Wagner-Meerwein Rearrangements of Longipinane Derivatives

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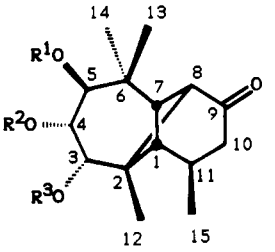
Tricyclic strained substances, such as longipinene derivatives[1] offer the possibility to generate new structures because of bond migrations can be promoted to release the four-membered ring strain. Thus, we undertook the study of the molecular rearrangements in longipinene derivatives of natural occurrence, mainly from plants belonging to the genus Stevia.[2-6] In this paper we report the Wagner-Meerwein rearrangement of rastevione (**1a**), a highly functionalized longipinene derivative,[6] and of the three related compounds **1b**, **2a**, and **3a**.

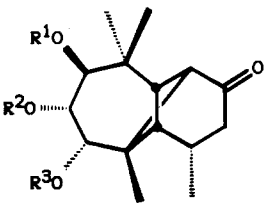
Results and Discussion

The structural[6] and conformational[7] evaluation of **1a** reveals that this compound fully meets the requirements[8] for undergoing a rearrangement. Thus, when **1a** was treated in acid media, it rearranged to afford **4a** whose formation involves the displacement of the previously protonated hydroxyl group at C3 of **1a** by the antiperiplanar C1-C2 bond, followed by the formation of a double bond between C2 and C12. Furthermore, isomerization of the 2-methyl-2(*Z*)-butenoyl esters (ang) to the 2*E* isomers (tigl) occurred during the treatment. Both ester groups were removed by an alkaline hydrolysis to afford endiolone **4b**.

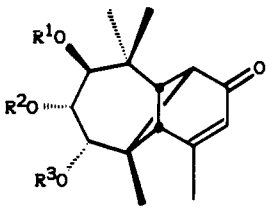
In order to obtain information on the influence of this reaction by changes in the stereochemistry at C11 and in the electron density at the C10-C11 bond of longipinenes, compounds **1b**, **2a**, and **3a** were prepared and treated under the same rearrangement conditions. Diacetates **1b** and **3a** were prepared by selective esterification of triols **1c** and **3c**,[5] respectively. Diacetate **2a** was obtained as the unique product from hydrogenation of **3b**[5] to yield **2b**, followed by hydrolysis and selective[7] acetylation of **2c**. The best comparative results in the rearrangement of **1b**, **2a**, and **3a** were obtained when using $Et_2O{\cdot}BF_3$ as the catalyst. While the saturated derivatives **1b** and **2a** afforded **4d** and **5a**, respectively, in good yields, the unsaturated compound **3a** gave a complex mixture of products from which **6a** could be isolated in only low yields. These results reveal that changes in the stereochemistry at C11 of longipinene derivatives do not affect the reaction products. However, the electron density due to the double bond at C10-C11 is critical during the course of the reaction. This behavior could be explained by a carbonium ion, formed at C2 after migration of the C1-C2 bond, which delocalizes involving the double bond to give untractable compounds.



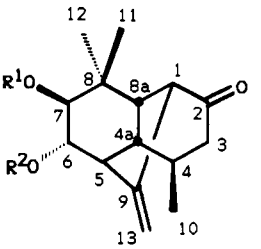
1a : $R^1 = R^2 =$ Ang; $R^3 = H$
1b : $R^1 = R^2 =$ Ac; $R^3 = H$
1c : $R^1 = R^2 = R^3 = H$



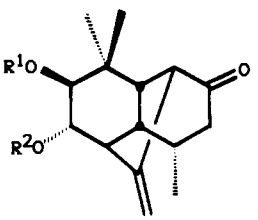
2a : $R^1 = R^2 =$ Ac; $R^3 = H$
2b : $R^1 = R^2 = R^3 =$ Ac
2c : $R^1 = R^2 = R^3 = H$



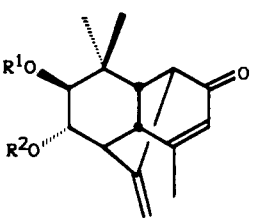
3a : $R^1 = R^2 =$ Ac; $R^3 = H$
3b : $R^1 = R^2 = R^3 =$ Ac
3c : $R^1 = R^2 = R^3 = H$



4a : $R^1 = R^2 =$ Tigl
4b : $R^1 = R^2 = H$
4c : $R^1 = H$; $R^2 =$ Ts
4d : $R^1 = R^2 =$ Ac



