The Sakurai Reaction of 4-Acetoxycyclopentenone – Synthesis of *trans*-3-Allyl-4-vinylcyclopentanone

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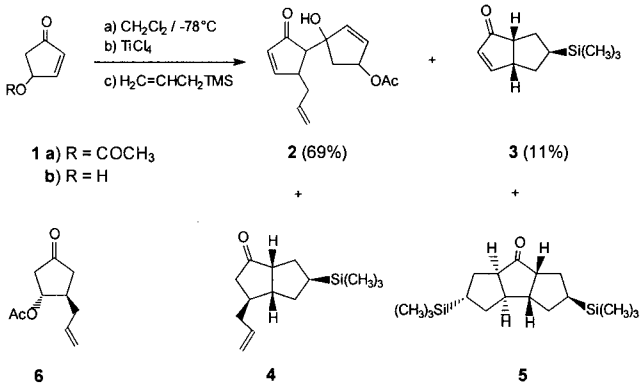
Abstract: The Sakurai reaction of 4-acetoxycyclopentenone **1a** leads to the aldol **2** and the bicyclic product **3**. Retroaldol reaction leads to 4-allylcyclopentenone **7**, from which the title compound **9** was prepared in 28% overall yield. Further transformations of **3** are reported.

Key words: allyltrimethylsilane, 4-acetoxycyclopentenone, aldol products, 5-trimethylsilyl-bicyclo[3.3.0]octan-1-one, stereoelectronic control

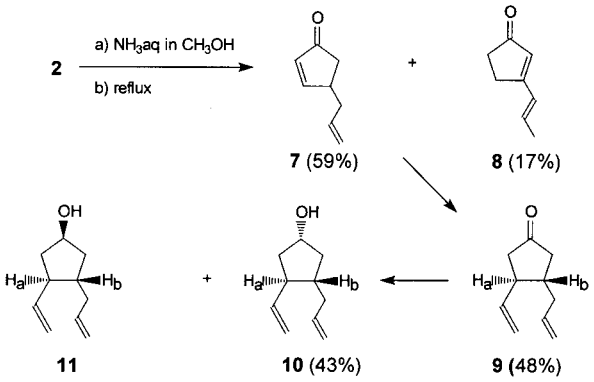
In the course of our continuing efforts to prepare polyquinanes and to study their properties, we visualized *trans*-1-allyl-2-vinylcyclopentane with a functionality in the non adjacent position like **9** as an attractive intermediate.[1-5] To prepare this target compound in a few steps we considered the readily available 4-acetoxycyclopent-2-enone **(1a)** as the key synthon.[6-7] Allylation of enones by $TiCl_4$ induced reaction with allyltrialkylsilanes according to Sakurai is well established and should lead in the case of **1a** to the intermediate **6**, which after base induced elimination of the β-acetoxy group is ready for stereoselective Cu(I) promoted *trans*-addition of a vinyl anion.[8] Most recently Robertson has reported an intriguing alternative to $TiCl_4$.[9] Here we report our surprising results of the $TiCl_4$ induced reaction of 4-acetoxycyclopent-2-enone **(1a)** with allyl-trimethylsilane leading preferentially to the aldol product **2** accompanied by the bicyclic compound **3**. The successful preparation of *trans*-3-allyl-4-vinylcyclopentanone **9** from **2** and further transformations of **3** are described.



