Highly *threo*-Selective Pinacol Coupling of Tricarbonylchromium Complexes of Benzaldehyde with Samarium(II) Diiodide

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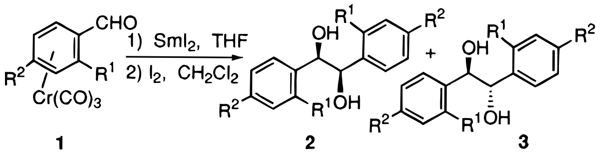
Received June 14, 1996

The intermolecular coupling of various aldehydes or ketones to give high yields of the corresponding pinacols can be achieved by lanthanoid metals or low valent transition metals.[1] Although this reaction has been extensively studied, highly diastereoselective formation of 1,2-diols is not so easy under most conventional reductive coupling methods.[2] But, utilization of some modified reducing agents and/or aldehydes possessing chelating functional groups resulted in high stereoselectivity for the intermolecular pinacol coupling.[3] However, the *threo*-pinacols cannot be obtained essentially in an enantiomerically active form by this type of coupling of aldehydes or ketones, while the osmium tetroxide-mediated catalytic asymmetric dihydroxylation of olefins has become one of most useful method for the preparation of enantiomerically active 1,2-diols.[4] In this communication, we wish to report that the intermolecular pinacol coupling of planar chiral tricarbonyl(benzaldehyde)chromium complexes in the presence of samarium(II) diiodide gives highly selective *threo*-pinacols in enantiomerically pure form.

Thus, reaction of tricarbonyl(benzaldehyde)chromium (**1**) with 2.5 equiv of samarium(II) diiodide[5] gave the corresponding pinacol, 1,2-diphenyl-1,2-ethanediol (**2**, **3**), as a diastereomeric mixture in a ratio of 91:9 after oxidative demetalation with I_2 (Scheme 1). The major product was assigned the *threo* configuration by comparison with an authentic sample.[6] Reaction results of the pinacol coupling of the tricarbonylchromium complexes of *o*- or *p*-substituted benzaldehydes are summarized in Table 1, and several facts are worthy of comment. In addition to the benzaldehyde complex, (*ortho*- or *para*-substituted benzaldehydes)chromium complexes afforded predominantly the corresponding *threo*-pinacols. Slightly reduced *threo* selectivities were observed in the case of benzaldehyde chromium complexes substituted with heteroatoms at the *ortho* position. In striking contrast to the *threo* selectivity for these complexes, the *o*-bromobenzaldehyde chromium complex gave the corresponding *erythro*-pinacol as the major product without reductive removal of the bromine atom (entries 10, 11). Interestingly, the homo-coupling of (benzaldehyde)$Cr(CO)_3$ complexes in the presence of 5 equiv of HMPA resulted in reversed *erythro* predominance (entries 5, 7). These results show that the *threo* coupling products can be predominantly obtained by simple chromium complexation of benzaldehydes except for the *o*-bromobenzaldehyde, and addition of HMPA to the reaction media changed the predominance to *erythro*.

Scheme 1



In order to clarify the reaction mechanism of the pinacol coupling of tricarbonylchromium-complexed benzaldehydes, the relative stereochemistry of both *threo*- and *erythro*-tricarbonylchromium-complexed pinacols derived from racemic (*o*-brombenzaldehyde)$Cr(CO)_3$ was investigated. Tricarbonylchromium complexes of both *threo*- and *erythro*-pinacols could possibly exist as three stereoisomers based on two-plane chirality and two stereogenic centers, respectively. In practice, however, either *threo*- or *erythro*-pinacol was derived from racemic (*o*-brombenzaldehyde)$Cr(CO)_3$ as a single compound, respectively (Scheme 2). The relative stereochemistry of both compounds was finally confirmed by X-ray crystallography.[7] The *threo*-pinacol **5** has a $1(S^*),\alpha(S^*),\alpha'(S^*),1'(S^*)$-configuration, while the stereochemistry of *erythro*-pinacol **6** was found to be the $1(R^*),\alpha(R^*),\alpha'(S^*),1'(S^*)$-configuration. These stereochemical results indicate that each benzylic stereogenic center of either stereoisomeric coupling product has the same configuration as its adjacent planar chirality, respectively. In other words, the *threo*-pinacol **5** was obtained by homocoupling of the same planar chiral (*o*-bromobenzaldehyde)$Cr(CO)_3$, while the *erythro*-pinacol **6** was formed by the heterocoupling of different planar chiral (η^6-arene)chromium complexes.

These stereochemical results of chromium-complexed pinacols predict that an enantiomerically pure (*o*-substituted benzaldehyde)$Cr(CO)_3$ could produce only *threo*-pinacols as a single product, irrespective of the nature of the *ortho* substituent. Indeed, enantiomerically pure (*S*)-(+)-(*o*-bromobenzaldehyde)$Cr(CO)_3$ (**7**)[8] and (*R*)-(−)-(*o*-methylbenzaldehyde)$Cr(CO)_3$ (**9**)[8,9] were treated with samarium(II) diiodide to give the corresponding *threo*-

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[7] The authors have deposited atomic coordinates for the structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1Ez, UK.

