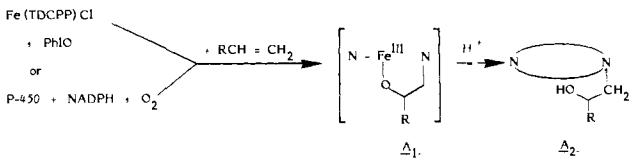
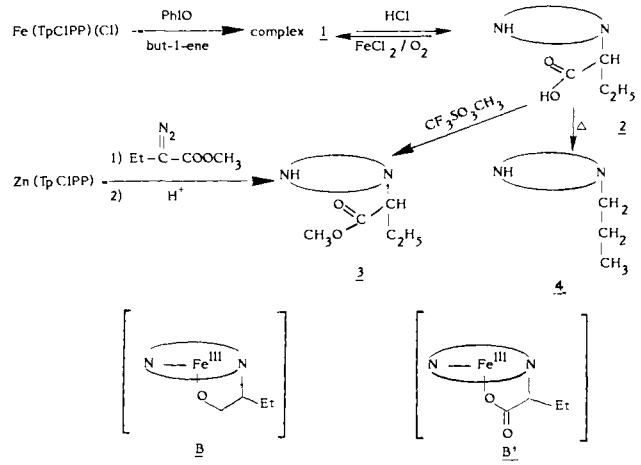
**Scheme I**



**Scheme II**



(Scheme II). Second, the simple heating of **2** in $CH_3OH$ containing HCl for 1 h at 50 °C led to its decarboxylation. The structure of the *N*-propyl-TpClPPH, **4**, was clearly shown by its $^1H$ NMR and mass spectra.[8] The easy decarboxylation of **2**[9] could explain at least in part its instability.

Metalation of **2** by $FeCl_2$ in aerated THF gave an unstable complex exhibiting a UV-visible spectrum superimposable on that of complex **1**. Moreover, the analogy of this spectrum with those of previously reported iron(III) porphyrins involving a five-membered NCCOFe metallocycle[2,10] suggests the NCHEt-COOFe structure proposed for this complex (structure B′ of Scheme II).

Preliminary $^1H$ NMR and mass spectroscopy studies on the *N*-alkylporphyrins formed during oxidation of 4-methylpent-1-ene and hex-1-ene by PhIO catalyzed by Fe(TPP)(Cl) or Fe(TpClPP)(Cl)[4] indicated a N-CH(COOH)R porphyrin structure as in **2**. Thus, it appears that two kinds of *N*-alkylporphyrins can be isolated from 1-alkene oxidation by PhIO catalyzed by iron porphyrins: the N-$CH_2$CHROH porphyrins found upon oxidation of several 1-alkenes (3-methylbut-1-ene, 4,4-dimethylpent-1-ene, and dec-1-ene) by Fe(TDCPP)Cl[2] and the N-CHRCOOH porphyrins found upon oxidation of various alkenes (but-1-ene, hex-1-ene, and 4-methylpent-1-ene) by Fe(TPP or TpClPP)Cl (this work). Much work is still needed to determine the mechanism of formation of these N-CHRCOOH porphyrins. However, it is likely that complex **1** has the structure B′ indicated in Scheme II. It could be formed by oxidation in the medium containing PhIO, from a precursor B (a regioisomer of $A_1$ with R = Et), deriving formally from an addition of a pyrrole nitrogen to the internal carbon and the iron-activated oxygen[11] to the terminal carbon of the alkene double bond.

The above results show for the first time that *N*-alkylporphyrins deriving from the binding of a pyrrole nitrogen to the more substituted vinylic carbon of alkenes are formed during oxidation of these substrates by PhIO catalyzed by certain iron porphyrins. They suggest that the structure of the final *N*-alkylporphyrins formed in such reactions is critically dependent on the nature of the iron environment in the catalyst and on the fate of the intermediate complexes in the highly oxidizing medium.

