Tetrahedron Vol. 39, No. 6, pp. 935 to 947, 1983
Printed in Great Britain.

0040-4020/83/060935-13$03.00/0
Pergamon Press Ltd.

SCOPE AND STEREOCHEMICAL COURSE OF THE (TRIMETHYLSILYL)CYCLOPENTENE ANNULATION

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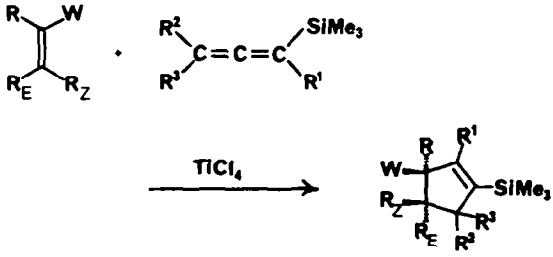
(*Received in U.S.A. 26 May 1982*)

Abstract—A new, regiospecific [3 + 2] annulation approach to highly substituted 5-membered carbocycles has been developed. The "TMS-cyclopentene annulation" involves the reaction of (trimethylsilyl)allenes with electron-deficient alkenes and alkynes in the presence of titanium tetrachloride to afford, in a single step, a functionalized and highly substituted TMS-cyclopentene derivative. Annulations employing α, β-unsaturated ketones proceed stereoselectively *via* suprafacial addition to the enone. Some useful transformations of the annulation products are also described; for example, treatment with K_2CO_3-methanol or HF in acetonitrile effects isomerization and desilylation yielding α,β-unsaturated ketones.

The identification of the prostaglandins, steroids, and related natural products as important synthetic targets has stimulated the development of an impressive methodology for the synthesis of 5-membered carbocycles.[1] Unfortunately, the design of *general, single-step* [3 + 2] annulation approaches to cyclopentane derivatives has proven to be an elusive goal.[2] At present there exists no 5-membered ring forming reaction which rivals in regioselectivity, stereoselectivity, and scope of application the highly esteemed Diels–Alder strategy for the synthesis of cyclohexane derivatives.

Recently we described a new regiocontrolled [3 + 2] annulation approach to 5-membered carbocycles involving the combination of (trimethylsilyl)allenes and electron-deficient alkenes in the presence of titanium tetrachloride.[3] A unique feature of this "*TMS-cyclopentene annulation*" is its capacity to regiospecifically generate in a single step 5-membered rings substituted at each position and functionally equipped for further synthetic elaboration.

In this report we now provide full details of our investigation defining the scope and stereochemical course of the TMS-cyclopentene annulation. As formulated in Eqn (1), *the reaction proceeds with remarkably high stereoselectivity via the effective suprafacial addition of the three carbon allene component to an electron-deficient olefin* ("*allenophile*").

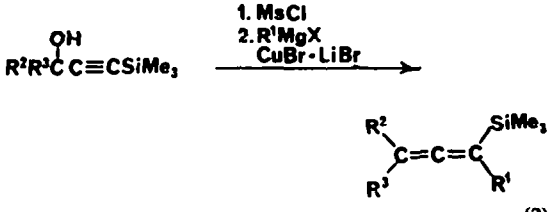


(1)

RESULTS

Preparation of (trimethylsilyl)allenes

The synthetic utility of the TMS-cyclopentene annulation obviously depends on the availability of efficient routes to (trimethylsilyl)allenes possessing a wide range of substitution and functionality patterns. Fortunately, considerable progress has recently been made in the development of general synthetic approaches to (trimethylsilyl)allenes[4–6] as well as specialized routes to specific functionalized derivatives.[7] For this investigation the requisite 1-substituted (trimethylsilyl)allenes **2a–e** were conveniently prepared employing the method of Westmijze and Vermeer (Eqn 2).[4a] Since



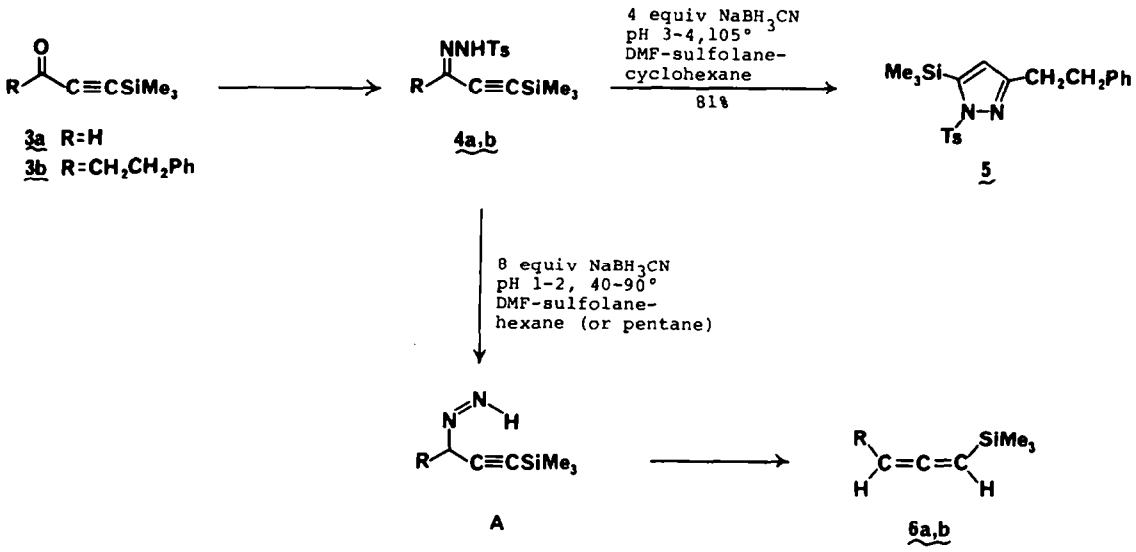
(2)

a R^1 = Me, R^2, R^3 = H
b R^1 = *i*Pr, R^2, R^3 = H
c R^1, R^2 = Me, R^3 = H
d R^1 = Me, R^2 = Et, R^3 = H
e R^1, R^2, R^3 = Me

no satisfactory procedure was available for the synthesis of *pure* (trimethylsilyl)allene itself,[8] we have developed a new approach which involves an adaptation of Hutchin's method for the reductive deoxygenation of α,β-unsaturated carbonyl compounds.[9] This reaction proceeds *via* a *concerted* [1, 5] sigmatropic rearrangement of a propargylic diazene intermediate (A) (Scheme 1) and thus furnishes (trimethylsilyl)allene (**6a**) as well as its 3-alkyl derivatives (e.g. **6b**) free of their acetylenic isomers.

Thus, reaction of hydrocinnamyl chloride with cuprous (trimethylsilyl)acetylide[10] gave the ketone **3b**, which was converted to the tosylhydrazone **4b** (81–86% overall yield) by treatment with 1.1 equiv of $TsNHNH_2$ in diethyl ether at 25°. Although reaction of **4b** with sodium cyanoborohydride according to Hutchin's procedure led to the formation of the pyrazole **5**[11,12] (mp 97–98°), rearrangement to the desired allene **6b** could be effected in 78–84% yield by employing the indicated modified procedure. (Trimethylsilyl)allene (**6a**) was prepared in 51% yield from the aldehyde **3a**[13] in a similar fashion.

†Alfred P. Sloan Research Fellow, 1981–83.



Scheme I.

Optimal conditions for the TMS-cyclopentene annulation

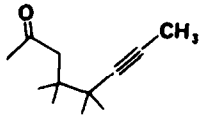
The TMS-cyclopentene annulation is typically carried out by rapidly adding 1.5 equiv of distilled titanium tetrachloride[14,15] to a solution of the "allenophile" and 1.0–1.5 equiv of a (trimethylsilyl)allene in methylene chloride. With the more reactive allenophiles annulation is best effected at −78° in order to minimize further reaction of the TMS-cyclopentene products. Higher reaction temperatures proved necessary to achieve complete conversion in the case of the less reactive (e.g. sterically hindered) allenophiles (*vide infra*). The progress of the annulation is conveniently followed by thin layer chromatography; upon completion the reaction is quenched by transferring the reaction mixture *via* cannula to a rapidly stirred mixture of diethyl ether and water.

Scope of the TMS-cyclopentene annulation

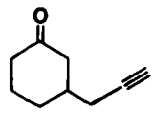
Tables 1 and 2 delineate the scope of the TMS-cyclopentene annulation. Addition of allene **2a** to methyl vinyl ketone proceeds smoothly at −78° to furnish the (trimethylsilyl)cyclopentene 7 in 71–75% yield after chromatographic purification. The structure of the annulation product was established by spectral characterization (Experimental) and by conversion to 1-acetyl-2-methylcyclopentene (*vide infra*; semicarbazone m.p. 220.0–220.5°, lit.[16] m.p. 220–221°).

The TMS-cyclopentene annulation can be applied to the synthesis of a wide variety of highly substituted 5-membered carbocyclic compounds. Both cyclic and acyclic enones participate in the annulation, indicating that it is not necessary for the enone to be able to attain *s*-cis geometry in order for reaction to occur. α-Alkylidene ketones undergo annulation to provide access to spiro-fused systems, and acetylenic allenophiles react to form cyclopentadiene derivatives. Although no reaction occurs upon exposure of β,β-disubstituted enones to (trimethylsilyl)allenes at −78°, in many cases annulation does proceed in good yield provided that the reaction is carried out at room temperature. However, more hindered enones such as isophorone fail to participate in the annulation. The formation of the highly congested TMS-cyclopentene **15** in low yield demarcates the steric limit of the annulation; the acetylenic ketone **18** was the principal product isolated in this reaction.

The TMS-cyclopentene annulation proceeds most efficiently using 1-substituted (trimethylsilyl)allenes. Very highly substituted 5-membered rings are generated in annulations employing allenes **2c-e**; reactions with **2e** proceed regiospecifically to afford (trimethylsilyl)cyclopentenes containing quaternary centers. Disappointingly, the parent allene **6a** reacts with cyclohexenone to produce the annulation product **17** in only 17–19% yield together with the acetylenic ketone **19** (30%).

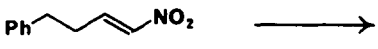


18

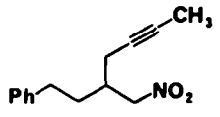


19

The reaction of (trimethylsilyl)allenes with α-nitro olefins was also investigated in the hope that the latter might function as ketene equivalents in the TMS-cyclopentene annulation. In the event, reaction of the nitro alkene **20**[17] with the allene **2a** at −78° in the presence of $TiCl_4$ produced the acetylene **21** (58% yield) rather than



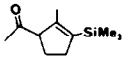
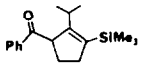
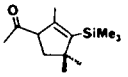
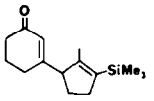
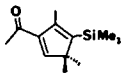
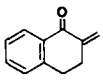
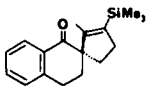
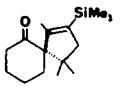
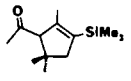
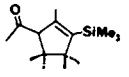
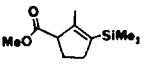
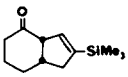
20



21

the desired TMS-cyclopentene. This result suggests, however, that (trimethylsilyl)allenes may serve as useful

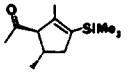
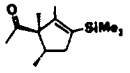
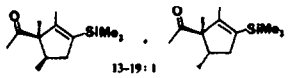
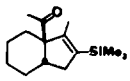
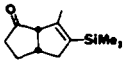
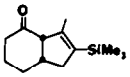
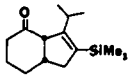
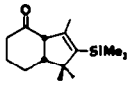
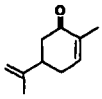
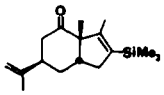
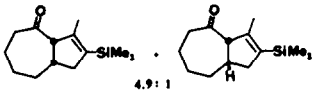
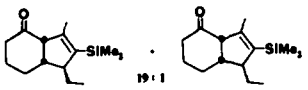
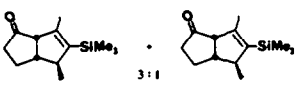
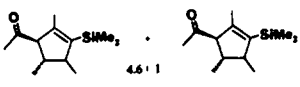
Table 1. Scope of the TMS-cyclopentene annulation

entry	allenophile	allene	annulation product	% yield
1		2a	 7	71-75
2		2b	 8	69-73
3		2e	 9	80
4		2a	 10	66
5		2e	 11	53
6		2a	 12	80-84
7		2a	 13	86
8		2a	 14	65
9		2e	 15	7
10		2a	 16	49
11		6a	 17	17-19

propargylic anion equivalents in Michael-type additions to nitro olefins.[18]

Attempts to extend the TMS-cyclopentene annulation to α,β-unsaturated aldehydes have thus far proved unsuccessful. For example, reaction of methacrolein with allene **2a** in the presence of $TiCl_4$ at $-78°$ results in the formation of a complex mixture of products. However, addition of methyl acrylate to **2a** at 25° does proceed as expected to afford the TMS-cyclopentene **16** in 49% yield. This annulation proceeds considerably more

Table 2. Stereochemical course of the TMS-cyclopentene annulation

entry	allenophile	allene	annulation product(s)	% yield
1		2a	 22	79
2		2a	 23	71
3		2a	 13–19 : 1 24 23	68
4		2a	 25	91
5		2a	 26	48
6		2a	 27	85
7		2b	 28	81–85
8		2c	 29	63
9		2a	 30	87
10		2a	 4.9 : 1 31a 31b	90–94
11		2d	 19 : 1 32a 32b	79
12		2c	 3 : 1 33a 33b	68
13		2c	 4.6 : 1 34a 34b	82

slowly than the analogous reaction employing methyl vinyl ketone. Other investigators have reported unsuccessful efforts to achieve the electrophilic substitution of allylic silanes with α,β-unsaturated esters.[19,20] The application of highly reactive aldehyde and carboxylic acid equivalents in the TMS-cyclopentene annulation will be the subject of a future communication from our laboratory.

