from the diaminoaralkyl residue at position 4 and chirality of residue 5.

We have prepared many 14-membered cyclic analogues of the parent Tyr-c[D-A$_2$bu-Gly-Phe-(L and D)-Leu].[19-21] While most of these molecules exhibit only trans amide structures, we have shown in this communication that three of the eight peptides shown in Figure 1 exhibit cis amide containing isomers. In addition, we demonstrate, with the use of proton NMR, that it is possible to assign the specific bonds involved in the cis structures. The full understanding of the origin of these structural effects will require much more research into the energies and steric constraints of such molecules.[22,23]

Acknowledgment. We would like to thank Dr. Peter Schiller of the Clinical Research Institute of Montreal for many helpful discussions in the design of the molecules examined here. We acknowledge the support of the National Institutes of Health (DK 15410). One of us (E.R.F.) acknowledges a research fellowship from Ciba-Geigy Ltd.

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Homogeneous Sonochemistry in Radical Chain Reactions. Sonochemical Hydrostannation and Tin Hydride Reduction

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Irradiation of homogeneous liquids with high-intensity ultrasound[1] produces characteristic thermal nonequilibrium[2] conditions by creating localized superheated sonochemical cavities, wherein a maximum temperature over 2000 K can be readily realized. In contrast to its heterogeneous counterpart,[3] homogeneous sonochemistry[4] has remained virtually unexplored as a means for effecting chemical reactions[5]—a consequence of its poor efficiency due to the very small size and the exceedingly short lifetime (<2 μs) of the cavities. We have investigated the possibilities of utilizing homogeneous sonochemistry for the controlled initiation of radical chain reactions: radicals generated in the short-lived "hot spots"[3] undergo chain reactions in the bulk medium in such a way that the low concentration of the initial radical species may be compensated by the length of the chain. We report here the first synthetic application of this concept by describing hydrostannation (Scheme I) and tin hydride reduction initiated by sonochemical thermolysis of R$_3$SnH.[6]

Scheme I

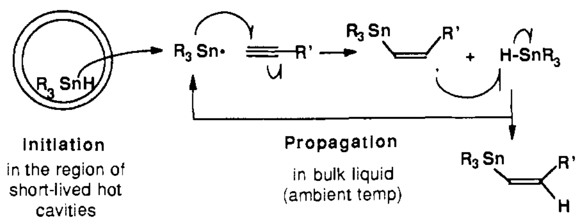
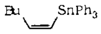
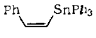
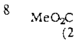
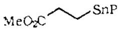
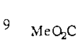
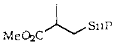
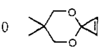
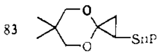


Table I. Sonochemical Hydrostannylation with Ph$_3$SnH[a]

entry	substrate (equiv)	solv	sonochemical time (h)	sonochemical temp (°C)	%yield[c] (%cis)[d]	major product	control temp (°C)	control %yield[e]	acceln[b]
1	n-BuC≡CH (5)	neat	3	7	95 (92)		0	1	>1 x 10^2
2		toluene[f]	2	7	86 (91)		7	3	1 x 10^2
3		THF	0.25	7	72(93)				
4	PhC≡CH (3)	toluene	4	-8	50 (≥92)		7	13[c]	-10
5		THF[f]	1.5	-55	61 (87)				
6	Me$_3$SiC≡CH (3)	toluene	5	-8	78 (8)		0	0	>6 x 10^2
7	Me$_3$SiC≡CH	THF[f]	8	-55	39[g] (17)		-70	<1	1 x 10^2
8	 (2)	toluene[f]	2.5	6	94		8	<2	1 x 10^2
9	 (2)	toluene	5	7	63		0	<1	1 x 10^2
10	 (0.5)	toluene	5	7	83		0	6	>1 x 10

[a] The reaction was carried out in a 0.5 M solution except in entry 2 where a 0.25 M solution was used. Temperatures refer to those measured with a thermocouple immersed in the reaction mixture. In low-yield runs, high levels of material balance were observed. [b] Approximation rate acceleration assuming first-order kinetics. [c] Isolated yield except in entries 2 and 3 where GLC yields are reported. [d] Determined by GLC except in entries 4 and 5 where the ratio was determined by ^{13}C NMR. [e] Determined by NMR or GLC. [f] With AIBN (10 mol %). [g] Ca. 10% of Ph$_3$SnH was recovered.

