REACTION OF 8-AMINO-3-PHENYL-1-AZAAZULENE WITH CHLORO-, PHENYL-, AND DIPHENYLKETENE[†]

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Abstract - Chloroketene reacted with 8-amino-3-phenyl-1-azaazulene (**1**) to give 2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one derivative (**2a**), as a cycloadduct, along with ethyl (3-phenyl-1-azaazulen-8-yl)aminocarboxylate (**3a**) and 8-chloroacetylamino-3-phenyl-1-azaazulene (**4a**).   Compound (**2a**) was formed by the reaction of **4a** with chloroketene.   Formation mechanism of **2a**, **3a** and **4** was discussed.   Phenylketene and diphenylketene reacted with **1** to give 8-phenylacetylamino- (**4b**) and 8-diphenylacetylamino-3-phenyl-1-azaazulene (**6**) as major products, respectively.   Further treatment of **6** with diphenylketene gave 2-diphenylmethylene-4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulene (**7**).

INTRODUCTION

Much attention about the azaazulenes has been attracted regarding their interesting chemical and physical natures as well as their physiological properties.[1]   For synthetic strategy of fuzed heterocycles, cycloaddition reactions are served as excellent methods,[2—8] including the reactions of ketenes.[8—10]   We have been studied on cycloadditions of 1-azaazulenes and reported that the reactions afforded a wide variety of cycloadducts attended by a nature of the substituents on 1-azaazulenes and the reaction conditions.[1]   We previously showed that 2-amino-1-azaazulenes underwent interesting cycloadditions with halo- and phenylketenes to give cycloadducts such as 4,4a-dihydro-1,4a-diazacyclopent[*a*]azulen-4-one derivatives and *anhydro*-2-chloroacetyl-1-ethyl-3-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide.[11]   To expand the reaction of 1-azaazulenes with ketenes, we examined the reactions of 8-amino-3-phenyl-1-azaazulene with chloro-, phenyl-, and diphenylketenes, and found that the 8-amino-1-azaazulene reacted with two equivalents of the ketenes to give novel fused heterocycles.

RESULTS AND DISCUSSION

In the reaction of 8-amino-1-azaazulene with chloroketene, the ketene was generated *in situ* by the treatment of chloroacetyl chloride with triethylamine in chloroform.   Thus, the treatment of 8-amino-3- phenyl-1-

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[†] Dedicated to Professor Yuichi Kanaoka on occasion of his 75th birthday.

azaazulene[12] (**1**) with chloroketene at 0   for 30 min under ice-cooling followed by quenching with water gave a complex mixture.   Chromatography of the mixture with chloroform as an eluent afforded 1-chloro-4-phenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one (**2a**) (3%), ethyl (3-phenyl-1-azaazulen-8-yl)aminocarboxylate (**3a**) (7.5%), 8-chloroacetylamino-3-phenyl-1-azaazulene (**4a**) (3%) and 8-amino-3-phenyl-1-azaazulene hydrochloride (**5**) (5%) (Entry 1).