Stereochemical course of the TMS-cyclopentene annulation

As formulated in eqn (1), the TMS-cyclopentene annulation proceeds with a strong preference for *suprafacial* addition of the allene to the two-carbon "allenophile". The high selectivity displayed by the reaction permits the stereocontrolled synthesis of a variety of mono- and polycyclic systems (Table 2).

The reactions of *E* and *Z*-3-methyl-3-penten-2-one illustrate the stereochemical course of the annulation. These ketones are easily prepared by the reaction of methyllithium at 0° with tiglic and angelic acid. Thus, annulation employing the *E* enone affords a single TMS-cyclopentene (**23**), while reaction of the corresponding *Z* isomer generates primarily (93–95%) the diastereomeric annulation product (**24**). The stereochemistry of these ketones was assigned by analysis of their ^{13}C NMR spectra: the Me group attached to C_3 in **23** appears upfield (δ13.2 or 14.6) relative to the corresponding Me group in **24** (δ 20.9).[21]

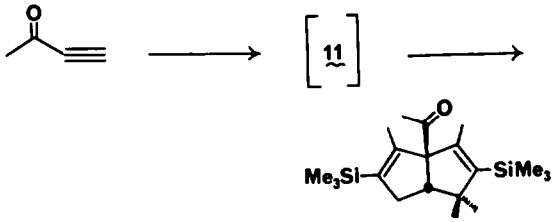
Reactions employing acetylcyclohexene, cyclopentenone, and cyclohexenone (entries 4–9) yield in each case a single annulation product. Molecular models indicate that the intermediates involved in these reactions (*vide infra*) are constrained to cyclize to *cis*-fused adducts. The coupling constants for the ring fusion protons in hydrindanes **27**, **28**, **29**, and **32** (J = 6.2–7.3 Hz) and bicyclo[3.3.0]octanes **26** and **33** (J = 7.3–8.1 Hz) support the assignment of *cis* ring fusion stereochemistry in these compounds. Annulation with carvone also affords a single product (**30**); the orientation of the isopropenyl group in this adduct was assigned by analogy with related conjugate additions to carvone.[22] Finally, addition of allene **2a** to cycloheptenone gave a 4.9 : 1 mixture of hydroazulenes **31a** and **31b**. Epimerization of the *cis*-fused adduct cannot be ruled out as the source of the small amount of *trans*-fused isomer, although thus far we have been unable to inhibit its formation through modifications in the reaction and workup procedures.

Annulations employing allenes **2c** and **2d** also proceed stereoselectively to produce TMS-cyclopentene derivatives containing a third stereocenter (Table 2, entries 11–13). The stereochemistry of bicyclo[3.3.0]octanes **33a** and **33b** was assigned by analysis of their ^{13}C NMR spectra: in **33b** the endo methyl and C_4 carbons appear upfield relative to the corresponding carbon atoms in the exo-methyl isomer **33a**.[23] The stereochemistry of annulation products **32a,b** and **34a,b** could not be established with certainty, and the structures proposed in Table 2 were assigned by analogy with the preceding results.

Synthetic elaboration of TMS-cyclopentene annulation products

The TMS-cyclopentene annulation products are readily transformed into a variety of synthetically valuable systems. One useful transformation involves the conversion of the annulation products to α,β-unsaturated ketones (Table 3). Exposure of the TMS-cyclopentenes to either potassium carbonate in methanol (25°, 2.5–21 hr; method A) or a dilute solution of hydrofluoric acid in acetonitrile (25°, 2–48 hr; method B) results in isomerization followed by desilylation of the intermediate γ-trimethylsilyl-α,β-unsaturated ketones. Although complete conversion to the α,β-enones was achieved in most cases, treatment of TMS-cyclopentene **8** with excess potassium carbonate at 25° for 14 d afforded an 89 : 11 mixture of **36** and the corresponding β,γ-enone isomer.[24] As expected, exposure of bicyclo[3.3.0]octenones **33a,b** to hydrofluoric acid results in desilylation without isomerization to produce **45a,b** in 92% yield. In this system, the β,γ-enone is thermodynamically favored because of the additional ring strain associated with the conjugated isomer.[25] Hydrofluoric acid can also be employed to effect the desilylation of TMS-cyclopentenes in which isomerization is blocked by substitution (e.g. entry 5).

Acetylenic allenophiles participate in one-pot "double annulations" to generate bicyclo[3.3.0]octadiene derivatives. For example, sequential treatment of 3-butyn-2-one with allenes **2e** and **2a** at −78° to −30° in the presence of titanium tetrachloride furnished the bis-annulation product **46** in 38% yield.



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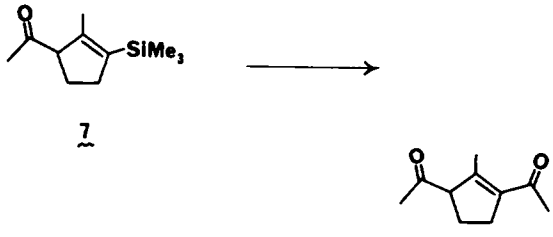
The vinylsilane moiety incorporated in the annulation products can serve as the basis for a variety of other interesting synthetic transformations. For example, vinylsilanes undergo regiospecific electrophilic substitution with great facility employing a wide range of electrophilic species.[26,27] Treatment of the TMS-cyclopentene **7** with 1.5 equiv of acetyl chloride and 2.5 equiv of $AlCl_3$ in CH_2Cl_2 at 0° for 1 hr thus provides 1,3-diacetyl-2-methylcyclopentene (**47**) in 95% yield after



7

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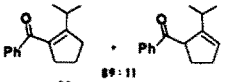
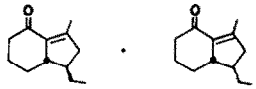
chromatographic purification. Santelli and Pardo have recently described alternate routes to this compound which they suggest should serve as a valuable intermediate in natural product synthesis.[28]

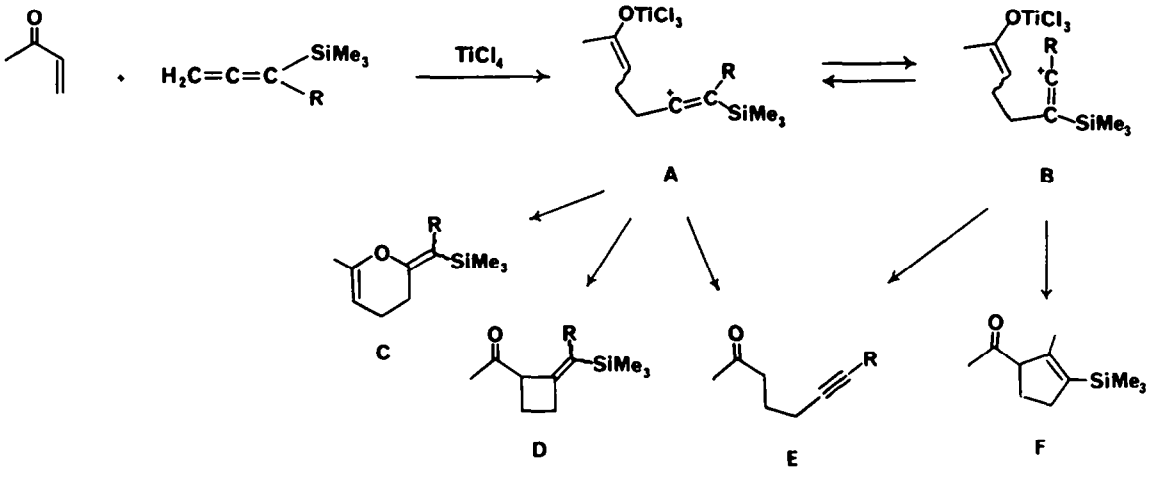
DISCUSSION

Scheme 2 outlines the general mechanistic course of the TMS-cyclopentene annulation employing methyl vinyl ketone as prototypal allenophile. The reaction likely

Table 3. Isomerization-desilylation of TMS-cyclopentene annulation products

entry	TMS-cyclopentene	method	product	% yield
1	7	A	 35	68
2	8	A	 89:11 36	68
3	9	B	 37	66
4	22	A	 38	64
5	25	B	 39	96
6	27	A	 40	86
7	28	A	 41	75
8	29	B	 42	94
9	31a,b	A	 43	91
10	32a,b	B	 44a 44b	88-91
11	33a,b	B	 45a 45b	92

involves initial complexation of the enone and titanium tetrachloride to generate an alkoxy allylic carbocation. Regiospecific electrophilic substitution[26,27b] of this cation at C_3 of the (trimethylsilyl)allene then provides a vinyl cation stabilized by interaction with the adjacent carbon-silicon bond. The C–Si bond in (trimethylsilyl)allenes is oriented coplanar to the allylic π bond but orthogonal to the vinylic π system, and therefore can afford direct stabilization only to the transition state resulting from electrophilic attack at C_3.[29] A 1,2 shift of the trimethyl-



Scheme 2.

silyl group[30,31] then occurs to afford an isomeric vinyl cation (B) which is intercepted by the titanium enolate to produce the new 5-membered ring.

Inspection of molecular models indicates that cyclization of the initial intermediate (A) is disfavored by the large distance separating the cationic center and nucleophilic carbon. These reactive centers are well situated for ring closure in the isomeric cation (B). Interestingly, Santelli and Jellal have recently reported the isolation in low (12%) yield of a cyclobutane derivative (type D) from the reaction of acetylcyclopentene and (trimethylsilyl)allene.[20] These workers also obtained a small amount (4% yield) of a pyran derivative (product C) in a related reaction. We have not detected the formation of type C products in any of the annulations examined in our laboratory including those (Table 1, entries 6,7) proceeding *via* enolates whose geometry should most favor O-alkylation.

The disappointing yield of TMS-cyclopentene product observed in the reaction of (trimethylsilyl)allene itself (Table 1, entry 11) is attributable to the relative instability of the terminal vinyl cation B (R = H) involved in this case. The major product isolated in this reaction is thus the acetylene (E) generated by desilylation of the more stable vinyl cation (A).

A complete understanding of the basis for the high stereoselectivity displayed in the TMS-cyclopentene annulation requires a more definitive investigation of the mechanism of the reaction. Apparently cyclization proceeds more rapidly than conformational interconversion in the intermediate cations. Additional studies are underway in our laboratory to further extend the scope of the reaction, and to implement the TMS-cyclopentene annulation in the synthesis of natural products.

EXPERIMENTAL

Instrumentation. IR spectra were obtained using a Perkin–Elmer 283B grating spectrophotometer. ^{1}H NMR spectra were measured with Perkin–Elmer R-24B (60 MHz) and Bruker WM-250 (250 MHz) spectrometers. ^{13}C NMR spectra were determined on JEOL FX-90Q (22.5 MHz) and Bruker WM-250 (62.8 MHz) spectrometers. Chemical shifts are expressed in ppm (δ) downfield from TMS as an internal standard. Low resolution mass spectra (MS) were determined on a Varian MAT 44 instrument; high resolution mass spectra were measured with a DuPont CEC-110B spectrometer. M.ps and b.ps are uncorrected.

