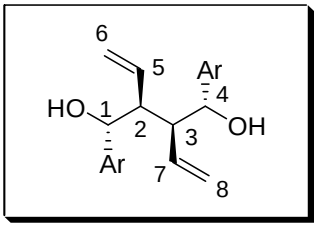
Electronic supplementary materials *Mendeleev Commun*., 2011, **21**, 1 – 3

Diastereoselectivity of allylboration of aromatic aldehydes with 1,6-bis(dipropylboryl)-2,4-hexadiene

Alexander N. Anfimov, Sergey Yu. Erdyakov, Mikhail E. Gurskii, Anatolii V. Ignatenko, Konstanin A. Lyssenko and Yurii N. Bubnov*



5a *rel*-(1*R*,2*S*,3*S*,4*R*)-1,4-diphenyl-2,3-divinylbutane-1,4-diol. Colorless oil. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 2.00 (s, 2H, OH), 2.19 (dd, 2H, H-2, *J* 9.1, 9.1 Hz), 4.42 (d, 2H, H-1, *J* 9.1 Hz), 5.14 (dd, 2H, H-6, *J* 12.8, 1.46 Hz), 5.40 (dd, 2H, H-6, *J* 10.2, 1.46 Hz), 5.92 (ddd, 2H, H-5, *J* 12.8, 10.2, 9.1 Hz), 7.01-7.18 (m, 4H, Ar), 7.20-7.43 (m, 6H, Ar); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 52.1 (C-2), δ 74.7 (C-1), 121.3 (C-6), 135.3 (C-5), 127.5, 128.1, 128.4, 141.2 (Ar). Found (%): C, 81.45; H, 7.38. Calc. for $C_{20}H_{22}O_2$ (%): C, 81.60; H, 7.53.

6a *rel*-(1*R*,2*S*,3*S*,4*R*)-1,4-di(*p*-methoxyphenyl)-2,3-divinylbutane-1,4-diol. Colorless oil. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 2.14 (dd, 2H, H-2, *J* 8.8, 8.8 Hz), 2.29 (s, 2H, OH), 3.81 (s, 6H, OCH_3), 4.32 (d, 2H, H-1, *J* 8.8 Hz), 5.08 (d, 2H, H-6, *J* 16.8 Hz), 5.34 (d, 2H, H-6, *J* 10.2 Hz), 5.85 (ddd, 2H, H-5, *J* 16.8, 10.2, 8.8 Hz), 6.83 (d, 4H, Ar, *J* 8.4), 6.99 (d, 4H, Ar, *J* 8.4); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 52.1 (C-2), 55.1 (OCH_3), 74.0 (C-1), 113.6, 120.7 (C-6), 135.5 (C-5), 122.0, 128.6, 133.5, 159.2 (Ar). Found (%): C, 74.29; H, 7.25. Calc. for $C_{22}H_{26}O_4$ (%): C, 74.55; H, 7.39.

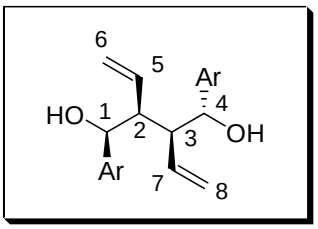
7a *rel*-(1*R*,2*S*,3*S*,4*R*)-1,4-bis(3,4-dimethoxyphenyl)-2,3-divinylbutane-1,4-diol. White solid, mp 139-140 °C. ^{1}H NMR (200.13 MHz, CD_3OD) δ: 2.07 (dd, 2H, H-2, *J* 9.2, 9.2 Hz), 3.60 and 3.80 (s, 12H, OMe), 4.30 (d, 2H, H-1, *J* 9.2 Hz), 5.03 (d, 2H, H-6, *J* 17.1 Hz), 5.21 (d, 2H, H-6, *J* 10.2 Hz), 5.77 (ddd, 2H, H-5 *J* 17.1, 10.2, 9.2 Hz), 6.47 (s, 2H, Ar), 6.64 (d, 2H, Ar, *J* 8.3 Hz), 6.81 (d, 2H, Ar, *J* 8.3 Hz); ^{13}C NMR (50.32 MHz, CD_3OD) δ: 53.1 (C-2), 56.0 and 56.4 (OCH_3), 75.8 (C-1), 119.6 (C-6), 137.9 (C-5), 111.2, 112.0, 121.7, 137.1, 149.9, 150.4 (Ar). Found (%): C, 69.25; H, 7.05. Calc. for $C_{24}H_{30}O_6$ (%): C, 69.54; H, 7.30.

