H), 2.71 (dd, J = 7, 14 Hz, 1 H), 2.84 (dd, J = 6, 14 Hz, 1 H), 2.92 (dd, J = 8, 14 Hz, 1 H), 3.06 (dd, J = 5, 14 Hz, 1 H), 3.88–3.98 (m, 1 H), 4.60 (d, J = 8 Hz, 1 H, NH), 5.03 (s, 2 H), 6.91 (d, J = 8 Hz, 2 H), 7.10 (d, J = 8 Hz, 2 H), 7.29–7.44 (m, 5 H). Anal. Calcd for $C_{23}H_{29}NO_4S$: C, 66.48; H, 7.03; N, 3.37. Found: C, 66.67; H, 7.18; N, 3.32.

(*S*)-3-(Benzyloxy)-2-[(*tert*-butoxycarbonyl)amino]propyl ethanethioate (3e): 95%; oily substance; $[\alpha]_D$ +17.9° (c 1, $CHCl_3$); ^1H NMR δ ($CDCl_3$) 1.43 (s, 9 H), 2.33 (s, 3 H), 3.11 (dd, J = 7, 13.5 Hz, 1 H), 3.17 (dd, J = 6, 13.5 Hz, 1 H), 3.47 (dd, J = 5, 9 Hz, 1 H), 3.56 (dd, J = 4, 9 Hz, 1 H), 3.86–3.96 (m, 1 H), 4.50 and 4.52 (ABq, J = 12 Hz, 2 H), 4.92 (d, J = 7.5 Hz, 1 H, NH), 7.26–7.38 (m, 5 H); ^{13}C NMR δ ($CDCl_3$) 28.4 (q), 30.5 (q), 31.0 (t), 50.3 (d), 70.9 (t), 73.3 (t), 79.5 (s), 127.7 (d), 128.4 (d), 137.9 (s), 155.4 (s), 195.6 (s); MS (SIMS) m/z 340 $(M + H)^+$.

(2*S*,3*R*)-3-(Benzyloxy)-2-[(*tert*-butoxycarbonyl)amino]-butyl ethanethioate (3f): 97%; oily substance; $[\alpha]_D$ +11.0° (c 1, $CHCl_3$); ^1H NMR δ ($CDCl_3$) 1.21 (d, J = 6 Hz, 3 H), 1.43 (s, 9 H), 2.33 (s, 3 H), 3.06 (dd, J = 8, 13 Hz, 1 H), 3.11 (dd, J = 6, 13 Hz, 1 H), 3.65–3.75 (m, 2 H), 4.40 and 4.60 (ABq, J = 11.5 Hz, 2 H), 4.87 (d, J = 9.5 Hz, 1 H, NH), 7.27–7.39 (m, 5 H); ^{13}C NMR δ ($CDCl_3$) 16.2 (q), 28.4 (q), 30.5 (q), 31.6 (t), 54.6 (d), 71.0 (t), 74.7 (d), 79.3 (s), 127.8 (d), 127.9 (d), 128.4 (d), 138.2 (s), 155.9 (s), 195.5 (s); MS (SIMS) m/z 354 $(M + H)^+$.

Preparation of 3c via (*S*)-2-[(Benzyloxycarbonyl)-amino]-3-phenylpropyl Methanesulfonate (4c): To an ice-cooled solution of **2c** (50 mmol) and Et_3N (55 mmol) in CH_2Cl_2 (200 mL) was added a solution of MsCl (52 mmol) in CH_2Cl_2 (50 mL) dropwise over 30 min. The mixture was evaporated in vacuo, and the residue was treated with EtOAc and H_2O. The separated organic layer was washed with 5% aqueous $NaHCO_3$ and brine. After drying over Na_2SO_4, the solvent was evaporated in vacuo to give the crystalline methanesulfonate **4c** in 97% yield: mp 109–110 °C; $[\alpha]_D$ −21.1° (c 1, $CHCl_3$); ^1H NMR δ ($CDCl_3$) 2.84–2.97 (m, 2 H), 2.95 (s, 3 H), 4.13 (dd, J = 4, 10 Hz, 1 H), 4.15–4.22 (m, 1 H), 4.26 (dd, J = 3.5, 10 Hz, 1 H), 5.00 (d, J = 9 Hz, 1 H), 5.07 and 5.09 (ABq, J = 12.5 Hz, 2 H), 7.18–7.38 (m, 10 H). Anal. Calcd for $C_{18}H_{21}NO_5S$: C, 59.49; H, 5.82; N, 3.85. Found: C, 59.17; H, 5.83; N, 3.69.