Materials. Methylene chloride, benzene, acetonitrile, triethylamine, dimethylformamide, chlorotrimethylsilane, and dimethyl sulfide were distilled from CaH_2. THF and diethyl ether were distilled from sodium benzophenone ketyl or dianion. MeOH was stored over 3Å molecular sieves. Sulfolane, $TiCl_4$, MsCl, and all acid chlorides, ketones, aldehydes, and esters were distilled before use. Powdered molecular sieves were heated with a Bunsen burner at 0.1 torr before use. LiBr and CuBr were dried at 100° (0.1 torr) for 15 hr. Column chromatography was performed using E. Merck silica gel 60 (230–400 mesh). Chromatographic purifications of $\leq$0.100 g of material were carried out in disposable pipettes containing *ca.* 1 g of silica gel.

All reactions were carried out in flame-dried glassware under an atmosphere of argon or nitrogen with the aid of magnetic stirring.

Preparation of (trimethylsilyl)allenes via Westmijze-Vermeer method

3-Trimethylsilyl-2-propyn-1-ol (**1a**). To a soln of propargyl alcohol (22.4 g, 400 mmol) in 800 mL THF at 0° was added dropwise over 1.5 hr n-BuLi soln (2.38 M in hexane, 336 mL, 800 mmol). The resulting mixture was treated dropwise over 1 hr with chlorotrimethylsilane (86.8 g, 800 mmol), allowed to warm to 25° over 0.5 hr, and stirred 0.5 hr further. The mixture was then poured into 600 mL 3 M HCl and stirred at 25° for 0.5 hr. The organic phase was separated and washed with water, satd $NaHCO_3$ aq, and satd NaCl aq, dried over $MgSO_4$, filtered, and distilled to yield 46.2 g (90%) of **1a**[32] as a pale yellow oil (b.p. 64–67°/10 torr) with spectral characteristics identical to that previously reported for this compound.[33]

1-Methyl-1-(trimethylsilyl)allene (**2a**). To a soln of **1a** (46.2 g, 360 mmol) and Et_3N (54.7 g, 540 mmol) in 1100 mL CH_2Cl_2 at −50° was added dropwise over 0.5 hr methanesulfonyl chloride (55.0 g, 480 mmol). The resulting mixture was allowed to warm to 25° over 1.5 hr and stirred 0.5 hr further at that temp. The mixture was then poured into 600 mL water, the aqueous phase was separated and extracted with CH_2Cl_2, and finally the combined organic layers were washed with water and satd NaCl aq, dried over $MgSO_4$, filtered, and concentrated to afford 74.3 g of the mesylate as a pale yellow oil used in the next step without purification.

To a soln of LiBr (34.4 g, 400 mmol) and cuprous bromide (56.8 g, 400 mmol) in 1000 mL THF at −10° was added dropwise over 1 hr MeMgBr soln (3.0 M in ether, 132 mL, 400 mmol). The resulting suspension was stirred at −10° for 1 hr, cooled to −60°, and treated dropwise over 20 min with a soln of the mesylate prepared above in 120 mL of THF. The mixture was next stirred at −60° for 0.5 hr, allowed to warm to 25° over 1 hr, maintained at 25° for 1 hr further, and then poured into 1000 mL satd NH_4Cl aq (adjusted to pH 8 by addition of NH_4OH). The resulting mixture was stirred at 25° for 0.75 hr, and the organic phase was then separated and washed with satd pH 8 NH_4Cl aq until the extracts were no longer blue. The combined aqueous layers were back-extracted with CH_2Cl_2, and the combined organic

phases were finally washed with water and satd NaCl aq, dried over $MgSO_4$, filtered, and concentrated by careful distillation of the solvent at atmospheric pressure. Distillation then gave 23.8 g (52% overall from **1a**) of **2a**[34] as a colorless oil: b.p. 52–53° (90 torr); IR (tf) 2955, 2920, 2900, 2860, 1935, 1440, 1400, 1250, 935, 880, 830, 805, 750, and 685 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 1.71 (t, 3 H, J = 3), and 4.27 (q, 2 H, J = 3).

4-Trimethylsilyl-3-butyn-2-ol (**1c**). To a soln of (trimethylsilyl)-acetylene (15.0 g, 153 mmol) in 135 mL THF and 75 mL hexane at 0° was added dropwise over 1 hr n-BuLi soln (2.27 M in hexane, 61.2 mL, 139 mmol). The mixture was cooled to −70°, treated dropwise over 1 hr with a soln of acetaldehyde (18.4 g, 417 mmol) in 40 mL THF, and then stirred at −70° for 2 hr and at 25° for 16 hr. The resulting mixture was diluted with water and the aqueous phase was separated and extracted with ether. The combined organic layers were washed with satd NaCl aq, dried over $MgSO_4$, filtered, and concentrated to afford 23.8 g of a brown oil. Column chromatography on silica gel (elution with EtOAc–hexane) furnished 16.3 g (76%) of **1c**[35] as a yellow oil: IR (tf) 3340, 2975, 2955, 2930, 2900, 2160, 1445, 1405, 1365, 1320, 1245, 1110, 1070, 1040, 940, 860, 835, 750, and 690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 1.42 (d, 3 H, J = 7), 2.0 (br s, 1 H), and 4.2–4.75 (m, 1 H).

1,3-Dimethyl-1-(trimethylsilyl)allene (**2c**). Reaction of **1c** (16.3 g, 115 mmol) with methanesulfonyl chloride (17.5 g, 153 mmol) and Et_3N (17.4 g, 172 mmol) in 250 mL of CH_2Cl_2 according to the procedure described for the preparation of **2a** gave 25 g of the mesylate as a brown oil used in the next step without purification.

Reaction of 23 g of this mesylate with the organocopper reagent prepared from LiBr (10.9 g, 125 mmol), CuBr (17.9 g, 125 mmol), and MeMgBr soln (3.0 M in ether, 41.6 mL, 125 mmol) in 400 mL of THF at −50° for 1 hr and then at 25° for 12 hr according to the procedure described for the preparation of **2a** provided 9.4 g (65% overall from **1c**) of **2c** as a colorless oil: b.p. 58–59° (48 torr); IR (tf) 2955, 2920, 2890, 2860, 1935, 1440, 1360, 1240, 970, 865m 830, 750, 730, and 680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 1.65 (d, 3 H, J = 7), 1.72 (d, 3 H, J = 2.5), and 4.75 (m, 1 H).

1-Trimethylsilyl-1-pentyn-3-ol (**1d**). Reaction of (trimethylsilyl)acetylene (9.8 g, 100 mmol) with n-BuLi soln (2.39 M in hexane, 40.1 mL, 96 mmol) and then propionaldehyde (5.57 g, 96 mmol) in 375 mL THF according to the procedure described for the preparation of **1c** provided 12.4 g (80%) of **1d**[36] as a pale yellow oil with spectral data identical to that reported previously.

1-Ethyl-3-methyl-3-(trimethylsilyl)allene (**2d**). Reaction of **1d** (8.9 g, 57 mmol) with methanesulfonyl chloride (8.64 g, 76 mmol) and Et_3N (8.64 g, 86 mmol) in 250 mL CH_2Cl_2 according to the procedure described for the preparation of **2a** gave 13.3 g of the mesylate as a yellow oil used in the next step without purification.

Reaction of this mesylate with the organocopper reagent prepared from LiBr (4.95 g, 57 mmol), CuBr (8.18 g, 57 mmol), and MeMgBr soln (3.0 M in ether, 19 mL, 57 mmol) in 180 mL of THF at −60° for 0.75 hr and then at 25° for 1.5 hr according to the procedure described above for the preparation of **2a** gave 6.53 g (74% overall from **1d**) of **2d** as a colorless oil: b.p. 55–57° (30 torr); IR (tf) 2955, 2930, 2910, 2890, 2850, 1935, 1440, 1390, 1360, 1300, 1245, 930, 855, 830, 745, and 680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 1.05 (t, 3 H, J = 7), 1.72 (d, 3 H, J = 3), 2.02 (m, 2 H), and 4.82 (m, 1 H).

2-Methyl-4-trimethylsilyl-3-butyn-2-ol (**1e**). Prepared by the reaction of $Me_3SiC{\equiv}CMgBr$ and acetone as described previously[37]: m.p. 41°; IR (tf) 3350, 2980, 2955, 2930, 2900, 2870, 2130, 1450, 1360, 1250, 1215, 1160, 965, 910, 840, 750, 730, and 690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 1.52 (s, 6 H), and 2.18 (s, 1 H).

1,1,3-Trimethyl-3-(trimethylsilyl)allene (**2e**). To a soln of **1e** (6.3 g, 41 mmol) and LiBr (3.57 g, 41 mmol) in 100 mL of THF at −60° was added dropwise over 0.5 h n-BuLi soln (1.44 M in hexane, 28.5 mL, 41 mmol). The resulting soln was stirred at −60° for 40 min, treated dropwise over 0.5 hr with methanesulfonyl chloride (3.14 g, 41 mmol), and then stirred at −60° for 2 hr further.

To a soln of LiBr (8.93 g, 103 mmol) and CuBr (14.8 g, 103 mmol) in 250 mL of THF at −30° was added dropwise over 0.5 hr MeMgBr soln (2.8 M in ether, 36.8 mL, 103 mmol), and the resulting mixture was stirred at −30° for 0.5 hr and then cooled to −40°. This yellow suspension was transferred by cannula over 1 hr into the mesylate soln (prepared above) maintained at −60°. The resulting mixture was stirred at −30° for 1 hr, at 25° for 1 hr, and then worked up as described in the preparation of **2a** to afford 4.1 g (65%) of **2e** as a colorless oil: b.p. 40–41° (20 torr); IR (tf) 2950, 2920, 2900, 2850, 1945, 1440, 1400, 1350, 1240, 1190, 1050, 935, 830, 740, and 680 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.18 (s, 9 H) and 1.72 (s, 9 H).

Preparation of (trimethylsilyl)allenes via reductive deoxygenation method

3-(Trimethylsilyl)propynal (**3a**). This aldehyde was prepared in 80% yield by the reaction of $Me_3SiC{\equiv}CMgBr$ and dimethylformamide[13]: b.p. 44° (15 torr); IR (tf) 2970, 2910, 2860, 2740, 2160, 1670, 1390, 1260, 1000, 850, and 765 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.30 (s, 9 H) and 9.28 (s, 1 H).

[3-(Trimethylsilyl)-2-propynylidene]-4-methylbenzenesulfonyl hydrazide (**4a**). A soln of **3a** (25.1 g, 200 mmol) and *p*-toluenesulfonylhydrazine (41.6 g, 220 mmol) in 200 mL of EtOH was heated at reflux for 3.5 hr. The resulting suspension was concentrated at ≤25° (15 torr) to *ca.* 40 mL and the ppt was collected by filtration and dried at 25° (0.1 torr) to afford 55.5 g (94%) of **4a** as yellow crystals used in the next step without further purification: ^1H NMR (60 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 2.46 (s, 3 H), 6.66 (s, 1 H), 7.64 (AB, 4 H), and 8.68 (br s, 1 H).

(Trimethylsilyl)allene (**6a**). Sodium cyanoborohydride (48.0 g, 800 mmol), **4a** (31.0 g, 100 mmol), and bromocresol green (*ca.* 0.005 g) were dissolved in 460 mL of a 1 : 1 mixture of DMF and sulfolane. Pentane (460 mL) was added, and the resulting two-phase mixture was treated dropwise with *ca.* 5 mL of conc HCl so that the indicator changed from blue to yellow and some H_2 evolution was observed (pH 1–2). The mixture was then heated at 40–45° for 10 hr (bath temp 50°) while 2.5 mL portions of conc HCl were added at intervals of 1 hr. The resulting mixture was next heated at 40–45° for 20 hr and then at 55–60° (bath temp 80°) for 48 hr. The mixture was allowed to cool to room temp, diluted with water, and extracted with pentane. The combined organic phases were washed with satd NaCl aq, dried over Na_2SO_4, filtered, and the pentane was removed by careful distillation at atmospheric pressure. Distillation of the product of several runs gave 11.5 g (51% overall from **3a**) of **6a** as a colorless oil: b.p. 90–93° (760 torr); IR (tf) 2955, 2900, 1935, 1250, 1210, 1055, 840, 800, 750, and 690 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 4.27 (d, 2 H, J = 7.7), and 4.88 (dd, 1 H, J = 6.6, 7.7).

