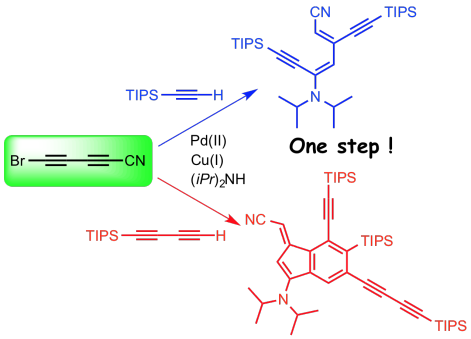
Synthesis and reactivity of bromocyanobutadiyne: from interstellar chemistry to synthetic organic methodology

YANN TROLEZ

Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7
yann.trolez@ensc-rennes.fr

Some cyanopolyynes (the formula of which is R-(C≡C)$_n$-CN with R = H or Me) have been detected in the interstellar medium (ISM)[1] and on Titan for some of them.[2,3] Our laboratory has been studying from several years these compounds by synthesizing them and studying their chemical or photochemical reactivity. However, despite the low number of atoms these compounds possess, their synthesis in laboratory still remains a scientific challenge. Thus, we have recently described a synthetic pathway for cyanopolyynes having two conjugated C≡C triple bonds (n = 2),[4,5,6] but their superior counterparts (n = 3) stay elusive so far.

To solve this problem, we synthesized the bromocyanobutadiyne (5-bromopenta-2,4-diynenitrile ; Br-C≡C-C≡C-CN) and reacted it with different terminal alkynes under Cadiot-Chodkiewicz conditions.[7] Surprisingly, the corresponding cyanopolyynes were not obtained but more complex compounds, resulting from cascade reactions, were isolated. In particular, a diene was obtained stereoselectively when using trialkylsilylacetylenes. When using triisopropylsilylbutadiyne, a functionalized benzofulvene was obtained. The characterization of these unexpected products is based on X-ray crystallography, among other usual techniques. The mechanisms of formation of these products, which were studied both experimentally and theoretically, will be discussed.



References

[1] P. Thaddeus, M. C. McCarthy, M. J. Travers, C. A. Gottlieb, W. Chen, *Faraday Discuss.* **1998**, *109*, 121-135
[2] A. Coustenis, T. Encrenaz, B. Bézard, B. Bjoraker, G. Graner, G. Dang-Nhu, E. Arié, *Icarus*, **1993**, *102*, 240-260
[3] V. Vuitton, R. V. Yelle, V. G. Anicich, *Astrophys. J.* **2006**, *647*, L175-L178
[4] Y. Trolez, J.-C. Guillemin, *Angew. Chem. Int. Ed.* **2005**, *44*, 7224-7226
[5] N. Kerisit, L. Toupet, Y. Trolez, J.-C. Guillemin, *Chem. Eur. J.* **2013**, *19,* 17683-17686
[6] N. Kerisit, C. Rouxel, S. Colombel-Rouen, L. Toupet, J.-C. Guillemin, Y. Trolez, *J. Org. Chem.* **2016**, *81*, 3560-3567
[7] N. Kerisit, L. Toupet, P. Larini, L. Perrin, J.-C. Guillemin, Y. Trolez, *Chem. Eur. J.* **2015**, *21*, 6042-6047