

TRANSFER HYDROCYANATION OF α - AND α,β -SUBSTITUTED STYRENES CATALYZED BY BORON LEWIS ACIDS

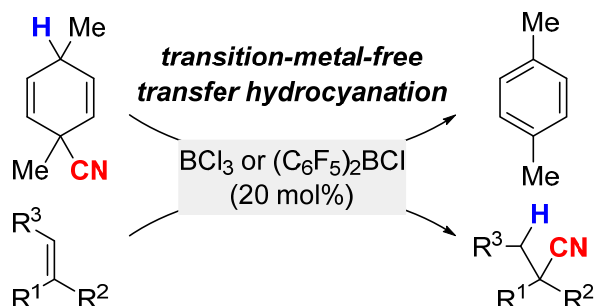
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Nitriles are synthetically versatile building blocks, which are readily converted into amines or various carbonyl compounds. While transition-metal-catalyzed hydrocyanation of alkenes using hydrogen cyanide (HCN) is widely used in industry, the same approach is less appealing in academic laboratories due to safety concerns.[1] Recently, surrogates of HCN were explored in order to overcome these issues, resulting in transition-metal-catalyzed transfer hydrocyanation processes.[2]

Our group has shown that adequately substituted cyclohexadienes undergo *irreversible* transfer processes when treated with boron Lewis acids, exploiting the rearomatization energy of these molecules.[3]

We report here a new strategy to convert alkenes into nitriles by metal-free transfer hydrocyanation using a substituted cyclohexa-1,4-diene as surrogate (see Scheme). These surrogates are bench-stable and can formally release HCN, rearomatizing in the presence of boron Lewis acids.[4] The transfer of HCN across the 1,1-di- and tri-substituted alkenes occurs with Markovnikov selectivity, affording highly substituted nitriles in good to excellent yields. Mechanistic evidence, in agreement with a cationic mechanism, will also be presented.



[1] L. Bini, C. Müller, D. Vogt, *Chem. Commun.* **2010**, 46, 8325–8334.

[2] a) A. Falk, A.-L. Göderz, H. G. Schmalz, *Angew. Chem. Int. Ed.* **2013**, 52, 1576–1580. b) X. Fang, P. Yu, B. Morandi, *Science* **2016**, 351, 832–836. c) A. Bhunia, K. Bergander, A. Studer, *J. Am. Chem. Soc.*, **2018**, 140, 16353–16359.

[3] For selected examples, see: a) M. Oestreich, *Angew. Chem. Int. Ed.* **2016**, 55, 494–499. b) I. Chatterjee, Z.-W. Qu, S. Grimme, M. Oestreich, *Angew. Chem. Int. Ed.* **2015**, 54, 12158–12162. c) S. Keess, M. Oestreich, *Chem. Eur. J.* **2017**, 23, 5925–5928. d) S. Keess, M. Oestreich, *Chem. Sci.* **2017**, 8, 4688–4695. e) W. Yuan, P. Orecchia, M. Oestreich, *Chem. Commun.* **2017**, 53, 10390–10393.

[4] P. Orecchia, W. Yuan, M. Oestreich, *Angew. Chem. Int. Ed.* **2019**, doi.org/10.1002/anie.201813853.