Synthesis of a Tetrasubstituted Cyclohexene from a Bicyclo[2.2.2]octa-2,5-diene

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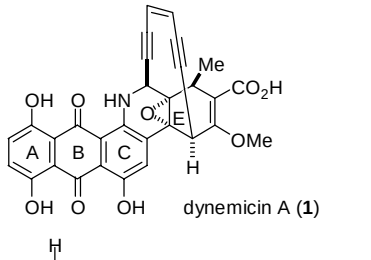
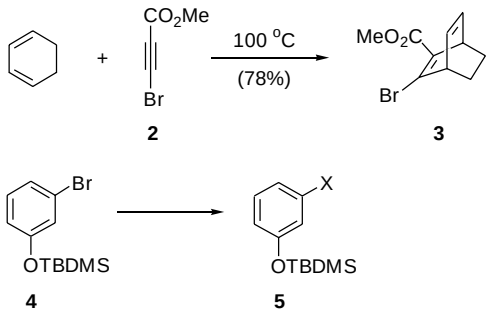
Abstract. A palladium-catalyzed cross-coupling reaction between the arylstannane **5c** and the bicyclic vinyl bromide **3**, which was obtained by a Diels–Alder reaction, provided the substituted bicyclo[2.2.2]octa-2,5-diene **6**. A subsequent ozonolysis of the less substituted double bond of **6** followed by reduction of the intermediate with sodium borohydride provided the highly functionalized cyclohexene **8**. This compound can be viewed as a substructure of the antitumor antibiotic *dynemicin A*.

Polysubstituted cyclohexanes and -hexenes represent important substructures in a number of natural products. Among several strategies for synthesizing such compounds, the tactical combination of a Diels–Alder reaction between a cyclic 1,3-diene and a suitable dienophile followed by cleavage of the bicyclic structure has been widely used [1]. As a consequence the stereochemistry of the two substituents that originate from cleavage of the bridge are *cis* to each other. This structural situation can be found, for example in the E-ring of the antitumor antibiotic *dynemicin A* [2, 3]. The known total syntheses of *dynemicin A* have addressed this issue in different ways [4–8]. In the course of the synthesis of analogs [9] of *dynemicin A* (Scheme 1) we planned to use the above mentioned strategy for establishing the array of rings spanning C–E. One of the two functional groups resulting from the cleavage of the bridge will be transformed to a methyl group, while the other one would be used to fashion the enediyne (cf. structures A and B). In this paper, we report on initial studies in this direction resulting in the cyclohexene **8**.

As a dienophile methyl 3-bromopropiolate (**2**) was used [10]. This was converted to the bicyclic vinyl bromide **3** by a Diels–Alder reaction [11]. The problem in subsequent functionalization reactions of **3** is the possible aromatization reaction through a retro Diels–Alder reaction with the elimination of ethylene. For the substitution of the bromide with an aryl group the aryl metal derivatives **5a**–**c** were prepared from the bromide **4** [12, 13] (Scheme 2). The corresponding zinc derivative **5a** was not isolated and used directly [yield not determined (ND)] [14].



Scheme 1 Dynemicin A as a lead compound for analog design



compound	X	conditions	yield (%)
5a	ZnBr	1. *n*-BuLi, THF, – 78 °C 2. $ZnBr_2$	ND
5b	$B(OH)_2$	1. *n*-BuLi, THF, – 60 °C, $B(OMe)_3$ 2. NH_4Cl	45
5c	$SnBu_3$	1. *n*-BuLi, THF, – 78 °C 2. $ClSnBu_3$	99

Scheme 2 Preparation of the bicyclic vinyl bromide **3** and the aryl metal compounds **5**

