a heptet at δ 4.30. The highest fragment observed in the EI mass spectrum is M - F^+ at m/e 379.

Anal. Calcd for $[(CF_3)_2CHO]_2SO_2$: S, 8.05; F, 57.28. Found: S, 8.15; F, 58.0.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with 1,1,1,3,3,3-Hexafluoro-2-propanol [$(CF_3)_2CHOH$]. 1,1,1,3,3,3-Hexafluoro-2-propanol (2 mmol, 0.34 g) and triethylamine (2 mmol, 0.20 g) were condensed in a Pyrex reaction vessel at -196 °C and warmed to room temperature for 20 min. The mixture was then frozen at -196 °C and 2,2,2-trifluoroethyl fluorosulfate (2 mmol, 0.36 g) added, whereupon the mixture was warmed slowly to room temperature with stirring. After the mixture was heated to 60 °C with stirring for 2-3 h, the volatiles were removed at -30 °C. The product, a colorless to pale yellow liquid, was analyzed by gas chromatography-mass spectroscopy and found to be 93.4% CF_3CH_2O-$SO_2OCH(CF_3)_2$, 4.0% unreacted $(CF_3)_2CHOH{\cdot}N(CH_2CH_3)_3$ (eluted at 120 °C as one component), and 2.6% $(CF_3CH_2O)_2SO_2$. The vapor pressure of 1,1,1,3,3,3-hexafluoroisopropyl 2,2,2-trifluoroethyl sulfate is approximately 5 mm at room temperature. The infrared spectrum for this new sulfate is as follows: 2980 (w), 1441 (s), 1370 (s), 1297 (vs), 1212 (vs-br), 1112 (m), 1069 (s), 1038 (vs), 970 (s), 911 (sh), 893 (s), 854 (s), 746 (w), 698 (s), 673 (w), 624 (m), 597 (m), 576 (m), 539 (m) cm^{-1}. The ^{19}F NMR shows a doublet centered at ϕ -75.2 ($^3J_{HF}$ = 5.4 Hz, 6 F), and a triplet at ϕ -76.0 (^3J = 7.3 Hz, 3 F). The ^1H NMR consists of a heptet at δ 5.23 (1 H) and a quartet at δ 4.62 (2 H). The CI mass spectrum shows a quasi-molecular ion at m/e 331 (base peak), as well as prominent fragments at m/e 311 (M - F^+, 88.6%), 231 (M - $CF_3CH_2^+$, 8.1%), 211 (M - $C_2H_2F_3^+$, 6.9%), 163 (M - $(CF_3)_2CHO^+$, 10.9%), 101 ($CF_3CH_2OH_2^+$, 12%), 81 (CF_3C^+, 36.9%), and 69 (CF_3^+, 16%).

Anal. Calcd for $C_5H_3F_9O_4S$: C, 18.18; H, 0.91; F, 51.8. Found: C, 19.19; H, 1.19; F, 53.7.

Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with Methanethiol (CH_3SH). A Pyrex reaction vessel was charged with CH_3SH (4 mmol, 0.20 g), triethylamine (2 mmol, 0.20 g), and 2,2,2-trifluoroethyl fluorosulfate (2 mmol, 0.36 g), at -196 °C, and warmed slowly with stirring, to room temperature. Immediately, the volatile products were removed at 0 °C, and the volatile and involatile products were analyzed by GC/MS. In addition to unreacted fluorosulfate (46.6%), trifluoroethanol (as triethylamine adduct, 1.8%), bis(2,2,2--trifluoroethyl) sulfate (trace), SO_2 (6.3%), dimethyldisulfane (14.0%), and methyl 2,2,2-trifluoroethyl sulfide (31.4%) were found. Spectral data for $CF_3CH_2SCH_3$: ^{19}F NMR ϕ -68.5 (t, ^3J = 9.7 Hz); ^1H NMR δ 3.03 (q, ^3J = 9.9 Hz, 2 H), 2.24 (s, 3 H); mass spectrum (CI), m/e 131 (M + 1, 57.6%), 111 (M - F^+, 100%), 61 (M - CF_3^+, 10.6%); infrared spectrum 3005 (w, 2950 (w), 1423 (w), 1321 (s), 1288 (s), 1265 (s), 1188 (w), 1142 (vs), 1100 (sh), 992 (w), 861 (w), 752 (m), 658 (m), 497 (w) cm^{-1}. The molecular weight of $CF_3CH_2SCH_3$ was found to be 132 (calcd 130). When the mixture was allowed to react for approximately 2 days prior to analysis, the amount of bis(2,2,2-trifluoroethyl) sulfate increased to about 10% and the sulfide to about 45% of the mixture with an accompanying decrease in the amount of unreacted fluorosulfate and triethylamine. Trace amounts of a substance of molecular weight 158 were also found in the mass spectrum; however, no compound was isolated.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation (Grant CHE-8100156), and the Air Force Office of Scientific Research (82-0247) for support of this research.

Registry No. $CF_3CH_2OSO_2F$, 66950-71-8; Me_2NH, 124-40-3; $CF_3CH_2OSO_2NMe_2$, 66950-70-7; $MeNH_2$, 74-89-5; $CF_3CH_2OSO_2NHMe$, 92720-78-0; NH_3, 7664-41-7; $CF_3CH_2OSO_2NH_2$, 92720-79-1; CF_3CH_2OH, 75-89-8; $(CF_3CH_2O)_2SO_2$, 665-97-4; MeONa, 124-41-4; $CF_3CH_2OSO_2OMe$, 92720-80-4; $(CF_3)_2CHOSO_2F$, 38252-04-9; $[(CF_3)_2CHO]_2SO_2$, 92720-81-5; $CF_3CH(OH)CF_3$, 920-66-1; $(CF_3)_2CHOSO_2OCH_2CF_3$, 92720-82-6; MeSH, 74-93-1; CF_3CH_2SMe, 5187-55-3.

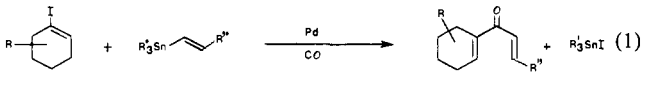
Palladium-Catalyzed Carbonylative Coupling of Vinyl Triflates with Organostannanes. A Total Synthesis of (±)$\Delta^{9(12)}$-Capnellene

G. T. Crisp, William J. Scott, and J. K. Stille*

Contribution from the Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523. *Received June 11, 1984*

Abstract: The palladium-catalyzed carbonylative coupling of vinyl triflates with alkyl-, vinyl-, allyl-, and arylstannanes gives good yields of the cross-coupled ketone products. Regioselectively formed vinyl triflates can be used to produce divinyl ketones as regioisomerically pure compounds. The *E* and *Z* geometry of the vinylstannane is maintained during the coupling reaction. This methodology was applied to a total synthesis of the marine natural product $\Delta^{9(12)}$-capnellene.

Divinyl ketones are important intermediates in organic synthesis since they can act as Michael acceptors for a diverse range of nucleophiles[1] or participate in Nazarov reactions to give cyclopentenones.[2] We reported recently that the palladium-catalyzed carbonylative coupling of vinyl ioides with vinylstannanes afforded unsymmetrical divinyl ketones in good yields (eq 1).[3]



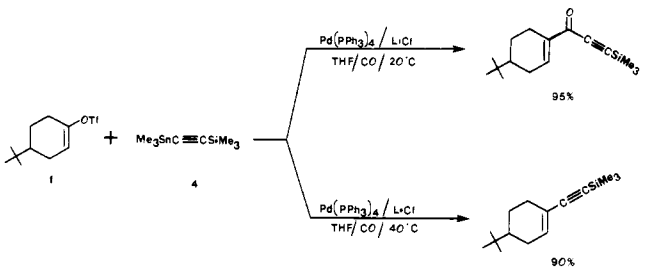
(1)

However, an expeditious route for the regioselective generation of a cyclic vinyl iodide is not currently available. For example, cyclic vinyl iodides have traditionally been prepared from the corresponding cycloalkanone via a two-step sequence involving hydrazone formation and subsequent oxidation with iodine in the presence of triethylamine.[4] This procedure gives only moderate yields of the desired vinyl iodide, the major side product being the geminal diiodide. More recently, a modification of this procedure which significantly increases the yield of the vinyl iodide has been reported.[5] The regioselective generation of a cyclic vinyl iodide from a hydrazone precursor utilizing this methodology was

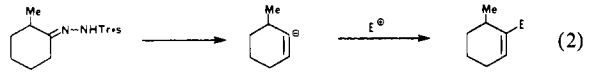
(1) Bergman, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179-555.
(2) Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429-442.
(3) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.*, in press.
(4) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989-1003.
(5) Barton, D. H. R.; Bashiardes, G.; Fourrey, J.-L. *Tetrahedron Lett.* **1983**, *24*, 1605-1608.

