °C (0.1 torr). The 2- and 4-alkylpyridines are readily distinguished by GCMS since the 2-alkyl derivatives have a pronounced M⁺ - H peak while 4-alkyl derivatives give mainly M⁺.¹³

(11) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* 1969, 91, 5646.

(12) Reaction of 5-hexenylmercury chloride with 1 equiv of TMPDA formed a mixture of 5-hexenyl- and cyclopentylcarbinyl products. Although reaction of PhCH₂HgCl with C₅H₅N forms mainly PhCH₂CH₂Ph from the reaction PhCH₂ + PhCH₂HgCl → PhCH₂CH₂Ph + HgCl₂ with the more reactive TMPDA (1 equiv), the benzylated product (80%) and PhCH₂CH₂Ph (7%) were formed (GC yields). Toward PhCH₂, TMPDA was 6 times as reactive as Me₂C=NO₂⁻, giving a reactivity series toward PhCH₂· of Me₂C=NO₂⁻ (1) > TMPDA (0.16) > PhCH₂HgCl (<0.01) > C₅H₅N (<10⁻⁴).

Cyclohexene (1.64 g) was added to a stirred solution of 6.36 g of Hg(OAc)₂ in 20 mL of MeOH. After 10 min, 8 mL of C₅H₅N was added and the solution irradiated 40 h with the sunlamp to yield 3.0 g of Hg and 2.1 g of a mixture of *o*- and *p*-(2-methoxycyclohexyl)pyridine, bp 95–115 °C (2 torr). A more rapid reaction and higher yield was observed using Hg(O₂CCF₃)₂.

TMPDA (1.09 g, 6.6 mmol) and 2.15 g of PhCH₂HgCl (6.5 mmol) in 40 mL Me₂SO were irradiated by sunlamp for 40 h. Workup provided 1.19 g (70%) of the benzyl derivative, bp 125–145 °C (0.01 torr).

(13) McDonald, F. R.; Widecora, A.; Cook, G. L. *Appl. Spectrosc.* 1968, 22, 325, 329.

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Thermal, Four-Carbon + Three-Carbon Cycloaddition Reaction of Cyclopropenone Ketals. Total Synthesis of Deacetamidocolchicine: Formal Total Synthesis of Colchicine

Summary: A total synthesis of deacetamidocolchicine, constituting a formal total synthesis of colchicine, is described and is based on the implementation of a thermal, four-carbon + three-carbon cycloaddition of α-pyrone 4 with the cyclopropenone ketal 3 in a process proceeding by way of the reversible, thermal generation of a three-carbon 1,3-dipole best represented as a nucleophilic and delocalized singlet vinylcarbene.

Sir: Colchicine (1), a potent mitotic inhibitor exhibiting a characteristic and specific binding with tubulin which prevents microtubule assembly and spindle formation, has been the subject of extensive synthetic,² biosynthetic,³ and biochemical investigations.³ Most recent efforts have focused on defining the complete spectrum of colchicine's

(1) (a) Searle Scholar Recipient, 1981–1985. National Institutes of Health research career development award recipient, 1983–1988 (CA 00898/01134). Alfred P. Sloan research fellow, 1985–1989. Correspondence regarding this work should be addressed to this author at the following address: Department of Chemistry, Purdue University, West Lafayette, IN 47907. (b) National Institutes of Health predoctoral fellow, 1981–1984 (GM 07775).

(2) Structure determination: (a) Dewar, M. J. S. *Nature (London)* 1945, 155, 141. Total synthesis: (b) Schreiber, J.; Leimgruber, W.; Pesaro, M.; Schudel, P.; Threlfall, T.; Eschenmoser, A. *Helv. Chim. Acta* 1961, 44, 540. (c) van Tamelen, E. E.; Spencer, F. A.; Allen, O. S.; Orvis, R. L. *Tetrahedron* 1961, 14, 8. (d) Sunagawa, G.; Nakamura, T.; Nakazawa, J. *Chem. Pharm. Bull.* 1962, 10, 291. Nakamura, T. *Ibid.* 1962, 10, 299. (e) Scott, A. I.; McCapra, F.; Buchanan, R. L.; Day, A. C.; Young, D. W. *Tetrahedron* 1965, 21, 3605. Scott, A. I.; McCapra, F.; Nabney, J.; Young, D. W.; Day, A. C.; Baker, A. J.; Davidson, T. A. *J. Am. Chem. Soc.* 1963, 85, 3040. (f) Woodward, R. B. *Harvey Lect.* 1963, 31. (g) Martel, J.; Toromanoff, E.; Huynh, C. *J. Org. Chem.* 1965, 30, 1752. (h) Matsui, M.; Yamashita, K.; Mori, K.; Kaneko, S. *Agric. Biol. Chem.* 1967, 31, 675. Kaneko, S.; Matsui, M. *Ibid.* 1968, 32, 995. (i) Kato, M.; Kido, F.; Wu, M. D.; Yoshikoshi, A. *Bull. Chem. Soc. Jpn.* 1974, 47, 1516. (j) Kotani, E.; Miyazak, F.; Tobinaga, S. *J. Chem. Soc., Chem. Commun.* 1974, 300. Tobinaga, S. *Bioorg. Chem.* 1975, 4, 110. (k) Evans, D. A.; Hart, D. J.; Koelsch, P. M. *J. Am. Chem. Soc.* 1978, 100, 4593. Evans, D. A.; Tanis, S. P.; Hart, D. J. *Ibid.* 1981, 103, 5813. (l) For resolution methods in the conversion of deacetamidocolchicine (2b) to colchicine with resolution of deacetylcolchicine; see: Corrodi, H.; Hardegger, E. *Helv. Chim. Acta* 1957, 40, 193.

(3) For a recent review, see: Capraro, H.-G. "Alkaloids"; Academic Press: Orlando, Florida, 1984; Vol. 23, pp 1–70.