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SELECTIVE CLEAVAGE OF BENZYL ESTER BY TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE CATALYST

Hiroshi SUGIYAMA,* Shinji TSUCHIYA, and Shuichi SETO
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai
Yasuhisa SENDA, and Shin IMAIZUMI
Department of Applied Science, Tohoku University, Sendai, JAPAN

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The studies of homogeneous hydrogenation catalyst have been developed very much,[1] but those are almost limited to the reduction of unsaturated carbon-carbon bonds and the other kinds are very few.[2] We have examined the reductive cleavage of benzyl ester with Et_3SiH and $(Ph_3P)_3RhCl$ catalyst and have found that this reaction has the selectivity due to the functional group participation. The studies of the selective reduction due to the functional group participation are also very few.[3]

Refluxing of amino acid benzyl esters with the Rh complex in Et_3SiH for 3 hr under N_2 atomosphere and then in methanol for 1 hr gave corresponding amino acids as in the Table. However, the ammonium salt of alanine benzyl ester or N-benzoylglycine benzyl ester could not be cleaved. As a result, it can be concluded that the amino group of amino acids plays an important role in this reaction. Hence, it is interesting to replace an amino group to phenolic or alcoholic hydroxyl groups. Benzyl o-hydroxybenzoate and benzyl lactate were cleaved, but the yield of lactic acid was relatively low. In the case of benzyl p-hydroxybenzoate and of benzyl cinnamate, the cleavage reaction did not proceed under the present condition. Those facts suggest that the facility of this reaction is proportional to the chelating power of a parent acid.[4] This cleavage reaction with other metal salts and complexes is under investigation.

Table. The yield and condition of the benzyl ester cleavage.

Benzyl ester (mg)	Rh complex (mg)	Et_3SiH (ml)	Reaction time (hr)	Yield (%)
glycinate 30	5	1.5	3	quantitativ
alaninate 30	5	1.5	3	quantitativ
N-Cbz-β-asparatate 40	5	1.5	3	quantitativ
N-Cbz-β-benzylasparatyl alnine benzyl ester 30	5	1.5	12	quantitativ
p-toluenesulfonate salt of alaninate 50	5	1.5	20	0
hippurate 20	5	1.5	20	0
o-hydroxybenzoate 25	5	1.5	3	quantitativ
p-hydroxybenzoate 25	5	1.5	3	0
lactate 50	10	1.5	3	60
cinnamate 50	10	1.5	3	0

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