0002-7863/84/1506-7500$01.50/0

Scheme I



attempted during the synthesis of pentalenolactone E, but a mixture of regioisomers was obtained.[6] An alternate procedure, in which a modified Shapiro reaction is used to generate a vinyl anion regioselectively and is followed by trapping with various electrophiles (e.g., water, *n*-butyl bromide, *N,N*-dimethylformamide, but not iodine), was reported as giving only one product (eq 2).[7] However, in our hands, an analogous reaction with the trisylhydrazone of 3,3-dimethylcyclohexanone gave a mixture of regioisomers.[8]

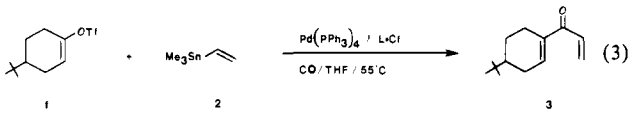


(2)

It would be advantageous to be able to utilize the oxygen of an enolate as the leaving group in a metal-catalyzed coupling.[9] The regioselective generation of vinyl triflates (trifluoromethanesulfonates) is precedented,[10] as is the direct coupling between a vinyl triflate and an organostannane.[11] These results suggested that a coupling between vinyl triflates and organostannanes in the presence of carbon monoxide might serve as a means of introducing the carbonyl functionality between organic fragments and that such a coupling might be regiospecific. For the examination of the utility of this reaction the total synthesis of the marine natural product $\Delta^{9(12)}$-capnellene was undertaken.

Results and Discussion

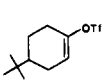
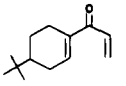
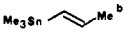
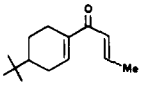
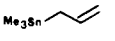
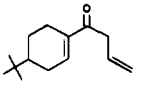
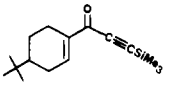
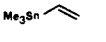
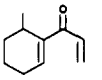
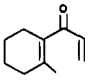
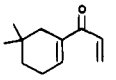
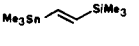
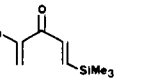
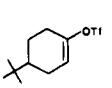
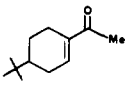
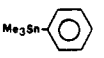
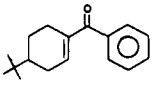
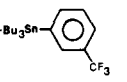
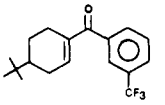
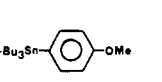
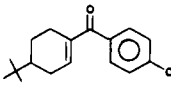
The reaction between vinyl triflate **1** and trimethylvinyltin (**2**) at 55 °C in tetrahydrofuran (THF) in the presence of 3 mol % tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, and 15 psi carbon monoxide did not take place, as evidenced by gas chromatographic (GC) analysis of the mixture. However, upon addition of 2–3 equiv of lithium chloride to the mixture, complete consumption of vinyl triflate **1** occurred within 18 h affording **3** and Me_3SnCl as the only products observable by GC analysis (eq 3).



(3)

A number of features of this reaction are worth mentioning. Formation of **3** was extremely slow at temperatures below 45 °C, while at temperatures above 65 °C a considerable quantity of the non-carbonylated coupled product was observed. Although $Pd(PPh_3)_4$ proved to be the most convenient catalyst for the reaction, bis(dibenzylideneacetone)palladium(0) and 2 equiv of triphenylphosphine were equally efficacious. Surprisingly, $PhCH_2PdCl(PPh_3)_2$,[12] was not a particularly efficient catalyst, with only low conversions of **1** to **3** being realized after 18 h. In

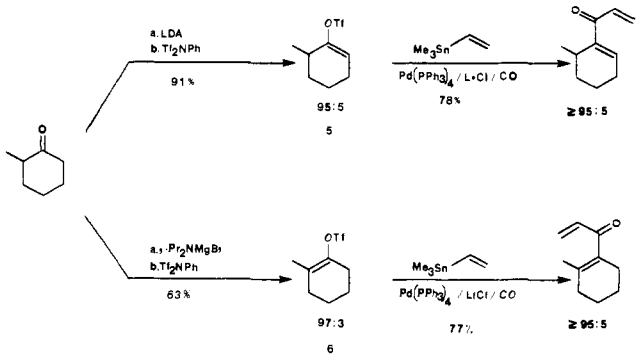
Table I. Palladium-Catalyzed Carbonylative Coupling of Vinyl Triflates with Organostannanes[a]

EXAMPLE	TRIFLATE	ORGANOSTANNANE	PRODUCT	ISOLATED YIELD (%)
1				78
2				70[c]
3				95[d]
4				95[e]
5				78
6				77
7				73
8				77
9				73[d]
10				93[d]
11				76[d]
12				88[d]

[a] Reactions carried out at 55 °C in THF under 15 psi carbon monoxide and in the presence of 3 mol % $Pd(PPh_3)_4$, unless otherwise stated. [b] The vinylstannane was a 2:1 mixture of *Z*:*E* isomers. [c] The product was a 2:1 mixture of *Z*:*E* isomers. [d] Reactions carried out at 75 °C in THF under 50 psig of carbon monoxide in the presence of 3 mol % $Pd(PPh_3)_4$ and 1 equiv of $ZnCl_2$. [e] Reaction carried out at 20 °C in THF under 50 psig of carbon monoxide in the presence of 3 mol % $Pd(PPh_3)_4$.

(6) Paquette, L. A.; Annis, G. D.; Schostarez, H. *J. Am. Chem. Soc.* **1982**, *104*, 6646–6653.
(7) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147–154.
(8) Scott, W. J.; Stille, J. K, unpublished results.
(9) (a) For the palladium-catalyzed coupling of alanes with enol phosphates, see: Takai, K.; Sato, M.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 108–115. (b) For the nickel-catalyzed coupling of Grignard reagents with methyl vinyl ethers, see: Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246–2247. (c) For the nickel-catalyzed coupling of Grignard reagents with silyl enol ethers, see: Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915–3918.
(10) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979–982.
(11) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630–4632.
(12) $PhCH_2PdCl(PPh_3)_2$ has been used successfully for palladium-catalyzed couplings of organic halides with organostannanes: (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992–4998. (b) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833–4840.

Scheme II



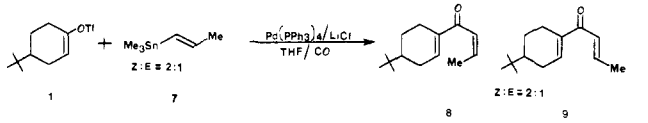
THF or acetonitrile quantitative conversions of **1** to **3** after 18 h were realized, whereas when the solvent was chloroform or benzene only partial conversions were achieved over this period.

The reaction is quite general, with both cyclic and acyclic vinyl triflates affording good, isolated yields of the corresponding divinyl ketones (Table I). Although little of the noncarbonylated coupled product was observed for reactions involving vinylstannanes under standard conditions, this was not true for the acetylenic stannane **4**. Thus, reaction between **1** and **4** in the temperature range 40–60 °C under 50 psig of carbon monoxide gave predominately the directly coupled product, whereas reactions carried out at 20 °C under 50 psig of carbon monoxide produced the desired carbonyl-containing product (Scheme I).

When vinyl triflate **1** was heated at 55 °C with tetramethyltin under the standard conditions, GC analysis of the mixture indicated that no reaction had taken place. Increasing the reaction temperature by heating dimethoxyethane or diglyme solutions of the reactants to reflux only caused decomposition of the vinyl triflate. This problem was alleviated, however, by the addition of 1 equiv of zinc chloride to the reaction mixture and increasing the carbon monoxide pressure to 50 psig. As shown in Table I, a good isolated yield of the desired methyl enone was realized. This same procedure was necessary for aryl stannanes, which also failed to react in the absence of zinc chloride. Although the exact role of zinc chloride remains to be clarified, the possible intermediacy of an organozinc species is assumed.[13]

An important aspect of this work is the ability to generate a vinyl triflate regioselectively utilizing well-known enolate chemistry,[10] and couple this with an organostannane under a carbon monoxide atmosphere to give only one regioisomeric product (Scheme II). Thus, 2-methylcyclohexanone was converted into the kinetic triflate, **5**, and into the thermodynamic triflate, **6**. Carbonylative coupling of these triflates with trimethylvinyltin (**2**) gave the desired divinyl ketones as greater than or equal to 95% isomerically pure products as shown by ^1H or ^{13}C NMR.

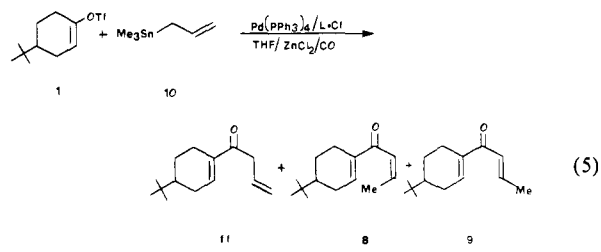
In an effort to determine whether the regiochemical integrity of the vinylstannane was maintained during the course of the coupling, a 2:1 mixture of the *Z*:*E* isomers of trimethylpropenyltin (**7**) was allowed to react with vinyl triflate **1**. Capillary GC analysis of the product mixture indicated that two products were obtained in the ratio of 2:1. These were shown, by the ^1H NMR spectrum, to be the *Z* compound **8** (doublets of quartets at 5.94 and 6.29 ppm, J = 12 Hz) and the *E* compound **9** (doublets of quartets at 6.52 and 6.69 ppm, J = 15 Hz), respectively (eq 4).