(8) **4**: N-($CH_2CH_2CH_3$)TpClPPH; mass spectrum, *m/e* 796 (100%, $MH^+$ + 1) 754 (78% $TpClPPH_3^+$ + 1); $^1H$ NMR ($CD_2Cl_2$) -0.74 (3 H, t, $J$ = 7.5 Hz), -1.60 (2 H, m), -4.57 (2 H, t, $J$ = 7 Hz); ortho and meta H, 8-8.11 (2 H, m), 8.11-8.33 (4 H, m), 7.81 (4 H, d, $J$ = 8.5 Hz), 7.67-7.9 (6 H, m); pyrrole H, 8.76 (2 H, s), 8.61 and 8.42 (4 H, AB system, $J$ = 4.5 Hz), 7.43 (2 H, s).

(9) Callot, H. J. *Tetrahedron Lett.* **1979**, 3093-3096.

(10) Battioni, J. P.; Artaud, I.; Dupré, D.; Leduc, P.; Akhrem, I.; Mansuy, D.; Fischer, J.; Weiss, R.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1986**, *108*, 5598-5607.

(11) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884-2886.

## Free Energy Increments for Hydrogen Bonds in Nucleic Acid Base Pairs

Douglas H. Turner,*† Naoki Sugimoto,† Ryszard Kierzek,‡ and Scott D. Dreiker†

*Department of Chemistry, University of Rochester Rochester, New York 14627*
*Institute of Bioorganic Chemistry*
*Polish Academy of Sciences, 60-704 Poznan*
*Noskowskiego 12/14, Poland*

*Received January 21, 1987*

Contributions of hydrogen bonds to the stability of folded forms of macromolecules are not known.[1-3] Studies on small molecules have been interpreted as indicating either a favorable[4,5] or a negligible[6] free energy contribution from hydrogen bonds. Recent improvements in methods for synthesis of ribooligonucleotides permit synthesis of small double helixes with and without particular hydrogen-bonding groups.[7] For example, substitution of inosine (I) for guanosine (G) removes the 2-amino group involved in hydrogen bonding in a GC base pair. We report here thermodynamic parameters for duplex formation by self-complementary oligomers, ICCGGC, CGGCCI, ICCGG, and GGCCI. Comparison with previous results[8,9] on corresponding oligomers with I replaced by G suggests hydrogen bonds make substantial, sequence-dependent contributions to $\Delta G°$ of duplex formation.

Oligomers were synthesized as described previously[7] and purified by HPLC.[10] Thermodynamic parameters for duplex formation were derived from measurements of optical melting curves as described previously.[8,11] For a two-state transition, the inverse melting temperature in $K^{-1}$ is related to $\Delta H°$ and $\Delta S°$ by $T_M^{-1} = (2.3R/\Delta H°) \log C_T + \Delta S°/\Delta H°$. Here $C_T$ is total strand concentration. Appropriate plots are available as supplementary material, and results are listed in Table I. Similar results were obtained by analyzing shapes of melting curves (see Table II in supplementary material).

Empirical free energy increments for hydrogen bonds in base pairs, $\Delta\Delta G°_{HB}$, can be derived from Table I in two ways. First, $\Delta G°$'s for duplex formation by oligomers with identical core sequences but terminal GC or IC pairs can be subtracted. For example,

$$\Delta\Delta G°_{HB} = (1/2)[\Delta G°(GCCGGC) - \Delta G°(ICCGGC)] \quad (1)$$

† University of Rochester.

‡ Polish Academy of Sciences.

(1) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry Part I: The Conformation of Biological Macromolecules*; W. H. Freeman: San Francisco, 1980.

(2) Fersht, A. R.; Shi, J.-P.; Knill-Jones, J.; Lowe, D. M.; Wilkinson, A. J.; Blow, D. M.; Brick, P.; Carter, P.; Wage, M. M. Y.; Winter, G. *Nature (London)* **1985**, *314*, 235-238.

(3) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969.

(4) Schellman, J. A. *C. R. Lab. Carlsberg, Ser. Chim.* **1955**, *29*, 223.

(5) Robinson, D. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1965**, *87*, 2462-2470.

(6) Klotz, I. M.; Franzen, J. S. *J. Am. Chem. Soc.* **1962**, *84*, 3461-3466.

