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CYCLOADDITION REACTIONS OF 1-AZA- AND 1,3-DIAZAAZULENIUM 1-METHYLIDES[†]

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Abstract - 2-Chloro-, 2-methoxy-, and 2-amino-1-azaazulenium 1-methylides and 1,3-diazaazulenium 1-methylide were generated by the treatment of the corresponding 1-trimethylsilylmethyl-1-azaazulenium triflates and 1-trimethylsilylmethyl-1,3-diazaazulenium triflate with CsF; the triflates were prepared from the corresponding 1-azaazulenes and 1,3-diazaazulene with trimethylsilylmethyl triflate. The 1,3-dipolar cycloadditions of the 2-chloro-1-azazaazulenium 1-methylide, prepared *in situ*, with acetylenic esters gave 2a-azabenz[*cd*]azulene derivatives and 3a-azacyclopenta[*a*]naphthalene derivatives as major products, whereas 2-piperizino-1-azaazulenium 1-methylide underwent extended dipolar cycloaddition with acetylenic esters and afforded 9b-azacyclopent[*a*]azulene derivatives as major products.

INTRODUCTION

Heteroaromatic *N*-ylides[1-3] and heteroaromatic *N*-imines[4-8], which are highly useful synthetic intermediate for the construction of fused heterocycles *via* 1,3-dipolar cycloaddition reaction.[9,10] We previously reported about the synthesis and reactions of 1-azaazulene *N*-imine (**1**) where interesting dipolar cycloadditions were observed.[11] Although a non-alternant heteroaromatic *N*-ylide has large potential for the construction of new heterocyclic nuclei, which have an interesting function such as bioactivity and

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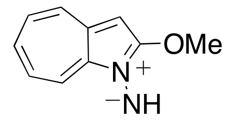
[†] Dedicated to Professor Steven M. Weinreb occasion of his 65th birthday.

dye, the investigation was rarely reported. Recently, we communicated the generation of 1-azaazulenium 1-methylides (**2a,c**).[12] For the development of azaazulene chemistry[13] and for an interest in the construction of new fused heterocycles, we advanced the investigation to the reactions of 1-azaazulenium 1-methylides, and we wish report the full detail herein.

RESULTS AND DISCUSSION

Generation of azomethine ylide by desilylation from α-silyliminium salts is interesting and a facile route to pyrrolidines and pyrroles was reported recently.[14] Because *N*-alkylations of 1-azaazulene are known,[15,16] we intend to make a 1-azaazulenium 1-methylide by *N*-trimethylsilylmethylation of 1-azaazulene followed by desilylation. Thus 2-chloro-1-azaazulene (**3a**) was treated with trimethylsilylmethyl triflate in dichloromethane for 48 h, and 2-chloro-1-trimethylsilylmethyl-1-azaazulenium triflate (**4a**) was obtained in 87% yield. The structure was deduced on the basis of the spectroscopic data as well as elemental analyses. In the ^{1}H NMR spectrum of **4a**, rather low resonated proton signals were seen at δ 7.68 (s, H-3), 8.51 (dd, J 10.1 and 9.8, H-7), 8.60 (dd, J 10.2 and 9.9, H-5), 8.71 (dd, J 10.2 and 9.8, H-6), 9.06 (d, J 9.9, H-4), and 9.47 (1H, d, J 10.1, H-8) together with silylmethyl signals at δ 0.14 (9H, s) and a methylene signal at δ 4.59 (2H, s). This suggests that the cationic charge on **4a** delocalized to 1-azaazulene ring.

Similar treatment of the 1-azaazulenes (**3b**-**3e**) with trimethylsilylmethyl triflate in dichloromethane for 48 h gave **4b** (90%), **4c** (92%), **4d** (96%), and **4e** (64%), respectively.



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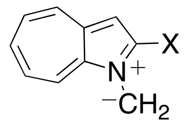
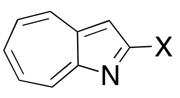
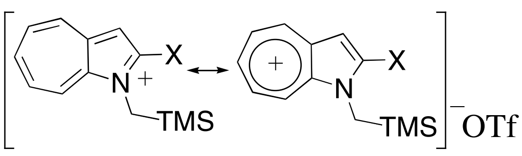


2a : X = Cl
2b : X = OMe
2c : X = piperidino
2d : X = ethylamino
2e : X = amino



3a : X = Cl
3b : X = OMe
3c : X = piperidino
3d : X = ethylamino
3e : X = amino



4a : X = Cl
4b : X = OMe
4c : X = piperidino
4d : X = ethylamino
4e : X = amino

Desilyation of the salt (**4**) would produce the ylide (**2**). To consider the character of 1-azaazulenium 1-methylides, we carried out the molecular orbital calculation of 2-substituted 1-azaazulenium 1-methylides (**2a,c**) by Spartan'02 with RHF/6-31G* basis set.[17] Calculated bond lengths and electron densities were shown in Figure 1. From the consideration of bond lengths, **2c** would have a character as for heptafulvene and amidinium ion, where large bond alternation than that of **2a** is seen. Atomic charges at C-2, C-8, and C-8a are nearly equal on **2a**, whereas C-2 is highly positive on **2c**.

