Pergamon

TETRAHEDRON

Tetrahedron 57 (2001) 5091–5095

Studies on transannular rearrangement pathways in the bicyclo[4.4.1]undecane ring system: a novel entry into the bicyclo[4.2.1]nonene ring system

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Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

Received 2 February 2001; revised 19 March 2001; accepted 20 March 2001

Abstract—Several novel transannular bond reorganization pathways have been observed in various bicyclo[4.4.1]undecane substrates during attempted α-ketol and pinacol rearrangement reactions. © 2001 Elsevier Science Ltd. All rights reserved.

The bicyclo[4.4.1]undecane ring system is a prominent substructural feature in several families of diterpene and sesterterpene natural products and its construction has presented formidable challenges to the synthetic chemist.[1] In recent years our laboratory has developed an efficient and very general entry into this intriguing ring system that exploits a chromium(0)-promoted [6π+4π] cycloaddition reaction for the construction of this otherwise difficult to access species (Fig. 1).[2]

One of the particular virtues of this transformation is its adaptability to a wide range of substituted reaction partners, making available bicyclic products exhibiting a virtually unlimited variety of substitution patterns. This feature of these transformations was exploited in a series of rearrangements that were designed to convert the bicyclo[4.4.1]undecane ring into the isomeric bicyclo[5.3.1]undecane and bicyclo[5.4.0]undecane systems, which are characteristic of the taxane and tigliane (phorbol) diterpenes, respectively[3] (Scheme 1). We now wish to report on another rearrangement manifold available within the bicyclo[4.4.1]undecane framework that involves a novel transannular bond reorganization leading to highly substituted bicyclo[4.2.1]nonene systems that can become the major pathway in certain circumstances.[4]

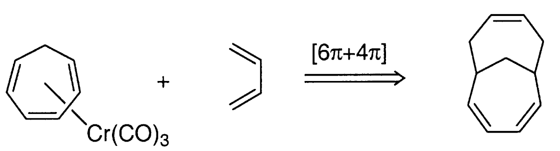
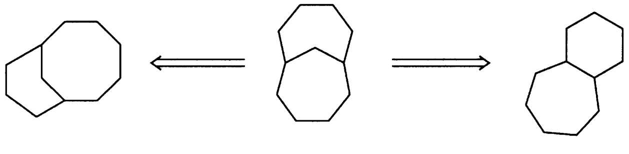
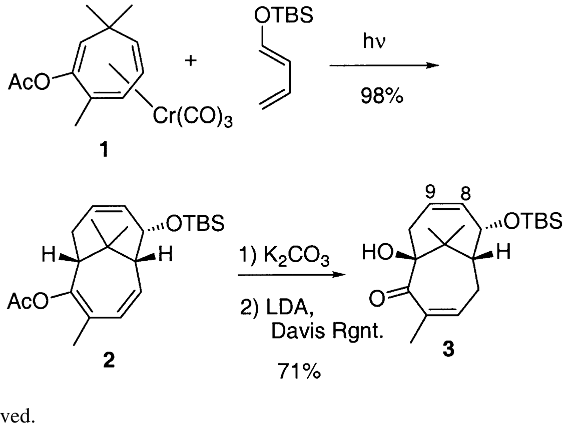


Figure 1. Cr(0)-promoted entry into the bicyclo[4.4.1]undecane system.

This new reaction channel was first observed during an attempted α-ketol rearrangement of the highly functionalized bicyclic intermediate **3** prepared via a highly stereo- and regioselective photo-[6π+4π] cycloaddition between complex **1** and the corresponding silyloxybutadiene partner to give cycloadduct **2**, which was subsequently α-hydroxylated using the Davis oxaziridine reagent[5] via the corresponding bridgehead enolate as reported previously (Eq. (1)).[3] Compound **3** was then treated with excess aluminum triisopropoxide in refluxing benzene to afford an 80% overall yield of a mixture of recovered starting material (60%) and a new compound, assigned structure **4** (22%), in which the original [4.4.1]undecane skeleton had undergone a profound bond reorganization to give a vinyl substituted bicyclo[4.2.1]nonene species.



