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[3+2] Cycloadditions of Allylsilanes - 4.[1]

Dual Reactivity of Allyltrimethylsilane: Sakurai Reaction versus Trimethylsilylcyclopentane Annulation

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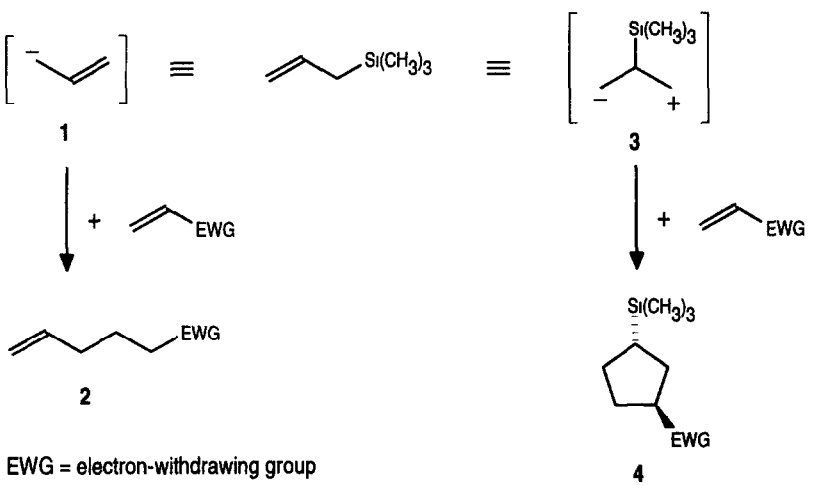
Abstract: The Lewis-acid-promoted reaction of allyltrimethylsilane with enones is shown to afford the 3-allyl ketone derivatives (Sakurai products) along with the trimethylsilylcyclopentanes ([3+2] cycloaddition products) The stereochemistry of the [3+2] cycloaddition products is determined by X-ray analysis

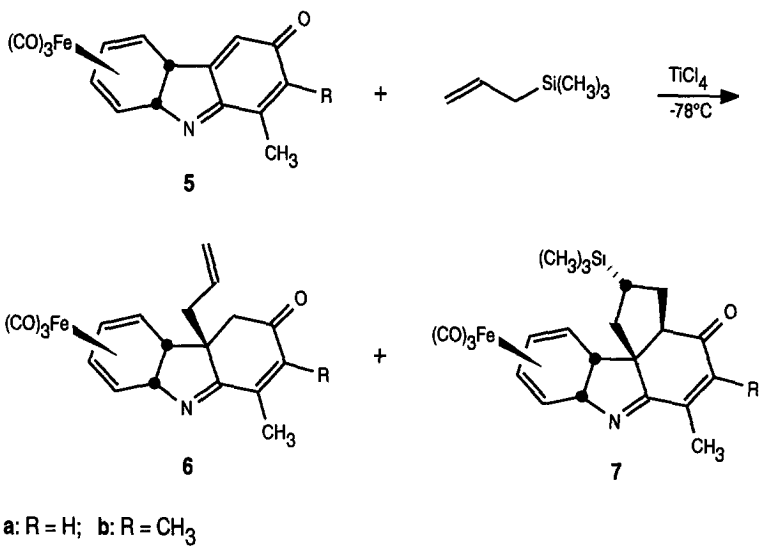
We have shown that allyltrimethylsilane exhibits dual reactivity on titanium-tetrachloride-promoted addition to α,β-unsaturated ketones, providing the allyl derivatives **2** as well as the cyclopentanes **4** (Scheme 1).



Scheme 1

The Lewis acid is used to activate the enone by coordination to the carbonyl oxygen. In the course of the Sakurai reaction[2] allyltrimethylsilane serves as a synthetic equivalent for the allyl anion **1** and adds in a 1,4-fashion to the electron-deficient double bond. Desilylation with regeneration of the double bond takes place by nucleophilic attack of chloride at the silicon atom and affords **2**. In our methodology allyltrimethylsilane is regarded as a synthetic equivalent for the 2-trimethylsilyl-substituted 1,3-dipole **3**, resulting in trimethylsilylcyclopentanes **4** by [3+2] cycloaddition to the electron-deficient double bond. This cycloaddition generally takes place with a high degree of stereoselectivity, providing the product with the trimethylsilyl group *anti* relative to the electron-withdrawing group.

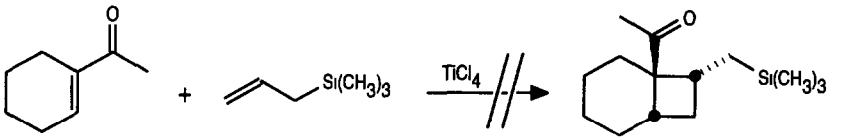
In 1990 we described[3] the previously unprecedented formation of trimethylsilylcyclopentanes as by-products in the course of the Sakurai reaction. We entered this field while investigating the Sakurai addition of allyltrimethylsilane to the tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-ones **5**. This reaction provided diastereoselectively the desired 4a-allyl derivatives **6** along with the trimethylsilylcyclopentanes **7** (Scheme 2).[4] The constitution as well as the stereochemistry of **7a** was confirmed by an X-ray analysis. The cycloaddition of the 1,3-dipole **3** at the 4,4a-double bond of **5** occurs stereoselectively from the *convex* face of the molecule (*syn* relative to the tricarbonyliron moiety) and gives exclusively the product with the trimethylsilyl group *anti* to the keto group.



a: R = H; **b**: R = CH_3

Scheme 2

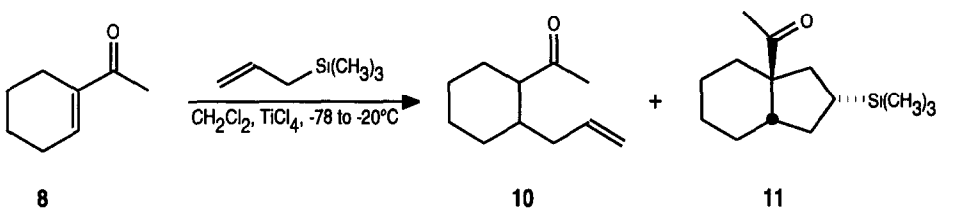
Prior to our discovery there had been several reports that erroneously described the formation of trimethylsilylmethylcyclobutanes as by-products of the Sakurai reaction.[5-11] The structural assignments of these by-products were essentially based on Santelli's original report (*e.g.* the cyclization to **9** on reaction with 1-acetylcyclohexene **8**, Scheme 3).[5] We have unequivocally demonstrated that the compounds described by Santelli have to be reassigned as trimethylsilylcyclopentanes[3] and the additional results presented herein show that there are no grounds for assuming a cyclization to a silylcyclobutane in any of the examples previously reported.[5-11]



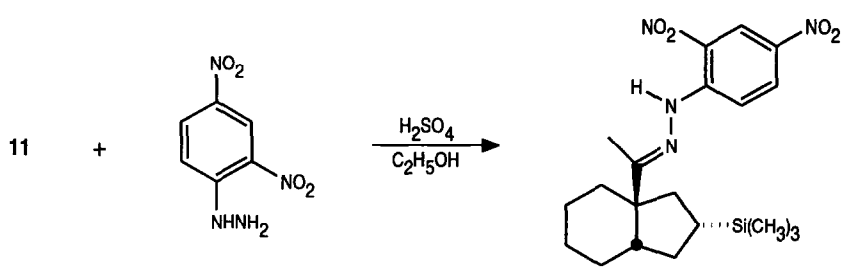
8 9

Scheme 3

First, we reinvestigated the titanium-tetrachloride-promoted addition of allyltrimethylsilane to 1-acetylcyclohexene **8**. Our optimized experimental procedure involves addition of a solution of the enone in dichloromethane to a solution of titanium tetrachloride in dichloromethane at -20°C in order to generate the Lewis acid-enone complex. At -78°C a solution of the allylsilane is added and the reaction temperature slowly raised to -20°C. After a total reaction time of 19h the addition is quenched by addition of aqueous ammonium chloride solution. Standard workup and separation by flash chromatography afforded the expected Sakurai product, the allyl derivative **10**, as a mixture of diastereomers (76% yield) along with the "silyl group containing by-product" **11** in 18% yield (Scheme 4).



