Tetrahedron Letters 45 (2004) 2051–2052

Tetrahedron Letters

Comments on ‘Unusual oxidative rearrangement of 1,5-diazadecalin’

Tammo Winkler*

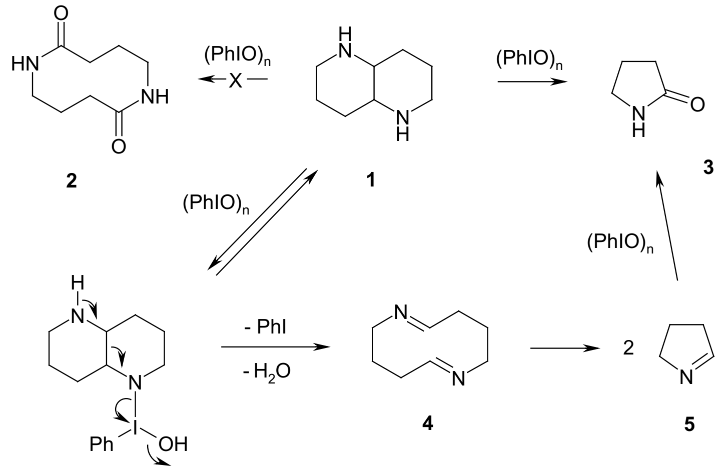
Syngenta Crop Protection AG, CH 4002 Basel, Switzerland

Received 9 January 2004; revised 14 January 2004; accepted 16 January 2004

Abstract—Oxidation of *cis* or *trans* 1,5-diazadecalin with $(PhIO)_n$ yields 2-pyrrolidinone and not 1,6-diaza-2,7-cyclodecadione, as reported. This is shown by a comparison of the NMR data of the reaction product with those of 2-pyrrolidinone and 1,6-diaza-2,7-cyclodecadione.

It was recently reported[1] in this journal that oxidation of *cis* or *trans* 1,5-diazadecalin (**1**) with $(PhIO)_n$ yields the ring expanded bislactam 1,6-diaza-2,7-cyclodecadione (**2**) (Scheme 1). The reaction product was described as an oil and its NMR data were given. 1,6-Diaza-2,7-cyclodecadione, however, is a high-melting solid, whose X-ray structure analysis has been published.[2] Furthermore, the ^{1}H and ^{13}C NMR data given[1] for the reaction product are those of 2-pyrrolidinone **3**, as can easily be seen by a comparison with literature data of 2-pyrrolidinone[3] and of **2**[4] (see Table 1). At room temperature, the ^{1}H NMR spectrum of **2** in $CDCl_3$ shows six separate signals for the axial and equatorial protons of the three nonequivalent CH_2 groups due to the stable centrosymmetrical crown conformation of the macrocyclic ring. A detailed analysis of this spectrum has been published in 1982 in a study of the solution conformation of **2**.[4]

The formation of 2-pyrrolidinone can be explained by the decay of the postulated[1] intermediate bisimine **4** to the monomeric 1-pyrroline (**5**) or its hydrate, which is in



Scheme 1.

Keywords: Diazadecalins; Macrocyclic bislactams; NMR; Conformational analysis.

* Tel.: +41-613-235047; fax: +41-613-233704; e-mail: tammo.winkler@syngenta.com

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.01.062

Table 1. ^{13}C and ^{1}H NMR chemical shifts of **2** and **3** in $CDCl_3$

	C(2)	C(3)	C(4)	C(5)
2[a]	175.4	35.7	26.6	39.4
3[1]	179.8	30.5	21.2	42.7
3[3]	179.59	30.28	20.75	42.44
	H-3	H-4	H-5	
2[b]	2.01 t, 2.32 d	2.17 q, 1.80 d	4.10 q, 2.91 d	
3[1]	2.25 t	2.08 quintet	3.36 t	
3[3]	2.29 t	2.12 quintet	3.40 t	

[a] This work; cf. ^{13}C NMR chemical shifts in DMSO-d_6 or EtOH-d_6[4].

[b] The chemical shift of the axial protons is listed first. At 25 °C, a slight exchange broadening is observed: Therefore only the multiplicities caused by the large geminal and trans diaxial vicinal coupling constants are given (cf. the analysis[4] of the spectrum at 0 °C).

turn oxidized to 2-pyrrolidinone as shown[5] by Ochiai et al. (see Scheme 1).

References and notes

1. Li, X.; Xu, Z.; DiMauro, E. F.; Kozlowski, M. C. *Tetrahedron Lett.* **2002**, *43*, 3747–3750.
2. Tereshko, V.; Monserrat, J. M.; Pérez-Folch, J.; Aymamí, J.; Fita, I.; Subirana, J. A. *Acta Crystallogr., Sect. B* **1994**, *B50*, 243–251.
3. Pouchert, C. J.; Behnke, J. In *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Aldrich Chemical Company: Milwaukee, 1993; Vol. 1, p 1285, spectra B.
4. Winkler, T.; Leutert, T. *Helv. Chim. Acta* **1982**, *65*, 1760–1763.
5. Ochiai, M.; Inenaga, M.; Nagao, Y.; Moriarty, R. M.; Vaid, R. K.; Duncan, M. P. *Tetrahedron Lett.* **1988**, *29*, 6917–6920.