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# SUPPLEMENTARY MATERIAL

## A Multicomponent Redox System Accounts for the First Nozaki-Hiyama-Kishi Reactions Catalytic in Chromium

**Alois Fürstner* and Nongyuan Shi**

*Max-Planck-Institut für Kohlenforschung*

*Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany*

**Gerneral.** All reactions were carried out under Ar using Schlenk techniques. **$CrCl_2$**: The $CrCl_2$ used should be colorless; pale-green batches result in lower yields. Samples of good quality were purchased from Alfa - Johnson Matthey Co. (99.9% purity). **Mn powder**: Aldrich, ca 150 μ. The **solvents** were dried by distillation over the following drying agents and were transferred under Ar: DME (Na/K alloy). The **DMF** must be thorougly purified: best results were obtained by distilling pre-dried DMF over Desmodur-15® (Bayer AG) and dibutyltin laurate at 70-80 °C under reduced pressure. **TMSCl** (Janssen), the commercially available aldehydes, iodobenzene, iodothiophene, allylbromide, and ethyl (2-bromomethyl) propenoate were distilled prior to use. Cyanopropyldimethylchlorosilane (Aldrich) was used as received. **Substrates**: 2-Trifluoromethylsulfonyloxy-1-octene and 2-trifluoromethylsulfonyloxy-1-hexene were prepared according to a literature procedure.[17] 2-Iodo1-hexene was obtained upon reaction of 1-hexyne with 9-iodo-9-BBN, followed by de-borylation with HOAc.[18] **Flash chromatography**: Merck silica gel 60 (230-400 mesh) with hexane/ethyl acetate in various proportions as eluent. **Instrumental analyses**: NMR: Spectra were recorded on a Bruker AC 200 spectrometer at 200.1 MHz ($^1H$) and 50.3 MHz ($^{13}C$) in $CDCl_3$. Chemical shifts δ

are given in ppm relative to TMS. IR: Nicolet FT-7199, wavenumbers in $cm^{-1}$. MS: Varian CH-5 (70 eV).

**Representative Procedure.** A solution of 4-methoxybenzaldehyde (340 mg, 2.5 mmol), 2-trifluoromethylsulfonyloxy-1-hexene (1.06 g, 4.6 mmol) and TMSCl (0.75 mL, 6.0 mmol) in DMF (1.5 mL) and DME (5 mL) was dropped into a suspension of Mn powder (230 mg, 4.2 mmol), $CrCl_2$ (46 mg, 0.38 mmol) and $NiCl_2$ (10 mg, 0.07 mmol) in DME (5 mL) at 50 °C. After stirring for 5 h at that temperature, the mixture was quenched with water (15 mL), extracted with ethyl acetate (150 mL in three portions) and the combined organic layers were washed with brine. Aqueous n-$Bu_4NF$ (75% w/w) was added and the solution was stirred at room temperature until TLC showed complete desilylation of the crude product. Standard work-up followed by flash chromatography with hexane/ethyl acetate (15/1) as eluent afforded 2-methylene-1-(4-methoxyphenyl)hexan-1-ol as colorless syrup (420 mg, 76%).

**Diphenylmethanol:** m.p. 64-66°C. $^1H$ NMR: δ 2.23 (1H), 5.84 (s, 1H), 7.36 (m, 10H). $^{13}C$ NMR: δ 75.9, 126.2, 127.2, 128.2, 143.5. IR: 3388, 1598, 1494, 1454, 1269, 1181, 1172, 1035, 1018, 754, 735, 699, 653, 602. MS *m/z* (relative intensity) 184 (55, [$M^+$]), 165 (11), 105 (100), 79 (29), 77 (46), 51 (14).

**1-Phenyl-1-octanol:** Colorless syrup. $^1H$ NMR: δ 0.92 (t, 3H), 1.31 (m, 8H), 1.79 (m, 2H), 1.97 (s, 1H), 4.69 (t, 1H), 7.37 (s, 5H). $^{13}C$ NMR: δ 13.7, 22.3, 25.5, 28.9, 29.2, 31.5, 38.8, 74.3, 125.6, 127.1, 128.0, 144.6. IR: 3360, 1600, 1500, 1450, 1060, 1030, 760, 700. MS *m/z* (relative intensity) 206 (3, [$M^+$]), 107 (100), 79 (25), 77 (12).

