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On the Oxazaborolidine-Catalyzed Borane Reduction of 1-Tetralone-$Cr(CO)_3$ Complexes: The Control of the Reagent over a Strong Substrate

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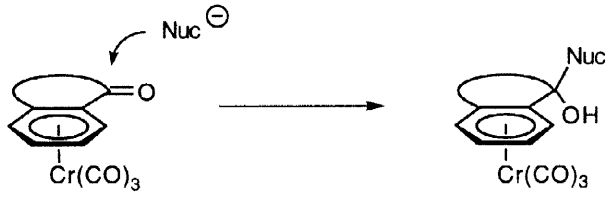
Abstract: The oxazaborolidine-catalyzed enantioselective borane reduction (CBS reduction) of 1-tetralone-$Cr(CO)_3$ derivatives was investigated. The kinetic resolution of the racemic substrates was possible but the enantiomeric purity of the recovered ketone was only 40-48%*e.e.* (at 50-56% conversion). On complete conversion, a ca. 52:48-mixture of the *endo*- and *exo*-tetralol complexes was obtained (80-99 %*e.e.*). It was shown that each substrate enantiomer gives selectively rise to a particular diastereomer (reagent control). The formation of the *endo*-isomer involves an unprecedented hydride transfer from the complexed face of the ligand and was exploited for the (diastereoselective) preparation of enantiomerically pure *exo*-6,7-dimethoxytetralol-$Cr(CO)_3$.

Planar chiral η^6-arene-$Cr(CO)_3$ complexes[1] enjoy an increasing recognition, especially as building blocks for the stereoselective synthesis of complex molecules[2] and as ligands for enantioselective catalysis.[3] Besides the chemical activation of the arene ligand, it is above all the stereodirecting effect of the metal unit which establishes the value of these compounds.[4] Thus, transformations of the complexed arene ligands proceed notoriously *substrate controlled*[5] – in many cases with virtually complete diastereoselectivity. As an example, the addition of nucleophiles to benzocycloalkenone-$Cr(CO)_3$ complexes of type **1** gives rise to products of type **2** (Scheme 1) because the nucleophile attacks the prochiral carbonyl center always from the unhindered face.[6]



1 **2**

Scheme 1: Diastereoselective nucleophilic addition to benzocycloalkenone-$Cr(CO)_3$ derivatives as an example for a substrate controlled reaction.

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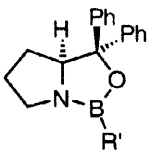
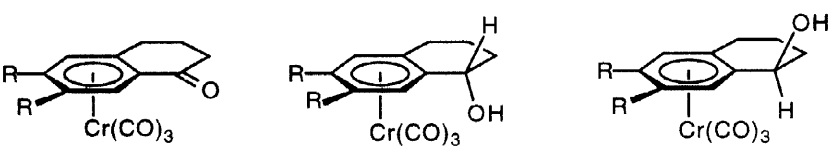
As a powerful method, which is capable to effectively differentiate the π-faces of prochiral carbonyl compounds under *reagent control*, the borane reduction catalyzed by chiral oxazaborolidines such as **3** (Itsuno-Corey reduction, sometimes also called CBS reduction)[7] has found broad application in enantioselective synthesis in recent years. However, in contrast to other catalytic-enantioselective methods (e.g. the Sharpless epoxidation[8]) the Itsuno-Corey reduction has, to our best knowledge, never been used for the kinetic resolution of racemic substrates.



3a (R' = Me)
3b (R' = Ph)

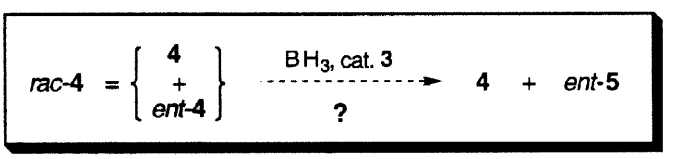
In connection with our interest in non-racemic 1-tetralone-$Cr(CO)_3$ complexes of type **4**[9,2b] and having in mind that reductions of such compounds with hydride reagents[6] are known to afford exclusively *endo*-products of type **5** (and no *exo*-isomers **6**), we asked ourselves if the Itsuno-Corey reduction could eventually be used for (non-enzymatic)[10] kinetic resolutions of complexes of type *rac*-**4** (Scheme 2).