Scheme 1

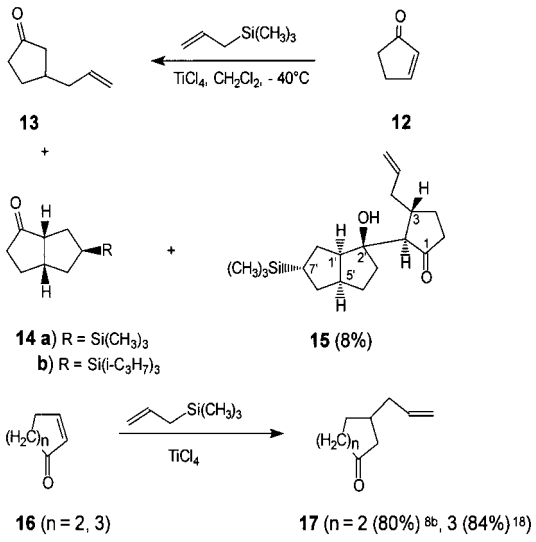
Addition of allyltrimethylsilane to a mixture of **1a** and titanium tetrachloride in dichloromethane at -78°C gave **2** and **3** in 69% and 11% yield, respectively (Scheme 1). In addition, small amounts of **1b** and of the dimer of cylcopentadienone have been detected. When the reaction was run with a large excess of allyltrimethylsilane for 2d small amounts of **4** (8%) and **5** (5%) were isolated as well. Neither the expected 3-allyl-4-acetoxy-cyclopentane **6** nor the elimination product **7** were found.

Surprisingly, the enolate intermediate of the Sakurai reaction, formed by normal allylation reacted with a second molecule of **1a** leading after elimination of acetic acid to the aldol product **2** obtained as a mixture of stereoisomers. A single isomer of unknown configuration was isolated by HPLC. The product of the annulation reaction and elimination of the acetoxy group, **3** is obtained as a single stereoisomer (see below). The structure of **2** suggested that the 4-allylcyclopent-2-enone **7** might be obtained by a retroaldol reaction. Treatment of **2** with a variety of bases did not lead to the desired cleavage. However, reaction of **2** with ammonia at r.t. gave the desired **7** accompanied by **8** in 59% and 17% yield, respectively. The subsequent Cu(I) induced 1,4-addition of vinyl magnesiumbromide to **7** gave the target compound **9** in 69% yield, with an overall yield of 28% for the transformation **1a** → **9**. Since the NMR spectra of **9** did not give a conclusive answer about the stereochemistry, the carbonyl group was reduced to the two stereoisomeric hydroxy compounds **10** and **11** (Scheme 2). The H atoms in both stereoisomers have been assigned from their H-H- and C-H COSY NMR spectra.



Scheme 2

Comparison of the chemical shifts of the bridgehead protons in the ^{1}H NMR spectra and NOE interactions revealed the *trans* configuration of the allyl and the adjacent vinyl group: In **10** as well as in **11** the tertiary H atoms *trans* to the hydroxy group (**10**: H_a, **11**: H_b) showed a NOE interaction with the H atom adjacent to the hydroxy group. The bicyclic compound **3** is formed as a minor product in the stereoselective reaction of **1a** with allyltrimethylsilane. The exo position of the trimethylsilyl substituent is suggested by the absence of a NOE signal between the adjacent H atom and the bridgehead H atoms as well as by the close analogy to the reaction of cyclopentenone **12** with tris(isopropyl)-allylsilane which gives **14b** as the major product.[10] Although **12** reacts with allyltrimethylsilane to 3-allylcyclopentanone **13** in good yield, we surmised that the bicyclic product **14a** with an *exo*-TMS substituent might be present as well (Scheme 3). If so, it would support the exo configuration of the trimethylsilyl group in analogy to the tris(isopropylsilyl) group in **14b**.



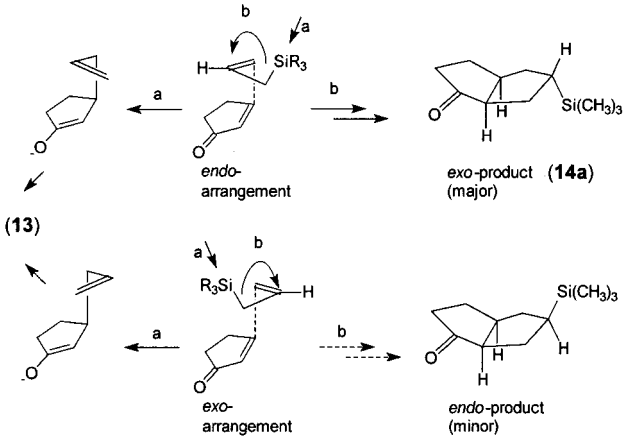
Scheme 3

Cyclopentenone (**12**) was treated with allyltrimethylsilane and $TiCl_4$ according to the known procedures.[8, 11-12] After workup the crude product was purified not by distillation but by CC, instead.[13] A mixture of **13** (GC-yield 20%) and **14a** (GC-yield 7%) was eluted first. Then, the crystalline aldol product **15** was isolated in 8% yield. The formation of **15** is most likely due to the direct reaction of the titaniumenolate, produced by allylation of **12**, with bicyclic ketone **14a**.