(*S*)-2-[(Benzyloxycarbonyl)amino]-3-phenylpropyl Ethanethioate (3c). A solution of **4c** (30 mmol) and KSAc (33 mmol) in DMF (150 mL) was stirred at room temperature for 20 h. The reaction mixture was poured into water and extracted with EtOAc. The extract was washed with H_2O, 5% aqueous $NaHCO_3$, and brine. After drying over Na_2SO_4, the solvent was evaporated in vacuo to give a crystalline solid **3c** (96%), mp 89–90 °C, $[\alpha]_D$ −5.2° (c 1, $CHCl_3$).

General Preparation of 2-Substituted Taurines 5a–f. To a performic acid solution, prepared by mixing and stirring 30% H_2O_2 (9 mL) and 98% HCOOH (90 mL) at room temperature for 1 h and cooled in an ice bath, were added acetylthio derivatives **3a–f** (15 mmol) in 98% HCOOH (20 mL) dropwise, keeping the temperature at 0 °C. After the mixture was stirred at 0 °C for additional 2 h and at room temperature for 20 h, 10% Pd–C (0.5 g) was added in order to decompose the remaining peroxide. After the mixture was stirred for a further 20 h under a hydrogen atmosphere at room temperature, the catalyst was removed by suction and the filtrate was evaporated in vacuo. The residue was crystallized from aqueous EtOH to give the pure 2-substituted taurines **5a–f**.

(*S*)-2-Amino-3-methylbutanesulfonic acid (5a): mp >330 °C; $[\alpha]_D$ +29.8° (c 1, H_2O); for $C_5H_{13}NO_3S$ [lit.[4] mp 325–326 °C dec; $[\alpha]_D$ +29.8° (c 1, H_2O); for $C_5H_{13}NO_3S$].

(2*S*,3*S*)-2-Amino-3-methylpentanesulfonic acid (5b): mp 292–293 °C; $[\alpha]_D$ +24.8° (c 1, H_2O); ^1H NMR δ (0.2 N NaOD) 0.86 (d, J = 7.5 Hz, 3 H), 0.89 (t, J = 7.5 Hz, 3 H), 1.12–1.24 (m, 1 H), 1.31–1.42 (m, 1 H), 1.46–1.57 (m, 1 H), 2.75 (dd, J = 10, 15 Hz, 1 H), 3.03 (dd, J = 2, 15 Hz, 1 H), 3.15–3.20 (m, 1 H). Anal. Calcd for $C_6H_{15}NO_3S$: C, 39.76; H, 8.34; N, 7.73. Found: C, 39.81; H, 8.52; N, 7.62.

(*S*)-2-Amino-3-phenylpropanesulfonic acid (5c): mp >330 °C; $[\alpha]_D$ −3.6° (c 1, H_2O); for $C_9H_{13}NO_3S$ [lit.[4] mp >330 °C dec; $[\alpha]_D$ −3.5° (c 1, H_2O); for $C_9H_{13}NO_3S$].

(*S*)-2-Amino-3-(4-hydroxyphenyl)propanesulfonic acid (5d): mp >330 °C; $[\alpha]_D$ −4.7° (c 1, H_2O); ^1H NMR δ (0.2 N NaOD) 2.50 (dd, J = 8, 14 Hz, 1 H), 2.69 (dd, J = 5.5, 14 Hz, 1 H), 2.83 (dd, J = 9, 14 Hz, 1 H), 3.06 (dd, J = 3, 14 Hz, 1 H), 3.38–3.45 (m, 1 H), 6.56–7.03 (m, 4 H). Anal. Calcd for $C_9H_{13}NO_4S$: C, 46.75; H, 5.76; N, 6.06. Found: C, 46.68; H, 5.86; N, 6.16.

(*S*)-2-Amino-3-hydroxypropanesulfonic acid (5e; D-cysteinolic acid): mp 279–281 °C; $[\alpha]_D$ +7.3° (c 1, H_2O); for $C_3H_9NO_4S$ [lit.[4] mp 279–281 °C; $[\alpha]_D$ +7.5° (c 1, H_2O); $C_3H_9NO_4S$].