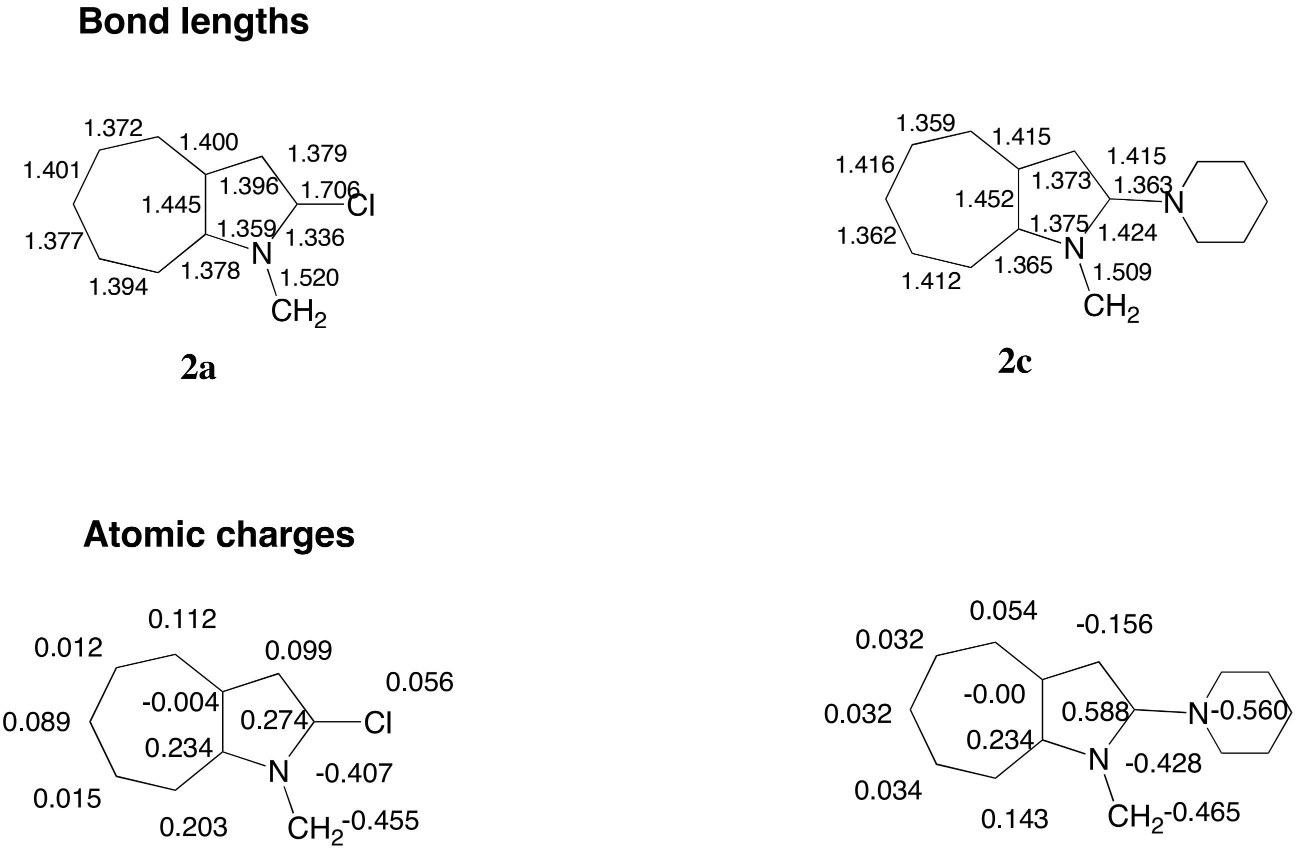
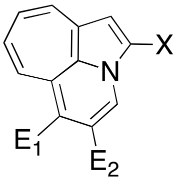


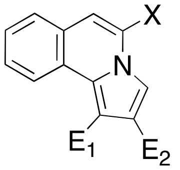
Figure 1. Bond lengths (Å) (upper) and atomic charges (lower) of 1-azaazulenium 1-methylides. Calculations were performed by Spartan'02 (RHF / 6-31G*).

1-Azaazulenium 1-methylide (**2a**) could not be obtained by the treatment of **4a** with pottasium carbonate or tetrabutylammonium fluoride. It was very difficult to isolate a clear product. It is known that pyridinium methylides generated by the treatment of *N*-(trimethylsilylmethyl)pyridinium triflates with CsF.[18-20] Therefore, the desilylation of **4** with CsF or KF and the trapping experimrnts in the presence of acetylenic esters were carried out as follows. The treatment of **4a** with CsF, dried before use, in the presence of dimethyl acetylenedicarboxylate (DMAD) in acetonitrile at 0 ℃ for 6 h gave 2a-azabenz[*cd*]azulene derivatives (**5aa**) (5%), 3a-azacyclopenta[*a*]naphthalene (**6aa**) (7%), and 9b-azacyclopent[*a*]azulene derivatives (**7**) (3%) (Run 1). The yield was slightly improved at elevated reaction temperature and **5aa** (8%) and **6aa** (11%) was obtained, instead **7** was not obtained (Run 2). When the reaction was performed in *N*,*N*-dimethylacetoamide (DMA), yields were slightly change and the compounds (**5aa**) (5%), (**6aa**) (7%), (**7**) (2%), and (**8**) (0.4%) were obtained (Run 3). It is considered that **8** would be a secondary cycloadduct from the reaction of **5** and/or **7** with DMAD. Compounds (**5**) and (**7**) were expected to be precursors of **8**. Indeed **7** reacted with DMAD to give **8** in 12% yield. But its yield was not good. During the process from **7** to **8**, dehydrogenation needs to proceed. We previously reported that the reaction of **10** with DMAD gave cycloadduct (**11**).[21]

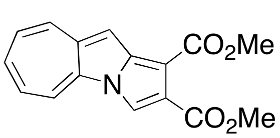
Therefore, we thought their yields would be improved somewhat higher when cycloaddition was carried out in the presence of oxidants such as tetrachloro-*p*-benzoquinoneone (chloranil) or 2,3-dichiloro-5,6-dicyano-*p*-benzoquinone (DDQ). Thus **4a** was treated with CsF and DMAD in acetonitrile at room temperature for 22 h, then the mixture was treated with chloranil for 24 h gave **5aa** (7%) and **6aa** (19%) (Run 5). In this case, the yields of **5aa** and **6aa** were slightly improved, but **7** and **8** were not obtained. As shown as above, **7** could undergo cycloaddition.



5aa : X = Cl, $E_1 = E_2 = CO_2Me$
5ba : X = OMe, $E_1 = E_2 = CO_2Me$
5ca : X = piperidino, $E_1 = E_2 = CO_2Me$
5ab : X = Cl, $E_1 = CO_2Me$, $E_2 = H$



6aa : X = Cl, $E_1 = E_2 = CO_2Me$
6ba : X = OMe, $E_1 = E_2 = CO_2Me$
6ca : X = piperidino, $E_1 = E_2 = CO_2Me$
6ab : X = Cl, $E_1 = CO_2Me$, $E_2 = H$



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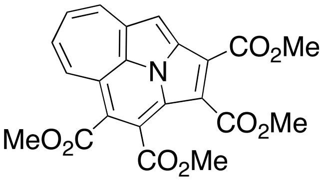

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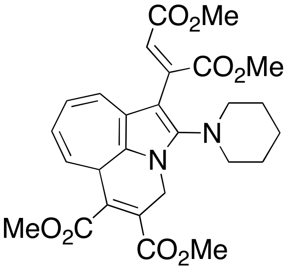

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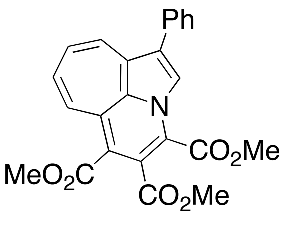

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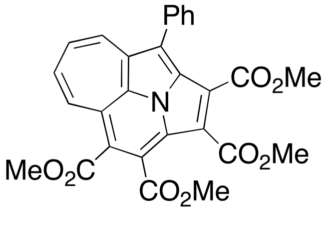

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Therefore, it is thought that **7** would consumed by the reaction with chloranil. Indeed, when **7** was treated with chloranil, **7** was disappeared but clear products were not obtained. As shown in Runs 5-8, a clear solvent effect was not obtained. Using excess molar of DMAD in the reaction improved the yields (Runs 10-13), and increasing of the yield of **8** was observed on the reaction at 0 °C (Run 12).