8 10 11



12

Scheme 4

The DEPT experiment revealed that a signal of a CH group was significantly shifted to high field (α-TMS CH· 23.55 ppm) rather than a signal of a CH_2 group, as one would have expected for the trimethylsilylcyclobutane **9**. The structure of the trimethylsilylcyclopentane **11** was unambiguously confirmed by an X-ray crystal structure determination of its 2,4-dinitrophenylhydrazone derivative **12** (Figure 1).[12] The crystal structure also established for the first time that exclusively the *anti* diastereoisomer has been formed in this annulation process (*syn* and *anti* give the position of the silyl group relative to the acetyl group).

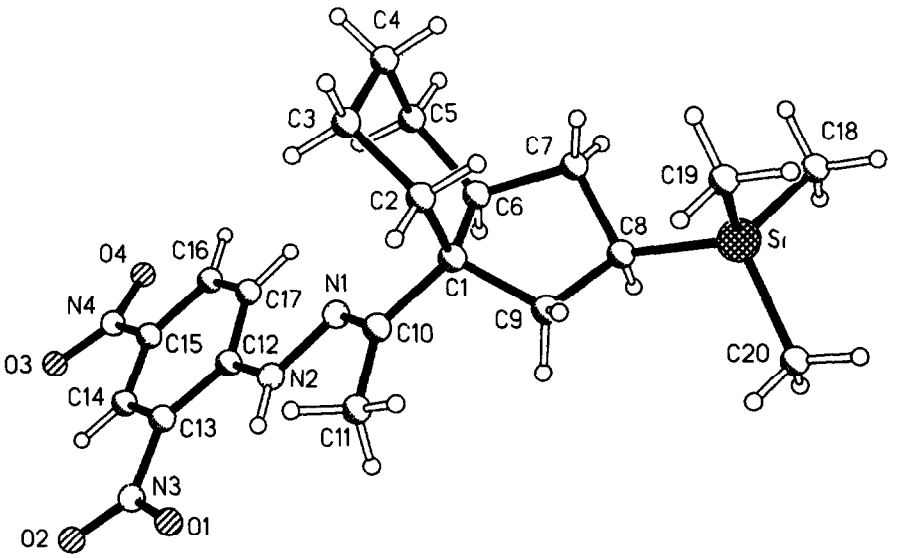
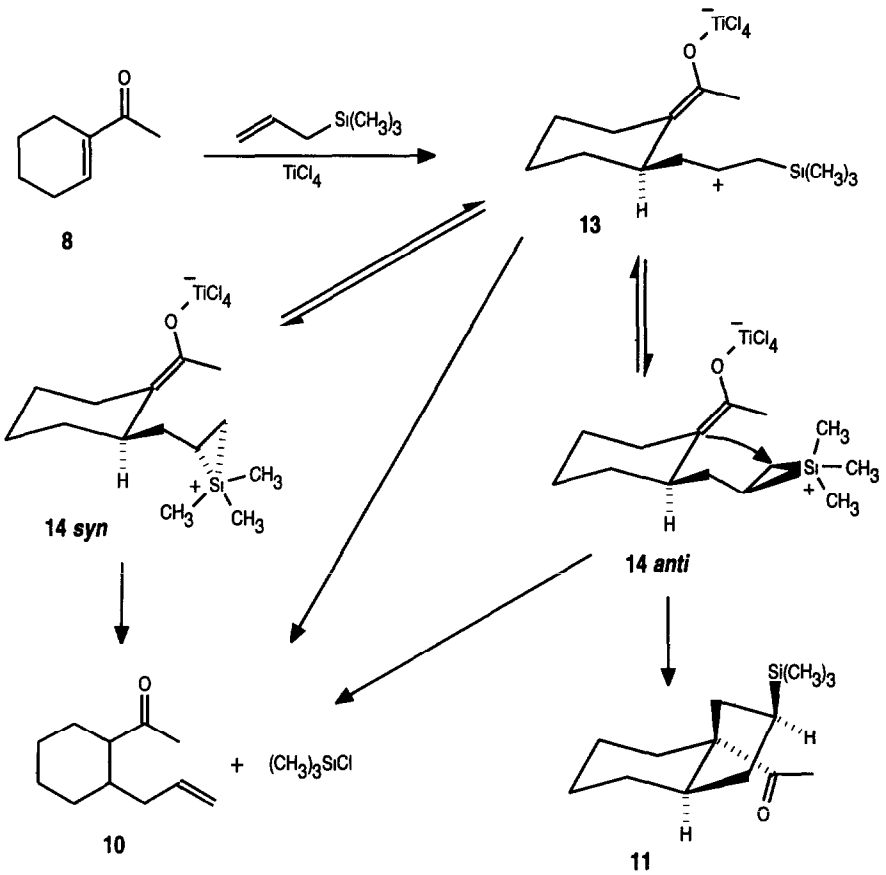


Figure 1

The most important impact of silicon in organic chemistry is clearly its ability to stabilize a positive charge on the β-carbon atom, the so called β-effect. Three different mechanisms have been suggested to contribute to the β-effect.[13] 1. Silicon is more electropositive than carbon and therefore may stabilize the positive charge in the β-position by through-bond σ-induction. 2. The carbon-silicon σ-bond is able to stabilize the positive charge by hyperconjugation (donation of C-Si σ-electrons to the empty carbon p-orbital) due to its high polarizability, vertical stabilization according to Traylor. 3. Silicon may stabilize the positive charge by internal nucleophilic neighboring group participation to form a siliranium ion, non-vertical stabilization according to Traylor. The siliranium ion represents a bridged non-classical pentavalent silicon cation,[14] in which the pentavalency of silicon is permitted by its d-orbitals.

We proposed the pentavalent silicon cation as an intermediate of the trimethylsilylcyclopentane annulation three years ago when we reported the first examples.[3] The stereochemical outcome of the [3+2] cycloaddition of allylsilanes (*anti* selectivity) as well as the cyclization involving a cationic 1,2-silyl shift[15] is explained by the proposed mechanism presented in Scheme 5. The titanium-tetrachloride-promoted addition of allyltrimethylsilane to 1-acetylcyclohexene **8** by nucleophilic attack of the allylsilane at the β-enone position provides the β-silyl cation **13**. Non-vertical stabilization of the positive charge by the silicon atom provides the two diastereomeric bridged non-classical pentavalent silicon cations **14** ***syn*** and **14** ***anti***, which can interconvert *via* the open form **13**. Intermolecular attack of a chloride anion at the silicon atom of either one of the three cationic species leads by elimination of chlorotrimethylsilane and subsequent hydrolysis to the Sakurai product **10**. We found in an extensive optimization of the [3+2] cycloaddition of allylsilanes that the Sakurai reaction is suppressed by having bulky substituents at the silicon atom.[16] The cyclization to the trimethylsilylcyclopentane is a highly stereospecific process, since it requires an "attack from the back" by collinear approach of the titanium enolate β-carbon at the unsubstituted carbon atom of the siliranium ion in the direction to the carbon-silicon bond (5-*exo*-*tet* cyclization)[17] and therefore, occurs with retention of configuration of the carbon-silicon bond. For stereoelectronic reasons the **14** ***anti*** isomer cyclizes much

faster by intramolecular nucleophilic attack of the titanium enolate onto carbon atom of the pentavalent silicon cation and affords on aqueous workup exclusively the *anti*-configurated bicyclo[4.3.0]nonane **11**.

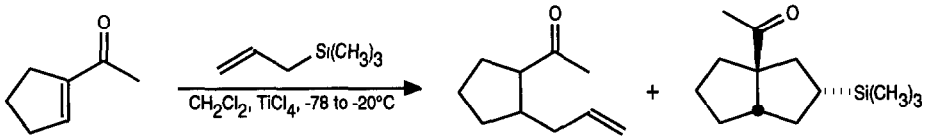


Scheme 5

The [3+2] cycloaddition of allylsilanes involves a β-silyl-cation-induced 1,2-silyl shift *via* an intermediate siliranium ion and is terminated by the nucleophilic attack of the titanium enolate at the pentavalent silicon cation. Therefore, the overall process might be considered a sila-Wagner-Meerwein rearrangement. The same mechanism as described above has been used by others in order to explain further examples of this cycloaddition[18] that have been reported subsequent to our first communication.[3]

Next we investigated the dependence of the ratio Sakurai product/cycloaddition product on the temperature used for hydrolyzing the reaction mixture, which has been described by House and Majetich for their examples of "silicon-containing byproducts".[8,9] Warming the reaction mixture to room temperature prior to hydrolysis, according to those reports, should increase the yield of our cycloadduct at the expense of the Sakurai product. The best results were obtained by addition of the cold (-78°C) reaction mixture to refluxing dichloromethane and subsequent quenching.[8] However, in our hands none of the alternative workup procedures[8,9] led to an improvement of the yield of the cyclopentane **11**.