(2*S*,3*R*)-2-Amino-3-hydroxybutanesulfonic acid (5f): mp 220–222 °C; $[\alpha]_D$ +15.5° (c 1, H_2O); ^1H NMR δ (0.2 N NaOD) 1.17 (d, J = 6.5 Hz, 3 H), 2.83 (dd, J = 9, 14 Hz, 1 H), 3.10 (dd, J = 2.5, 14 Hz, 1 H), 3.11–3.17 (m, 1 H), 3.77–3.84 (m, 1 H). Anal. Calcd for $C_4H_{11}NO_4S$: C, 28.40; H, 6.55; N, 8.28. Found: C, 28.10; H, 6.35; N, 7.95.

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Registry No. **1a**, 24210-19-3; **1b**, 42807-91-0; **1c**, 35909-92-3; **1d**, 27513-44-6; **1e**, 80963-10-6; **1f**, 137719-70-1; **2a**, 6216-65-5; **2b**, 6216-62-2; **2c**, 6372-14-1; **2d**, 66605-58-1; **2e**, 79069-15-1; **2f**, 79069-63-9; **3a**, 137719-71-2; **3b**, 137719-72-3; **3c**, 82001-62-5; **3d**, 137719-73-4; **3e**, 137719-74-5; **3f**, 137719-75-6; **4c**, 135731-20-3; **5a**, 126301-31-3; **5b**, 137719-76-7; **5c**, 126301-32-4; **5d**, 137719-77-8; **5e**, 16421-58-2; **5f**, 137719-78-9; performic acid, 107-32-4.

Supplementary Material Available: ^{13}C NMR spectra for compounds **3e** and **3f** (2 pages). Ordering information is given on any current masthead page.

An Improved Procedure for the Synthesis of Macrocyclic Poly(thialactones). The Dramatic Effect of Reactant Mixing[1]

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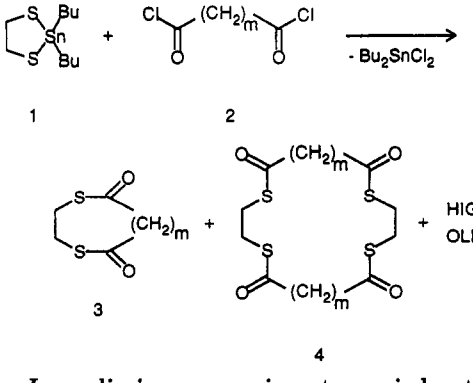
In the course of our studies aimed at modeling the behavior of systems where simultaneous macrocyclization and polymerization takes place,[2] our attention was attracted by the reaction of the stannadithiane **1** with diacyl chlorides **2** as an example of a kinetically controlled[3] double ring-closure reaction of the type A---A + B---B.



In preliminary experiments carried out with pimeloyl chloride (**2**, m = 5) and azelaoyl chloride (**2**, m = 7), the effect of the reactant mixing technique was investigated by performing the reaction batchwise, by simultaneous

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Table I. Reaction of the Stannadithiane 1 with Diacyl Chlorides 2. Isolated % Yields of Monomeric Dithialactones 3 and Dimeric Tetrathialactones 4

	$m = 5$		$m = 7$	
mixing technique[a]	3	4	3	4
BW[b]	12	25	30	12
1C-DP (A)	10	12	16	9
1C-DP (B)	58[c]	27[c]	82	15
2C-DP	67	13	93	5

[a] For an explanation of symbols see text. In all cases the overall amounts of reactants were 0.05 mol/L of solvent. [b] See ref 8. [c] To be compared with a 9.2 and 22% yield of 3 and 4, respectively, reported in the literature.[3]

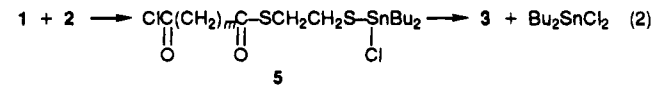
addition of both components into the reaction medium and by using a combination of the slow addition of one component to the other. The procedure variation had such a dramatic influence on yields of monomeric dithialactones 3 that we were prompted to communicate our observations.