8a *rel*-(1*R*,2*S*,3*S*,4*R*)-1,4-di(*p*-chlorophenyl)-2,3-divinylbutane-1,4-diol. White solid, mp 90-91°C. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 2.06 (s, 2H, OH), 2.12 (m, 2H, H-2), 4.40 (d, 2H, H-1, *J* 8.7 Hz), 5.12 (dd, 2H, H-6, *J* 15.7, 1.46 Hz), 5.42 (d, 2H, H-6, *J* 9.8, 1.46 Hz), 5.90 (ddd, 2H, H-5, *J* 15.7, 9.8, 8.7 Hz), 6.98 (d, 4H, Ar, *J* 8.4 Hz), 7.45 (d, 4H, Ar, *J* 8.4 Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$)

δ: 52.5 (C-2), 73.9 (C-1), 121.8 (C-6), 134.7 (C-5), 122.0, 129.0, 131.5, 141.2 (Ar). Found (%): C, 66.22; H, 5.39. Calc. for $C_{20}H_{20}Cl_2O_2$ (%): C, 66.12; H, 5.55.

9a *rel*-(1*R*,2*S*,3*S*,4*R*)-1,4-di(*p*-bromophenyl)-2,3-divinylbutane-1,4-diol. White solid, mp 111-112 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.94 (s, 2H, OH), 2.10 (dd, 2H, H-2, *J* 8.7, 8.7 Hz), 4.40 (d, 2H, H-1, *J* 8.7 Hz), 5.12 (dd, 2H, H-6, *J* 15.7, 1.74 Hz), 5.42 (dd, 2H, H-6, *J* 10.2, 1.74 Hz), 5.90 (ddd, 2H, H-5, *J* 15.7, 10.2, 8.7 Hz), 6.98 (d, 4H, Ar, *J* 8.4 Hz), 7.45 (d, 4H, Ar, *J* 8.4); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 52.5 (C-2,3), 73.9 (C-1,4), 121.8 (C-6,8), 134.7 (C-5,7), 122.0, 129.1, 131.5, 141.2 (Ar). Found (%): C, 53.41; H, 4.53. Calc. for $C_{20}H_{20}Br_2O_2$ (%): C, 53.12; H, 4.46.

10a *rel*-(1*R*,2*S*,3*S*,4*R*)-1,4-di(*m*-nitrophenyl)-2,3-divinylbutane-1,4-diol. Yellow oil. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 2.22 (dd, 2H, H-2, *J* 7.3, 7.3 Hz), 2.45 (s, 2H, OH), 4.72 (d, 2H, H-1, *J* 7.3 Hz), 5.16 (dd, 2H, H-6, *J* 15.6, 1.46 Hz), 5.41 (dd, 2H, H-6, *J* 10.4, 1.46 Hz), 5.97 (ddd, 2H, H-5, *J* 15.6, 10.4, 7.3 Hz), 7.47 and 8.09 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$): 53.4 (C-2,3), 73.1 (C-1,4), 121.8 (C-6,8), 133.1 (C-5,7), 121.1, 122.9, 132.6, 133.8, 143.8 , 148.1 (Ar). Found (%): C, 62.22; H, 5.05; N, 7.29. Calc. for $C_{20}H_{20}N_2O_2$ (%): C, 62.49; H, 5.24; N, 7.29.



