# SYNTHESIS AND SOME REACTIONS OF ETHYL (2-AlKYL-IMINO-1,2-DIHYDRO-1-AZAAZULEN-1-YL)ACETATES†

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**Abstract** — Ethyl (2-alkylimino-1,2-dihydro-1-azaazulen-1-yl)acetates (**3**) were synthesized from 2-alkylamino-1-ethoxycarbonylmethyl-1-azaazulenium salts, which were produced from 2-alkylamino-1-azaazulenes with ethyl bromoacetate. Reaction of **3** with acid anhydrides gave the mesoionic *anhydro*-3-acyl-1-alkyl-2-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide. Polar cycloaddition of **3** with methyl propiolate gave methyl 2-alkyl-1-oxo-1,2-dihydro-2,9b-diazaindeno[3,3a,4,5-*bcd*]azulene-8-carboxylate and 3-ethyl 5-methyl 2-alkylamino-2a-azabenz[*cd*]azulene-3,5-dicarboxylate.

## INTRODUCTION

Heteroaromatic *N*-ylides,[1] which possess an azomethine ylide moiety,[2] are highly useful synthetic intermediates for preparation of fused nitrogen-bridged heterocycles, as well as heterocyclic *N*-imines.[3] Recently we reported the synthesis and reactions of 1-amino-2-imino-1,2-dihydro-1-azaazulene,[4] where some interesting fused heterocycles were obtained. Previously, we also reported that the reactions of 2-amino-1-azaazulenes with $\alpha$-bromoacetophenone and potassium carbonate gave 1,3a-diazacyclopent[*a*]azulene systems.[5] As a continuation of our studies on the preparation of new azaazulene-fused heterocycles,[6] we are interested in the synthesis and reaction of ethyl (2-alkylimino-1,2-dihydro-1-azaazulen-1-yl)acetate, which could act as a polar species[7] in the presence of a base.

## RESULTS AND DISCUSSION

It is known that 1-azaazulenes were alkylated at N-1 by the treatment with alkyl halide.[6] Therefore, we treated 2-alkylamino-1-azaazulenes (**1a**, **b**) with ethyl bromoacetate and obtained 2-alkylamino-1-ethoxycarbonylmethyl-1-azaazulenium salts (**2a**, **b**) in excellent yields. Treatment of the salts with potassium carbonate in acetonitrile at room temperature gave ethyl (2-alkylimino-1,2-dihydro-1-azaazulen-

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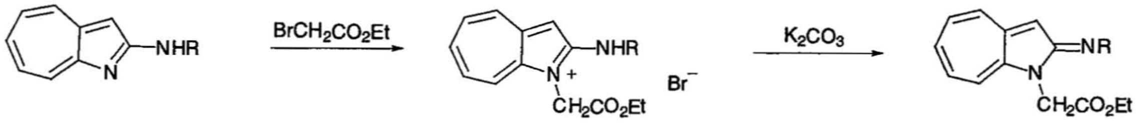
† Dedicated to Professor James P. Kutney on occasion of his 70th birthday.

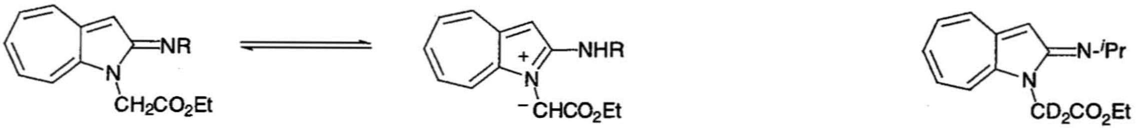
1-yl)acetates (**3a**, **b**), quantitatively. It is known that the hydrogen adjacent to the imine nitrogen of α-amino ester imine is highly acidic and the migration of the proton furnishes azomethine ylide.[2] Therefore it is considered that compound (**3**) would tautomerise to the ylide (**4**); indeed the methylene protons of **3** were acidic and the treatment of **3a** with deuterium oxide in the presence of potassium carbonate gave **3c**. In the IR spectrum of **3a**, the carbonyl signal appeared at 1736 $cm^{-1}$. In its $^1H$ NMR spectrum, a methylene signal appeared at 4.67 (2H, s), and 1H singlet at $\delta$ 6.00 (1H, s) and the seven-membered protons at $\delta$ 5.84 (1H, d, $J$ 9.1), 6.18 (1H, dd, $J$ 11.0 and 8.3), 6.51 (1H, dd, $J$ 11.2 and 8.3), 6.57 (1H, dd, $J$ 11.0 and 9.1), and 6.82 (1H, d, $J$ 11.2) were seen together with ethyl ester and isopropyl signals. Its electronic spectra resembled to 1-methyl-1-azaazulen-2(1*H*)-one. From these results, we concluded that the compound (**3a**) exist mainly in the imino-form.