Scheme 1.



(1)

Keywords: cycloadditions; ketols; rearrangements; transannular reactions.

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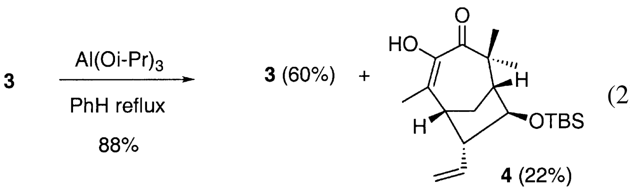
PII: S0040-4020(01)00356-8



(2)

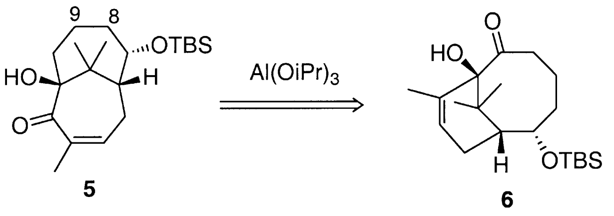
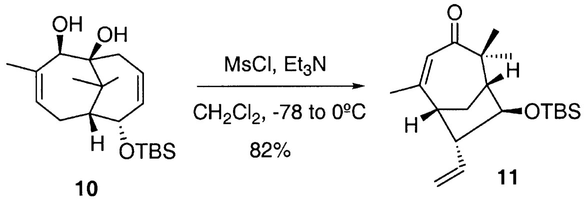


Figure 2. 'Normal' rearrangement pathway for the bicyclo[4.4.1]undecane system.

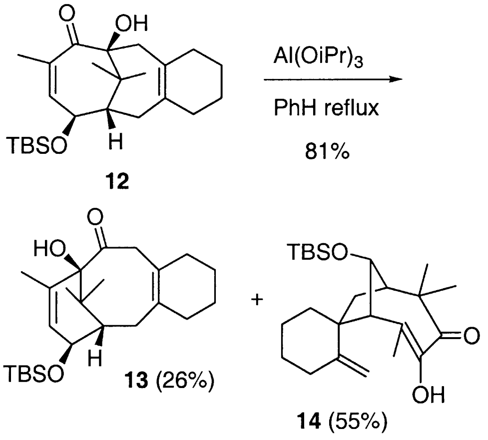
The structure of **4** was assigned based on the presence in the ^{1}H NMR spectrum of a three spin system centered at approximately 5.45 ppm, typical of a terminal vinyl group,[6] as well as bands in the IR spectrum consistent with the presence of an α-diketone (3343, 1716, 1657 cm^{-1}). The structural assignment for **4** was further substantiated by a complete set of proton–proton decoupling and 2D NMR experiments which confirmed the connectivity as shown. The production of **4** in this case is quite intriguing in light of the fact that a bicyclic starting material identical to **3** in all respects except for the absence of a second double bond at C8–C9 led cleanly to a bicyclo[5.3.1]undecane product (Fig. 2).[3]

The distinct reaction channels followed by compounds **3** and **5** when exposed to aluminum triisopropoxide suggest the involvement of a transannular process in the former substrate that is precluded in the latter material due to the absence of the unsaturation at C8–C9. Transannular reactions are frequently observed in medium-sized rings and, in fact, are often difficult to avoid in these types of systems.[7] It is noteworthy that this reaction was the first instance in our experience of a transannular process in the bicyclo[4.4.1]undecane system. A possible rationale for the production of **4** from compound **3** is depicted in Scheme 2. A crucial feature of this proposed mechanism is the role played by the Lewis acid in dictating the reactive conformation of the bicyclic species. Indeed, the chelation of the trivalent aluminum center with the vicinal oxygen functions in **3** appears to strongly enforce the corresponding boat conformation **7**, bringing the alkene close to the developing cation. The development of electron deficiency at C4 in **7** that presumably occurs as the reaction proceeds could be subjected to transannular trapping by the alkene function situated directly across the ring at C8. Subsequent bond cleavage, as indicated in intermediate **8**, would ultimately afford the observed product (**8**⇒**9**⇒**4**).

