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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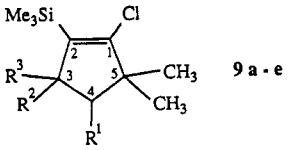
0022-3263/92/1957-0768$03.00/0

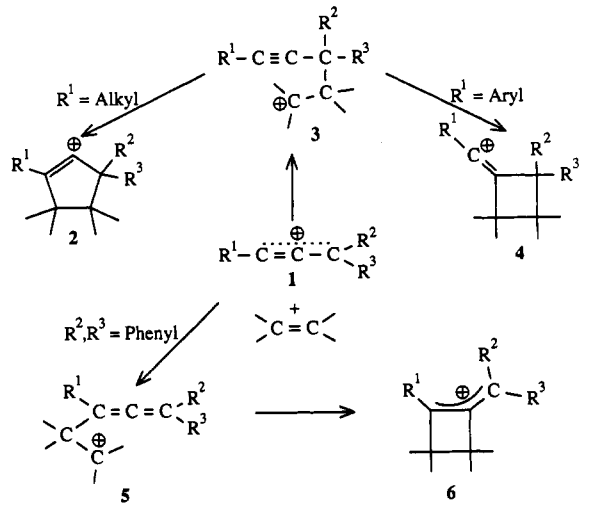
Table I. ^{13}C NMR Chemical Shifts for the 2-Chloro-2-(trimethylsilyl)cyclopentenes 9 ($CDCl_3$)[a]



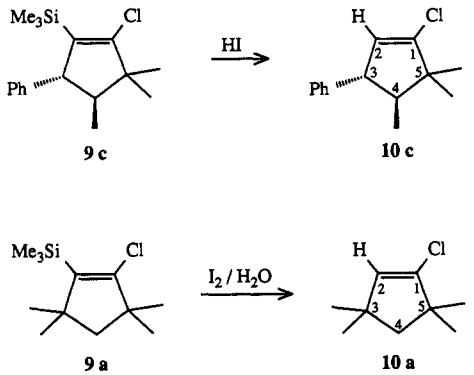
formula	R^1	R^2	R^3	C-1	C-2	C-3	C-4	C-5	R^1	R^2	R^3	5-CH_3	$SiMe_3$
9a	H	CH_3	CH_3	150.52	142.09	48.32*	55.48	47.53*		30.94*	30.94*	28.64*/28.64*	0.45
9b	CH_3	CH_3	CH_3	151.37	142.54	52.99*	49.84	50.39*	8.77	27.54*	29.21*	23.51/21.72	0.52
9c	CH_3	H	Ph	153.65	136.30	54.85*	60.33*	50.78	12.04		*b*	26.03*/20.42*	−0.82
9d	CH_3	H	CH_3	151.47	137.21	51.64*	48.30*	50.61	12.73*		19.95*	26.42*/20.07*	−0.06
9e	$-(CH_2)_3-$		CH_3	148.94	141.24	58.35	61.10	49.50	26.01		22.51	29.67/30.64	−0.08
									30.52				
									41.33				

[a] Asterisk indicates uncertain assignment. [b] 145.36 (i), 128.22 (o,m), 126.22 (p).

Scheme I

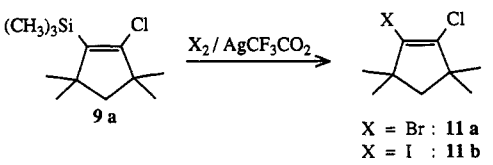


Scheme II

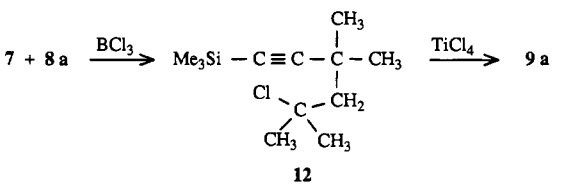


only by polymeric material. There was no evidence for the formation of isomeric products with the positions of $SiMe_3$ and Cl interchanged. Products of that type might arise via trimethylsilyl migration during cyclization, in analogy to the [3 + 2] annulations previously described by Danheiser.[6] Proof for the constitution of the unsymmetrical