These structures were deduced from the results of their spectroscopic data as well as elemental analyses. The compound (**2a**) was analyzed as $C_{17}H_{10}NOCl$ by the inspections of its MS spectrum and elemental analysis.   In the IR spectrum of **2a**, a carbonyl absorption is seen at 1731 and 1723 cm^{-1}, and no NH band appears.   The ^{1}H NMR spectrum of **2a** shows the signals at δ 6.99 (dd, *J* 10.7 and 9.2, H-6), 7.31 (dd, *J* 10.8 and 9.2, H-7), 7.36 (1H, s, H-3), 7.40—7.50 (6H, m, H-5 and phenyl) and 7.55 (1H, d, *J* 10.8, H-8).   From the results, we assigned **2a** as 1-chloro-4-phenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one.
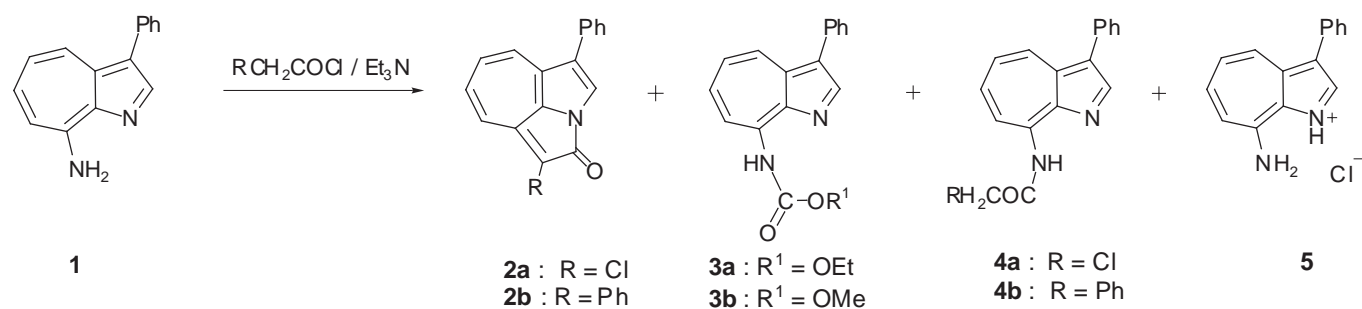

| | | **2a** : R = Cl | **3a** : R^1 = OEt | **4a** : R = Cl | **5** |
| **1** | | **2b** : R = Ph | **3b** : R^1 = OMe | **4b** : R = Ph | |

Table 1

Entry	1 : RCH$_2$COCl : R$_3$N		CHCl$_3$	Temperature	Yield (%)				
1	1 : 6 : 12	(Et$_3$N)	CaCl$_2$ dried	0 rt	**2a** (3)	**3a** (7.5)	**4a** (3)	**5** (5)	**1** (—)
2	1 : 6 : 12	(Et$_3$N)	CaCl$_2$ dried	0	**2a** (1)	**3a** (9)	**4a** (3)	**5** (3)	**1** (—)
3	1 : 6 : 12	(Et$_3$N)	CaCl$_2$ dried	rt	**2a** (—)	**3a** (—)	**4a** (44)	**5** (—)	**1** (—)
4	1 : 3 : 6	(Et$_3$N)	CaCl$_2$ dried	0	**2a** (4)	**3a** (1)	**4a** (7.5)	**5** (5)	**1** (13)
5	1 : 6	(—)	CaCl$_2$ dried	0 rt	**2a** (—)	**3a** (—)	**4a** (45)	**5** (—)	**1** (15)
6	1 : 6 : 12	(Et$_3$N)	ethanol free	0	**2a** (2)	**3a** (12)	**4a** (15)	**5** (6)	**1** (—)
7	1 : 6 : 12	(Et$_3$N)	+ ethanol	0	**2a** (6)	**3a** (13)	**4a** (8)	**5** (6)	**1** (—)
8	1 : 6 : 12	(Pr$_3$N)	ethanol free	0	**2a** (6)	**3a** (8)	**4a** (trace)	**5** (—)	**1** (—)
9	1 : 6 : 12	(Et$_3$N)	ethanol free	0	**2a** (4)	**3b** (2)	**4a** (trace)	**5** (—)	**1** (—)
10	1 : 6 : 12	(Pr$_3$N)	ethanol free	0	**2a** (6)	**3b** (2)	**4a** (trace)	**5** (—)	**1** (—)

The IR spectrum of **3a** shows a carbonyl absorption is seen at 1731 cm^{-1}, and NH band appears at 3299 cm^{-1}. In the ^{1}H NMR spectrum of **3a**, ethyl signals were seen at δ 1.39 (t, *J* 7.1) and 4.35 (q, *J* 7.1).

Therefore, it is thought that the compound (**3a**) has a ethylcarbamate moiety, and the structure was assigned as ethyl (3-phenyl-1-azaazulen-8-yl)aminocarboxylate.   To confirm the structure, we treated **1** with ethyl

chloroformate, and the obtained compound was identical with **3a**.