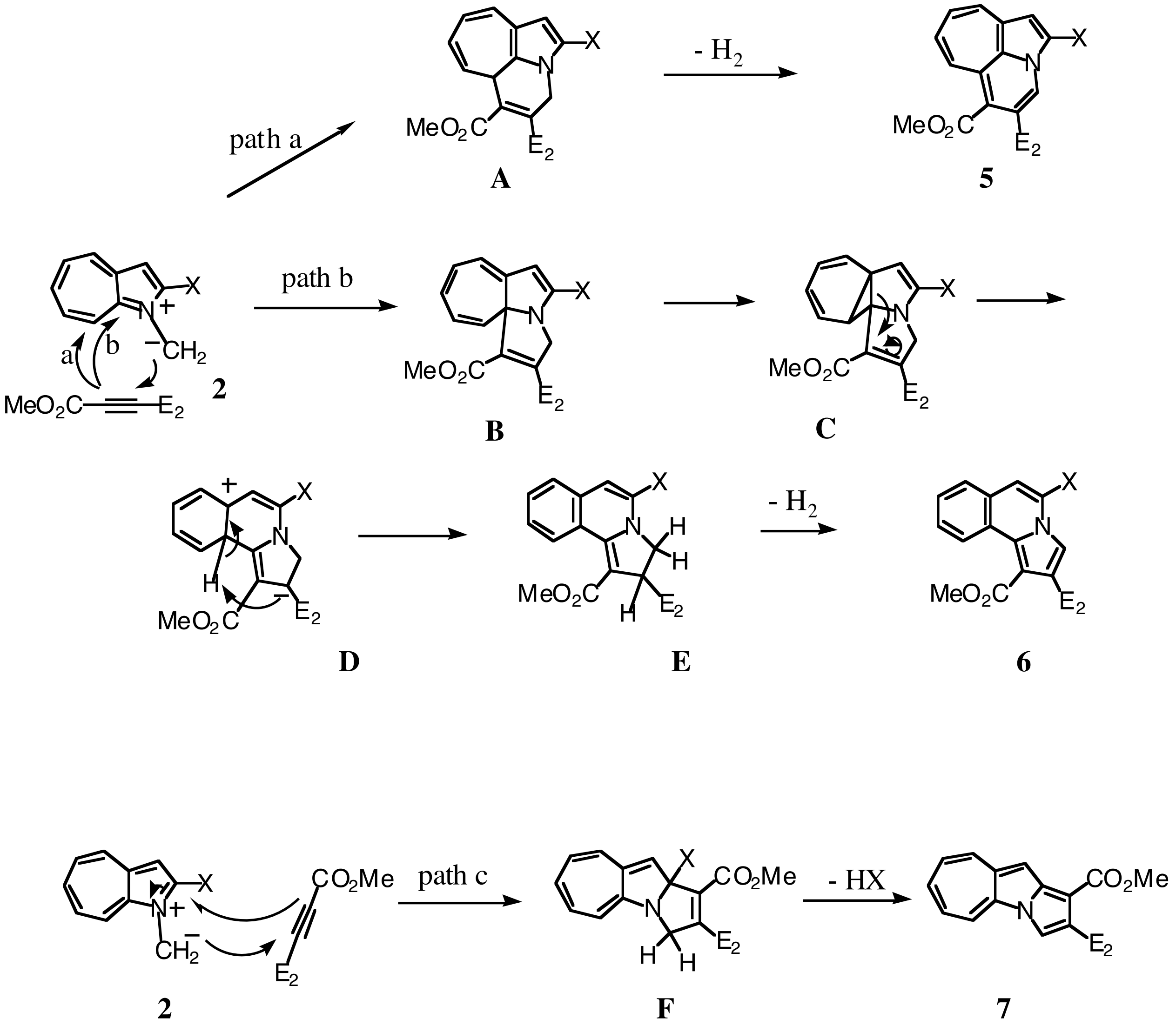
The structures of **5-7** were established on the basis of the spectroscopic data. In the ^{1}H NMR spectrum of **5aa**, rather high-field resonated signals of seven-membered ring protons appeared at δ 4.95 (H-7), 5.28 (H-8), 5.59 (H-9), and 5.72 (H-6), which have a large divergence of the coupling constants ($J_{5\text{-}6}$ = 11.2,

$J_{6-7} = 7.8$, and $J_{7-8} = 12.8$) showing the presence of the bond-alternation in the seven-membered ring, together with two 1H singlets, at δ 6.07 (H-1) and 7.36 (H-3), and two methyl signals. In the ^{1}H NMR

Table 1. Reactions of 1-azaazulenium methylides with reactive acetylenes

Run	Reactant	Acetylene	Ratio	Oxidant	Reaction conditions			Products (Yield / %)
					Solvent	Temp. / ℃	Time / h	
1	**4a**	DMAD	1 : 1.3		MeCN	0	6	**5aa**(5) **6aa** (7) **7** (3)
2	**4a**	DMAD	1 : 1.0		MeCN	reflux	1	**5aa**(8) **6aa** (11)
3	**4a**	DMAD	1 : 1.3		DMA	0	6	**5aa**(10) **6aa**(18) **7** (2) **8**(0.4)
4	**4a**	DMAD	1 : 1.5		THF	-90 → 10	51	**5aa**(6) **6aa**(15)
5	**4a**	DMAD	1 : 2.4	chloranil	MeCN	rt	22	**5aa**(9) **6aa**(17)
6	**4a**	DMAD	1 : 2.4	chloranil	dioxane	rt	21	**5aa**(8) **6aa**(22)
7	**4a**	DMAD	1 : 2.4	chloranil	DMF	rt	22	**5aa**(7) **6aa**(24)
8	**4a**	DMAD	1 : 1.5	chloranil	DMSO	rt	24	**5aa**(8) **6aa**(20)
9	**4a**	DMAD	1 : 1.5	DDQ	MeCN	rt	22	**5aa**(10) **6aa**(13)
10	**4a**	DMAD	1 : 5	chloranil	MeCN	rt	22	**5aa**(10) **6aa**(31)
11	**4a**	DMAD	1 : 5	chloranil	DMA	rt	22	**5aa**(10) **6aa**(29)
12	**4a**	DMAD	1 : 5	chloranil	MeCN	0	22	**5aa**(23) **6aa**(27) **8**(6)
13	**4a**	DMAD	1 : 10	chloranil	MeCN	rt	22	**5aa**(23) **6aa**(32)
14	**4b**	DMAD	1 : 1.5		MeCN	rt	20	**5ba**(7) **6ba**(1) **7**(14)
15	**4b**	DMAD	1 : 3	chloranil	MeCN	rt	22	**6ba**(8)
16	**4c**	DMAD	1 : 2		DMA	0	6	**7**(8)
17	**4c**	DMAD	1 : 2		DMA	0	12	**7**(10) **9**(1.5)
18	**4c**	DMAD	1 : 1.3		MeCN	0	22	**7**(22)
19	**4c**	DMAD	1 : 1.3	chloranil	MeCN	rt	22	No distinct product
20	**4d**	DMAD	1 : 1.3		DMA	rt	6	No distinct product
21	**4e**	DMAD	1 : 1.3		MeCN	rt	24	No distinct product
22	**4a**	MP	1 :1.4	chloranil	MeCN	rt	21	**6ab**(3)
23[a]	**4a**	MP	1: 1.3		DMA	rt	60	**5ab**(2) **6ab**(4)
24	**4d**	MP	1 : 1.5		MeCN	rt	24	No distinct product
25[a]	**4a**	EB	1: 1.3		DMA	rt	144	No distinct product
26	**4a**	EB	1 : 2	chloranil	MeCN	reflux	2	No distinct product