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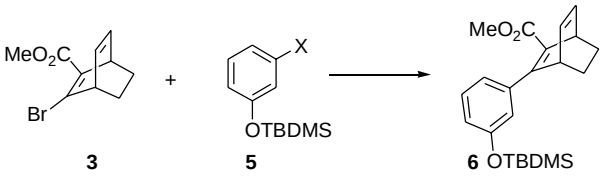
The crucial cross-coupling reaction between the bicyclic bromide **3** and the aryl metal compounds **5** was studied under various conditions (Table 1). Initially, we tried to add the aryl group *via* the cuprate, derived from the organozinc compound **5a** [14]. However, this led to destruction of **3**. On the other hand, palladium-catalyzed reactions were successful. For example, reaction of the organozinc compound **5a** with **3** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) and triphenylphosphine gave the desired compound **6** in 40% yield. A somewhat better yield could be realized with the arylboronic acid **5b**. With the same palladium catalyst but the weakly coordinating triphenylarsine as an additive and under basic conditions, the coupling product **6** could be obtained in 45% yield. The Stille coupling, finally, of the aryl stannane **5c** with **3** gave the best results. We used conditions that had been advantageous in our hands for the coupling of α-iodoenones with aryl metal compounds [15]. That is, use of the relatively stable $Pd_2(dba)_3{\cdot}\,CHCl_3$, triphenylarsine as a coligand, the polar solvent *N*-methylpyrrolidinone (NMP) and copper iodide facilitated the coupling reaction. In order to suppress the unwanted aromatization reaction, the temperature was kept below 45 °C.

Table 1 Cross-coupling reactions of the bromide **3** with aryl metal compounds **5** with $Pd_2(dba)_3 \cdot CHCl_3$ as catalyst

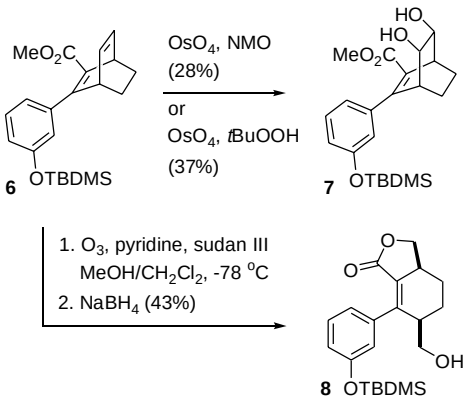


3 **5** **6**

entry	aryl metal compounds	conditions	yield of **6** (%)
1	ZnBr	PPh_3, THF room temp., 15 h	40
2	$B(OH)_2$	$AsPh_3$, Na_2CO_3 dioxane, 45 °C, 90 min	45
3	$SnBu_3$	$AsPh_3$, CuI, NMP 45 °C, 44 h	60

With the substituted oxabicyclooctadiene **6** in hand, we turned to the oxidative cleavage of the less substituted double bond (Scheme 3). Using the VanRheenen conditions [16], that is catalytic amounts of osmium tetroxide in the presence of *N*-methylmorpholine *N*-oxide (NMO) the diol **7** was isolated in moderate yield. Such yields are not seldom for the dihydroxylation of bicyclic olefins [16]. In analogy to the dihydroxylation of other bicyclic olefins, the reaction was assumed to take place *anti* to the ethano bridge [17]. The yield of the dihydroxylation reaction was somehow higher with *tert*-butyl hydroperoxide as oxidizing agent [18].

Since the yield could not be further improved, unfolding of the bicyclic structure by dihydroxylation and oxidative cleavage of the diol was not pursued further. Instead, cleavage of the double bond by ozonolysis and reductive work-up proved to be more efficient. In order to check for overoxidation, the end point of the ozonolyis was determined with an indicator [19]. Without isolation the intermediate was reduced with sodium borohydride. Treatment with acid induced lactonization to compound **8**. This way the two hydroxymethyl groups could be differentiated.



Scheme 3 Selective functionalization of the less substituted double bond of the bicyclic olefin **6**

In summary, we developed an efficient synthetic route to the highly functionalized cyclohexene **8** by oxidative cleavage of the Diels–Alder adduct **6**. Further work is underway to apply this strategy to the synthesis of *dynemicin A* analogs.

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Experimental

^{1}H NMR: Varian Unity 500 (500 MHz), Varian Gemini 2000 (400 MHz), Varian Gemini 200 (200 MHz); all spectra were recorded in $CDCl_3$ as solvent with tetramethylsilane as internal standard. – ^{13}C NMR: Varian Unity 500 (125 MHz), Varian Gemini 2000 (100 MHz), Varian Gemini 200 (50 MHz), broad-band decoupling. The signal multiplicities were determined by means of the DEPT 135 or the APT technique; + for CH or CH_3, – for CH_2, × for C. – IR: Perkin-Elmer Spectrum 1000. – Flash chromatography: J. T. Baker silica gel 30–60 mm. – Thin-layer chromatography: Macherey, Nagel & Co precoated TLC plates Polygram SIL G/UV_{254}. – All experiments were carried out under nitrogen or argon. Petroleum ether with a boiling range of 35–65 °C was used; THF

was distilled from sodium benzophenone ketyl immediately before use. The following reagents were prepared according to literature procedures: methyl 3-bromopropiolate (**2**) [10], aryl bromide **4** [12, 13], aryl stannane **5c** [13], $Pd_2(dba)_3$ $CHCl_3$ [20].

Methyl 3-bromobicyclo[2.2.2]octa-2,5-dien-2-carboxylate (**3**)

A mixture of the bromide **2** (8.46 g, 51.9 mmol) and cyclohexadiene (4.99 g, 62.3 mmol) was stirred at 100 °C for 18.5 h. After cooling to room temperature, the volatiles were removed *in vacuo*. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, gradient elution, 15:1 to 4:1) gave 9.84 g (78%) of **3** as a colorless oil. – TLC (petroleum ether/ethyl acetate, 8:1): R_f = 0.52. – ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 1.32–1.39 (m, 2H, CH_2), 1.43–1.50 (m, 1H, CH_2), 1.56–1.60 (m, 1H, CH_2), 3.76 (s, 3H, OCH_3), 3.87–3.90 (m, 1H, CH), 4.29–4.31 (m, 1H, CH), 6.27–6.30, 6.32–6.35 (2 m, 1H each, vinyl CH).

2-[3-(tert-Butyldimethylsilyloxy)phenyl]boronic acid (**5b**)

To a solution of the aryl bromide **4** [12] (14.2 g, 49.5 mmol) in THF (80 ml) was added dropwise *n*-butyllithium (1.6M in *n*-hexanes, 43 ml, 69 mmol) at –78 °C. After being stirred for 15 min at that temperature, trimethyl borate (15.4 g, 0.149 mol) was added. The mixture was stirred for 2.5 h while it warmed to –60 °C, and for 4 h at room temperature. Hydrolysis was performed at 0 °C by adding satd. NH_4Cl solution (50 ml). After being stirred for 5 min, the mixture was filtered, and the filtrate extracted with ethyl acetate (3 × 50 ml). The combined organic layers were washed with water (100 ml), dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, gradient elution, 10:1 to 1:1) to provide 6.37 g (51%) of **5b** as a yellow oil. – TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.33. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 0.26 [s, 6H, $Si(CH_3)_2$], 1.03 [s, 9H, $SiC(CH_3)_3$], 7.04–7.10 (m, 1H, aromatic H), 7.34–7.42 (m, 1H, aromatic H), 7.66–7.68 (m, 1H, aromatic H), 7.78–7.83 (m, 1H, aromatic H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = –4.30 [+, $Si(CH_3)_2$], 18.27 (×, $SiCMe_3$), 25.77 [+, $SiC(CH_3)_3$], 124.62, 126.65, 128.55, 129.24 (+, aromatic CH), 155.43 (×, aromatic C). – MS (EI), *m/z* (%): 252 (1) [M^+], 251 (2) [M^+ – H], 224 (15), 167 (100). – IR (film): ν/cm^{-1} = 3 220 (m, OH), 3 064 (w), 2 955, 2 931, 2 894 (s, CH_3). – $C_{12}H_{21}BO_3Si$ (252.2): an elemental analysis was not obtained.