Isolated yields of monomeric 3 and dimeric 4 poly(thialactones) are given in Table I as a function of the mixing technique. All experiments were carried out under strictly comparable conditions in that the total reaction time was 1.5 h and the number of moles of reactants reacted per unit volume was the same in all cases. In the batchwise experiment (BW) 2.5 mmol of dichloride 2 in 5 mL of $CHCl_3$ were added all at once to a boiling solution of 2.5 mmol of the stannadithiane 1 in 45 mL of the same solvent, so that the initial concentration of both reactants was 0.05 M. In the two-component influx procedure, which according to Rossa and Vogtle's proposal[4] is a 2C-DP (two-component dilution principle) reaction, two solutions of 2.5 mmol of each reactant in 10 mL of $CHCl_3$ were added simultaneously to 30 mL of boiling $CHCl_3$ over 1 h by means of two identical syringes operated by a syringe pump. In variant A of the 1C-DP procedure, 2.5 mmol of 1 in 10 mL of $CHCl_3$ were added over 1 h by syringe to a boiling solution of 2.5 mmol of 2 in 40 mL of $CHCl_3$, whereas in variant B mixing of reactants was carried out in the reverse order. All influx experiments were completed by refluxing the reaction mixtures for an additional 30 min to ensure complete reaction.

Table I shows that yields of the 13-membered dithialactone 3 ($m = 7$) are consistently higher than those of the 11-membered homologue 3 ($m = 5$). This is easily understood on the basis of the well-known concept[5] that medium-sized rings (8- to 11-membered) are less easily formed than the less strained large rings. It is apparent that a substantial improvement has been achieved with respect to a previous report[3] (see footnote c to Table I) where a mixing technique corresponding to variant B of our 1C-DP technique was employed.

The dramatic increase in yields of monomeric lactones of the 2C-DP over the BW technique is in accordance with the dilution principle.[4,5] What is less immediately understood is the unprecedented difference between the two variants of the 1C-DP technique. Whereas variant B afforded results which are almost as good as those obtained with the 2C-DP technique, variant A was even less effective than the BW technique.

To gain an insight into the origin of the effect, kinetic considerations are appropriate. The reaction mechanism is unknown, but a resonable sequence of steps for the conversion of reactants into monomeric dithialactone is that given in eq 2. The bifunctional species 5 is the key



intermediate which can undergo first-order cyclization to 3 (eq 3) or second-order intermolecular reactions with both 1 and 2, as well as with the –COCl and $-SSn(Cl)Bu_2$ end groups of the various oligomeric species which accumulate in the reaction medium in the time course of the reaction (eq 4).[6] It is the competition between these intra- and intermolecular processes which determines the outcome of the macrocyclization reaction (eq 5).

$$v_{intra} = k_{intra}[5] \quad (3)$$

$$v_{inter} = 2k_{inter}[1][5] + 2k'_{inter}[2][5] + k'_{inter}[5]([-COCl] + [-SSn(Cl)Bu_2]) \quad (4)$$

$$\frac{v_{intra}}{v_{inter}} = k_{intra}/[2k_{inter}[1] + 2k'_{inter}[2] + k'_{inter}([-COCl] + [-SSn(Cl)Bu_2])] \quad (5)$$

In order to obtain some evidence for the existence of 5, as well as some information on the relative values of k_{inter} and k'_{inter}, the reaction between 1 and the monofunctional species AcCl (eq 6) was investigated by ^1H NMR spec-

$$1 \xrightarrow[2k_{inter}]{AcCl} \underset{6}{[AcSCH_2CH_2SSn(Cl)Bu_2]} \xrightarrow[k'_{inter}]{AcCl} \underset{7}{AcSCH_2CH_2SAc} + Bu_2SnCl_2 \quad (6)$$

troscopy. Reaction of 1 mol equiv of 1 with 1 mol equiv of AcCl afforded a mixture of 0.5 mol equiv of the diester 7 and of Bu_2SnCl_2, plus 0.5 mol equiv of unreacted 1. No trace was found of the unsymmetrical intermediate 6. Other experiments carried out with different proportions of reactants in all cases confirmed that a clean reaction of 1:2 stoichiometry took place. This finding demonstrates that the reactivity of 6 (or any other intermediate) is much greater than that of 1, namely, $k'_{inter} \gg k_{inter}$. Thus, 1 is a synthetic equivalent of an ethanedithiol dianion $^-SCH_2CH_2S^-$, where the nucleophilicity of the first reacting thiolate group is much lower than that of the second. This is an important result, which provides an explanation for the peculiar effect found in the 1C-DP procedures. When applied to the two variants of the 1C-DP technique, eq 5 reduces to the simpler forms of eqs 7 and 8. Equation 7,

$$\left(\frac{v_{intra}}{v_{inter}}\right)_A = \frac{k_{intra}}{2k'_{inter}[2] + k'_{inter}([-COCl] + [-SSn(Cl)Bu_2])} \quad (7)$$