To test the generality of this rearrangement in related systems, compound **3** was converted into the corresponding *cis*-1,2-diol **10** via Luche reduction,[8] and then treated with methanesulfonyl chloride and triethylamine at low temperature. Under these conditions, a bond reorganization occurred rapidly to provide bicycle **11** in 82% yield. This reaction is presumed to proceed through a pathway not unlike the one suggested for the conversion of **3** into **4**.

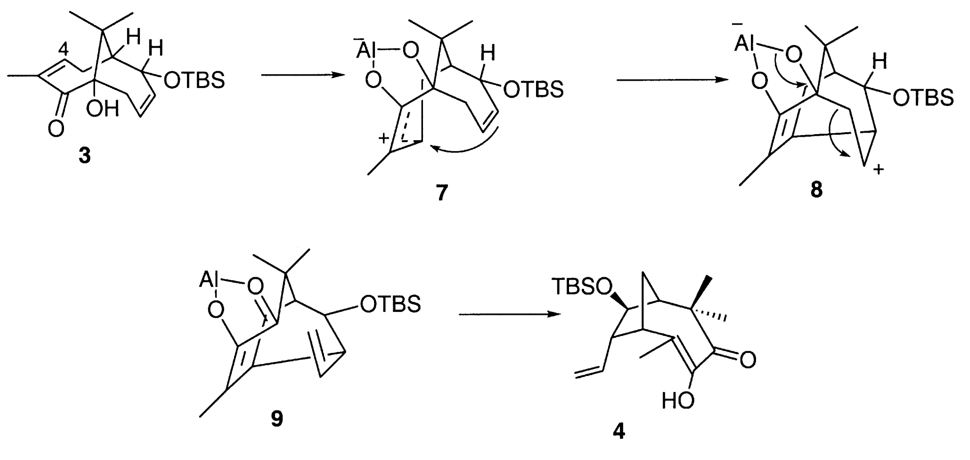


(3)



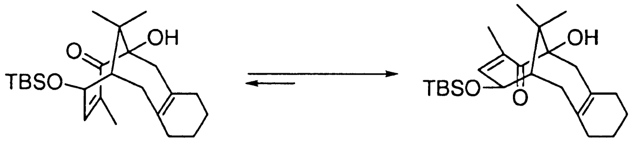
(4)

To study this fascinating rearrangement in a more complex

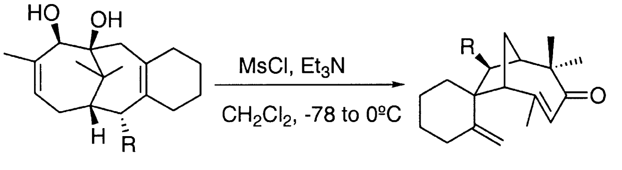


Scheme 2.

context, the functionalized tricycle **12**, reported previously,[3] was exposed to Al(OiPr)$_3$ in refluxing benzene. In the event, this reaction provided a mixture of compounds comprised of the taxane-like **13** and the novel spirotricycle **14** with the latter material being formed preferentially. Both compounds were produced in stereochemically homogeneous form. Models were examined to gain further insight into the conformational effects at play in this reaction, and these indicated that conformation **12b** should be preferred over **12a** so as to better accommodate the bulky OTBS group in a pseudo-equatorial orientation. However, once again it is believed that chelation of the aluminum reagent to the keto-alcohol function helps to increase the amount of conformer **12a** present in the reaction mixture, allowing the transannular reaction to proceed with reasonable efficiency as before.