The titanium-tetrachloride-promoted addition of allyltrimethylsilane to 1-acetylcyclopentene **15**[19] afforded, under the same reaction and workup conditions as described above for **8**, a diastereomeric mixture of the Sakurai product **16**[5,8] along with the bicyclo[3.3.0]octane **17**, which was obtained as one diastereoisomer in 4% yield (Scheme 6).

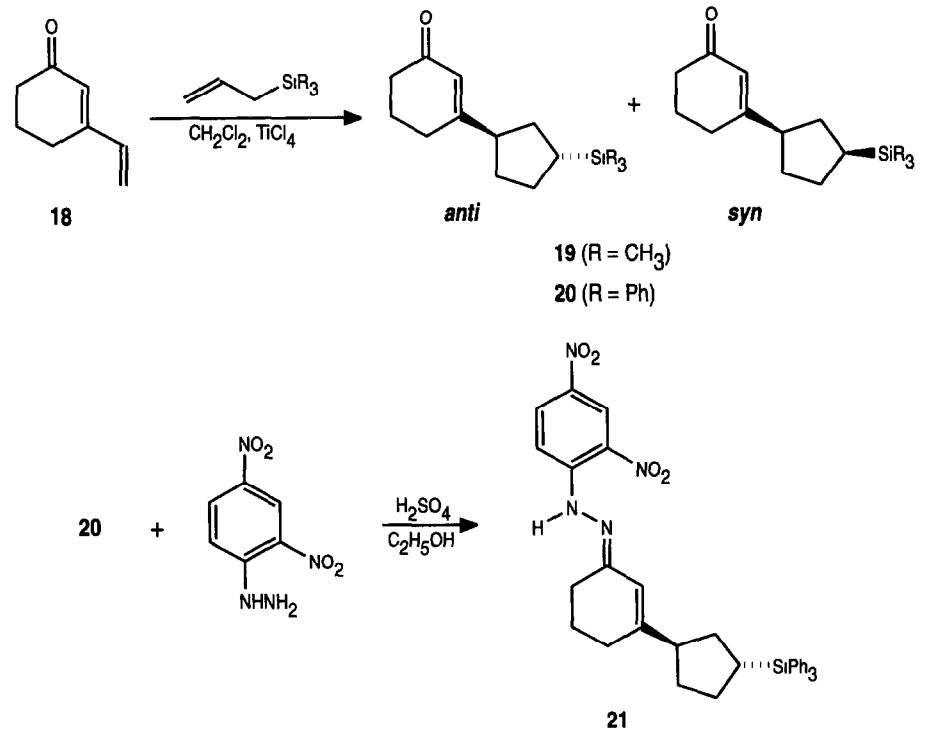


15 **16** **17**

Scheme 6

The structure and the stereochemistry of **17** have been assigned based on comparison of its ^{13}C-NMR data (α-TMS CH: 28.1 ppm) with those of the bicyclo[4.3.0]nonane **11** and those of analogous compounds.[16] The alternative workup procedure as reported by House[8] was also checked for this example, but transfer of the reaction mixture into a refluxing solution of dichloromethane prior to hydrolysis gave the same result (4% yield of **17**).

In the $TiCl_4$-promoted addition of allyltrimethylsilane to 3-vinyl-2-cyclohexen-1-one **18**[20], the formation of a trimethylsilylmethylcyclobutane derivative has also been reported.[9] The dienone **18** offered for the first time the possibility of investigating a vinylogous case of our [3+2] cycloaddition of allylsilanes (Scheme 7).

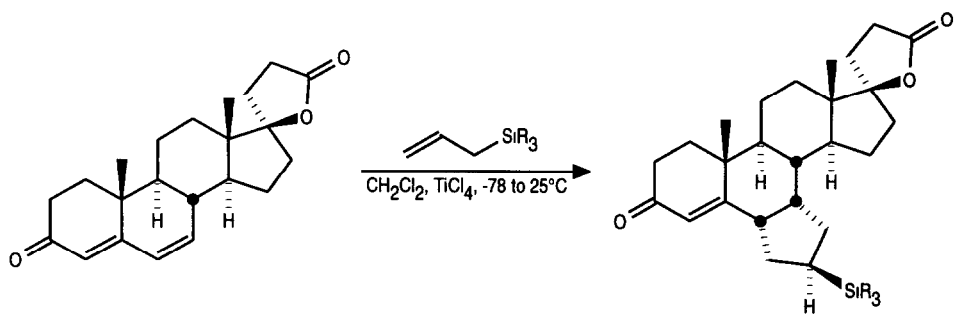


18 ***anti*** ***syn*** **21**

Scheme 7

First, we repeated the reaction originally described by Majetich and co-workers[9] in order to prove that the structure of the product has to be reassigned. In this reaction the titanium tetrachloride-dienone complex was prepared by addition of titanium tetrachloride to a solution of the dienone **18** in dichloromethane at -78°C ("*normal addition*"). Subsequent addition of the allyltrimethylsilane at -78°C and workup by pouring the cold reaction mixture into refluxing dichloromethane before aqueous hydrolysis provided two diastereoisomers **19** ***anti*** and **19** ***syn*** in a ratio of approximately 1:1.4 (10% yield). The structure assignment was based on the ^{1}H-NMR and ^{13}C-NMR spectra (α-TMS CH: 25.28 and 26.24 ppm). In our extensive study of optimization of the silylcyclopentane annulation which we reported recently,[16] we have shown that allyltriphenylsilane leads to considerably improved yields of the cycloadducts. However, by using the same procedure as described above for allyltrimethylsilane ("*normal addition*" for the preparation of the Lewis acid complex) a 1:1.3 mixture of the two diastereoisomers **20** ***anti*** and **20** ***syn*** was obtained in the same yield (10%). If the Lewis acid-dienone complex was prepared by addition of a solution of the dienone **18** to a solution of titanium tetrachloride in dichloromethane ("*inverse addition*", according to our optimized standard procedure[16]) the cycloaddition with allyltriphenylsilane afforded a 10:1 ratio of the two diastereoisomers **20** ***anti*** and **20** ***syn***. The major diastereoisomer of this mixture has been successfully transformed to its 2,4-dinitrophenylhydrazone derivative **21**. The structure assignments are based on spectral comparison with related systems reported by us previously.[1,3,4,16] Our present knowledge of the [3+2] cycloaddition with allylsilanes suggests that the low yield observed in the reaction with **18**, even under optimized conditions, is a general trend for 2-cycloalkenone type systems (see below).

Next we investigated the titanium-tetrachloride-promoted addition of allyltrimethylsilane to the steroidal 3-oxo-4,6-diene **22** (kindly provided by Dr. G. Sauer, Schering AG, Berlin). For this reaction Laurent et al. reported the formation of a trimethylsilylmethylcyclobutane annulation product along with the expected 7α-allyl derivative.[10] However, our own results with the steroid dienone **22** demonstrated that the initial structural assignment has to be corrected.