$$\left(\frac{v_{intra}}{v_{inter}}\right)_B \approx \frac{k_{intra}}{2k_{inter}[1] + k'_{inter}([-COCl] + [-SSn(Cl)Bu_2])} \quad (8)$$

which applies to variant A, immediately follows from the

(1) Group 14 Organometallic Reagents. 12. Part 11: Roelens, S.; Dalla Cort, A.; Mandolini, L. *J. Org. Chem.*, in press.
(2) Ercolani, G.; Mandolini, L.; Mencarelli, P. *J. Chem. Soc., Perkin. Trans. 2* **1990**, 747.
(3) Shanzer, A.; Libman, J. *Synthesis* **1984**, 140.
(4) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 1.
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(6) In eqs 3 and 4 k_{inter} is the rate constant for reaction of a –COCl end group with 1, whereas k'_{inter} is the corresponding quantity for reaction of a –COCl end group with a $-SSn(Cl)Bu_2$ end group. It should be noted that (i) k_{inter} and k'_{inter} are statistically corrected, (ii) $[-SSn(Cl)Bu_2]$ represents the concentration of end groups rather than of actual species, (iii) [–COCl] represents the concentration of end groups except those of the diacyl chloride reactant 2, and (iv) the assumption is made that the reactivity of end groups is independent of chain length.

fact that $k_{inter}[1] \ll k'_{inter}[2]$. In variant B, 2 is slowly added to a solution of 1. It is clear that not only in the early stages of the reaction, but also during a large part of its time course, the product $k'_{inter}[2]$ is small compared to the product $k_{inter}[1]$, in spite of the fact that k'_{inter} is larger than k_{inter}. Hence, the approximate eq 8 applies to variant B. Combination of eq 7 with eq 8 gives eq 9, where the nu-

$$\frac{(v_{intra}/v_{inter})_B}{(v_{intra}/v_{inter})_A} \approx \frac{2k'_{inter}[2] + k'_{inter}([\text{-COCl}] + [\text{-SSn(Cl)Bu}_2])}{2k_{inter}[1] + k'_{inter}([\text{-COCl}] + [\text{-SSn(Cl)Bu}_2])} \quad (9)$$

merator of the fraction in the right-hand side is much greater than the denominator because $k'_{inter} \gg k_{inter}$. This shows that the advantage of variant B over variant A, as measured by the corresponding (v_{intra}/v_{inter}) ratios, is a consequence of the reactivity increase of the tin thiolate intermediate 5 relative to the stannadithiane reactant 1. In other words, the advantage of variant B is that in this case macrolactonization to the monomeric dithialactones 3 competes with a slower intermolecular reaction.

Concluding Remarks

It was found that macrocyclic dithialactones can be prepared in remarkably high yields by reaction of 1 with 2 provided that reactant mixing is carried out according to the 2C-DP technique. It should be stressed that highly efficient macrocyclization can be achieved by a proper adjustment of experimental conditions, even in the absence of yield-enhancing factors, such as template effects. Reaction of 1 with 2 is actually a double ring-closure reaction of the type A---A′ + B---B, where A′ is a latent functionality that is more reactive than the parent functionality A. This has important consequences on yields whenever reactant mixing is carried out according to a 1C-DP technique, which is widely used in macrocyclization reactions.[4] In this case the correct order of mixing is the slow addition of the symmetrical reactant to a solution of the reactant in which equivalence of the two ends is lost in the reaction. The advantage of the correct procedure over the uncorrect one is greater, the larger the reactivity difference between A and A′.

Experimental Section

Instruments, Techniques, and Materials. ^{1}H NMR and ^{13}C NMR spectra were recorded at 7.1 T in $CDCl_3$. Positive FAB-MS spectra were obtained with a standard FAB source (Argon 7 kV). Melting points are uncorrected. Column chromatography of the reaction mixtures was performed on silica gel 60, mesh size 70–230. Ethanedithiol and dibutyltin oxide were commercial samples. Reagent-grade samples of acid chlorides were distilled before use.

2,2-Dibutyl-1,3,2-dithiastannolane (1). Ethanedithiol (3.76 g, 40 mmol) and dibutyltin oxide (9.95 g, 40 mmol) were azeotropically dehydrated in toluene (100 mL) in a Dean-Stark apparatus, until the reaction was complete. Toluene was removed in vacuo and the resulting solid was crystallized from hexane to afford 13 g (50% yield) of a colorless solid, mp 57.5–58 °C (lit.[7] mp 59–60 °C).