5-Phenyl-1-(trimethylsilyl)-1-pentyn-3-one (**3b**). To a soln of (trimethylsilyl) acetylene (2.70 g, 27.5 mmol) in 100 mL THF at 0° was added dropwise over 0.25 hr n-BuLi soln (2.43 M in hexane, 10.25 mL, 25 mmol). A soln of $CuBr \cdot Me_2S$[38] (5.66 g, 27.5 mmol) in 75 mL Me_2S was then added dropwise over 0.75 hr and the resulting mixture was stirred at 0° for 1 hr. Hydrocinnamyl chloride (4.80 g, 29 mmol) was then added and the mixture was stirred at 25° for 12 hr. The resulting mixture was then diluted with ether and satd NH_4Cl aq (adjusted to pH 8 with NH_4OH) and stirred vigorously for 0.25 hr. The organic phase was separated and washed with pH 8 satd NH_4Cl aq until the extracts were no longer blue. The combined aqueous layers were backextracted with ether, and the combined organic phases were then washed with water and satd NaCl solution, dried over Na_2SO_4, filtered, and concentrated to afford 6.54 g of **3b** as a yellow oil used in the next step without purification.

[1-(2-Phenylethyl)-3-(trimethylsilyl)-2-propynylidene]-4-methyl benzenesulfonyl hydrazide (**4b**). A soln of crude **3b** (6.5 g) and *p*-toluenesulfonylhydrazine (5.1 g, 28 mmol) in 50 mL diethyl ether was stirred at 25° for 14 d. Concentration and recrystallization from 95% EtOH afforded 8.1 g (81%)[39] of **4b** as white crystals: m.p. 105.5–107°; IR (CH_2Cl_2)3260, 3055, 3030, 1600, 1495, 1450, 1385, 1340, 1280, 1245, 1185, 1165, 1080, 1060, 920, 840, and 805 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.22 (s, 9 H), 2.40 (s, 3 H), 2.72 (m, 4 H), 7.16 (br s, 5 H), 7.55 (AB, 4 H), and 8.27 (s, 1 H).

1-(2-Phenylethyl)-3-(trimethylsilyl)allene (**6b**). The tosylhy-

drazone **4b** (8.0 g, 20 mmol) was reduced with sodium cyanoborohydride (10.0 g, 160 mmol) in 100 mL of 1 : 1 DMF-sulfolane as described for the preparation of **6a** except that hexane was substituted for pentane, and the reaction was carried out at (bath temp) 50° for 9 hr (addition of 1 mL conc HCl at 2 hr intervals), and then at 50° for 16 hr and 90° for 20 hr. Column chromatography on silica gel (elution with hexane) afforded 3.02 g (69%)[40] of **6b** as a colorless oil: IR (tf) 3085, 3060, 3025, 2950, 2850, 1940, 1605, 1495, 1450, 1245, 860, 840, 760, 755, 745, and 700 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 2.3–2.4 (m, 2 H), 2.77 (t, 2 H, J = 7.6), 4.88 (q, 1 H, J = 6.7), 4.99 (dt, 1 H, J = 3.7, 6.7), and 7.3 (m, 5 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 209.9, 141.9, 128.4, 128.3, 125.8, 83.0, 82.8, 36.0, 29.7, and −1.0; MS *m/e* 216 (M^+).

General procedure for TMS-cyclopentene annulation

3-Acetyl-2-methyl-1-(trimethylsilyl)cyclopentene (**7**). To a soln of methyl vinyl ketone (2.24 g, 32 mmol) and 1-methyl-1-(trimethylsilyl)allene (4.04 g, 32 mmol) in 150 mL CH_2Cl_2 at −78° was added dropwise over 5 min $TiCl_4$ (5.28 mL, 48 mmol). The resulting red soln was stirred at −78° for 1 hr and then transferred over 2 min by cannula into a flask containing 800 mL of a rapidly stirred 1 : 1 mixture of diethyl ether and water. The aqueous phase was separated and extracted with ether, and the combined organic layers were then washed with satd NaCl aq, dried over Na_2SO_4, filtered, and concentrated to afford 5.69 g of a yellow oil. Column chromatography on silica gel (elution with THF–hexane) gave 4.5 g (71%) of **7** as a colorless oil: IR (tf) 2957, 2908, 2850, 1708, 1615, 1350, 1250, 1160, 1065, 835, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.67 (dt, 3 H, J = 1.1, 2.1), 2.00 (s, 3 H), 1.79–2.08 (m, 2 H), 2.33–2.58 (m, 2 H) and 3.39 (br t, 1 H, J = 7.0); an exact mass determination gave *m/e* 196.1284 (Calc. for $C_{11}H_{20}OSi$: 196.1283).

3 - Benzoyl - 2 - isopropyl - 1 - (trimethylsilyl)cyclopentene (**8**). Reaction of 1-phenyl-2-propen-1-one (0.132 g, 1.00 mmol) with 1-isopropyl-1-(trimethylsilyl)allene[4a] (0.232 g, 1.50 mmol) and $TiCl_4$ (0.286 g, 1.50 mmol) in 4 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure furnished 0.209 g (73%) of **8** as a colorless oil: IR (tf) 3085, 3060, 3025, 2955, 2860, 2840, 1680, 1600, 1595, 1580, 1465, 1445, 1330, 1245, 1205, 1070, 990, 910, 845, 830, 750, 710, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 0.78 (d, 3 H, J = 7.0), 0.99 (d, 3 H, J = 7.0), 1.86–1.96 (m, 1 H), 2.03–2.19 (m, 1 H), 2.39 (ddd, 1 H, J = 2.6, 8.5, 15.8), 2.49–2.63 (m, 1 H), 2.88 (sept, 1 H, J = 7.0), 4.52 (dm, 1 H, J = 9.9), 7.39–7.54 (m, 3 H), and 7.96–8.0 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 202.0, 157.7, 138.8, 137.1, 132.5, 128.4, 128.3, 53.2, 36.6, 31.1, 30.6, 22.2, and −0.4; an exact mass determination gave *m/e* 286.1753 (Calc. for $C_{18}H_{26}OSi$: 286.1753).

3 - Acetyl - 2,5,5 - trimethyl - 1 - (trimethylsilyl)cyclopentene (**9**). Reaction of methyl vinyl ketone (0.035 g, 0.50 mmol) with 1,1,3-trimethyl-3-(trimethylsilyl)allene (0.085 g, 0.55 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure provided 0.090 g (80%) of **9** as a colorless oil: IR (tf) 2955, 2900, 2865, 1710, 1595, 1360, 1245, 1160, 1120, 1000, 830, 755, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 1.03 (s, 3 H), 1.14 (s, 3 H), 1.70 (dd, 1 H, J = 8.9, 12.9), 1.71 (d, 3 H, J = 1.3), 1.88 (dd, 1 H, J = 8.9, 12.9), 2.09 (s, 3 H), and 3.51 (br t, 1 H, J = 8.9).

3 - (2' - Methyl - 3' - trimethylsilyl - 2' - cyclopentene - 1' - yl) - 2 - cyclohexen-1-one (**10**). Reaction of 3-vinyl-2-cyclohexen-1-one[41] (0.249 g, 2.0 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.353 g, 2.8 mmol) and $TiCl_4$ (0.33 mL, 3.0 mmol) in 8 mL of CH_2Cl_2 at −20° for 1 hr according to the general procedure gave 0.327 g (66%) of **10** as a colorless oil: IR (tf) 2950, 2865, 1670, 1610, 1455, 1425, 1415, 1370, 1345, 1245, 1190, 1130, 1065, 1005, 965, 885, 835, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 1.65 (dt, 3 H, J = 1.1, 2.2), 1.7–2.3 (m, 6 H), 2.3–2.5 (m, 4 H), 3.3 (m, 1 H), and 5.84 (s, 1 H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 200.1, 168.7, 147.9, 138.5, 125.8, 61.1, 37.6, 37.3, 29.9, 26.6, 22.9, 15.5, and −0.8; an exact mass determination gave *m/e* 248.1613 (Calc. for $C_{15}H_{24}OSi$: 248.1596).

2-Acetyl - 3,5,5 - trimethyl - 4 - trimethylsilyl - 1,3 - cyclopentadiene (**11**). Reaction of 3-butyn-2-one (0.034 g, 0.50 mmol) with 1,1,3-trimethyl-3-(trimethylsilyl)allene (0.077 g, 0.50 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure afforded 0.059 g (53%) of **11** as a pale yellow oil: IR (tf) 2960, 2925, 2895, 2835, 1725, 1595, 1380, 1365, 1330, 1255, 1250, 1190, 1160, 1050, 1000, 935, 925, 900, 835, 760, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.23 (s, 9 H), 1.23 (s, 6 H), 2.20 (s, 3 H), 2.37 (s, 3 H), and 7.07 (s, 1 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 197.3, 161.9, 150.9, 147.0, 142.3, 55.9, 28.3, 21.9, 16.5, and 1.1; an exact mass determination gave *m/e* 222.1443 (Calc. for $C_{13}H_{22}OSi$: 222.1440).

2 - Methyl - 3 - (trimethylsilyl)spiro[2 - cyclopentene - 1,2' - α - tetralone] (**12**). Reaction of 2-methylene-α-tetralone[42] (0.140 g, 0.88 mmol, *ca.* 95% pure) with 1-methyl-1-(trimethylsilyl)allene (0.166 g, 1.32 mmol) and $TiCl_4$ (0.250 g, 1.32 mmol) in 4 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure furnished 0.201 g (80–84%) of **12** as a colorless oil: IR (tf) 3060, 3020, 2950, 2915, 2850, 1675, 1615, 1600, 1450, 1375, 1350, 1305, 1280, 1245, 1225, 1155, 1115, 1070, 1020, 975, 925, 900, 830, 750, 735, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 1.67 (t, 3 H, J = 2.0), 1.82 (ddd, 1 H, J = 3.0, 4.6, 13.2), 1.9–2.06 (m, 2 H), 2.26–2.4 (m, 3 H), 2.90 (ddd, 1 H, J = 3.0, 4.6, 16.9), 3.12 (ddd, 1 H, J = 4.6, 12.4, 16.9), 7.21 (d, 1 H, J = 7.8), 7.28 (dd, 1 H, J = 7.5, 7.8), 7.43 (ddd, 1 H, J = 1.3, 7.5, 7.8), and 8.02 (dd, 1 H J = 1.3, 7.8); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 200.7, 150.7, 143.6, 137.5, 133.0, 132.3, 128.5, 127.8, 126.6, 64.9, 34.8, 33.7, 31.7, 26.5, 14.1, −0.6; an exact mass determination gave *m/e* 284.1578 (Calc. for $C_{18}H_{24}OSi$: 284.1596).

2-Isopropylidenecyclohexanone. A suspension of 2-(1-hydroxy-1-methylethyl)cyclohexanone[43] (0.340 g, 2.2 mmol), *p*-toluenesulfonic acid monohydrate (0.170 g, 0.9 mmol) and powdered 3Å molecular sieves (0.340 g) in 4 mL of benzene was heated at 50° for 1 hr. The mixture was allowed to cool to room temp, filtered through celite, and washed with satd $NaHCO_3$ aq and NaCl aq, dried over Na_2SO_4, filtered, and concentrated to afford 0.260 g of a pale yellow oil. Column chromatography on silica gel (elution with ether-pentane) gave 0.230 g (77%) of 2-isopropylidenecyclohexanone as a colorless oil with spectral data identical to that previously reported.

1,4,4 - Trimethyl - 2 - (trimethylsilyl)spiro[4.5]dec - 1 - en - 6 - one (**13**). Reaction of 2-isopropylidenecyclohexanone (0.095 g, 0.69 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.173 g, 1.37 mmol) and $TiCl_4$ (0.197 g, 1.03 mmol) in 2 mL CH_2Cl_2 at 25° for 1 hr according to the general procedure afforded 0.157 g (86%) of **13** as a colorless oil: IR (tf) 2955, 2870, 2840, 1700, 1620, 1470, 1450, 1425, 1370, 1315, 1290, 1250, 1210, 1070, 890, 860, 835, 750 and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 0.83 (s, 3 H), 1.25 (s, 3 H), 1.67 (t, 3 H, J = 1.6), and 1.6–2.5 (m, 10 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 212.0, 152.2, 133.9, 71.0, 51.6, 44.4, 42.7, 30.6, 27.1, 25.9, 25.7, 21.9, 15.2, and −0.8; an exact mass determination gave *m/e* 264.1913 (Calc. for $C_{16}H_{28}OSi$: 264.1909).