5a : $R^1 = R^2 =$ Ac
5b : $R^1 = R^2 = H$



6a : $R^1 = R^2 =$ Ac
6b : $R^1 = R^2 = H$

Since the rearranged products posses a new carbon skeleton, it was desirable to obtain further support to their structures by X-ray diffraction analysis. Monotosylate **4c** prepared by treatment of **4b** with *p*-toluenesulfonyl chloride and diendiolone **6b** obtained from hydrolysis of **6a** afforded good quality prisms to achieve X-ray crystallographic analyses. Perspective views of both structures are given in Figures 1 and 2. Furthermore, to confirm the structure of diacetate **5a**, a chemical correlation with **6b** was made. Thus regioselective catalytic hydrogenation of **6b** afforded **5b** (**4b** was also obtained) which was identical with the product of hydrolysis of **5a**. The ^1H NMR spectral data of the new substances are listed in Tables I and II, while the ^{13}C NMR data are listed in Tables III and IV. The assignment of the NMR spectra was done with the aid of $^{13}C/^1H$ heteronuclear chemical shift correlation diagrams for **1b**, **1c**, **2a**, **4a**, **4c**, **4d**, and **5b** and ^1H-^1H COSY contour plots of **2c**, **4a-d**, **5b**, and **6a**. The remaining spectral data are given in the supplementary material.

Experimental Section

Melting points are uncorrected. NMR measurements were obtained from $CDCl_3$ solutions with the exception of **8b** (DMSO-d_6). $(CH_3)_4Si$ was used as the internal standard. Ex-

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Table I. ^{1}H NMR Chemical Shifts,[a] Multiplicity,[b] and Coupling Constants[b] for Longipinene Derivatives

compd	H-1	H-3	H-4	H-5	H-7	H-8	H-10α	H-10β	H-11	H-12	H-13	H-14	H-15
1b[c]	2.19	3.77	5.32	5.36	1.80	3.05	2.12	2.57	2.35	1.04	1.05	0.91	1.10
2a[d]	2.35	3.81	5.37	5.32	1.63	3.06	2.23	2.90	2.35	1.19	1.07	0.90	1.22
2b[e]	2.44	5.30	5.30	5.30	1.68	3.04	2.23	2.92	2.37	1.01	1.06	0.90	1.23
2c[f]	2.21	3.83	3.83	3.62	1.60	2.91	2.22	2.90	2.34	1.19	0.99	0.95	1.21
3a[g]	2.70	3.88	5.30	5.40	2.31	3.16	5.81		–	1.15	1.08	0.89	2.05

[a] In ppm at 300 MHz. [b] Couplings are in hertz: H-1 (br d, J = 7), H-3 (d, J = 3), H-4 (dd, J = 11, 3), H-5 (d, J = 11), H-7 (br s), H-8 (d, J = 7), H-10α for **1b** (dd, J = 18, 6), H-10α for **2a**, **2b**, and **2c** (dd, J = 20, 5), H-10 for **3a** (m), H-10β for **1b** (dd, J = 18, 9), H-10β for **2a**, **2b**, and **2c** (dd, J = 20, 11), H-11 (m), H-12 (s), H-13 (s), H-14 (s), H-15 for **1b**, **2a**, **2b**, and **2c** (d, 7), H-15 for **3a** (d, 2). [c] OH 2.48 (br s); acetates, 2.09, 2.07 (2 s). [d] OH, 2.63 (br s); acetates, 2.10, 2.06 (2 s). [e] Acetates, 2.15, 2.06, 1.95 (3 s). [f] OH, 3.22, 2.8, 2.53 (3 s). [g] OH, 2.47 (br s); acetates, 2.10, 2.07 (2 s).