[a] 0.1 Equivalent molar of Yb(CF$_3$SO$_3$)$_3$ was used as catalyst.



Scheme 1

spectrum of **6aa**, two 1H singlets, at δ 7.06 (H-5) and 8.12 (H-3), and protons assignable to benzene ring were seen at δ 7.14-7.56 (m, H-6, 7, and 8) and 8.19 (d, *J* 8.0, H-9) together with two methyl singlets. The structures of **5aa** and **6aa** were confirmed by X-Ray crystallographic analysis, and the results were previously reporetd.[12]

When 2-methoxy-1-trimethylsilylmethyl-1-azaazulenium triflate (**4b**) was treated with CsF and DMAD at room temperature for 20 h, compounds (**5ba**, **6ba**, and **7**) were obtained in 7%, 1%, and 14% yields, respectively (Run 14).

Reaction of 2-piperidino-1-trimethylsilylmethyl-1-azaazulenium triflate (**4c**) with CsF and DMAD in DMA gave **7** (10%) and **9** (1.5%), and the rearrangement product (**6ca**) was not obtained (Run 17). It seems that using longer reaction time improved the yield, and the yield of **7** increased to 22% (Run 18). Using of cloranil again resulted in disappearance of **7** (Run 19).

When KF was used as a desilylation reagent of **4a** in the presence 18-crown-6-ether, the cycloadducts (**5aa** and **6aa**) were obtained in only trace yields.

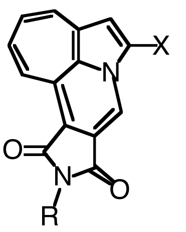
Reactions of **4d** and **4e** with CsF and DMAD gave no distinct product (Runs 16-18). These results were different from the case of 1-amino-2-alkylamino- and 1,2-diamino-1-azaazulenium salts with base and reactive acetylenes, where cycloaddition was observed.[22]

For the examination of regioselectivity in the cycloaddition of **2** to acetylenes,, we investigate the reaction of **2** with methyl propiolate (MP) and ethyl butynolate (EB) as reactive acetylenes. When **4a** was treated with MP in the presence of CsF in acetonitrile for 21 h at room temperature, followed by treatment with chloranil, **6ab** was obtained in 3% yield (Run 22). For expecting to improve the reaction by addition of Lewis acid, the reaction of **4a** with MP in the presence of $Yb(CF_3SO_3)_3$ was performed in DMA for 60 h at room temperature, but the yields were low and **5ab** and **6ab** were obtained in 2% and 4% yields (Run 23). In the ^1H NMR spectra of **5ab** and **6ab**, H-6 proton of **5ab** and H-9 proton of **6ab** were resonated at low field (δ 7.16 and δ 9.82, respectively) compared with those of **5aa** and **6aa** (δ 5.72 and δ 8.19, respectively), which would be influenced by anisotropy of ester group situated at peri-position. It is known that the ester groups at C-5 of **5aa** and at C-1 of **6aa** were situated nearly perpendicular with rings,[12] where steric repulsion between esters at C-4 and C-5 of **5aa** and esters at between at C-1 and C-2 of **6aa** would exist. Absence of the ester group at C-4 of **5aa** and at C-2 of **6aa** affords dissolution of the steric repulsion of the esters of **5ab** and **6ab** and, the esters at C-5 of **5aa** and at C-1 of **6aa** would be situated in co-planer with the rings. Reactions using EB was scarcely proceeded, and distinct product was not obtained (Runs 25 and 26).

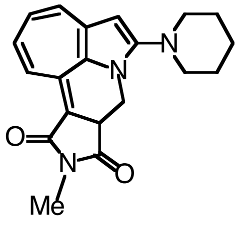
Although yields were low, it is indicated that the reaction of **4a** with MP proceeded regioselectively. A plausible formation mechanism of **5**, **6**, and **7** is shown in Scheme 1. From the consideration of the results (Table 1), it considered that the cycloaddition reaction was strongly affected by the functional group located at C-2 of the 1-azaazulenium 1-methylides (**10**). The results show that reaction of the 2-chloro-1-azazaazulenium 1-methylide gave 2a-azabenz[*cd*]azulene derivatives (**5**) and 3a-azacyclopenta[*a*]naphthalene derivatives (**6**) as major products, whereas 2-piperizino-1-azazaazulenium 1-methylide afforded 9b-azacyclopent[*a*]azulene derivative (**7**) as major product. Reaction of 2-methoxy-1-azazaazulenium 1-methylide gave **5**, **6**, and **7**.

Next, for the investigation of streoselectivity in the cycloaddition of **2** to acetylenes, we examined the reaction of electron deficient olefins such as *N*-phenyl maleimide (PM) and *N*-methyl maleimide (MM). Treatment of **4a** with CsF in the presence of PM in DMA for 1 h gave a complex mixture of yellow oils and a green compound. The structures of yellow oils could not be characterized because they were unstable. The green compound (**12aa**) was isolated in 31% yield by chromatography and the structure was deduced on the basis of the spectroscopic data. In the similar manner, reaction of **4a** with MM and the reaction of **4c** with PM gave **12ab** (20%) and **12ca** (14%), respectively. The obtained compounds (**12aa-ca**) were aromatized products and the stereoselectivity on the reaction could not be defined. In the reaction of **4c** with MM, the red oil (**13cb**) was obtained. In its ^{1}H NMR spectrum, methine and methylene protons were observed at δ 3.33 (dd, 12.3 and 10.8, H-7), 3.57 (dd, J 12.3 and 6.3, H-7), and 4.79 (dd, J 10.8 and 6.3, H-7a). The seven-membered ring protons were appeared at δ 6.41 (dd, J 10.8 and 8.3, H-3), 6.72 (dd, J 12.1 and 8.3, H-2), 7.02 (d, J 10.8, H-4), and 8.28 (1H, d, J 12.1, H-1). These data of **13cb** suggested that there is bond-alternation, and **13cb** is thought to have a heptafulvene structure. In this case, proton migration occurred and the stereoselectivity on the reaction could not be defined again.