**1a** : R = *iso*-Pr
**1b** : R = Et

**2a** : R = *iso*-Pr
**2b** : R = Et

**3a** : R = *iso*-Pr
**3b** : R = Et



**3**

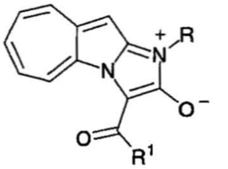
**4**

**3c**

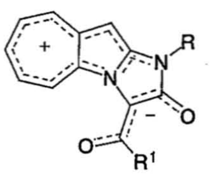
Treatment of **3a** with acetic anhydride in acetonitrile under reflux for 4 days gave the dark red compound (**5a**) in 70% yield. The presence of a base accelerated the reaction; when the reaction was performed in the presence of potassium carbonate for 20 h under reflux, **5a** was obtained in 95% yield. These results suggest that in the former acetic acid would react with the ylide (**4**), and in the latter acetic acid would react with the anion **6** at first; the reaction proceeded *via* a polar cyclization.[7] The compound (**5a**) was analyzed as $C_{16}H_{16}N_2O_2 \cdot 2H_2O$ from its elemental analysis. In the $^1H$ NMR spectrum of **5a**, the protons of the seven-membered ring resonated at rather low field, at $\delta$ 7.53 (1H, dd, $J$ 10.0 and 9.8), 7.67 (1H, t, $J$ 10.0), 7.75 (1H, dd, 10.0 and 9.8), 8.23 (1H, d, $J$ 10.0), and 10.97 (1H, d, $J$ 10.0); this showed that the seven-membered ring had a cationic tropylium character. The IR spectrum showed the signals at 1662 and 1616 $cm^{-1}$ assignable to carbonyl group. From the result, the structure of **5a** was deduced as *anhydro*-3-acetyl-1-isopropyl-2-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide. Fyrthermore, its precise structure was confirmed by X-Ray structure analysis. The ORTEP drawing[8] of **5a** is shown in Figure 1, and the bondlengths are shown in Figure 2. The bondlengths of the seven-membered ring did not show the bond-alternation. The bondlengths of the two carbonyl groups are equivalent and slightly lengthened (1.237 and 1.245 Å), and the bond of C(2)—C(15) is rather short as $sp^2$—$sp^2$ single bond (1.402 Å). These results showed that compound (**5a**) have a mesoionic structure as **5A**.

In the similar manner, the reaction of **3a** and **3b** with benzoic anhydride gave the corresponding mesoionic compounds (**5c**) (94%) and (**5d**) (90%), respectively.

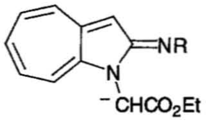
Treatment of **3b** with succinic anhydride in the presence of potassium carbonate gave **7** in the 45% yield. In the $^1$H NMR spectrum of **7**, the hydrogen bonding proton was observed at $\delta$ 12.00.



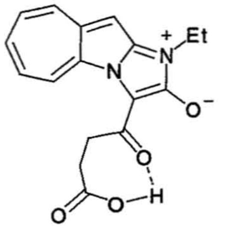
**5a** : R = *iso*-Pr, $R^1$ = Me
**5b** : R = Et, $R^1$ = Me
**5c** : R = *iso*-Pr, $R^1$ = Ph
**5d** : R = Et, $R^1$ = Ph



**5A**



**6**



**7**

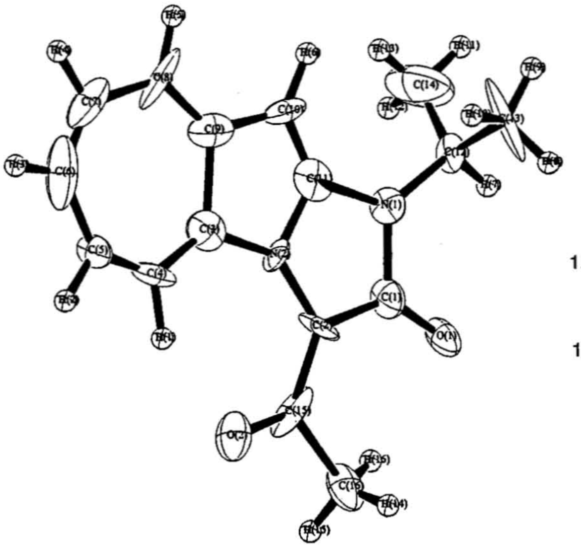


Figure 1. An ORTEP drawing of **5a** with thermal ellipsoids (50% probability).

