

THE REACTION OF 2-CHLORO-1-AZAAZULENES WITH GRIGNARD REAGENTS

Noritaka AbeDepartment of Chemistry, Yamaguchi University, Yoshida,
Yamaguchi, 753, Japan

Reaction of 2-chloro-1-azaazulenes with phenylmagnesium bromide gave addition-type products, and dehydrogenation thereof afforded 4-, 6-, and 8-phenyl-2-chloro-1-azaazulenes. It is concluded from product yields that the reactivity of the ring position of the 2-chloro-1-azaazulene system towards this reagent increases in the order of $C(8) \gg C(4) > C(6)$.

Like halogen-substituted azulenes, their 1-aza-analogues are known to react with some nucleophiles, such as amines, alkoxides, or mercaptides, producing the corresponding substitution products by replacement of the halogen atom with a nucleophile (1,2,3,4). However, it has been recently disclosed (5,6,7) that diethyl azulene-1,3-dicarboxylates underwent addition-type reactions upon treatment with some carbanions and 1,3-diazaazulene underwent addition reactions with Grignard reagents. The study was extended to the 2-chloro-1-azaazulene system and it was found that this heteroazulene also underwent addition reaction upon treatment with Grignard reagents.

Treatment of 2-chloro-1-azaazulene (Ia) with 2.5 molar equiv.

of phenylmagnesium bromide in THF at room temperature gave a mixture of air-sensitive dihydro-1-azaazulenes. Dehydrogenation of this mixture with tetrachloro-o-benzoquinone followed by silica gel chromatography with benzene gave 2-chloro-4-phenyl-1-azaazulene (IIa) [orange needles, m.p. 123-124°], 2-chloro-6-phenyl-1-azaazulene (IIIa) [orange needles, m.p. 137.5-138.5°], and 2-chloro-8-phenyl-1-azaazulene (IVa) [orange needles, m.p. 120-121°], in 4, 3, and 88 % yield, respectively. Likewise, ethyl 2-chloro-1-azaazulene-3-carboxylate (Ib) gave ethyl 2-chloro-4-phenyl-1-azaazulene-3-carboxylate (IIb) [orange prisms, m.p. 115.5-116.5°], ethyl 2-chloro-6-phenyl-1-azaazulene-3-carboxylate (IIIb) [yellow needles, m.p. 167-169°], and ethyl 2-chloro-8-phenyl-1-azaazulene-3-carboxylate (IVb) [yellow needles, m.p. 154-155.5°], in 8, 7, and 77 % yield, respectively.

These structures were assigned on the basis of the spectral data shown in Tables 1 and 2, as well as the microanalytical data (8) and some chemical evidences that deethoxycarbonylation of the compounds IIb, IIIb, and IVb with hot hydrobromic acid afforded the compounds IIa, IIIa, and IVa, respectively. The corresponding 2-phenyl-1-azaazulenes, which would be expected to be formed by displacement of the chlorine atom with the nucleophile, could not be isolated even in a trace amount. The foregoing results, which sharply contrast with the behaviour of 2-chloroazulene itself towards a Grignard reagent (5) or sodium acetylide (6), show that the reactivity of the ring position towards the Grignard reagent increases in the order of $C(8) \gg C(4) > C(6)$.

However, this order of reactivity does not agree with the result derived from the MO calculation for the 1-azaazulene system which predicts the C(4)-position to be most reactive towards nucleophiles

Table 1. The nmr data for the phenyl-1-azaazulenes at 100 MHz in CDCl_3 compounds δ ppm (intensity, pattern, coupling const. Hz, assignment)

IIa	6.97(1H, s, H-3) 7.40-7.60(5H, m, phenyl) 7.64-7.98(3H, m, H-5,6,7) 8.59(1H, dm, 9.0, H-8)
IIIa	7.17(1H, s, H-3) 7.40-7.70(5H, m, phenyl) 7.81(1H, dd, 10.8, 1.8, H-5) 7.92(1H, dd, 10.2, 1.8, H-7) 8.40(1H, d, 10.8, H-4) 8.55(1H, d, 10.2, H-8)
IVa	7.18(1H, s, H-3) 7.30-7.90(8H, m, H-5,6,7, and phenyl) 8.40(1H, d, 9.7, H-4)
IIb	1.06(3H, t, 7.0, CH_3CH_2-) 3.59(2H, q, 7.0, CH_3CH_2-) 7.43(5H, s, phenyl) 8.60-8.03(3H, m, H-5,6,7) 8.65(1H, dm, 10.0, H-8)
IIIb	1.50(3H, t, 7.2, CH_3CH_2-) 4.49(2H, q, 7.2, CH_3CH_2-) 7.40-7.65(5H, m, phenyl) 8.13(2H, dd, 10.3, 1.5, H-5,7) 8.69(1H, dd, 10.3, 1.5, H-8) 9.55(1H, dd, 10.3, 1.5, H-4)
IVb	1.47(3H, t, 7.0, CH_3CH_2-) 4.46(2H, q, 7.0, CH_3CH_2-) 7.36-8.06(8H, m, H-5,6,7, and phenyl) 9.58(1H, dm, 9.5, H-4)

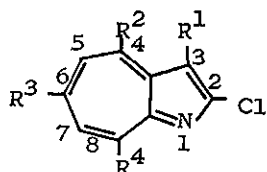
Ia: $\text{R}^1=\text{R}^2=\text{R}^3=\text{R}^4=\text{H}$ Ib: $\text{R}^1=\text{CO}_2\text{C}_2\text{H}_5$ IIa: $\text{R}^1=\text{R}^3=\text{R}^4=\text{H}$ $\text{R}^2=\text{R}^3=\text{R}^4=\text{H}$ $\text{R}^2=\text{Ph}$ IIb: $\text{R}^1=\text{CO}_2\text{C}_2\text{H}_5$, $\text{R}^2=\text{Ph}$, $\text{R}^3=\text{R}^4=\text{H}$ IIIa: $\text{R}^1=\text{R}^2=\text{R}^4=\text{H}$ $\text{R}^3=\text{Ph}$ IIIb: $\text{R}^1=\text{CO}_2\text{C}_2\text{H}_5$, $\text{R}^3=\text{Ph}$, $\text{R}^2=\text{R}^4=\text{H}$ IVa: $\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$ $\text{R}^4=\text{Ph}$ IVb: $\text{R}^1=\text{CO}_2\text{C}_2\text{H}_5$, $\text{R}^4=\text{Ph}$, $\text{R}^2=\text{R}^3=\text{H}$

Table 2. The electronic spectral data for the phenyl-1-azaazulenes compounds $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ nm(log ϵ)

IIa	228(3.76)	275(4.68)	308(3.73, sh)	337(3.75)	470(3.37)
IIIa	226(3.24)	273(4.58)	307(4.39)	346(4.12)	361(4.15)
	476(3.36)				
IVa	228(3.80)	268(4.51)	292(4.24)	338(3.74)	357(3.46, sh)
IIb	230(4.32)	283(4.68)	337(3.89)	468(3.44)	
IIIb	283(4.49, sh)	298(4.55)	313(4.57)	345(4.34)	361(4.36)
	443(3.34)				
IVb	279(4.56)	300(4.42, sh)	338(4.01, sh)	447(3.20)	

(9). It is suggested that coordination of the ring nitrogen atom with the Grignard reagent may be responsible for the observed high reactivity of the C(8)-position.

The reaction described herein is considered to be a convenient synthetic method for 8-aryl-1-azaazulenes which are otherwise difficult to obtain.

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