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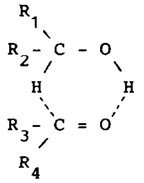
Diastereoselective Hydrogen Transfer from Alcohols to Ketones over Liquid Indium

Hydrogen transfer reactions between alcohols and ketones over liquid indium catalysts have been extensively studied by Miyamoto (*1*). Through deuterium isotope experiments and molecular orbital calculations, he proposed a six-membered ring transition state model for the reaction (*1*, *2*):



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It has been inferred that the six-membered ring sits flat on the liquid indium surface (*1*–*3*). The differences between the hydrogen transfer mechanisms over metal oxide catalysts (*4*) and over liquid indium catalyst have been discussed (*2*). A cyclic configuration such as **1** is likely to provoke steric hindrance among some of the alkyl groups R_1 through R_4, when one or more of them are sufficiently bulky. Such a stereochemical effect has been observed in alkoxide-catalyzed Meerwein–Ponndorf–Verley reactions (*5*) as well as in the liquid indium-catalyzed hydrogen transfer from various alcohols to ketones (*1*, *2*) including enantiomer-differentiating hydrogen transfer from several alcohols to menthone (*3*, *6*). The present work extends the examination of the stereochemical hydrogen transfer reactions over liquid indium catalysts further to diastereo-differentiating reactions.

Gas-phase reaction experiments were performed at atmospheric pressure using a flow reactor previously reported (*6*). Catalyst preparation also followed a previous description (*7*). Reagents employed were commercially obtained and were used as received. The partial pressures of the reactants were fixed at 0.018 atm for alcohol, 0.027 atm for ketone, and 0.345 atm for the solvent cumene, the balance being the carrier gas, helium. Total flow rate was fixed at 0.148 mol/h. Reaction temperatures were varied from 723 to 793 K, although most of the data were taken at either 743 or 753 K. Products were analyzed by gas chromatography using a stainless-steel capillary column (Ucon oil, 0.25 mm × 45 m) and a flame ionization detector.

Prior to the examination of asymmetric reactions, the molecular size effect in the alcohol-to-ketone hydrogen transfer was examined. For this purpose (−)-menthol was used as a hydrogen donor and ketones of various molecular sizes as hydrogen acceptors. Figure 1 plots the conversion of each ketone to the corresponding alcohol against the molar volume of the starting ketone at 293 K, calculated by using Kopp's method. The monotonous decrease of the alcohol yield with the ketone molar volume is understood by supposing the transition state model, **1**. Namely, changing the alkyl group R_3 and/or R_4 in the formula means that the facileness of the transition state formation is varied: the bulkier the R_3 and/or R_4 groups are, the more severe the steric hindrance in the transition state becomes, resulting in the higher potential barrier for its formation. This would give lower conversion for bulkier ketones, in accordance with the results found in Fig. 1.

The possibility of the diastereoface differentiation over liquid indium catalysts was

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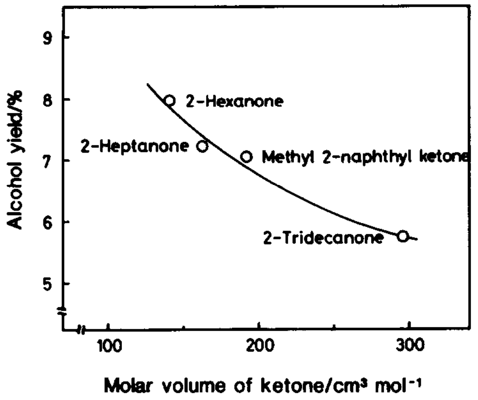

FIG. 1. Molecular volume dependency of hydrogen transfer from (−)-menthol to various ketones over liquid indium at 753 K.

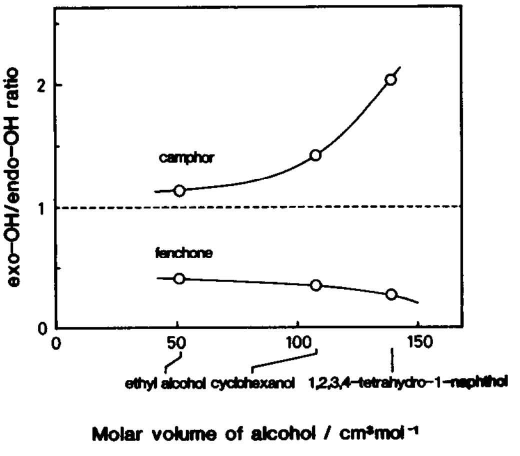

FIG. 2. Diastereoface differentiation in the hydrogen transfer from various alcohols to camphor or fenchone over liquid indium at 753 K.

TABLE 1

Comparison of the Camphor Yield from Borneol and from Isoborneol in Dehydrogenation or in Hydrogen Transfer over Liquid Indium at 743 K

	Dehydrogenation (%)	Hydrogen transfer to ethyl methyl ketone (%)
Borneol	29.3	55.6
Isoborneol	16.0	27.5

examined for hydrogen transfer reactions from alcohols of different molecular sizes, viz., ethyl alcohol, cyclohexanol, and 1, 2, 3, 4-tetrahydro-1-naphthol, to two ketones, camphor and fenchone. These two ketones were chosen because the face selectivity for the carbonyl group hydrogenation is expected to be opposite to each other when one assumes the formation of the transition state **1**. In the case of camphor the Cram rule dictates that the hydrogen transfer from endo-side (si-face) is preferred to that from the exo-side (re-face) due to the large steric hindrance on the exo-side. This would favor the production of isoborneol (exo-OH) over that of borneol (endo-OH). In the case of fenchone, in contrast, its exo-side (si-face) would be less crowded for the formation of the transition state than its endo-side (re-face): thus the production of β-fenchol (endo-OH) would be preferred to the production of α-fenchol (exo-OH).

These expectations are apparently met, as is obvious in Fig. 2. For the camphor–alcôhol system the product isoborneol/borneol ratio (exo-OH/endo-OH) is larger than unity for all the three alcohols examined. For the fenchone–alcohol system the α-fenchol/β-fenchol (exo-OH/endo-OH) ratio is less than unity, indicating face selectivity opposite to that in the case of camphor. In both cases, it is shown in the figure that the deviations of the exo-OH/endo-OH ratios from unity become larger with increasing molar volume of donor alcohol, calculated using Kopp's method for 293 K, in accordance with the higher potential barrier expected for bulkier reagents to form the transition state **1**.

Finally, the kinetic differences between two diastereomers, borneol and isoborneol, in dehydrogenation and in hydrogen transfer over liquid indium were examined. Table 1 lists the camphor yield by dehydrogenation and by hydrogen transfer to ethyl methyl ketone over liquid indium at 743 K. In either reaction, borneol, with endo-OH, is more quickly converted to camphor than isoborneol, which has exo-OH. In the case of hydrogen transfer this is easily understood by taking into account the facileness of the transition state formation. For dehydrogenation one may consider the transition state similar to **1**, except that in this case it consists of a four-membered ring without the C=O group (*8*).

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