The thermally initiated radical hydrostannation of alkynes represents an important synthetic entry to vinylstannanes.[7] The reaction is normally carried out by heating a mixture of an organotin hydride and an alkyne at 50–100 °C in the presence of an initiator.[8] High-intensity ultrasound now has been found to smoothly initiate the reaction even below 0 °C through the selective thermolysis of the tin hydride reagent in the region of the short-lived hot spots. Thus, sonochemical irradiation of a mixture of Ph$_3$SnH (0.44 g, 1.25 mmol) and 1-hexyne (0.72 mL, 6.25 mmol) under argon for 3 h (0 °C bath; 7 °C internal temperature) gave the desired vinylstannane in 95% yield (0.51 g) with 92% cis selectivity (Table I, entry 1).[9] Without irradiation, <1%

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(1) Cf.: Suslick, K. S.; Hammerton, D. A.; Cline, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5641.

(2) On the growing interests in nonequilibrium processes, see: Freeman, G. R., Ed *Kinetics of Nonhomogeneous Processes*; Wiley: New York, 1987.

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(4) (a) Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73. Suslick, K. S. *Mod. Synth. Methods* **1986**, *4*, 1. (b) Lorimer, J. P.; Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 239.

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(6) Cf. ESR detection of radical species upon thermolysis of R$_4$Sn and ditins: Rehorek, D.; Janzen, E. G. *J. Organomet. Chem.* **1984**, *268*, 135.

(7) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47. van der Kerk, G. J. M.; Noltes, J. G. *Ibid.* **1959**, *9*, 106. Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285. Leusink, A. J.; Budding, H. A.; Drenth, W.; *Ibid.* **1967**, *9*, 295.

(8) A recent method for chemical initiation: Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547.

(9) (a) The reactions were carried out under argon with an immersion-type ultrasound generator (20 kHz, 200 W used at $^1/_{10}$ to $^4/_{10}$ of the full power without grossly affecting the efficiency, with a tapered titanium horn) using a glass reactor installed with a thermocouple similar to the one described by Suslick.[4a] A cup horn apparatus (fitted to the above generator[3b,4b]) and a common "ultrasound cleaner" (27 kHz, 150 W) gave qualitatively the same results.

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Table II. Sonochemical Tin Hydride Reduction[a]

entry	halide	tin hydride (equiv)	solv	time, h	sonochemical temp, °C	sonochemical % yield[b]	control temp, °C	control % yield[b]
1	1-iododecane	Bu_3SnH (1.2)	toluene	1	6	90	0	5
2	1-iododecane	Ph_3SnH (1.1)	toluene	2	4	65	0	15
3	1-iododecane	Ph_3SnH (2)	THF	2	−64	88		
4	5-bromodecane	Bu_3SnH (1.2)	toluene	11	14	73	0	8
5	1-bromodecane	Bu_3SnH (1.2)	toluene	16	14	66		
6	*p*-iodoanisole	Bu_3SnH (1.2)	toluene	12	40	14	40	1

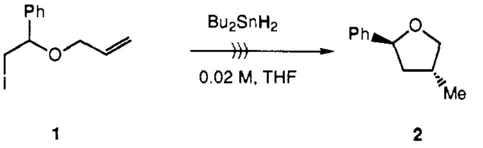
[a] The reaction was carried out in a 0.2 M solution for the halide except in entry 3 (0.5 M). In low-yield runs, high levels of material balance were observed. [b] Determined by GLC yield.

conversion occurred under otherwise identical conditions. Large rate accelerations were also observed in toluene and THF solutions (entries 2 and 3). The sonochemical hydrostannation of phenylacetylene (entries 4 and 5) and (trimethylsilyl)acetylene[10] (entry 6 and 7) also proceeded very smoothly at low temperatures. *The reactions carried out using irradiation proceed 100–600 times faster than those without.* It is particularly noteworthy that these reactions take place even at −50 °C (entries 5 and 7).[11]

The stereochemistry of the hydrostannation reactions (1-hexyne, 0 °C, THF) serves to illustrate the difference between the sonochemical methods and photochemical initiation. Thus, while the former showed very high kinetic cis selectivity (entry 3), the latter (400-W high-pressure Hg lamp, Pyrex filter) produced a ~1:1 mixture of cis and trans isomers (95%) owing to very rapid photochemical equilibration of the product.