22

23 (R = CH_3)
24 (R = *i*-Pr)

Scheme 8

The structure of the "silicon-containing by-product" has been determined as the trimethylsilylcyclopentane **23** by the ^{13}C-NMR spectrum in combination with the DEPT experiment (α-TMS CH: 14.39 ppm). The stereochemistry of **23** has been unequivocally confirmed by an X-ray crystal structure analysis (Figure 2).[12]

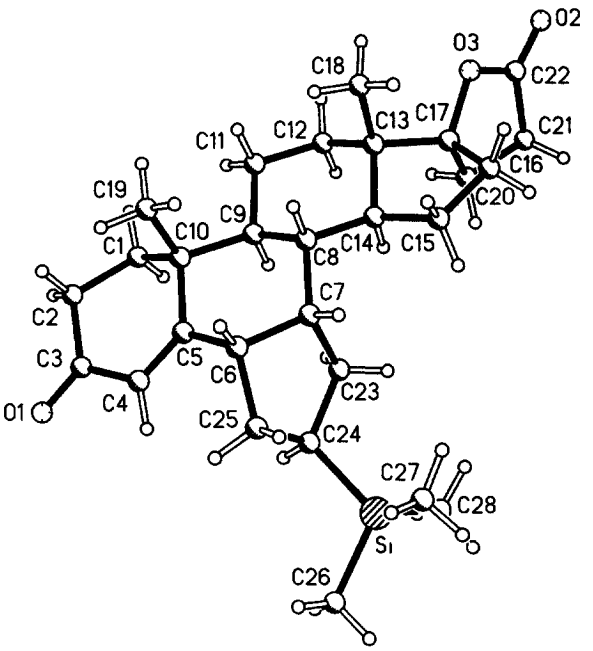
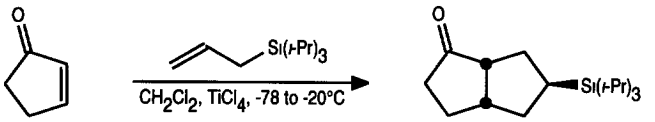


Figure 2

The cycloadditions of allylsilanes to the steroid dienone **22** proceed with complete stereoselectivity, in contrast to the analogous reactions of the dienone **18**. This difference is ascribed to the considerably increased rigidity of the dienone system in **22** compared to that of compound **18**. The cycloaddition of allyltrimethylsilane with **22** afforded only 7% of the cyclopentane **23**. In order to improve the yield of this annulation we used allyltriisopropylsilane, which we found[1,16] to give almost exclusively the [3+2] cycloadduct, in some cases with quantitative yields. By using the same reaction conditions as for the cycloaddition to **23** the hexacyclic steroid derivative **24** was obtained in 32% yield. Based on spectral comparison with **23**, the stereochemistry of **24** was assigned as the *anti*-silyl derivative (α-TMS CH: 15.55 ppm). It is interesting to note at this point that the cycloadditions of the steroid dienone **22** with allylsilanes stereoselectively provide the products with *exo*-orientation of the trialkylsilyl group (sterically less hindered diastereoisomer). We had already observed the same *exo*-configuration for the trimethylsilylcyclopentanes resulting from cycloadditions with the iminoquinones **5**.[3,4] On the other hand, the cycloadditions of allylsilanes to 1-acetylcycloalkenes stereoselectively afford the corresponding bicyclic ring systems with an *endo*-configuration of the silyl group (sterically more hindered diastereoisomer). This can be rationalized by considering that both types of enones lead with preference to the cycloadducts exhibiting an *anti* arrangement of the silyl substituent and the electron-withdrawing group. Compared to other cycloadditions recently reported from our laboratories,[1,16] the yield for the annulation of the triisopropylsilylcyclopentane ring to **24** was disappointing. As mentioned above for the cycloadditions with the dienone **18**, this appears to be a general problem of our allylsilane annulation with 2-cycloalkenone type systems, although they give rise to products with the silyl substituent in the less hindered position.

A similar result arises from the titanium-tetrachloride-promoted cycloaddition of the parent 2-cyclohexenone with allyltriisopropylsilane, which gave only traces of the corresponding bicyclo[4.3.0]nonane derivative. The more reactive 2-cyclopentenone **25** however, provided the bicyclo[3.3.0]octane **26** in at least 41% yield (Scheme 9).



25 **26**

Scheme 9

The stereochemistry of **26** was assigned based on comparison of the ^{1}H-NMR and ^{13}C-NMR spectral data with those of related systems described above and earlier.[1,16] Most significant was the chemical shift of the signal for the CH α to the triisopropylsilyl group (δ = 21.66 ppm).

Conclusion: A series of trimethylsilylmethylcyclobutanes as by-products of conventional Sakurai reactions has been reported in the literature (7 examples).[5-11] In our preliminary communication on the trimethylsilylcyclopentane annulation[3] we were already convinced that all of these structures have to be reassigned. In this paper we provide unambiguous evidence for 4 of those examples[5,8,9,10] that the structures of these by-products have to be reassigned as trimethylsilylcyclopentanes. The structure of a further "silyl-group-containing by-product" of the Sakurai reaction, which had been reported by Majetich,[11] has already been corrected[18d] according to our original findings.[3] Based on the evidence reported in this paper and earlier[1,3,4,16] it is obvious that the two remaining "cyclobutanes" reported by Sakurai[6] and Danishefsky[7] also have to be reassigned as cyclopentanes. Moreover, we have additional evidence that the [2+2] cycloadduct of an allylsilane reported even more recently by Monti[21] is in fact a [3+2] cycloadduct.[22] Recent results from our laboratories[1,16] have demonstrated that by variation of the substituents at the silicon atom the [3+2] cycloaddition of allylsilanes becomes a powerful synthetic method.

EXPERIMENTAL SECTION

Flash chromatography: Baker silica gel (0.03-0.06 mm). Melting points: Reichert hot stage. UV: Beckman 3600. IR: Bruker IFS 25 and IFS 88 (FTIR), Perkin-Elmer 882 and 1710 (FTIR). ^{1}H-NMR and ^{13}C-NMR: Bruker WP 200, AM 300, and AM 400; internal standard: chloroform; coupling constants in Hz. Mass spectra: Finnigan MAT-312 and MAT-90; ionization potential: 70 eV. Elemental analyses: Heraeus CHN-Rapid. All reactions were carried out by using dry solvents in an inert gas atmosphere.

1-Acetyl-8-trimethylsilylbicyclo[4.3.0]nonane (11)

A solution of 1-acetylcyclohexene **8** (500 mg, 4.03 mmol, 0.52 ml) in dichloromethane (2 ml) was added to a stirred solution of titanium tetrachloride (840 mg, 4.43 mmol, 0.49 ml) in dichloromethane (5 ml) at -20°C. The formation of the titanium-tetrachloride-enone complex was indicated by the intense yellow color of the resulting suspension. The reaction mixture was cooled to -78°C and a solution of allyltrimethylsilane (690 mg, 6.04 mmol, 0.96 ml) in dichloromethane (6 ml) was added (this caused a spontaneous change of the

color to red violet). The temperature of the reaction mixture was kept for further 4 h at -78°C and then for 15 h at -20°C. After an overall reaction time of 19 h the cold reaction mixture was quenched by addition of an aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted three times with cold dichloromethane. The combined organic layers were dried over magnesium sulfate. Removal of the solvent *in vacuo* and flash chromatography (light petroleum/diethyl ether, 7:1) of the residue on silica gel provided 174 mg (18%) of the bicyclo[4.3.0]nonane **11** as the less polar fraction (colorless oil) and 510 mg (76%) of the allyl derivative **10** as the more polar fraction (colorless oil).

11: IR (film, NaCl): ν 2931, 2862, 1700, 1449, 1350, 1300, 1282, 1248, 1229, 1216, 1149, 1133, 1031, 972, 945, 920, 901, 840, 749, 734, 640 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ -0.03 (s, 9 H), 0.97-1.26 (br m, 1 H), 1.30-1.85 (m, 11 H), 1.88 (dd, J = 13.2, 10.7, 1 H), 2.13 (s, 3 H), 2.44 (br m, 1 H); ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ -2.94 (3 CH_3), 22.07 (CH_2), 23.55 (CH), 23.59 (CH_2), 25.47 (CH_3), 26.60 (CH_2), 31.30 (CH_2), 32.02 (CH_2), 37.70 (CH_2), 41.61 (CH), 58.53 (C), 213.05 (C=O); MS (25°C): *m/z* 238 (M^+, 7), 223 (3), 197 (11), 195 (4), 125 (25), 121 (29), 73 (100), 43 (11); HRMS calcd for $C_{14}H_{26}OSi$ (M^+): 238.1753, found: 238.1753.

10: spectral data, see ref.[5].