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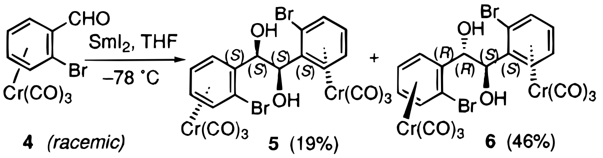
S0022-3263(96)01121-8 CCC: $12.00

Table 1. Pinacol Coupling of (Benzaldehyde)Cr(CO)$_3$ Complexes with SmI$_2$

entry	substrate **1**	temp (°C)	additive	yields (%) (coupling, demetalation)	ratio (**2**:**3**)
1	$R^1 = R^2 = H$	−78	none	78, 92	91:9
2	$R^1 = R^2 = H$	0	none	78, 92	90:10
3	$R^1 = Me, R^2 = H$	−78	none	85, 91	95:5
4	$R^1 = Me, R^2 = H$	0	none	83, 91	95:5
5	$R^1 = Me, R^2 = H$	0	HMPA	80, 85	20:80
6	$R^1 = OMe, R^2 = H$	0	none	81, 91	80:20
7	$R^1 = OMe, R^2 = H$	0	HMPA	81, 89	8:92
8	$R^1 = OPr\textit{i}, R^2 = H$	rt	none	79, 90	79:21
9	$R^1 = NMe_2, R^2 = H$	−78	none	74, 92	73:27
10	$R^1 = Br, R^2 = H$	rt	none	84, 89	16:84
11	$R^1 = Br, R^2 = H$	0	none	85, 89	34:66
12	$R^1 = H, R^2 = Br$	−78	none	75, 82	71:29
13	$R^1 = H, R^2 = Me$	0	none	78, 93	98:2
14	$R^1 = H, R^2 = OMe$	0	none	73, 91	91:9

Scheme 2. Pinacol Coupling of Racemic 4



pinacol complexes **8** and **10** in 75% and 71% yields, respectively, without formation of the *erythro* isomer (Scheme 3).

The stereoselectivity the pinacol coupling reactions of (benzaldehyde)tricarbonylchromium complexes is proposed to occur as follows (Figure 1). The carbonyl oxygen of chromium-complexed *ortho*-substituted benzaldehydes possessing the electron-donating substituents tends to be *anti* to the *ortho* substituents (**11**) in both solid and solution states due to the stereoelectronic effect.[10] An *exo*-attack of samarium onto the carbonyl would give the ketyl radical **12**, which possesses substantial exocyclic double bond character (**14**) owing to an interaction of the d-orbital on the chromium with the p-orbital of the benzylic carbon. This, in turn, implies that rotation about the $C_\alpha-C_{ipso}$ bond, giving **13**, will be restricted. The generated chromium-stabilized ketyl intermediate **12** is coupled with another (benzaldehyde)Cr(CO)$_3$ from the opposite side of the tricarbonylchromium fragment, for which both tricarbonylchromium-complexed arene rings are located in an *anti*-orientation to each other due to a dipole−dipole repulsion. Similar dipole−dipole interaction has been proposed in highly enantioselective reactions of metalcarbonyl-coordinated substrates.[11] Taking into account the Newman model, the two arenes couple via an intramolecular coordination (**15**) of the samarium with the carbonyl oxygen, giving the *threo*-pinacol. In the case of the chromium complexes possessing hetero atoms at the *ortho* position, both coordination transition states (**15** and **16)** would be competitive, giving coupling products in varying ratios. The presence of HMPA, however, precludes such coordination in the transition state. Therefore, it seems reasonable to assume that the

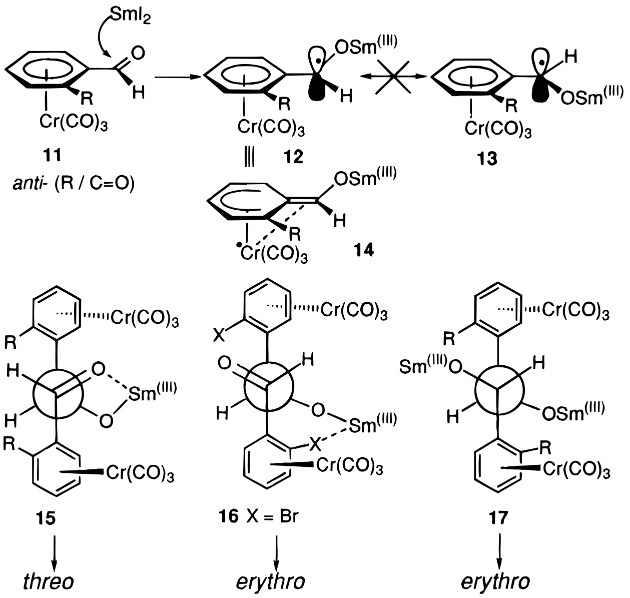
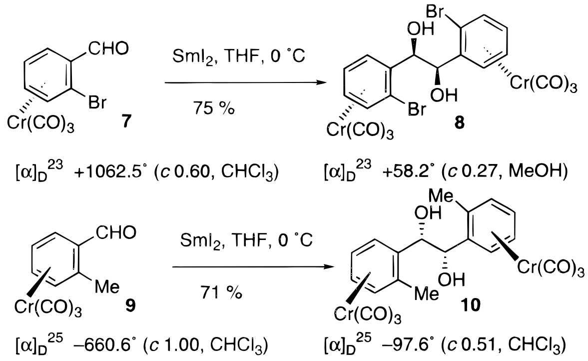


Figure 1. Proposed transition states.

Scheme 3. Pinacol Coupling of Enantiomerically Pure (Arene)Cr(CO)$_3$



erythro-pinacols are formed by bimolecular coupling of the generated radical **12** via the transition state **17** with minimized stereoelectronic conformation. This is the first example of reaction of tricarbonylchromium-stabilized benzylic radicals without stereochemical isomerization at the benzylic position, although the chromium stabilized benzylic carbocation[12] and carbanion[13] intermediates are known to be configurationally stable.

Acknowledgment. Partial financial support of this work was provided by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

Supporting Information Available: Experimental procedures and spectroscopic data for compounds **2**, **5**, **6**, **8**, and **10** (5 pages).

JO961121D

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