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UNACTIVATED 2-AZA-1,3-DIENES: HALOGENATION AND FACE SELECTIVITY IN DIELS-ALDER REACTIONS

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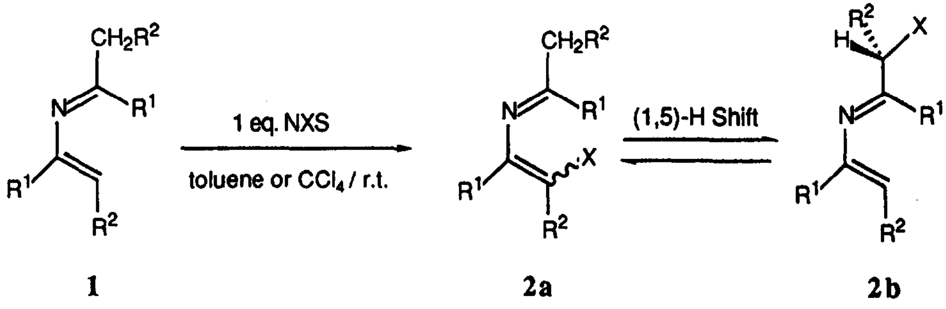
Summary: The synthesis of monohalogenated 2-aza-1,3-dienes 2 is described.The first example of face selectivity in Diels-Alder reactions of dienes 2 with diethyl azodicarboxylate and benzaldehyde is also reported.

Over the last years an increasing interest is being observed in the study of the face selectivity in Diels-Alder reactions of cyclic and acyclic 1,3-carbodienes.[1] However,as far as we are aware, nothing is known about this study in heterodienes and, particularly, in 2-aza-1,3-dienes.[2]

We have recently developed a simple synthesis of unactivated 2-aza-1,3-dienes 1 and shown their reactivity in [4+2]-cycloaddition reactions toward different dienophiles, as well as in other types of processes.[3] In order to extend the synthetic utility of these systems, we report the monohalogenation of 2-aza-dienes 1[4] in this letter and the results of the Diels-Alder reaction of the new dienes formed 2 with diethyl azodicarboxylate and benzaldehyde.

The halogenation of 2-aza-1,3-dienes 1 (10 mmol) (R^1= Ph, *p*-Tolyl; R^2= Me, Et) was performed with 1 equivalent of N-halo succinimide (NXS, X=Cl, Br, I) in toluene or CCl_4 overnight at room temperature, the yield of isolated product being higher than 90% (Scheme I).

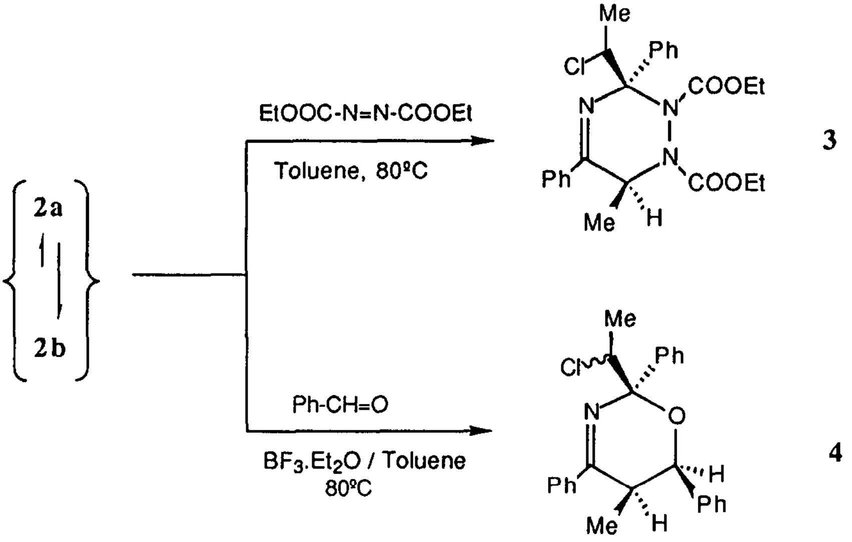


Scheme I

The halogenated 2-aza-1,3-dienes 2 were isolated as a mixture of two isomers **2a** and **2b**. The transformation of **2a** to **2b** probably takes place by a 1,5-sigmatropic shift of hydrogen.

The structure of **2** was ascertained by chemical and spectroscopic methods.[5] Thus, when **2** was treated with H_2SO_4 6N (80ºC, 2h), a 1:1 mixture of the corresponding ketones was obtained.

We tested the reactivity of **2** with different dienophiles and found that the treatment of **2** (10 mmol) (*i.e.* R^1= Ph, R^2= Me, X= Cl) with diethyl azodicarboxylate (10 mmol) (toluene, 80ºC, 12h) led to the compound **3** [5] (85% yield) with apparently complete diastereoselectivity. [6] Similarly, a 83:17 mixture of two epimers **4** [5] (90% yield) were formed when **2** was allowed to cycloadd to benzaldehyde (10 mmol) in the presence of boron trifluoride (1.5 mmol) (toluene, 80ºC, 12h) (Scheme II).



Scheme II

The formation of **3** and **4** takes place from the more reactive trisubstituted tautomer **2b**. The high stereoselectivity observed can be understood in terms of face selectivity arising from a favourable *anti* conformation of chlorine and nitrogen atoms in the tautomer **2b** (Scheme I).

References and notes.

1. M.J. Fisher, W.J. Hehre, S.D. Kahn, and L.E. Overman, *J. Am. Chem. Soc.*,1988,*110*,4625 and references cited therein.
2. (a) D.L. Boger, *Tetrahedron*, 1983, *39*, 2869;(b) D.L. Boger and S. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis", Academic Press, N.Y., 1987, pp 101 - 103.
3. (a) J.Barluenga, *Bull. Soc. Chim. Belg.*, 1988, *97*, 545; (b) J. Barluenga, J. Joglar, F.J. González, V. Gotor, and S. Fustero, *J. Org. Chem.*, 1988, *53*, 5960 and references cited therein.
4. Whereas the halogenation of imino compounds has been extensively reviewed by De Kimpe, very little is known about the halogenation of 2-aza-1,3-dienes. See, N. De Kimpe, and N. Schamp, *Org. Prep. Proced. Int.*, 1983, *15 (1-2)*,71 and references cited therein.
5. Satisfactory ^1H, ^{13}C NMR and Mass Spectra were obtained for all new compounds 2, 3, and 4 reported.
6. In the absence of definitive evidence, the tentative stereochemical assignment in the carbon bonded to the chlorine atom in 3 was made on the basis of a preferential attack through the *anti* conformation in the tautomer 2b.

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