

# Reactions of diethyl azulene-1,3-dicarboxylate derivatives and 1-azaazulene derivatives with Grignard reagents, and alkyl- and aryllithium

Tadayoshi Morita,<sup>\*a</sup> Noritaka Abe<sup>\*b</sup> and Kahei Takase<sup>a</sup>

<sup>a</sup> Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-Ku, Sendai 980–8578, Japan

<sup>b</sup> Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753–8512, Japan

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Reactions of diethyl azulene-1,3-dicarboxylate (**1**) and diethyl 2-chloroazulene-1,3-dicarboxylate (**11**) with Grignard reagents, followed by dehydration with tetrachloro-1,2-benzoquinone, gave 2-, 4-, and 6-substituted addition–oxidation products. Grignard reagents have a tendency to react with **1** at the positions in the order of 2 > 4 > 6, while steric hindrance has a greater influence at the positions in order of 2 > 4 > 6. Reactions of **1** and **11** with phenyllithium and methyllithium gave similar results. On the other hand, on the reaction of diethyl 2-methoxyazulene-1,3-dicarboxylate (**15**), Grignard reagents attacked preferentially at the methoxy group, and 2-substituted products were obtained. Use of excess molar equivalents of Grignard reagents led to diaryl-substituted products. Reaction of 2-chloro-1-azaazulenes with Grignard reagents also gave similar addition–oxidation products, and reacted at the positions in the order 8 ≧ 4 > 6, whereas reaction of 2-methoxy-1-azaazulene with a Grignard reagent gave 1-azaazulene-2(1*H*)-one.

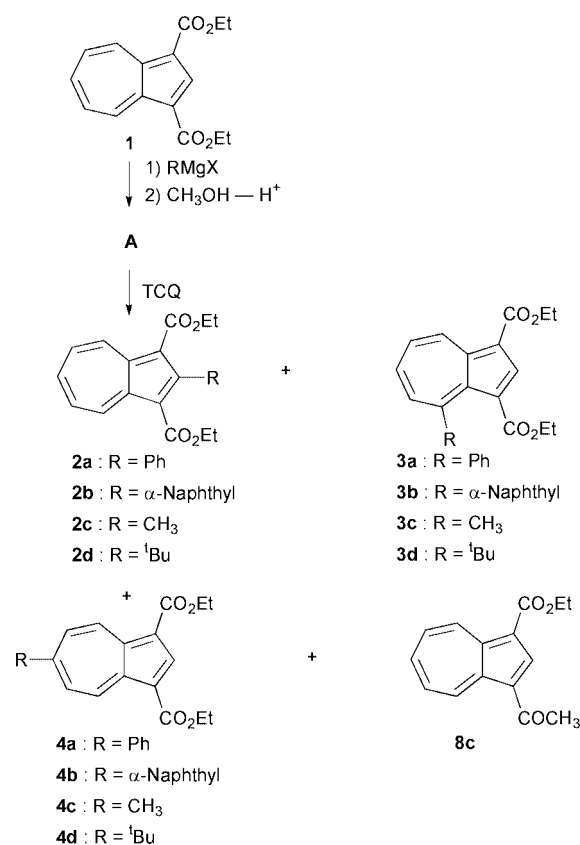
## Introduction

In azulene chemistry, very few methods for introduction of alkyl and aryl substituents are known. However, the reaction of haloazulenes, alkoxyazulene and haloazaazulenes with some nucleophilic reagents such as alkoxides, amines and sulfides gave the corresponding substitution products by replacement of the halogen or alkoxy substituent with the nucleophile.<sup>1–12</sup> On the other hand, addition-type reactions have also been reported for azulenes and 1-azaazulenes with some carbanions<sup>13–17</sup> and 1,3-diazaazulene with Grignard reagents.<sup>18</sup> We have also communicated that the reactions of diethyl azulene-1,3-dicarboxylate,<sup>19</sup> diethyl 2-chloroazulene-1,3-dicarboxylate<sup>20</sup> and 1-azaazulenes<sup>21</sup> with Grignard reagents proceeded by addition-type reaction and diethyl 2-methoxyazulene-1,3-dicarboxylate with Grignard reagents proceeded by substitution reaction.<sup>20</sup> We wish to report the full details herein.