3 - Acetyl - 2,4,4 - trimethyl - 1 - (trimethylsilyl)cyclopentene (**14**). Reaction of mesityl oxide (0.049 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.126 g, 1.0 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL CH_2Cl_2 at 25° for 1 hr according to the general procedure provided 0.073 g (65%) of **14** as a colorless oil: IR (tf) 2955, 2925, 2900, 2870, 2840, 1705, 1615, 1365, 1355, 1250, 1160, 1070, 1035, 835, 750, and 690 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.99(s, 3 H), 1.11 (s, 3 H), 1.72 (ddd, 3 H, J = 0.7, 1.8, 2.6), 2.04 (s, 3 H), 2.2–2.3 (m, 1 H), 2.43 (dquin, 1 H, J = 2.2, 15.8), and 3.01 (br s, 1 H); an exact mass determination gave *m/e* 224.1596 (Calc. for $C_{13}H_{24}OSi$: 224.1596).

3 - Acetyl - 2,4,4,5,5 - pentamethyl - 1 - (trimethylsilyl)cyclopentene (**15**) and *4,4,5,5-tetramethyl-6-octyn-2-one* (**18**). Reaction of mesityl oxide (0.049 g, 0.50 mmol) with 1,1,3-trimethyl-3-(trimethylsilyl)allene (0.154 g, 1.0 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL of CH_2Cl_2 at 25° for 1 hr according to the general procedure afforded 0.104 g of a yellow oil. Preparative thin layer chromatography (elution with ether–pentane) gave 0.008 g (7%) of **15** and 0.023 g (25%) of **18** as colorless oils. For **15**: IR (tf) 2960, 2950, 2905, 2865, 1705, 1595, 1465, 1445, 1390, 1370, 1365, 1350, 1260, 1245, 1180, 1160, 1035, 995, 960, 935, 835, 755, 675 and 660 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 0.73 (s, 3 H), 0.86 (s, 3 H), 0.90 (s, 3 H), 1.03 (s, 3 H), 1.70 (d, 3 H, J = 1.1), 2.12 (s, 3 H), and 3.40 (br s, 1 H); an exact mass

determination gave 252.1907 (calc. for $C_{15}H_{28}OSi$: 252.1909). For **18**: IR (tf) 2970, 2920, 2880, 2855, 1710, 1460, 1390, 1370, 1360, 1350, 1300, 1240, 1200, 1155, 1130 and 1040 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.05 (s, 6 H), 1.11 (s, 6 H), 1.77 (s, 3 H), 2.15 (s, 3 H), and 2.52 (s, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 209.9, 85.6, 76.7, 50.1, 38.9, 33.0, 24.6, 21.7 and 3.5; an exact mass determination gave *m/e* 180.1517 (Calc. for $C_{12}H_{20}O$: 180.1514).

3 - *Carbomethoxy* - 2 - *methyl* - 1 - (*trimethylsilyl*)*cyclopentene* (**16**). Reaction of methyl acrylate (0.043 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.095 g, 0.75 mmol) and $TiCl_4$ (0.190 g, 1.0 mmol) in 2 mL of CH_2Cl_2 at 25° for 13.5 hr according to the general procedure gave 0.052 g (49%) of **16** as a colorless oil: IR (tf) 2950, 2900, 2840, 1735, 1615, 1435, 1245, 1195, 1160, 1070, 1040, 1005, 830, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 1.79 (dt, 3 H, J = 1.1, 1.8), 2.0–2.1 (m, 2 H), 2.3–2.6 (m, 2 H), 3.41 (br t, 1 H, J = 7), and 3.69 (s, 3 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 175.3, 145.5, 138.4, 57.7, 51.5, 37.3, 28.4, 15.7, and −0.7; an exact mass determination gave *m/e* 212.1237 (Calc. for $C_{11}H_{20}O_2Si$: 212.1233).

cis-8-(*Trimethylsilyl*)*bicyclo*[4.3.0]*non*-8-*en*-2-*one* (**17**) and 3-(2-*propynyl*)*cyclohexanone* (**19**). Reaction of 2-cyclohexen-1-one (0.48 g, 0.50 mmol) with (trimethylsilyl)allene (0.084 g, 0.75 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure furnished 0.021 g (19%, *ca* 95% pure) of **17** and 0.020 g (30%) of **19** as pale yellow oils. For **17**: IR (tf) 2950, 2860, 1700, 1635, 1455, 1405, 1310, 1240, 1220, 830, 760, 745, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.6–2.6 (m, 7 H), 2.7–2.9 (m, 1 H), 3.05 (dddd, 1 H, J = 0.8, 2.7, 9.1, 15.9), 3.7 (m, 1 H), and 5.44 (q, 1 H, J = 2.7); an exact mass determination gave 208.1267 (Calc. for $C_{12}H_{20}OSi$: 208.1283). For **19**: IR (tf) 3285, 2930, 2865, 2110, 1710, 1450, 1425, 1345, 1310, 1225, 1055, and 865 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.45–1.75 (m, 2 H) and 1.95–2.5 (m, 10 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 210.6, 81.4, 70.4, 47.0, 41.0, 37.8, 30.3, 25.4, and 24.8; an exact mass determination gave *m/e* 136.0884 (Calc. for $C_9H_{12}O$: 136.0888).

5-*Nitromethyl*-7-*phenyl*-2-*heptyne* (**21**). Reaction of 1-nitro-4-phenyl-1-butene (0.177 g, 1.0 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.253 g, 2.0 mmol) and $TiCl_4$ (0.570 g, 3.0 mmol) in 4 mL CH_2Cl_2 at −78° for 15 min according to the general procedure provided 0.133 g (58%) of **21** as a colorless oil: IR (tf) 3090, 3065, 3030, 2925, 2765, 1605, 1550, 1495, 1455, 1435, 1380, 1355, 1195, 1030, 745, and 700 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.78 (t, 3 H, J = 2.4), 1.65–1.85 (m, 2 H), 2.3–2.45 (m, 3 H), 2.5–2.75 (m, 2 H), 4.35 (dd, 1 H, J = 5.9, 12.5), 4.51 (dd, 1 H, J = 7.0, 12.5), and 7.15–7.3 (m, 5 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 141.5, 128.6, 128.4, 126.2, 78.7, 74.5, 36.4, 32.7, 32.6, 20.9, and 3.3; an exact mass determination gave *m/e* 231.1256 (Calc. for $C_{14}H_{17}NO_2$: 231.1259).

trans - 3 - *Acetyl* - 2,4 - *dimethyl* - 1 - (*trimethylsilyl*) *cyclopentene* (**22**). Reaction of *E*-3-penten-2-one (90%, 0.042 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.063 g, 0.50 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure gave 0.075 g (79%) of **22** as a colorless oil: IR (tf) 2960, 2915, 2875, 2845, 1705, 1615, 1355, 1250, 1210, 1160, 1065, 1030, 830, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9 H), 0.99 (d, 3 H, J = 7.0), 1.65 (br s, 3 H), 2.02 (s, 3 H), 1.95–2.05 (m, 1 H), 2.25–2.4 (m, 1 H), 2.70 (ddquin, 1 H, J = 2.2, 8.1, 16.1), and 3.02 (br d, 1 H, J = 4.6); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 210.9, 145.4, 138.3, 75.4, 46.1, 36.8, 27.3, 21.4, 16.2, and −0.8; an exact mass determination gave *m/e* 210.1439 (Calc. for $C_{12}H_{22}OSi$: 210.1440).

E-3-*Methyl*-3-*penten*-2-*one*. To a soln of *E*-2-methyl-2-butenoic acid (7.12 g, 71.1 mmol) in 130 mL of THF at 0° was added dropwise over 2 hr MeLi soln (1.32 M in ether, 130 mL, 158 mmol). The resulting soln was stirred at 0° for 3.5 hr and then transferred dropwise *via* cannula over 2.3 hr to a soln of 250 mL of 0.4 M HCl maintained at 0°. The aqueous phase was satd with NaCl and extracted with ether. The combined organic layers were washed with satd NaCl aq, dried over Na_2SO_4, filtered, and the solvent was removed by distillation through an 18 in vigreux column. Distillation provided 4.8 g (69%) of *E*-3-methyl-3-penten-2-one as a colorless oil, b.p. 45–47° (29 torr) with spectral data identical to that previously reported.[44]

trans - 3 - *Acetyl* - 2,3,4 - *trimethyl* - 1 - (*trimethylsilyl*)*cyclopent* - *ene* (**23**). Reaction of *E*-methyl-3-penten-2-one (0.049 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.063 g, 0.5 mmol) and $TiCl_4$ (0.082 mL, 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure afforded 0.080 g (71%) of **23** as a colorless oil: IR (tf) 2955, 2915, 2840, 1700, 1610, 1445, 1380, 1350, 1250, 1160, 1100, 835, 750, and 690 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.91 (d, 3 H, J = 7), 0.95 (s, 3 H), 1.63 (br t, 3 H), 1.97–2.08 (m, 1 H), 2.08 (s, 3 H), and 2.4–2.65 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 212.7, 152.2, 137.2, 69.2, 44.3, 40.4, 25.5, 14.6, 14.3, 13.2, and −0.8; an exact mass determination gave *m/e* 224. (Calc. for $C_{13}H_{24}OSi$: 224.1596).

Z-3-*Methyl*-3-*penten*-2-*one*. To a soln of *Z*-2-methyl-2-butenoic acid (0.510 g, 5.1 mmol) in 16 mL diethyl ether at 0° was added dropwise over 0.25 hr MeLi soln (1.32 M in ether, 8.45 mL, 11.2 mmol). The resulting soln was stirred at 0° for 2 hr and then transferred dropwise *via* cannula over 50 min to 20 mL of 0.4 M HCl maintained at 0°. The aqueous phase was separated and extracted with ether, and the combined organic layers were washed with satd NaCl aq, dried over Na_2SO_4, filtered, and the solvent was removed by careful distillation through a 6 in vigreux column. Kugelrohr distillation (50–60°, 30 torr) provided 0.291 g (58%) of *Z*-3-methyl-3-penten-2-one[44a] as a colorless oil: IR (tf) 2960, 2920, 1680, 1620, 1490, 1355, 1230, 1140, and 820 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.86–1.93 (m, 6 H), 2.26 (s, 3 H), and 5.85 (qq, 1 H, J = 1.3, 7.4); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 202.6, 136.2, 133.4, 29.9, 20.7, and 15.5.

cis-3-*Acetyl*-2,3,4 - *trimethyl* - 1 - (*trimethylsilyl*)*cyclopentene* (**24**). Reaction of *Z*-3-methyl-3-penten-2-one (0.049 g, 0.5 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.077 g, 0.61 mmol) and $TiCl_4$ (0.082 mL, 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure furnished 0.070 g (68%) of a 13–19 : 1 mixture of **24** and **23** as a colorless oil. For **24**: IR (tf) 2960, 2935, 2905, 2840, 1700, 1610, 1450, 1380, 1350, 1250, 1210, 1160, 1105, 835, 755, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 0.93 (d, 3 H, J = 7.0), 1.11 (s, 3 H), 1.64 (br t, 3 H), 1.98 (s, 3 H), 2.04–2.24 (m, 2 H), and 2.67 (ddq, 1 H, J = 1.5, 7.4, 13.6); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 212.3, 152.7, 138.8, 69.5, 45.4, 44.4, 28.3, 20.9, 14.7, and −0.9; an exact mass determination gave *m/e* 224.1 (Calc. for $C_{13}H_{24}OSi$: 224.1596).

cis-6-*Acetyl*-7-*methyl*-8-(*trimethylsilyl*)*bicyclo*[4.3.0]*non*-7-*ene* (**25**). Reaction of 1-acetylcyclohexene (0.062 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.076 g, 0.60 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure provided 0.114 g (91%) of **25** as a colorless oil: IR (tf) 2965, 2855, 1700, 1605, 1450, 1345, 1245, 1150, 830, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9 H), 1.04–1.2 (m 1 H), 1.2–1.45 (m, 6 H), 1.59 (dd, 3 H, J = 1.9, 2.2), 2.02 (s, 3 H), 2.0–2.1 (m, 1 H), 2.16 (ddq, 1 H, J = 2.2, 7.8, 15.6), 2.37 (ddq, 1 H, J = 1.9, 7.4, 15.6), and 2.5–2.6 (m, 1 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 212.2, 152.5, 137.5, 68.7, 41.7, 41.0, 28.0, 27.1, 26.4, 22.2, 21.8, 14.4, and −0.6; an exact mass determination gave *m/e* 250.1777 (Calc. for $C_{15}H_{26}OSi$: 250.1753).