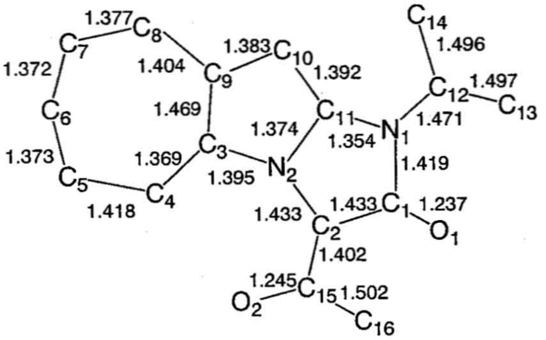


Figure 2. The bondlengths of **5a**.

As compound (**3**) was reacted as a dipolar species (in the absence of a base) or a polar species (in the presence of a base) as above, we next examined the cycloaddition of **3**.

Treatment of **3a** with dimethyl acetyenedicarboxylate under reflux gave a complex mixture and no distinct product was isolated. Reaction of **3a** with methyl plopiolate (MP) for 16 days in refluxing dichloromethane gave two cycloadducts (**8a**) (2%) and (**9a**) (10%), and the reaction was accelerated in the acetonitrile (Table 1). The structures of these compounds were deduced from the inspections of spectroscopic data as well as elemental analyses and MS spectral data..

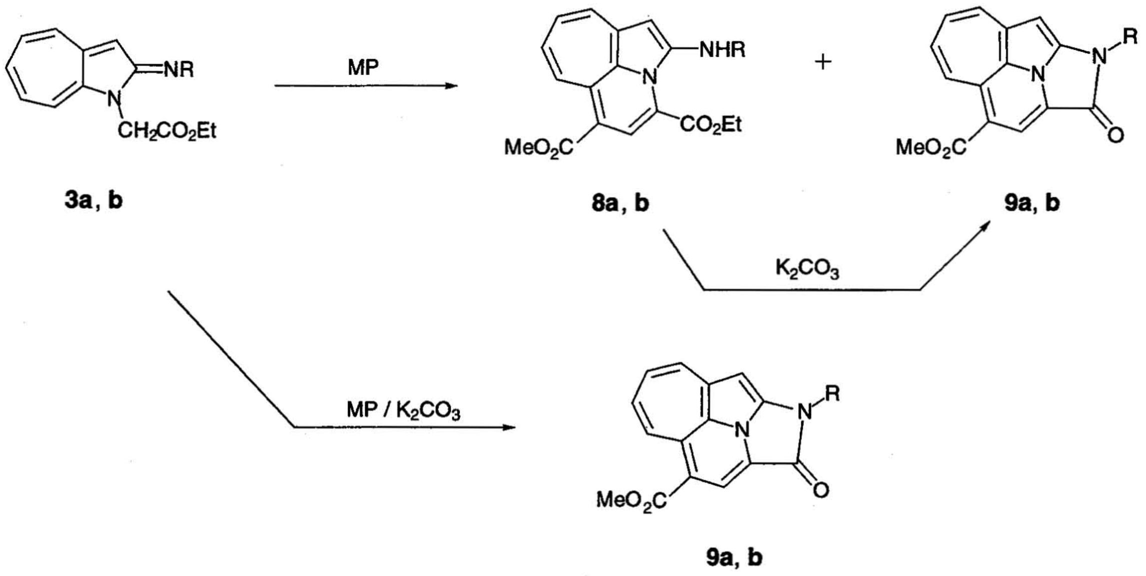


Table 1. Reactions of **3a** and **3b** with methyl propiolate (MP).

| Run | Compounds | Reaction conditions |  |  | Products (yield / %) |  |
|---|---|---|---|---|---|---|
|  |  | ratio (**3** : MP : $K_2CO_3$) | solvent | reaction time |  |  |
| 1 | **3a** | 1 : 3 : – | $CH_2Cl_2$ | 16 d | **8a**(2) | **9a**(10) |
| 2 | **3a** | 1 : 3 : – | $CHCl_3$ | 12 d | **8a**(3) | **9a**(8) |
| 3 | **3a** | 1 : 3 : – | MeCN | 3 d | **8a**(4) | **9a**(8) |
| 4 | **3a** | 1 : 3 : 1 | MeCN | 3 d | **8a**(–) | **9a**(3) |
| 5 | **3b** | 1 : 3 : – | MeCN | 8 h | **8b**(23) | **9b**(–) |
| 6 | **3b** | 1 : 3 : 1 | MeCN | 4 h | **8b**(4) | **9b**(3) |
| 7 | **3b** | 1 : 3 : 1 | MeCN | 8 h | **8b**(1) | **9b**(7) |
| 8 | **3b** | 1 : 3 : 1 | MeCN | 16 h | **8b**(–) | **9b**(11) |

The treatment of **3b** with MP gave similar results and **8b** and **9b** were obtained (Table 1). From the above results, it is considered that **8** are produced at first and then converted to **9** by the base. Indeed the compound (**8a**) was quantitatively converted to **9a** by the treatment with potassium carbonate in refluxing acetonitrile for 24 h.

