[Tetrahedron Lett., **36**, 3465-3468 (1995)] [Lab. of Medicinal Chemistry]

Selective Inhibition of Benzyl Ether Hydrogenolysis with Pd/C Due to the Presence of Ammonia, Pyridine or Ammonium Acetate.

HIRONAO SAJIKI

Benzyl ethers are widely used protective groups. Although a number of catalysts have been employed for the hydrogenolysis of O-benzyl ethers, the selectivity of cleavage (or resistance) in the presence of other reducible functionalities within a molecule is usually poor. In this paper, ammonia, pyridine and ammonium acetate were found to be extremely effective as inhibitors of Pd/C catalyzed benzyl ether hydrogenolysis. While olefin, Cbz, benzyl ester and azide functionalities were hydrogenated smoothly, benzyl ethers were not cleaved in the presence of these additives at ordinary pressure and temperature.

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Carbon-carbon bond formation and reduction of aldehydes, ketones and acetals with silylated nucleophiles catalysed by tetracyanoethylene.

TSUYOSHI MIURA, YUKIO MASAKI*

Tetracyanoethylene catalyses the reactions of aldehydes, ketones and acetals with silylated nucleophiles such as trimethylsilyl cyanide, allyltrimethylsilane, aryl methyl ketone trimethylsilylenol ethers and triethylsilane to promote carbon-carbon bond formation and reduction under neutral conditions. All the evidence strongly suggested that the reactions occur through single electron transfer (SET) mechanism based on UV spectroscopic measurements.

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Monothioacetalization of Acetals Catalyzed by Dicyanoketene Acetals.

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A type of capto-dative olefin, dicyanoketene acetal such as dicyanoketene dimethyl acetal and ethyleneacetal is introduced to be a novel type of π-acid catalyst for the monothioacetalization of acetals as well as the corresponding α,β-unsaturated systems. Particularly, the catalytic activity of dicyanoketene ethylene acetal was found to be superior to that of tetracyanoethylene and highly chemoselective in the crossover reaction of a ketone-, aldehyde-acetal, an alcohol THP-, and MOM-ether providing a ketone monothioacetal favorably.