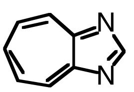
For the comparison with the case of 1-azaazulene, we next synthesized 1-trimethylsilylmethyl-1,3-diazaazulenium triflate (**15**) from 1,3-diazaazulene (**14**) in 79% yield. In the similar manner as for **4**, 3a,5-diazacyclopenta[*a*]naphthalene derivative (**15**) was treated with CsF in the presence of DMAD for 24 h at room temperature, and only **16** was isolated in 9% yield. The reaction would proceed as a similar case to **4b**.



12aa : X = Cl, R = Ph
12ab : X = Cl, R = Me
12ca : X = piperidino, R = Ph



13cb



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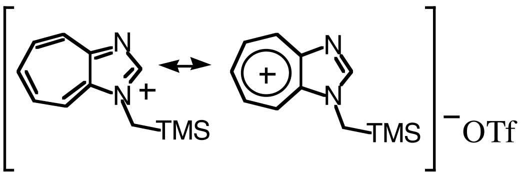

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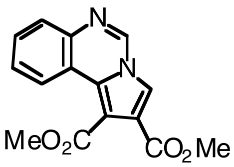

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CONCLUSION

In summary, 1-azaazulenium 1-methylides (**2**) were trapped by acetylenic esters and three types of cycloadducts, 2a-azabenz[*cd*]azulene derivatives, 3a-azacyclopent[*a*]naphthalene derivatives, and 9b-azacyclopent[*a*]azulene, were obtained. The selectivity of the reaction site on the cycloaddition of 1-azaazulenium 1-methylides was affected by the substituents at C-2 of **2**.

EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra (including HH-COSY and CH-COSY NMR)) were recorded on a Bruker AVANCE 400S (400 MHz) and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard; *J* values are recorded in Hz. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410 unless otherwise stated. Electronic spectra were recorded with Shimadzu UV-1600PC spectrophotometer. MS spectra were taken with on a LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Synthesis of 1-trimethylsilylmethyl-1-azaazulenium triflates

Typical procedure - Under argon atmosphere, a mixture of 2-chloro-1-azaazulene (**3a**) (2.062 g, 12.6 mmol), trimethylsilylmethyl triflate (3.02 mL, 15.1 mmol) in dry CH_2Cl_2 (60 mL) was stirred for 48 h at rt. To the mixture Et_2O (200 mL) was added, and stirring was continued for 5 h. The precipitate was collected by filtration and 2-chloro-1-trimethylsilylmethyl-1-azaazulenium triflate (**4a**) (4.823 g, 87%) was obtained.

4a: Yellow plates (Et_2O-CH_2Cl_2), mp 143-144 ℃; δ_H 0.14 (9H, s, SiMe), 4.59 (2H, s, $SiCH_2N$), 7.68 (1H, s, H-3), 8.51 (1H, dd, *J* 10.1 and 9.8, H-7), 8.60 (1H, dd, *J* 10.2 and 9.9, H-5), 8.71 (1H, dd, *J* 10.2 and 9.8, H-6), 9.06 (1H, d, *J* 9.9, H-4), and 9.47 (1H, d, *J* 10.1, H-8); δ_C -1.8, 39.2, 112.0, 135.3, 137.5, 137.9, 142.1, 143.3, 143.8, 144.9, and 146.3. *Anal.* Calcd for $C_{14}H_{17}NO_3ClF_3SSi$: C, 42.05 H, 4.28; N, 3.50. Found: C, 42.33; H, 4.37; N, 3.44.

In the similar manner, compounds **4b** (90%), **4c** (92%), **4d** (96%), **4e** (64%), and **4f** (79%) were obtained.

4b: Yellow oil; δ_H 0.32 (9H, s, SiMe), 4.42 (2H, s, $SiCH_2N$), 4.65, (3H, s, OMe), 7.51 (1H, s, H-3), 8.37 (1H, dd, *J* 10.1 and 9.7, H-7), 8.47 (1H, dd, *J* 10.1 and 9.9, H-5), 8.56 (1H, dd, *J* 10.1 and 9.7, H-6), 9.05 (1H, d, *J* 9.9, H-4), and 9.09 (1H, d, *J* 10.1, H-8); δ_C –2.1, 35.9, 60.9, 93.1, 129.4, 135.6, 136.4, 138.9, 141.2, 142.5, 145.6, and 165.6. *Anal.* Calcd for $C_{15}H_{20}NO_4F_3SSi$: C, 42.56 H, 5.10; N, 3.54. Found: C, 42.46; H, 5.02; N, 3.45.

4c: Orange prisms (Et_2O-CH_2Cl_2), mp 132-133 ℃; δ_H 0.00 (9H, s, SiMe), 1.76-1.88 (6H, m, H-3', 4', and 5'), 3.52 (4H, t, *J* 5.7, H-2' and 6'), 4.27 (2H, s, $SiCH_2N$), 6.99 (1H, s, H-3), 7.87-7.98 (2H, m, H-5 and 7), 8.10 (like t, *J* 9.9, H-6), 8.46 (1H, d, *J* 9.9, H-4), and 8.66 (1H, d, *J* 9.9, H-8); δ_C –1.5, 23.5, 25.3, 38.8, 52.5, 116.1, 119.3, 122.5, 128.1, 134.7, 135.8, 136.3, 139.4, 145.8, 146.0, and 162.2. *Anal.*

Calcd for $C_{19}H_{27}NO_3F_3SSi$: C, 50.87 H, 6.07; N, 6.24. Found: C, 50.90; H, 5.87; N, 6.35.

4d: Orange prisms (Et_2O-CH_2Cl_2), mp 186-187 ℃; δ_H 0.13 (9H, s, SiMe), 1.41 (3H, t, *J* 7.2, Me), 3.63 (2H, qd, *J* 7.2 and 6.8, $MeC\underline{H}_2NH$), 4.11 (2H, s, $SiCH_2N$), 6.50 (1H, s, H-3), 7.48-7.66 (4H, m, H-4, 5, 6, and 7), 7.96 (1H, d, *J* 10.2, H-8), and 8.67 (1H, br t, *J* 6.8); δ_C –1.9, 14.3, 35.1, 40.2, 95.9, 120.4, 131.7, 132.3, 134.5, 134.7, 145.9 and 158.1. *Anal.* Calcd for $C_{16}H_{23}N_2O_3F_3SSi$: C, 47.04 H, 5.67; N, 6.86. Found: C, 47.40; H, 5.61; N, 6.73.