## EXPERIMENTAL

Mps are measured using Yanagimoto micro-melting apparatus and uncorrected. $^1$H NMR spectra (400 MHz) and $^{13}$C NMR spectra (100.6 MHz) were recorded on Bruker AVANCE 400S using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. Electronic spectra were taken with Shimadzu 1600PC spectrophotometer. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410. MSspectra were taken with on an LC-MS Waters Integrity System 2690. Elemental analyses were taken with Perkin Elmer 2400II. Kieselgel 60 and was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

### Reaction of 2-alkylamino-1-azaazulene (1) with ethyl bromoacetate

*Typical procedure* — A solution of 2-isopropylamino-1-azaazulene (**1a**) (1.896 g, 10.2 mmol) with ethyl bromoacetate (3.410 g, 20.4 mmol) in dry acetonitrile (90 mL) was refluxed for 24 h, then evaporated. The residue was chromatographed. Elution with chloroform gave **1a** (0.038 g, 2%), and elution with acetone gave 1-(ethoxycarbonylmethyl)-2-isopropylamino-1-azaazulenium bromide (**2a**) as yellow prisms (3.060 g, 85 %).

In a similar manner, the reaction of 2-ethylamino-1-azaazulene (**1a**) (1.963 g, 11.4 mmol) with ethyl bromoacetate (4.770 g, 28.6 mmol) in dry acetonitrile (140 mL) gave **1b** (0.075 g, 3%) and **2b** (3.495 g, 90%).

**2a**: Yellow prisms (from dichloromethane—benzene), mp 192—195 ℃, $\delta_H$ 1.32 (3H, t, *J* 7.2), 1.59 (6H, d, *J* 6.6), 3.97 (1H, dsep, *J* 7.8 and 6.6), 4.29 (2H, q, *J* 7.2), 6.05 (1H, br s), 6.47 (1H, s), 7.41—7.75 (4H, m), 7.88 (1H, d, *J* 10.6), and 10.07 (1H, br d, *J* 7.8); $\delta_C$ 14.5, 22.6, 47.3, 50.0, 63.1, 97.4, 120.1, 132.3, 133.9, 134.9, 135.7, 146.3, 147.7, 158.6, and 167.0; $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 203 (4.32), 216 (4.29), 237 (4.18), 270 (4.45), 295 (4.27), and 422 (4.14); $\nu_{max}$ / cm$^{-1}$ 3164 (NH) and 1744 (C=O). *Anal.* Calcd for $C_{16}H_{21}N_2O_2Br$: C, 54.40; H, 5.99; N, 7.93. Found: C, 54.26; H, 5.99; N, 7.80.

**2b**: Yellow prisms (from dichloromethane—hexane), mp 192—196 ℃, $\delta_H$ 1.35 (3H, t, *J* 7.1), 1.47 (3H, t, *J* 7.3), 3.64 (2H, m), 4.30 (2H, q, *J* 7.1), 5.91 (2H, s), 6.46 (1H, br s), 7.44—7.55 (4H, m), 7.90 (1H, d, *J* 10.7), and 10.49 (1H, br); $\delta_C$ 14.5, 14.9, 40.4, 46.9, 63.2, 97.0, 120.1, 132.4, 133.9, 135.0, 135.8, 146.2, 147.8, 159.2, and 166.8; $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 203 (4.31), 216 (4.28), 237 (4.17), 270 (4.44), 294 (4.26), and 421 (4.12); $\nu_{max}$ / cm$^{-1}$ 3167 (NH) and 1743 (C=O). *Anal.* Calcd for $C_{15}H_{19}N_2O_2Br$: C, 53.11; H, 5.65; N, 8.26. Found: C, 53.05; H, 5.74; N, 8.12.

### Synthesis of ethyl (2-alkylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3)

*Typical procedure* — A mixture of **2a** (2.310 g, 6.54 mmol) and potassium carbonate (2.339 g, 16.9 mmol) in dry acetonitrile (200 mL) was stirred for 24 h at rt, then filtered. The filtrate was evaporated and the residue was dissolved in hexane. The solution was washed with water, dried over sodium sulfate, and evaporated. Recrystallization of the residue from hexane gave ethyl (2-isopropylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (**3a**) (1.513 g, 85%) as red needles.