## Results and discussion

Diethyl azulene-1,3-dicarboxylate<sup>22</sup> (**1**) was reacted with phenylmagnesium bromide to give an unstable yellow oily mixture of dihydroazulene-type addition products **A**. Dehydrogenation of the oil **A** with tetrachloro-1,2-benzoquinone (TCQ) gave three phenylazulene derivatives, diethyl 2-phenylazulene-1,3-dicarboxylate (**2a**), diethyl 4-phenylazulene-1,3-dicarboxylate (**3a**) and diethyl 6-phenylazulene-1,3-dicarboxylate (**4a**) in 10%, 70% and 2% yields, respectively (Scheme 1). On alkaline hydrolysis, followed by decarboxylation upon heating, **2a** and **3a** gave 2-phenylazulene<sup>23,24</sup> (**5**) and 4-phenylazulene<sup>12</sup> (**6**), respectively. Deesterification of **2a** with 100% phosphoric acid gave **5** together with ethyl 2-phenylazulene-1-carboxylate (**7**). On the basis of this chemical evidence and the spectral data (see Experimental), we have assigned the structures.

By careful separation of **A** with silica gel chromatography with benzene, two oily compounds, diethyl 2-phenyl-1,2-

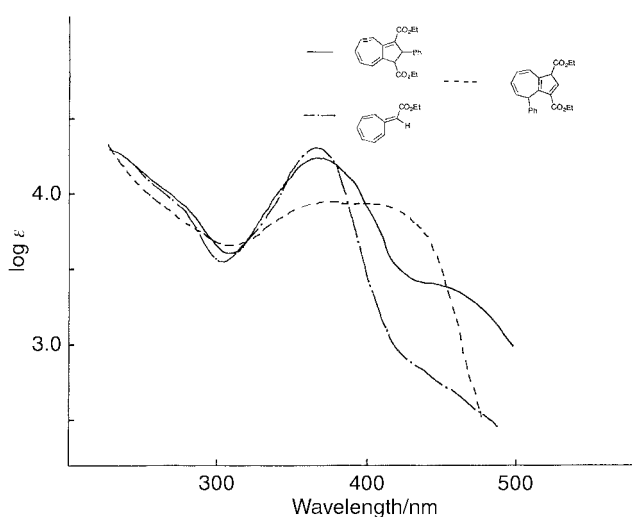
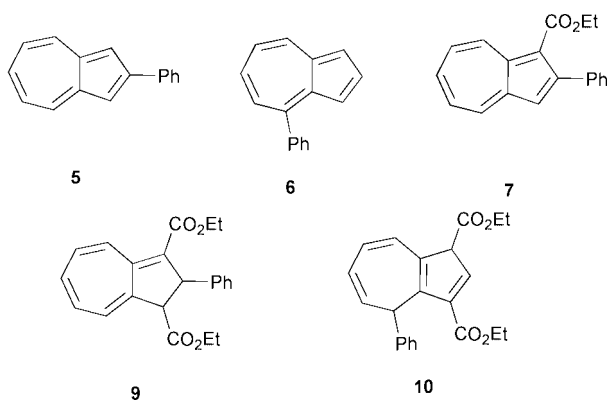


Scheme 1

dihydroazulene-1,3-dicarboxylate (**9**) and diethyl 4-phenyl-1,4-dihydroazulene-1,3-dicarboxylate (**10**), were isolated. In the <sup>1</sup>H NMR spectrum of **9**, a pair of AB doublets at  $\delta$  3.45 and 4.50