4e: Orange prisms (Et_2O-CH_2Cl_2), mp 221-222 ℃; δ_H 0.13 (9H, s, SiMe), 4.02 (2H, s, $SiCH_2N$), 6.85 (1H, s, H-3), 7.46-7.56 (4H, m,H-4, 5, 6, and 7), 7.92-9.94 (1H, m, H-8), and 7.95 (2H, br s, NH). *Anal.* Calcd for $C_{14}H_{19}N_2O_3F_3SSi$: C, 44.20 H, 5.03; N, 7.36. Found: C, 44.35; H, 5.21; N, 7.16.

Generation and reaction of 1-azaazulene *N*-methylides with dimethyl acetylenedicarboxylate (DMAD)

Typical procedure A – Under argon atmosphere, a mixture of CsF (0.281 g, 1.85 mmol), DMAD (0.171 g, 1.20 mmol), **4a** (0.370 g, 0.92 mmol), and *N*,*N*-dimethylacetamide (DMA) (10 mL) in a sealed tube was stirred for 6 h. To the mixture was added water, then the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and the solvent was evaporated. Chromatography of the residue with hexane-AcOEt (2 : 1) gave **5aa** (0.029 g, 10%), **6aa** (0.052 g, 18%), **7** (0.006 g, 2%), and **8** (0.0016 g, 0.4%), successively.

Typical procedure B – Under argon atmosphere, a mixture of CsF (0.082 g, 0.54 mmol), DMAD (0.08 mL, 0.65 mmol), **4a** (0.149 g, 0.37 mmol), and MeCN (3 mL) in a sealed tube was stirred for 22 h. Then, *p*-chloranil (0.103 g, 0.042 mmol) was added to the mixture, and stirring was continued for 24 h. To the mixture was added water, then the mixture was extracted with AcOEt. The extract was dried over Na_2SO_4, and the solvent was evaporated. Chromatography of the residue with hexane-AcOEt (3 : 1) gave **5aa** (0.010 g, 9%) and **6aa** (0.020 g, 17%), successively.

5aa: Dark violet prisms (hexane-CH_2Cl_2), mp 138-140 ℃; δ_H 3.73, (3H, s, Me), 3.77 (3H, s, Me), 4.95 (1H, dd, *J* 11.2 and 7.8, H-8), 5.28 (1H, ddd, *J* 12.8, 7.8, and 0.7, H-7), 5.59 (1H, d, *J* 12.8, H-9), 5.72 (1H, dd, *J* 11.2 and 0.7, H-6), 6.07 (1H, s, H-1), and 7.36 (1H, s, H-3); δ_C 52.2, 52.3, 111.2, 111.3, 112.2, 119.1, 121.5, 123.7, 124.3, 128.5, 133.2, 134.0, 137.3, 139.1, 164.8, and 167.6; ν(C=O) / cm^{-1} 1725 and 1714; λ_{max} (MeCN) nm (log ε) 233 (4.62), 356 (4.01), and 550 (2.48); *m/z* (rel intensity) 319 (M^+, 38), 317 (M^+, 100), 286 (39), 271 (30), 200 (33), and 164 (20). *Anal.* Calcd for $C_{16}H_{12}NO_4Cl$: C, 60.48; H, 3.82; N, 4.41. Found: C, 60.36; H, 4.03; N, 4.44.

6aa: Yellow prisms (hexane- CH_2Cl_2), mp 183-184 ℃; δ_H 3.91, (3H, s, Me), 4.06 (3H, s, Me), 7.06 (1H, s, H-5), 7.14-7.56 (3H, m, H-6, 7, and 8), 8.12 (1H, s, H-3), and 8.19 (1H, d, *J* 8.0, H-9); δ_C 52.0, 53.0, 111.4, 113.4, 117.4, 117.5, 123.3, 123.8, 124.4, 126.8, 127.8, 128.0, 128.5, 129.5, 163.8, and 167.5;

ν(C=O) / cm^{-1} 1723 and 1710; λ_{max} (MeCN) nm (log ε) 264 (4.78), 307 (3.87), and 320 (3.84); *m/z* (rel intensity) 317 (M$^+$, 28), 317 (M$^+$, 75), 286 (100), 256 (21), 227 (10), 214 (10), and 164 (34). *Anal.* Calcd for $C_{16}H_{12}NO_4Cl$: C, 60.48; H, 3.82; N, 4.41. Found: C, 60.22; H, 3.98; N, 4.57.

7: Green needles (hexane-CH_2Cl_2), mp 165-166 ℃; δ_H 3.91, (3H, s, Me), 3.92 (3H, s, Me), 6.73 (1H, dd, *J* 11.2 and 8.3, H-7), 6.82 (1H, dd, *J* 11.2 and 8.5, H-8), 6.92 (1H, dd, *J* 11.3 and 8.3, H-6), 6.98 (1H, s, H-4), 7.40 (1H, d, *J* 8.5, H-9), 7.51 (1H, d, *J* 11.3, H-5), and 8.04 (1H, s, H-1); δ_C 51.3, 52.0, 107.6, 115.6, 115.8, 122.1, 126.7, 127.0, 133.1, 133.4, 139.3, 139.9, 146.1, 151.8, 164.0, and 164.5; ν(C=O) / cm^{-1} 1701 and 1673; *m/z* (rel intensity) 283 (M$^+$, 100), 252 (90), 225 (18), 222 (11), 194 (18), 180 (13), 167 (34), 166 (25), and 139 (16). *Anal.* Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.56; H, 4.57; N, 4.98.

8: Reddish violet needles (hexane-CH_2Cl_2), mp 209-210 ℃; δ_H 4.03, (3H, s, Me), 4.04 (3H, s, Me), 4.07 (3H, s, Me), 4.08 (3H, s, Me), 6.56 (1H, dd, *J* 11.1 and 8.7, H-8), 6.85 (1H, dd, *J* 12.1 and 8.7, H-7), 7.22 (1H, d, *J* 12.1, H-6), 7.57 (1H, dd, *J* 11.1, H-9), and 7.73 (1H, s, H-3); ν(C=O) / cm^{-1} 1725, 1705, and 1697; *m/z* (rel intensity) 423 (M$^+$,100), 392 (34), 377 (13), 217 (24), 190 (12), 189 (22), and 188 (17). *Anal.* Calcd for $C_{22}H_{17}NO_8$: C, 62.41; H, 4.05; N, 3.31. Found: C, 62.53; H, 4.12; N, 3.13.

5ba: Dark violet prisms (hexane-CH_2Cl_2), mp 124-127 ℃; δ_H 3.68, (3H, s, Me), 3.72 (3H, s, Me), 3.82 (3H, s, Me), 4.91 (1H, dd, *J* 11.2 and 7.9, H-8), 5.26 (1H, dd, *J* 12.8 and 7.9, H-7), 5.35 (1H, s, H-1), 5.71 (1H, d, *J* 12.8, H-9), 5.72 (1H, dd, *J* 11.2, H-6), and 7.02 (1H, s, H-3); ν(C=O) / cm^{-1} 1727 and 1703. *Anal.* Calcd for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.04; H, 4.88; N, 4.63.