(7) Kierzek, R.; Caruthers, M. H.; Longfellow, C. E.; Swinton, D.; Turner, D. H.; Freier, S. M. *Biochemistry* **1986**, *25*, 7840-7846.

(8) Freier, S. M.; Alkema, D.; Sinclair, A.; Neilson, T.; Turner, D. H. *Biochemistry* **1985**, *24*, 4533-4539.

(9) Freier, S. M.; Burger, B. J.; Alkema, D.; Neilson, T.; Turner, D. H. *Biochemistry* **1983**, *22*, 6198-6206.

(10) Ikuta, S.; Chattopadhyaya, R.; Dickerson, R. E. *Anal. Chem.* **1984**, *56*, 2253-2256.

(11) Petersheim, M.; Turner, D. H. *Biochemistry* **1983**, *22*, 256-263.

0002-7863/87/1509-3783$01.50/0 

**Table I.** Thermodynamic Parameters for Duplex Formation in 1 M NaCl[a]

| sequence | ref | $-\Delta H°$, kcal/mol | $-\Delta S°$, eu | $-\Delta G°_{37}$, kcal/mol | $T_M$ at $10^{-4}$ M, °C |
|---|---|---|---|---|---|
| ICCGGC | | 53.6 | 146.9 | 8.03 | 51.3 |
| ICCGG | | 36.1 | 101.2 | 4.72 | 29.0 |
| GCCGGp | 8 | 32.5 | 88.9 | 4.99 | 30.6 |
| CCGG | 11 | 34.2 | 95.6 | 4.55 | 27.1 |
| CCGGCp | 9 | 39.8 | 111.3 | 5.30 | 34.1 |
| GCCGGCp | 8 | 62.7 | 166.0 | 11.24 | 67.2 |
| CGGCCI | | 53.0 | 143.2 | 8.55 | 54.8 |
| GGCCI | | 57.7 | 157.9 | 8.76 | 54.5 |
| GGCCGp | 9 | 53.6 | 143.9 | 8.98 | 57.4 |
| GGCC | 9 | 35.8 | 98.1 | 5.37 | 34.4 |
| CGGCCp | 8 | 30.6 | 79.9 | 5.78 | 38.0 |
| CGGCCGp | 8 | 54.1 | 142.6 | 9.90 | 63.3 |

[a] Buffer is 1 M NaCl, 0.01 M $Na_2HPO_4$, 0.5 mM $Na_2EDTA$, pH 7. Parameters were determined from $T_M^{-1}$ vs. log $C_T$ plots. Estimated errors are ±5% for $\Delta H°$ and $\Delta S°$ and ±2% for $\Delta G°$.

The $^1/_2$ arises because each duplex contains two I to G substitutions. This assumes stacking interactions involving terminal GC and IC pairs are identical. This cannot be proven. Thermodynamic parameters for duplex formation by oligomers with terminal unpaired G's or I's (dangling ends), however, provide a comparison of stacking interactions for G and I. For example, $\Delta G°$'s for duplex formation by GCCGG and ICCGG and by GGCCG and GGCCI are essentially identical (see Table I). Thus G and I have similar stacking interactions in these oligomers. In using data in Table I, we also assume 3'-terminal phosphates have negligible effects on stability, as demonstrated previously.[9] Application of eq 1 to the data in Table I provides $\Delta\Delta G°_{HB}$'s of −1.6 and −0.7 kcal/mol respectively for the hydrogen bond formed by the 2-amino group in the terminal GC base pairs of GCCGGC and CGGCCG.

A second method for estimating $\Delta\Delta G°_{HB}$ is to compare the stability of duplexes formed with terminal base pairs to that of duplexes formed with corresponding dangling ends and to that of duplexes formed from the core sequences.[11,12] For example, $\Delta\Delta G°_{ST}(3'C) = (1/2)[\Delta G°(CCGGC) - \Delta G°(CCGG)]$ and $\Delta\Delta G°_{ST}(5'I) = (1/2)[\Delta G°(ICCGG) - \Delta G°(CCGG)]$ provide measures of the contributions of stacking by the 3'C and 5'I, respectively, to the stability of ICCGGC. These contributions are subtracted from the stability of the terminal base pair, $(1/2)[\Delta G°(ICCGGC) - \Delta G°(CCGG)]$, to provide a measure of stability provided by hydrogen bonds between I and C. For example, from data for ICCGGC,

$$\Delta\Delta G°_{HB} = [1/2(2)][\Delta G°(ICCGGC) - \Delta G°(CCGGC) - \Delta G°(ICCGG) + \Delta G°(CCGG) - 2(1.9)] \quad (2)$$