1-Acetyl-8-trimethylsilylbicyclo[4.3.0]nonane-(2,4-dinitrophenylhydrazone) (12)

A solution of 2,4-dinitrophenylhydrazine (270 mg, 1.36 mmol) in conc. sulfuric acid (0.5 ml) / ethanol (2.5 ml) was added to a stirred solution of the bicyclo[4.3.0]nonane **11** (156 mg, 0.66 mmol) in ethanol (3 ml) at room temperature. The reaction mixture was left for 1 h at room temperature and subsequently warmed for 30 min at 45°C. The precipitate was separated by filtration, washed with a small amount of cold ethanol and with much water. Recrystallization from ethyl acetate/diethyl ether/ethanol (1:2:3) and drying in high vacuum afforded 256 mg (93%) of the dinitrophenylhydrazone **12** as bright yellow plates, mp 166°C. UV (MeOH): λ 227, 260 (sh), 362 nm. IR (KBr): ν 3320, 3108, 2932, 2861, 1620, 1592, 1519, 1510 (sh), 1425, 1338, 1311, 1290, 1274, 1248, 1223, 1136, 1086, 923, 861, 834 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.00 (s, 9 H), 1.10 (m, 1 H), 1.39-1.92 (m, 12 H), 2.03 (s, 3 H), 2.54 (m, 1 H), 7.96 (d, J = 9.61, 1 H), 8.31 (ddd, J = 9.61, 2.56, 0.67, 1 H), 9.14 (d, J = 2.56, 1 H), 11.09 (s, 1 H); ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ -2.92 (3 CH_3), 13.25 (CH_3), 22.37 (CH_2), 23.14 (CH), 23.20 (CH_2), 26.54 (CH_2), 32.27 (CH_2), 32.35 (CH_2), 38.72 (CH_2), 42.28 (CH), 52.88 (C), 116.51 (CH), 123.57 (CH), 129.04 (C), 130.05 (CH), 137.56 (C), 145.55 (C), 162.10 (C=N); MS (160°C): *m/z* 418 (M^+, 6), 345 (1), 304 (4), 287 (13), 257 (9), 245 (9), 229 (1), 180 (4), 147 (3), 120 (8), 73 (100); HRMS calcd for $C_{20}H_{30}N_4O_4Si$ (M^+): 418.2036, found: 418.2037. Anal. Calcd for $C_{20}H_{30}N_4O_4Si$: C, 57.39; H, 7.22; N, 13.39. Found: C, 57.46; H, 7.14; N, 13.02.

X-ray crystal structure determination for 12

Formula: $C_{20}H_{30}N_4O_4Si$; crystal size: 0.9 · 0.5 · 0.2 mm; monoclinic; space group: $P2_1/n$; a = 7.473(2) Å, b = 7.562(2) Å, c = 39.977(10) Å; β = 94.94(2)°; V = 2250.8(10) $Å^3$; Z = 4; ρ_{calcd} = 1.235 g/cm^3; T = 178 K; μ = 0.130 mm^{-1}; Mo-K_α radiation (graphite monochromator); 2Θ range: 6° < 2Θ < 50°; independent reflections: 3937, observed: 2816 [$F > 4\sigma(F)$]; R = 4.54%; wR = 5.27% [$w^{-1} = \sigma^2(F) + 0.0003\ F^2$]; maximal residual electron density: 0.39 e/$Å^3$.

Data collection and calculations were carried out using a Siemens R3m/V four-circle diffractometer with a Micro VAX II computer and Siemens SHELXTL PLUS software.[12]

Table 1. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement factors (pm^2) for **12**

	x	y	z	U(eq)
Si	203(1)	3965(1)	2060.8(2)	432(3)
N(1)	2694(3)	1309(3)	699.7(4)	312(7)
N(2)	2967(3)	1676(3)	367.4(4)	323(7)
N(3)	3545(3)	2280(3)	-341.1(5)	396(8)
N(4)	1232(3)	-3589(3)	-593.9(5)	363(7)
O(1)	3867(3)	3539(2)	-146.3(4)	473(7)
O(2)	3812(3)	2359(3)	-638.3(4)	642(8)
O(3)	1694(3)	-3395(3)	-879.1(4)	465(7)
O(4)	379(3)	-4883(3)	-507.6(4)	476(7)
C(1)	2897(3)	2146(3)	1280.2(5)	314(8)
C(2)	4772(4)	1983(4)	1479.2(6)	425(9)
C(3)	5711(4)	235(4)	1419.7(7)	526(11)
C(4)	4586(4)	-1329(4)	1515.1(7)	507(11)
C(5)	2762(4)	-1295(3)	1313.5(6)	418(9)
C(6)	1779(3)	460(3)	1336.7(5)	329(8)
C(7)	1049(3)	856(3)	1675.9(6)	393(9)
C(8)	483(4)	2813(3)	1652.7(6)	379(9)
C(9)	1819(3)	3674(3)	1431.4(5)	354(8)
C(10)	3160(3)	2522(3)	914.7(6)	298(8)
C(11)	3936(4)	4274(3)	825.6(6)	379(9)
C(12)	2582(3)	412(3)	132.8(5)	289(8)
C(13)	2833(3)	650(3)	-212.5(5)	298(8)
C(14)	2402(3)	-667(3)	-447.3(5)	317(8)
C(15)	1725(3)	-2229(3)	-345.0(5)	299(8)
C(16)	1476(3)	-2539(3)	-6.8(6)	339(8)
C(17)	1904(3)	-1246(3)	224.6(5)	327(8)
C(18)	-1369(5)	2656(5)	2299.8(7)	744(14)
C(19)	2422(5)	4149(5)	2307.8(7)	761(14)
C(20)	-759(5)	6190(4)	1969.7(8)	805(15)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2. Bond lenghts (pm) of **12**

Si-C(8)	187.7 (3)	Si-C(18)	186.1 (4)
Si-C(19)	186.1 (4)	Si-C(20)	185.3 (3)
N(1)-N(2)	138.9 (3)	N(1)-C(10)	128.4 (3)
N(2)-C(12)	135.2 (3)	N(3)-O(1)	124.0 (3)
N(3)-O(2)	122.3 (3)	N(3)-C(13)	145.4 (3)
N(4)-O(3)	122.8 (3)	N(4)-O(4)	123.3 (3)
N(4)-C(15)	145.6 (3)	C(1)-C(2)	155.5 (3)
C(1)-C(6)	155.2 (3)	C(1)-C(9)	156.0 (3)
C(1)-C(10)	151.8 (3)	C(2)-C(3)	152.5 (4)
C(3)-C(4)	151.8 (4)	C(4)-C(5)	152.3 (4)
C(5)-C(6)	152.3 (4)	C(6)-C(7)	153.4 (3)
C(7)-C(8)	154.0 (4)	C(8)-C(9)	153.5 (4)
C(10)-C(11)	150.2 (4)	C(12)-C(13)	142.1 (3)
C(12)-C(17)	141.2 (3)	C(13)-C(14)	138.8 (3)
C(14)-C(15)	136.2 (3)	C(15)-C(16)	140.0 (3)
C(16)-C(17)	136.5 (3)		

Table 3. Bond angles (°) of **12**

C(8)-Si-C(18)	108.8(1)	C(8)-Si-C(19)	109.6(1)
C(18)-Si-C(19)	109.9(1)	C(8)-Si-C(20)	108.7(1)
C(18)-Si-C(20)	109.4(2)	C(19)-Si-C(20)	110.4(2)
N(2)-N(1)-C(10)	116.3(2)	N(1)-N(2)-C(12)	118.8(2)
O(1)-N(3)-O(2)	122.3(2)	O(1)-N(3)-C(13)	119.1(2)
O(2)-N(3)-C(13)	118.7(2)	O(3)-N(4)-O(4)	123.2(2)
O(3)-N(4)-C(15)	118.4(2)	O(4)-N(4)-C(15)	118.4(2)
C(2)-C(1)-C(6)	109.5(2)	C(2)-C(1)-C(9)	109.4(2)
C(6)-C(1)-C(9)	104.4(2)	C(2)-C(1)-C(10)	108.8(2)
C(6)-C(1)-C(10)	114.2(2)	C(9)-C(1)-C(10)	110.4(2)
C(1)-C(2)-C(3)	113.3(2)	C(2)-C(3)-C(4)	111.3(2)
C(3)-C(4)-C(5)	110.1(2)	C(4)-C(5)-C(6)	113.4(2)
C(1)-C(6)-C(5)	116.0(2)	C(1)-C(6)-C(7)	101.8(2)
C(5)-C(6)-C(7)	115.7(2)	C(6)-C(7)-C(8)	104.6(2)
Si-C(8)-C(7)	116.4(2)	Si-C(8)-C(9)	115.5(2)
C(7)-C(8)-C(9)	104.7(2)	C(1)-C(9)-C(8)	107.0(2)
N(1)-C(10)-C(1)	117.4(2)	N(1)-C(10)-C(11)	124.0(2)
C(1)-C(10)-C(11)	118.6(2)	N(2)-C(12)-C(13)	123.1(2)
N(2)-C(12)-C(17)	120.4(2)	C(13)-C(12)-C(17)	116.4(2)
N(3)-C(13)-C(12)	122.3(2)	N(3)-C(13)-C(14)	116.1(2)
C(12)-C(13)-C(14)	121.6(2)	C(13)-C(14)-C(15)	119.4(2)
N(4)-C(15)-C(14)	119.1(2)	N(4)-C(15)-C(16)	119 7(2)
C(14)-C(15)-C(16)	121.3(2)	C(15)-C(16)-C(17)	119.4(2)
C(12)-C(17)-C(16)	121.9(2)		