Similarly, the treatment of **2b** with potassium carbonate gave **3b** in 91% yield.

**3a**: Red needles (from hexane), mp 98—99 ℃; $\delta_H$ 1.13 (6H, d, *J* 6.3), 1.26 (3H, t, *J* 7.1), 3.60 (1H, sep., *J* 6.3), 4.20 (2H, q, *J* 7.1), 4.67 (2H, s), 5.84 (1H, d, *J* 9.1), 6.00 (1H, s), 6.18 (1H, dd, *J* 11.0 and 8.3), 6.51 (1H, dd, *J* 11.2 and 8.0), 6.57 (1H, dd, *J* 11.0 and 9.1), and 6.82 (1H, d, *J* 11.2); $\delta_C$ 14.6, 25.1, 42.1, 50.9, 61.7, 101.3, 105.0, 124.2, 126.3, 131.9, 145.0, 158.1, and 169.0; $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 263 (4.43), 304 (4.01), 407 (4.14), 430 (4.01, sh), 481 (3.24), 518 (2.95), and 560 (2.19, sh); $\nu_{max}$ / cm$^{-1}$ 1736 (C=O); *m/z* (rel intensity) 272 (M$^+$, 11), 257 (100), 243 (17), 229 (42), 185 (18), 169 (9), and 130(11). *Anal.* Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.57; H, 7.94; N, 10.15.

**3b**: Red needles (from hexane), mp 122—123 ℃; $\delta_H$ 1.19 (3H, t, *J* 7.3), 1.27 (3H, t, *J* 7.2), 3.38 (2H, q, *J* 7.3), 4.21 (2H, q, *J* 7.2), 4.69 (2H, s), 5.90 (1H, d, *J* 9.0), 6.03 (1H, s), 6.23 (1H, dd, *J* 11.0 and 8.4), 6.56 (1H, dd, *J* 11.2 and 8.4), 6.61 (1H, dd, *J* 11.0 and 9.0), and 6.87 (1H, d, *J* 11.2); $\delta_C$ 14.6, 17.2, 42.0, 45.4, 61.8, 100.9, 105.4, 124.5, 126.5, 132.0, 132.2, 145.0, 149.4, 159.6, and 168.8; $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 264 (4.45), 305 (4.03), 408 (4.16), 430 (4.03), 479 (3.33), 516 (3.05), and 556 (2.54); $\nu_{max}$ / cm$^{-1}$ 1737 (C=O); *m/z* (rel intensity) 258 (M$^+$, 59), 243 (100), 229 (16), 214 (70), 185 (24), 171 (17), 157 (11), and 130 (38). *Anal.* Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.82; H, 7.08; N, 10.75.

### Reaction of ethyl (2-isopropylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3a) with acetic anhydride

a) To the mixture of **3a** (0.134 g, 0.49 mmol) and potassium carbonate (0.075 g, 0.55 mmol) in acetonitrile (30 mL) was added acetic anhydride (0.169 g, 1.66 mmol), and the mixture was refluxed for 20 h. The insoluble material was filtered off, and the filtrate was evaporated. The residue was chromatographed on alumina with chloroform, and *anhydro*-3-acetyl-2-hydroxy-1-isopropyl-1,3a-diazacyclopent[*a*]azulenium hydroxide (**5a**) (0.127 g, 95%) was obtained.

b) A solution of **3a** (0.120 g, 0.44 mmol) and acetic anhydride (0.169 g, 1.66 mmol) in acetonitrile (30 mL) was refluxed for 4 days, then evaporated. Chromatography of the residue on alumina with chloroform gave **5a** (0.083 g, 70%)

**5a**: Dark red prisms (from benzene), mp 211—212 ℃; $\delta_H$ 1.57 (6H, d, *J* 7.0), 5.00 (1H, sep., *J* 7.0), 6.83 (1H, s), 7.53 (1H, dd, *J* 10.0 and 9.8), 7.67 (1H, t, *J* 10.0), 7.75 (1H, dd, *J* 10.0 and 9.8), 8.23 (1H, d, *J* 10.0), and 10.97 (1H, d, *J* 10.0); $\delta_C$ 19.5, 25.7, 42.2, 90.3, 105.5, 128.3, 129.2, 130.5, 133.5, 136.2, 142.6, 142.7, 161.3, and 180.4; $\nu_{max}$ / cm$^{-1}$ 1662, 1616 (C=O); $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 230 (4.36), 246 (4.35), 268 (4.43), 285 (4.11), 295 (4.10), 359 (4.55), and 444 (3.62); *m/z* (rel intensity) 268 (M$^+$, 100), 253 (9), 226 (72), 211 (66), 199 (10), 183 (22), 155 (38) and 128 (22). *Anal.* Calcd for $C_{16}H_{16}N_2O_2 \cdot 2H_2O$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.44; H, 6.63; N, 9.24.