(4)

Thus, no loss of regiochemistry occurred during the course of the coupling, nor at the product stage. This result contrasts with that reported for the carbonylative coupling of vinyl iodides with vinylstannanes, in which a loss of regiochemical integrity was observed at the product stage for an analogous *Z* isomer.[3]

The carbonylative coupling of vinyl triflate **1** with trimethylallyltin (**10**) required special reaction conditions. Under standard conditions (such as those employed for vinylstannane coupling) **10** was completely consumed but a quantitative recovery of vinyl triflate **1** was realized with negligible formation of the desired compound **11**. Upon addition of zinc chloride to the mixture a fast reaction took place to give, in addition to the desired product **11**, both isomeric divinyl ketones **8** and **9**, the relative ratios between **8**, **9**, and **11** depending upon the reaction time (eq 5).

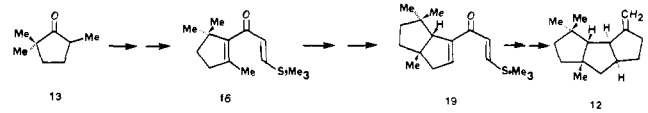


(5)

If the mixture was worked up immediately, all of the vinyl triflate **1** was consumed and only trace amounts of **8** and **9** were observed. However, on heating **11** in the presence of zinc chloride substantial quantities of **8** and **9** were detected by ^1H and ^{13}C NMR spectroscopy.

(±)$\Delta^{9(12)}$-Capnellene. The previous results suggested that a combination of a carbonylative coupling of vinyl triflates with vinylstannanes and a Nazarov reaction[2] might be expeditiously applied to an iterative three-carbon annulation procedure for the synthesis of fused polycyclopentanoids.[15] Thus, a total synthesis of the marine natural product $\Delta^{9(12)}$-capnellene (**12**) was undertaken.

The sesquiterpene **12** is the parent hydrocarbon for a series of cis-anti-cis ring-fused complexes possessing the tricyclo[6.3.0.0^{2,6}]undecane structure which have been isolated from the soft coral *capnella imbricata*.[16] A number of elegant syntheses of **12** have been reported recently.[17] Our approach to capnellene was based on two intermediates, **16** and **19**, which were envisioned as arising from a carbonylative coupling of a vinyl triflate with vinylstannane (eq 6).



(6)

The readily prepared trimethylcyclopentanone **13**[18] was converted into vinyl triflate **14** in 85% yield with triflic anhydride and the sterically hindered base 2,6-di-*tert*-butyl-4-methyl-

(13) (a) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spigel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254–2256. (b) Godschalx, J. P.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599–2602.

(14) Krafft, M. E.; Holton, R. A. *Tetrahedron Lett.* **1983**, *24*, 1345–1348.

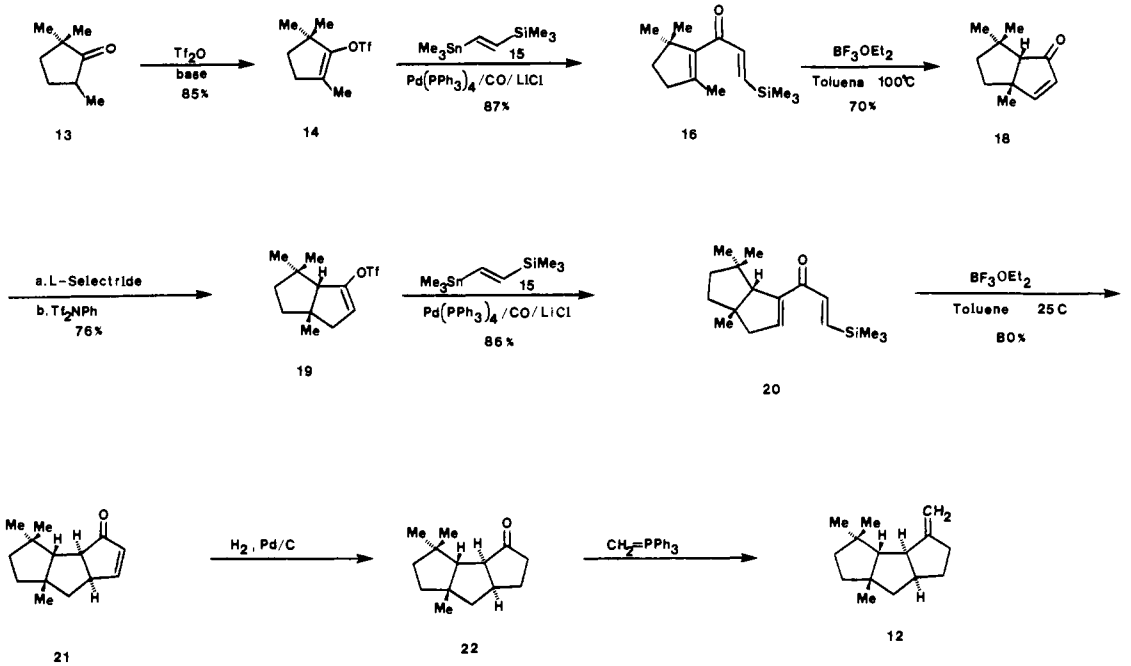
(15) For a comprehensive listing of references on iterative three-carbon annulation and polycyclopentanoids, see: (a) Greene, A. E.; Luche, M.-J.; Deprês, J.-P. *J. Am. Chem. Soc.* **1983**, *105*, 2435–2439. (b) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141–170.

(16) (a) Kaisin, M.; Sheikh, Y. M.; Durham, L. J.; Djerassi, C.; Tursch, B.; Daloze, D.; Braekman, J. C.; Losman, D.; Karlsson, R. *Tetrahedron Lett.* **1974**, 2239–2242. (b) Sheikh, Y. M.; Singy, G.; Kaisin, M.; Eggert, H.; Djerassi, C.; Tursch, B.; Daloze, D.; Braekman, J. C. *Tetrahedron* **1976**, *32*, 1171–1178. (c) Sheikh, Y. M.; Djerassi, C.; Braekman, J. C.; Daloze, D.; Kaisin, M.; Tursch, B.; Karlsson, R. *Tetrahedron* **1977**, *33*, 2115–2117.

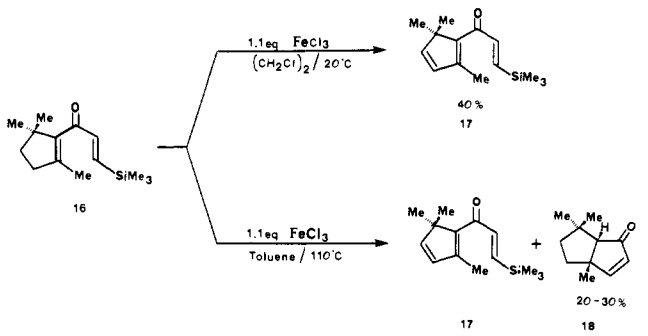
(17) For previous total syntheses of (±)$\Delta^{9(12)}$-capnellene, see: (a) Paquette, L. A.; Stevens, K. E. *Tetrahedron Lett.* **1981**, *22*, 4393–4396. Paquette, L. A.; Stevens, K. E. *Can. J. Chem.*, submitted for publication. (b) Little, R. D.; Carroll, G. L. *Tetrahedron Lett.* **1981**, *22*, 4389–4392. Little, R. D.; Carroll, G. L.; Petersen, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 928–932. (c) Oppolzer, W.; Battig, K. *Tetrahedron Lett.* **1982**, *23*, 4669–4672. (d) Huguet, J.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 2413–2421. (e) Mehta, G.; Reddy, D. S.; Murty, A. N. *J. Chem. Soc., Chem. Commun.* **1983**, 824–825. (f) Piers, E.; Karunaratne, V. *Can. J. Chem.* **1984**, *62*, 629–631.

(18) Dubois, J. E.; Fort, J. F. *Tetrahedron* **1972**, *28*, 1653–1663.

Scheme III



Scheme IV



pyridine[19] (Scheme III). The palladium-catalyzed carbonylative coupling between vinyl triflate **14** and (trimethylsilyl)vinylstannane (**15**)[20] afforded the desired divinyl ketone **16** in 87% yield. Compound **16** appeared to be an ideal candidate for a silicon-directed Nazarov reaction.[21] However, addition of 1.1 equiv of $FeCl_3$ to a dichloroethane solution of **16** at room temperature gave, unexpectedly, the cyclopentadienyl compound **17** and only traces of the desired enone **18** (Scheme IV). When **16** was heated to reflux in toluene in the presence of 1.1 equiv of $FeCl_3$, both **17** and **18** were formed in varying yields. Under these conditions **17** appeared to decompose and a 20–30% yield of **18** was occasionally realized. This problem was circumvented by changing the Lewis acid. Thus, heating a toluene solution of dienone **16** and $BF_3{\cdot}OEt_2$ at reflux for 36 h gave the desired enone, **18**, in 70% yield. With **18** in hand, it was now necessary to repeat the palladium-catalyzed coupling and demonstrate the utility of this sequence for iterative three-carbon annulations. Vinyl triflate **19** was prepared in 76% yield by conjugate reduction[23] of enone **18** with L-Selectride (Aldrich) followed by trapping of the enolate with *N*-phenyltriflimide.[10] Coupling between vinyl triflate **19** and vinylstannane **14**[20] in the presence of $Pd(PPh_3)_4$ and carbon monoxide afforded divinyl ketone **20** in 88% yield. The addition of $BF_3{\cdot}OEt_2$ to **20** at room temperature effected the desired cyclization to give enone **21** in high yield (88%). The double bond emerged at the least substituted position, as expected for a silicon-directed Nazarov reaction,[21] and the cis-anti-cis ring-fused arrangement was formed exclusively. A compound very similar to **20**, but lacking the trimethylsilyl group, was reported not to cyclize under the influence of Lewis acids.[17a] The hydrogenation of **21** and olefination of **22** were performed in accord with previous procedures[17a-d] and resulted in the formation of (±)$\Delta^{9(12)}$-capnellene.[24]

Thus, the palladium-catalyzed carbonylative coupling of vinyl triflates with various organostannanes gives good yields of the desired products, is regiospecific, and shows synthetic potential as a means of introducing a carbonyl group between unsaturated organic fragments.