5b *rel*-(1*R*,2*R*,3*R*,4*S*)-1,4-diphenyl-2,3-divinylbutane-1,4-diol. White solid. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.72, 2.67 (s, 1H, OH), 1.48, 2.83 (m, 2H, H-2,3), 4.63-5.49 (m, 6H, H-1,4,6,8), 5.54 (m, H-7), 5.82 (m, H-5), 7.26-7.38 (10H, Ar); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 54.2, 54.9 (C-2,3), 74.5 (C-1,4), 116.2, 118.3 (C-6,8), 135.0, 137.3 (C-5,7), 125.7, 127.0, 127.1, 127.4, 127.7, 128.0, 142.1, 142.2 (Ar). Found (%): C, 81.35; H, 7.31. Calc. for $C_{20}H_{22}O_2$ (%): C, 81.60; H, 7.53.

6b *rel*-(1*R*,2*R*,3*R*,4*S*)-1,4-di(*p*-methoxyphenyl)-2,3-divinylbutane-1,4-diol. White solid, mp 128-129ºC. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.76, 2.14 (both s, 1H, OH), 2.22 (ddd, 1H, H-3, *J* 10.4, 9.2, 9.2 Hz), 3.10 (ddd, 1H, H-2, *J* 10.6, 9.2, 9.2 Hz), 3.77, 3.84 (2s, 3H, OCH_3), 4.44-4.54 (m, 6H, H-1,4,6,8), 4.61 (d, 1H, H-8A[1], *J* 16.1 Hz), 4.95 (d, 1H, H-8B, *J* 10.4 Hz), 5.41 (d, 1H, H-6A, *J* 16.8 Hz), 5.47 (d, 1H, H-6B, *J* 10.6 Hz), 5.55 (ddd, 1H, H-7, *J* 16.1, 10.4, 10.4 Hz), 6.00 (ddd, 1H, H-5, *J* 16.8, 10.6, 10.6 Hz), 6.78 (d, 2H, Ar, *J* 8.4 Hz), 6.91 (d, 2H, Ar, *J* 8.4 Hz), 7.02 (d, 2H, Ar, *J* 8.4 Hz), 7.27 (s, 2H, Ar); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 51.5, 52.1 (C-2, 3), 55.1, 55.2 (OCH_3), 74.6, 74.8 (C-1,4), 120.7, 119.1 (C-6,8), 135.3, 136.3 (C-5,7), 113.8, 113.4, 128.7, 128.1, 134.0, 134.9, 158.9, 159.2 (Ar). Found (%): C, 74.32; H, 7.35. Calc. for $C_{22}H_{26}O_4$ (%): C, 74.55; H, 7.39.

[1] Vinyl protons described as ABX-spin system

7b *rel*-(1*R*,2*R*,3*R*,4*S*)-1,4-di(3,4-dimethoxyphenyl)-2,3-divinylbutane-1,4-diol. Yellow oil. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 2.04 (s, 2H, OH), 2.33-2.56 (m, 2H, H-3), 2.52-2.78 (m, 2H, H-2, OH), 3.87 (br s, 12H, OMe), 4.61 (d, 1H, H-4, *J* 8.0 Hz) 4.87 - 5.28 (m, 4H, H-1, H-8A, H-8B, H-6A, H-6B), 5.54 (ddd, 1H, H-7, *J* 16.7, 10.4, 10,4 Hz), 6.08 (ddd, 1H, H-5, *J* 17.7, 9.4, 9,4 Hz), 6.63-6.98 (m, 6H, Ar); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 54.1, 55.5 (C-2,3), 55.8 (OMe), 74.2, 75.2 (C-1,4), 117.3, 118.7 (C-6,8), 109.9, 110.1, 110.4, 119.5, 120.1, 134.8, 136.0, 137.4, 148.4 (C-5,7, Ar). Found (%): C, 69.35; H, 7.15. Calc. for $C_{24}H_{30}O_6$ (%): C, 69.54; H, 7.30.