### Reaction of ethyl (2-ethylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3b) with acetic anhydride

To a mixture of **3b** (0.150 g, 0.58 mmol) and potassium carbonate (0.088 g, 0.64 mmol) in acetonitrile

(30 mL) was added acetic anhydride (0.191 g, 1.87 mmol), and the mixture was refluxed for 1 h. The insoluble material was filtered off, and the filtrate was evaporated. The residue was chromatographed on alumina with chloroform, and **5b** (0.138 g, 94%) was obtained.

**5b**: Dark red needles (from benzene), mp 198—199 ℃; $\delta_H$ 1.46 (3H, t, *J* 7.3), 2.68 (3H, s), 4.11 (2H, q, *J* 7.3), 6.78 (1H, s), 7.54 (1H, dd, *J* 10.3 and 9.8), 7.69 (1H, dd, *J* 10.3 and 9.1), 7.77 (1H, dd, *J* 10.3 and 9.1), 8.25 (1H, d, *J* 10.3), and 10.99 (1H, d, *J* 9.8); $\delta_C$ 14.3, 31.4 36.3 90.5, 107.5, 130.0, 132.3, 135.0, 138.0, 138.5, 144.2, 145.5, 163.0, and 181.9; $\nu_{max}$ / $cm^{-1}$ 1661, 1627 (C=O and C=N),; $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 230 (4.36), 247 (4.34), 267 (4.42), 285 (4.10), 295 (4.10), 359 (4.55), and 443 (3.63). *Anal.* Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.52; H, 5.78; N, 10.88.

### Reaction of ethyl (2-isopropylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3a) with benzoic anhydride

To the mixture of **3a** (0.139 g, 0.51 mmol) and potassium carbonate (0.088 g, 0.64 mmol) in acetonitrile (30 mL) was added benzoic anhydride (0.347 g, 1.53 mmol), and the mixture was refluxed for 4 h. The insoluble material was filtered off, and the filtrate was evaporated. The residue was chromatographed on alumina with chloroform, and **5c** (0.158 g, 94%) was obtained.

**5c**: Dark violet needles (from dichloromethane—hexane), mp 179—180 ℃; $\delta_H$ 1.53 (6H, d, *J* 7.0), 4.76 (1H, sep, *J* 7.0), 6.85 (1H, s), 7.36—7.48 (4H, m), 7.59 (1H, dd, *J* 10.0 and 9.3), 7.70 (1H, t, *J* 10.0), 7.78 (1H, dd, *J* 10.0 and 9.3), 8.28 (1H, d, *J* 10.0), and 10.42 (1H, d, *J* 10.0); $\delta_C$ 21.1, 43.8, 92.0, 106.3, 127.9, 129.3, 130.1, 130.7, 131.4, 134.8, 137.6, 137.8, 140.7, 145.0, 145.6, 162.3, and 180.5; $\nu_{max}$ / $cm^{-1}$ 1676 and 1618 (C=O); $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 230 (4.52), 274 (4.21), 366 (4.48), and 448 (3.77); *m/z* (rel intensity) 330 ($M^+$, 100), 315 (8), 287 (100), 271 (12), 259 (16), 245 (15), 231 (17), 185 (20), 155 (17), 128 (14), 105 (65), and 77 (57). *Anal.* Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.12; H, 5.58; N, 8.33.

### Reaction of ethyl (2-ethylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3b) with benzoic anhydride

To the mixture of **3b** (0.131 g, 0.51 mmol) and potassium carbonate (0.074 g, 0.54 mmol) in acetonitrile (30 mL) was added benzoic anhydride (0.141 g, 0.623 mmol), and the mixture was refluxed for 4 h. The insoluble material was filtered off, and the filtrate was evaporated. The residue was chromatographed on alumina with chloroform, and **5d** (0.145 g, 90%) was obtained.

**5d**: Black prisms (from dichloromethane-hexane), mp 252—253 ℃; $\delta_H$ 1.41 (3H, d, *J* 7.3), 4.03 (2H, q, *J* 7.3), 6.80 (1H, s), 7.25—7.48 (2H, m), 7.60 (1H, dd, *J* 10.0 and 9.4), 7.72 (1H, dd, *J* 10.0 and 9.8), 7.80 (1H, t, *J* 10.0), 7.84—7.86 (3H, m), 8.29 (1H, d, *J* 10.0), and 10.49 (1H, d, *J* 10.0); $\delta_C$ 14.2, 36.3, 90.6, 106.8, 127.9, 129.3, 130.2, 130.7, 131.4, 135.0, 137.9, 138.1, 140.4, 144.9, 146.8, 162.4, and 180.4; $\nu_{max}$ / $cm^{-1}$ 1679 and 1622 (C=O); $\lambda_{max}$ (MeCN) nm (log $\varepsilon$) 230 (4.50), 274 (4.23), 365 (4.46), and 447 (3.76). *Anal.* Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.77; H, 5.25; N, 8.68.