1-Acetyl-3-trimethylsilylbicyclo[3.3.0]octane (17)

A solution of 1-acetylcyclopentene **15** (1.85 ml, 1.77 g, 16.1 mmol) in dichloromethane (8 ml) was added to a stirred solution of titanium tetrachloride (1.94 ml, 3.36 g, 17.7 mmol) in dichloromethane (20 ml) at -20°C. The reaction mixture was cooled to -78°C and a solution of allyltrimethylsilane (3.85 ml, 2.76 g, 24.2 mmol) in dichloromethane (24 ml) was added. After stirring for 19 h at -20°C the cold mixture was poured into a cold dilute aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted three times with cold dichloromethane (50 ml). The combined organic layers were dried over magnesium sulfate. Removal of the solvent and flash chromatography (light petroleum/diethyl ether, 20:1) of the residue on silica gel provided 157 mg (4%) of the bicyclo[3.3.0]octane **17** as the less polar fraction (colorless oil) and 1.14 g (47%) of the allyl derivative **16** as the more polar fraction (colorless oil).

17: IR (film, NaCl): ν 2951, 2860, 1695, 1446, 1352, 1246, 1157, 910, 870, 836 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ -0.03 (s, 9 H), 0.86 (m, 1 H), 0.97 (m, 1 H), 1.13 (tr, J = 13.3, 1 H), 1.52 (m, 1 H), 1.66 (m, 5 H), 2.03 (m, 1 H), 2.17 (s, 3 H), 2.28 (ddd, J = 12.9, 5.8, 2.0, 1 H), 2.79 (m, 1 H); ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ -3.0 (3 CH_3), 24.8 (CH_2), 25.9 (CH_3), 28.1 (CH), 33.1 (CH_2), 37.1 (CH_2), 37.2 (CH_2), 39.7 (CH_2), 47.6 (CH), 69.2 (C), 212.0 (C=O); MS (25°C): *m/z* 224 (M^+, 8), 183 (38), 135 (16), 117 (20), 111 (41), 73 (100), 43 (25); HRMS calcd for $C_{13}H_{24}OSi$ (M^+): 224.1596; found: 224.1578.

16: spectral data, see ref.[5,8].

3-(3-Trimethylsilylcyclopentyl)-2-cyclohexen-1-one (19)

Titanium tetrachloride (366 µl, 3.33 mmol) was added to a stirred solution of 3-vinyl-2-cyclohexen-1-one **18** (370 mg, 3.03 mmol) in dichloromethane (12 ml) at -78°C. Allyltrimethylsilane (578 µl, 3.63 mmol) was added over a period of 10 min and the reaction mixture was subsequently stirred for further 5 min at -78°C. After this time the mixture was poured into refluxing dichloromethane (6 ml) and refluxed for 20 min. The mixture was hydrolyzed by addition of water (2 ml) and extracted several times with dichloromethane. The combined organic layers were washed with a dilute aqueous $NaHCO_3$ solution and dried over magnesium sulfate. Evaporation of the solvent and flash chromatography (diethyl ether/light petroleum, 1.2) of the residue on silica gel gave 71 mg (10%) of **19** as a light yellow oil. IR (film, NaCl): ν 2948, 2865, 1670, 1621, 1454, 1429, 1417, 1374, 1344, 1325, 1285, 1249, 1192, 1039, 969, 911, 887, 834 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ -0.03 (s, 9H), 1.32-2.04 (m, 9H), 2.34 (m, 4H), 2.59 (m, 1H), 5.90 (m, 1H); ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ -3.12 (3 CH_3), 22.93/ 22.99 (CH_2), 25.28/ 26.24 (CH), 26.78 (CH_2), 28.47/ 28.63 (CH_2), 31.31/ 32.99 (CH_2), 32.19/ 34.04 (CH_2), 37.55 (CH_2), 48.06/ 49.54 (CH), 123.75/ 123.89 (CH), 169.57/ 170.02 (C), 200.14 (C=O); MS (25°C): *m/z* 236 (M^+, 6), 221 (12), 196 (16), 195 (100), 72 (81); HRMS calcd for $C_{14}H_{24}OSi$ (M^+): 236.1596, found: 236.1597.

3-(3-Triphenylsilylcyclopentyl)-2-cyclohexen-1-one (20)

A solution of 3-vinyl-2-cyclohexen-1-one **18** (1.0 g, 8.1 mmol) in dichloromethane (15 ml) was added to a stirred solution of titanium tetrachloride (1.84 g, 9.72 mmol, 1.07 ml) in dichloromethane (5 ml) at -78°C. A solution of allyltriphenylsilane (3.65 g, 12.2 mmol) in dichloromethane (12 ml) was added slowly to the reaction mixture. The temperature was kept at -78°C for further 15 min and then slowly warmed to room temperature over a period of 1 h. The reaction mixture was hydrolyzed with water, the organic layer was separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over magnesium sulfate. Removal of the solvent and flash chromatography (light petroleum/diethyl ether, 5:1) of the residue on silica gel provided 260 mg (8%) of **20** as a yellow oil. IR ($CHCl_3$) ν 3405, 3071, 3053, 3006, 2949, 2868, 1654, 1615, 1587, 1481, 1449, 1425, 1374, 1343, 1326, 1303, 1282, 1253, 1236, 1188, 1108, 1026, 968, 886 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) [major diastereomer]: δ 1.32-2.10 (m, 8 H), 2.15-2.41 (m, 6 H), 5.88 (s, 1 H), 7.33-7.46 (m, 9 H), 7.54-7.60 (m, 6 H); ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$) [major diastereomer]: δ 21.80 (CH), 22.92 (CH_2), 28.64 (CH_2), 29.20 (CH_2), 32.67 (CH_2), 32.94 (CH_2), 37.54 (CH_2), 47.94 (CH), 123.93 (CH), 127.91 (CH), 129.52 (CH), 134.65 (C), 135.91 (CH), 169.37(C), 200.22 (C=O); MS (25°C): *m/z* 422 (M^+, 2), 381 (8), 277 (10), 276 (45), 260 (6), 259 (25), 200 (18), 199 (100), 122 (16), 78 (6), 77 (10); HRMS calcd for $C_{29}H_{30}OSi$ (M^+): 422.2066, found: 422.2043.