Sonochemical hydrostannation of electron-deficient olefins also proceeded smoothly.[7,12] Thus, addition of Ph_3SnH to unsaturated esters proceeded in good yield at 7–8 °C (Table I, entries 8 and 9). Hydrostannation of a thermally unstable cyclopropenone ketal[13] (entry 10) was also accomplished very cleanly.[14]

Ultrasound initiates tin hydride reduction of organic halide[15] at low ambient temperature. For instance, ultrasound irradiation of a mixture of Bu_3SnH and 1-iodododecane in toluene at 0–6 °C (internal) for 1 h resulted in rapid and quantitative formation of decane (Table II, entry 1). Various halides could be reduced similarly at temperatures as low as −60 °C (entry 3). A variety of tin hydrides—Bu_3SnH, Ph_3SnH, and Bu_2SnH_2—can serve as a hydride source, and 10- to 50-fold rate acceleration was generally observed. The low-temperature sonolysis is particularly useful for enhancing the stereoselectivity of radical cyclizations—an important issue in these versatile synthetic reactions.[16] For instance, the sonochemical cyclizations of **1** (eq 1) at 6 °C and at −55 °C gave the tetrahydrofuran **2** in 60–70% yield with trans/cis ratios of 87:13 and 94:6, respectively, while the cyclization under thermal conditions (AIBN, 70 °C, 1 h) gave a 79:21 mixture (77% yield).



(1)

trans:cis = 87:13 (6 °C, 2 h)
94:6 (-55 °C, 13 h)

The high levels of the observed product selectivities indicate that the dominant fraction of the reaction product has been formed in the cold bulk liquid phase and not in the hot cavities (cf. Scheme I). In contrast to the normal thermal conditions, wherein both the initiation and the propagation steps necessarily take place under an identical thermal environment, the sonochemical conditions permit these steps to be carried out under very different thermal environments.[17]

Acknowledgment. We thank Professor Yoshihiko Hatano for helpful discussions on the physicochemical aspects of sonochemistry.

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(10) (Trimethylsilyl)acetylene is particularly liable to the formation of a trans adduct (cf. ref 6).

(11) The presence of AIBN, which is not essential in any of the reactions reported herein, was found sometimes beneficial in reactions at low temperatures.

(12) van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 356.

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(14) Cyclopropenone ketals are good radical acceptors: unpublished results by S. Yamago and S. Ejiri.

(15) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth & Co. Ltd.: London, 1987. Neumann, W. P. *Synthesis* **1987**, 665.

(16) Interest in this field has been renewed in the past several years: Stork, G. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon Press: Oxford, England, 1983. Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564. For pertinent recent references, see: RajanBabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759. Reviews: Curran, D. P. *Synthesis* **1988**, 417, 489. Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541.

(17) The cavity temperature can be controlled by the vapor pressure of the solvent: Suslick, K. S.; Gawienowski, J. J.; Schubert, P. F.; Wang, H. H. *Ultrasonics* **1984**, *22*, 33.

Synthesis and Metal-Dependent Condensation Reactions of $M(CO)_4(\eta^2\text{-}HC{\equiv}CH)$ (M = Ru, Os): Formation of Diosmacyclobutene and Heterodimetallacyclopentenones

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It is well documented that the reaction of iron group carbonyls with alkynes gives a myriad of organometallic complexes and a large variety of carbonyl-containing cyclic organic compounds.[1] Yet the isolation of the simple ternary acetylene–tetracarbonyl species $M(CO)_4(\eta^2\text{-}HC{\equiv}CH)$ (**1**), a most plausible intermediate in the reaction with acetylene, has so far remained elusive.[2,3] Here we report the successful synthesis of such molecules for M = Ru (**1a**) and Os (**1b**) and communicate some early results that reveal unexpected reactivity of these coordinatively saturated species.

Photolysis of the respective pentacarbonyls in hydrocarbon solution at low temperature, while purging with acetylene, gives the corresponding acetylene–tetracarbonyl compounds (eq 1).

$$M(CO)_5 \xrightarrow[\text{pentane, }-60\,°\text{C}]{h\nu,\ \lambda > 370\text{ nm}} M(CO)_4(\eta^2\text{-}HC{\equiv}CH) \qquad (1)$$

M = Ru, **1a**; M = Os, **1b**

[†] NSERC Undergraduate Research Awardee.

[‡] Feodor-Lynen Fellow.

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(2) A limited number of ternary alkyne–tetracarbonyl species are known. (a) Pannell, K. M.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251 ($M(CO)_4(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3$, M = Fe). (b) Ball, R.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 1918 ($M(CO)_4(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$, M = Ru, Os). (c) Gagné, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561 ($M(CO)_4(\eta^2\text{-}CF_3C{\equiv}CCF_3)$, M = Ru, Os).

(3) Recently, $Fe(CO)_2(PR_3)_2(\eta^2\text{-}HC{\equiv}CH)$ (R = Et, OMe) type compounds have been reported by Berke et al. (a) Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1988**, *121*, 471. (b) Birk, R.; Grössmann, U.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1988**, *345*, 321.

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