Macrocyclization Reactions. These were carried out as described in the text. Slow additions were carried out by means of a motor-driven syringe pump. After completion of additions, reflux was continued for 30 min to ensure complete reaction. The mixture was then cooled, and Bu_2SnCl_2 was removed by complexation with 2,2′-dipyridyl. Concentration in vacuo and chromatography of the residue on silica gel with toluene containing increasing amounts of EtOAc (from 0 to 30%) led to the isolation of the pure macrocyclic products.[8]

1,4-Dithiacycloundecane-5,11-dione (3, m = 5): mp 79–80 °C (lit.[3] mp 75–78 °C).

1,4-Dithiacyclotridecane-5,13-dione (3, m = 7): mp 90–91 °C; ^{1}H NMR δ 3.25 (s, 2 H), 2.55 (m, 2 H), 1.75, 1.33 (m, 14 H); ^{13}C NMR (75 MHz) δ 199.5, 44.0, 27.8, 27.4, 27.2, 25.2; IR (Nujol) 1675 cm^{-1}; mass spectrum m/e M$^+$, 246. Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.66; H, 7.32. Found: C, 53.60; H, 7.38.

1,4,12,15-Tetrathiacyclodocosane-5,11,16,22-tetrone (4, m = 5): mp 134–135 °C (lit.[3] mp 125–129 °C).

1,4,14,17-Tetrathiacyclohexacosane-5,13,18,26-tetrone (4, m = 7): mp 109–110 °C; ^{1}H NMR δ 3.0 (s, 4 H), 2.54 (t, J = 7 Hz, 4 H), 1.66, 1.31 (m, 28 H); ^{13}C NMR (75 MHz) δ 198.8, 43.8, 28.7, 28.6, 28.2, 25.5; IR (Nujol) 1680 cm^{-1}; mass spectrum m/e M + 1, 493. Anal. Calcd for $C_{22}H_{36}O_4S_4$: C, 53.66; H, 7.32. Found: C, 53.54; H, 7.48.

Registry No. 1, 7191-30-2; 2 (m = 5), 142-79-0; 2 (m = 7), 123-98-8; 3 (m = 5), 89863-24-1; 3 (m = 7), 137516-82-6; 4 (m = 5), 74190-60-6; 4 (m = 7), 74190-59-3; 7, 10017-60-4; ethanethiol, 540-63-6; dibutyltin oxide, 818-08-6.

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(8) Combined HPLC and FAB-MS analyses of the crude mixtures obtained with the BW technique showed the presence of higher cyclic oligomers with polymerization degree up to 7. This work will be presented elsewhere.

Synthesis of Cyclopentenes via [3 + 2]-Cycloadditions of Silylated Propargyl ↔ Allenyl Cations with Alkenes†

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The construction of 5-membered carbocycles by combination of 3C and 2C fragments has attracted considerable attention in recent years.[1] One possible approach, [3 + 2]-cycloadditions of [allenyl ↔ propargyl] cations with alkenes, has been accomplished by treating trialkylpropargyl chlorides with Lewis acids in the presence of alkenes.[2] This reaction sequence proceeds via the cyclization **3** → **2**,[2] in spite of the fact that 1-cyclopentenyl cations are highly unstable and are not formed during solvolyses of 1-cyclopentenyl triflates.[3] The vinyl cations **2** are not the only cycloadducts arising from [allenyl ↔ propargyl] cations, however, and for other substitution patterns of 1, [2 + 2]-cycloadditions with formation of **4** or **6** have been observed (Scheme I).[4]

Because of the well-known β-effect of trialkylsilyl groups,[5] the intermediate cations **3** (R^1 = $SiMe_3$) can be expected to undergo exclusive 5-*endo-dig* cyclizations with formation of 1-cyclopentenyl cations, thus providing a convenient access to cyclopentenes with a functionalized double bond. We report now on Lewis acid promoted reactions of 3-chloro-3-methyl-1-(trimethylsilyl)-1-butyne (**7**) with various CC-double bonded compounds and describe some reactions of the resulting 1-chloro-2-(trimethylsilyl)cyclopentenes **9**.

When the propargyl chloride **7** is combined with one of the alkenes **8a–e** in the presence of $TiCl_4$, the cyclopentenes **9a–e** are produced (Tables I and II), accompanied

† This work is dedicated to Prof. Michael Hanack on the occasion of his 60th birthday.

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