Table II. ^{1}H NMR Chemical Shifts,[a] Multiplicity,[b] and Coupling Constants[b] for 1,5-Methanonaphthalene Derivatives

compd	H-1	H-3α	H-3β	H-4	H-4a	H-5	H-6	H-7	H-8a	H-10	H-11[c]	H-12[c]	H-13	H-13′
4a[d]	3.42	2.72	1.84	2.13	1.95	2.86	5.02	5.08	2.30	1.06	1.09	0.97	5.08	5.21
4b[e]	3.30	2.72	1.85	2.06	1.90	2.66	3.68	3.12	2.16	1.05	1.04	1.00	5.13	5.14
4c[f]	3.27	2.68	1.82	2.05	1.88	2.92	4.62	3.40	2.17	1.04	1.03	0.98	5.12	5.12
4d[g]	3.38	2.70	1.83	2.06	1.95	2.80	4.96	4.90	2.26	1.06	1.06	0.96	5.12	5.21
5a[h]	3.40	2.20	2.20	2.10	1.77	2.98	4.93	4.93	2.33	1.06	1.07	0.94	5.09	5.15
5b[i]	3.31	2.30	2.14	2.06	1.72	2.88	3.64	3.17	2.23	1.06	1.03	1.02	5.10	5.04
6a[j]	3.51	5.68		–	2.08	2.77	5.01	4.96	2.82	2.02	1.05	0.94	5.10	5.35
6b[k]	3.20	5.54		–	1.90	2.50	2.97	3.54	2.76	1.97	0.88	0.88	4.98	4.98

[a] In ppm at 300 MHz. [b] Couplings are in hertz: H-1 (br s), H-3α for **4a–d** (dd, J = 17, 4), H-3α for **5a** (m), H-3α for **5b** (dd, J = 16, 12), H-3 for **6a** and **6b** (m), H-3β for **4a–d** (dd, J = 17, 4), H-3β for **5a** (m), H-3β for **5b** (dd, J = 16, 6), H-4 (m), H-4a (br s), H-5 (br s), H-6 for **4a–d**, **5a**, **5b**, and **6a** (dd, J = 10, 3), H-6 for **6b** (dd, J = 8, 4), H-7 for **4a–d**, **5a**, **5b**, and **6a** (d, J = 10), H-7 for **6b** (d, J = 8), H-8a (br s), H-10 for **4a–d** (d, J = 7), H-10 for **5a**, and **5b** (d, J = 6), H-10 for **6a** and **6b** (d, J = 1), H-11 (s), H-12 (s), H-13 (s), H-13′ (s). [c] May be interchanged. [d] Tiglates: 6.82, 6.78 (2 qq, J = 7, 2), 1.78–1.75 (m). [e] OH: 1.97, 1.93 (2 br s). [f] Tosylate: 7.83, 7.35 (2 d, J = 9), 2.45 (s). OH: 2.04 (br s). [g] Acetates: 2.03, 2.03 (s). [h] Acetates: 2.05, 2.03 (2 s). [i] OH: 2.36, 2.36 (s). [j] Acetates: 2.04, 2.04 (s). [k] OH: 4.75, 4.45 (2 br s).

Table III. ^{13}C NMR Chemical Shifts for Longipinene Derivatives (at 75.4 MHz)

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15
1b[a]	44.3	45.8	75.0	71.6	71.2	35.0	46.3	51.6	211.5	41.9	26.7	20.4	19.7	27.0	19.6
2a[b]	44.6	44.6	75.1	71.6	71.1	35.4	52.7	51.4	211.3	41.5	32.9	22.7	19.5	26.8	20.9
2b[c]	44.4	43.6	74.4	70.6[d]	69.1[d]	34.9	52.1	51.9	210.0	41.1	32.4	19.0[e]	19.2[e]	26.3	21.6
2c	44.5	44.3	76.4	71.1[d]	70.6[d]	35.8	52.9	51.4	212.3	41.7	33.0	23.0	18.3	27.3	21.0
3a[f]	48.1	55.3	75.0	71.6	70.8	36.3	65.5	52.3	202.6	122.9	169.5	20.8	19.7	26.5	23.3

[a] Acetates: 170.0, 169.5, 20.9, 20.8. [b] Acetates: 170.0, 169.5, 20.9, 20.8. [c] Acetates: 170.4, 169.4, 169.3, 20.4, 20.3, 20.2. [d,e] May be interchanged. [f] Acetates: 170.0, 169.7, 21.8, 20.9 ppm.

