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THE SELECTIVE DISTINCTION OF DIETHYLISOPROPYLSILYL ETHER IN HYDROGENOLYSIS

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Summary: The diethylisopropylsilyl ether was distinguished from *t*-butyldimethysilyl, *t*-butyldiphenylsilyl and benzyl ethers with high selectivity in hydrogenolysis by use of $Pd(OH)_2$ as a catalyst.

Selection of the suitable protecting groups sometimes becomes key problem in the synthesis of complex natural products and silyl ethers are amongst the most useful protective groups1). Recently, we have reported the some advantages of the diethylisopropylsilyl (DEIPS) group which was a novel silyl group for hydroxyl function in organic synthesis2,3). In this communication, we wish to demonstrate that DEIPS ether was highly distinguished from *t*-butyldimethysilyl (TBS)4), *t*-butyldiphenylsilyl (TBDPS)5) and benzyl ethers in hydrogenolysis using $Pd(OH)_2$ as a catalyst under neutral condition.

The benzyl ether was cleaved cleanly without deprotection of DEIPS group in hydrogenolysis in the presence of catalytic amounts of $Pd(OH)_2$6) in ***dioxane*** 3a)(entries 1 in Table 1 and 2). In contrast to this fact, DEIPS group was removed smoothly with deprotection of benzyl ether in ***MeOH*** (entries 2 in Table 1 and 2). The change of the solvent made it possible to control the high selective distinction of DEIPS ether from benzyl ether.

Our next attention was turned to the selective deprotection of DEIPS group in the presence of TBDPS and TBS groups, which were widely used silyl protecting groups, in hydrogenolysis. The results summarized as entries 3 and 4 in Table 1 and 2 showed that DEIPS group was distinguished from these protecting groups with high selectivity and deprotected in ***MeOH*** in both primary and secondary positions. Although reaction times were not constant, the selectivities of the reactions were not significantly influenced by the reaction times.

These results indicated that DEIPS group was highly distinguished from TBS, TBDPS and benyl ethers under neutral condition.

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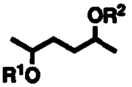
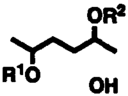
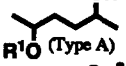
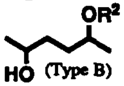
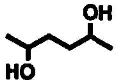
References and Notes:
1) T. W. Green, "*Protective Groups in Organic Synthesis*", John Willy and Sons, New York, 1981.
2) (a) K. Toshima, K. Tatsuta, and M. Kinoshita, *Tetrahedron Lett.*, **27**, 4741 (1986): (b) K. Toshima, K. Tatsuta, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **61**, 2369 (1988).
3) (a) K. Toshima, S. Mukaiyama, M. Kinoshita, and K. Tatsuta, *Tetrahedron Lett.*, **30**, 6413 (1989): (b) K. Toshima, M. Misawa, K. Ohta, K. Tatsuta, M. Kinoshita, *Tetrahedron Lett.*, **30**, 6417 (1989).

Table 1.[7,8]

Entries	1	2	3	4
	R^1=Bn R^2=DEIPS	R^1=Bn R^2=DEIPS	R^1=TBDPS R^2=DEIPS	R^1=TBS R^2=DEIPS
Reaction Conditions Products	***dioxane*** 26°C, 4.5h	***MeOH*** 26°C, 6h	***MeOH*** 26°C, 1h	***MeOH*** 40°C, 1h
	0%	0%	0%	0%
 (Type A)	0%	0%	99%	71%
 (Type B)	98%	0%	0%	12%
	0%	93%	0%	15%

Table 2.[7,8]

Entries	1	2	3	4
	R^1=Bn R^2=DEIPS	R^1=Bn R^2=DEIPS	R^1=TBDPS R^2=DEIPS	R^1=TBS R^2=DEIPS
Reaction Conditions Products	***dioxane*** 26°C, 3h	***MeOH*** 26°C, 3h	***MeOH*** 26°C, 1h	***MeOH*** 26°C, 1h
	0%	0%	0%	0.5%
 (Type A)	0%	0%	98%	75%
 (Type B)	96%	0%	0%	3%
	0%	91%	0%	13%

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4) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

5) S. Hanessian and P. Lavallee, *Can. J. Chem.*, **53**, 2975 (1975).

6) Purchased from Aldrich Chemical Company, Inc..

7) All new products were purified by silica gel column chromatography and were fully characterized by spectroscopic means.

8) Isolated yield after column chromatography on slica gel. The ratio of type A and type B was determined by ^{1}H-NMR analysis.

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