At first, we thought that ethoxy group of **3a** was introduced by the attack of a trace amount of ethanol in chloroform. Interestingly, in spite of the presence or the absence of ethanol in the reaction solvent, an ethoxy group was introduced to the product (**3a**) (Entries 1, 2, 4, 6 and 7). When tripropylamine was used as base, the results were similar as above. When triethylamine was absent, only mono-acetylated product (**4a**) was obtained in 45% yield (Entry 5). When the reaction was performed at rt, **4a** was obtained in 44% yield, (Entry 3); this suggests that the acetylation is preffered to the formation of chloroketene. These suggest that the ethyl group was not derived from the reaction solvent or the amine. Furthermore, when the quenching of the reaction mixture was done using methanol, ethyl (3-phenyl-1-azaazulen-8-yl)aminocarboxylate (**3b**) was not obtained. We next tried to separate the reaction mixture by chromatography using methanol-containing benzene as an eluent and obtained **3b** instead of **3a** (Entries 9 and 10). This shows that the addition of the alcohol occurred on silica gel chromatography. Thus it is concluded that the ethoxy group of **3a** is derived from the ethanol containing in the chloroform. The compound (**3b**) was identical with the compound by the reaction of **1** with methyl chloroformate. The reaction of **1** with chloroacetyl chloride in the absence of triethylamine gave **4a** in 45% yield (Entry 5). Treatment of **4a** with chloroketene gave **2a** in 2% yield. From the results, the following plausible mechanism is considered (Scheme 1). Reaction of the ketene on the amino group at C-8 of **1** gave **4**, and a successive reaction of a second molecule of chloroketene with **4** leads to an intermediate (**A**). Intramolecular cyclization of **A** gives **B**, and a successive elimination of amido group furnishes **2**. On the
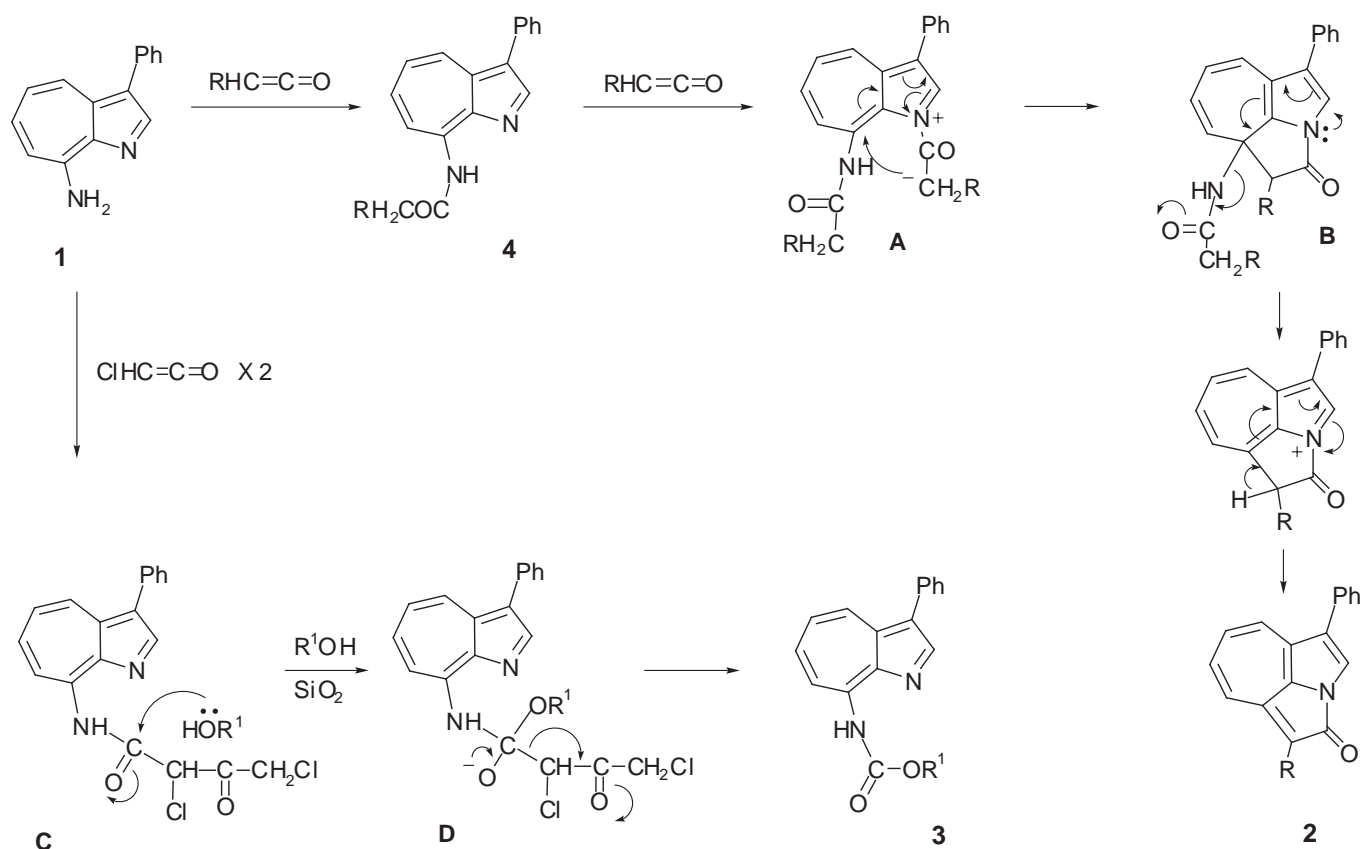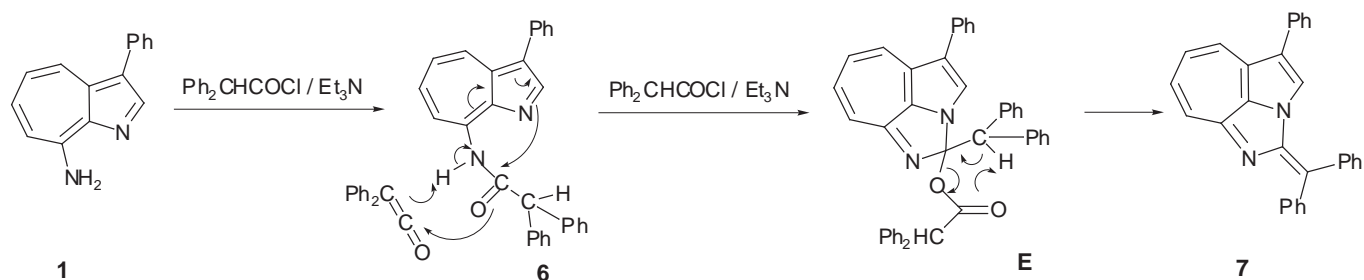