Table IV. ^{13}C NMR Chemical Shifts for 1,5-Methanonaphthalene Derivatives (at 75.4 MHz)

compd	C-1	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-9	C-10	C-11[a]	C-12[a]	C-13
4a[b]	58.1	208.7	41.7	31.8	52.3	51.2	75.4	75.5	38.5	45.2	145.1	22.3	25.6	23.0	112.1
4b	58.6	209.3	41.8	31.8	52.1	54.2	75.4	78.3	38.2	45.5	146.7	22.4	25.6	21.9	110.3
4c[c]	58.2	208.7	41.6	31.6	51.6	51.9	86.0	74.6	38.8	45.2	144.3	22.3	25.6	21.9	112.4
4d[d]	58.3	208.2	41.6	31.6	52.0	51.2	75.2	75.5	38.3	45.1	144.7	22.3	25.7	22.9	112.2
5a[e]	57.9	208.4	42.0	33.7	44.9	44.8	75.4	75.6	38.6	57.7	146.0	19.2	25.4	22.8	110.9
5b	58.4	209.2	42.4	34.0	47.8	45.5	75.8	78.7	38.6	58.1	148.4	19.3	25.4	21.9	108.7
6a[f]	59.0	197.5	124.7	163.3	57.1	47.9	74.9	75.1	38.4	47.1	143.6	23.1	25.2	22.3	114.0
6b	59.0	201.0	123.7	169.6	57.9	51.1	75.1	77.1	–[g]	48.1	146.6	23.6	25.8	22.2	112.6

[a] The signals of the *gem*-dimethyl groups are not assigned specifically. [b] Tiglates: 167.6, 167.3, 138.2, 137.4, 128.4, 128.3, 14.5, 14.3, 12.1, 11.8. [c] Tosylate: 145.0, 134.0, 129.9, 127.6, 21.7. [d] Acetates: 170.6, 170.2, 21.0, 20.8. [e] Acetates: 170.5, 170.2, 20.8, 20.7. [f] Acetates: 170.6, 170.2, 21.0, 20.8. [g] Overlapped by the DMSO-d_6 signal.

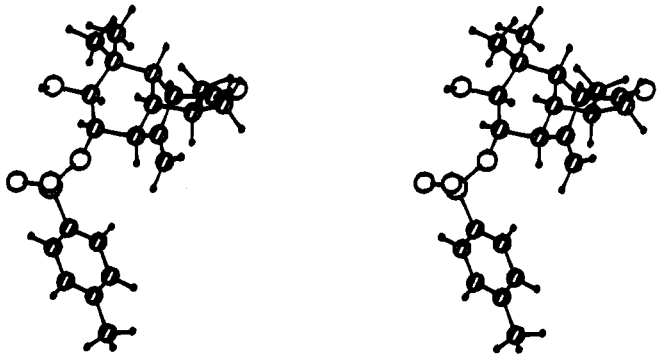

Figure 1. Stereoview of the molecular structure of **4c**.

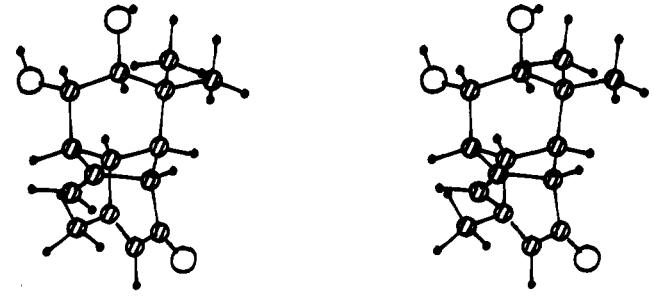

Figure 2. Stereoview of the molecular structure of **6b**.

tractions were made using ethyl acetate (EtOAc) unless otherwise stated. Organic layers were dried using anhydrous Na_2SO_4.

Analytical samples were obtained by crystallizations from $CHCl_3$–hexane unless other solvent indicated.

[1*R*-(1α,4aβ,4aβ,5α,6α,7β,8aβ)]-Octahydro-4,8,8-trimethyl-6,7-bis[(2-methyl-2(*E*)-butenoyl)oxy]-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (4a). A solution of **1a**[6] (500

mg, 1.16 mmol) in C_6H_6 (40 mL) was treated with *p*-toluenesulfonic acid (100 mg, 0.58 mmol). The reaction mixture was refluxed during 1 h, removing H_2O by means of a Stark–Dean trap, concentrated to a small volume, diluted with H_2O, and extracted. The organic layer was washed with H_2O, dried, filtered, and evaporated giving **4a** (450 mg, 93%) as a colorless oil. Chromatography on silica (SiO_2) afforded the pure sample of **4a** as a colorless oil.

[1*R*-(1α,4β,4aβ,5α,6α,7β,8aβ)]-Octahydro-6,7-dihydroxy-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2-(1*H*)-one (4b). A solution of **4a** (3.8 g, 9.17 mmol) in CH_3OH (150 mL) was treated with KOH (4 g, 71.4 mmol) in H_2O (8 mL). The reaction mixture was refluxed during 2 h. Usual workup for hydrolysis[5] gave **4b** (400 mg) as white needles, mp 139–141 °C. Chromatography of the mother liquors through alumina (25 g) afforded **4b**, 300 mg, 31% overall yield. The analytical sample showed mp 142–143 °C. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; O, 19.17. Found: C, 71.73; H, 8.72; O, 19.30.

[1*R*-(1α,4β,4aβ,5α,6α,7β,8aβ)]-Octahydro-7-hydroxy-4,8,8-trimethyl-9-methylene-6-[[(4-methylphenyl)sulfonyl]-oxy]-1,5-methanonaphthalen-2(1*H*)-one (4c). A solution of **4b** (1 g, 4.0 mmol) in pyridine (py, 12 mL) was treated with *p*-toluenesulfonyl chloride (2 g, 10.50 mmol) at 0 °C. The reaction mixture was stored at 4 °C during 24 h, poured over ice, and extracted. Usual workup for tosylations[5] afforded **4c** (1.2 g, 74%) as a white powder, mp 162–164 °C. The analytical sample showed mp 163–164 °C. Anal. Calcd for $C_{22}H_{28}O_5S$: C, 65.33; H, 6.98; O, 19.78; S, 7.91. Found: C, 65.17; H, 6.84; O, 19.88; S, 8.01.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11β)]-4,5-Bis(acetyloxy)-3-hydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (1b). A solution of **1c**[5] (1 g, 3.73 mmol) in py (4 mL) was treated with $(CH_3CO)_2O$ (4 mL). The reaction mixture was stored at 4 °C during 4 h and worked up as usual for acetylations[5] to yield **1b** (850 mg, 65%) as white needles, mp 183–185 °C. The pure sample showed mp 199–201 °C. Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01; O, 27.24. Found: C, 64.57; H, 8.06; O, 27.09.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11α)]-3,4,5-Tris(acetyloxy)-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (2b). A solution of **3b**[5] (1.90 g, 4.84 mmol) in EtOAc (160 mL) was stirred in the presence of prehydrogenated 10% Pd on activated charcoal (200 mg) under an H_2 atmosphere at room temperature and normal pressure until the uptake of the H_2 ceased. The catalyst was removed by filtration, and the solvent was evaporated to dryness. Crystallization from acetone–hexane gave **2b** (1.37 g, 72%) as white needles, mp 178–180 °C. The analytical sample, from acetone–hexane, showed mp 185–186 °C. Anal. Calcd for $C_{21}H_{30}O_7$: C, 63.94; H, 7.66; O, 28.39. Found: C, 64.01; H, 7.74; O, 28.72.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11α)]-3,4,5-Trihydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (2c). As described for the preparation of **4b**, reaction of **2b** (900 mg, 2.28 mmol) in CH_3OH (50 mL) with KOH (900 mg, 16.07 mmol) in H_2O (4 mL) gave **2c** (520 mg, 85%) as white prisms. The pure sample showed mp 164–168 °C. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01; O, 23.85. Found: C, 67.09; H, 8.85; O, 23.90.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11α)]-4,5-Bis(acetyloxy)-3-hydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (2a). As described for the preparation of **1b**, reaction of **2c** (460 mg, 1.71 mmol) in py (2 mL) with $(CH_3CO)_2O$ (2 mL) afforded **2a**, 320 mg, 53%. The pure sample, from EtOH–$CHCl_3$–hexane, showed mp 218–220 °C. Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01; O, 27.24. Found: C, 64.87; H, 8.09; O, 27.18.

[1*R*-(1β,2α,3α,4α,5β,7β,8α)]-4,5-Bis(acetyloxy)-3-hydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undec-10-en-9-one (3a). As described for the preparation of **1b**, reaction of **3c**[5] (500 mg, 1.88 mmol) in py (2 mL) with $(CH_3CO)_2O$ (2 mL) gave **3a** (320 mg, 48%) as white needles. The analytical sample showed mp 183–184 °C. Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48; O, 27.39. Found: C, 65.00; H, 7.54; O, 27.25.

