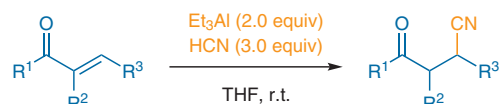


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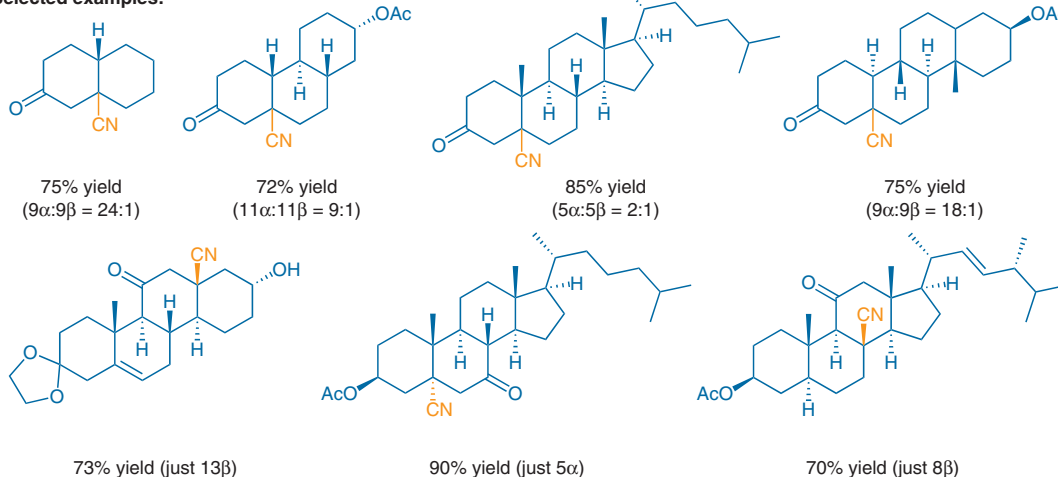
Eine neue Hydrocyanierungs-Methode

Tetrahedron Letters **1962**, *11*, 461–466, DOI: 10.1016/S0040-4039(00)70493-X.

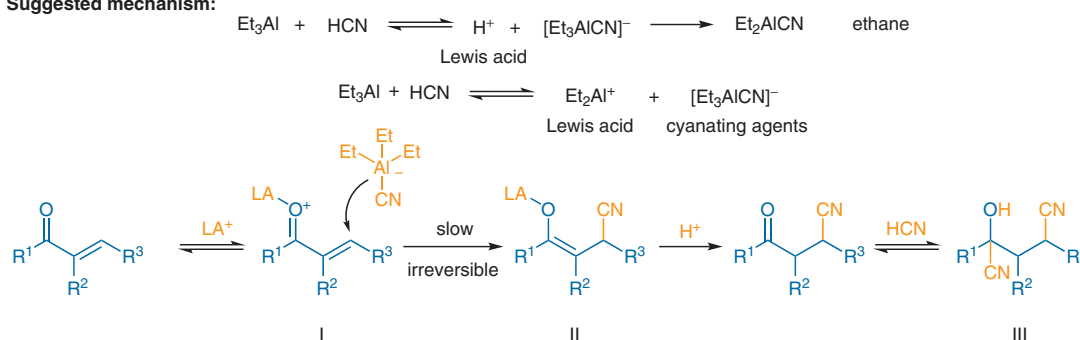
Nagata Hydrocyanation: Synthesis of β -Cyanoketones



Selected examples:



Suggested mechanism:



Significance: In 1962 Nagata et al. reported a method for the hydrocyanation of demanding α,β -unsaturated ketones for the synthesis of β -cyanoketones. This reaction employed a mixture of HCN and triethylaluminum in THF at room temperature as a new reagent that performed better than alkali cyanides (commonly used reagents at the time) in terms of yield and diastereoselectivity. This method has become known as Method A for hydrocyanation of unsaturated ketones.

Comment: Interesting mechanistic observations were made. It was suggested that polar solvent (THF) leads to a cyanotriethylaluminum, which was deemed to be the active cyanating reagent. Et_2Al^+ or a simple proton were proposed as Lewis acids. A slow and irreversible addition of cyanide ion gave II as an intermediate, which was quenched with HCN present in situ to give the expected product. Cyanohydrin III was also observed. The reaction proceeded with gas evolution and formation of diethylaluminumcyanide. This compound in inert solvent would become known as Method B and is the only commercially available reagent for Nagata hydrocyanation.

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Key words

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