Scheme 1

other hand, the reaction of two equivalents of chloroketene with **1** gives **C**. Reaction of **C** with alcohol on silica gel and a successive elimination of 1,3-dichloro-2-propanone from **D** furnish **3**.

In the reaction of 2-amino-1-azaazulene with ketenes, the behavior of phenylketene and diphenylketene was rather different from that of chloroketene.[11] Therefore we next examined the reaction of **1** with phenylketene. Treatment of **1** with phenylketene, prepared from phenylacetyl chloride with triethylamine, in dry chloroform at 0 for 30 min gave 1,4-diphenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one (**2b**) (3%) and 8-phenylacetylamino-3-phenyl-1-azaazulene (**4b**) (88%). Further treatment of **4b** with excess phenylketene for 2 h gave **2b** in 14% yield along with recovery of **4b** (64%). The results resembled to the case of chloroketene.

Similar treatment of **1** with diphenylketene, prepared from diphenylacetyl chloride with triethylamine, gave **6** in 88% yield. Although the treatment of **6** with triethylamine did not proceeded any reaction, further treatment of **6** with excess diphenylketene caused cyclization and gave 2-(diphenylmethylene)-4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulene (**7**) in 43% yield. The compound (**7**) was analyzed as $C_{29}H_{20}N_2$ by the inspection of its MS spectrum (*m/z* 396, M$^+$) and elemental analysis. In the IR spectrum of **7**, carbonyl and NH absorptions were not observed. In the ^{1}H NMR spectrum of **7**, the seven-membered ring protons appear at δ 6.25 (m, H-7), 7.11 (d, *J* 11.0, H-5), 7.27—7.38 (m, H-6) and 7.37 (dd, *J* 12.7 and 1.4, H-8) and show a large divergence of coupling constants. These results support the structure. Large steric hindrance of diphenylketene would obstruct the formation of intermediate like **A**, and a hydrogen abstraction on amido group and a successive cyclization would be preferred to give **E**, and the elimination of the carboxylica cid furnished to **7** (Scheme 2).

Scheme 2

EXPERIMENTAL

All reactions were carried out under argon atmosphere. Melting points were measured using Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra were recorded on Bruker AVANCE 400S (400 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. IR spectra were recorded for KBr pellets on a Hitachi 270-50 infrared spectrophotometer and Nicolet FT-IR Impact 410. MS spectra were taken with LC-MS Waters Integrity System. Kieselgel 60 was used for column chromatography, and the chloroform using for the column chromatography was used a commercially available chloroform with no further purification. Dry chloroform as the reaction solvent was prepared by distillation from calcium hydride after treatment with calcium chloride and Molecular sieves 4A. Ethanol free chloroform was prepared as follows; commercially

available chloroform was treated with conc. H_2SO_4, aq. NaOH, and water, successively, and dried over calcium chloride.　Then the chloroform was distilled from phosphorous pentoxide.

Reaction of 8-amino-3-phenyl-1-azaazulene (1) with chloroketene

Typical procedure — To a solution of 8-amino-3-phenyl-1-azaazulene[12] (**1**) (0.424 g, 1.93 mmol) and triethylamine (2.400 g, 12.2 mmol) in dry chloroform (25 mL) was added dropwise over a period of 25 min chloroacetyl chloride (1.380 g, 12.2 mmol) in dry chloroform (10 mL) at 0 ℃.　After being stirred for 30 min at 0 ℃, the mixture was poured into ice-water (200 mL) and extracted with dichloromethane.　The extract was dried over sodium sulfate and evaporated.　The residue was chromatographed with chloroform to give 1-chloro-4-phenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one (**2a**) (0.007 g, 1%), ethyl (3-phenyl-1-azaazulen-8-yl)aminocarboxylate (**3a**) (0.048 g, 9%), 8-chloroacetylamino-3-phenyl-1-azaazulene (**4a**) (0.017 g, 3%) and 8-amino-3-phenyl-1-azaazulene hydrochloride (**5**) (0.017 g, 3%).

The results of the reaction of **1** with chloroketene and phenylketene were listed in Table 1.

2a: Brown needles (from ethanol—dichloromethane), mp 168—171 ℃; δ_H 6.99 (1H, dd, *J* 10.7 and 9.2), 7.31 (1H, dd, *J* 10.8 and 9.2), 7.36 (1H, s), 7.40—7.50 (6H, m) and 7.55 (1H, d, *J* 10.8); ν_{max} / cm⁻¹ 1731 and 1723 (C=O); *m/z* (rel. intensity) 281 ($C_{17}H_{10}NO^{37}Cl$, M⁺, 33), 279 ($C_{17}H_{10}NO^{35}Cl$, M⁺, 100), 245 (6), 216 (20), 214 (12), and 189 (12).　*Anal*.　Calcd for $C_{17}H_{10}NOCl$: C, 73.00; H, 3.60; N, 5.01.　Found: C, 73.24; H, 3.53; N, 5.31.