cis-8-*Methyl*-7(*trimethylsilyl*)*bicyclo*[3.3.0] - *oct* - 7 - *en* - 2 - *one* (**26**). Reaction of 2-cyclopenten-1-one (0.041 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.063 g, 0.50 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL CH_2Cl_2 at −20° for 2 hr according to the general procedure afforded 0.050 g (48%) of **26** as a colorless oil: IR (tf) 2960, 2915, 2895, 2845, 1735, 1615, 1445, 1410, 1380, 1245, 1210, 1145, 1050, 1010, 830, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9 H), 1.45–1.6 (m, 1 H), 1.79 (dt, 3 H, J = 1.1, 2.2), 2.0–2.3 (m, 4 H), 2.70 (ddquin, 1 H, J = 2.3, 8.1, 16.4), 2.83–2.96 (m, 1 H), 3.10 (br d, 1 H, J = 8.1); an exact mass determination gave *m/e* 208.1289 (Calc. for $C_{12}H_{20}OSi$: 208.1283).

cis-9-*Methyl*-8-(*trimethylsilyl*) *bicyclo*[4.3.0]*non*-8-*en*-2 - *one* (**27**). Reaction of 2-cyclohexen-1-one (0.048 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.095 g, 0.75 mmol) and $TiCl_4$ (0.143 g, 0.75 mol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure gave 0.094 g (85%) of **27** as a colorless oil: IR (tf) 2950, 2925, 2855, 1705, 1610, 1445, 1245, 1215, 1200, 1070, 1055, 1010, 830, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9 H), 1.3–1.45 (m, 1 H), 1.5–1.7 (m, 2 H), 1.66 (m, 3 H), 1.75–1.9 (m, 1 H), 2.0–2.15 (m, 2 H), 2.2–2.35 (m, 1 H), 2.4–2.45

(m, 1 H), 2.5–2.62 (m, 1 H), and 3.18 (br d, 1 H, J = 6.2); an exact mass determination gave *m/e* 222.1416 (Calc. for $C_{13}H_{22}OSi$: 222.1440).

cis - 9 - *Isopropyl* - 8 - (*trimethylsilyl*)*bicyclo*[4.3.0]*non* - 8 - *en* 2-*one* (**28**). Reaction of 2-cyclohexen-1-one (0.096 g, 1.0 mmol) with 1-isopropyl-1-(trimethylsilyl)allene (0.232 g, 1.5 mmol) and $TiCl_4$ (0.286 g, 1.5 mmol) in 4 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure furnished 0.212 g (85%) of **28** as a colorless oil: IR (tf) 2955, 2925, 2865, 1700, 1590, 1455, 1445, 1360, 1310, 1250, 1225, 1055, 1020, 865, 835, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.03 (s, 9 H), 0.86 (d, 3 H, J = 7.0), 0.96 (d, 3 H, J = 7.0), 1.37–1.63 (m, 3 H), 1.75–1.85 (m, 1 H), 2.03 (ddd, 1 H, J = 1.9, 2.7, 15.6), 2.2–2.4 (m, 3 H), 2.45–2.55 (m, 1 H), 2.79 (sept, 1 H, J = 7.0), and 3.37 (br d, 1 H, J = 7.3); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 214.6, 156.7, 136.5, 61.6, 43.0, 42.5, 41.3, 31.5, 28.6, 24.3, 21.5, 20.4, and −0.6; an exact mass determination gave *m/e* 250.1756 (Calc. for $C_{15}H_{26}OSi$: 250.1753).

cis - 7,7,9 - *Trimethyl* - 8 - (*trimethylsilyl*)*bicyclo*[4.3.0]*non* - 8 - *en* - 2 - *one* (**29**). Reaction of 2-cyclohexen-1-one (0.048 g, 0.5 mmol) with 1,1,3-trimethyl-3-(trimethylsilyl)allene (0.116 g, 0.75 mmol) and $TiCl_4$ (0.143 g. 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure provided 0.079 g (63%) of **29** as a colorless oil: IR (tf) 2950, 2870, 2810, 1705, 1595, 1455, 1445, 1375, 1315, 1245, 1200, 830, 755, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 0.94 (s, 3 H), 1.02 (s, 3 H), 1.27–1.55 (m, 2 H), 1.66 (d, 3 H, J = 1.4), 1.57–1.71 (m, 1 H), 1.85–1.95 (m, 1 H), 1.98–2.13 (m, 2 H), 2.30 (dm, 1 H, J = 14.8), and 3.34 (br d, 1 H, J = 7.0); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 213.7, 145.2, 144.3, 63.6, 53.8, 52.6, 40.9, 26.7, 24.2, 24.0, 23.8, 16.2, and 1.4.

cis - 4 - exo - *Isopropenyl* - 1,9 - *dimethyl* - 8 - (*trimethylsilyl*) *bicyclo*[4.3.0]*non* - 8 - *en* - 2 - *one* (**30**). Reaction of carvone (0.075 g, 0.5 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.095 g, 0.75 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure afforded 0.120 g (87%) of **30** as a colorless oil: IR (tf) 3080, 2950, 2920, 1700, 1640, 1610, 1440, 1375, 1245, 885, 830, 750, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 1.10 (s, 3 H), 1.65 (t, 3 H, J = 2.2), 1.68 (m, 3 H), 1.65–1.72 (m, 2 H), 2.10 (dm, 1 H, J = 12.4), 2.15–2.25 (m, 1 H), 2.27–2.31 (m, 2 H), 2.45–2.57 (m, 2 H), 4.63 (m, 1 H), and 4.72 (m, 1 H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 215.6, 151.5, 147.7, 136.1, 110.4, 64.8, 46.1, 43.9, 42.0, 39.8, 32.4, 21.3, 21.1, 14.4 and −0.7; an exact mass determination gave *m/e* 276.1891 (Calc. for $C_{17}H_{28}OSi$: 276.1909).

10 - *Methyl* - 9 - (*trimethylsilyl*)*bicyclo*[5.3.0]*dec* - 9 - *en* - 2 - *one* (**31a,b**). Reaction of 2-cyclohepten-1-one (0.055 g, 0.50 mmol) with 1-methyl-1-(trimethylsilyl)allene (0.095 g, 0.75 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure produced 0.111 g (94%) of an inseparable mixture of **31a** and **31b** as a colorless oil: IR (tf) 2950, 2925, 2860, 1705, 1450, 1325, 1245, 1065, 845, 830, 750, and 685 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.04 (s, 9 H, **31b**), 0.06 (s, 9 H, **31a**), 1.36–1.63 (m, 1 H), 1.62 (br s, 7 H, **31b**), 1.64 (br s, 7 H, **31a**), 1.8–2.04 (m, 1 H), 2.1–2.36 (m, 3 H), 2.43–2.65 (m, 2 H), 3.60 (br d, 1 H, **31a**, J = 9.1), and 3.68 (br d, 1 H, **31b**, J = 9.6); an exact mass determination gave *m/e* 236.1568 (Calc. for $C_{14}H_{24}OSi$: 236.1596).

cis - 7 - *Ethyl* - 9 - *methyl* - 8 - (*trimethylsilyl*)*bicyclo*[4.3.0]*non* - 8 - *en* - 2 - *one* (**32a,b**). Reaction of 2-cyclohexen-1-one (0.048 g, 0.50 mmol) with 1-ethyl-3-methyl-3-(trimethylsilyl)allene (0.077 g, 0.50 mmol) and $TiCl_4$ (0.143 g, 0.75 mmol) in 2 mL CH_2Cl_2 at −78° for 1 hr according to the general procedure gave 0.099 g (79%) of an inseparable mixture of **32a** and **32b** as a colorless oil: IR (tf) 2950, 2890, 2865, 1700, 1590, 1455, 1445, 1380, 1360, 1315, 1245, 1230, 1170, 1140, 990, 830, 755, and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.10 (s, 9 H, **32a**), 0.11 (s, **32b**), 0.82 (t, 3 H, **32b**, J = 7.0). 0.84 (t, 3 H, **32a**, J = 7.0), 1.2–1.41 (m, 2 H), 1.64 (br s, 3 H), 1.43–1.75 (m, 3 H), 1.85–2.1 (m, 2 H), 2.30 (dm, 1 H, J = 14.7), 2.46–2.63 (m, 2 H), 3.07 (br d, 1 H, **32a**, J = 6.3), and 3.33 (br d, 1 H, **32b**, J = 6.7).

cis-6,8-*Dimethyl*-7-(*trimethylsilyl*)*bicyclo*[3.3.0] *oct*-7-*en*-2-*one* (**33a,b**). Reaction of 2-cyclopenten-1-one (0.840 g, 10.0 mmol) with 1,3-dimethyl-1-(trimethylsilyl)allene (2.12 g, 15.0 mmol) and $TiCl_4$ (2.88 g, 15.0 mmol) in 40 mL CH_2Cl_2 at −78° for 3 hr according to the general procedure furnished 1.51 g (68%) of an inseparable mixture of **33a** and **33b** as a colorless oil: IR (tf) 2950, 2870, 1730, 1600, 1450, 1405, 1370, 1245, 1145, 830, 750 and 680 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.10 (s, 9 H, **33a**), 0.12 (s, 9 H, **33b**), 0.96 (d, 3 H, **33a**, J = 7.0), 1.07 (d, 3 H, **33b**, J = 7.3), 1.4–3.0 (m, 6 H), 1.8 (m, 3 H), 3.03 (br d, 1 H, **33b**, J = 7.8) and 3.20 (br d, 1 H, **33a**, J = 7.3); ^{13}C NMR (22.5 MHz, $CDCl_3$): for **33a**: δ 217.9, 143.5, 143.0, 64.8, 52.2, 48.2, 38.2, 27.8, 21.7, 15.3 and 0.45, for **33b**: δ 218.5, 144.0, 143.5, 65.0, 48.0, 44.2, 38.4, 21.8, 15.4, 15.2 and 0.50; an exact mass determination gave *m/e* 221.1425 (Calc. for $C_{13}H_{22}OSi$: 222.1440).

3 - *Acetyl* - 2,4,5 - *trimethyl* - 1 - (*trimethylsilyl*)*cyclopentene* (**34a,b**). Reaction of *E*-3-penten-2-one (90% pure, 0.084 g, 1.0 mmol) with 1,3-dimethyl-1-(trimethylsilyl)allene (0.140 g, 1.0 mmol) and $TiCl_4$ (0.286 g, 1.50 mmol) in 4 mL of CH_2Cl_2 at −78° for 1 hr according to the general procedure provided 0.165 g (82%) of **34a,b** as a colorless oil: IR (tf) 2965, 2930, 2880, 1715, 1610, 1450, 1380, 1355, 1250, 1210, 1165, 1090, 1025, 840, 760, and 690 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) for **34a**: δ 0.11(s, 9 H), 0.78 (d, 3 H, J = 7.0), 0.95 (d, 3 H, J = 7.0), 1.66 (br s, 3 H), 2.09 (s, 3 H), 2.43 (dquin, 1 H, J = 7.0, 10.3), 2.72 (quin, 1 H, J = 7.0), and 3.22 (d, 1 H, J = 10.3); for **34b**: δ 0.12 (s, 9 H), 1.03 (d, 3 H, J = 7.0), 1.04 (d, 3 H, J = 7.0), 1.68 (m, 3 H), 1.76–1.87 (m, 1 H), 2.11 (s, 3 H), 2.25–2.34 (m, 1 H), and 3.03 (d, 1 H, J = 5.9); ^{13}C NMR (22.5 MHz, $CDCl_3$) for **34a**: δ 211.6, 145.9, 71.2, 47.1, 41.8, 28.2, 16.1, 14.7, 14.1, and −0.3; for **34b**: δ 210.6, 145.0, 143.2, 74.2, 53.7, 45.3, 28.2, 21.5, 20.6, 16.5, and 0.1; an exact mass determination gave *m/e* 224.1600 (Calc. for $C_{13}H_{24}OSi$: 224.1596).

General procedure for desilylation and isomerization-method A

1-*Acetyl*-2-*methylcyclopentene* (**35**). A soln of **7** (0.118 g, 0.6 mmol) and anhyd K_2CO_3 (0.042 g, 0.3 mmol) in 3 mL MeOH was stirred at 25° for 9 hr. The mixture was then diluted with water and extracted with diethyl ether. The combined organic phases were washed with satd NaCl aq, dried over $MgSO_4$, filtered, and concentrated to afford 0.099 g of a yellow oil. Column chromatography on silica gel (elution with ether–pentane) gave 0.051 g (68%) of **35** as a colorless oil: semicarbazone m.p. 220–220.5° (lit.[16] 220–221°); IR (tf) 2945, 2910, 2845, 1675, 1650, 1610, 1430, 1355, 1300, 1255, 1210, 1015 and 960 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.80 (quin, 2 H, J = 7.5), 2.06 (m, 3 H), 2.22 (s, 3 H), 2.48 (br t, 2H, J = 7.5), and 2.64 (m, 2 H).