**Phenylcyclohexylcarbinol:** $^1H$ NMR: δ 0.78 -1.45 (m, 6H), 1.48 - 1.85 (m, 4H), 1.95 (b, 1H), 2.00 (s, 1H), 4.33 (d, 1H), 7.29 (m, 5H). $^{13}C$ NMR: δ 25.8, 26.1, 28.5, 29.0, 44.6, 79.0, 126.4, 127.0, 127.8, 143.3. IR: 3395, 3028, 2924, 2852, 1603, 1493, 1451, 1259, 1068, 1017, 893, 760, 701, 578. MS *m/z* (relative intensity) 190 (4, [$M^+$]), 107 (100), 79 (28).

**1-Acetoxy-6-chloro-1-phenylhexane:** Colorless syrup. $^1$H NMR: δ 1.22 - 1.59 (m, 4H), 1.70 - 2.05 (m, 4H), 2.11 (s, 3H), 3.54 (t, 2H), 5.79 (t, 1H), 7.36 (s, 5H). $^{13}$C NMR: δ 20.9, 24.5, 26.2, 32.0, 35.8, 44.5, 75.5, 126.1, 127.5, 128.1, 140.3, 170.0. IR: 3065, 3033, 2941, 2863, 1737, 1495, 1455, 1372, 1239, 1073, 1024, 964, 760, 700, 650, 553. MS *m/z* (relative intensity) 254 (6, [M$^+$]), 212 (34), 149 (39), 117 (35), 107 (100), 43 (84).

**6-Chloro-1-phenyl-1-hexanol:** Colorless syrup. $^1$H NMR: δ 1.21 - 1.54 (m, 4H), 1.62 - 1.91 (m, 5H), 3.50 (t, 2H), 4.66 (t, 2H), 7.33 (s, 5H). $^{13}$C NMR: δ 24.7, 26.4, 32.1, 38.5, 44.6, 74.1, 125.5, 127.2, 128.1, 144.4. IR: 3374, 3029, 2937, 2860, 1603, 1493, 1454, 1310, 1282, 1201, 1028, 914, 762, 701, 650. MS *m/z* (relative intensity) 184 (2, [M$^+$]), 107 (100), 79 (29).

**1-(2-Thienyl)-1-octanol:** Colorless syrup. $^1$H NMR: δ 0.90 (t, 3H), 1.29 (m, 10H), 1.86 (m, 2H), 2.04 (b, 1H), 4.92 (t, 1H), 6.98 (m, 3H), 7.24 (m, 2H). $^{13}$C NMR: δ 13.7, 22.3, 25.4, 28.8, 29.0, 31.4, 39.0, 69.7, 123.3, 124.1, 126.2, 148.7. IR: 3377, 2955, 2927, 1465, 1415, 1378, 1231, 1039, 853, 830, 697. MS *m/z* (relative intensity) 212 (10, [M$^+$]), 113 (100), 85 (22).

**(4-Ethoxycarbonylphenyl)phenylmethanol:** Colorless syrup. $^1$H NMR: δ 1.36 (t, 3H), 2.65 (b, 1H), 4.33 (q, 2H), 5.84 (s, 1H), 7.31 (m, 5H), 7.43 (d, 2H), 7.99 (d, 2H). $^{13}$C NMR: δ 14.0, 60.6, 75.5, 125.9, 126.3, 127.5, 128.3, 129.4, 143.0, 148.3, 166.1. IR: 3461, 3062, 3030. 2982, 1716, 1700, 1611, 1453, 1413, 1368, 1279, 1176, 1106, 1019, 873, 755, 701. MS *m/z* (relative intensity) 256 (16, [M$^+$]), 211 (14), 183 (13), 177 (30), 165 (11), 151 (100), 123 (32), 105 (63), 77 (27).

**8-Hydroxy-7-methylene-pentadecane:** Colorless syrup. $^1$H NMR: δ 0.88 (m, 3H), 1.29 - 1.55 (m, 23H), 2.00 (m, 2H), 4.05 (t, 1H), 4.83 (d, 1H), 5.00 (d, 1H). $^{13}$C NMR δ 13.7, 22.3, 25.4, 27.7, 28.9, 29.2, 31.0, 31.4, 31.5, 35.2, 75.2, 108.7, 152.0. IR: 3354, 2956, 2927, 2857, 1646, 1466, 1378, 1122, 1047, 1020, 900, 724. MS *m/z*

(relative intensity) 240 (3, [M+]), 169 (12), 155 (18), 141 (29), 127 (26), 123 (20), 95 (17), 81 (35) 71 (100).

**2-Methylene-1-(4-methoxyphenyl)-1-hexanol:** Colorless syrup. $^1$H NMR: δ 0.83 (t, 3H), 1.15-1.45 (m, 4H), 1.72- 2.05 (m, 2H), 2.18 (b, 1H), 3.77 (s, 3H), 4.94 (s, 1H), 5.05 (s, 1H), 5.22 (s, 1H), 6.85 (d, 2H), 7.25 (d, 2H). $^{13}$C NMR: δ 13.6, 22.1, 29.6, 31.4, 54.9, 76.4, 108.7, 113.2, 127.7, 134.2, 151.0, 158.8. IR: 3410, 2957, 2931, 2871, 1630, 1611, 1511, 1465, 1249, 1172, 1036, 910, 830. MS *m/z* (relative intensity) 220 (100, [M+]), 177 (13), 163 (26), 137 (86), 109 (17).

**2-Methylene-1-(3,4-methylenedioxyphenyl)-1-hexanol:** Colorless syrup. $^1$H NMR: δ 0.85 (t, 3H), 1.17-1.46 (m, 4H), 1.65-2.04 (m, 3H), 4.95 (s, 1H), 5.04 (s, 1H), 5.24 (s, 1H), 5.93 (s, 2H), 6.80 (m, 3H). $^{13}$C NMR: δ 13.6, 22.1, 29.6, 31.3, 76.7, 100.6, 106.8, 107.6, 108.9, 120.0, 136.0, 146.7, 147.4, 150.8. IR: 3390, 2957, 2930, 2873, 1650, 1503, 1487, 1442, 1247, 1094, 1041, 951, 933, 809. MS *m/z* (relative intensity) 234 (100, [M+]), 177 (14), 151 (67), 123 (11), 93 (15).

**1-Undecen-4-ol:** Colorless syrup. $^1$H NMR: δ 0.81 (m, 3H), 1.21 (m, 8H), 1.38 (m, 2H), 2.00 - 2.34 (m, 3H), 3.63 (m, 1H), 5.05 (m, 1H), 5.13 (m, 1H), 5.69-5.90 (m, 1H). $^{13}$C NMR: δ 13.7, 22.3, 25.3, 28.9, 29.2, 31.5, 36.4, 41.5, 70.5, 117.6, 134.5. IR: 3357, 3077, 2957, 2928, 2856, 1641, 1466, 1438, 1378, 1342, 1126, 1074, 1044, 994, 912. MS *m/z* (relative intensity) 170 (0.3, [M+]), 129 (24), 111 (22), 69 (100), 55 (36).

**2-Methylene-4-(2-phenyl-1-ethyl)butyrolactone:** Colorless syrup. $^1$H NMR: δ 1.82-2.31 (m, 2H), 2.58 and 3.04 (dtAB-system, 2H, J = 2.5, 7.8, 17), 2.76 (m, 2H), 4.52 (m, 1H), 5.62 (t, 1H, J = 2.5), 6.23 (t, 1H, J = 2.5), 7.15-7.34 (m, 5H). $^{13}$C NMR: δ 31.0, 33.2, 37.7, 76.2, 121.8, 125.9, 128.1, 128.2, 134.3, 140.3, 169.9. IR: 3027, 2932, 2861, 1762, 1665, 1603, 1497, 1454, 1398, 1342, 1278, 1265, 1164, 1128, 1023, 937, 814, 752, 701, 627. MS *m/z* (relative intensity) 202 (18, [M+]), 117 (100), 91 (71).

**1,2-Bis(4-methoxycarbonylphenyl)-1,2-ethanediol**: ratio of isomers ≈ 3 : 1. $^{1}H$ NMR: ([resolved signals, minor stereoisomer]) δ 3.79 (s), [3.81 (s)], [4.68 (br d)], 4.75 (br d), [5.57 (br d)], 5.67 (br d), 7.21 (d, J = 7.5), [7.33 (d, J = 8)], 7.75 (d, J = 7.5), [7.82 (d, J = 8)]. $^{13}C$ NMR ([resolved signals, minor stereoisomer]): δ [166.1], 166.0, [148.1], 147.4, 128.1, 128.0, 127.9, 127.8, 127.4, 127.1, 76.4, [76.2], 51.8. IR: 3482, 3038, 2956, 2872, 1694, 1609, 1577, 1435, 1415, 1313, 1292, 1194, 1119, 1052, 1019, 963, 863, 803, 772, 737, 700. MS *m/z* (relative intensity) 299 (5, [(M-OMe)$^{+}$]), 166 (100).

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