MECHANISTIC INVESTIGATION OF AN OXIME ETHER ELECTROCYCLIZATION

Helena Mora-Radó, Lia Sotorrió, Matthew P. Ball-Jones, Laurent Bialy, Werngard Czechtizky, María Méndez, Enrique Gómez-Bengo, and Joseph P. A. Harrity

aDepartment of Chemistry, University of Sheffield, S3 7HF, U.K.
bDepartment of Organic Chemistry I, University of the Basque Country (UPV/EHU), Donostia, 20018, Spain
cIntegrated Drug Discovery R&D, Sanofi Aventis Deutschland GmbH, Industriepark Höchst 65926 Frankfurt, Germany
dRespiratory, Inflammation, Autoimmunity IMED Biotech Unit, AstraZeneca, 431 50 Gothenburg, Sweden

A range of functionalized heteroaromatic boronic acid derivatives is readily accessed by a diboration/π-electrocyclization sequence [1]. This study revealed the surprising observation that there is a direct relationship between oxime ether stereochemistry and reactivity towards electrocyclization. Specifically, E-oxime ethers are found to be significantly more reactive than their Z-counterparts.

In contrast, the configuration at the azatriene alkene terminus has little impact on reaction rates Computational analysis offers a rationale for this observation; a \( N_{\text{lone pair}} \rightarrow \pi^* \) orbital interaction lowers the energy of the transition state in the electrocyclization of E-oxime ethers. The aromaticity of the transition state of the reaction was also studied, calculating the NICS index and performing AICD calculations [2], which lead to the classification of this reaction as pseudopericlyclic.

Figure 1. Synthesis of borylated thienopyridines.

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