The second 2 in the denominator arises because IC pairs can form two hydrogen bonds. The −2(1.9) kcal/mol is a configurational free energy correction term[12] added because 3'-terminal nucleotides are likely to be rigidly fixed for both dangling and paired ends, but 5'-terminal nucleotides are only fixed when paired.[8,11-13] Application of eq 2 to the data in Table I provides $\Delta\Delta G°_{HB}$'s of −1.6 and −0.8 kcal/mol respectively for the average of the two hydrogen bonds in the IC pairs of ICCGGC and CGGCCI. The agreement between these values and those above indicates the $\Delta\Delta G°$ of −1.9 kcal/mol nucleotide suggested previously[12] for fixing a 5'-terminal nucleotide in a base pair is reasonable.

It has been suggested that $\Delta\Delta G°_{HB}$ is more favorable when stacking interactions are less favorable.[12] Figure 1 is a plot of $\Delta\Delta G°_{HB}$ derived here and previously[12] from equivalents of eq 1 and 2 vs. $\Delta\Delta G°_{3'ST}$ for the appropriate 3'-dangling end.[9] A linear relationship is observed. Points based on comparison of GC and IC pairs involve fewer assumptions than the others but are within

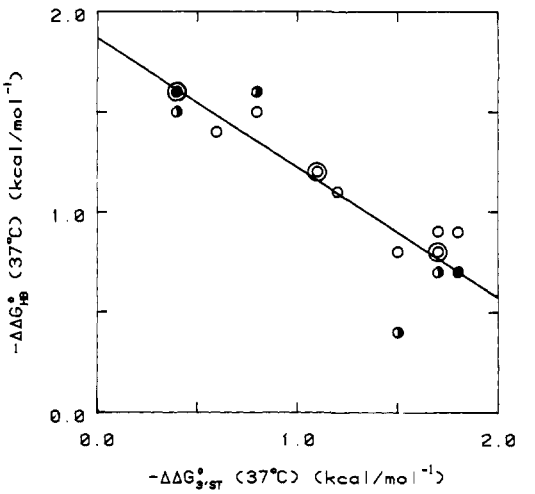



**Figure 1.** Plot of free energy increments for hydrogen bonds, $\Delta\Delta G°_{HB}$, vs. free energy increments for stacking of appropriate 3'-dangling ends, $\Delta\Delta G°_{3'ST}$. Data from Table I and ref 9 and 12, $\Delta\Delta G°_{HB}$ calculated by comparing terminal GC and IC (●) or AU (◑) base pairs (e.g., see eq 1); (○) $\Delta\Delta G°_{HB}$ calculated by comparing terminal base pairs with dangling ends (e.g., see eq 2). Circles within circles indicate two overlapping points.

experimental error of the least-squares line. This suggests assumptions used previously are reasonable.[14] Evidently, stacking and hydrogen bonding compete in a base pair. For example, strong stacking may favor geometries not optimum for hydrogen bonding. The intercept when $\Delta\Delta G°_{3'ST}$ is 0 is −2 kcal/mol. This is predicted to be the maximum $\Delta\Delta G°_{HB}$.

Results presented here are for terminal base pairs in ribooligonucleotides. Several results suggest hydrogen bonds inside a double helix have similar strengths. Free energy increments for terminal and interior base pairs in RNA oligomers seem to be the same.[12,15] Moreover, literature data indicate addition or subtraction of hydrogen bonds for interior pairs in DNA oligomers changes $\Delta G°$ for duplex formation by −0.5 to −1.9 kcal/mol hydrogen bond,[16-19] consistent with the range in Figure 1.