### Reaction of ethyl (2-ethylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3b) with succinic anhydride

To a mixture of **3b** (0.134 g, 0.52 mmol) and potassium carbonate (0.077 g, 0.56 mmol) in acetonitrile (30 mL) was added succinic anhydride (0.166 g, 1.70 mmol), and the mixture was refluxed for 3.5 h, then the solvent was evaporated. The residue was washed with water, then recrystallized from chloroform to give **7** (0.073 g, 45%).

**7**: Dark brown prisms (from chloroform), mp 187 ℃ (decomp); $\delta_H$ (DMSO-$d_6$) 1.33 (3H, t, *J* 6.9), 2.55 (2H, t, *J* 6.8), 3.14 (2H, t, *J* 6.8), 4.03 (2H, q, *J* 6.9), 7.39 (1H, s), 7.70 (1H, dd, *J* 10.1 and 9.9), 7.78 (1H, dd, *J* 10.3 and 9.9), 7.91 (1H, dd, *J* 10.3 and 9.8), 8.23 (1H, d, *J* 10.1), 10.76 (1H, d, *J* 9.9), and 12.00 (1H, s); $\delta_C$ (DMSO-$d_6$) 14.0, 29.1, 33.2, 36.0, 92.0, 105.7, 129.4, 130.7, 131.4, 135.8, 137.5, 138.6, 143.8, 145.6, 162.0, 174.9, and 180.3; $\nu_{max}$ / cm$^{-1}$ 3104 (OH), 1699, 1656, 1625 (C=O). *Anal.* Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.46; H, 5.48; N, 8.78.

### Reaction of ethyl (2-isopropylimino-1,2-dihydro-1-azaazulen-1-yl)acetate (3a) with methyl propiolate (MP)

*Typical procedure* — a) A mixture of **3a** (0.272 g, 1.00 mmol) and MP (0.271 g, 3.22 mmol) in acetonitrile (50 mL) was refluxed for 3 days, then the solvent was evaporated. Chromatography of the residue with chloroform gave **8a** (0.015 g, 4%) and **9a** (0.024 g, 8%), successively.

b) A mixture of **3a** (0.274 g, 1.01 mmol) and MP (0.269 g, 3.20 mmol) in acetonitrile (50 mL) was refluxed for 3 days in the presence of potassium carbonate (0.158 g, 1.14 mmol), then the insoluble material was filtered off, and the filtrate was evaporated. Chromatography of the residue with chloroform gave **9a** (0.008 g, 3%).

**8a**: Green needles (from hexane), mp 93—96 ℃; $\delta_H$ 1.27 (6H, d, *J* 6.3), 1.37 (3H, t, *J* 7.1), 3.56 (1H, dsep, *J* 6.3 and 6.0), 4.31 (2H, q, *J* 7.1), 5.05 (1H, br d, *J* 6.0), 5.83 (1H, dd, *J* 10.7 and 8.1), 5.90 (1H, s), 6.25 (1H, dd, *J* 12.6 and 8.1), 6.71 (1H, d, *J* 10.7), 7.78 (1H, s), and 7.81 (1H, d, *J* 12.6); $\delta_C$ 14.7, 23.2, 46.5, 51.5, 61.3, 66.0, 95.5, 101.9, 115.0, 125.3, 129.1, 129.7, 131.3, 134.3, 135.0, 135.9, 141.5, 144.8, 163.3, and 166.5; $\nu_{max}$ / cm$^{-1}$ 3416 (NH), 1660, and 1616 (C=O); *m/z* (rel intensity) 354 (M$^+$, 100), 323 (5), 311 (37), 281 (36), 265 (41), 239 (57), 223 (13), 207 (14), and 179 (17). *Anal.* Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.65; H, 6.28; N, 7.84.