4a (R = H)
4b (R = OMe)

5a (R = H)
5b (R = OMe)

6a (R = H)
6b (R = OMe)



Scheme 2: Concept for the kinetic resolution of 1-tetralone-$Cr(CO)_3$ derivatives by enantioselective oxazaborolidine-catalyzed borane reduction.

Applying the reliable stereochemical model for the Itsuno-Corey reduction[11], one would predict that in the presence of catalyst **3** only one enantiomer of the substrate (*ent*-**4**)[12] should react smoothly, because only in this case substrate control (SC) and reagent control (RC) would point into the same direction (→ *ent*-**5**) as shown in figure 1A ("matched case"[13]). With the enantiomeric substrate (**4**), a "mismatched" situation would arise (figure 1B and 1C) leading either (under SC and against unfavorable steric interactions between substrate and catalyst) to the *endo*-configurated complex **5** or, alternatively (under RC and through attack of the hydride from the complexed face of the ligand), to the *exo*-configurated product **6**. The formation of *ent*-**6**, however, would be very unlikely, as a particularly unfavorable arrangement of the reaction partners in the transition state would be necessary (figure 1D).

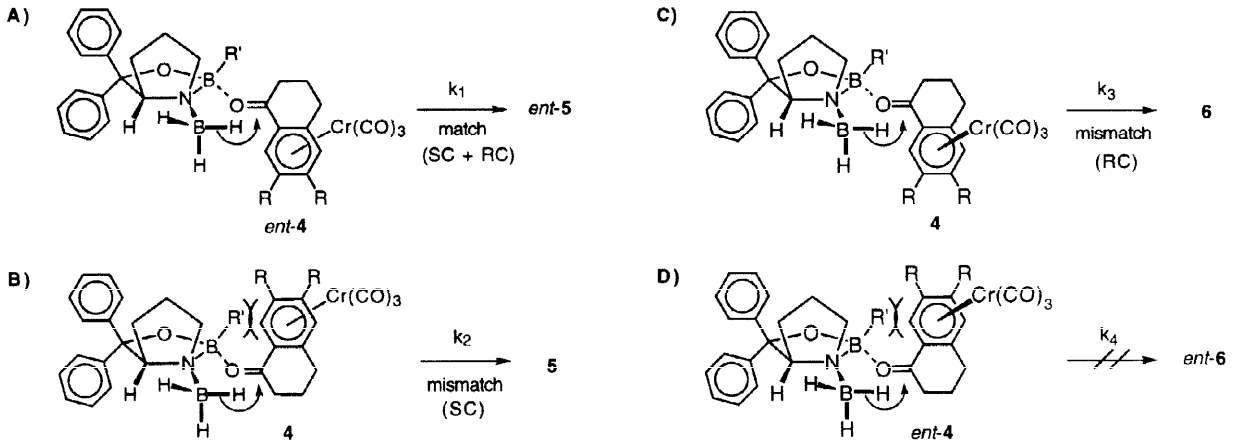


Figure 1

In order to investigate the projected kinetic resolution (Scheme 2), a first series of experiments was carried out employing *rac*-**4a** as substrate and **3a** as catalyst (see experimental part). By limiting the amount of borane, the conversion of the rather fast reactions was kept at about 50%. After ^{1}H NMR spectroscopic analysis of its composition the crude product (which was usually obtained in more or less quantitative yield) was chromatographically separated and the enantiomeric purity of the components was determined by HPLC using a chiral column.[14] The absolute configuration of the products was confirmed by comparison of the molecular rotations of selected samples with literature data.[9a] The results of these experiments are summarized in Table 1. It was remarkable that the product mixtures always contained significant amounts of the *exo*-diastereomer **6a** (10-14%), besides the unchanged ketone **4a** (44-54%) and the expected *endo*-product *ent*-**5a** (36-42%). While the enantiomeric excess of the reisolated ketone **4a** was rather low (33-48 %*e.e.*; depending on the conversion[8a,15,16]), the *endo*-product (*ent*-**5a**) was obtained with up to 91 %*e.e.* and the *exo*-product (**6a**) in all cases with ≥ 98 %*e.e.*.