The $\Delta\Delta G°_{HB}$ values reported here can be compared with literature values of $\Delta\Delta G°$'s attributed to hydrogen bonds. Fersht et al. report increments from −0.5 to −1.2 kcal/mol for uncharged hydrogen bonds involved in binding substrate to the transition state of tyrosyl-tRNA synthetase.[2] The similar range suggests equilibrium and transition-state hydrogen bonds may be similar. Based on kinetic data, Cech and coworkers,[20,21] estimate $\Delta\Delta G°$'s ranging from −1.4 to −2.2 kcal/mol hydrogen bond for removal of hydrogen bonding groups from substrates for self-splicing RNA. The similarity with values in Figure 1 supports their interpretation that hydrogen bonds provide a major contribution to binding of these substrates.

**Acknowledgment.** This work was supported by National Institutes of Health Grant GM 22939. We thank I. Tinoco, Jr.,

(12) Freier, S. M.; Sugimoto, N.; Sinclair, A.; Alkema, D.; Neilson, T.; Kierzek, R.; Caruthers, M. H.; Turner, D. H. *Biochemistry* **1986**, *25*, 3214–3219.

(13) Petersheim, M.; Turner, D. H. *Biochemistry* **1983**, *22*, 269–277.

(14) The limited scatter in Figure 1 also suggests the different types of hydrogen bonds in base pairs contribute similar free energy increments. This is because various points represent different combinations of hydrogen bonds. This suggestion is also consistent with comparisons of stabilities of terminal GC and GU pairs. Freier, S. M.; Kierzek, R.; Caruthers, M. H.; Neilson, T.; Turner, D. H. *Biochemistry* **1986**, *25*, 3209–3213.

(15) Freier, S. M.; Kierzek, R.; Jaeger, J. A.; Sugimoto, N.; Caruthers, M. H.; Neilson, T.; Turner, D. H. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 9373–9377.

(16) Gaffney, B. L.; Marky, L. A.; Jones, R. A. *Tetrahedron* **1984**, *40*, 3–13.

(17) Martin, F. H.; Castro, M. M.; Aboul-ela, F.; Tinoco, I., Jr. *Nucleic Acids Res.* **1985**, *13*, 8927–8938.

(18) Aboul-ela, F.; Koh, D.; Tinoco, I., Jr.; Martin, F. H. *Nucleic Acids Res.* **1985**, *13*, 4811–4824.

(19) Kawase, Y.; Iwai, S.; Inoue, H.; Miura, K.; Ohtsuka, E. *Nucleic Acids Res.* **1986**, *14*, 7727–7736.

(20) Bass, B. L.; Cech, T. R. *Nature (London)* **1984**, *308*, 820–826.

(21) Tanner, N. K.; Cech, T. R. *Biochemistry*, in press.

for suggesting experiments with inosine.

**Supplementary Material Available:** One figure containing plots of $T_M^{-1}$ vs. log $C_T$ for ICCGGC, CGGCCI, ICCGG, and GGCCI and Table II containing "temperature-independent" and temperature-dependent thermodynamic parameters for the oligomers listed in Table I (2 pages). Ordering information is given on any current masthead page.

## Intramolecular Palladium-Catalyzed Cyclizations of Esters Containing Vinyl Triflate and Vinylstannane Groups at the Termini: Synthesis of Large-Ring Lactones

