Computational insights into cycloadditions of thioisomunchnones with acetylenes: how does sulfur escape from cycloadducts?

The spontaneous loss of sulfur or isocyanate from transient 7-thia-2-azabicyclo[2.2.1]hept-5-en-3-ones, which are initially formed by 1,3-dipolar cycloadditions of thioisomünchnones with acetylenic dipolarophiles, is the key step in the chemoselective syntheses of pyridin-2-ones or thiophenes. The way by which sulfur is released has been the subject of previous studies pointing to a concerted retro-cheletropic mechanism as a more favorable route than the alternative stepwise pathway. The latter however, is apparently prevalent for elimination of isocyanate. Working with a conformationally-restricted bicyclic thioisomünchnone that undergoes facile cycloaddition with acetylenes, sulfur elimination has now been interrogated by experiment and theoretical calculations at the M06-2X and M11 methods in combination with the 6-311++G(d,p) basis set, which unveil rather a sigmatropic shift via the intermediacy of thiirane species. These results provide new vistas and synthetic opportunities in mesoionic cycloadditions.

$$\begin{bmatrix} R^1 \\ O \\ N \\ R^2 \\ R^3 \end{bmatrix} \longrightarrow \begin{bmatrix} R^1 \\ O \\ N \\ R^4 \end{bmatrix}^{\ddagger} \longrightarrow \begin{bmatrix} R^1 \\ O \\ N \\ R^3 \end{bmatrix} \xrightarrow{-S_8} \begin{bmatrix} R^1 \\ O \\ N \\ R^3 \end{bmatrix}$$

Fuente de la publicación:

• Juan García de la Concepción, Martín Avalos, Reyes Babiano, Pedro Cintas, José L. Jiménez, Mark E. Light, Juan C. Palacios. (2016). <u>Tetrahedron</u> [1] 72 4665-4670. https://doi.org/10.1016/j.tet.2016.06.041 [2]

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Ligações

[1] https://www.journals.elsevier.com/tetrahedron [2] https://doi.org/10.1016/j.tet.2016.06.041