12a **12b**



15a, R=H
15b, R=OTBS

16a, R=H (68%)
16b, R=OTBS (66%)

(5)

If this rearrangement pathway proved to be general in even more structurally elaborate substrates, a number of intriguing ring systems could be assembled in short order. *cis*-Diols **15a**, **b** were then prepared to test this notion, and the corresponding pinacol rearrangements proceeded smoothly and rapidly on each compound to deliver the expected spirotricyclic products **16a**, **b** in good yields. These latter observations serve to reinforce the supposition that these transannular rearrangement pathways indeed represent an important aspect of the reaction profile of the bicyclo[4.4.1]undecane skeleton.

In summary, the bicyclo[4.4.1]undecane ring system has been shown to be a particularly rich source of interesting bond reorganizations, and further work on exploiting these rearrangement products to synthetic advantage is currently underway in our laboratory.

1. Experimental[9]

1.1. General

1.1.1. ***rac*[1*R*,6*R*,8*R*]-8-[(*tert*-Butyldimethylsilyl)oxy]-7-ethenyl-4-hydroxy-2,2,5-trimethylbicyclo[4.2.1]nona-4-ene-3-one (4).** To a boiling solution of **3** (0.022 g, 0.063 mmol) in benzene (5 mL, freshly distilled from CaH$_2$) was added in one portion aluminum triisopropoxide (0.064 g, 0.314 mmol) and the resulting mixture was heated at reflux under N$_2$ for 20 h. The reaction mixture was cooled to room temperature and a saturated aqueous solution of Rochelle salt (5 mL) was added and the mixture was stirred for 20 min and diluted with Et$_2$O (20 mL). The organic phase was separated and the aqueous phase was extracted into Et$_2$O (2×10 mL). All organic extracts were combined, rinsed with brine (10 mL), dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexanes–EtOAc, 40:1) to afford 0.012 g (60%) of the starting ketol **3** and 0.006 g (22%) of the transannular product **4**: colorless oil; R$_f$=0.25 (hexanes–Et$_2$O, 10:1); IR (neat) ν 3373, 3074, 2928, 1716, 1647, 1604, 1088, 836 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.60 (dt, *J*=12, 9.9 Hz, 1H), 5.20 (dd, *J*=9.9, 2.1 Hz, 1H), 3.95 (dd, *J*=6.9, 2.5 Hz, 1H), 2.71 (ddd, *J*=6.6, 5.7, 0.9 Hz, 1H), 2.64 (ddd, *J*=9.9, 6.9, 6.6 Hz, 1H), 2.24 (ddd, *J*=12, 9.9, 5.7 Hz, 1H), 2.01 (dd, *J*=9.9, 2.5 Hz, 1H), 2.00 (s, 1H, D$_2$O exchangeable), 1.99 (dd, J=12, 0.9 Hz, 1H), 1.93 (s, 3H), 1.36 (s, 3H), 1.26 (s, 3H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 201.4 (CO), 144.5 (C), 138.9 (C), 131.9 (CH$_2$), 118.0 (CH), 81.3 (CH), 60.4 (CH), 56.2 (CH), 51.3 (CH$_3$), 48.8 (CH). 32.9 (CH$_2$), 30.1 (CH$_2$), 26.7 (CH$_3$), 25.9 (CH$_3$), 22.4 (CH$_3$), 17.9 (CH$_3$), −2.8 (CH$_3$), −4.5 (C); MS *m/e* (rel. int.) 350 (13), 293 (92), 265 (35); HRMS calcd for $C_{20}H_{34}O_3Si$ (M$^+$) 350.2277, found 350.2281.