6ba: Yellow prisms (hexane-CH_2Cl_2), mp 146-147 ℃; δ_H 3.89, (3H, s, Me), 4.04 (3H, s, Me), 4.12 (3H, s, Me), 6.14 (1H, s, H-5), 7.43-7.53 (2H, m, H-7 and 8), 7.52 (1H, dd, *J* 7.9 and 1.2, H-6), 8.00 (1H, s, H-3), and 8.19 (1H, d, *J* 7.4, H-9); ν(C=O) / cm^{-1} 1725 and 1711; *m/z* (rel intensity) 313 (M$^+$, 100), 298 (69), 282 (91), 267 (56), 181 (19), and 126 (13). *Anal.* Calcd for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.28; H, 4.78; N, 4.50.

6ca: Yellow oil; δ_H 1.13-1.18 (6H, m, H-3', 4', and 5'), 1.75-1.77 (4H, m, H-2' and 6'), 3.83, (3H, s, Me), 3.97 (3H, s, Me), 6.34 (1H, s, H-5), 7.30-7.50 (3H, m, H-6, 7, and 8), 7.86 (1H, s, H-3), and 8.10 (1H, d, *J* 9.4, H-9); ν(C=O) / cm^{-1} (Neat) 1730 and 1728; *m/z* (rel intensity) 366 (M$^+$, 100), 335 (16), 303 (15), 285 (13), 149 (27), and 87 (23).

9: Red oil; δ_H 1.50-1.57 (6H, m, H-3', 4', and 5'), 2,97-3.02 (2H, m, H-2' and 6'), 3.20-2.25 (2H, m, H-2' and 6'), 3.55 (3H, s, Me), 3.64, (3H, s, Me), 3.67 (3H, s, Me), 3.76 (3H, s, Me), 4.18 (1H, d, *J* 15.4, H-3), 4.25 (1H, d, *J* 15.4, H-3), 5.32 (1H, d, *J* 10.3, H-9), 5.69 (1H, s, vinylic-H), 5.83 (1H, dd, *J* 11.0 and 6.7, H-7), 5.94 (1H, d, *J* 7.4, H-5a), 6.08 (1H, dd, *J* 10.3 and 6.7, H-8), and 6.28 (1H, dd, *J* 11.0 and 7.4, H-6). ν(C=O) / cm^{-1} (Neat) 1720 1713, 1698, and 1680; *m/z* (rel intensity) 510 (M$^+$, 100).

Reaction of 7 with DMAD

A mixture of **7** (0.045 g, 0.16 mmol) and DMAD (0.046 g, 0.32 mmol) in MeCN (5 mL) was stirred for 21 h at rt, and evaporated. Chromatography of the residue with hexane-AcOEt (2 : 1) gave **8** (8 mg, 12%) and **7** (0.030 g, 67%).

Generation and reaction of 1-azaazulene *N*-ylides with methylplopiolate (MP)

Procedure A – Under argon atmosphere, a mixture of CsF (0.211 g, 1.39 mmol), MP (0.135 g, 0.78 mmol), **4a** (0.278 g, 0.69 mmol), $Yb(CF_3SO_3)_3$ (0.043 g, 0.07 mmol), and DMA (10 mL) in a sealed tube was stirred for 60 h. To the mixture was added water, then the mixture was extracted with CH_2Cl_2. The extract was dried over sodium sulfate, and the solvent was evaporated. Chromatography of the residue with hexane-ethyl acetate (10 : 1) gave **5ab** (0.0026 g, 2%) and **6ab** (0.0074 g, 4%).

Procedure B – Under argon atmosphere, a mixture of CsF (0.172 g, 1.12 mmol), MP (0.11 mL, 1.20 mmol), **4a** (0.306 g, 0.77 mmol), and MeCN (6 mL) in a sealed tube was stirred for 21 h. Then, *p*-chloranil (0.211 g, 0.86 mmol) was added to the mixture, and stirring was continued for 24 h. To the mixture was added water, then the mixture was extracted with AcOEt. The extract was dried over Na_2SO_4, and the solvent was evaporated. Chromatography of the residue with benzene gave **6ab** (0.006 g, 3%).

5ab; Dark violet prisms (hexane-CH_2Cl_2), mp 118-120 ℃; δ_H 3.72, (3H, s, Me), 5.19 (1H, dd, *J* 10.9 and 7.9, H-8), 5.61 (1H, dd, *J* 13.0 and 7.9, H-7), 6.01 (1H, d, *J* 10.9, H-9), 6.09 (1H, s, H-1), 6.42 (1H, d, *J* 7.6, H-4), 6.67 (1H, d, *J* 7.6, H-3), 7.16 (1H, d, *J* 13.0, H-6); ν(C=O) / cm^{-1} (Nujol) 1714; *m/z* (rel intensity) 261 (M^+, 38), 259 (M^+, 100). *Anal.* Calcd for $C_{14}H_{10}NO_2Cl$: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.52; H, 3.65; N, 5.57.

6ab: Yellow oil; δ_H 3.95, (3H, s, Me), 7.13 (1H, s, H-5), 7.34 (1H, d, *J* 3.3, H-2), 7.50-7.63 (3H, m, H-6, 7, and 8), 7.65 (1H, d, *J* 3.3, H-3), and 9.82 (1H, d, *J* 7.9, H-9); ν(C=O) / cm^{-1} (Neat) 1715; *m/z* (rel intensity) 261 (M^+, 33), 259 (M^+, 82), 228 (100), 201 (22), and 172 (22).

Generation and reaction of 1-azaazulene *N*-ylides with electron-deficient olefins

Typical procedure A – Under argon atmosphere, a mixture of CsF (0.525 g, 3.46 mmol), *N*-phenylmaleimide (0.390 g, 2.25 mmol), **4a** (0.692 g, 1.73 mmol), and DMA (20 mL) in a sealed tube was stirred for 1 h. To the mixture was added water, then the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and the solvent was evaporated. Chromatography of the residue with benzene gave **12aa** (0.186 g, 31%).

Typical procedure B – Under argon atmosphere, a mixture of cesium fluoride (0.144 g, 0.95 mmol), *N*-methylmaleimide (0.113 g, 1.02 mmol), **4a** (0.260 g, 0.65 mmol), and MeCN (6 mL) in a sealed tube was stirred for 21 h. Then, *p*-chloranil (0.179 g, 0.73 mmol) was added to the mixture, and stirring was continued for 24 h. To the mixture was added water, then the mixture was extracted with AcOEt. The extract was dried over sodium sulfate, and the solvent was evaporated. Chromatography of the residue with benzene gave **12ab** (0.010 g, 5%).