3-(3-Triphenylsilylcyclopentyl)-2-cyclohexen-1-one-(2,4-dinitrophenylhydrazone) (21)

A solution of 2,4-dinitrophenylhydrazine (257 mg, 1.3 mmol) in conc. sulfuric acid (0.65 ml) / ethanol (5 ml) was added to a solution of **20** (250 mg, 0.59 mmol) in ethanol (7 ml). The reaction mixture was left for 1 h at room temperature and subsequently warmed to 45°C. The precipitate was separated by filtration, washed with much water and with a small amount of ethanol. Recrystallization from ethanol/diethyl ether (3:2) and drying in high vacuum gave 263 mg (74%) of the dinitrophenylhydrazone **21** as orange crystals, mp 157-158°C. IR (KBr): ν 3313, 3070, 2937, 2865, 1614, 1588, 1513, 1425, 1331, 1309, 1288, 1259, 1131, 1108,

1079, 701, 550 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.22-2.68 (m, 14 H), 6.13 (s, 1 H), 7,36-7.45 (m, 9 H), 7.56-7.58 (m, 6 H), 7.98 (d, *J* = 9.6, 1 H), 8.28 (dd, *J* = 9.6, 2.4, 1 H), 9.12 (d, *J* = 2.4, 1 H), 11.23 (br s, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.51 (CH_2), 21.84 (CH), 24.16 (CH_2), 27.59 (CH_2), 29.26 (CH_2), 32.74 (CH_2), 32.85 (CH_2), 48.06 (CH), 116.41 (CH), 120.53 (CH), 123.63 (CH), 127.89 (CH), 129.08 (C), 129.48 (CH), 129.93 (CH), 134.79 (C), 135.94 (CH), 137.57 (C), 144.67 (C), 155.48 (C), 156.47 (C). MS (220°C): *m/z* 602 (M^+, 9), 260 (18), 259 (100); HRMS calcd for $C_{35}H_{34}SiN_4O_4$ (M^+): 602.2349, found: 602.2333.

Trimethylsilylcyclopentanosteroid (23)

Titanium tetrachloride (3.1 ml, 28.2 mmol) was added to a stirred solution of the steroid dienone **22** (2.0 g, 5.87 mmol) in dichloromethane (100 ml) at -78°C. After 10 min of stirring a solution of allyltrimethylsilane (5.6 ml, 35.2 mmol) in dichloromethane (5 ml) was added over a period of 15 min. The reaction mixture was stirred for 1.5 h at -78°C, the cooling bath was removed, and after further stirring for 1 h the mixture was hydrolyzed by addition of water (3 ml). The reaction mixture was extracted three times with dichloromethane, the combined organic layers were washed with a dilute $NaHCO_3$ solution and dried over magnesium sulfate. Evaporation of the solvent and flash chromatography (light petroleum/ethyl acetate, 3:1) of the residue on silica gel afforded 188 mg (7%) of the trimethylsilylcyclopentane **23** as the less polar fraction (colorless prisms) and 970 mg (43%) of the 7α-allyl derivative as the more polar fraction (colorless crystals).

23: mp >275°C (dec.). IR (KBr): ν 3042, 2952, 2890, 2874, 1774, 1672, 1606, 1457, 1422, 1380, 1316, 1293, 1249, 1178, 1136, 1106, 1021, 973, 916, 853, 834 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.08 (s, 9 H), 0.95 (s, 3 H), 1.17 (s, 3 H), 1.05-1.74 (m, 11 H), 1.79-2.06 (m, 7 H), 2.18-2.39 (m, 5 H), 2.51 (m, 2 H), 2.72 (m, 1 H), 5.88 (d, *J* = 1.6, 1 H); ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ -3.36 (3 CH_3), 14.39 (CH), 17.47 (CH_3), 18.87 (CH_3), 20.42 (CH_2), 22.81 (CH_2), 23.81 (CH_2), 29.28 (CH_2), 29.54 (CH_2), 31.28 (CH_2), 31.64 (CH_2), 33.59 (CH_2), 34.97 (CH), 35.52 (CH_2), 35.76 (CH_2), 38.99 (C), 43.67 (CH), 43.90 (CH), 45.72 (C), 46.12 (CH), 46.68 (CH), 95.71 (C), 122.59 (CH), 169.98 (C), 176.66 (C=O), 199.46 (C=O); MS (180°C): *m/z* 454 (M^+, 5), 439 (5), 416 (10), 415 (35), 413 (100), 383 (2), 382 (2), 341 (27), 73 (61); HRMS calcd for $C_{28}H_{42}O_3Si$ (M^+): 454.2903, found: 454.2904. Anal. Calcd for $C_{28}H_{42}O_3Si$: C, 73.96; H 9.31. Found: C, 73.23; H, 9.19.

7α-allyl derivative: spectral data, see ref.[10].

X-ray crystal structure determination for 23

Formula: $C_{28}H_{42}O_3Si$; crystal size: 0.5 · 0.35 · 0.3 mm; monoclinic; space group: $P2_1$; a = 6.118(2) Å, b = 11.639(5) Å, c = 17.318(7) Å; β = 90.67(3)°; V = 1233.2(8) $Å^3$; Z = 2; ρ_{calcd} = 1.225 g/cm^3; T = 178 K; μ = 0.117 mm^{-1}; Mo-K_α radiation (graphite monochromator); 2Θ range: 6° < 2Θ < 55°; independent reflections: 5098, observed: 4263 [F > 4σ(F)]; R = 3.65%; wR = 3.86% [$w^{-1} = \sigma^2(F) + 0.0003\ F^2$]; maximal residual electron density: 0.29 e/$Å^3$; absolute configuration by η refinement [η = +1.0(2)].

Data collection and calculations were carried out using a Siemens R3m/V four-circle diffractometer with a Micro VAX II computer and Siemens SHELXTL PLUS software.[12]

Table 4. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement factors (pm^2) for **23**

	x	y	z	U(eq)
Si	3992(1)	9000	1966.6(3)	260(2)
C(1)	2201(3)	4580(2)	4803(1)	297(7)
C(2)	2883(4)	5200(2)	5542(1)	339(7)
C(3)	3809(4)	6370(2)	5381(1)	323(7)
C(4)	3000(3)	6943(2)	4680(1)	288(6)
C(5)	1496(3)	6512(2)	4196(1)	242(6)
C(6)	385(3)	7249(2)	3585(1)	249(6)
C(7)	107(3)	6622(2)	2803(1)	254(6)
C(8)	-751(3)	5391(2)	2868(1)	224(6)
C(9)	567(3)	4693(2)	3463(1)	213(6)
C(10)	650(3)	5272(2)	4278(1)	233(6)
C(11)	-178(3)	3426(2)	3487(1)	252(6)
C(12)	-237(3)	2861(2)	2690(1)	251(6)
C(13)	-1603(3)	3548(2)	2114(1)	212(6)
C(14)	-717(3)	4781(2)	2088(1)	224(6)
C(15)	-1935(4)	5346(2)	1409(1)	324(7)
C(16)	-2351(4)	4347(2)	838(1)	364(7)
C(17)	-1421(3)	3261(2)	1240(1)	278(6)
C(18)	-4036(3)	3504(2)	2340(1)	310(7)
C(19)	-1638(3)	5332(2)	4641(1)	302(7)
C(20)	842(4)	2943(2)	941(1)	348(7)
C(21)	307(5)	2211(2)	237(1)	430(8)
C(22)	-1838(4)	1681(2)	431(1)	407(8)
C(23)	2349(4)	6769(2)	2424(1)	335(7)
C(24)	3309(4)	7916(2)	2738(1)	288(7)
C(25)	1621(4)	8338(2)	3335(1)	301(6)
C(26)	5653(4)	10179(2)	2398(1)	407(8)
C(27)	1453(4)	9624(3)	1540(1)	476(9)
C(28)	5561(4)	8299(2)	1179(1)	349(7)
O(1)	5103(3)	6845(2)	5822(1)	417(5)
O(2)	-2751(4)	873(2)	133(1)	613(7)
O(3)	-2756(3)	2257(1)	1027(1)	348(5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 5. Bond lenghts (pm) of **23**

Si-C(24)	188.8 (2)	Si-C(26)	185.9 (3)
Si-C(27)	186.0 (3)	Si-C(28)	186.6 (2)
C(1)-C(2)	152.4 (3)	C(1)-C(10)	153.5 (3)
C(2)-C(3)	150.2 (3)	C(3)-C(4)	146.5 (3)
C(3)-O(1)	122.5 (3)	C(4)-C(5)	133.6 (3)
C(5)-C(6)	151.6 (3)	C(5)-C(10)	154.0 (3)
C(6)-C(7)	154.6 (3)	C(6)-C(25)	154.0 (3)
C(7)-C(8)	153.0 (3)	C(7)-C(23)	153.7 (3)
C(8)-C(9)	153.3 (3)	C(8)-C(14)	152.7 (3)
C(9)-C(10)	156.4 (3)	C(9)-C(11)	154.5 (3)
C(10)-C(19)	154.3 (3)	C(11)-C(12)	152.8 (3)
C(12)-C(13)	152.1 (3)	C(13)-C(14)	153.5 (3)
C(13)-C(17)	155.6 (3)	C(13)-C(18)	154.4 (3)
C(14)-C(15)	153.3 (3)	C(15)-C(16)	154.5 (3)
C(16)-C(17)	154.8 (3)	C(17)-C(20)	153.0 (3)
C(17)-O(3)	147.0 (3)	C(20)-C(21)	152.1 (3)
C(21)-C(22)	149.2 (4)	C(22)-O(2)	120.7 (3)
C(22)-O(3)	135.8 (3)	C(23)-C(24)	155.4 (3)
C(24)-C(25)	155.0 (3)		