Scheme III



Scheme IV



Scheme V

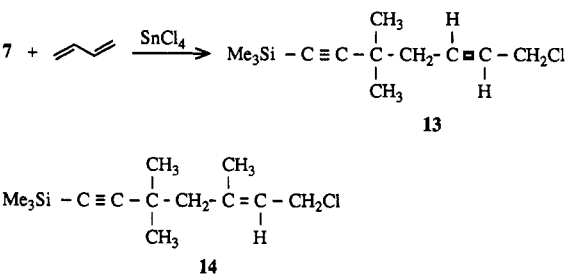


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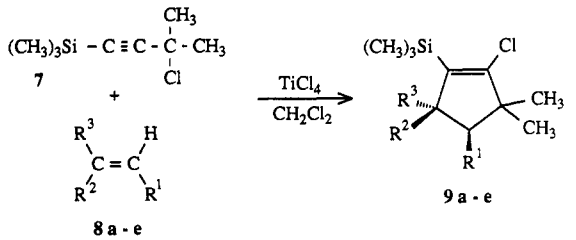
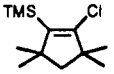
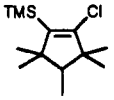
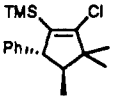
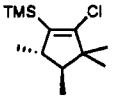
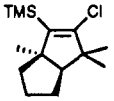
Table II



alkene	condns (°C)	product	yield (%)
 **8a**	0	 **9a**	38
 **8b**	0	 **9b**	45
 **8c**	0	 **9c**	35
 **8d**	−20 → 0	 **9d**	16
 **8e**	−78[a]	 **9e**	54

[a] BCl_3 was used instead of $TiCl_4$; the $TiCl_4$-catalyzed reaction at 0 °C gave 20% of **9e** contaminated by an unidentified product.

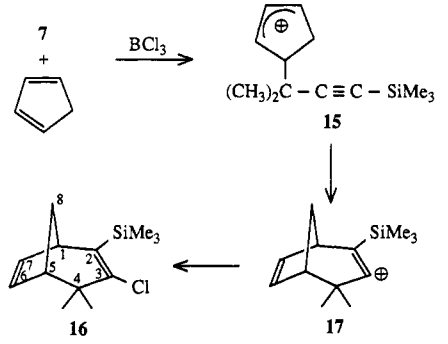
cyclopentene **9c** has been obtained by conversion of **9c** into **10c** (Scheme II). A cross-correlated heteronuclear 2D spectrum[7] of **10c** revealed a ^3J(C,H) coupling between C-1 and the protons of the 5-methyl groups. If the substitutents at the double bond of **9c** were in the alternative positions, the desilylated product should show a ^3J(C,H) coupling between the unsubstituted vinyl carbon and the 5-methyl-protons.

At room temperature, **9a** does not react with either Br_2 or I_2 in CH_2Cl_2, and the formation of some **10a** was observed when **9a** was heated with iodine in refluxing CH_2Cl_2. Probably traces of moisture account for this reaction (Scheme II), since treatment of **9a** with iodine and water[8] in boiling dichloromethane gave **10a** in 70% yield.

Replacement of the trimethylsilyl group by halogens has been achieved by reaction of **9a** with $Br_2/AgCF_3CO_2$ or $I_2/AgCF_3CO_2$,[9] respectively.

For the formation of the cyclopentenes **9a–e**, a stepwise [3 + 2]-cycloaddition sequence is suggested, as indicated in the upper left of Scheme I. In accord with this hypothesis, the acyclic adduct **12** is isolated in 74% yield, when **7** and **8a** are combined in presence of BCl_3 instead of $TiCl_4$. Under these conditions, the intermediate **3** can be trapped by Cl^-, since BCl_4^- is more nucleophilic than $TiCl_5^-$. Treatment of **12** with $TiCl_4$ gave **9a** in 84% yield; analogous silicon-directed cyclizations have been reported.[10]

Scheme VI



The $SnCl_4$-catalyzed reaction of **7** with 1,3-butadiene gave 41% of the acyclic adduct **13**, containing an *E*-configurated double bond. Yields of 10–40% were obtained with BCl_3 at −78 °C, but the $TiCl_4$-catalyzed reaction at 0 °C yielded only polymers. Attempts to cyclize **13** by treatment with Lewis acids have failed under a variety of conditions. An analogous adduct from **7** and isoprene could not be produced, since the primarily produced adduct **14** is ionized to a greater extent than **7** and therefore gives rise to the formation of polymeric material.[11]