**Table 1** Reactions of azulene and 1-azaazulene derivatives with Grignard reagents and phenyl- and methyllithium

Run	Reactant	Reagent	Conditions reactant : reagents	Product yield (%)
1	<b>1</b>	PhMgBr	1 : 2.5	<b>2a</b> (10) <b>3a</b> (70) <b>4a</b> (2)
2	<b>1</b>	$\alpha$ -NaphthylMgBr	1 : 2.5	<b>2b</b> (6) <b>3b</b> (45) <b>4b</b> (7)
3	<b>1</b>	CH <sub>3</sub> MgI	1 : 2.5	<b>2c</b> (16) <b>3c</b> (5) <b>4c</b> (1) <b>8c</b> (2)
4	<b>1</b>	<sup>t</sup> BuMgBr	1 : 2.5	<b>3d</b> (1) <b>4d</b> (23)
5	<b>11</b>	PhMgBr	1 : 2.5	<b>12a</b> (94) <b>13a</b> (3)
5	<b>11</b>	PhMgBr	1 : 1	<b>12a</b> (7) <b>13a</b> (2) <b>11</b> (70)
6	<b>11</b>	$\alpha$ -NaphthylMgBr	1 : 2.5	<b>12b</b> (76) <b>13b</b> (9)
7	<b>11</b>	CH <sub>3</sub> MgI	1 : 2.5	<b>12c</b> (20) <b>13c</b> (1) <b>14c</b> (2)
8	<b>11</b>	<sup>t</sup> BuMgBr	1 : 2.5	<b>12d</b> (1) <b>13d</b> (30)
9	<b>15</b>	PhMgBr	1 : 1.5	<b>2a</b> (72) <b>16</b> (22)
10	<b>15</b>	PhMgBr	1 : 3.3	<b>17a</b> (46) <b>18a</b> (5)
11	<b>15</b>	$\alpha$ -NaphthylMgBr	1 : 1	<b>2b</b> (75) <b>16</b> (10)
12	<b>15</b>	MeMgI	1 : 1	<b>2c</b> (72) <b>17c</b> (2) <b>16</b> (12)
13	<b>2a</b>	PhMgBr	1 : 2.5	<b>17a</b> (67) <b>18a</b> (1) <b>19a</b> (1)
14	<b>2c</b>	PhMgBr	1 : 2.5	<b>17c</b> (47) <b>19c</b> (3)
15	<b>21</b>	PhMgBr	1 : 2.5	<b>22</b> (5) <b>23</b> (8) <b>24</b> (12)
16	<b>25</b>	PhMgBr	1 : 1	<b>25</b> (98)
17	<b>26</b>	PhMgBr	1 : 3.5	<b>27</b> (85)
18	<b>1</b>	PhLi	1 : 3.0	<b>2a</b> (10) <b>3a</b> (70) <b>4a</b> (2)
19	<b>1</b>	MeLi	1 : 3.0	<b>2c</b> (70) <b>3c</b> (2) <b>8c</b> (3)
20	<b>11</b>	PhLi	1 : 3.0	<b>12c</b> (80) <b>13c</b> (2)
21	<b>11</b>	MeLi	1 : 3.0	<b>12c</b> (34) <b>13c</b> (2)
22	<b>29</b>	PhMgBr	1 : 2.5	<b>30</b> (4) <b>31</b> (3) <b>32</b> (88)
23	<b>33</b>	PhMgBr	1 : 2.5	<b>34</b> (8) <b>35</b> (7) <b>36</b> (77)
24	<b>37</b>	PhMgBr	1 : 1.2	<b>38</b> (100)
25	<b>39</b>	PhMgBr	1 : 1.2	<b>40</b> (100)