Table 6. Bond angles (°) of **23**

C(24)-Si-C(26)	109.5(1)	C(24)-Si-C(27)	110.6(1)
C(26)-Si-C(27)	108.7(1)	C(24)-Si-C(28)	110.2(1)
C(26)-Si-C(28)	109.5(1)	C(27)-Si-C(28)	108.3(1)
C(2)-C(1)-C(10)	114.3(2)	C(1)-C(2)-C(3)	111.9(2)
C(2)-C(3)-C(4)	116.2(2)	C(2)-C(3)-O(1)	122.3(2)
C(4)-C(3)-O(1)	121.4(2)	C(3)-C(4)-C(5)	125.0(2)
C(4)-C(5)-C(6)	121.7(2)	C(4)-C(5)-C(10)	121.6(2)
C(6)-C(5)-C(10)	116.5(2)	C(5)-C(6)-C(7)	112.8(2)
C(5)-C(6)-C(25)	116.4(2)	C(7)-C(6)-C(25)	101.0(2)
C(6)-C(7)-C(8)	114.3(2)	C(6)-C(7)-C(23)	103.4(2)
C(8)-C(7)-C(23)	116.4(2)	C(7)-C(8)-C(9)	111.5(2)
C(7)-C(8)-C(14)	111.2(2)	C(9)-C(8)-C(14)	109.6(2)
C(8)-C(9)-C(10)	112.9(2)	C(8)-C(9)-C(11)	111.8(2)
C(10)-C(9)-C(11)	113.1(2)	C(1)-C(10)-C(5)	109.9(2)
C(1)-C(10)-C(9)	108.8(2)	C(5)-C(10)-C(9)	109.2(2)
C(1)-C(10)-C(19)	109.8(2)	C(5)-C(10)-C(19)	107.6(2)
C(9)-C(10)-C(19)	111.6(2)	C(9)-C(11)-C(12)	113.0(2)
C(11)-C(12)-C(13)	111.9(2)	C(12)-C(13)-C(14)	108.6(2)
C(12)-C(13)-C(17)	118.7(2)	C(14)-C(13)-C(17)	98.2(2)
C(12)-C(13)-C(18)	109.9(2)	C(14)-C(13)-C(18)	112.4(2)
C(17)-C(13)-C(18)	108.6(2)	C(8)-C(14)-C(13)	113.6(2)
C(8)-C(14)-C(15)	117.9(2)	C(13)-C(14)-C(15)	104.8(2)
C(14)-C(15)-C(16)	104.0(2)	C(15)-C(16)-C(17)	105.7(2)
C(13)-C(17)-C(16)	103.4(2)	C(13)-C(17)-C(20)	117.2(2)
C(16)-C(17)-C(20)	112.1(2)	C(13)-C(17)-O(3)	111.6(2)
C(16)-C(17)-O(3)	109.6(2)	C(20)-C(17)-O(3)	103.0(2)
C(17)-C(20)-C(21)	102.7(2)	C(20)-C(21)-C(22)	103.4(2)
C(21)-C(22)-O(2)	129.0(2)	C(21)-C(22)-O(3)	109.9(2)
O(2)-C(22)-O(3)	121.1(2)	C(7)-C(23)-C(24)	106.4(2)
Si-C(24)-C(23)	114.3(1)	Si-C(24)-C(25)	114.5(1)
C(23)-C(24)-C(25)	104.7(2)	C(6)-C(25)-C(24)	105.1(2)
C(17)-O(3)-C(22)	110.5(2)		

Triisopropylsilylcyclopentanosteroid (24)

Titanium tetrachloride (0.53 ml, 0.91 g, 4.8 mmol) was added to a stirred solution of the steroid dienone **22** (341 mg, 1 mmol) in dichloromethane (20 ml) at -78°C. After 15 min of stirring a solution of allyltriisopropylsilane (0.98 ml, 784 mg, 4 mmol) in dichloromethane (1 ml) was added over a period of 10 min. The reaction mixture was stirred for 1.5 h at -78°C, the cooling bath was removed, and after further stirring for 1 h the mixture was quenched by addition of an aqueous ammonium chloride solution. After extraction with dichloromethane (three times) the combined organic layers were dried over magnesium sulfate and subsequently filtered through a short path of Celite. Removal of the solvent *in vacuo* and flash chromatography (light petroleum/ethyl acetate, 3:1) of the residue on silica gel provided 170 mg (32%) of the triisopropylsilylcyclopentane **24** as colorless crystals, mp 108-110°C. IR (KBr): ν 3403, 2942, 2864, 1773, 1669, 1608, 1464, 1383, 1316, 1261, 1177, 1044, 917, 883, 666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3 H), 0.99-1.08 (m, 21 H), 1.18 (s, 3 H), 1.28-2.54 (m, 25 H), 2.74 (tr, J = 5, 1 H), 5.85 (d, J = 1.6, 1 H); ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ 11.03 (3 CH), 14.33 (CH_3), 15.55 (CH), 17.26 (CH_3), 19.23 (3 CH_3), 19.27 (3 CH_3), 20.30 (CH_2), 22.75 (CH_2), 24.50 (CH_2), 29.25 (CH_2), 30.93 (CH_2), 31.22 (CH_2), 31.50 (CH_2), 33.59 (CH_2), 34.87 (CH), 35.44 (CH_2), 35.69 (CH_2), 38.94 (C), 43.42 (CH), 43.46 (CH), 45.69 (C), 45.93 (CH), 46.53 (CH), 95.70 (C), 122.37 (CH), 169.87 (C), 176.70 (C=O), 199.41

(C=O); MS (170°C): *m/z* 538 (M^+, 1), 511 (6), 497 (14), 496 (36), 495 (100); HRMS calcd for $C_{34}H_{54}O_3Si$ (M^+): 538.3842, found: 538.3862.

7-Triisopropylsilylbicyclo[3.3.0]octan-2-one (26)

A solution of 2-cyclopenten-1-one **25** (326 µl, 331 mg, 4.03 mmol) in dichloromethane (2 ml) was added to a stirred solution of titanium tetrachloride (0.49 ml, 840 mg, 4.43 mmol) in dichloromethane (5 ml) at -20°C. The reaction mixture was cooled to -78°C and a solution of allyltriisopropylsilane (1.46 ml, 1.2 g, 6.04 mmol) in dichloromethane (5 ml) was added. The temperature was slowly raised to -20°C and the mixture was stirred at this temperature for 19 h. The cold reaction mixture was poured into an aqueous solution of ammonium chloride. After separation of the organic layer the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over magnesium sulfate and then filtered through a short path of Celite. Evaporation of the solvent and flash chromatography (*n*-hexane/diethyl ether, 7:1) of the residue on silica gel afforded 460 mg (41%) of the bicyclo[3.3.0]octane **26** as a colorless oil. IR (film, KBr): ν 3458, 2942, 2890, 2866, 1738, 1463, 1383, 1256, 1130, 1072, 1015, 999, 883, 780, 666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.92-1.05 (m, 22 H), 1.30-1.40 (m, 1 H), 1 63-1.85 (m, 3 H), 2.03-2.28 (m, 4 H), 2.50 (t, *J* = 9.5, 1 H), 2.80 (quin, *J* = 7.8, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 11 31 (3 CH), 19.09 (6 CH_3), 21.66 (CH), 27.36 (CH_2), 33.60 (CH_2), 37.30 (CH_2), 39.53 (CH_2), 40.66 (CH), 52.44 (CH), 223.05 (C=O); MS (35°C): *m/z* 280 (M^+, 5), 238 (17), 237 (100), 195 (10); HRMS calcd for $C_{17}H_{32}OSi$ (M^+): 280.2222, found: 280.2229.

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