The X-ray structure analysis of **15** clearly reveals an *exo*-configuration of the trimethylsilyl group. Under controlled GC conditions **15** underwent a retro aldol reaction giving the bicyclic ketone **14a** as well as 3-allylcyclopentanone **13**. Hydrogenation of **3** led to a product, which according to its ^{1}H NMR sprectrum was identical with that of **14a**.

With the bicyclic compound **3** at hand, the further reaction with allyltrimethylsilane was of interest. When **3** was treated with titanium tetrachloride and allyltrimethylsilane the bi- and tricyclic compounds **4** and **5** were formed in 53% and 24% yield respectively. The stereochemistry of the triquinane **5** is based on its C_2 symmetry compatible with the 2 signals in the GC on a chiral GC-column and the 7 ^{13}C NMR signals observed.

Taking into account the results and mechanistic interpretations of Knölker, Danheiser and Meyers, the highly stereoselective processes by which **3, 14a** and others are formed, can be described by a stereoelectronically controlled attack of the allylsilane in the 3-position of the activated enone in a synplanar or an antiplanar conformation (Scheme 4, shown only for an antiplanar conformation of the enone).[9, 14-15] A priori the allylsilane can adopt an '*endo*'- or an '*exo*'-orientation. Whereas allylation could proceed by nucleophilic attack at the silyl group (process a) from the *endo*- as well as from *exo* arrangement, an endo orientation of the allyltrialkylsilane is required for the observed exclusive formation of the cyclopentane ring with the carbonyl and silyl group *trans* to each other (**14a**).[16] This ring formation becomes the dominant process (process b) by use of bulky alkylsubstituents at Si.



Scheme 4

The Sakurai reaction has proven to be a valuable addition to the arsenal of reliable and efficient synthetic methods.[8] Specifically the cycloalkenones **12** and **16** (n = 2, 3) give upon treatment with $TiCl_4$ and allyltrimethylsilane the 3-allylcycloalkanones in high yield (**13**: 70 %[8b]; **17** n = 2: 80 %[8b], **17** n = 3: 84 %[18]). Depending on the structure of the enone and the bulk of the trialkylsilyl group allylation is accompanied by a competing annulation reaction .[10,14-15] This latter reaction becomes the dominant path when the trimethylsilyl substituent of the allylsilane is replaced by bulkier trialkylsilyl groups. For the reaction of cyclopentenone **12** with allyltrimethylsilane our more detailed investigation has revealed a more complex reactivity pattern. Whether this is due to the formation of binary or higher Ti(IV)complexes in the course of the reaction is an unsolved question.[19] Nevertheless, the high yield as well as the control of the chemo- and stereoselectivity ob-

served in the reaction of enones with allyltrialkylsilanes is the basis for its synthetic importance.

In contrast to this high selectivity 4-acetoxycyclopent-2-enone **1a** reacts preferentially to **2** and the annulation product **3** rather than to the expected Sakurai product **6** or **7**. The aldol compound **2** can be cleaved upon treatment with a weak base to give the desired 4-allylcyclopent-2-enone **7** directly in good yield, from which 3-allyl-4-vinylcyclopentanone **9** can be readily prepared.