Experimental Section

^1H NMR spectra were recorded on an IBM WP270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on an IBM WP270 (68 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. Coupling constants for ^{13}C–^1H were obtained from gated decoupled spectra. Infrared spectra were recorded on a Beckman 4250 spectrometer as neat films on sodium chloride plates. Gas-chromatographic analyses were conducted on a Varian 3700 equipped with a 0.25 mm × 50 m SE-30 capillary column. Low-resolution mass spectra (LRMS) were performed on a V.G. Micromass 16 spectrometer. High-resolution mass spectra (HRMS) were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Tetrahydrofuran (THF) was distilled from potassium under argon. Pentane and hexane were distilled from potassium permanganate. *N*-Phenyltriflimide was either purchased (PCR Research Chemicals, Inc.) and recrystallized from hexane or prepared following known methods.[24] All reactions were carried out under argon unless otherwise stated.

2,2,5-Trimethylcyclopentanone[18] and 2,6-di-*tert*-butyl-4-methylpyridine[19] were prepared according to literature methods.

Organostannanes. The following compounds were prepared by literature procedures: trimethylvinylstannane (**2**),[25] 1-(trimethylstannyl)-prop-1-ene (**7**) (*Z*:*E*, 2:1),[25] trimethylallylstannane (**10**),[26] trimethylphenylstannane,[27] (4-methoxyphenyl)tri-*n*-butylstannane,[28] (3-(tri-

(19) Scott, W. J. Ph.D. Dissertation, Cornell University, Ithaca, NY, 1983.
(20) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1978**, *144*, 1–12.
(21) (a) Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642–2645. (b) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1984**, *66*, 2377–2396. (c) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1984**, *66*, 2397–2411.
(22) (a) Ganem, B. *J. Org. Chem.* **1975**, *40*, 146–147. (b) Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194–2200.
(23) NMR spectra of **12** were identical with spectra of authentic $\Delta^{9(12)}$-capnellene. The authors thank Professors Djerassi, Paquette, and Little for copies of NMR spectra.
(24) Hendriksson, J. B.; Bair, K. W.; Bergeron, R.; Giga, A.; Skipper, P. L.; Sternbach, D. D.; Waring, J. A. *Org. Prep. Procedures* **1977**, *9*, 173–207.
(25) Seyferth, D.; Vaughan, L. G. *J. Organomet. Chem.* **1963**, *1*, 138–152.
(26) Abel, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199–229.

fluoromethyl)phenyl)tri-*n*-butylstannane,[29] 1-(trimethylsilyl)-2-(trimethylstannyl)acetylene (**4**),[30] and (*E*)-1-(trimethylsilyl)-2-(trimethylstannyl)ethylene (**15**).[20]

Vinyl Triflates. The following vinyl triflates were prepared according to literature methods: 4-*tert*-butylcyclohex-1-en-1-yl triflate (**1**),[19] hex-1-en-2-yl triflate,[31] and 6-methylcyclohex-1-en-1-yl triflate.[10]

2-Methylcyclohex-1-en-1-yl Triflate (6). To a solution of diisopropylamine (3.0 mL, 2.1 mmol) in ether (250 mL) at 0 °C was added ethylmagnesium bromide (21 mL, 1.0 N in ether, 2.1 mmol), and the resulting mixture was allowed to warm to room temperature and stirred for 18 h. After the mixture was cooled to 0 °C, hexamethylphosphoramide (8.0 mL, 4.6 mmol) was added, followed by 2-methylcyclohexanone (2.4 g, 2.2 mmol). This mixture was warmed to room temperature and stirred for 6 h, and then solid *N*-phenyltriflimide (7.5 g, 2.1 mmol) was added. The mixture was stirred for 15 h at room temperature and heated at reflux for 6 h. The resulting solution was washed with 10% hydrochloric acid (2 × 50 mL), water (50 mL), 10% sodium hydroxide (2 × 50 mL), water (2 × 50 mL), and brine (50 mL). The solution was dried over $MgSO_4$ and concentrated to give an oil which was filtered through a pad of silica gel eluting with hexane. Bulb-to-bulb distillation (55 °C (0.55 mm)) gave **6**[32] (3.3 g, 63%): IR (neat) 1710, 1450, 1410, 1345, 1250, 1200, 1140 cm^{-1}; ^1H NMR δ 1.57–1.63 (m, 2 H), 1.70–1.76 (m, 2 H), 1.73 (s, 3 H), 2.08–2.12 (m, 2 H), 2.25–2.31 (m, 2 H); ^{13}C NMR δ 16.6, 21.8, 23.3, 27.7, 30.7, 118.4 (q, J = 319 Hz), 126.4, 143.4; LRMS m/z 244 (M^+, 5%). Anal. Calcd for $C_8H_{11}F_3O_3S$: C, 39.34; H, 4.54. Found: C, 39.49; H, 4.39.

5,5-Dimethylcyclohex-1-en-1-yl Triflate. To a THF (50 mL) solution of 5,5-dimethylcyclohex-2-en-1-one[33] (1.0 g, 8.1 mmol) at −78 °C was added L-Selectride (8.3 mL, 1 M in THF, 8.3 mmol). The solution was stirred at −78 °C for 1.5 h, and solid *N*-phenyltriflimide (3.0 g, 8.3 mmol) was added. After the solution was stirred overnight at room temperature it was diluted with pentane (100 mL) and washed with a saturated sodium bicarbonate solution (2 × 25 mL). The combined aqueous layers were back extracted with pentane (1 × 50 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated to give a cloudy oil. Filtration of this material through a pad of silica gel with the aid of pentane, followed by bulb-to-bulb distillation (55 °C, 0.8 mm), gave the product as a colorless oil (1.94 g, 93%): IR (neat) 1690, 1415, 1210, 1140 cm^{-1}; ^1H NMR δ 0.97 (s, 6 H), 1.33 (t, J = 6 Hz, 2 H), 2.07 (t, J = 2 Hz, 2 H), 2.14–2.21 (m, 2 H), 5.69–5.73 (m, 1 H); ^{13}C NMR δ 21.7, 27.7 (2 C), 31.1, 31.6, 34.0, 41.2, 117.0, 118.7 (q, J = 322 Hz), 148.7; LRMS m/z 258 (M^+, 1%). Anal. Calcd for $C_9H_{13}F_3O_3S$: C, 41.86; H, 5.07. Found: C, 41.37; H, 4.97.

1-(4-*tert*-Butylcyclohex-1-en-1-yl)-2-propen-1-one (3, Entry 1). To a mixture of LiCl (0.20 g, 4.8 mmol) and $Pd(PPh_3)_4$ (0.060 g, 0.052 mmol, 3 mol %) was added a THF (30 mL) solution of triflate **1** (0.50 g, 1.8 mmol) and trimethylvinyltin (**2**) (0.33 g, 1.8 mmol). Carbon monoxide was bubbled through the solution for 15 min, and a static pressure of 15 psi of carbon monoxide was maintained over the reaction mixture by means of a Fisher rubber gas bag. The mixture was heated at 55 °C for 18 h, cooled to room temperature, and diluted with pentane (50 mL). This solution was washed with water (2 × 20 mL) and brine (2 × 20 mL) and then dried over Na_2SO_4 and concentrated. The resulting oil was passed through a short pad of silica gel, eluting with 10% ethyl acetate/hexane. The solution was concentrated to give 0.25 g (76%) of **3** as a colorless oil: IR (neat) 1665, 1645, 1612 cm^{-1}; ^1H NMR δ 0.81 (s, 9 H), 1.21–2.65 (m, 7 H), 5.58 (d, J = 9 Hz, 1 H), 6.14 (d, J = 17 Hz, 1 H), 6.75–7.00 (m, 2 H); ^{13}C NMR δ23.3 (t, J = 126 Hz), 24.6 (t, J = 129 Hz), 26.9 (q, J = 127 Hz), 27.8 (t, J = 127 Hz), 32.0 (s), 43.4 (d, J = 136 Hz), 127.1 (t, J = 161 Hz), 131.5 (d, J = 158 Hz), 139.4 (s), 141.1 (d, J = 153 Hz), 190.8 (s). Anal. Calcd for $C_{13}H_{20}O$: C, 81.25; H, 10.42. Found: C, 81.50; H, 10.30.