**Fig. 1** Electronic spectra of **9**, **10** and ethyl heptafulvene-8-carboxylate.

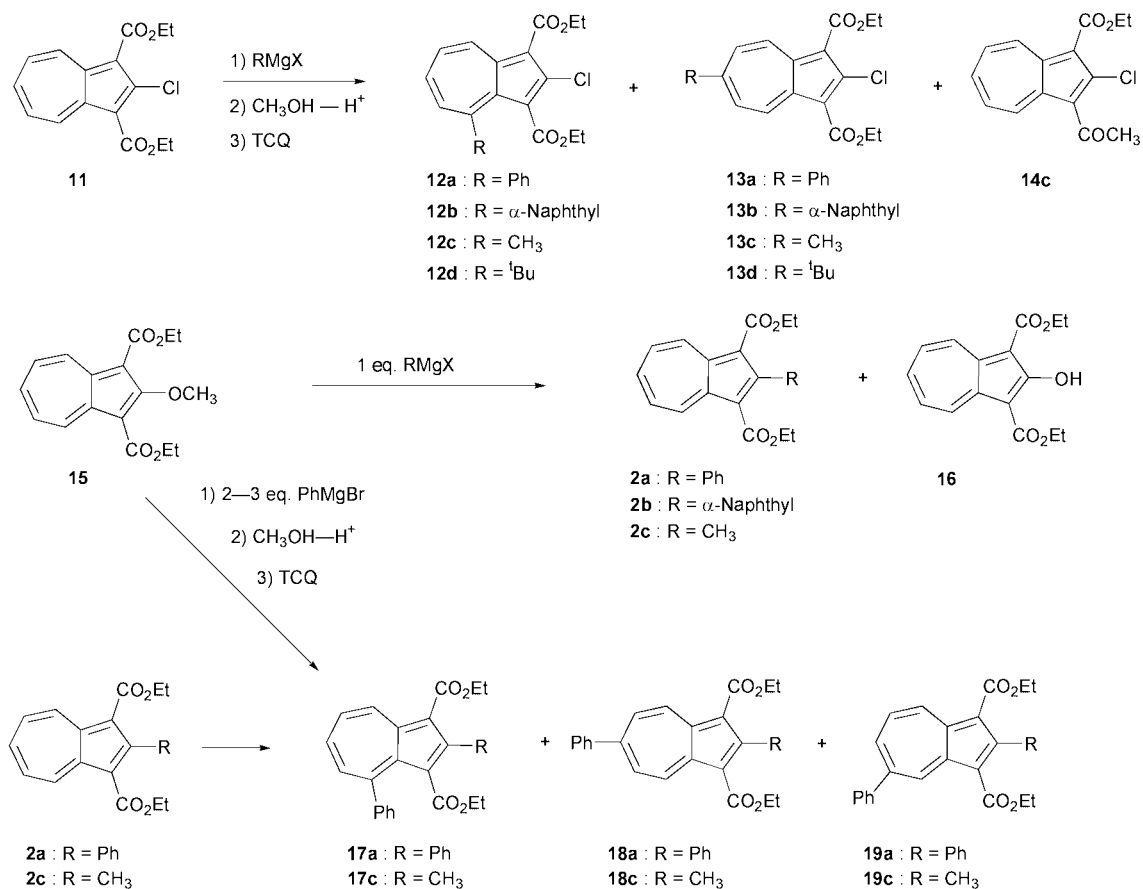
(each 1H, *J* 3.6) were observed, and seven-membered ring protons were seen at  $\delta$  6.0–6.4 (4H, m) and 7.62 (1H, br d, *J* 12.0). In its IR spectrum, two ester carbonyl peaks were observed at 1736 and 1689  $\text{cm}^{-1}$ , the former is a non-conjugated ester signal

and the latter is a conjugated ester signal. The mass spectrum of **9** showed its molecular peak at  $m/z$  350, and dehydrogenation of **9** with TCQ afforded **2a**. Furthermore, the UV-vis spectrum of **9** resembles that of ethyl heptafulvene-8-carboxylate<sup>25</sup> † (Fig. 1). The <sup>1</sup>H NMR spectrum of **10** showed rather complex features, but peaks assigned to benzylic and allylic protons were observed at  $\delta$  3.67 (1H, br) and 4.20 (1H, br). In the IR spectrum of **10**, two ester carbonyl peaks were observed at 1706 and 1695  $\text{cm}^{-1}$ . The maximum at the longest wavelength in the absorption band for **10** is observed at 402 nm, and this suggests that **10** has higher conjugated double bonds. The mass spectrum of **10** also showed its molecular peak at  $m/z$  350, and dehydrogenation of **10** with TCQ afforded **3a**. From these results the structures were assigned.

In a similar manner as with phenylmagnesium bromide, the reaction of **1** with some other Grignard reagents, such as  $\alpha$ -naphthylmagnesium bromide, methylmagnesium iodide and *tert*-butylmagnesium bromide, gave the corresponding substituted azulene derivatives (Scheme 1, Table 1). On the reaction of **1** with *tert*-butylmagnesium bromide, no 2-substituted product was obtained. Further, in the case of the reaction of methylmagnesium iodide, ethyl 3-acetylazulene-1-carboxylate (**8c**), which should be formed by attack of the reagent at the ester group, was obtained along with the addition-elimination products. Relative yields of the azulene derivatives indicate that the bulkiness of the reagents affected the positions of the azulene nucleus attacked, for example, the less bulky methyl Grignard reagent gave mainly 2-substituted azulene (**2c**), while the more bulky *tert*-butyl Grignard reagent gave mainly 6-substituted azulene (**4d**). These facts suggested that Grignard reagents have a tendency to react with diethyl azulene-1,3-dicarboxylate (**1**) at the positions in order of  $2 > 4 > 6$ , while steric hindrance has a greater influence at the positions in order of  $2 > 4 > 6$ .