1.1.2. ***rac*[1*R*,6*R*,7*R*,8*S*]-8-[(*tert*-Butyldimethylsilyl)oxy]-7-ethenyl-2,2,5-trimethyl bicyclo[4.2.1]nona-4-ene-3-one (11).** To a solution of **10** (0.028 g, 0.080 mmol) in CH$_2$Cl$_2$ (2 mL) were added respectively triethylamine (0.013 mL, 0.096 mmol) and methanesulfonyl chloride (0.009 mL, 0.095 mmol) and the resulting mixture was stirred at 0°C for 2 h. The reaction mixture was quenched with water (5 mL) and diluted with CH$_2$Cl$_2$ (25 mL) and the organic phase was separated. The aqueous phase was extracted into CH$_2$Cl$_2$ (2×10 mL), and the combined organic phases were rinsed with brine (10 mL), dried over anhydrous MgSO$_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexanes–EtOAc, 40:1) to afford 0.022 g (82%) of the enone: mp=50–51°C (methanol); R$_f$=0.14 (hexanes–EtOAc, 40:1); IR (neat) ν 3074, 2928, 1641, 1433, 1093, 836 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.86 (6rs, 1H), 5.59 (ddd, *J*=17.1, 10.5, 8.1 Hz, 1H), 5.16 (dd, *J*=12, 2.0, Hz, 1H), 5.12 (dd, *J*=10.5, 2.0 Hz, 1H), 3.92 (dd, *J*=5.7, 2.0 Hz, 1H), 2.65 (m, 2H), 2.19 (ddd, *J*=13.0, 9.5, 5.0 Hz, 1H), 2.15 (d, *J*=13.0 Hz, 1H), 2.02 (dd, *J*=9.5, 2.0 Hz, 1H), 1.87 (d, *J*=1.2 Hz, 3H), 1.25 (s, 3H), 1.17 (s, 3H), 0.85 (s,9H), 0.01 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 206.4 (CO), 157.4 (C), 137.8 (C), 129.2 (CH$_2$), 117.9 (CH), 81.6 (CH), 60.2 (CH), 56.6 (CH), 51.8 (CH), 49.5 (CH$_3$), 32.6 (CH$_3$), 29.7 (CH$_3$), 29.3 (CH$_2$), 28.5 (CH$_3$), 26.1 (CH$_3$), 25.9 (CH$_3$), −3.1 (CH$_3$), −4.6 (C); MS *m/e* (rel. int.) 335 (M+1, 2), 319 (2), 277 (65), 249 (17), 133 (40), 75 (100); HRMS calcd for $C_{20}H_{35}O_2Si$ (M$^+$+1) 335.2406, found 335.2413. Anal. Calcd for $C_{20}H_{35}O_2Si$: C,71.81; H, 10.24. Found: C, 71.46; H, 10.19.

1.1.3. ***rac*-[1*R*,11*R*,14*S*]-14-[(*tert*-Butyldimethylsilyl)oxy]-11-hydroxy-12,15,15-trimethyltricyclo[9.3.1.0^{3,8}]pentadeca-3(8),12-diene-10-one (13), and *rac*-[1*R*,1′*R*,6′*S*,9′*R*]-spiro{2-methylenocyclohexane-1,7′-9′-[(*tert*-butyldimethyl-**

silyl)oxy]-4-hydroxy-2′2′,5′-trimethylbicyclo[4.2.1]nona-4′-ene-3′one} (14). To a solution of α-ketol **12** (0.040 g, 0.1 mmol) in benzene (10 mL) was added aluminum isopropoxide (0.060 g, 0.300 mmol) and the resulting mixture was heated at reflux under standard conditions. The progress of the reaction was monitored by the disappearance of the starting material as indicated by TLC analysis. When the starting material had completely disappeared (4 h), the reaction mixture was cooled to room temperature, quenched with a saturated aqueous solution of Rochelle salt (5 mL) and diluted with Et_2O (50 mL). Work-up as before provided a crude mixture, which was purified by flash column chromatography (silica gel, hexanes–EtOAc, 10:1) to afford 0.010 g (26%) of the taxane substructure **13** and 0.022 g (55%) of the spiro product **14**.