The following compounds were prepared in an analogous manner.

(*E*)- and (*Z*)-1-(4-*tert*-butylcyclohex-1-en-1-yl)-but-2-en-1-one (entry 2): IR (neat) 1665, 1642, 1622 cm^{-1}; (*Z*) ^1H NMR δ 0.68 (s, $(CH_3)_3C$), 1.67 (dd, J = 1, 7 Hz, CH_3), 0.75–2.50 (m), 5.94 (dq, J = 7, 12 Hz, $-CH{=}CH(CH_3)$), 6.29 (dq, J = 2, 12 Hz, $-CH{=}CH(CH_3)$), 6.67 (m); (*E*) ^1H NMR δ 0.66 (s, $(CH_3)_3C$), 1.80 (dd, J = 2, 7 Hz, CH_3), 0.75–2.50 (m), 6.52 (dq, J = 1, 15 Hz, $-CH{=}CH(CH_3)$), 6.69 (dq, J = 7, 15 Hz, $-CH{=}CH(CH_3)$), 6.70 (m); LRMS m/z 206 (M^+, 11%). Anal. Calcd for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 81.44; H, 10.88.

1-(6-Methylcyclohex-1-en-1-yl)-prop-2-en-1-one (entry 5): IR (neat) 1660, 1631, 1604 cm^{-1}; ^1H NMR δ 0.95 (d, J = 7 Hz, 3 H), 1.56 (m, 4 H), 2.18 (m, 2 H), 2.80 (m, 1 H), 5.62 (dd, J = 2, 10 Hz, 1 H), 6.14 (dd, J = 2, 17 Hz, 1 H), 6.75 (m, 2 H); ^{13}C NMR δ 17.6 (t, J = 123 Hz), 19.8 (q, J = 127 Hz), 26.1 (t, J = 125 Hz), 26.9 (d, J = 126 Hz), 29.6 (t, J = 129 Hz), 127.3 (t, J = 158 Hz), 132.8 (d, J = 158 Hz), 139.9 (d, J = 155 Hz), 144.6 (s), 191.9 (s); LRMS m/z 150 (M^+, 3%). Anal. Calcd for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.83; H, 9.28.

1-(2-Methylcyclohex-1-en-1-yl)-prop-2-en-1-one (entry 6): IR (neat) 1680, 1660, 1605 cm^{-1}; ^1H NMR δ 1.60 (m, 4 H), 1.67 (s, 3 H), 2.05–2.25 (m, 4 H), 5.85 (dd, J = 2,10 Hz, 1 H), 6.15 (dd, J = 2,17 Hz, 1 H), 6.42 (dd, J = 10,17 Hz, 1 H); ^{13}C NMR δ 21.2 (q, J = 125 Hz), 22.2 (t, J = 125 Hz), 22.4 (t,J = 125 Hz), 26.9 (t, J = 127 Hz), 31.8 (t, J = 125 Hz), 129.2 (t, J = 159 Hz), 132.3 (s), 136.5 (d, J = 158 Hz), 137.3 (s), 199.5 (s); LRMS m/z 150 (M^+, 18%); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1044.

1-(5,5-Dimethylcyclohex-1-en-1-yl)-prop-2-en-1-one (entry 7): IR (neat) 1665, 1640, 1615 cm^{-1}; ^1H NMR δ 0.89 (s, 6 H), 1.33 (t, J = 6 Hz, 2 H), 2.05 (s, 2 H), 2.27 (m, 2 H), 5.64 (dd, J = 2, 11 Hz, 1 H), 6.18 (dd, J = 2, 17 Hz, 1 H), 6.88 (m, 2 H); ^{13}C NMR δ 24.1 (t, J = 126 Hz), 28.0 (q, J = 123 Hz), 29.6 (s), 34.2 (t, J = 126 Hz), 36.8 (t, J = 131 Hz), 127.3 (t, J = 161 Hz), 131.8 (d, J = 160 Hz), 138.7 (s), 139.6 (d, J = 160 Hz), 191.4 (s); LRMS m/z 164 (M^+, 2%). Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.76. Found: C, 80.42; H, 9.96.

1-(Trimethylsilyl)-4-butylpenta-1,4-dien-3-one (entry 8): IR (neat) 1662, 1623 cm^{-1}; ^1H NMR δ 0.06 (s, 9 H), 0.81 (m, 3 H), 1.27 (m, 4 H), 2.25 (t, J = 8 Hz, 2 H), 5.67 (s, 1 H), 5.86 (s, 1 H), 6.97 (q, J = 19 Hz,,2 H); ^{13}C NMR δ −2.0 (q, J = 119 Hz), 13.7 (q, J = 125 Hz), 22.2 (t, J = 125 Hz), 30.3 (t, J = 131 Hz), 31.0 (t, J = 130 Hz), 123.5 (t, J = 164 Hz), 137.9 (d, J = 160 Hz), 147.4 (d, J = 142 Hz), 149.2 (s), 191.6 (s); LRMS m/z 210 (M^+, 1%). Anal. Calcd for $C_{12}H_{22}SiO$: C, 68.57; H, 10.48. Found: C, 68.44; H, 10.25.

1-(4-*tert*-Butylcyclohex-1-en-1-yl)-3-(trimethylsilyl)propyn-1-one (Entry 4). To a mixture of LiCl (0.20 g, 4.7 mmol) and $Pd(PPh_3)_4$ (0.060 g, 0.052 mmol, 3 mole %) in a Fischer Porter tube was added a THF (30 mL) solution of triflate **1** (0.50 g, 1.8 mmol) and 1-(trimethylsilyl)-2-(trimethylstannyl)ethyne (**4**) (0.48 g, 1.8 mmol). The reaction tube was pressured to 50 psig with carbon monoxide, and the mixture was stirred for 48 h at room temperature. Carbon monoxide was then vented and the solution diluted with pentane (100 mL), washed with water (3 × 50 mL) and brine (2 × 50 mL), and dried over $MgSO_4$. The residue was purified by chromatography on silica gel eluting with 10% ethyl acetate/hexane to give 0.44 g (95%) of product: IR (neat) 2060, 1637 cm^{-1}; ^1H NMR δ 0.08 (s, 9 H), 0.73 (s, 9 H), 0.80–2.50 (m, 7 H), 7.20 (m, 1 H); ^{13}C NMR δ −0.8 (q, J = 121 Hz), 23.0 (t, J = 129 Hz), 23.6 (t, J = 129 Hz), 26.9 (q, J = 127 Hz), 28.2 (t, J = 128 Hz), 31.9 (s), 43.5 (d, J = 124 Hz), 97.0 (s), 100.4 (s), 140.2 (s), 147.5 (d, J = 157 Hz), 178.4 (s); LRMS m/z 262 (M^+, 3%); HRMS calcd for $C_{10}H_{26}SiO$ 262.1754, found 262.1755. Anal. Calcd for $C_{16}H_{26}SiO$: C, 73.28; H, 9.92. Found: C, 73.57; H, 9.80.

1-(4-*tert*-Butylcyclohex-1-en-1-yl)but-3-en-1-one (11, Entry 3). To a mixture of LiCl (0.20 g, 4.7 mmol) and $Pd(PPh_3)_4$ (0.060 g, 0.052 mmol, 3 mol %) in a Fischer Porter tube was added a THF (20 mL) solution of triflate **1** (0.50 g, 1.8 mmol) and trimethylallyltin **10** (0.36 g, 1.8 mmol). The reaction tube was pressured to 50 psig with carbon monoxide, and the solution was stirred for 15 min. Carbon monoxide was vented and $ZnCl_2$ (0.24 g, 1.8 mmol) was added. The reaction tube was then pressured to 50 psig with carbon monoxide and heated at 75 °C for 2 h. The solution was cooled to room temperature, carbon monoxide was vented, and the solution was diluted with pentane (100 mL). Washing the solution with water (2 × 30 mL) and brine (2 × 30 mL) and drying over Na_2SO_4 followed by concentration gave 0.34 g (95%) of product **11**: IR (neat) 1678, 1655, 1640 cm^{-1}; ^1H NMR δ 0.80 (s, 9 H), 0.83–2.00 (m, 7 H), 3.32 (dt, J = 1, 7 Hz, 2 H), 5.00 (m, 2 H), 5.87 (ddt, J = 7, 10, 17 Hz, 1 H), 6.84 (m, 1 H); ^{13}C NMR δ 23.3 (t, J = 129 Hz), 24.6 (t, J = 125 Hz), 26.9 (q, J = 127 Hz), 27.7 (t, J = 127 Hz), 31.9 (s), 42.1 (t, J = 125 Hz), 43.4 (d, J = 127 Hz), 117.4 (t, J = 155 Hz), 131.7 (d, J = 157 Hz), 138.7 (s), 140.3 (d, J = 155 Hz), 198.2 (s); HRMS calcd for $C_{14}H_{22}O$ 206.1672, found 206.1672.