In contrast, the BCl_3-catalyzed reaction of **7** with cyclopentadiene gave 26% of the bicyclo[3.2.1]octadiene **16**. Like **14**, the allyl chloride derived from **15** is not isolable, but the allylic cation **15** does not exclusively react with external nucleophiles (i.e., cyclopentadiene) to give higher adducts or polymers; because of the endo-fixed conformation it can also undergo cyclization with formation of the vinyl cation **17**, the precursor of **16**. Bicyclo[3.2.1]-octadienes with hydrogen or alkyl groups at C-2 have analogously been prepared from cyclopentadiene and alkyl-substituted propargyl chlorides.[12]

Conclusion

The $TiCl_4$-catalyzed reaction of the propargyl chloride **7** with 1,1-dialkylated or trialkylated ethylenes provides a convenient access to highly alkylated 1-chloro-2-(trimethylsilyl)cyclopentenes, which are of interest as possible cyclopentyne precursors. Because of the low S_N1 reactivity of **7**,[13] the scope of this reaction is rather limited, however, and the choice of alkenes that give [1:1]-products is considerably smaller than in analogous reactions with trialkyl or phenyl substituted propargyl chlorides.[2,14]

Experimental Section

3-Chloro-3-methyl-1-(trimethylsilyl)-1-butyne (7) has been synthesized in 77% yield from 30 g of 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol and 83 mL of concd hydrochloric acid according

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(13) Propargyl chloride **7** solvolyzes only 2.3 times faster than *t*-BuCl (100% EtOH, 25 °C): Dau-Schmidt, J. P.; Mayr, H.; Bentley, T. W. Unpublished results.

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to ref 15, bp 61–63 °C (20 mmHg) [lit.[15] bp 54.5–55 °C (17 mmHg)]. For the preparation of 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol a procedure developed by Shostakovskii[16] was used: A Grignard reagent was prepared from magnesium turnings (29.2 g, 1.20 mol) and bromoethane (133 g, 1.22 mol) in 600 mL of THF. The solution was cooled at 0 °C (formation of a precipitate), and a solution of 50.0 g (0.594 mol) of 2-methyl-3-butyn-2-ol in THF (50 mL) was added dropwise within 30 min. The cooling bath was removed, and stirring was continued for 6 h with occasional warming in a water bath to improve blending of the viscous suspension. The suspension, which had become fluid during this period, was cooled at 0 °C, and after addition of CuCl (0.6 g) and Hg_2Cl_2 (1.2 g), chlorotrimethylsilane (65.0 g, 0.598 mol) was added dropwise within 30 min. Stirring was continued for 12 h at ambient temperature and for 5 h at reflux. After the mixture was cooled, 160 mL of hydrochloric acid (concd HCl:H_2O = 1:3) and 150 mL of aqueous NH_4Cl solution (concd NH_4Cl:H_2O = 1:1) were successively added to dissolve the precipitate. The orange organic layer was separated, washed with two 200-mL portions of saturated aqueous NaCl solution, dried over Na_2SO_4, and evaporated in vacuo. Bulb-to-bulb distillation of the residue gave 56.3 g (61%) colorless, asbestos-like fibers with mp 41.5–42.5 °C [lit.[16] 42–42.5 °C].

1-Chloro-3,3,5,5-tetramethyl-2-(trimethylsilyl)cyclopentene (9a) (Typical Procedure). A solution of **7** (26.5 g, 152 mmol) and isobutene (**8a**) (9.90 g, 176 mmol) in dry CH_2Cl_2 (270 mL) was added dropwise within 3 h to a cooled (0 °C) solution of $TiCl_4$ (9.0 g, 47 mmol) in CH_2Cl_2 (90 mL). After 2 h at 0 °C, the solution was poured into water (200 mL). The organic layer was separated, washed with 200 mL of water, and dried over $CaCl_2$. Evaporation of the solvent gave 29.0 g of a dark brown oil, which could not be distilled because of heavy foaming. The product was, therefore, dissolved in petroleum ether (bp 35–45 °C) and filtered through a small amount of silica. Distillation over a 10-cm Vigreux column gave **9a** (13.3 g, 38%), a colorless oil with bp 88–90 °C (20 mmHg): IR (neat) 2970, 2940, 2900, 2870, 1580, 1470, 1460, 1450, 1365, 1315, 1250, 1030, 915, 880, 840, 765, 730 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 1.13 (s, 6 H, 2 CH_3), 1.15 (s, 6 H, 2 CH_3), 1.72 (s, CH_2); ^{13}C NMR see Table I; MS (96 eV) m/e (rel intensity) 230, 232 (32, 11, M^+), 215, 217 (100, 36), 179 (6), 159, 161 (28, 9), 143, 145 (18, 5), 122 (58), 121 (32), 117 (34), 107 (54), 95 (20), 93 (49), 91 (25), 73 (60). Anal. Calcd for $C_{12}H_{23}ClSi$: C, 62.44; H, 10.04. Found: C, 62.40; H, 9.94.

