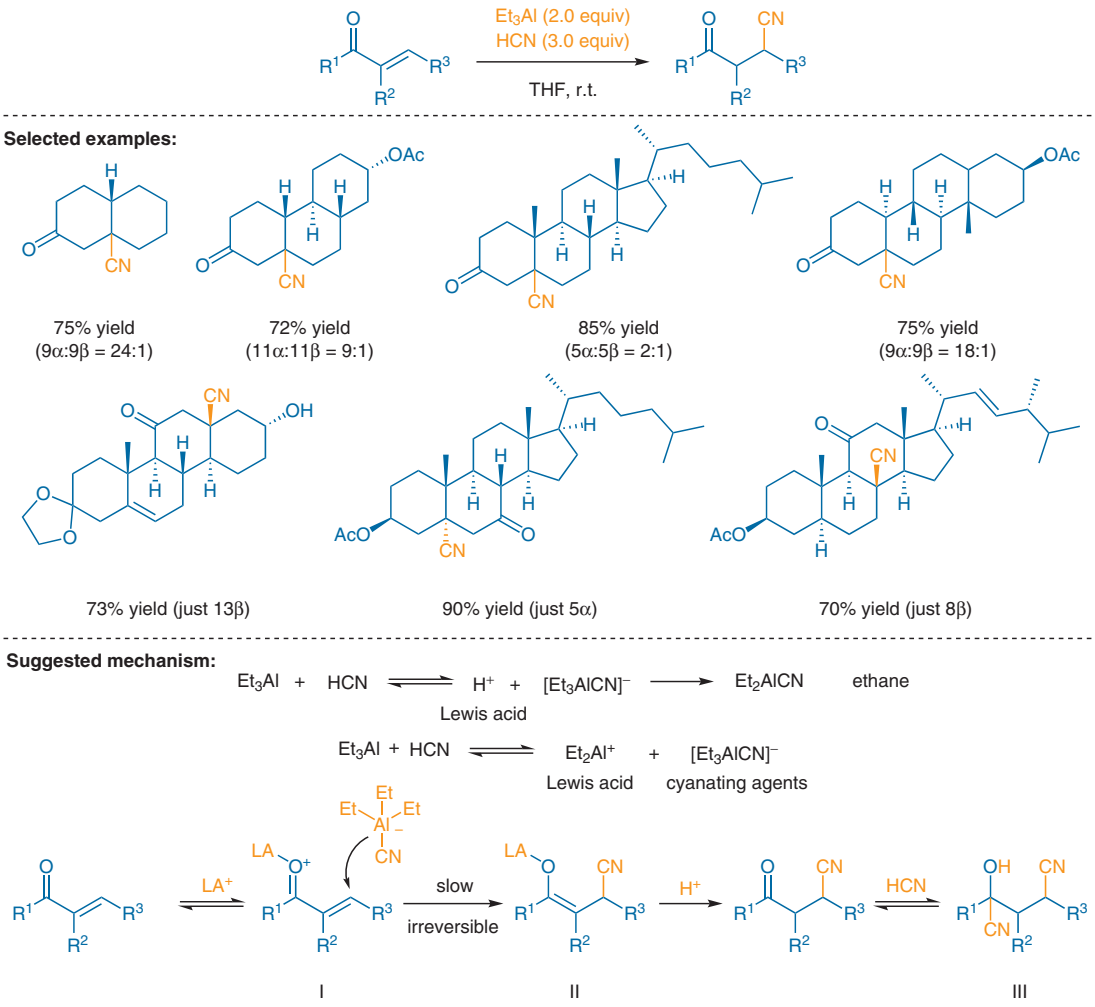
W. NAGATA, M. YOSHIOKA, S. HIRAI* (SHIONOGI RESEARCH LABORATORY, OSAKA, JAPAN)

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

Nagata Hydrocyanation: Synthesis of β-Cyanoketones



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 triethylaluminium 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 cyanotriethylaluminate, 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. Cyanohydrine **III** was also observed. The reaction proceeded with gas evolution and formation of diethylaluminiumcyanide. This compound in inert solvent would become known as Method B and is the only commercially available reagent for Nagata hydrocyanation.

SYNFACTS Contributors: Paul Knochel, Dimitrije Djukanovic
Synfacts 2021, 17(06), 0669 Published online: 18.05.2021
DOI: 10.1055/s-0040-1720514; **Reg-No.:** P05521SF

© 2021. Thieme. All rights reserved.
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.