1-Acetyl-4-*tert*-butylcyclohex-1-ene (Entry 9). This compound was prepared in a manner similar to that described for entry 3, except the mixture was heated at 75 °C for 24 h. Bulb-to-bulb distillation (70 °C (0.5 mm)) gave a 73% yield of product:[34] IR (neat) 1720, 1672 cm^{-1}; ^1H NMR δ 0.78 (s, 9 H), 1.80–2.20 (m, 7 H), 2.16 (s, 3 H), 6.80 (m, 1 H); ^{13}C NMR δ 23.3 (t, J = 129 Hz), 24.4 (t, J = 126 Hz), 25.0 (q,

(27) Eaborn, C.; Waters, J. A. *J. Chem. Soc.* **1962**, 1131–1132.
(28) Wardell, J. L.; Ahmed, S. *J. Organomet. Chem.* **1974**, *78*, 395–404.
(29) Barnard, M.; Smith, P. J.; White, R. F. M. *J. Organomet. Chem.* **1974**, *77*, 189–197.
(30) Menz, G.; Wrackmeyer, B. *Z. Naturforsch., B* **1977**, *32B*, 1400–1407.
(31) Summerville, R. H.; Senkler, C. A.; Schleyer, P. v. R.; Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 1100–1110.
(32) Hanack, M.; Fuchs, K.-A.; Collins, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 4008–4017.
(33) Hiegel, G. A.; Burk, P. *J. Org. Chem.* **1973**, *38*, 3637–3639.
(34) House, H. O.; Umen, M. J. *J. Org. Chem.* **1973**, *38*, 3893–3901.

J = 126 Hz), 27.0 (q, J = 127 Hz), 27.8 (t, J = 127 Hz), 32.0 (s), 43.4 (d, J = 127 Hz), 139.6 (s), 140.8 (d, J = 156 Hz), 198.6 (s); LRMS m/z 180 (M^+, 2%). Anal. Calcd for $C_{12}H_{20}O$: C, 80.00; H, 11.11. Found: C, 79.88; H, 10.90.

1-Benzoyl-4-*tert*-butylcyclohex-1-ene (Entry 10). This compound was prepared as described for entry 9 and was purified by chromatography on silica gel eluting with 5% ethyl acetate/hexane to give a 93% yield of product:[35] IR (neat) 1655, 1645 cm^{-1}; ^1H NMR δ 0.88 (s, 9 H), 1.10–2.70 (m, 7 H), 6.60 (m, 1 H), 7.33–7.62 (m, 5 H); ^{13}C NMR δ 23.5 (t, J = 128 Hz), 25.5 (t, J = 128 Hz), 27.1 (q, J = 125 Hz), 27.8 (t, J = 125 Hz), 32.1 (s), 43.6 (d, J = 121 Hz), 127.9 (d, J = 162 Hz), 129.0 (d, J = 164 Hz), 131.1 (d, J = 163 Hz), 138.6 (s), 138.8 (s), 143.9 (d, J = 158 Hz), 197.7 (s); LRMS m/z 242 (M^+, 7%). Anal. Calcd for $C_{17}H_{22}O$: C, 84.30; H, 9.09. Found: C, 84.09; H, 9.21.

1-(3-(Trifluoromethyl)benzoyl)-4-*tert*-butylcyclohex-1-ene (Entry 11). This compound was prepared as described for entry 9 and was purified by vigorous stirring of an ether solution of product with 50% aqueous KF (to convert tributylchlorostannane to insoluble tributylfluorostannane) followed by drying over $MgSO_4$ and bulb-to-bulb distillation (130 °C (0.2 mm)) to give a 76% yield of product: IR (neat) 1725, 1655, 1640, 1615 cm^{-1}; ^1H NMR δ 0.86 (s, 9 H), 1.12–2.70 (m, 7 H), 6.55 (m, 1 H), 7.49 (t, J = 8 Hz, 1 H), 7.68 (d, J = 8 Hz, 1 H), 7.74 (d, J = 8 Hz, 1 H), 7.82 (s, 1 H); ^{13}C NMR δ 23.3 (t, J = 124 Hz), 25.3 (t, J = 130 Hz), 27.0 (q, J = 127 Hz), 28.0 (t, J = 127 Hz), 32.1 (s), 43.5 (d, J = 122 Hz), 125.7 (d, J = 161 Hz), 127.6 (d, J = 163 Hz), 128.0 (s), 128.5 (d, J = 168 Hz), 130.4 (s), 132.1 (d, J = 165 Hz), 139.0 (q, J = 168 Hz), 145.1 (d, J = 157 Hz); LRMS m/z 310 (M^+, 27%). Anal. Calcd for $C_{18}H_{21}F_3O$: C, 69.68; H, 6.77. Found: C, 69.70; H, 6.78.

1-(4-Methoxybenzoyl)-4-*tert*-butylcyclohex-1-ene (Entry 12). This compound was prepared as described for entry 11 and purified by bulb-to-bulb distillation (140 °C (0.2 mm)) to give an 88% yield of product:[35] IR (neat) 1737, 1650, 1610 cm^{-1}; ^1H NMR 0.86 (s, 9 H), 1.04–2.32 (m, 7 H), 3.80 (s, 3 H), 6.46 (m, 1 H), 6.86 (d, J = 9 Hz, 2 H), 7.64 (d, J = 9 Hz, 2 H); ^{13}C NMR δ 23.6 (t, J = 127 Hz), 25.9 (t, J = 129 Hz), 27.0 (q, J = 124 Hz), 27.6 (t, J = 129 Hz), 32.1 (s), 43.6 (d, J = 130 Hz), 55.3 (q, J = 143 Hz), 113.3 (d, J = 162 Hz), 131.1 (s), 131.4 (d, J = 161 Hz), 138.6 (s), 141.4 (d, J = 161 Hz), 162.5 (s), 196.6 (s); LRMS m/z 272 (M^+, 5%).

2,5,5-Trimethylcyclopent-1-en-1-yl Triflate (14). To a dichloromethane (300 mL) solution of 2,2,5-trimethylcyclopentanone[18] (5.0 g, 40 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (14 g, 68 mmol) was added dropwise triflic anhydride (17 g, 60 mmol). The resulting brown solution was heated at reflux for 36 h, cooled to room temperature, and concentrated almost to dryness. The dark brown slurry was diluted with pentane (300 mL), and triflic acid was added dropwise until no 2,6-di-*tert*-butyl-4-methylpyridine could be detected by GLC. Filtration and concentration of the solution left a brown residue which was chromatographed on silica gel, eluting with hexane to give 10 g (85%) of colorless product: IR (neat) 1705, 1415, 1230, 1060 cm^{-1}; ^1H NMR δ 1.13 (s, 6 H), 1.73 (s, 3 H), 1.81 (t, J = 7 Hz, 2 H), 2.30 (t, J = 7 Hz, 2 H); ^{13}C NMR δ 12.7, 25.8, 30.6, 37.1, 43.2, 118.7 (q, J = 325 Hz), 126.9, 149.1; LRMS m/z 258 (M^+, 1%). Anal. Calcd for $C_9H_{13}F_3O_3S$: C, 41.82; H, 5.03. Found: C, 41.94; H, 5.08.

1-(2,5,5-Trimethylcyclopent-1-en-1-yl)-3-(trimethylsilyl)prop-2-en-1-one (16). To a mixture of LiCl (1.0 g, 24 mmol) and $Pd(PPh_3)_4$ (0.14 g, 0.13 mmol, 3 mol %) was added a THF (50 mL) solution of triflate **14** (1.5 g, 5.8 mmol) and (*E*)-2-(trimethylsilyl)-1-(trimethylstannyl)-ethylene (**15**) (1.6 g, 6.0 mmol). Carbon monoxide was bubbled through the solution for 15 min, and a static pressure of 15 psi of carbon monoxide was maintained over the reaction mixture by means of a Fischer gas bag. The mixture was heated at 55 °C for 36 h, cooled to room temperature, and diluted with pentane (50 mL). The solution was washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na_2SO_4, and concentrated. The resulting oil was bulb-to-bulb distilled (100 °C (0.5 mm)) to give 1.2 g (87%) of product: IR (neat) 1650 cm^{-1}; ^1H NMR δ 0.08 (s, 9 H), 1.10 (s, 6 H), 1.63 (t, J = 7 Hz, 2 H), 1.72 (s, 3 H), 2.30 (m, 2 H), 6.60, 6.90 (AB, J = 19 Hz, 2 H); ^{13}C NMR δ −1.9, 16.7, 27.2, 29.7, 36.9, 40.3, 144.1, 144.5, 145.1, 146.7, 195.2; LRMS m/z 236 (M^+, 1%). Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.19; H, 10.17. Found: C, 71.07; H, 10.26.