1-Chloro-3,3,4,5,5-pentamethyl-2-(trimethylsilyl)cyclopentene (9b) was prepared in 45% yield from **7** (9.67 g, 55.3 mmol), 2-methyl-2-butene (**8b**) (4.36 g, 62.2 mmol), and $TiCl_4$ (3.3 g, 17 mmol) as described for **9a**: bp (bath) 77–79 °C (0.4 mmHg); IR (neat) 2980, 2880, 1580, 1475, 1465, 1370, 1255, 1210, 1035, 905, 865, 850, 770 cm^{-1}; ^1H NMR (CCl_4) δ 0.24 (s, 9 H, $Si(CH_3)_3$), 0.88 (d, partially masked, $J \approx 7$ Hz, 4-CH_3), 0.96 (s, 6 H, 2 CH_3), 1.06 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.63 (q, J = 7 Hz, 1 H, 4-H); ^{13}C NMR see Table I; MS (96 eV) m/e (rel intensity) 244, 246 (14, 5, M^+), 229, 231 (47, 16), 169, 167 (5, 2), 170, 172 (8, 2), 159, 161 (21, 7), 136 (62), 135 (44), 121 (100), 117 (22), 105 (15), 93 (39), 73 (70). Anal. Calcd for $C_{13}H_{25}ClSi$: C, 63.76; H, 10.29. Found: C, 64.09; H, 10.08.

1-Chloro-4,5,5-trimethyl-3-phenyl-2-(trimethylsilyl)-cyclopentene (9c). Following the typical procedure, compound **7** (2.90 g, 16.6 mmol), (*E*)-1-phenylpropene (**8c**) (2.21 g, 18.7 mmol), and $TiCl_4$ (1.0 g, 5 mmol) were combined to give **9c** (1.70 g, 35%) with bp (bath) 80–100 °C (0.01 mmHg), which crystallized in the refrigerator. Colorless needles from pentane with mp 46–47 °C; IR (KBr) 3050, 3020, 2950, 2890, 2860, 1575, 1475, 1465, 1440, 1350, 1235, 1220, 1200, 1145, 1100, 1075, 1055, 1015, 980, 965, 930, 900, 880, 855, 825, 805, 765, 745, 720, 685 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ −0.10 (s, 9 H, $Si(CH_3)_3$), 0.87 (d, J = 7 Hz, 3 H, 4-CH_3), 0.94 (s, 3 H, 5-CH_3), 1.09 (s, 3 H, 5-CH_3), 1.74 (mc, 1 H, 4-H), 3.24 (d, J = 9 Hz, 1 H, 3-H), 7.13 (mc, 5 H, C_6H_5); ^{13}C NMR see Table I; MS (90 eV) m/e (rel intensity) 292, 294 (39, 15, M^+), 277, 279 (19, 8), 257 (4), 241 (11), 219, 221 (20, 7), 218, 220 (17, 7), 185 (28), 184 (63), 183 (56), 170 (54), 169 (84), 161 (20), 159 (54), 155 (32), 154 (30), 153 (28), 152 (21), 143 (18), 142 (19), 141 (42), 129 (26), 128 (35), 119 (37), 117 (58), 115 (45), 105 (37), 95 (56), 93 (71), 91 (55), 77 (33), 74 (42), 73 (100). Anal. Calcd for $C_{17}H_{25}ClSi$: C, 69.71; H, 8.60. Found: C, 69.27; H, 8.43.