Experimental details.[20]

3-Allyl–2-[1-hydroxy-4-acetoxycyclopent-2-enyl]-cyclopent-4-enone **(2)**. To a solution of 3.40g (24.0 mmol) **1a**[7] in 140ml CH_2Cl_2 was injected 4.54g (24.0 mmol) freshly distilled $TiCl_4$ at -78ºC under vigourous stirring. After stirring for 20 min a cooled (-78ºC) solution of 6.40g (48.0 mmol) allyltrimethylsilane in 80ml CH_2Cl_2 was slowly added during 1h. The reaction mixture was warmed to -25ºC and stirred for 20h. Hydrolysis with an ice cold solution of $NaHCO_3$ and extraction with CH_2Cl_2 (3x) gave after work up and CC with hexane-ether (1:1) 4.35g (69%) **2** and 0.52g (11%) **3**. In addition traces of **1b** and dicyclopentadienone were isolated. A pure isomer of **2** was isolated by HPLC: R_f (hexane-ether = 1:1): 0.17. IR: 3600 (w), 1730(ws), 1690(vs), 1370(s), 1245(vs), 1020(s). MS: 262(M^+, 3), 220(12), 205(27), 202(19), 184(5), 174(5), 171(6), 161(10), 141(10), 123(22), 122(100), 121(20), 107(34), 94(40), 86(73), 84(82), 81(59), 79(29), 53(12), 49(15), 47(21), 43(29), 18(10). ^{1}H NMR**:** 7.68(dd, J=5.5, 2.3, 1H), 6.25(dd, J=5.5, 1.8, 1H), 6.05-5.97 (m, 2H), 5.80-5.62 (m, 1H), 5.54-5.46(m, 1H), 5.17-5.04 (m, 2H), 4.60(s, 1H), 2.10-2.50(m, 5H), 2.05(s, 3H), 1.84 (dd, J =15.1, 3.3, 1H). ^{13}C-NMR: 217(s), 170.8(s), 168.4(d), 139.6(d), 134.2(d), 134.1(d), 132.4(d), 118.4(t), 84.8(s), 77.4(d), 56.3(d), 44.3(d), 42.0(t), 37.9(t), 21.1(q). HR-MS: 262.1205 (calc. $C_{15}H_{18}O_4$ 262.1205).

3: R_f (hexane-ether = 1:1): 0.73. M.p: 24-28ºC. IR: 1705(vs), 1250(s). MS: 194(M^+, 100), 79(56), 105(10), 153(50), 75(43), 73(80), 47(17), 28(22), 18(43). ^{1}H NMR: 7.48 (dd, J_1=5.5, J_2=2.8, 1H), 6.15 (dd, J_1=5.5, J_2=1.8, 1H), 3.40-3.33 (m, 1H), 2.66 dd, J_1=9.7, J_2=5.4, 1H), 1.91 (dd, J=12.9, 5.9, 1H), 1.62 (ddt, J=12.9, 5.9, 1.3, 1H), 1.55-1.43 (m, 2H), 0.72-0.61 (m, 1H), 0.00 (s, 9H). ^{13}C-NMR**:** 214.0(s), 167.6(d), 135.1(d), 50.7(d), 47.7(d), 32.2(t), 31.2(t), 22.4(d), -3.0(q). HR-MS: 194.1309 (calc. for $C_{11}H_{18}OSi$ 194.1307).

4-Allylcyclopent-2-enone (**7**): After addition of 2.86g (10.9 mmol) **2** in 10ml CH_3OH to a mixture of 80ml aqueous NH_3 (25%) and 100ml CH_3OH in 15 min the solution was refluxed for ~ 1.5 h. The organic phase obtained by dilution of the reaction mixture with ice cold aqueous $NaHCO_3$ and extraction with hexane (3x) was treated with 2N HCl (3x). CC with hexane-ether (1:1) gave 0.785g (59%) **7** and 0.226g (17%) **8**[21]. **7**: R_f (hexane-ether = 1:1): 0.38. IR**:** 1710(vs). ^{1}H NMR: 7.65(dd, J_1=5.6, J_2=2.6, 1H), 6.19(dd, J_1=5.6, J_2=1.9, 1H), 5.78(m, 1H), 5.13(m, 2H), 3.05(m, 1H), 2.53(dd, J=18.7, 6.2, 1H), 2.27(m, 2H), 2.05(dd, J=18.7, 2.2, 1H). ^{13}C-NMR: 214.1(s), 167.6(d), 134.9(d), 134.2(d), 117.5(t), 40.8(d), 40.3(t), 38.5(t).