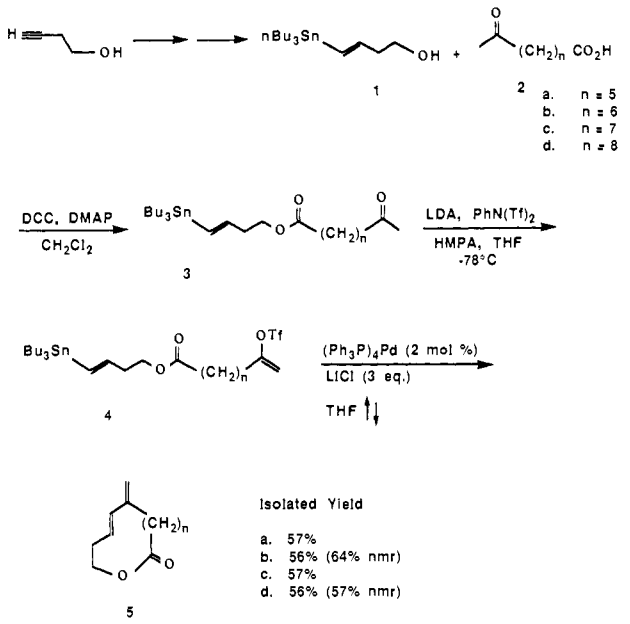
J. K. Stille* and Masahide Tanaka

*Department of Chemistry, Colorado State University*
*Fort Collins, Colorado 80523*
*Received March 13, 1987*

The construction of large-ring compounds, particularly macrocyclic lactones, in relatively high yields is an important procedure, since these compounds occur widely in nature and possess a variety of biological activity.[1] Several approaches to this problem have been utilized, the most prevalent of which is the cyclization of an ω-hydroxy carboxylic acid derivative by some transesterification procedure. An alternate approach to macrolide synthesis is the intramolecular formation of a carbon–carbon bond from an acyclic ester. For example, excellent yields of macrolides can be obtained by reactions such as the Dieckman and Thorpe–Zielger condensations,[2] alkylations,[3] acylations,[4] Horner–Emmons coupling,[5] and Reformatski condensations[6]—particulary that utilizing samarium iodide.[6c] Transition-metal-mediated coupling reactions,[7] especially those arising from the alkylation of an $\eta^3$-allylpalladium complex with a soft anion,[7b-e] have the advantage that the reaction occurs under relatively mild conditions.

The palladium-catalyzed reaction of a variety of organic electrophiles and organostannanes takes place to give high yields of cross-coupled products under mild conditions.[8] Furthermore, this reaction is relatively insensitive to moisture and air, tolerates a variety of functional groups on either coupling partner, and is both stereospecific and regioselective. Thus, this reaction appeared to be ideal for the synthesis of a variety of large-ring compounds. As an initial reaction type, the intramolecular coupling of an ester bearing vinyl triflate and vinylstannane[9] groups at the termini was explored. It was anticipated that the palladium catalyst would act as a template to assemble the ends of the molecule through an oxidative addition and coordination of the vinylstannane unit prior to transmetalation. Extrusion of palladium by reductive elimination would simultaneously generate a carbon–carbon bond while reducing the ring size.

**Scheme I**




The substrates **4** for cyclization were synthesized as shown in Scheme I. The linear esters **3** were obtained by the DCC coupling of the keto acids **2**[10] with an alcohol, (*E*)-4-(tributylstannyl)-3-buten-1-ol (**1**) containing a vinyl tin group. Tin reagent **1** was obtained by the stereospecific stannylmagnesation of 4-(1-ethoxyethoxy)-1-butyne[11] followed by deprotection of the alcohol. The methyl ketone functionality in **3** was converted to the kinetic enolate with LDA at low temperatures and trapped with *N*-phenyltriflimide to give **4**.[9] Both the ketone precursor **3** and the vinyl triflate substrate **4** could be obtained analytically pure by chromatography. The *E*-double-bond geometry was maintained in **4** ($J$ = 19 Hz), the conversion to triflate being carried out without cleavage of the vinnylstannane group.

Cyclization of **4** containing the vinyl tin and vinyl triflate groups at the termini of the ester chain was accomplished with tetrakis(triphenylphosphine)palladium (2 mol %) in the presence of lithium chloride under high dilution ($10^{-3}$ M) in refluxing THF. Good yields of pure products **5** could be obtained; remarkably, the yield was insensitive to the ring size. Especially noteworthy was the observation that a 57% *isolated yield* of the 12-membered ring was achieved, since this is a ring size that is difficult to generate, the rate of cyclization being the slowest of the 12- through 21-membered rings.[12] Under these mild reaction con-

(1) For reviews, see: (a) Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683. (b) Back, T. G. *Tetrahedron* **1977**, *33*, 3041. (c) Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585. (d) Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569.

(2) Hurd, R. N.; Shah, D. H. *J. Org. Chem.* **1973**, *38*, 390.