1-Chloro-3,4,5,5-tetramethyl-2-(trimethylsilyl)cyclopentene (9d). A solution of **7** (5.02 g, 28.7 mmol) and of (*E*)-2-butene **8d** (7.0 g, 125 mmol) in dry CH_2Cl_2 (80 mL) was added dropwise within 75 min to a solution of $TiCl_4$ (1.55 g, 8.2 mmol) in 75 mL of CH_2Cl_2 at −78 °C. The mixture was then stirred at −20 °C (16 h) and warmed to 0 °C within 5 h. Workup as described (see typical procedure) gave 3.28 g of distilled material, a mixture of products, from which **9d** (1.04 g, 16%) was isolated by medium-pressure liquid chromatography (silica 20 μm, hexane): colorless liquid with bp (bath) 20–40 °C (0.4 mmHg); IR (neat) 2954, 2923, 2898, 2868, 1580, 1466, 1453, 1361, 1249, 1101, 1013, 906, 870, 838 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.19 (s, 9 H, $Si(CH_3)_3$), 0.85 (s, 3 H, 5-CH_3), 0.95 (d, J = 7.0 Hz, 3 H, 4-CH_3), 1.04 (s, 3 H, 5-CH_3), 1.1 (d, J = 6.7 Hz, 3 H, 3-CH_3), 1.41 (qd, J = 7.0 Hz, J = 8.3 Hz, 1 H, 4-H), 2.25 (qd, J = 6.7 Hz, J = 8.3 Hz, 1 H, 3-H); ^{13}C NMR see Table I; MS (70 eV) m/e (rel intensity) 230, 232 (5, 2, M^+), 215 (6), 122 (30), 121 (25), 107 (100), 93 (31), 73 (85). Anal. Calcd for $C_{13}H_{23}ClSi$: C, 62.44; H, 10.04. Found: C, 61.60; H, 9.60.

3-Chloro-1,4,4-trimethyl-2-(trimethylsilyl)bicyclo[3.3.0]-oct-2-ene (9e). Solutions of **7** (1.75 g, 10.0 mmol) in 10 mL of CH_2Cl_2 and of **8e** (0.83 g, 10.1 mmol) in 20 mL of CH_2Cl_2 were successively added to a solution of BCl_3 (1.20 g, 10.2 mmol) in 15 mL of CH_2Cl_2 at −78 °C. After being stirred for 18 h at −78 °C, the solution was poured into ice/water. The organic layer was separated, and the aqueous layer was extracted with 50 mL of CH_2Cl_2. The organic layers were dried over $MgSO_4$, the solvent was evaporated, and the residue was distilled [bp (bath) 40 °C (0.04 mbar)] to give 1.40 g (54%) of a colorless liquid **9e**: IR (neat) 2946, 2859, 1582, 1448, 1369, 1260, 1249, 1038, 1026, 840, 761 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.21 (s, 9 H, $Si(CH_3)_3$), 1.01 (s, 3 H, 1-CH_3), 1.14, 1.22 (2 s, 6 H, 4-CH_3), 1.3–1.9 (m, 7 H, 5-H, 6-H, 7-H, 8-H); ^{13}C NMR see Table I; MS (70 eV) m/e (rel intensity) 256, 258 (13, 5, M^+), 241, 243 (25, 9), 182, 184 (11, 4), 147 (16), 133 (19), 117 (10), 93 (26), 81 (18), 73 (100). Anal. Calcd for $C_{14}H_{25}SiCl$: C, 65.46; H, 9.81. Found: C, 65.70; H, 9.48.

1-Chloro-3,3,5,5-tetramethylcyclopentene (10a). A solution of **9a** (0.23 g, 1.0 mmol), I_2 (0.12 g, 0.47 mmol), and water (0.20 g, 11 mmol) in 5 mL of CH_2Cl_2 was refluxed for 20 h, and the reaction mixture was poured into aqueous $Na_2S_2O_3$ solution (30 mL). The layers were separated, and the aqueous layer was extracted with two 15-mL portions of CH_2Cl_2. The organic layers were dried over Na_2SO_4, the solvent was evaporated, and the residue was distilled [bp (bath) 25–45 °C (23 mmHg)] to give 0.11 g (70%) of the colorless liquid **10a**: IR (neat) 2960, 2860, 1630, 1465, 1455, 1370, 1330, 1200, 1000, 910, 855, 700 cm^{-1}; ^1H NMR (CCl_4) δ 1.10 (s, 6 H), 1.13 (s, 6 H), 1.73 (s, 2 H, 4 H), 5.35 (s, 1 H, 2-H); ^{13}C NMR ($CDCl_3$) δ 28.03 (q), 30.12 (q), 41.38 (s), 46.62 (s), 52.90 (t), 133.87 (d), 139.12 (s); MS (96 eV) m/e (rel intensity) 158, 160 (15, 4, M^+), 143, 145 (100, 31), 107 (28), 91 (16). Anal. Calcd for $C_9H_{15}Cl$: C, 68.13; H, 9.53. Found: C, 68.41; H, 9.34.

