Reaction of 1-azaazulenes with benzyne

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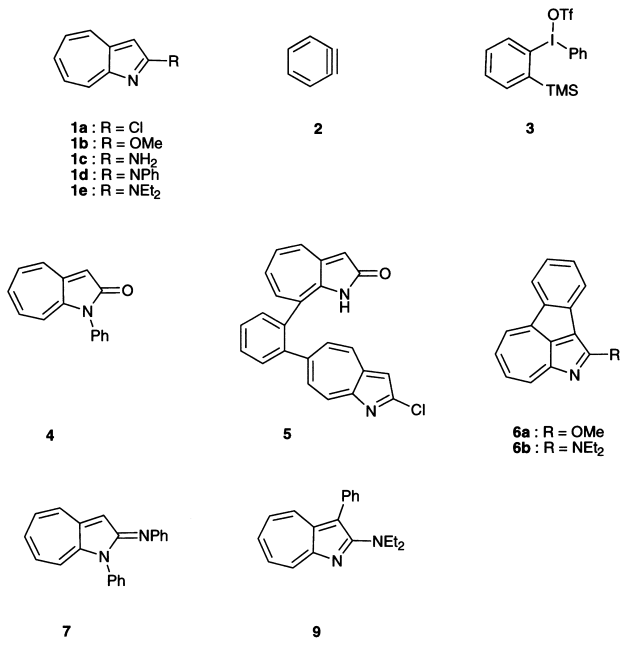
The reaction of 2-chloro-1-azaazulene **(1a)** with the benzyne prepared from (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate with tetrabutylammonium fluoride gave 1-phenyl-1-azaazulen-2(1*H*)-one and 8-[2-(2-chloro-1-azaazulen-6-yl)phenyl]-1-azaazulen-2(1*H*)-one **(5)**, whereas the reaction of **1a** with the benzyne prepared from benzenediazonium-2-carboxylate gave 6,10b-etheno-1-azabenz[e]azulen-2(3*H*)-one **(11)** together with **12**.

Keywords: 1-azaazulenes, benzyne, cycloaddition, phenylation

Cycloadditions of 1-azaazulenes are interesting; various reaction types, such as 1,n-dipolar cycloadditions and Diels–Alder type reactions, have been found and they are affected by the nature of the functional groups and the reaction conditions.[1] In this paper we report that the reaction of 1-azaazulenes with benzyne proceed by a different path depending upon both the nature of the functional group and also the generation method of the benzyne.

Treatment of 2-chloro-1-azaazulene **(1a)** with the benzyne **2**, prepared from (phenyl)[o-(trimethylsilyl)phenyl]iodonium triflate **(3)** and tetrabutylammonium fluoride (TBAF) (Kitamura's method[5]), gave 1-phenyl-1-azaazulen-2(1*H*)-one **(4)** and 8-[2-(2-chloro-1-azaazulen-6-yl)phenyl]-1-azaazulen-2(1*H*)-one **(5)** in low yields together with recovered **1a** (Scheme 1). Similar treatment of 2-methoxy-1-azaazulene **(1b)** gave **4** and 1-methoxy-2-azaindeno[1,2,3-*cd*]azulene **(6a)**, and the treatment of 2-diethylamino-1-azaazulene **(1e)** gave 1-methoxy-2-azaindeno[1,2,3-*cd*]azulene **(6a)** and 2-diethylamino-3-phenyl-1-azaazulene **(9)**. Unlike the reaction of **1a**, the product of reaction at N-1 was not obtained in the reaction of **1e**. Reaction of 2-amino-1-azaazulene **(1c)** gave only 1-phenyl-2-(phenylimino)-1,2-dihydro-1-azaazulene **(7)** as a distinct product.



1a : R = Cl
1b : R = OMe
1c : R = NH_2
1d : R = NPh
1e : R = NEt_2

2 **3**

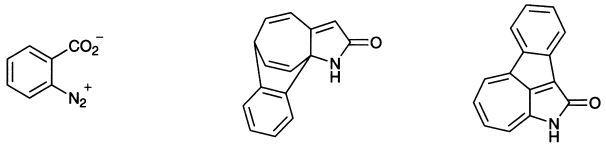
4 **5**

6a : R = OMe
6b : R = NEt_2

7 **9**

Scheme 1

Next, we examined the reaction of 1-azaazulenes with the benzyne prepared from benzenediazonium-2-carboxylate **10** (Scheme 2).[8] When a reaction of **1a** and **10** in refluxing 1,2-dichloroethane was performed for 1 h, **5** and 6,10b-etheno-1-azabenz[e]azulen-2(1*H*)-one **11** were isolated together with **1a**. Similar reaction of 2-methoxy-1-azaazulene **1b** gave **11** and 2-azaindeno[1,2,3-*cd*]azulen-1(2*H*)-one **12**.



10 **11** **12**

Scheme 2

Tables: 2

References: 9

Techniques used: ^{1}H and ^{13}C NMR, MS, IR, chromatography.

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References cited in this synopsis:

1 N. Abe, *Recent Research Developments in Organic and Bioorganic Chemistry: Recent Progress in the Chemistry of Azaazulenes*, Vol. 4, pp. 14-48, Transworld Research Network, 2001; N. Abe, *Cycloaddition Reactions of Azaazulenes: Trends in Heterocyclic Chemistry*, Vol. 7, Research Trend, 2001, in press; T. Nishiwaki and N. Abe, *Heterocycles,* 1981, **15**, 547.
5 T. Kitamura and M. Yamane, *J. Chem. Soc., Chem. Commun*., 1995, 983.
8 I. Tabushi, K. Okazaki and R. Oda, Tetrahedron, 1969, **25**, 4401; L. Friedman, *J. Am. Chem. Soc*., 1967, **89**, 3071.

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