Diethyl azulene-1,3-dicarboxylate (**1**) reacted with Grignard reagents to give dihydroazulene-type addition products at first as discussed above. On the other hand, it is known that

† The IUPAC name for ethyl heptafulvene-8-carboxylate is ethyl 2-cyclohepta-2,4,6-trien-1-ylideneacetate.



Scheme 2

2-haloazulenes usually react with nucleophilic reagents to give the corresponding substitution products.<sup>1,5,7</sup> Therefore, the reaction of Grignard reagents with azulene derivatives with a halogen substituent capable of acting as an anionic leaving group, were investigated in order to study substitution *versus* addition reactions. Thus we treated diethyl 2-chloroazulene-1,3-dicarboxylate<sup>22</sup> (**11**) with 2.5 molar equivalents of phenylmagnesium bromide (run 5), and a pale yellow oily mixture of dihydroazulene-type addition products was obtained. Dehydrogenation of this mixture with TCQ gave two kinds of phenylazulene derivatives, diethyl 2-chloro-4-phenyl- (**12a**) (94%) and diethyl 2-chloro-6-phenylazulene-1,3-dicarboxylate (**13a**) (3%). When an equimolar amount of phenylmagnesium bromide was used, a fair amount of the starting material **11** was recovered, accompanied by the formation of small amounts of **12a** and **13a**, after dehydrogenation.

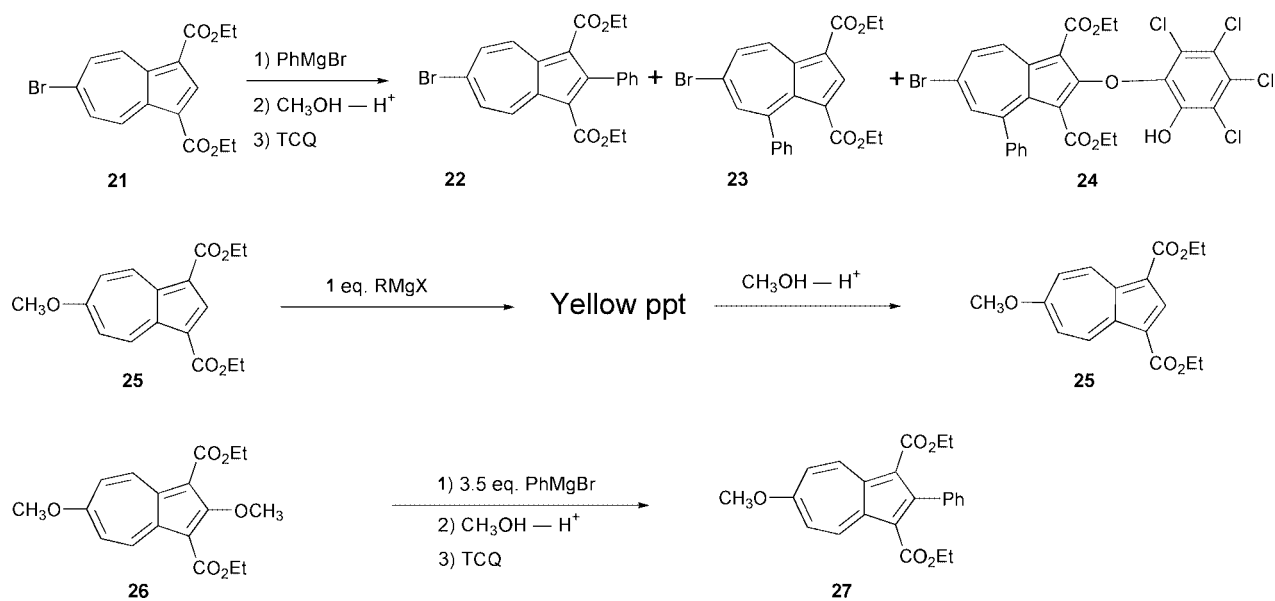
Similar treatment of **11** with some other Grignard reagents, such as  $\alpha$ -naphthylmagnesium bromide, methylmagnesium iodide and *tert*-butylmagnesium bromide, gave the corresponding 4- and 6-substituted azulene derivatives (run 6–8). In these reactions no corresponding 2-substituted products, expected to be formed by displacement of the chloro substituent, were obtained. This indicates that in the reaction of 2-chloro derivative **11** with Grignard reagents displacement of the chloro substituent at the 2-position did not occur, but addition of the reagents took place at the 4- or 6-position (Scheme 2).