Compound 13. Colorless oil; R_f=0.28 (hexanes–EtOAc, 10:1); IR (neat) ν 3438, 1688, 1644, 1463, 1252, 1055, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.72 (dq, *J*=5.0, 1.0 Hz, 1H), 4.56 (s, D_2O exchangeable, 1H), 3.89 (d, *J*=5.0 Hz, 1H), 3.69 (d, *J*=11.5 Hz, 1H), 2.71 (d, *J*=11.5 Hz, 1H), 2.25 (dd, *J*=14.5, 7.5 Hz, 1H), 2.17 (dd, *J*=14.5, 10.5 Hz, 1H), 2.05–1.96 (m, 6H), 1.66 (m, 2H), 1.58 (d, *J*=1.0 Hz, 3H), 1.24 (s, 3H), 0.89 (s, 9H), 0.87 (m, 1H), 0.76 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.3 (CO), 136.3 (C), 135.4 (C), 128.1 (CH_2), 124.6 (C), 85.7 (CH), 71.1 (C), 47.8 (CH), 44.3 (CH), 39.9 (C), 38.7 (C), 31.8 (CH_2), 31.0 (CH_2), 30.3 (CH_2), 25.8 (CH_2), 22.7 (CH_2), 22.6 (CH_3), 18.4 (CH_3), 18.0 (CH_3), −4.6 (CH_3), −4.9 (C); MS *m/e* (rel. int.) 404 (23), 376 (30), 347 (65), 267 (100); HRMS calcd for $C_{24}H_{40}O_3Si$ (M^+) 404.2746, found 404.2739.

Compound 14. Colorless oil; R_f=0.37 (hexanes–EtOAc, 10:1); IR (neat) ν 3372, 2930, 1694, 1644, 1251, 839 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.75 (s 1H), 4.74 (dd, *J*=8.5, 5.5 Hz, 1H), 4.54 (s, 1H), 2.95 (d, *J*=5.5 Hz, 1H), 2.33–2.29 (m, 2H), 2.25–2.19 (m, 2H), 2.00 (bd, *J*=14.0 Hz, 1H), 1.87 (s 3H), 1.69–1.58 (m, 1H), 1.58–1.53 (m, 1H), 1.42 (s 3H), 1.40–1.31 (m, 1H), 1.27–1.20 (m, 1H), 0.79 (s, 9H), 0.04 (s, 6H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.2 (CO), 151.5 (C), 146.2 (C), 120.9 (C), 108.1 (CH_2), 73.6 (CH), 56.0 (CH), 49.5 (CH), 47.1 (CH_2), 43.9 (CH_2), 38.7 (CH_2), 36.9 (CH_2), 35.9 (CH_2), 29.8 (CH_2), 28.6 (CH_2), 27.9 (CH_3), 25.7 (CH_3), 22.7 (CH_3), 21.6 (CH_3), 17.9 (CH_3), −5.0 (C); MS *m/e* (rel. int.) 404 (4), 376 (5), 347 (18), 305 (11), 267 (26), 75 (100); HRMS calcd for $C_{24}H_{40}O_3Si$ (M^+) 404.2746, found 404.2755.

1.1.4. ***rac*[1*R*,1′*R*,6′*S*]-Spiro{2-methylenocyclohexane-1,7′-2′,2′,5′-trimethylbicyclo[4.2.1]nona-4′-ene-3′one} (16a).** To a solution of diol **15a** (0.017 g, 0.061 mmol) in CH_2Cl_2 (1 mL) were added triethylamine (0.017 mL, 0.122 mmol) and methanesulfonyl chloride (0.006 mL, 0.074 mmol) and the resulting mixture was stirred at −78°C for 10 min, slowly warmed to −20°C, stirred for another 0.5 h and then warmed to 0°C. After stirring for 1.5 h at 0°C, the reaction mixture was quenched with 5% aqueous hydrochloric acid solution (2 mL) and diluted with CH_2Cl_2 (20 mL). Work-up as before afforded a crude product, which was purified by flash column chromatography (silica gel, hexanes–EtOAc, 10:1) to deliver 0.011 g (68%) of spiro product **16a:** mp=80–81°C (colorless needles, Et_2O–hexanes); R_f=0.38 (hexanes–EtOAc, 10:1); IR (CH_2Cl_2) ν 3081, 2931, 1729, 1637, 1447, 1380, 893 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.84 (s, 1H), 4.74 (s, 1H), 4.59 (s, 1H), 2.83 (d, *J*=5.5 Hz, 1H), 2.31–2.00 (m, 3H), 2.12 (m, 1H), 2.04–1.95 (m, 3H), 1.87 (s, 3H), 1.61 (m, 1H), 1.48 (dd, *J*=13.5, 8.5 Hz, 1H), 1.40–1.26 (m, 2H), 1.25 (m, 1H), 1.21 (dd, *J*=13.5, 4.0 Hz, 1H), 1.16 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.2 (CO), 159.4 (C), 150.8 (CH), 130.7 (C), 108.0 (CH_2), 54.3 (C), 50.8 (C), 49.8 (CH), 41.9 (CH), 38.7 (CH_2), 37.6 (CH_2), 36.0 (CH_2), 33.5 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.3 (CH_2), 26.0 (CH_3), 22.1 (CH_3); MS *m/e* (rel. int.) 258 (18), 230 (36), 215 (17), 187 (35), 147 (100); HRMS calcd for $C_{18}H_{26}O$ (M^+) 258.1983, found 258.1979.