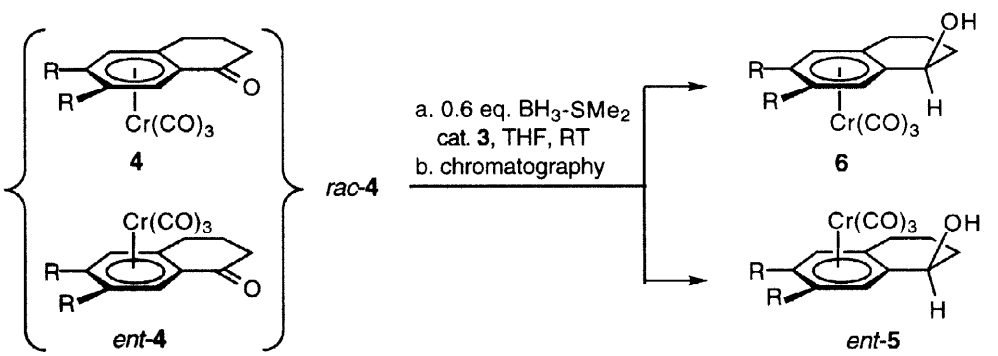
Table 1: Results of the kinetic resolution experiments of *rac*-**4a** according to Scheme 2[a)]

entry	eq. **3a**	conversion	composition of the product mixture [b)]		
1	0.3	46%	**4a** (54%; 33 %*e.e.*)	*ent*-**5a** (36%; 91 %*e.e.*)	**6a** (10%; 98 %*e.e.*)
2	0.3	56%	**4a** (44%; 48 %*e.e.*)	*ent*-**5a** (42%; 87 %*e.e.*)	**6a** (14%; 99 %*e.e.*)
3	0.2	51%	**4a** (49%; 40 %*e.e.*)	*ent*-**5a** (41%; 81 %*e.e.*)	**6a** (10%; 99 %*e.e.*)
4	0.1	53%	**4a** (47%; 47 %*e.e.*)	*ent*-**5a** (42%; 74 %*e.e.*)	**6a** (11%; 99 %*e.e.*)
5	0	100%[c)]	---	*rac*-**5a** (91%)	*rac*-**6a** (9%)
6	0	100%[d)]	---	*rac*-**5a** (100%)	---

a) All reactions were performed in THF at RT using 0.3 eq. of BH_3-SMe_2; b) the relative yields were determined by ^{1}H NMR analysis of the crude product mixture; the *e.e.*-values of the components were determined by HPLC after chromatographic separation[14]; c) in this case, *rac*-**4a** was stirred for 7 h with 0.7 eq. of BH_3-SMe_2 in THF at RT in the absence of catalyst; d) in this case, *rac*-**4a** was stirred for 0.5 h with 0.7 eq. BH_3-SMe_2 and a catalytic amount of $NaBH_4$ (5 mol%) in THF at RT.

The interpretation of these results is easily possible based on the analysis presented above (Figure 1). Obviously, the reaction path leading from *ent*-**4a** to *ent*-**5a** (k_1) is the fastest one, but surprisingly, the reagent controlled conversion of **4a** to **6a** (k_3) also takes place to a considerable degree. On the other hand, k_2 plays only a minor role and k_4 must be (as predicted) very small as it is indicated by the very high optical purity of the *exo*-product **6a**.

In a second set of experiments we addressed the question, what will happen when the reactions are allowed to reach complete conversion. Thus, *rac*-**4a** was subjected to the same reaction conditions as before except that the double amount of borane was used (Scheme 3). As shown in Table 2 (entry 1) the reduction of *rac*-**4a** in the presence of **3a** (0.3 eq.) as catalyst afforded a product mixture containing comparable amounts of two diastereomeric alcohols (51% of *ent*-**5a** and 49% of **6a**) which could very easily be separated by flash chromatography. The enantiomeric purity of the *endo*-product (*ent*-**5a**) was 93 % *e.e.* and that of the *exo*-product (**6a**) ≥99 %*e.e.*. This indicates that both substrate enantiomers (**4a** and *ent*-**4a**) were highly selectively converted to different diastereomers (reagent control). As Table 2 further demonstrates, the amount of catalyst could be reduced to 0.1 eq without significant loss of selectivity. With the B-phenyl substituted catalyst (**3b**) lower selectivities were observed. The synthetic relevant substrate *rac*-**4b**[9b] was also reduced in remarkable enantiomeric excess.