8b *rel*-(1*R*,2*R*,3*R*,4*S*)-1,4-di(*p*-chlorophenyl)-2,3-divinylbutane-1,4-diol. Colorless solid, mp 90-91^{o}C. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.91, 2.25 (both s, 2H, OH), 2.15 (ddd, 1H, H-3, *J* 10.1, 8.7, 8.7), 3.06 (ddd, 1H, H-2, *J* 10.4, 8.7, 8.7 Hz), 4.48-4.56 (m, 2H, H-1, H-4), 4.61 (d, 1H, H-8A, *J* 17.7 Hz), 4.97 (d, 1H, H-8B, *J* 10.1 Hz), 5.41 (d, 1H, H-6A, *J* 16.6 Hz), 5.47 (d, 1H, H-6B, *J* 10.4 Hz), 5.59 (ddd, 1H, H-7, *J* 17.7, 10.1, 10.1 Hz), 5.95 (ddd, 1H, H-5, *J* 16.6, 10.4, 10,4 Hz), 7.02 (d, 2H, Ar, *J* 8.0 Hz), 7.15-7.37 (m, 6H, Ar); ^{13}C NMR ($CDCl_3$): 51.64 (C-2,3), 74.42, 74.69 (C-1,4), 119.5, 120.1 (C-6,8), 134.6, 135.4 (C-5,7), 128.7, 129.6, 131.2, 131.5, 133.9, 134.3, 142.2, 142.6 (Ar). Found (%): C, 66.30; H, 5.48. Calc. for $C_{20}H_{20}Cl_2O_2$ (%): C, 66.12; H, 5.55.

9b *rel*-(1*R*,2*R*,3*R*,4*S*)-1,4-di(*p*-bromophenyl)-2,3-divinylbutane-1,4-diol. Colorless oil. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 1.89, 2.26 (both s, 1H, OH), 2.16 (ddd, 1H, H-3, *J* 10.4, 9.6, 9.6 Hz), 3.06 (ddd, 1H, H-2, *J* 10.4, 9.6, 9.6 Hz), 4.46-4.53 (m, 2H, H-1, H-4 Hz), 4.61 (d, 1H, H-8A, *J* 17.2 Hz), 4.99 (d, 1H, H-8B, *J* 10.4 Hz), 5.42 (d, 1H, H-6A, *J* 16.6 Hz), 5.60 (ddd, 1H, H-7, *J* 17.2, 10.4, 10.4 Hz), 5.97 (ddd, 1H, H-5, *J* 16.6, 10.4, 10,4 Hz), 6.98 (d, 1H, Ar, *J* 7.6 Hz), 7.22 (d, 1H, Ar, *J* 7.6 Hz) 7.39 (d, 1H, Ar, *J* 8.3 Hz), 7.50 (d, 1H, Ar, *J* 8.3 Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 51.6, 51.5 (C-2,3), 73.9, 77.6 (C-1,4), 119.8, 121.6 (C-6,8), 125.5, 129.0, 131.2, 131.5, 134.7, 145.5, 145.7 (C-5,7, Ar). Found (%): C, 53.96; H, 4.53; Br, 35.02. Calc. for $C_{20}H_{20}Br_2O_2$ (%): C, 53.12; H, 4.46.

10b *rel*-(1*R*,2*R*,3*R*,4*S*)-1,4-di(*m*-nitrophenyl)-2,3-divinylbutane-1,4-diol. Yellow oil. ^{1}H-^{1}H COSY (600.13 MHz, $CDCl_3$) δ: 2.26 (ddd, 1H, H-3, *J* 10.8, 10.2, 9.0 Hz), 2.47 and 2.57 (both s, 1H, OH), 3.08 (ddd, 1H, H-2, *J* 10.2, 10.2, 7.8 Hz), 4.63 (d, 1H, H-8A, *J* 16.8 Hz), 4.67 (d, 1H, H-4, *J* 9.0 Hz), 4.77 (d, 1H, H-1, *J* 7.8 Hz), 5.02 (d, 1H, H-8B, *J* 10.8 Hz), 5.32 (d, 1H, H-6A, *J* 16.8 Hz), 5.43 (d, 1H, H-6B, *J* 10.2 Hz), 5.66 (ddd, 1H, H-7, *J* 16.8, 10.8, 10.8 Hz), 5.97 (ddd, 1H, H-5, *J* 16.8, 10.2, 10.2 Hz), 7.41 (t, 1H, H-5(4-Ar), *J* 7.8 Hz), 7.47 (d, 1H, H-6(4-Ar), *J* 7.8 Hz), 7.52 (t, 1H, H-5(1-Ar), *J* 7.8 Hz), 7.67 (d, 1H, H-6(4-Ar), *J* 7.2 Hz), 7.96 (s, 1H, H-2(4-Ar)), 8.04 (d, 1H, H-4(4-Ar), *J* 7.8 Hz), 8.14 (d, 1H, H-5(1-Ar), *J* 7.8 Hz), 8.17 (s, 1H, H-2(1-Ar)); ^{13}C NMR ($CDCl_3$, 150.90 MHz): 52.09 (C-2), 53.35 (C-3), 74.41 (C-1), 74.48 (C-4), 120.47 (C-8), 121.94 (C-6), 134.07 (C-5),