1-*Benzoyl*-2-*isopropylcyclopentene* (**36**). Reaction of **8** (0.175 g, 0.61 mmol) and K_2CO_3 (0.252 g, 1.83 mmol) in 5 mL MeOH at 25° for 14 d according to procedure A provided 0.089 g (68%) of an 89 : 11 mixture of **36** and 3-benzoyl-2-isopropylcyclopentene: for **36**: IR (tf) 3075, 3055, 3020, 2960, 2865, 1640, 1595, 1575, 1455, 1445, 1335, 1260, 1230, 1170, 1020, 1000, 885, 830, 785, 705 and 690 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.93 (d, 6 H, J = 6.7), 1.88 (quin, 2 H, J = 7.3), 2.45–2.52 (m, 2 H), 2.59–2.71 (m, 3 H), 7.37–7.53 (m, 3 H), and 7.75–7.79 (m, 2 H); an exact mass determination gave *m/e* 214.1350 (Calc. for $C_{15}H_{18}O$: 214.1358).

General procedure for desilylation-method B

1-*Acetyl*-2,4,4-*trimethylcyclopentene* (**37**). A soln of **9** (0.085 g, 0.38 mmol) and 0.2 mL of 48% HF in 2 mL MeCN was stirred at 25° for 48 hr. The mixture was diluted with water and extracted with ether. The combined organic phases were washed with satd NaCl aq, dried over Na_2SO_4, filtered, and concentrated to afford 0.074 g of a yellow oil. Column chromatography on silica gel (elution with THF–hexane) gave 0.038 g (66%) of **37** as a colorless oil: IR (tf) 2950, 2920, 2900, 2860, 1675, 1650, 1610, 1460, 1425, 1360, 1240, and 1215 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.04 (s, 6 H), 2.01 (m, 3 H), 2.17 (s, 3 H), 2.27 (m, 2 H), and 2.43 (m, 2 H); an exact mass determination gave *m/e* 152.1182 (Calc. for $C_{10}H_{16}O$: 152.1201).

1-*Acetyl*-2,5-*dimethylcyclopentene* (**38**). Reaction of **22** (0.059 g, 0.28 mmol) and K_2CO_3 (0.040 g, 0.28 mmol) in 2 mL MeOH at 25° for 23 hr according to procedure A gave 0.025 g (64%) of **38** as a pale yellow oil: IR (tf) 2950, 2860, 2830, 1670, 1650, 1610, 1450, 1430, 1355, 1245, 1210, and 1115 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.04 (d, 3 H, J = 7.0), 1.3–1.45 (m, 1 H), 2.0 (br s, 3 H), 1.95–2.1 (m, 1 H), 2.24 (s, 3 H), 2.2–2.38 (m, 1 H), 2.5–2.6 (m, 1 H), and 3.07 (br s, 1 H); an exact mass determination gave *m/e* 138.1052 (Calc. for $C_9H_{14}O$: 138.1045).

cis-6-*Acetyl*-7-*methylbicyclo*[4.3.0]*non*-7-*ene* (**39**). Reaction of **25** (0.132 g, 0.53 mmol) with 0.13 mL 48% HF in 2.5 mL MeCN at 25° for 16 hr according to procedure B furnished 0.090 g (96%) of **39** as a colorless oil: IR (tf) 3030, 2925, 2845, 1700, 1440, 1375, 1345, 1220, 1190, 1145, and 1005 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.2–1.5 (m, 7 H), 1.60 (br s, 3 H), 2.10 (s, 3 H), 2.07–2.18 (m, 2 H), 2.3–2.45 (m, 1 H), 2.6–2.73 (m, 1 H), and 5.52 (br s, 1 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 211.8, 143.7, 127.2, 65.0, 41.2, 35.7, 27.6, 27.3, 26.0, 21.6, 21.5, and 13.7; an exact mass determination gave *m/e* 178.1368 (Calc. for $C_{12}H_{18}O$: 178.1358).

9-*Methylbicyclo*[4.3.0]*non*-9(1)-*en*-2-*one* (**40**). Reaction of **27** (0.083 g, 0.37 mmol) with K_2CO_3 (0.026 g, 0.19 mmol) in 2.5 mL MeOH at 25° for 2.5 hr according to procedure A provided 0.048 g (86%) of **40**[45] as a colorless oil: IR (tf) 2925, 2860, 1675, 1615, 1450, 1430, 1370, 1340, 1320, 1260, 1240, 1175, 1105, 940 and 800 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.12–1.29 (m, 1 H), 1.33–1.5 (m, 1 H), 1.6–1.8 (m, 1 H), 1.87–2.28 (m, 5 H), 2.02 (br s, 3 H), 2.32–2.48 (m, 2 H), and 2.81 (m, 1 H); an exact mass determination gave *m/e* 150.1019 (Calc. for $C_{10}H_{14}O$: 150.1045).

9-*Isopropylbicyclo*[4.3.0]*non*-9(1)-*en*-2-*one* (**41**). Reaction of **28** (0.184 g, 0.73 mmol) with K_2CO_3 (0.153 g, 1.1 mmol) in 5 mL MeOH at 25° for 21 hr according to procedure A afforded 0.097 g (75%) of **41** as a colorless oil: IR (tf) 2940, 2860, 1675, 1610, 1460, 1325, 1255, 1175, 1105, and 805 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.99 (d, 3 H, J = 7.0), 1.02 (d, 3 H, J = 7.0), 1.18–1.46 (m, 2 H), 1.64–1.82 (m, 1 H), 1.9–2.5 (m, 7 H), 2.83 (br s, 1 H), and 3.59 (sept, 1 H, J = 7.0); an exact mass determination gave *m/e* 178.1345 (Calc. for $C_{12}H_{18}O$: 178.1358).

7,7,9-*Trimethylbicyclo*[4.3.0]*non*-9(1)-*en*-2-*one* (**42**). Reaction of **29** (0.079 g, 0.32 mmol) with 0.1 mL 48% HF in 2 mL MeCN at 25° for 2.5 hr according to procedure B gave 0.053 g (94%) of **42** as a colorless oil: IR (tf) 2955, 2935, 2865, 2815, 1675, 1615, 1455, 1425, 1360, 1340, 1320, 1265, 1215, 1160, 1120, 955, 920, 890, and 825 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.81 (s, 3 H), 1.07 (s, 3 H), 1.18–1.35 (m, 1 H), 1.52–1.74 (m, 2 H), 1.91–2.01 (m, 2 H), 2.04 (br s, 3 H), 2.08–2.2 (m, 1 H), 2.3–2.42 (m, 2 H), and 2.47–2.57 (m, 1 H); an exact mass determination gave *m/e* 178.1335 (Calc. for $C_{12}H_{18}O$: 178.1358).

10-*Methylbicyclo*[5.3.0]*dec*-10(1)-*en*-2-*one* (**43**). Reaction of **31a,b** (0.080 g, 0.34 mmol) with K_2CO_3 (0.023 g, 0.17 mmol) in 2.5 mL MeOH at 25° for 2.5 hr according to procedure A furnished 0.051 g (91%) of **43** as a colorless oil: IR (tf) 2920, 2860, 1670, 1610, 1445, 1430, 1370, 1320, 1270, 1245, 1180, 1160, and 865 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.19–1.57 (m, 4 H), 1.62–1.96 (m, 3 H), 2.02 (br s, 3 H), 2.03–2.12 (m, 1 H), 2.23–2.54 (m, 4 H), and 2.87 (br m, 1 H); an exact mass determination gave *m/e* 164.1194 (Calc. for $C_{11}H_{16}O$: 164.1201).

7-*Ethyl*-9-*methylbicyclo*[4.3.0]*non*-9(1)-*en*-2-*one* (**44a,b**). Reaction of **32a,b** (0.096 g, 0.38 mmol) with 0.1 mL 48% HF in 2 mL Me_3CN at 25° for 2 hr according to procedure B provided 0.062 g (91%) of **44a,b** as a colorless oil: IR (tf) 2960, 2930, 2865, 2825, 1675, 1620, 1460, 1430, 1370, 1315, 1270, 935, and 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.82 (t, 3 H J = 7.3), 0.9–1.1 (m, 1 H), 1.3–1.5 (m, 2 H), 1.55–1.8 (m, 2 H), 1.9–2.2 (m, 4 H), 2.01 (br s, 3 H), 2.3–2.4 (m, 1 H), 2.5 (br dd, 1 H, J = 7.5, 17), and 2.85–2.98 (m, 1 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 200.6, 151.5, 134.3, 50.0, 43.9, 41.0, 26.0, 24.0, 22.6, 16.2 and 12.2; an exact mass determination gave *m/e* 178.1343 (Calc. for $C_{12}H_{18}O$: 178.1358).

cis-6,8-*Dimethylbicyclo*[3.3.0]*oct*-7-*en*-2-*one* (**45a,b**). Reaction of **33a,b** (1.51 g, 6.80 mmol) with 1.3 mL 48% HF in 25 mL MeCN at 25° for 15 hr according to procedure B provided 0.740 g (92%) of **45a,b** as a colorless oil: IR (tf) 3020, 2945, 2860, 1730, 1640, 1445, 1405, 1370, 1275, 1170, 1140, 1125, 1085, 845, 830 and 810 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.91 (d, 3 H, **45a**, J = 6.7), 0.92 (d, 3 H, **45b**, J = 6.7), 1.61 (br s, 3 H), 1.5–1.77 (m, 1 H), 1.91–2.22 (br s, 3 H), 2.33–2.47 (m, **45a** 1 H, **45b** 2 H), 2.7–2.87 (m, **45a** 1 H), 2.93 (m, 1 H), 5.09 (m, 1 H, **45b**) and 5.19 (m 1 H, **45a**); ^{13}C NMR (62.8 MHz, $CDCl_3$) for **45a**: δ 217.5, 135.3, 132.6, 61.1, 48.2, 46.9, 37.3, 27.3, 20.8 and 14.4, for **45b**: δ 218.2, 135.1, 132.0, 62.3, 43.3, 41.1, 38.9, 22.1, 14.2 and 13.7; an exact mass determination gave *m/e* 150.1046 (Calc. for $C_{10}H_{14}O$: 150.1045).

1-*Acetyl*-2,4,4,8-*tetramethyl*-3,7-*bis*(*trimethylsilyl*)*bicyclo*[3.3.0]*octa*-2,7-*diene* (**46**). To a soln of 3-butyn-2-one (0.034 g, 0.5 mmol) and 1,1,3-trimethyl-3-(trimethylsilyl)allene (0.077 g, 0.5 mmol) in 2.5 mL CH_2Cl_2 at −78° was added rapidly dropwise $TiCl_4$ (0.143 g, 0.75 mmol). The resulting red soln was stirred at −78° for 0.5 hr and then treated with additional $TiCl_4$ (0.143 g, 0.75 mmol) and 1-methyl-1-(trimethylsilyl)allene (0.095 g, 0.75 mmol). The mixture was next stirred at −78° for 1 hr, allowed to warm to −30° over 0.5 hr, and then transferred *via* cannula to a 1:1 mixture of ether and water at 25°. The aqueous phase was separated and extracted with ether, and the combined organic layers were washed with satd NaCl aq, dried over Na_2SO_4, filtered, and concentrated to afford 0.168 g of a yellow oil. Column chromatography on a silica gel (elution with ether–pentane) furnished 0.067 g (38%) of **46** as a yellow oil: IR (tf) 2950, 2920, 2860, 1705, 1610, 1585, 1440, 1405, 1380, 1360, 1350, 1250, 1175, 1160, 1120, 1070, 1025, 840, 750 and 680 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 0.16 (s, 9 H), 0.93 (s, 3 H), 0.99 (s, 3 H), 1.74 (br s, 3 H), 1.80 (s, 3 H), 2.05 (s, 3 H), 2.30–2.33 (m, 2 H) and 2.49 (dd, 1 H, J = 5.2, 7.0); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 212.0, 148.3, 147.1, 146.6, 139.1, 88.5, 61.0, 51.9, 37.9, 30.5, 26.3, 24.2, 16.9, 16.2, 1.4 and −0.7; an exact mass determination gave *m/e* 348.2303 (Calc. for $C_{20}H_{36}OSi_2$: 348.2305).