***cis*-5,8,8-Trimethylbicyclo[3.3.0]oct-3-en-2-one (18).** To a toluene (30 mL) solution of dienone **16** (1.1 g, 4.7 mmol) was added $BF_3{\cdot}OEt_2$ (2.7 g, 19 mmol). The red solution was heated at reflux for 36 h, cooled to room temperature, and diluted with ether (100 mL). The solution was washed with sodium bicarbonate (2 × 50 mL), water (2 × 20 mL), brine (2 × 20 mL), dried over Na_2SO_4, and concentrated. The resulting brown oil was passed through a small pad of silica gel, eluting with 50% ethyl acetate/hexane. Bulb-to-bulb distillation (100 °C (0.5 mm)) gave 0.56 g (70%) of product:[17d] ^1H NMR δ 0.97 (s, 3 H), 1.06 (s, 3 H), 1.28 (s, 3 H), 1.41 (m, 2 H), 1.68 (m, 2 H), 1.82 (s, 1 H), 5.93 (d, J = 6 Hz, 1 H), 7.27 (d, J = 6 Hz, 1 H); ^{13}C NMR δ 25.5 (q, J = 126 Hz), 26.3 (q, J = 132 Hz), 30.1 (q, J = 127 Hz), 35.5 (t, J = 128 Hz), 40.1 (t, J = 126 Hz), 42.5 (s), 54.5 (s), 66.5 (d, J = 137 Hz), 132.2 (d, J = 171 Hz), 170.5 (d, J = 162 Hz), 211.1 (s); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1194.

1-(2,5,5-Trimethylcyclopenta-1,3-dien-1-yl)-3-(trimethylsilyl)prop-2-en-1-one (17). To a dichloroethane (30 mL) solution of dienone **16** (1.0 g, 4.2 mmol) was added $FeCl_3$ (0.73 g, 4.5 mmol). The resulting mixture was stirred at room temperature for 48 h, diluted with ether (50 mL), washed with brine (3 × 20 mL), and dried over Na_2SO_4. The residue was purified by chromatography on neutral alumina, eluting with 2% ethyl acetate/hexane to give 0.40 g (40%) of product: IR (neat) 1615 cm^{-1}; ^1H NMR δ 0.09 (s, 9 H), 1.22 (s, 6 H), 2.19 (s, 3 H), 6.10 (d, J = 5 Hz, 1 H), 6.48 (d, J = 5 Hz, 1 H), 6.91, 6.93 (AB, J = 19 Hz, 2 H); ^{13}C NMR δ −1.8 (q, J = 129 Hz), 17.3 (q, J = 128 Hz), 21.8 (q, J = 130 Hz), 55.4 (s), 132.3 (d, J = 165 Hz), 143.2 (d, J = 158 Hz), 143.9 (d, J = 140 Hz), 147.1 (s), 150.0 (s), 155.3 (d, J = 169 Hz), 187.1 (s); LRMS m/z 234 (M^+, 3%). Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.79; H, 9.40. Found: C, 71.68; H, 9.47.

***cis*-5,8,8-Trimethylbicyclo[3.3.0]oct-2-en-2-yl Triflate (19).** To a THF (20 mL) solution of enone **18** (0.47 g, 2.7 mmol) at −78 °C was added L-Selectride (2.7 mL, 1.0 M in THF, 2.7 mmol). The mixture was stirred at −78 °C for 30 min and solid *N*-phenyltriflimide (0.96 g, 2.7 mmol) was added. The slurry was warmed slowly (2 h) to room temperature and stirred for a further 12 h. Concentration gave a colorless oil which was chromatographed on silica gel, eluting with hexane to give 0.61 g (76%) of product: IR (neat) 1664, 1425, 1230, 1140 cm^{-1}; ^1H NMR δ 1.09 (s, 3 H), 1.13 (s, 3 H), 1.28 (s, 3 H), 1.52–2.33 (m, 7 H), 5.61 (m, 1 H); ^{13}C NMR δ 24.8 (q, J = 125 Hz), 29.6 (q, J = 126 Hz), 29.9 (q, J = 125 Hz), 39.5 (t, J = 133 Hz), 41.5 (t, J = 133 Hz), 43.0 (s), 43.5 (t, J = 169 Hz), 119.0 (q, J = 284 Hz), 116.9 (d, J = 169 Hz), 148.8 (s); LRMS m/z 298 (M^+, 0.1%). Anal. Calcd for $C_{12}H_{17}F_3O_3S$: C, 48.32; H, 5.70. Found: C, 48.12; H, 5.54.

***cis*-2-(3-(Trimethylsilyl)-1-oxoprop-2-en-1-yl)-5,8,8-trimethylbicyclo-[3.3.0]oct-2-ene (20).** To a mixture of LiCl (0.20 g, 4.7 mmol) and $Pd(PPh_3)_4$ (0.044 g, 0.038 mmol, 3 mol %) was added a THF (20 mL) solution of vinyl triflate **19** (0.39 g, 1.3 mmol) and vinyl stannane **15** (0.34 g, 1.3 mmol). Carbon monoxide was bubbled through the solution for 15 min, and a static pressure of 15 psi of carbon monoxide was maintained over the reaction vessel by means of a Fischer gas bag. The mixture was heated at 55 °C for 24 h, cooled to room temperature, and diluted with pentane (50 mL). The solution was washed with water (2 × 50 mL) and brine (3 × 50 mL), dried over Na_2SO_4, and concentrated to give 0.33 g (86%) of product. Bulb-to-bulb distillation (130 °C (0.2 mm)) gave an analytically pure sample: IR (neat) 1655, 1640, 1610 cm^{-1}; ^1H NMR δ 0.12 (s, 9 H), 0.62 (s, 6 H), 1.12 (s, 3 H), 1.30–2.70 (m, 7 H), 6.64 (m, 1 H), 6.97, 7.07 (AB, J = 19 Hz, 2 H); ^{13}C NMR δ −1.7 (q, J = 120 Hz), 25.4 (t, J = 122 Hz), 29.9 (q, J = 120 Hz), 30.3 (q, J = 120 Hz), 39.0 (t, J = 125 Hz), 42.3 (q, J = 120 Hz), 43.1 (s), 49.3 (t, J = 122 Hz), 51.0 (s), 66.9 (d, J = 131 Hz), 138.8 (d, J = 150 Hz), 142.9 (d, J = 150 Hz), 145.9 (d, J = 148 Hz), 146.8 (s), 188.4 (s); LRMS m/z 276 (M^+, 5%). Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.91; H, 10.14. Found: C, 73.80; H, 10.06.

8,11,11-Trimethylbicyclo[6.3.0.$0^{2,6}$]undec-4-en-3-one (21). To a toluene (5 mL) solution of dienone **20** (0.30 g, 1.0 mmol) was added $BF_3{\cdot}OEt_2$ (0.68 g, 4.8 mmol). The red solution was stirred at room temperature for 6 h, diluted with ether and washed with saturated sodium bicarbonate (2 × 20 mL), water (2 × 20 mL), and brine (2 × 20 mL), and dried over $MgSO_4$. Concentration gave a dark yellow oil which was filtered through a pad of silica gel, eluting with 50% ether/hexane to give 0.18 g (88%) of product:[17d] IR (neat) 1712 cm^{-1}; ^1H NMR 0.88 (s, 3 H), 0.89 (s, 3 H), 1.00 (s, 3 H), 1.00–1.90 (m, 7 H), 2.57 (d, J = 6 Hz, 1 H), 3.37 (m, 1 H), 5.98 (d, J = 6 Hz, 1 H), 7.77 (dd, J = 3,6 Hz, 1 H); ^{13}C NMR δ 25.4 (t, J = 129 Hz), 29.6 (s), 30.3 (q, J = 129 Hz), 31.1 (q, J = 129 Hz), 40.3 (q, J = 129 Hz), 41.4 (t, J = 129 Hz), 42.1 (s), 44.1 (t, J = 129 Hz), 49.5 (d, J = 139 Hz), 53.3 (d, J = 131 Hz), 65.7 (d, J = 134 Hz), 132.2 (d, J = 167 Hz), 168.7 (d, J = 164 Hz), 214.1 (s); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1527.

8,11,11-Trimethylbicyclo[6.3.0.$0^{2,6}$]undecan-3-one (22). This compound was prepared by catalytic hydrogenation of enone **21** over 5% palladium on carbon as described previously:[17b] ^1H NMR δ 0.90 (s, 3 H), 1.03 (s, 3 H), 1.07 (s, 3 H), 1.30–3.00 (m, 13 H); ^{13}C NMR δ 24.0 (t, J = 130 Hz), 26.1 (q, J = 122 Hz), 30.4 (q, J = 128 Hz), 30.9 (q, J = 120 Hz), 35.0 (t, J = 130 Hz), 40.2 (t, J = 126 Hz), 41.7 (t, J = 115 Hz), 42.0 (s), 42.4 (d, J = 137 Hz), 47.8 (t, J = 127 Hz), 53.0 (s), 57.3 (d, J = 126 Hz), 64.3 (d, J = 130 Hz), 196.7 (s); HRMS calcd for

(35) Charpentier-Morize, M.; Sansoulet, J. *Bull. Soc. Chim Fr.* **1977**, 331–332.

$C_{14}H_{22}O$ 206.1671, found 206.1661.

(±)-$\Delta^{9(12)}$-**Capnellene (12).** This compound was prepared as described previously:[17a] IR ($CDCl_3$) 2950, 2930, 2860, 1650, 1460 cm^{-1}; ^1H NMR δ 0.97 (s, 3 H), 1.05 (s, 3 H), 1.14 (s, 3 H), 1.50–2.70 (m, 13 H), 4.77 (s, 1 H), 4.88 (s, 1 H); ^{13}C NMR δ 26.1, 29.2, 31.7, 31.8, 40.6, 41.7, 42.4, 46.1, 48.1, 52.4, 53.4, 69.2, 105.0, 158.9; HRMS calcd for $C_{15}H_{24}$ 204.1882, found 204.1874.