3a: Red needles (from hexane—dichloromethane), mp 149—151 ℃; δ_H 1.39 (3H, t, *J* 7.1), 4.35 (2H, q, *J* 7.1), 7.35—7.65 (6H, m), 7.92 (1H, dd, *J* 10.4 and 9.9), 8.44 (1H, s), 8.60 (1H, d, *J* 9.9), 9.55 (1H, d, *J* 11.5); ν_{max} / cm⁻¹ 3299 (NH) and 1731 (C=O); *m/z* (rel. intensity) 292 (M⁺, 68), 263 (3), 247 (87), 246 (100), 220 (69), 204 (11), 193 (64), and 165 (24).　*Anal*.　Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58.　Found: C, 73.84; H, 5.44; N, 9.82.

3b: Red needles (from hexane—dichloromethane), mp 161—162 ℃; δ_H 3.92 (3H, s), 7.35—7.63 (6H, m), 7.94 (1H, dd, *J* 10.1 and 9.9), 8.45 (1H, s), 8.61 (1H, d, *J* 10.1), 9.04 (1H, d, *J* 11.5); ν_{max} / cm⁻¹ 3300 (NH) and 1730 (C=O); *m/z* (rel. intensity) 278 (M⁺, 85), 247 (100), 246 (88), 220 (6), 204 (4), 193 (18), and 165 (8).　*Anal*.　Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07.　Found: C, 73.44; H, 5.18; N, 9.96.

4a: Red brown oil; δ_H 4.76 (2H, s), 7.12 (1H, dd, *J* 10.6, 8.9), 7.40—7.58 (6H, m), 7.66 (1H, s), 7.72 (1H, d, *J* 12.0), 8.03 (1H, d, *J* 10.6); ν_{max} / cm⁻¹ (neat) 3106 (NH), 1714 and 1698 (C=O); *m/z* (rel. intensity) 298 ($C_{17}H_{13}N_2O^{37}Cl$, M⁺, 7), 296 ($C_{17}H_{13}N_2O^{35}Cl$, M⁺, 21), 261 (7), 260 (12), 248 (56), 247 (100), 232 (14), 220 (24), 205 (17), 204 (18), 193 (30), and 165 (19).　*Anal*.　Calcd for $C_{17}H_{13}N_2OCl$: C, 68.81; H, 4.42; N, 9.44.　Found: C, 68.73; H, 4.33; N, 9.71.

Reaction of 8-amino-3-phenyl-1-azaazulene (1) with ethyl chloroformate

A solution of 8-amino-3-phenyl-1-azaazulene (**1**) (0.063 g, 0.286 mmol) and ethyl chloroformate (0.058 g, 0.534 mmol) in ethanol (10 mL) was refluxed for 40 min, then evaporated.　To the residue water was added, and the mixture was neutralized with sodium hydrogencarbonate and extracted with chloroform.　The extract was dried over sodium sulfate and evaporated.　The residue was chromatographed with chloroform

to give **3a** (0.036 g, 45%) and recovered **1** (0.034 g, 54%)
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Reaction of 8-amino-3-phenyl-1-azaazulene (1) with methyl chloroformate

To a solution of 8-amino-3-phenyl-1-azaazulene (**1**) (0.110 g, 0.50 mmol) in dry chloroform (10 mL) was added methyl chloroformate (0.102 g, 1.02 mmol) in dry chloroform (5 mL) dropwise over a period of 10 min at 0   and was stirred at 0   for 1 h and poured into ice-water (200 mL).   The mixture was neutralized with sodium hydrogencarbonate and extracted with dichloromethane.   The extract was dried over sodium sulfate and evaporated.   The residue was chromatographed with chloroform to give **3b** (0.041 g, 29.5%) and recovered **1** (0.060 g, 55%).