Scheme 3: Reagent controlled, enantioselective reduction of complexes of type *rac*-**4** (compare Table 2).

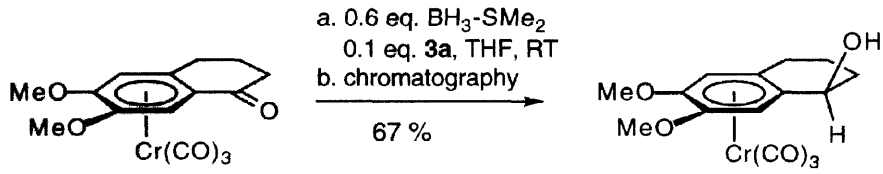
Table 2: Results of the enantioselective reduction experiments according to Scheme 3[a)]

entry	substrate	catalyst (eq.)	composition of the product mixture [b)]	
1	*rac*-**4a**	**3a** (0.3)	*ent*-**5a** (51%; 93 %*e.e.*)	**6a** (49%; 99 %*e.e.*)
2	*rac*-**4a**	**3a** (0.1)	*ent*-**5a** (53%; 89 %*e.e.*)	**6a** (47%; 99 %*e.e.*)
3	*rac*-**4a**	**3b** (0.3)	*ent*-**5a** (56%; 75 %*e.e.*)	**6a** (44%; 98 %*e.e.*)
4	*rac*-**4b**	**3a** (0.1)	*ent*-**5b** (55%; 79 %*e.e.*)	**6b** (45%; 99 %*e.e.*)
5	*rac*-**4b**	*ent*-**3a** (0.1)	**5b** (56%; 81 %*e.e.*)	*ent*-**6b** (44%; 99 %*e.e.*)

a) All reactions were performed in THF at RT using 0.6 eq. of BH_3-SMe_2; b) the relative yields were determined by ^1H NMR analysis of the crude product mixture; the *e.e.*-values of the components were determined by HPLC after chromatographic separation.[14]

The unexpected facility of the formation of the *exo*-complexes **6** (k_3) diminishes the value of the kinetic resolution approach for the preparation of optical active **4**. This compound is better accessible via diastereoselective complexation of the temporarily chirally modified ligand.[9a] On the other hand, the formation of **6a** deserves special attention: It represents the first case of a reagent controlled reaction overcoming the strong steric influence of the metal fragment upon nucleophilic attack to the ketone function of a benzocycloalkenone-$Cr(CO)_3$ complex.

As a demonstration for the preparative value of this reaction (which opens the first direct access to *exo*-tetralol-$Cr(CO)_3$ complexes) a sample of the optical active complex **4b** (70 %*e.e.*) was reduced under the established reaction conditions (Scheme 4). After chromatographic separation of the less polar *endo*-diastereomer the desired *exo*-diastereomer **6b** was isolated in 67% yield and high optical purity.



4b (70% *e.e.*) **6b** (99% *e.e.*)

Scheme 4

In conclusion we have demonstrated for the first time that the Itsuno-Corey reduction can be used for the non-enzymatic kinetic resolution of racemic ketones. More importantly, we have found an unprecedented case of *endo*-attack of a hydride to the carbonyl function of a benzocycloalkenone-$Cr(CO)_3$ complex (under reagent control in the "mismatched"-case). Further investigations may show if similar results can be obtained also with other classes of planar chiral ketones ("strong" substrates).