1.1.5. ***rac*[1*R*,1′*R*,6′*R*,8′*R*]-Spiro{2-methylenocyclohexane-1,7′-8′-[(*tert*-butyldimethylsilyl)oxy]-2′,2′,5′-trimethylbicyclo[4.2.1]nona-4′-ene-3′one} (16b).** To a solution of the diol **15b** (0.030 g, 0.07 mmol) in dry CH_2Cl_2 (1 mL) was added methanesulfonyl chloride (0.007 mL, 0.089 mmol) and triethylamine (0.031 mL, 0.22 mmol) and the resulting mixture was stirred for 1 h at −78°C. At this time, the reaction mixture was slowly warmed to 0°C and quenched with 5% aqueous hydrochloric acid solution (2 mL) and diluted with CH_2Cl_2 (20 mL). Extractive work-up procedure as above gave a crude product, which was purified by flash column chromatography (silica gel, hexanes–EtOAc, 10:1) to afford 0.019 g (66%) of the spiro product **16b** as a colorless oil: R_f=0.38 (hexanes–EtOAc, 10:1); IR (CH_2Cl_2) ν 3088, 2927, 1730, 1615, 1471, 1255, 835 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.84 (d, *J*=0.5 Hz, 1H), 4.85 (s, 1H), 4.74 (s, 1H), 4.53 (d, *J*=4.0 Hz, 1H), 2.86 (d, *J*=5.5 Hz, 1H), 2.40 (dd, *J*=10.5, 5.5 Hz, 1H), 2.37 (dd, *J*=10.5, 5.5 Hz, 1H), 2.32 (bd, *J*=14.0, Hz, 1H), 2.21 (ttd, *J*=13.5, 4.5, 1.5 Hz, 1H), 1.91 (dd, *J*=10.5, 3.5, Hz, 1H), 1.84 (d, *J*=1.5 Hz, 3H), 1.42 (d, *J*=5.5 Hz, 1H), 1.79–1.70 (m, 1H), 1.67 (dd, *J*=13.0, 4.0 Hz, 1H), 1.26 (s, 3H), 1.17 (s, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.8 (CO), 159.5 (C), 148.0 (CH), 130.4 (C), 108.8 (CH_2), 78.0 (CH), 56.1 (C), 53.2 (CH), 50.3 (CH), 50.1 (CH_2), 36.3 (CH_3), 31.7 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 27.5 (CH_2), 26.2 (CH_2), 26.0 (CH_3), 22.4 (CH_3), 18.4 (CH_3), −4.8 (CH_3), −4.6 (C); MS *m/e* (rel. int.) 388 (8), 331 (100), 303 (8), 249 (58); HRMS calcd for $C_{24}H_{40}O_2Si$ (M^+) 388.2798, found 388.2788.

Acknowledgements

The authors wish to thank the National Institutes of Health for their generous support of this research.

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