12a; Green prisms (hexane-CH_2Cl_2), mp 209-211 ℃; δ_H 5.48 (1H, dd, *J* 11.2 and 8.0, H-3), 5.90 (1H, dd, *J* 12.4 and 8.0, H-2), 6.19 (1H, d, *J* 11.2, H-4), 6.31 (1H, s, H-5), 7.18 (1H, d, *J* 12.4, H-1), 7.35-7.38 (3H, m, H-*m,p*-pheny), 7.45-7.49 (2H, m, H-*o*-phenyl), and 7.43 (1H, s, H-7); ν(C=O) / cm^{-1} (Nujol) 1744 and 1668; *m/z* (rel intensity) 348 (M$^+$, 38), 346 (M$^+$, 100), 302 (6), 301 (8), 267 (19), 266 (10), 237 (8), 199 (20), and 164 (25). *Anal.* Calcd for $C_{20}H_{11}N_2O_2Cl$: C, 69.27; H, 3.20; N, 8.08. Found: C, 69.37; H, 3.37; N, 7.99.

12ab: Green needles (hexane-CH_2Cl_2), mp 223-225 ℃; δ_H 3.05, (3H, s, Me), 5.42 (1H, dd, *J* 11.2 and 8.0, H-2), 5.84 (1H, dd, *J* 12.4 and 8.0, H-2), 6.13 (1H, d, *J* 11.2, H-4), 6.24 (1H, s, H-5), 7.07 (1H, d, *J* 12.4, H-1), and 7.43 (1H, s, H-7); ν(C=O) / cm^{-1} 1741 and 1698; *m/z* (rel intensity) 286 (M$^+$, 38), 284 (M$^+$, 100), 249 (1), 239 (13), 199 (28), and 164 (16). *Anal.* Calcd for $C_{15}H_9N_2O_2Cl$: C, 63.28; H, 3.19; N, 9.84. Found: C, 63.45; H, 3.38; N, 9.66.

12ca; Green fibers (hexane-CH_2Cl_2), mp 277-279 ℃; δ_H 1.58-1.63 (2H, m, H-4'), 1.69-1.74 (4H, H-3' and 5'), 2.82-2.80 (4H, m, H-2' and 6'), 5.43 (1H, dd, *J* 11.0 and 8.0, H-3), 5.88 (1H, dd, *J* 12.3 and 8.0, H-2), 5.87 (1H, s, H-5), 6.23 (1H, d, *J* 11.1, H-4), 7.15 (1H, d, *J* 12.3, H-1), 7.43 (1H, s, H-7), 7.32-7.38 (3H, m, H-*m,p*-pheny), and 7.44-7.48 (2H, m, H-*o*-phenyl); δ_C 24.4, 26.1, 52.4, 101.3, 102.6, 118.2, 120.7, 125.5, 126.7, 127.1, 128.1, 128.2, 129.2, 132.8, 135.5, 137.3, 138.3, 141.4, 142.8, 165.1, and 165.5; ν(C=O) / cm^{-1} (Nujol) 1730 and 1693. *Anal.* Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.77; H, 5.25; N, 10.56.

13cb; Orange oil; δ_H 1.70-1.83 (6H, m, H-3', 4', and 5'), 2.86-2.99 (4H, m, H-2' and 6'), 3.07 (3H, s, Me), 3.33 (1H, dd, 12.3 and 10.8, H-7), 3.57 (1H, dd, *J* 12.3 and 6.3, H-7), 4.79 (1H, dd, *J* 10.8 and 6.3, H-7a), 5.95 (1H, s, H-5), 6.41 (1H, dd, *J* 10.8 and 8.3, H-3), 6.72 (1H, dd, *J* 12.1 and 8.3, H-2), 7.02 (1H, d, *J* 10.8, H-4), and 8.28 (1H, d, *J* 12.1, H-1); *m/z* (rel intensity) 335 (M$^+$, 100).

Synthesis of 1-trimethylsilylmethyl-1,3-diazaazulenium triflate

Under argon atmosphere, a mixture of 1,3-diazaazulene (**14**) (0.127 g, 0.98 mmol), trimethylsilylmethyl triflate (0.277 mg 1.17 mmol) in dry CH_2Cl_2 (60 mL) was stirred for 48 h at rt. To the mixture Et_2O (300 mL) was added, and stirring was continued for 5 h. The precipitate was collected by filtration and 1-trimethylsilylmethyl-1,3-diazaazulenium triflate (**15**) (0.268 g, 79%) was obtained.

15: Colorless plates (hexane-dichloromethane), mp 137-138 ℃; δ_H 0.16 (9H, s, SiMe), 4.59 (2H, s,

$SiCH_2N$), 8.79 (1H, dd, *J* 10.0 and 9.8, H-7), 8.92 (1H, t, *J* 9.9, H-5), 9.01 (1H, dd, *J* 9.9 and 9.8, H-6), 9.09 (1H, s, H-2), 9.34 (1H, d, *J* 9.9, H-4), 9.74 (1H, d, *J* 10.0, H-8); δ_C –2.4, 39.6, 135.8, 140.7, 141.6, 144.1, 148.2, 149.3, 156.2, and 158.8. *Anal.* Calcd for $C_{14}H_{17}NO_3ClF_3SSi$: C, 42.61 H, 4.68; N, 7.64. Found: C, 42.46; H, 4.57; N, 7.48.

Generation and reaction of 1,3-diazaazulene 1-methylide (14) with DMAD

Under argon atmosphere, a mixture of CsF (0.168 g, 1.11 mmol), DMAD (0.118 g, 0.83 mmol), **15** (0.203 g, 0.55 mmol), and MeCN (10 mL) in a sealed tube was stirred for 5 h under cooling on ice-bath, then the stirring was continued for 24 h at rt. To the mixture was added water, then the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and the solvent was evaporated. Chromatography of the residue with hexane-AcOEt(2 : 1) gave **16** (0.014 g, 9%).

16: Colorless plates (hexane-CH_2Cl_2), mp 146-148 ℃; δ_H 3.91, (3H, s, Me), 4.03 (3H, s, Me), 7.56 (1H, ddd, *J* 8.3, 7.8 and 1.7, H-8), 7.58 (1H, ddd, *J* 8.3, 7.8, and 1.6, H-7), 7.81 (1H, s, H-3), 7.84 (1H, dd, *J* 7.8 and 1.6, H-9), 8.37 (1H, dd, *J* 7.8 and 1.7, H-6), and 8.64 (1H, s, H-4); *m/z* (rel intensity) 284 (M^+, 41), 253 (100), 221 (18), 194 (5), and 168 (6). *Anal.* Calcd for $C_{13}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.20; H, 3.92; N, 9.97.

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