Methyl 3-[3-(tert-butyldimethylsilyloxy)phenyl]bicyclo[2.2.2]octa-2,5-dien-2-carboxylate (**6**)

Using the arylzinc compound **5a**: To a solution of the aryl bromide **4** (0.450 g, 1.57 mmol) in dry THF (4 ml) was added dropwise *n*BuLi (1.6M in hexane, (0.98 ml, 1.6 mmol) at –78 °C. After being stirred for 15 min at that temperature, a solution of zinc bromide (353 mg, 1.57 mmol) in dry THF (3 ml) was added. The mixture was stirred for 5 min at 0 °C and then recooled to –78 °C before a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (31 mg, 60 µmol), triphenylphosphine (63 mg, 0.24 mmol) and the bromide **3** (293 mg, 1.21 mmol) in THF (3 ml) was added. The mixture was stirred for 15 h while it slowly warmed to room temperature. Then it was diluted with diethyl ether (100 ml), and washed with water (2 × 20 ml) and satd. NaCl solution (20 ml). The organic layers were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 20:1); yield of **6** 179 mg (40%).

Using the boronic acid **5b**: To a mixture of the bromide **3** (269 mg, 1.11 mmol), triphenylarsine (68 mg, 0.22 mmol), $Pd_2(dba)_3$ $CHCl_3$ (27 mg, 55 µmol) and the boronic acid **5b** (321 mg, 1.27 mmol) in dioxane (5 ml) was added aqueous Na_2CO_3 solution (2.0M, 1.2 ml). The reaction mixture was stirred in an oil bath for 90 min at 45 °C. Then it was cooled to room temperature and worked up as described above; yield of **6** 185 mg (45%).

Using the arystannane **5c**: A mixture containing the bromide **2** (9.13 g, 37.6 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.683 g, 1.31 mmol), CuI (5.36 g, 28.2 mmol) and triphenylarsine (1.61 g, 5.26 mmol) and NMP was degassed by carefully evaporating and flushing the apparatus with argon several times. After stirring for 10 min, the stannane **5c** (22.4 g, 45.1 mmol) was added and the flask lowered into an oil-bath (45 °C). The reaction mixture was stirred for 26 h at 45 °C, cooled to room temperature, poured into water (200 ml) and diethyl ether (100 ml). The aqueous phase was extracted with diethyl ether (4 × 100 ml). The combined organic layers were washed with brine (50 ml), dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatogrphy (petroleum ether/ethyl acetate, gradient elution, 50:1 to 15:1) to provide 8.32 g (60%) of 6 as a colourless oil. – TLC (petroleum ether/ethyl acetate, 8:1): R_f = 0.54. – ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 0.18 [s, 6H, $Si(CH_3)_2$], 0.97 [s, 9H, $SiC(CH_3)_3$], 1.38–1.46 (m, 2H, CH_2), 1.49–1.56 (m, 2H, CH_2), 3.53 (s, 3H, OCH_3), 3.79–3.82 (m, 1H, CH), 4.21–4.23 (m, 1H, CH), 6.36–6.39 (m, 1H, vinyl H), 6.43–6.46 (m, 1H, vinyl H), 6.64–6.65 (m, 1H, aromatic H), 6.72–6.77 (m, 2H, aromatic H), 7.14 (t, *J*/Hz = 7.8, 1H, aromatic H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm = –4.38 [+, $Si(CH_3)_2$], 18.17 (×, $SiCMe_3$), 24.64, 24.80 (–, CH_2), 25.68 [+, $SiC(CH_3)_3$], 38.93, 45.82 (+, CH), 51.15 (+, OCH_3), 118.99, 119.10, 120.43, 128.67 (+, aromatic CH, vinyl CH), 132.08 (×, aromatic C, vinyl C), 133.02, 135.22 (+, aromatic CH, vinyl CH), 141.01, 155.14, 155.97 (×, aromatic COMe, vinyl C), 166.85 (×, C=O). – MS (EI), *m/z* (%): 370 (12) [M^+], 342 (10) [$M^+ - C_2H_4$], 313 (4) [$M^+ - C_4H_9$], 285 (6) [$M^+ - C_2H_4 - C_4H_9$], 253 (100). – IR (film): ν/cm^{-1} = 3 058 (m), 2 953, 2 858 (s), 1 704 (s, C=O), 1 634 (m). – HRMS ($C_{22}H_{30}O_3Si$): calcd. 370.1964, found 370.1959.