1,3-*Diacetyl*-2-*methylcyclopentene* (**47**). To a suspension of anhyd $AlCl_3$ (0.770 g, 5.77 mmol) in 15 mL CH_2Cl_2 at 0° was added over 1 min AcCl (0.270 g, 3.46 mmol), and the resulting mixture was stirred at 0° for 3 min and then treated dropwise over 2 min with a soln of **7** (0.453 g, 2.31 mmol) in 5 mL CH_2Cl_2. The mixture was stirred at 0° for 1 hr and then transferred *via* cannula to a mixture of ether and 1 M HCl at 25°. After 10 min the aqueous phase was separated, saturated with NaCl, and extracted with ether. The combined organic layers were washed with satd NaCl aq, dried over Na_2SO_4, filtered, and concentrated to afford 0.413 g of a pale yellow oil. Column chromatography on silica gel (elution with EtOAc–hexane) gave 0.363 g (95%) of **47** as a colorless oil with spectral characteristics identical to that previously reported.

Acknowledgements—We thank the National Science Foundation and Eli Lilly and Co. for generous financial support. We are grateful to James T. Kadonaga and David W. Weinberg for assistance in the preparation of (trimethylsilyl)allenes. Richard J. Auchus carried out early studies on annulations involving carboxylic esters. High resolution mass spectra were provided by the facility supported by National Institutes of Health Grant RR 00317 (Principal investigator Prof. K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

REFERENCES

[1]For reviews of synthetic approaches to 5-membered carbocycles, see: [a]R. A. Ellison, *Synthesis* 397 (1973); [b]T.-L. Ho, *Synth. Commun.* **4**, 265 (1974); [c]J. S. Bindra and R. Bindra, *Prostaglandin Synthesis*. Academic Press, New York (1977); [d]A. Mitra, *The Synthesis of Prostaglandins*. Wiley-Interscience, New York (1977); [e]L. A. Paquette, *Topics Current Chem.* **79**, 41 (1979); [f]M. Ono. *J. Synth. Org. Chem. Japan* **39**, 872 (1981).

[2]Recently developed *single-step* [3 + 2] annulations include: [a]the Noyori α,α'-dibromo ketone cyclocoupling reaction: R. Noyori, *Acc. Chem. Res.* **12**, 61 (1979); R. Noyori, M. Nishizawa, F. Shimizu, Y. Hayakawa, K. Maruoka, S. Hashimoto, H. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.* **101**, 220 (1979); [b][3 + 2] annulations employing cyclopropyl phosphonium salts: P. L. Fuchs, *Ibid.* **96**, 1607 (1974); J. P. Marino and R. C. Landick, *Tetrahedron Letters* 4531 (1975); [c]the cyclopentenone annulation of H.-J. Altenbach, *Angew. Chem.* Int. Ed. **18**, 940 (1979); [d]the Trost methylenecyclopentane annulation: B. M. Trost and D. M. T. Chan, *J. Am. Chem. Soc.* **101**, 6429 (1979); [e]cyclopentenone annulations *via* Nazarov cyclizations: F. Cooke, R. Moerck, J. Schwindeman and P. Magnus, *J. Org. Chem.* **45**, 1046 (1980); M. Santelli, S. Hacini and R. Pardo, *Tetrahedron Lett* 4553 (1979); [f]Little diyl trapping reaction: R. D. Little, G. W. Muller, M. G. Venegas, G. L. Carroll, A. Bukhari, L. Patton and K. Stone, *Tetrahedron* **37**, 4371 (1981) and Refs. cited.

[3]R. L. Danheiser, D. J. Carini and A. Basak, *J. Am. Chem. Soc.* **103**, 1604 (1981).

[4a]H. Westmijze and P. Vermeer, *Synthesis* 390 (1979); see also [b]Y. Tanigawa and S.-I. Murahashi, *J. Org. Chem.* **45**, 4536 (1980) and [c]M. Montury, B. Psaume and J. Goré, *Tetrahedron Lett* **21**, 163 (1980).

[5]R. L. Danheiser and D. J. Carini, *J. Org. Chem.* **45**, 3925 (1980).

[6a]T. B. Patrick, E. C. Haynie and W. J. Probst, *J. Org. Chem.* **37**, 1553 (1972); [b]C. D. Beard and J. C. Craig *J. Am. Chem. Soc.* **96**, 7950 (1974); [c]X. Creary, Ibid **99**, 7632 (1977); [d]T. Yogo, J. Koshino and A. Suzuki, *Tetrahedron Letters*. 1781 (1979); [e]M. Montury and J. Goré, *Ibid.* 51 (1980); [f]I. Fleming, T. W. Newton and F. Roessler, *J. Chem. Soc.* Perkin I 2527 (1981); [g]J.-C. Clinet and G. Linstrumelle, *Synthesis* 875 (1981).

[7a]R. A. Ruden, *J. Org. Chem.* **39**, 3607 (1974); [b]B. Ganem, *Tetrahedron Letts.* 4467 (1974); [c]V. Y. Orlov, S. A. Lebedev, S. V. Ponomarev and I. F. Lutsenko, *Zh. Obshch. Khim.* **45**, 708 (1975), [d]K. A. Parker and R. W. Kosley, *Tetrahedron Letts.* 341 (1976); [e]C. C. Shen and C. Ainsworth, *Ibid.* 83, 87, 89, 93 (1979); [f]M. Bertrand, J.-P. Dulcere and G. Gil, *Ibid.* 1945 (1980); [g]J.-C. Clinet and G. Linstrumelle, *Ibid.* 3987 (1980); [h]R. G. Daniels and L. A. Paquette. *Ibid.* 1579 (1981); [i]J.-P. Dulcere, J. Grimaldi and M. Santelli, *Ibid.* 3179 (1981); [j]J.-P. Pillot, B. Bennetau, J. Dunogues and R. Calas, *Ibid.* 3401 (1981).

[8]Several methods have been reported for the synthesis of (trimethylsilyl)allene contaminated with isomeric acetylenes: [a]P. Bourgeois, G. Merault and J. Dunogues, *C. R. Hebd. Seances Acad. Sci. Ser. C* **274**, 1857 (1972); [b]F. Jaffe. *J. Organomet. Chem.* **23**, 53 (1970).

[9]R. O. Hutchins, M. Kacher and L. Rua, *J. Org. Chem.* **40**, 923 (1975); R. O. Hutchins and N. R. Natale, *Ibid.* **43**, 2299 (1978).

[10]M. W. Logue and G. L. Moore, *Ibid.* **40**, 131 (1975).

[11]No reaction occurred upon exposure of **4b** to catecholborane under a variety of conditions; see G. W. Kabalka, R. J. Newton, J. H. Chandler and D. T. C. Yang, *J. Chem. Soc. Chem. Commun.* 726 (1978) for the application of this reagent to the synthesis of allenes.

[12]For other examples of the formation of pyrazoles from α,β-acetylenic hydrazones, see: R. Fusco, *Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles, and Condensed Rings* (Edited by R. H. Wiley), pp. 16–19, Wiley, New York (1967).

[13]N. V. Komarov, O. G. Yarosh and L. N. Astaf'eva, *J. Gen. Chem. U.S.S.R.* **36**, 920 (1966).

[14]Reaction may also be achieved (although at a considerably slower rate) employing only 1.1 equiv of $TiCl_4$.

[15]Other Lewis acids which proved less effective or unsuitable for promoting the TMS-cyclopentene annulation include: $AlCl_3$, $SnCl_4$, $EtAlCl_2$, $Ti(iOPr)_4$, $NbCl_5$, $iPrOAlCl_2$, Me_3SiOTf, and $TiCl_4$-PhNHMe.

[16]I. Tabushi, K. Fujita and R. Oda, *Tetrahedron Letters* 4247 (1968).

[17]α-Nitro olefin **20** was prepared by the condensation of hydrocinnamaldehyde and nitromethane using the procedure of R. H. Wollenberg and S. J. Miller, *Tetrahedron Letters* 3219 (1978), followed by dehydration of the resulting nitro alcohol employing the method of J. Melton and J. E. McMurry, *J. Org. Chem.* **40**, 2138 (1975).

[18]For the related reaction of allylsilanes with α-nitro olefins, see: M. Ochiai, M. Arimoto and E. Fujita, *Tetrahedron Letters*, 1115 (1981).

[19]A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.* **99**, 1673 (1977).

[20]α,β-Unsaturated acyl cyanides are suitable electrophiles in these reactions: A. Jellal and M. Santelli, *Tetrahedron Letters*, 4487 (1980).

[21]The C_3 Me group in the ^{13}C NMR spectrum of **24** was identified by selectively decoupling the protons attached to this C.

[22]This assignment assumes antiparallel approach of the allene from the less hindered face of the alkoxy allylic carbocation intermediate; for a related process, see E. Siscovic and A. S. Rao, *Curr. Sci.* **37**, 286 (1968).

[23]For related assignments, see J. K. Whitesell and R. S. Matthews, *J. Org. Chem.* **42**, 3878 (1977).

[24]Hudlicky and Srnak have recently reported that neutral alumina is the reagent of choice for effecting complete isomerization in closely related enones: T. Hudlicky and T. Srnak, *Tetrahedron Letters* 3351 (1981).

[25]W. C. Agosta and S. Wolff, *J. Org. Chem.* **40**, 1699 (1975).

[26]For a review of electrophilic substitution of organosilicon compounds, see: T. H. Chan and I. Fleming, *Synthesis* 761 (1979).

[27]For reviews of the chemistry of vinylsilanes, see: [a]I. Fleming, *Comprehensive Organic Chemistry*, (Edited by D. N. Jones vol 3, pp 608–662. Pergamon Press, Oxford (1979); [b]E. Colvin, *Silicon in Organic Synthesis*, Butterworths, London (1981).

[28]R. Pardo and M. Santelli, *Tetrahedron Letters*, 3843 (1981).

[29]For other examples of electrophilic substitution of (trimethylsilyl)allenes, see Refs. 5 and 20 above, and also: P. Bourgeois, R. Calas and G. Merault, *J. Organomet. Chem.* **141**, 23 (1977); P. Bourgeois, *C. R. Hebd. Seances Acad. Sci., Ser. C.* **278**, 969 (1974).

[30]For a review of 1,2-cationic rearrangements in organosilicon compounds, see: A. G. Brook and A. R. Bassindale, *Rearrangements in Ground and Excited States* (Edited by P. de Mayo), vol II, pp. 190–192. Academic Press. New York (1980).

[31]For a review of migration across the double bond of vinyl cations, see: P. J. Stang, Z. Rappoport, M. Hanack and L. R. Subramanian, *Vinyl Cations* pp. 459–483. Academic Press, New York (1979).

[32]N. V. Komarov and M. F. Shostakovskii, *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1208 (1960).

[33]M. Ahmed, G. C. Barley, M. T. W. Hearn, E. R. H. Jones, V. Thaller and J. A. Yates, *J. Chem. Soc.* Perkin I 1981 (1974).

[34]For a previous low yield synthesis of this allene, see: J.-C. Masson, M. Le Quan and P. Cadiot, *Bull. Soc. Chim. Fr* 777 (1967).

[35]M. F. Shostakovskii, N. V. Komarov, V. B. Pukhnarevich and A. M. Sklyanova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1019 (1962).

[36]M. F. Shostakovskii, N. V. Komarov and V. B. Pukhnarevich, *Dokl. Acad. Nauk SSSR* **136**, 864 (1961).

[37]M. F. Shostakovskii, N. V. Komarov and O. G. Yarosh, *Izv. Akad. Nauk SSSR, Ser. Khim.* 101 (1966).

[38]H. O. House, C.-Y. Chu, J. M. Wilkins and M. J. Umen, *J. Org. Chem.* **40**, 1460 (1975).

[39]Yields varied from 81–86% in different runs.

[40]Some material was lost by spillage. Yields varied from 78–84% in other runs.

[41]C. Crisan and H. Normant, *Bull. Soc. Chim. Fr* 1451 (1957); I. N. Nazarov, I. V. Targov and G. P. Verholetova, *Dokl. Acad. Nauk SSSR* **112**, 1067 (1957).

[42]J.-L. Gras, *Tetrahedron Letters* 2111 (1978).

[43]W. G. Dauben, G. T. Rivers and W. T. Zimmerman, *J. Am. Chem. Soc.* **99**, 3414 (1977).

[44a]H. O. House and R. S. Ro, *Ibid.* **80**, 2428 (1958); [b]D. D. Faulk and A. Fry, *J. Org. Chem.* **35**, 364 (1970); [c]R. W. Hasbrouk and A. D. A. Kiessling, *Ibid.* **38**, 2103 (1973); [d]R. F. Childs, E. F. Lund, A. G. Marshall, W. J. Morrissey, and C. V. Rogerson, *J. Am. Chem. Soc.* **98**, 5924 (1976).

[45]F. Weisbach, *C. R. Hebd. Seances Acad. Sci., Ser. C.* **263**, 1234 (1966).