Acknowledgment. The authors gratefully acknowledge support for this research through Grant No. CHE-8305468 from the National Science Foundation. The palladium chloride was provided under the Johnson-Matthey Metal Loan Program. High-resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8211164). The authors thank Professor L. A. Paquette for providing a copy of his manuscript prior to publication.

Registry No. 1, 77412-96-5; **3**, 92622-56-5; **6**, 32363-21-6; **8**, 92622-57-6; **9**, 92622-58-7; **11**, 92622-59-8; (±)-**12**, 81370-78-7; (±)-**13**, 92622-67-8; **14**, 91158-82-6; **16**, 92622-68-9; **17**, 92622-66-7; (±)-**18**, 85544-98-5; (±)-**19**, 92622-69-0; (±)-**20**, 92622-70-3; (±)-**21**, 81332-28-7; (±)-**22**, 81331-89-7; $Me_3SNCH{=}CH_2$, 754-06-3; (*E*)-$Me_3SnCH{=}CHCH_3$, 4964-07-2; (*Z*)-$Me_3SnCH{=}CHCH_3$, 4964-06-1; $Me_3SnCH_2CH{=}CH_2$, 762-73-2; $Me_3SnC{\equiv}CSiMe_3$, 16035-50-0; (*E*)-$Me_3SnCH{=}CHSiMe_3$, 65801-56-1; Me_4Sn, 594-27-4; Me_3SnPh, 934-56-5; *m*-$CF_3C_6H_4SnBu_3$, 53566-38-4; *p*-$CH_3OC_6H_4SnBu_3$, 70744-47-7; $Pd(PPh_3)_4$, 14221-01-3; CO, 630-08-0; 1-(6-methylcyclohex-1-en-1-yl)-prop-2-en-1-one, 92622-61-2; 1-(2-methylcyclohex-1-en-1-yl)prop-2-en-1-one, 92622-62-3; 1-(5,5-dimethylcyclohex-1-en-1-yl)prop-2-en-1-one, 92622-63-4; 1-(trimethylsilyl)-4-butylpenta-1,4-dien-3-one, 92622-64-5; 1-acetyl-4-*tert*-butylcyclohex-1-ene, 37881-09-7; 1-benzoyl-4-*tert*-butylcyclohex-1-ene, 33809-30-2; 1-(3-(trifluoromethyl)benzoyl)-4-*tert*-butylcyclohex-1-ene, 92622-65-6; 1-(4-methoxybenzoyl)-4-*tert*-butylcyclohex-1-ene, 33809-31-3; 6-methylcyclohex-1-en-1-yl triflate, 76605-82-8; 5,5-dimethylcyclohex-1-en-1-yl triflate, 91158-80-4; hex-1-en-2-yl triflate, 37555-23-0; 5,5-dimethylcyclohex-2-en-1-one, 4694-17-1; 2-methylcyclohexanone, 583-60-8; *N*-phenyltriflimide, 456-64-4; 1-(4-*tert*-butylcyclohex-1-en-1-yl)-3-(trimethylsilyl)propyn-1-one, 92622-60-1.

Origins of Micellar Diastereoselectivity

Robert A. Moss,* Yuan-Ching P. Chiang, and Yongzheng Hui

Contribution from the Wright and Rieman Laboratories, Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. *Received May 21, 1984*

Abstract: Thiol-functionalized surfactant micelles (*n*-$C_{12}H_{25}N^+Me_2CH_2CH_2SH,Cl^-$) were used to cleave Z-Trp-Pro *p*-nitrophenyl dipeptide esters. Marked kinetic diastereoselectivity was observed in these reactions. For example at pH 8 and concentrations (~6–7) × 10^{-3} M, the micellar thiol cleaved the LL substrate 5–6 times more rapidly than its DL diastereomer. This kinetic diastereoselectivity was shown to develop at surfactant concentrations ~5 × 10^{-3} M, considerably above the cmc (~1 × 10^{-3} M), i.e., at a second "critical concentration". Dynamic light-scattering measurements showed that micelles which had reacted with the LL (but not the DL) substrate underwent a marked increase in apparent hydrodynamic diameter (from ~15 to 26 nm) near this second critical concentration. Similar phenomena could be induced upon addition of 2 × 10^{-5} M LL dipeptide surfactant *reaction product* to the thiol micelles. Micelles of *n*-$C_{12}H_{25}N^+Me_2CH_2CH_2OH,Cl^-$ or *n*-$C_{12}H_{25}N^+Me_3,Cl^-$ were unresponsive to such additions (light scattering). The results are discussed in terms of molecular and supramolecular interactions between surfactant and solubilizate molecules.

In order to expand the analogy between micelles and enzymes, many investigators sought to develop micellar reagents that would react with substrates rapidly and stereoselectively.[1] Following the original work of Bunton[2] and Brown,[3] most studies were devoted to enantioselective reactions between chiral nucleophiles and chiral substrates, usually activated amino acid esters.[4] Frequently, the nucleophiles were imidazole moieties, derived from hydrophobic histidine derivatives and solubilized in micellar surfactant carriers such as cetyltrimethylammonium (CTA) halides.[4a,c,e-h] Occasionally, fully functionalized histidine surfactant micelles,[3,5] micellar histidine dipeptide nucleophiles,[6] or other amino acid derived nucleophiles[7] were studied. Most recently, histidine and histidine dipeptide reagents were tested against activated esters of phenylalanine in vesicular or membrane aggregates.[8]

Impressive enantioselectivities have sometimes been observed. For example, *N*-Z-L-Leu-L-His cleaved L-methoxycarbonylphenylalanine *p*-nitrophenyl (PNP) ester 12.2 times more rapidly than its D enantiomer in micellar CTABr,[6b] whereas *N*-Z-L-Phe-L-His displayed an entioselectivity of 30 toward the *N*-decanoylphenylalanine PNP esters in vesicular (*n*-$C_{12}H_{25})_2N^+Me_2,Br^-$.[8a]

However, little is known about either the molecular level origins of these observed enantioselectivities or of the ways in which the micelles or vesicles elicit them. Ono et al. generalized that micellar stereoselectivity requires proximity of the nucleophile's chiral center and the active site, strong molecular interaction between the nucleophile and the substrate, and a reaction locus in the "hydrophobic field" of the micelle.[6a] Brown and Bunton offered a specific molecular model for an entioselective cleavage of *N*-acetylphenylalanine PNP by a micellar histidine reagent.[3,5] However, these examples are exceptions to the general lack of

(1) For a recent review, see: Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982; pp 309–322.
(2) Bunton, C. A.; Robinson, L.; Stam, M. F. *Tetrahedron Lett.* **1971**, 121.
(3) Brown, J. M.; Bunton, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 969.
(4) (a) Ihara, Y.; Hosako, R.; Nango, M.; Kuroki, N. *J. Chem. Soc., Perkin Trans. 2* **1983**, 5. (b) Ogino, K.; Tomita, I.; Madriya, K.; Tagaki, W. *Chem. Lett.* **1982**, 1875. (c) Ihara, Y.; Hosako, R.; Nango, M.; Kruoki, N. *J. Chem. Soc., Chem. Commun.* **1981**, 393. (d) Ihara, Y.; Nango, M.; Kuroki, N. *J. Org. Chem.* **1980**, *45*, 5011. (e) Ihara, Y. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1483. (f) Yamada, K.; Shoshenji, H.; Ihara, H.; Otsubo, Y. *Tetrahedron Lett.* **1979**, 2529. (g) Yamada, K.; Shosenji, H.; Ihara, H. *Chem. Lett.* **1979**, 491. (h) Ihara, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 984.
(5) Brown, J. M.; Elliott, R. L.; Griggs, C. G.; Helmchen, G.; Nill, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 890.
(6) (a) Ono, S.; Shosenji, H.; Yamada, K. *Tetrahedron Lett.* **1981**, *22*, 2391. (b) Ihara, Y.; Kunikiyo, N.; Kunimasa, T.; Nango, M.; Kuroki, N. *Chem. Lett.* **1981**, 667. (c) Ohkubo, K.; Sugihara, K.; Yoshinaga, K.; Ueoka, R. *J. Chem. Soc., Chem. Commun.* **1980**, 637.
(7) Ihara, H.; Ono, S.; Shosenji, H.; Yamada, K. *J. Org. Chem.* **1980**, *45*, 1623.
(8) (a) Ohkubo, K.; Matsumoto, N.; Ohta, H. *J. Chem. Soc., Chem. Commun.* **1982**, 739. (b) Murakami, Y.; Nakano, A.; Yoshimatsu, A.; Fukuya, K. *J. Am. Chem. Soc.* **1981**, *103*, 728. (c) Ueoka, R.; Matsumoto, Y.; Ninomiya, Y.; Nakagawa, Y.; Inoue, K.; Ohkubo, K. *Chem. Lett.* **1981**, 785.

0002-7863/84/1506-7506$01.50/0