Methyl 3-[3-(tert-Butyldimethylsilyloxy)phenyl]-5,6-dihydro-xybicyclo[2.2.2]oct-2-en-2-carboxylate (**7**)

Oxidation with NMO: To a solution of the alkene **6** (200 mg, 0.540 mmol) and NMO (70 mg, 0.59 mmol) in THF/*t*BuOH/water (7 ml, 5:2:1) was added a solution of OsO_4 (3.9 mM, 4.1 ml, 16 µmol) at 0 °C. The reaction mixture was stirred for 23 h while reaching room temperature. For the isolation of **7**, the mixture was treated with satd. $Na_2S_2O_3$ solution (5 ml) and then most of the solvent was removed *in vacuo*. The residue was diluted with water (5 ml) and then extracted with diethyl ether (2 × 20 ml). The combined organic layers were washed with brine (10 ml), dried with Na_2SO_4, filtered, and

concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to yield 61 mg (28%) of **7** as a colourless oil.

*Oxidation with t*BuOOH: To a solution of the bicyclic alkene **6** (245 mg, 0.661 mmol) in acetone (10 ml) were added dropwise solutions of *t*BuOOH (70% in water, 0.14 ml, 1.1 mmol) and OsO_4 in *t*BuOH (3.9 mM, 0.34 ml, 1.3 µmol) at 0 °C. The mixture was stirred for 45 min at 0 °C and then for 20 h at room temperature. After that another portion of the *t*BuOOH solution (0.14 ml, 1.1 mmol) was added, the mixture stirred for 1 h, treated with $Na_2S_2O_3$ solution (5 ml) and then concentrated *in vacuo* to remove most of the solvent. Work-up and isolation were performed as described above to yield 98 mg (37%) of **7** as colourless oil. – TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.27. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 0.18 [s, 6H, $Si(CH_3)_2$], 0.96 [s, 9H, $SiC(CH_3)_3$], 1.40–1.47 (m, 2H, CH_2), 1.50–1.56 (m, 3H, CH_2, OH), 2.51 (d, *J*/Hz = 4.9, 1H, OH), 3.02–3.05 (m, 1H, CH), 3.29–3.30 (m, 1H, CH), 3.57 (s, 3H, OCH_3), 3.90–3.93 (m, 1H, CHOH), 3.99–4.00 (m, 1H, CHOH), 6.73–6.75 (m, 1H, aromatic H), 6.80–6.81 (m, 1H, aromatic H), 6.89–6.92 (m, 1H, aromatic H), 7.14–7.18 (m, 1H, aromatic H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = –4.56 [+, $Si(CH_3)_2$], 18.02 (×, $SiCMe_3$), 21.10, 21.28 (–, CH_2), 25.55 [+, $SiC(CH_3)_3$], 39.46, 45.89 (+, CH), 51.47 (+, OCH_3), 70.11, 70.16 (+, CHOH), 119.19, 119.46, 120.85 (+, aromatic C), 127.62 (×, aromatic C, vinyl C), 128.78 (+, aromatic C), 141.55, 152.56, 155.31 (×, aromatic C, vinyl C), 166.24 (×, C=O). – MS (EI), *m/z* (%): 404 (31) [M^+], 372 (13) [M^+ – MeOH], 344 (15) [M^+ – MeOH – H_2O], 255 (100). – IR (film): ν/cm^{-1} = 3 433 (s, br, OH), 3 062 (m), 2 953, 2 860 (s), 1 705 (s, C=O). – HRMS ($C_{22}H_{32}O_5Si$): calcd. 404.2019, found 404.2033.