Reaction of 8-amino-3-phenyl-1-azaazulene (1) with chloroacetyl chloride

To a solution of 8-amino-3-phenyl-1-azaazulene (**1**) (0.221 g, 1.00 mmol) in dry chloroform (10 mL) was added chloroacetyl chloride (0.658 g, 5.83 mmol) in dry chloroform (10 mL) dropwise over a period of 10 min at 0   .   After being stirred for 1 h at rt, the mixture was worked up, as described above, to give **4** (0.135 g, 45%) and recovered **1** (0.034 g, 15%).

Reaction of 8-chloroacetylamino-3-phenyl-1-azaazulene (4a) with chloroketene

To a solution of 8-chloroacetylamino-3-phenyl-1-azaazulene (**4a**) (0.092 g, 0.31 mmol) and triethylamine (0.188 g, 1.86 mmol) in dry chloroform (10 mL) was added dropwise over a period of 15 min chloroacetyl chloride (1.380 g, 12.2 mmol) in dry chloroform (10 mL) at 0   .   After being stirred for 30 min at 0   , the mixture was poured into ice-water (200 mL) and extracted with dichloromethane.   The extract was dried over sodium sulfate and evaporated.   The residue was chromatographed with chloroform to give 1-chloro-4-phenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one (**2a**) (0.002 g, 2%), and 8-chloroacetylamino-3-phenyl-1-azaazulene (**4a**) (0.012 g, 13%).

Reaction of 8-amino-3-phenyl-1-azaazulene (1) with phenylketene

To a solution of 8-amino-3-phenyl-1-azaazulene (**1**) (0.110 g, 0.50 mmol) and triethylamine (0.607 g, 6.0 mmol) in dry chloroform (10 mL) was added dropwise over a period of 20 min phenylacetyl chloride (0.410 g, 3.0 mmol) in dry chloroform (5 mL) at 0   .   After being stirred for 30 min under at 0   , the mixture was poured into ice-water (200 mL) and extracted with dichloromethane.   The extract was dried over sodium sulfate and evaporated.   The residue was chromatographed with chloroform to give 1,4-diphenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one (**2b**) (0.005 g, 3%) and 8-phenylacetylamino-3-phenyl-1-azaazulene (**4b**) (0.148 g, 88%).

2b: Purple needles (from hexane—ethyl acetate), mp 241—242   ; δ_H 6.95 (1H, dd, J 10.6 and 9.1), 7.22 (1H, dd, J 11.0 and 9.1), 7.31 (1H, t, J 8.1), 7.41—7.55 (9H, m), 7.71 (1H, dd, J 8.1 and 1.8), and 7.73 (1H, d, J 11.0); δ_C 112.6, 119.2, 124.7, 127.2, 128.2, 128.5, 129.0, 129.4, 130.9, 131.6, 132.9, 133.0, 136.4, 136.5, 142.7, and 165.0; ν_{max} / cm^{-1} 1694 (C=O); m/z (rel. intensity) 321 (M$^+$, 100), 320 (90), 292 (29), 291 (27), 290 (20), 289 (20), 263 (7), and 145 (16).   *Anal.*   Calcd for $C_{23}H_{15}NO$: C, 85.96; H, 4.70; N, 4.36.   Found: C, 85.75; H, 4.46; N, 4.50.

4b: Anorange powder (from hexane—dichloromethane), mp 102—103 ; δ_H 3.98 (2H, s), 7.35—7.58 (11H, m), 7.93 (1H, dd, J 11.4 and 9.7), 8.43 (1H, s), 8.62 (1H, d, J 9.8), 9.34 (1H, d, J 11.4), and 9.7—10.5 (1H, br); ν_{max} / cm^{-1} 3267 (NH) and 1698 (C=O); m/z (rel. intensity) 338 (M$^+$, 3), 247 (100), 220 (4), 193 (7), and 165 (3). *Anal.* Calcd for $C_{23}H_{18}N_2O$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.76; H, 5.46; N, 8.18.