134.39 (C-7), 128.81 (C-5(4-Ar)), 132.87 (C-6(4-Ar)), 129.25 (C-5(1-Ar)), 133.22 (C-6(1-Ar)), 121.80 (C-2(4-Ar)), 122.80 (C-2(1-Ar)), 122.58 (C-4(4-Ar)), 122.78 (C-4(1-Ar)), 144.11 (C-1(1-Ar)), 144.99 (C-1(4-Ar)), 148.04 (C-3(4-Ar)), 148.27 (C-3(1-Ar)). Found (%): C, 62.32; H, 5.09; N, 7.23. Calc. for $C_{20}H_{20}N_2O_2$ (%): C, 62.49; H, 5.24; N, 7.29.

X-Ray diffraction experiments for **6b, 8a, 9a and 9a_2** were carried out with Bruker SMART APEX II CCD, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 100K. Reflection intensities were integrated using SAINT software and absorption correction was applied semi-empirically using SADABS program [1]. The structure was solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for no-hydrogen atoms. The positions of hydrogen atoms of hydroxyl group were located from the Fourier density synthesis while others were calculated from geometrical point view. In the crystal of **9a_2** the unknown disordered solvent which is probably the superposition of ethyl acetate and cyclohexane was removed by SQUEEZE program. Crystal data and structure refinement parameters for **6b, 8a, 9a and 9a_2** are given in Table S1. All calculations were performed using the SHELXTL software. [2]

Table S1. Crystal data and structure refinement parameters for **6b**, **8a** and **9a.**

	6b	**8a**	**9a**	**9a_2**
Formula	$C_{22}H_{26}O_4$	$C_{20}H_{21.33}Cl_2O_{2.67}$	$C_{20}H_{19}Br_2O_2$	$C_{20}H_{20}Br_2O_2$
M	354.43	375.27	451.17	452.18
T, K	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	C2	Cc	C2/c
Z	4	6	4	28
a, Å	11.3682(6)	21.861(2)	21.040(3)	14.9581(6)
b, Å	22.3724(11)	11.6979(11)	13.537(2)	26.3815(10)
c, Å	7.8701(4)	11.3240(11)	6.4754(12)	35.8063(14)
α, °	90.00	90.00	90.00	90.00
β, °	104.1970(10)	90.338(2)	101.633(5)	94.6859(8)
γ, °	90.00	90.00	90.00	90.00
V, $Å^3$	1940.50(17)	2895.8(5)	1806.5(5)	14082.6(10)
d_{calc}, $g \cdot cm^{-3}$	1.213	1.291	1.659	1.493
Linear absorption, μ (cm^{-1})	0.82	3.49	44.96	40.38
F(000)	760	1180	900	6328
$2\theta_{max}$, °	60	58	57	55
Reflections measured	9584	17035	8790	100665
Independent reflections	2821	7606	4325	16187
Observed reflections [$I > 2\sigma(I)$]	2400	4422	4037	11154
Parameters	256	355	227	760
R1	0.0372	0.0524	0.0255	0.0434
wR2	0.0903	0.0847	0.0637	0.0957
GOF	1.020	0.941	1.028	1.023
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.260/-0.183	0.377/-0.495	0.932/-0.490	1.604/-1.054

1. G.M. Sheldrick, SADABS, 1997, Bruker AXS Inc., Madison, WI-53719, USA

2. G.M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA