Intramolecular Chromium(II)-Catalyzed Pinacol Cross Coupling of 2-Methylene-α,ω-dicarbonyls[1]

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Abstract: Using only 10% of $CrCl_2$ as catalyst, manganese-powder as reducing agent and TMSCl as scavenger, 2-methylene-α,ω-dialdehydes and -ketones can be coupled to form cyclic diols diastereoselectively. The diastereomeric excess strongly depends on the ring size and the substituents of the ω-carbonyl group. The greater the ring size the higher diastereoselectivities are observed. In all cases *cis*-diols are preferentially formed.

Key words: chromium, catalysis, cross-coupling, cyclizations, pinacols

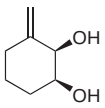
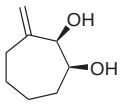
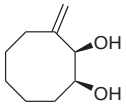
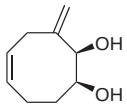
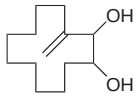
Many pharmacologically active natural products include 1,2-diol substructures occurring in cyclic systems. 1,2-Diols can be generated in general by bishydroxylation of olefinic double bonds[2] or reductive coupling of carbonyl compounds.[3] The last method plays an important role in the synthesis of HIV-protease inhibitors[4] and natural products[5] such as Taxol[6] and Cotylenol[7] and their derivates. For their synthesis this reaction has to be performed in a diastereoselective fashion.

However, most reported catalytic pinacol couplings[8] are limited to highly reactive aldehydes and even more important only symmetrically substituted pinacols can be obtained in intermolecular processes.

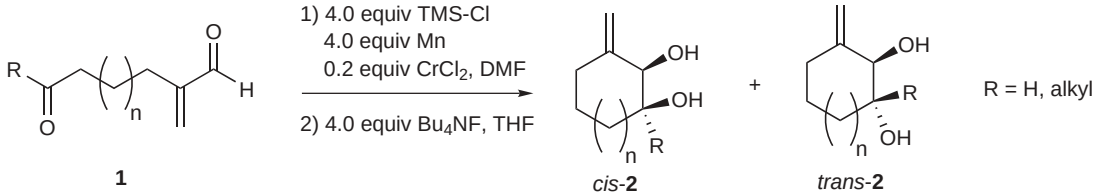
Previously, a Cr(II)-mediated pinacol-type cross coupling between α,β-unsaturated ketones and aldehydes has been reported.[9] The diastereoselectivity of this overstoichiometric process highly depends on the reaction temperature. Moreover, 4 equivalents of chromium chloride were necessary and no intramolecular example was given.

Recently, we reported a chromium catalyzed pinacol cross coupling of α,β-unsaturated carbonyl compounds and aldehydes to form 1,2-diols diastereoselectively.[10] The great advantage of this method is the decrease of the amount of chromium chloride to only 10% by using Fürstner's redox system[11] and the extention of Takai's method to acroleins and sterically demanding substrates. We now report an intramolecular coupling to form cyclic diols from small to mid-sized rings (Scheme 1).

Table 1 Cyclization of Dialdehydes **1** (R = H)

Entry	n	Pinacol **2**	Yield (%)[a]	*cis*/*trans*[b]	de (%)
1	1		60	59:41	18
2	2		55	71:29	42
3	3		75	80:20	60
4	3		65	92:8	84
5	7		–	–	–

[a] Yields refer to isolated products.
[b] Diastereomeric ratios were determined by isolation and/or NMR-spectroscopy.



1 *cis*-**2** *trans*-**2**

Scheme 1 Chromium(II)-catalyzed cross coupling of 2-methylene-α,ω-dicarbonyl compounds

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Application of the reported coupling conditions[10] to 2-methylene-α,ω-dialdehydes **1** predominantly produces *cis*-diols **2**. The diastereoselectivity strongly depends on the ring size. While 6-membered rings are formed with only 18% de, diastereoselectivities increase up to 84% de for 8-membered rings (Table 1).

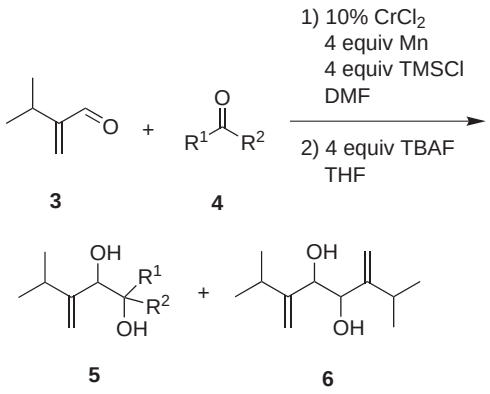
However, a 12-membered ring could not be obtained. In this case the reactive centers are too far from each other so that intermolecular couplings as well as homo couplings and other side reactions become dominant.

We were able to show[10] that substituted vinylketones as well as acroleins can be coupled with aliphatic aldehydes in good yields and with high selectivities.

However, when ketones are used instead of aldehydes yields decrease dramatically. In an attempt to cross couple 2-isopropylpropenal **3** (which reacts with aliphatic aldehydes in good yields up to 96%) with certain aromatic and aliphatic ketones such as **4** (Table 2), only 15% to 27% of the tertiary alcohol **5** could be obtained. Nevertheless the symmetrically substituted pinacol **6** resulting from homo coupling of acrolein **3** could be isolated in 35% to 63% yield with a *rac*/*meso*-ratio of 61:39 (22% de). Although the concentration of ketone is much higher than of acrolein, the acrolein itself acts as carbonyl compound to form the homo pinacol.

However, via the intramolecular pathway, we were able to obtain tertiary cyclic alcohols in high yields and with excellent diastereoselectivities. Starting from keto-acroleins **7** the corresponding cyclic pinacols **8** are obtained generally in better yields than in the case of the dialdehydes **1**. Some representative results are listed in Table 3.

Table 2 Cross-Coupling Between 2-Methylene-3-methylbutanal with Various Ketones

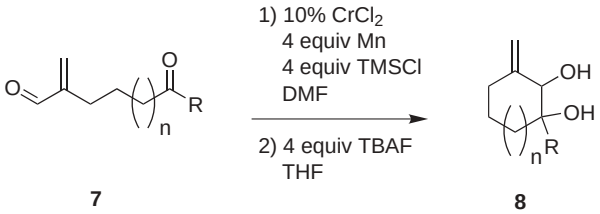


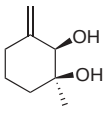
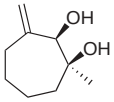
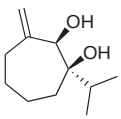
Entry	Ketone **4**	Pinacol **5** (%)[a]
1	Acetone	19
2	Cyclohexanone	24
3	Mesityl oxide	27
4	Acetophenone	15
5	*p*-NO_2-acetophenone	–

[a] Yields refer to isolated products.

Again, the diastereoselectivity depends on the ring size. Changing the ring size from n = 1 (entry 1) to n = 2 (entry 2) a dramatic increase in the diastereoselectivity from 10% to 86% is observed. But also the substituent of the keto group is important. Change of the substituent from

Table 3 Cyclization of Keto-acroleins **7**



Entry	n	R	Pinacol **8**	Yield (%)	*cis*/*trans*	de
1	1	Me		82	55:45	10
2	2	Me		75	93:7	86
3	2	*i*-Pr		30	>99:1	>98

[a] Yields refer to isolated products.
[b] Diastereoeric ratios were determined by isolation and/or NMR-spectroscopy.

R = H (Table 1, entry 1) to R = Me (Table 3, entry 1) results in a slight decrease in diastereoselectivity from 18% to 10% de for the 6-membered ring but a remarkable increase from 42% (Table 1, entry 2) to 86% de (Table 3, entry 2) for the 7-membered ring, respectively.

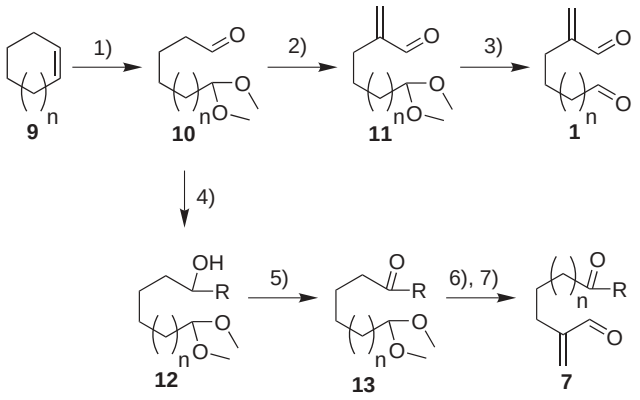
With R = *i*-Pr (Table 3, entry 3) the *cis*-diol is formed exclusively with more than 98% de. Unfortunately the yield is significantly lower (30%). The main product in this case is again the symmetrically substituted pinacol from the homo coupling of the acrolein, which could be isolated in 54% yield. The reactivity of the keto group is lowered by the sterically demanding and electron donating residue R = *i*-Pr so that the disfavored intermolecular homo coupling gains in importance.

In conclusion, the chromium(II)-catalyzed pinacol type cross coupling serves as an excellent method for the cyclization of 2-methylene-dicarbonyl compounds. In contrast to the intermolecular way even ketones can be coupled in good yields and high diastereoselectivities. The *cis*/*trans*-ratio strongly depends on the ring-size and the steric demand at the keto group. In all of these cases the *cis*-diol is preferred.

Application of this method to the total synthesis of Cotylenol is presently under investigation in our group.

Preparation of Starting Materials

Precursors for the cyclization can be easily obtained from cycloolefins in three steps for the aldehydes and five steps for the ketones, respectively (Scheme 2).



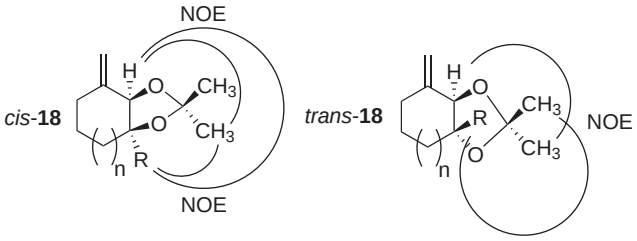
Scheme 2 Syntheses of the starting materials **1** and **7**. 1) a) O_3, CH_2Cl_2, MeOH, –78 °C; b) PTSA, –78 °C to r.t.; c) $NaHCO_3$; d) Me_2S; 2) Me_2NCH_2Cl, Et_3N, CH_2Cl_2, r.t.; 3) HCl, THF, r.t.; 4) RMgX, Et_2O, 0 °C to r.t.; 5) DMP, CH_2Cl_2, pyridine, r.t.; 6) HCl, THF, r.t.; 7) Me_2NCH_2Cl, Et_3N, CH_2Cl_2, r.t.

Cycloolefins **9** are converted to the monoprotected aldehydes **10** in a one-pot reaction by treatment with ozone in dichloromethane and methanol according to a procedure published by Schreiber et al.[12] in 80% to 95% yield. Mannich type reaction[13] of **10** with Eschenmoser-chloride[14] followed by deprotection with hydrochloric acid in tetrahydrofuran leads to α-methylene dialdehydes **1** in 55% to 65% yield.

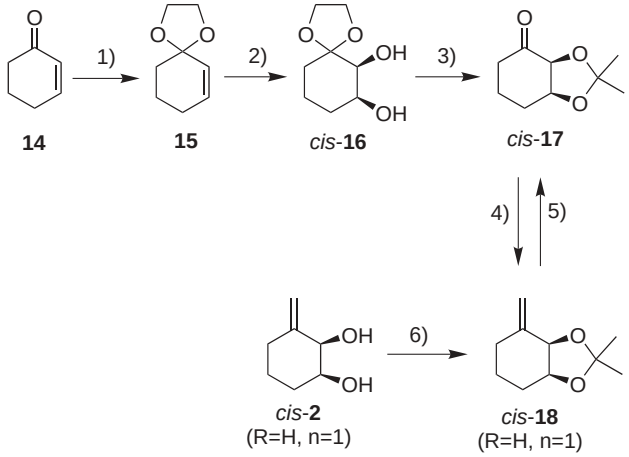
In case of the ketones the monoprotected aldehydes **10** are treated with a Grignard reagent to form the secondary alcohols **12** which are oxidized using Dess–Martin periodinane[15] to ketones **13**. Deprotection followed by Mannich reaction as described above leads to the corresponding keto-acroleins **7**. Under the chosen conditions only the aldehyde reacts with the Eschenmoser salt leaving the keto-group unchanged.

Determination of Relative Configurations

The relative configurations of the cyclic diols were determined by NOE-spectroscopy of the corresponding acetonides **18** (Scheme 3) and in the case of the 6-membered ring by comparison of the spectroscopic data with a reference substance obtained as shown in Scheme 4.



Scheme 3 Determination of relative configurations by NOE-spectroscopy.



Scheme 4 Preparation of reference substance. 1) $HOCH_2CH_2OH$, PTSA, toluene, reflux; 2) OsO_4, NMO, H_2O, acetone; 3) PTSA, acetone, r.t.; 4) $Cp_2Ti(CH_2)(Cl)AlMe_2$, THF, 0 °C to r.t.; 5) O_3, CH_2Cl_2, MeOH, Me_2S; 6) PPTS, 2,2-dimethoxypropane, acetone, r.t.

2-Cyclohexen-1-one (**14**) was protected to **15** and *cis*-hydroxylated using 1% osmium tetroxide and *N*-methylmorpholin-*N*-oxide as cooxidans.[16] Treatment of *cis*-**16** with catalytic amounts of *p*-toluenesulfonic acid in acetone led directly to the acetonide *cis*-**17**. The *cis*-configuration was validated by NOE-spectroscopy. The ketone *cis*-**17** can be converted to the allylic alcohol *cis*-**18** with

Tebbe's reagent.[17] Compound *cis*-**18** is also available by treatment of pinacol *cis*-**2** with pyridinium tosylate and 2,2-dimethoxypropane in acetone and can be converted into *cis*-**17** by ozonolysis.

General Coupling Procedure

All experiments were carried out under an argon atmosphere using Schlenk techniques.

4 mmol (220 mg) of manganese powder and 0.2 mmol (25 mg) of chromium dichloride were suspended in 8 mL of dry DMF. To the green mixture 4 mmol (435 mg, 0.51 mL) of TMSCl were added. The solution was allowed to stir at r.t. for 15 min. A solution of 1 mmol of the dicarbonyl compound in 2 mL of dry DMF was added over a period of 11 h via a syringe pump. After additional 4 h 20 mL of H_2O were added. The extraction with four 30 mL portions of Et_2O followed by drying with $MgSO_4$ and evaporation of the solvent afforded a colorless oil consisting of silylated pinacol and traces of DMF. For desilylation the oil was dissolved in 10 mL of THF and 4 mL of a 1 M solution of TBAF in THF were added. After 1 h 20 mL of H_2O were added and the diol was extracted with four 30 mL portions of Et_2O. After drying with $MgSO_4$ and evaporation the crude product was purified by column chromatography using 40 g of silica-gel with petroleum ether/EtOAc = 1:1 affording the *cis*-diol as a colorless oil and the *trans*-diol as colorless crystals.

For acetalization the diol was dissolved in 1 mL of acetone and 1 mL of 2,2-dimethoxypropane and a small amount of pyridinium tosylate was added. After 2 h approximately 0.5 g of silica-gel were added and the solvent was removed in vacuo. Purification by column chromatography using 4 g of silica-gel with petroleum ether/EtOAc = 9:1 afforded the acetonide as a colorless oil.

Representative spectroscopic data:

3-Methylenecyclohexane-1,2-diol (**2**; n = 1): *cis*-diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.33–1.37, 1.56–1.60, 1.71–1.78, 1.89–1.96, 2.22–2.27 (m, 6 H, 3 CH_2), 2.09 (br, 1 H, OH), 2.35 (br, 1 H, OH), 3.79, 4.08 [br, 2 H, 2 × C*H*(OH)], 4.83, 4.91 (s, 2 H, CH_2). ^{13}C (100 MHz, $CDCl_3$): δ = 22.60, 29.84, 31.49 (CH_2), 72.08, 74.61 (CHOH), 109.9 (CH_2), 147.5 (C); *trans*-Diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.33–1.37, 1.56–1.60, 1.71–1.78, 1.89–1.96, 2.22–2.27 (m, 6 H, 3 CH_2), 2.09 (br, 1 H, OH), 2.35 (br, 1 H, OH), 3.79, 3.31 [br, 2 H, 2 × C*H*(OH)], 4.76, 4.96 (s, 2 H, CH_2). ^{13}C (100 MHz, $CDCl_3$): δ = 24.30, 32.59, 33.80 (CH_2), 76.03, 77.76 (CHOH), 106.4 (CH_2), 147.7 (C). MS (EI, 70 eV): *m/z* (%) = 128 (2) [M^+], 110 (24) [$M^+ - H_2O$], 95 (19), 84 (44), 57 (62), 55 (60), 43 (87), 41(100). IR ($CDCl_3$): 3420, 3091, 2942, 2866, 1734, 1653, 1261, 1057, 991 cm^{-1}. Anal. Calcd for $C_7H_{12}O_2$ (128.17): C, 65.60; H, 9.44. Found: C, 65.12; H, 9.53.

Hexahydro-2,2-dimethyl-4-methylenebenzo[*d*][1,3]dioxole [**18**; acetonide of **2** (n = 1)]: *cis*-diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.37, 1.51 (s, 6 H, 2 CH_3), 1.21–1.83 (m, 4 H, 2 CH_2), 2.04–2.13, 2.30–2.38 (m, 2 H, CH_2), 4.23 [q, *J* = 5.0 Hz, 1 H, CH(OR)], 4.45 [d, *J* = 5.4 Hz, 1 H, CH(OR)]. ^{13}C (100 MHz, $CDCl_3$): δ = 20.9, 28.1, 30.5 (3 CH_2), 26.1, 27.9 (2 CH_3), 75.3, 77.4 [CH(OR)], 108.5 [$C(OR)_2$], 113.6 (CH_2), 144.9 (C).

1-Methyl-3-methylenecycloheptane-1,2-diol (**8**; R = CH_3, n = 2): *cis*-diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.26 (s, 3 H, CH_3), 1.49–1.77 (m, 6 H, 3 CH_2), 2.10–2.19, 2.49–2.55 (m, 2 H, CH_2), 2.92 (br, 2 H, 2 OH), 3.97 [s, 1 H, CH(OH)], 4.96, 5.02 (s, 2 H, CH_2). ^{13}C (100 MHz, $CDCl_3$): δ = 21.0, 27.4, 32.3, 39.4 (CH_2), 26.4 (CH_3), 73.5 [C(OH)], 81.0 [CH(OH)], 113.6 (CH_2), 148.7 (C). MS (EI, 70 eV): *m/z* (%) = 156 (1) [M^+], 138 (6) [$M^+ - H_2O$], 123 (7), 109 (33), 95 (51), 43 (100). *trans*-Diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.17 (s, 3 H, CH_3), 1.49–1.77 (m, 6 H, 3 CH_2), 2.10–2.19, 2.49–2.55 (m, 2 H, CH_2), 2.92 (br, 2 H, 2 OH), 4.07 [s, 1 H, C*H*(OH)], 4.96, 5.17 (s, 2 H, CH_2). ^{13}C (100 MHz, $CDCl_3$): δ = 21.4, 27.4, 33.3, 40.9 (CH_2), 26.4 (CH_3), 74.5 [C(OH)], 80.0 [CH(OH)], 112.5 (CH_2), 148.1 (C). MS (EI, 70 eV): *m/z* (%) = 156 (1) [M^+], 138 (9) [$M^+ - H_2O$], 123 (7), 109 (63), 95 (51), 43 (100). IR ($CDCl_3$): 3554, 3429, 2935, 2862, 1446, 1375, 1252 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$ (156.12): C, 69.19; H, 10.32. Found: C, 68.90; H, 10.51.

Hexahydro-2,2,3a-trimethyl-8-methylene-3a*H*-cyclohepta[*d*][1,3]dioxole [acetonide of **8** (R = CH_3, n = 2)]: *cis*-diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.31 (s, 3 H, CH_3), 1.39, 1.58 (s, 6 H, 2 CH_3), 1.18–1.77 (m, 6 H, 3 CH_2), 2.13 (dt, J^1 = 3.9 Hz, J^2 = 12.9 Hz, 1 H, CH_2), 2.45 (dt, J^1 = 4.7 Hz, J^2 = 12.5 Hz, 1 H, CH_2), 4.39 [s, 1 H, CH(OR)], 4.93, 4.94 (s, 2 H, CH_2). ^{13}C (100 MHz, $CDCl_3$): δ = 22.8 (CH_3), 26.2, 31.6, 31.8, 40.4 (CH_2), 27.2, 28.6 (CH_3), 83.4 [C(OR)], 88.0 [CH(OR)], 107.3 [$C(OR)_2$], 114.1 (CH_2), 147.0 (C). *trans*-Diol: ^{1}H (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, CH_3), 1.28, 1.35 (s, 6 H, 2 CH_3), 1.18–1.77 (m, 6 H, 3 CH_2), 2.13 (dt, J^1 = 3.9 Hz, J^2 = 12.9 Hz, 1 H, CH_2), 2.45 (dt, J^1 = 4.7 Hz, J^2 = 12.5 Hz, 1 H, CH_2), 4.43 [s, 1 H, CH(OR)], 4.86, 5.17 (s, 2 H, CH_2). ^{13}C (100 MHz, $CDCl_3$): δ = 22.8 (CH_3), 24.7, 31.6, 31.8, 40.4 (CH_2), 27.2, 28.6 (CH_3), 77.3 [C(OR)], 82.5 [CH(OR)], 107.3 [$C(OR)_2$], 109.1 (CH_2), 147.0 (C).

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