1-Chloro-4,5,5-trimethyl-3-phenylcyclopentene (10c). A solution of **9c** (220 mg, 0.751 mmol), H_2O (0.40 mL, 22.2 mmol), and HI (0.10 mL of a 57% aqueous solution, 0.74 mmol) in CH_2Cl_2 (10 mL) was heated under reflux for 4.5 h. The mixture was washed with 30 mL of concd aqueous $Na_2S_2O_3$ solution. After extraction of the aqueous phase with two 20-mL portions of CH_2Cl_2, the combined organic layers were dried over Na_2SO_4 and evaporated. Bulb-to-bulb distillation of the residue gave 150 mg (90%) of **10c** with bp (bath) 55–60 °C: IR (neat) 3017, 2951, 2919, 2862, 1617, 1491, 1465, 1450, 1361, 975, 905, 849, 749, 731, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (d, J = 7.8 Hz, 3 H, 4-CH_3), 0.99, 1.11 (2s, 6 H, 5-CH_3), 1.74–1.90 (m, 1 H, 4-H), 3.32 (dd, J = 9.4 Hz, J = 1.8 Hz, 1 H, 3-H), 5.64 (d, J = 1.8 Hz, 1 H, 2-H), 7.16–7.40 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 11.98 (q, 4-CH_3), 19.73, 25.59 (2q, 5-CH_3), 48.73 (s, C-5), 54.28 (d, C-4), 54.75 (d, C-3), 126.53 (d, C_p), 127.35 (d, C-2), 127.60, 128.35 (2d, C_o, C_m), 143.66, 143.70 (2s, C_i, C-1); MS (70 eV) m/e (rel intensity) 220, 222 (12, 5, M^+), 207, 205 (13, 32) 185 (100), 169 (30), 129 (21), 128 (22), 115 (30), 91 (39), 77 (20).

1-Bromo-2-chloro-3,3,5,5-tetramethylcyclopentene (11a). Silver trifluoroacetate (2.66 g, 12.0 mmol) was added to a solution

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of **9a** (2.30 g, 10.0 mmol) in 20 mL of CH_2Cl_2. During dropwise addition of a solution of Br_2 (0.62 mL, 12 mmol) in CH_2Cl_2 (50 mL) a precipitate is formed, and the mixture is stirred for 20 h at ambient temperature. After filtration, the solution is washed with 20% aqueous $NaHSO_3$ solution (2 mL) and concd aqueous ammonia (2 mL) and then dried over $CaCl_2$. Evaporation of the solvent and distillation yields 2.10 g (88%) of **11a** with a bp (bath) 80–100 °C (20 mmHg), which crystallizes in the refrigerator (mp 29.5–30 °C): ^1H NMR (CCl_4) δ 1.13 (s, 6 H), 1.17 (s, 6 H), 1.87 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.36 (q), 29.12 (q), 45.26 (s), 45.62 (s), 51.54 (t), 128.07 (s), 138.66 (s); MS (70 eV) *m/e* (rel intensity) 240, 238, 236 (2, 10, 8, M^+), 225 (11), 223 (49), 221 (38), 144 (31), 142 (100).

1-Chloro-2-iodo-3,3,5,5-tetramethylcyclopentene (11b). Silver trifluoroacetate (7.74 g, 35.0 mmol) was added to a solution of **9a** (4.90 g, 21.2 mmol) in 100 mL of CH_2Cl_2. A solution of I_2 (8.83 g, 34.8 mmol) in CH_2Cl_2 (150 mL) was added dropwise and stirred for 4 h at ambient temperature. The suspension was washed with 20% aqueous $NaHSO_3$ solution (100 mL), filtered, and once more washed with 20% aqueous $NaHSO_3$ solution (100 mL). The organic layer was then washed with water (200 mL) and concd aqueous NH_3 (150 mL) and was dried over $CaCl_2$. After evaporation of the solvent, the residue was distilled to give 5.25 g (87%) of **11b** with bp (bath) 90–105 °C (3.5 mmHg), which crystallizes in the refrigerator: mp 26–28 °C (from ether); ^1H NMR (CCl_4), δ 1.12 (s, 6 H), 1.20 (s, 6 H), 1.95 (s, 2 H); ^{13}C NMR δ 28.52 (q), 30.40 (q), 46.56 (s), 47.51 (s), 50.42 (t), 109.09 (s), 145.73 (s); MS (90 eV) *m/e* (rel intensity) 286, 284 (12, 43, M^+), 271 (31), 269 (100), 144 (43), 143 (25), 142 (48), 127 (27).