Reaction of 8-phenylacetylamino-3-phenyl-1-azaazulene (4b) with phenylketene

To a solution of 8-phenylacetylamino-3-phenyl-1-azaazulene (**4b**) (0.169 g, 0.50 mmol) and triethylamine (0.607 g, 6.0 mmol) in dry chloroform (10 mL) was added dropwise over a period of 20 min phenylacetyl chloride (0.464 g, 3.0 mmol) in dry chloroform (5 mL) at 0 . After being stirred for 2 h at 0 , the mixture was poured into ice-water (200 mL) and extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated. The residue was chromatographed with hexane-ethyl acetate to give 1,4-diphenyl-2,2a-dihydro-2a-azacyclopent[*cd*]azulen-2-one (**2b**) (0.023 g, 14%), and recovered **4b** (0.109 g, 64.5%).

Reaction of 8-amino-3-phenyl-1-azaazulene (1) with diphenylketene

To a solution of 8-amino-3-phenyl-1-azaazulene (**1**) (0.110 g, 0.50 mmol) and triethylamine (0.607 g, 6.0 mmol) in dry chloroform (10 mL) was added dropwise over a period of 20 min diphenylacetyl chloride (0.692 g, 3.0 mmol) in dry chloroform (10 mL) at 0 . After being stirred for 30 min at 0 , the mixture was poured into ice-water (200 mL) and extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated. The residue was chromatographed with chloroform to give 8-diphenylacetylamino-3-phenyl-1-azaazulene (**6**) (0.182 g, 88%).

6: Dark red prisms (from ethyl acetate), mp 149—150 ; δ_H 5.36 (2H, s), 7.32—7.57 (16H, m), 7.93 (1H, dd, J 11.4 and 9.6), 8.41 (1H, s), 8.62 (1H, d, J 9.8), 9.43 (1H, d, J 11.4); ν_{max} / cm^{-1} 3266 (NH), 1709 (C=O); m/z (rel. intensity) 414 (M$^+$, 6), 246 (98), 245 (100), 219 (17), 218 (13), 202 (9), 193 (17), 192 (13), 166 (30), 165 (30), and 152 (14). *Anal.* Calcd for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 84.12; H, 5.33; N, 6.71.

Reaction of 8-diphenylamino-3-phenyl-1-azaazulene (6) with diphenylketene

To a solution of 8-diphenylamino-3-phenyl-1-azaazulene (**6**) (0.166 g, 0.40 mmol) and triethylamine (0.503 g, 4.8 mmol) in dry chloroform (10 mL) was added dropwise over a period of 15 min diphenylacetyl chloride (0.558 g, 2.4 mmol) in dry chloroform (5 mL) at 0 . After being stirred for 30 min at 0 , the mixture was poured into ice-water (200 mL) and extracted with dichloromethane. The extract was dried over sodium sulfonate and evaporated. The residue was chromatographed with hexane—ethyl acetate (10 : 1) to give **6** (0.016 g, 10%) and 2-diphenylmethylene-4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulene (**7**) (0.068 g, 43%).

7: Brown needles (from hexane—ethyl acetate), mp 218—219 ; δ_H 5.73 (1H, s), 6.87 (2H, m), 7.11 (1H, d, J 11.0), 7.19 (2H, dd, J 8.0 and 1.2), 7.21 (1H, tdd, J 7.3, 1.2, and 1.0), 7.27—7.38 (7H, m), 7.37 (1H, dd, J 12.7 and 1.4), 7.46 (1H, tdd, J 7.4, 1.3 and 1.0), 7.56 (2H, ddd, J 8.0, 7.6 and 1.5), 7.70 (2H, dd, J

8.3 and 1.0); m/z (rel. intensity) 396 (M$^+$, 100), 319 (16), 287 (15), 176 (20), 165 (39), and 151 (22). *Anal*. Calcd for $C_{29}H_{20}N_2$: C, 87.85; H, 5.08; N, 7.07. Found: C, 87.67; H, 5.31; N, 6.78.

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