EXPERIMENTAL

General methods: Manipulations involving air sensitive compounds were carried out in anhydrous solvents in an argon atmosphere using Schlenk and syringe techniques. IR: *Nicolet* Magna FT-IR. ^1H NMR and ^{13}C NMR spectra: *Bruker* AM 270 or AM 400. Optical rotations: *Perkin-Elmer* 241 polarimeter, all measurements at 589 nm and 20 °C. HPLC: Merck-Hitachi; Preparative thin layer chromatography (PTLC): Chromatotron *Harrison Research.*

Preparation of the catalysts **3a** *and* **3b** (as BH_3 adducts):[17] A mixture of 1 mmol of diphenylprolinol, 1 mmol of methyl or phenyl boronic acid and 40 ml of toluene was heated to reflux for 24h under azeotropic removal of water (4 Å MS). After removal of the toluene in vacuo the resulting oxazaborolidine (**3a** or **3b**, respectively) was dissolved in 9 ml of dry THF. Addition of 1 ml of a 1M solution of BH_3-Me_2S in THF and stirring for 1h gave a 0.1M solution of **3**-BH_3 in THF which was used in the following experiments.

*Kinetic resolution of rac-***4a** *(typical procedure for Table 1)*: 4.35 ml (0.435 mmol) of a 0.1M solution of **3a**-BH_3 was diluted with 1.65 ml of THF and 423 mg (1.5 mmol) of *rac*-**4a**[9a] in 5 ml of THF were added all at once under stirring at room temperature. After 30 min 1 ml of methanol was added and stirring was continued for 15 min before the solvents were removed under reduced pressure. The crude product mixture was analyzed by ^1H NMR (see Table 1) before it was separated by PTLC (hexane/CH_2Cl_2/EtOAc = 10+10+2) to give pure samples of **4a** (48 *%e.e.*), *ent*-**5a** (87 *%e.e.*) and **6a** (99 *%e.e.*). The enantiomeric purity was determined in all cases by HPLC (conditions given below).

(4aS)-Tricarbonyl-[η^6*-3,4-dihydro-1(2H)-naphthalinone]-chromium(0)* (**4a**). IR: (ATR) $\tilde{\nu}$ = 1964s, 1881s, 1684s, 1524m; ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.04-2.25 (m, 2H), 2.45 (ddd, 1H, J = 6.5/11/17 Hz), 2.73 (ψt, 1H, J = 4 Hz), 2.77 (ψt, 1H, J = 4.3 Hz), 2.98 (ddd, 1H, J = 6/10/16 Hz), 5.15 (d, 1H, J = 6.4 Hz), 5.27 (ψdt, 1H, J = 1/6.5 Hz), 5.62 (ψdt, 1H, J = 1/6.5 Hz), 6.16 (dd, 1H, J = 7 Hz); HRMS calcd. for $C_{13}H_{10}CrO_4$: 281.9984; found: 282.0001; HPLC for *rac*-**4a** (hexane/2-propanol = 70+30, 0.8 ml/min, 256 nm): R_t(S) = 23.7 min, R_t(R) = 26.5 min.

(1R)-endo-Tricarbonyl-[η^6*-1,2,3,4-tetrahydro-1-naphthol]-chromium(0)* (*ent*-**5a**). mp.: 129°C; [α] = -13 (c = 0.7 in $CHCl_3$); IR: (ATR) $\tilde{\nu}$ = 1946s, 1870s, 1857s; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.59 (d, 1H, J = 10 Hz), 1.71 (m, 2H), 1.98 and 2.10 (m, 2H), 2.60 and 2.75 (m, 2H), 4.51 (m, 1H), 5.08 (d, 1H, J = 6.5 Hz), 5.13 (dt, 1H, J = 1/6.4 Hz), 5.51 (dt, 1H, J = 0.9/6.3 Hz), 5.83 (d, 1H, J = 6.4 Hz); HRMS calcd. for $C_{13}H_{12}CrO_4$: 284.0140; found: 284.0142; For the determination of the enantiomeric excess by HPLC, *ent*-**5a** was oxidized to *ent*-**4a** using the DMSO/Ac_2O reagent as described before.[9a,18]

(1R)-exo-Tricarbonyl-[η^6*-1,2,3,4-tetrahydro-1-naphthol]-chromium(0)* (**6a**): mp.: 63°C; [α] = -110 (c = 0.22); IR: (ATR) $\tilde{\nu}$ = 1956s, 1868s; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.73 (m, 2H), 2.05 (m, 3H), 2.65 (m, 2H), 4.64 (m, 1H), 5.19 (d, 1H, J = 6.3 Hz), 5.26 (ψt, 1H, J = 6.1 Hz), 5.35 (ψt, 1H, J = 6.1 Hz), 5.69 (d, 1H, J = 6.6 Hz); HRMS calcd. for $C_{13}H_{12}CrO_4$: 284.0140; found: 284.0141; HPLC for *rac*-**6a** (hexane/2-propanol = 80+20, 0.8ml/min, 256 nm): R_t(S) = 27.0 min, R_t(R) = 29.7 min.