5-Chloro-3,3,5-trimethyl-1-(trimethylsilyl)-1-hexyne (12). Isobutene (1.25 g, 22.3 mmol) was introduced into a 0.5 M solution of BCl_3 in dry CH_2Cl_2 (10 mL) at −78 °C. A solution of **7** (2.58 g, 14.8 mmol) in CH_2Cl_2 (20 mL) was added dropwise to give a brown solution. After being stirred at −78 °C for 2 d, the mixture was poured into water, and the organic layer was separated, washed with water, and dried over $CaCl_2/NaHCO_3$. Distillation gave 0.40 g of unreacted **7** and 2.12 g (74%, with respect to converted **7**) of **12** with bp (bath) 45–52 °C (0.01 mmHg): IR (neat) 2960, 2920, 2880, 2150, 1250, 885, 845, 790, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.10 (s, 9 H, $Si(CH_3)_3$), 1.31 (s, 6 H, 3-CH_3), 1.73 (s, 6 H, $C(CH_3)_2Cl$), 2.00 (s, 2 H, CH_2); MS (96 eV) *m/e* (rel intensity) 230, 232 (13, 4, M^+), 215, 217 (57, 19), 179 (7), 159, 161 (29, 9), 139 (22), 123 (22), 122 (47), 121 (38), 119 (19), 117 (52), 107 (67), 97 (73), 95 (23), 93 (68), 91 (28), 73 (100).

7-Chloro-3,3-dimethyl-1-(trimethylsilyl)hept-5(*E*)-1-ene (13). 1,3-Butadiene (1.08 g, 20.0 mmol) and $SnCl_4$ (1.0 g, 3.8 mmol) were dissolved in CH_2Cl_2 (30 mL) at −78 °C. A solution of **7** (3.50 g, 20.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise within 30 min, and the mixture was stirred for 4 h at −78 °C. The solution was poured into water (150 mL), and after separation of the two layers, the aqueous layer was extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and evaporated. Bulb-to-bulb distillation yielded **13** (1.89 g, 41%), a colorless liquid with bp (bath) 50 °C (0.1 mmHg): IR (neat) 3030, 2960, 2920, 2160, 1440, 1250, 970, 920, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.13 (s, 9 H, $Si(CH_3)_3$, 1.17 (s, 6 H, 3-CH_3), 2.15 (d, J = 7.0 Hz, 2 H, 4-H), 4.07 (d, J = 6.9 Hz, 2 H, 7-H), 5.60–5.95 (m, 2 H, 5-H, 6-H); ^{13}C NMR ($CDCl_3$) δ 0.26 (q, $Si(CH_3)_3$), 28.83 (q, 3-CH_3), 31.82 (s, C-3), 45.10, 45.62 (2 t, C-4, C-7), 84.01 (s, C-1), 113.64 (s, C-2), 128.70, 132.17 (2 d, C-5, C-6); MS (70 eV) *m/e* (rel intensity) 228, 230 (2, 1, M^+), 159, 161 (6, 3), 139 (100), 97 (83), 75 (27). Anal. Calcd for $C_{12}H_{21}ClSi$: C, 62.99; H, 9.25. Found: C, 62.26; H, 9.21.

3-Chloro-4,4-dimethyl-2-(trimethylsilyl)bicyclo[3.2.1]-octa-2,6-diene (16). A solution of **7** (2.62 g, 15.0 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a solution of BCl_3 (1.2 g, 10 mmol) in CH_2Cl_2 (20 mL) at −10 °C. Cyclopentadiene (0.99 g, 15.0 mmol) dissolved in CH_2Cl_2 (100 mL) was then added within 1 h, and the solution was stirred for another hour at −10 °C. The mixture was poured into water (100 mL), and the organic layer was extracted with two 50-mL portions of CH_2Cl_2. After the CH_2Cl_2 solutions were dried over $MgSO_4$, the solvent was evaporated, and the residue was dissolved in hexane (100 mL) and passed through silica (KG 60, 70–230 mesh, column l = 10 cm and d = 2.5 cm). Evaporation of the solvent and distillation yielded **16** (950 mg, 26%), a colorless oil with bp (bath) 50 °C (0.02 mmHg): IR (neat) 2960, 2860, 1570, 1250, 1055, 930, 920, 870, 840, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H, $Si(CH_3)_3$), 0.99, 1.27 (2s, 6 H, CH_3), 1.75–1.9 (m, 2 H, 8-H), 2.52 (mc, 1 H, 5-H), 2.87 (mc, 1 H, 1-H), 5.83 (1 H, dd, $J_{6,7}$ = 5.6 Hz, $J_{5,6}$ = 2.7 Hz, 1 H, 6-H), 6.22 (dd, $J_{6,7}$ = 5.6 Hz, $J_{1,7}$ = 2.7 Hz, 1 H, 7-H); ^{13}C NMR ($CDCl_3$) δ −0.21 (q, $Si(CH_3)_3$), 23.34, 28.52 (2 q, 4-CH_3), 39.45 (t, C-8), 42.21 (s, C-4), 43.78 (d, C-1), 51.72 (d, C-5), 131.18, 140.40 (2 d, C-6, C-7), 139.03 (s, C-2), 149.09 (s, C-3); MS (70 eV) *m/e* (rel intensity) 240, 242 (11, 4, M^+), 225, 227 (3, 1), 159, 161 (13, 5), 132 (40), 119, 121 (48, 15), 117 (71), 93 (37), 73 (100). Anal. Calcd for $C_{13}H_{21}ClSi$: C, 64.83; H, 8.79. Found: C, 64.76; H, 8.93.

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Registry No. **7**, 18387-63-8; **8a**, 115-11-7; **8b**, 513-35-9; **8c**, 873-66-5; **8d**, 624-64-6; **8e**, 693-89-0; **9a**, 137649-22-0; **9b**, 137649-23-1; **9c**, 137649-24-2; **9d**, 137649-25-3; **9e**, 137649-26-4; **10a**, 137649-27-5; **10c**, 137649-28-6; **11a**, 137649-29-7; **11b**, 137649-30-0; **12**, 137649-31-1; **13**, 137649-32-2; **16**, 137649-33-3; 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol, 5272-33-3; 2-methyl-3-butyn-2-ol, 115-19-5; 1,3-butadiene, 106-99-0; cyclopentadiene, 542-92-7.

Temperature-Controlled Synthesis of 4,7-Dioxatricyclo[3.2.1.0^{3,6}]octane Derivatives

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Interest in the chemistry of 7-oxanorbornenic systems has increased in recent years especially due to the large array of molecules of biological relevance that may be synthesized from these bicycles.[1] This has been possible because they contain valuable stereochemical information in their rigid skeleton and they are readily available as optically pure starting materials.[2] Additions of soft electrophiles to 7-oxanorbornenic derivatives have been thoroughly studied. In most cases the reaction occurs with complete regio- and stereocontrol to afford synthetically useful adducts (A or B) (Scheme I). This behavior has been attributed to the steric and electronic characteristics of the substituents at C-2.[3] These studies have been also extended to the norbornenic analogues.[4]

In connection with our interest in the development of new synthetic methodologies from oxanorbornenic derivatives,[5] particularly those with sulfur and selenium,[6] and with our broader interest in vinyl sulfoxides[7] we required efficient regiocontrolled routes to oxabicyclic functionalized vinyl sulfides,[8] immediate precursors of the corresponding sulfoxides and sulfones.[9] For this purpose, the facile but not highly selective intramolecular cyclization of 2-*exo*-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol (**1**, Table I, entry 1) upon reaction with PhSCl was considered an interesting possibility, provided we could render the cyclization synthetically useful. Furthermore, it was envisioned that subsequent deprotonation of the sulfur-containing oxetanes should produce oxanorbornenic vinyl sulfides by preferential β-elimination of the oxetane oxygen due to the highly strained character of the four-membered ring. On the other hand, control of the addition reaction would

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