7-[3-(tert-Butyldimethylsilyloxy)phenyl]-6-hydroxymethyl-1,3,3a,4,5,6-hexahydro-1-iso-benzofuranon (**8**)

Through a solution of the bicylic alkene **6** (379 mg, 1.02 mmol), pyridine (0.75 ml) and sudan III indicator (0.2 ml of a saturated solution in EtOH) in dry CH_2Cl_2 and MeOH (10 ml, 1:1) was passed ozone at –78 °C until the colour changes from red to yellow. The excess of ozone was removed by passing a slow stream of argon through the solution at room temperature. The solution was recooled to –78 °C, treated with sodium borohydride (135 mg, 3.58 mmol) and then stirred for 14 h during which it was allowed to reach room temperature. Following the addition of HCl (2 ml of an 10% aqueous solution), most of the solvent was removed *in vacuo* and the residue taken up in diethyl ether (100 ml). The organic layer was washed with HCl (15 ml of an 10% aqueous solution) and the aqueous phase extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (petroleum ether(ethyl acetate, gradient from 20:10 to 13:10). yield of **8** 163 mg (43%), colourless oil. – TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.47. – ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 0.16, 0.17 [s, 6H, $Si(CH_3)_2$], 0.95 [s, 9H, $SiC(CH_3)_3$], 1.34–1.44 (m, 1H, CH_2), 1.74–1.83 (m, 1H, CH_2), 1.89–1.95 (m, 1H, CH_2), 2.19–2.24 (m, 1H, CH_2), 2.70–2.75 (m, 1H, CH), 2.95–3.05 (m, 1H, CH), 3.33 (dd, *J*/Hz = 11.0, 7.4, 1H, CH_2O), 3.46 (dd, *J*/Hz = 11.0, 3.3, 1H, CH_2O), 3.79 (dd, *J*/Hz = 8.2, 10.3, 1H, CH_2O), 4.48 (t, *J*/Hz = 8.2, 8.2, 1H, CH_2O), 6.59–6.60 (m, 1H, aromatic H), 6.71–6.73 (m, 1H, aromatic H), 6.77–6.80 (m, 1H, aromatic H), 7.16–7.20 (m, 1H, aromatic H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = –4.69, –4.59 [+, $Si(CH_3)_2$], 17.99 (×, $SiCMe_3$), 21.27, 24.54 (–, CH_2), 25.54 [+, $SiC(CH_3)_3$], 39.27, 42.61 (+, CH), 64.23, 70.84 (+, CH_2O), 119.48, 119.98, 120.41 (+, aromatic CH), 126.06 (×, aromatic C, vinyl C), 129.34 (+, aromatic CH), 138.73, 148.68 (×, aromatic C, vinyl C), 155.55 (×, aromatic C), 168.63 (×, C=O). – MS (EI), *m/z* (%): 374 (3) [M^+], 359 (2) [$M^+ - CH_3$], 317 (100) [$M^+ - C_4H_9$], 287 (30), 269 (52). – IR (Film): ν/cm^{-1} = 3 436 (s, br, OH), 3 063 (m), 2 954, 2 931, 2 867 (s), 1 760 (s, C=O). – $C_{21}H_{30}O_4Si$ (374.6): an elemental analysis could not be obtained.

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