[1*R*-(1α,4β,4aβ,5α,6α,7β,8aβ)]-6,7-Bis(acetyloxy)octahydro-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (4d). A solution of **1b** (1 g, 2.84 mmol) in CH_2Cl_2 (12 mL) was treated with $Et_2O{\cdot}BF_3$ (3 mL) at 0 °C. The reaction mixture was stored at room temperature during 24 h, poured over ice, and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried, filtered, and evaporated. The residue was chromatographed on SiO_2 to yield **4d** (850 mg, 89%) as a colorless oil.

[1*R*-(1α,4α,4aβ,5α,6α,7β,8aβ)]-6,7-Bis(acetyloxy)octahydro-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (5a). As described for the preparation of **4d**, reaction of **2a** (50 mg, 0.14 mmol) in CH_2Cl_2 (0.6 mL) with $Et_2O{\cdot}BF_3$ (0.15 mL) yielded **5a**, 30 mg, 64%. Chromatography on SiO_2 afforded **5a** as a colorless oil.

[1*R*-(1α,4α,4aβ,5α,6α,7β,8aβ)]-Octahydro-6,7-dihydroxy-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2-(1*H*)-one (5b). As described for the preparation of **4b**, reaction of **5a** (30 mg, 0.09 mmol) in CH_3OH (10 mL) with KOH (30 mg, 0.54 mmol) gave, from acetone–hexane, **5b** (20 mg, 89%) as white needles: mp 154–156 °C. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.96; H, 8.86; O, 19.17. Found: C, 72.12; H, 8.69; O, 19.14.

[1*R*-(1α,4aβ,5α,6α,7β,8aβ)]-6,7-Bis(acetyloxy)-4a,5,6,7,8,8a-hexahydro-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (6a). As described for the preparation of **4d**, reaction of **3a** (500 mg, 1.43 mmol) in CH_2Cl_2 (6 mL) with $Et_2O{\cdot}BF_3$ (1.5 mL) gave an oily residue which showed in the ^1H NMR spectrum to be a complex mixture. This mixture was chromatographed through SiO_2. The fraction eluted with C_6H_6–EtOAc (3:1) was rechromatographed to yield **6a**, 100 mg, 21%.

[1*R*-(1α,4aβ,5α,6α,7β,8aβ)]-4a,5,6,7,8,8a-Hexahydro-6,7-dihydroxy-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (6b). As described for the preparation of **4b**, reaction of **6a** (100 mg, 0.30 mmol) in CH_3OH (5 mL) with KOH (100 mg, 1.78 mmol) in H_2O (0.5 mL) gave, from acetone–hexane, **6b** (33 mg, 44%) as white prisms: mp 226–229 °C.

Hydrogenation of 6b. As described for the preparation of **2b**, reaction of **6b** (100 mg, 0.40 mmol) in AcOEt (50 mL) with H_2, catalyzed by prehydrogenated 10% Pd on activated charcoal (10 mg), gave a mixture of **4b** and **5b** in a ratio of ca. 4:1. Chromatography on SiO_2 afforded from the fractions eluted with C_6H_6–EtOAc (9:1) **4b**, 38 mg, 37%, and from the fractions eluted with C_6H_6–EtOAc (3:1) **5b**, 9 mg, 10%.

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Registry No. **1a**, 80388-43-8; **1b**, 131657-27-7; **1c**, 131724-23-7; **2a**, 131724-24-8; **2b**, 131724-25-9; **2c**, 131724-26-0; **3a**, 131657-28-8; **3b**, 112420-81-2; **3c**, 97280-00-7; **4a**, 131657-29-9; **4b**, 131724-98-6; **4c**, 131657-30-2; **4d**, 131657-31-3; **5a**, 131724-27-1; **5b**, 131657-32-4; **6a**, 131657-33-5; **6b**, 131657-34-6.

Supplementary Material Available: IR and optical activity for all substances. UV spectral data for **3a**, **4a**, **4c**, **6a**, and **6b**. Tables containing crystal data, collection and refinement parameters, atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen atom coordinates, torsion angles, and labeled drawings of **4c** and **6b** (18 pages). Ordering information is given on any current masthead page.

Stereocontrolled Reductive Deoxygenation Using Low-Valent Titanium: Effects of Ultrasound Waves and Solvents

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Reductive deoxygenation of aldehydes and ketones with low-valent titanium is one of the most commonly used procedures for the preparation of alkenes and has been subjected to extensive synthetic and mechanistic investigations.[1] Occassional low yields and temperamental

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