**9a**: Green needles (from dichloromethane—hexane), mp 218—219 ℃; $\delta_H$ 1.56 (6H, d, *J* 6.8), 4.99 (1H, sep, *J* 6.8), 6.01 (1H, dd, *J* 10.7 and 8.8), 6.52 (1H, dd, *J* 12.4 and 8.8), 6.53 (1H, s), 7.10 (1H, d, *J* 10.7), 8.02 (1H, d, *J* 12.4), and 8.18 (1H, s); $\delta_C$ 22.2, 44.9, 52.1, 92.9, 108.9, 112.7, 123.6, 123.8, 124.1, 128.5, 129.1, 134.7, 136.5, 137.0, 142.7, 158.9, and 167.0; $\nu_{max}$ / cm$^{-1}$ 1672 and 1623 (C=O); *m/z* (rel intensity) 308 (M$^+$, 80), 266 (100), 235 (12), 223 (11), 207 (11), and 179 (10). *Anal.* Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.39; H, 5.27; N, 9.01.

In a similar manner, the reaction of **3b** with MP gave **8b** and **9b**. The results were listed in Table 1.

**8b**: Green needles (from hexane—dichloromethane), mp 110—111 ℃; $\delta_H$ 1.31 (3H, t, *J* 7.1), 1.38 (3H, t, *J* 7.1), 3.23 (1H, dq, *J* 7.1 and 6.0), 4.31 (2H, q, *J* 7.1), 5.07 (1H, br t, *J* 6.0), 5.83 (1H, dd, *J* 10.7

and 8.1), 5.91 (1H, s), 6.25 (1H, dd, *J* 12.6 and 8.1), 6.71 (1H, d, *J* 10.7), 7.77 (1H, s), and 7.80 (1H, d, *J* 12.6); $\delta_C$ 14.7, 15.0, 40.1, 51.5, 61.7, 95.2, 102.1, 115.1, 125.2, 129.2, 129.5, 134.1, 135.1, 136.0, 141.7, 142.1, 145.0, 163.3, and 166.5; $\nu_{max}$ / cm$^{-1}$ 3426 (NH), 1729, and 1655 (C=O); *m/z* (rel intensity) 340 (M$^+$, 60), 312 (4), 294 (32), 285 (4), 267 (13), 252 (17), 239 (30), 221 (100), 207 (9), and 179 (6). *Anal.* Calcd for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 67.23; H, 6.01; N, 8.20.

**9b**: Green needles (from dichloromethane—hexane), mp 209—210 ℃; $\delta_H$ 1.49 (3H, t, *J* 7.3), 3.85 (3H, s), 4.19 (2H, q, *J* 7.38), 5.99 (1H, dd, *J* 10.7 and 8.8), 6.49 (1H, s), 6.51 (1H, dd, *J* 12.3 and 8.8), 7.08 (1H, d, *J* 10.7), 8.00 (1H, d, *J* 12.3), and 8.16 (1H, s); $\delta_C$ 14.7, 37.4, 52.1, 91.5, 108.9, 112.7, 123.8, 124.3, 125.0, 128.5, 129.1, 134.9, 136.6, 137.1, 142.9, 159.3, and 167.0; $\nu_{max}$ / cm$^{-1}$ 1672 and 1625 (C=O); *m/z* (rel intensity) 294 (M$^+$, 100), 266 (14), 253 (14), 225 (3), and 207 (11). *Anal.* Calcd for $C_{17}H_{14}N_2O_3$: C, 69.78; H, 4.79; N, 9.52. Found: C, 70.01; H, 5.04; N, 9.46.

## Conversion of 8a to 9a with potassium carbonate

A mixture of **8a** (0.021 g, 0.06 mmol) and potassium carbonate (0.010 g, 0.07 mmol) in acetonitrile (10 mL) was refluxed for 1 d, then the insoluble material was filtered off, and the filtrate was evaporated. Chromatography of the residue with chloroform gave **9a** (0.018 g, 99%).

## X-Ray structure determination

**Crystal data of 4a**: Dark red prism, $C_{18}H_{20}N_2O_4$, $M$=328.37, triclinic, space group P-1, $a$=9.512(2), $b$=10.656(2), $c$=8.272(2) Å, $\alpha$=105.98(2)°, $\beta$=100.19(2)°, $\gamma$=99.29(2)°, $V$=773.5(4) Å$^3$, Z=2, $D_{calcd}$=1.410 g/cm$^3$, crystal dimensions 0.38 x 0.56 x 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-K$\alpha$ radiation. A total 3762 reflections (3547 unique) were collected using $\omega$–$2\theta$ scan technique with in a $2\theta$ range of 55.0°. The structure was solved by Patterson methods (DIRDIF92 ORIENT)[9] and expanded using Fourier thchniques,[10] and refined by a full-matrix least-squares methods using 199 variables refined with 1682 reflections [$I > 2\sigma(I)$]. The weighting scheme $\omega = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses. The final refinement converged to $R$ = 0.069 and $Rw$ = 0.062. All calculations were performed using the teXsan[11] crystallographic software package.

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