Trans-3-allyl-4-vinyl-cyclopentanone (**9**): To a mixture, prepared from 7.0 ml vinyl-MgBr in THF(15%, 7.00 mmol) and 0.119 g CuBr x $(CH_3)_2S$ in 18 ml THF at –70°C was slowly added 0.710g (5.8mmol) **7** in 10ml THF. After stirring for 1.5 h at -78ºC the reaction mixture was worked up, extracted with ether (3x) and the residue purified by FC with hexane-ether = 1:1 to give 0.60 mg (69%) **9**: R_f (hexane-ether = 1:1): 0.73. IR: 3010(m), 1740(vs), 920(s). ^{1}H NMR: 5.75(m, 2H), 5.08(m, 4H), 2.56-2.39(m, H_a + 3H), 2.19-1.85(m, 3H + H_b). ^{13}C NMR: 217.1(s), 139.3(d), 135.8(d), 116.7(t), 116.1(t), 46.5(d), 45.1(t), 44.0(t), 42.0(d), 37.0(t). FAB-MS: 150.0(M^+, 12), 149.0 (100). GC-MS: 150(M^+, 44), 135(30), 132(24), 108(14), 92(10), 81(14), 80(17), 79(15), 68(23), 67(37), 54(100), 41(32), 39(37), 27(22). Anal. calc. for $C_{10}H_{14}O$: C 79.94, H 9.40; found: C 79.65, H 9.38.

(rel-1R,3R,4S)-3-Allyl-4-vinyl-cyclopentanol (**10**) *and (rel-1S,3R,4S)-3-Allyl-4-vinyl-cyclopentanol* (**11**): A solution of 0.56 g (3.7mmol) **9** in 10ml methanol was slowly added to 0.156 g (4.1mmol) $NaBH_4$ in 20ml methanol. After 15 min 5ml dist. water was added and the reaction mixture worked up. HPLC gave 0.27 g (48%) **10** and 0.242 g (43%) **11**. **10**: R_f (hexane-ether = 1:1) : 0.28; k' (HPLC): 7.6. IR: 3615(s), 3480(s), 1010(vs), 915(vs). ^{1}H NMR: 5.90-5.75(m, 1H), 5.75-5.60(m, 1H), 5.10-4.9(m, 4H), 4.40-4.30(m, 1H), 2.60-2.50(m, H_a), 2.50-2.40(m, 1H), 2.40-2.30(m, 1H), 2.15-2.05(m, 1H), 2.00-1.90(ddt, 1H), 1.85-1.75(m, 1H), 1.75-1.70(m, H_b), 1.60(s, 1H), 1.45-1.35 (m, 1H). ^{13}C NMR: 141.5(d), 137.4(d), 115.5(t), 114.5(t), 72.2(d), 47.8(d), 44.0(d), 42.8(t), 41.5(t), 38.3(t). **11**: R_f 0.25 (hexane-ether = 1:1); k'(HPLC, hexane-ethylacetate = 20:1): 8.1. IR: 3610(m), 3450(s), 1330(m), 1070(m), 1010(vs), 915(vs). ^{1}H-NMR: 5.85-5.70(m, 2H), 5.05-4.90(m, 4H), 4.35-4.25(m, 1H), 2.40- 2.20(m, 2H), 2.15-2.00(m, H_a), 2.00-1.90(m, H_b), 1.90-1.78(m, 2H), 1.60-1.40(m, 3H).^{13}C-NMR: 142.1(d), 137.3(d), 115.5(t), 114.2(t), 72.2(d), 49.0(d), 42.9(d), 42.6(t), 41.7(t), 37.7(t). MS (mixture of **10** and **11**): 152(M^+, 5), 151([M-1]$^+$, 18), 137(17), 135(20), 124(42), 111(46), 110(39), 109(46), 91(64), 83(100). HR-MS: calc. for $C_{10}H_{16}O$ 152.120115, found 152.11850.