*Enantioselective reduction of rac-***4b** *(typical procedure for Table 2)*: 0.70 ml (0.07 mmol) of a 0.1M solution of **3a**-BH_3 was diluted with 1 ml of THF and 240 mg (0.7 mmol) of *rac*-**4b**[9a] in 5 ml of THF were added all at once under stirring at room temperature. After 45 min, 1 ml of methanol was added and stirring was continued for 15 min before the solvents were removed under reduced pressure. The crude product mixture was analyzed by ^1H NMR (see Table 2) before it was separated by PTLC (hexane/CH_2Cl_2/EtOAc = 10+10+2) to give pure samples of *ent*-**5b** (79 *%e.e.*) and **6b** (99 *%e.e.*). The enantiomeric purity was determined by HPLC (conditions given below).

(1R)-endo-Tricarbonyl-[η^6*-6,7-dimethoxy-1,2,3,4-tetrahydro-1-naphthol]-chromium(0)* (*ent*-**5b**): mp.: 142°C (decomp.); [α] = -4.3 (c = 0.25); IR: (ATR) $\tilde{\nu}$ = 1944 s, 1852s, 1548w; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.60 (m, 2H), 1.70 (d, 1H, J = 10.5 Hz), 1.93 and 2.06 (m, 2H), 2.54 and 2.72 (m, 2H), 3.78 and 3.84 (s, 6 H), 4.45 (m, 1H), 5.07 (s, 1H), 5.79 (s, 1H); HRMS calcd. for $C_{15}H_{16}CrO_6$: 344.0352; found: 344.0356; For the determination of the enantiomeric excess by HPLC, *ent*-**5b** was oxidized to *ent*-**4b** using the DMSO/Ac_2O reagent as described before.[9a,18] HPLC for *ent*-**4b** (hexane/2-propanol = 70+30,

0.8ml/min, 256 nm): $R_t(R)$ = 45 min, $R_t(S)$ = 57 min.

(1R)-exo-Tricarbonyl-[η^6-6,7-dimethoxy-1,2,3,4-tetrahydro-1-naphthol]-chromium(0) (**6b**): mp.: 106°C (decomp.); [α] = -93 (c = 0.31); IR: (ATR) $\tilde{\nu}$ = 1948s, 1859s; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.64 (m, 2H), 1.88 (m, 1H), 1.90 (d, 1H, J = 6.3 Hz), 2.09 (m, 1H), 2.61 (m, 2H), 3.79 and 3.80 (s, 6H), 4.64 (m, 1H), 5.12 (s, 1H), 5.63 (s, 1H); HRMS calcd. for $C_{15}H_{16}CrO_6$: 344.0352; found: 344.0354; HPLC for *ent*-**6b** (hexane/2-propanol = 70+30, 0.8ml/min, 256 nm): $R_t(S)$ = 50 min, $R_t(R)$ = 58 min.

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14. The enantiomeric excess was determined on a Chiracel OJ-column (*Daicel*). The separation conditions were always tested by the use of racemic mixtures (see experimental). For the analysis of the *endo*-tetralol complexes (**5**/*ent*-**5**) these alcohols were first oxidized to the ketone complexes (**4**/*ent*-**4**)[9a,18].
15. For the dependency of the enantiomeric excess on the conversion in kinetic resolutions, see, for example: Eliel, E.L.; Wilen, S.H. *Stereochemistry of Organic Compounds*, Wiley, New York **1994**, pp. 395.
16. In one experiment *rac*-**4a** was reduced using 0.4 eq BH_3 in the presence of 0.3 eq **3a** (73% conversion). In this case, the re-isolated ketone complex (**4a**) had an enantiomeric purity of 98% *e.e.*.
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