(3) (a) Takahashi, T.; Hashiguchi, S.; Kasuga, K.; Tsuji, J. *J. Am. Chem. Soc.* **1978**, *100*, 7424. (b) Takahashi, T.; Kasuga, K.; Tsuji, J. *Tetrahedron Lett.* **1978**, *19*, 4917. (c) Takahashi, T.; Kasuga, K.; Takahashi, M.; Tsuji, J. *J. Am. Chem. Soc.* **1979**, *101*, 5072. (d) Takahashi, T.; Nagashima, T.; Tsuji, J. *Chem. Lett.* **1980**, 369. (e) Takahashi, T.; Minami, I.; Tsuji, J. *Tetrahedron Lett.* **1981**, *22*, 2651. (f) Takahashi, T.; Ikeda, H.; Tsuji, J. *Tetrahedron Lett.* **1981**, *22*, 1363. (g) Sims, R. J.; Tischler, S. A.; Weiler, L. *Tetrahedron Lett.* **1983**, *24*, 253. (h) Trost, B. M.; Sato, T. *J. Am. Chem. Soc.* **1985**, *107*, 719.

(4) Gerlach, H. *Helv. Chim. Acta* **1977**, *60*, 3039.

(5) (a) Burri, K. F.; Cardone, R. A.; Chen, W. Y.; Rosen, P. *J. Am. Chem. Soc.* **1978**, *100*, 7069. (b) Stork, G.; Nakamura, E. *J. Org. Chem.* **1979**, *44*, 4010. (c) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R.; Petasis, N. A. *J. Org. Chem.* **1979**, *44*, 4011. (d) Meyers, A. I.; Roland, D. M.; Comins, D. L.; Henning, R.; Fleming, M. P.; Shimizu, K. *J. Am. Chem. Soc.* **1979**, *101*, 4732. (e) Meyers, A. I.; Comins, D. L.; Roland, D. M.; Henning, R.; Shimizu, K. *J. Am. Chem. Soc.* **1979**, *101*, 7104. (f) Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1981**, *103*, 1224. (g) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 2030. (h) Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1984**, *106*, 1148. (i) Tanaka, T.; Oikawa, Y.; Hamada, T.; Yonemitsu, O. *Tetrahedron Lett.* **1986**, *27*, 3651. (j) Oikawa, Y.; Tanaka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1986**, *27*, 3647. (k) Nakajima, N.; Hamada, T.; Tanaka, T.; Oikawa, Y.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 4645.

(6) (a) Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 7705. (b) Tsuji, J.; Mandai, T. *Tetrahedron Lett.* **1978**, *19*, 1817. (c) Tabuchi, T.; Kawamura, K.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 3889.

(7) (a) Corey, E. J.; Krist, H. A. *J. Am. Chem. Soc.* **1972**, *94*, 667. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1977**, *99*, 3867. (c) Trost, B. M.; Verhoeven, T. R. *Tetrahedron Lett.* **1978**, *26*, 2275. (d) Trost, B. M.; Brickner, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 568. (e) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 5940. (f) Ziegler, F. E.; Chakraborty, U. R.; Weisenfeld, R. B. *Tetrahedron* **1981**, *37*, 4035.

(8) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(9) (a) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (b) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

(10) (a) Bestmann, H. J.; Kunstmann, R.; Schultz, H. *Justus Liebigs Ann. Chem.* **1966**, *699*, 33 ($n$ = 5). (b) Burgstahler, A. W.; Weigel, L. O.; Bell, W. J.; Rust, M. K. *J. Org. Chem.* **1975**, *40*, 3456 ($n$ = 6). (c) Tsuji, J.; Kaito, M.; Yamada, T.; Mandai, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1915 ($n$ = 6). (d) Citterio, A.; Vismara, E. *Synthesis* **1980**, 751 ($n$ = 7, 8).

(11) Hibino, J.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetetrahedron Lett.* **1984**, *25*, 2151.

(12) Corey, E. J.; Brunelle, D. J.; Stork, P. J. *Tetrahedron Lett.* **1976**, *17*, 3405.

0002-7863/87/1509-3785$01.50/0 