4-exo-Allyl-7-exo-trimethylsilyl-*bicyclo[3.3.0]octan-2-one* (**4**) *and rel-(1R,3R,5S,7R,8R,10S)-5,10-bis-trimethylsilyl-tricyclo[6.3.0.0^{3,7}]-undecan-2-one* (**5**): A solution of 0.34 g (1.75 mmol) **3** in 5ml CH_2Cl_2 was added dropwise to a solution of 0.365g (1.93 mmol) $TiCl_4$ in 5ml CH_2Cl_2 at -78ºC. After slow addition of 0.30g (2.63 mmol) allyltrimethylsilane in 1ml CH_2Cl_2 the reaction mixture was stirred at -78ºC , warmed to -20ºC and stirred for 20h. Work up and CC with hexane-AcOEt = 20:1 gave 0.180 g(53%) **4** and 0.067 g (24%) **5**. **4**: R_f (hexane- AcOEt = 20:1): 0.65. IR: 1720(s), 1250(vs), 1150(s), 1100(vs), 910(s), 895(s), 850(vs). ^{1}H NMR: 6.00-5.85(m, 1H), 5.25-5.15(m, 1H), 2.90-2.80(m, 1H), 2.70-2.60(m, 1H), 2.55-2.35(m, 3H), 2.30-2.10(m, 2H), 2.00-1.85(m, 1H), 1.85-1.75(m, 1H), 1.70-1.55(m, 2H), 1.05-0.85(m, 1H), 0.05(s,

9H). ^{13}C NMR: 221.9(s), 136.5(d), 116.4(t), 53.5(d), 47.6(d), 45.8(t), 40.6(d), 40.2(t), 35.4(t), 32.3(t), 25.4(d), -3.0(q). MS: 236(M^+, 25), 221(12), 196(36), 195(100), 153(23), 123(27), 105(11), 86(45), 84(49), 75(15), 73(46), 47(12). HR-MS: 236.1592 (calc. for for $C_{16}H_{24}OS$ 236.1596). **5**: R_f (hexane- AcOEt = 20:1): 0.79. M.p.: 80-82°C. IR: 1725(vs), 1250(vs), 920(s), 850(vs). MS: 308(M^+, 8), 267(38), 235(15), 195(75), 194(22), 193(23), 179(23), 153(15), 105(15), 75(28), 73(100), 32(39), 28(96), 18(47). ^{1}H-NMR: 2.70-2.60(m, 2H), 2.40-2.30(m, 2H), 2.05-1.95(m, 2H),1.75-1.50(m, 6H), 0.90-0.80(m, 2H). ^{13}C-NMR: 228.3(s), 55.7(d), 48.8(d), 37.9(t), 33.9(t), 25.7(d), -3.0(q). HR-MS: 308.1996 (calc.$C_{17}H_{32}OSi_2$ 308.1992).

5-Trimethylsilyl-bicyclo[3,3,0] octan-1-one (**14a**).

a) via preparative GC: GC of **15** at 120 -130 °C (20% XF 1150)) gave **13** (t_R = 7.1 min) and **14a** (t_R = 15.78 min). **14a**: ^{1}H NMR: 2.80-2.95 (m, 1H) 2.55-2.65 (m, 1H) 2.10-2.40 m, 3H) 1.95 - 2.05 (ddd, 1H) 1.40 - 1.65 (m, 4H) 0.75 - 0.92 (m, 1H) -0.03 (s, 9H). ^{13}C NMR: 223.71 (s) 53.03 (d) 41.26 (d) 39.60 (t) 36.26 (t) 32.63 (t), 27.51 (t) 25.32 (d) -2.98 (q). MS: 196(M^+,10) 181(12), 155(81), 156(19), 75(40), 73(100) 54(25). HR-MS: calcd. for $C_{11}H_{20}OSi$: 196.128344; found 196.127610.

b) via hydrogenation: A solution of **3** (98 mg, 0.5 mmol) in ether (10 mL) was hydrogenated in the presence of 5% Pd/C (50 mg). The crude product (100 mg) was distilled in a Kugelrohr bp 110 °C (0.4 mm) purified by preparative GC. All spectral data (MS, ^{1}H NMR, ^{13}C NMR) identical with **14a** obtained from **15** by aldol cleavage.

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