On the other hand, the treatment of diethyl 2-methoxyazulene-1,3-dicarboxylate<sup>9</sup> (**15**) with an equimolar amount of phenylmagnesium bromide directly gave, after decomposition of the magnesium complex thereby formed, 2-phenylazulene derivative **2a** (72%) and diethyl 2-hydroxyazulene-1,3-dicarboxylate<sup>9</sup> (**16**) (22%) (run 9), and the dihydroazulene-type addition product was not obtained. Other Grignard reagents such as  $\alpha$ -naphthylmagnesium bromide and methylmagnesium iodide also gave the corresponding 2-substituted products

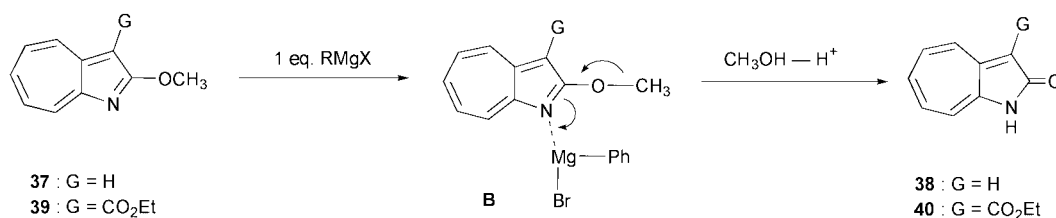
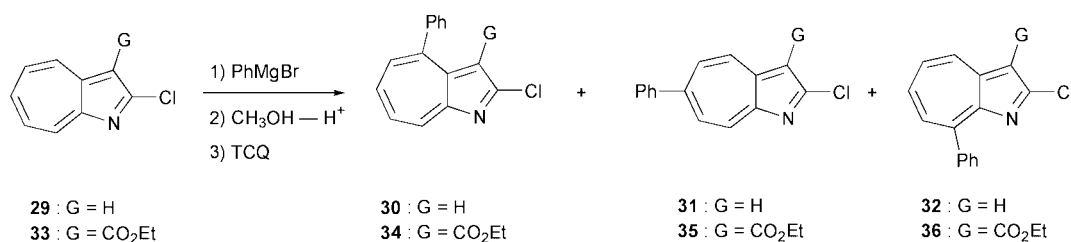
(run 11 and 12). Furthermore, the treatment of **2a** with excess molar equivalents of phenylmagnesium bromide, followed by dehydrogenation with TCQ, gave two kinds of diphenylazulene derivatives **17a** (46%) and **18a** (5%) (run 10). The same compounds **17a** and **18a** along with a minute amount of diethyl 2,5-diphenylazulene-1,3-dicarboxylate (**19a**) (run 13) were also obtained from the reaction of **2a** with phenylmagnesium bromide. These findings showed that in the reaction of 2-methoxyazulene **15** with Grignard reagents, the reagent first displaced the methoxy substituents at the 2-position to form the substitution products **2a**, and then the excess reagent added to **2a** at the 4-, 6- or 5-position. The formation of **16** is assumed to be caused by attack of Grignard reagents on the methyl carbon of the methoxy group, and resembles the reaction of deprotection of aromatic ethers by Grignard reagents.<sup>26</sup>

It is known that 6-haloazulenes and 4-alkoxyazulenes also undergo substitution with some nucleophiles.<sup>2,3,5,8</sup> Therefore, we next examined the reactions of 6-bromo-<sup>3,27</sup> (**21**), 6-methoxy-<sup>3</sup> (**25**), and 2,6-dimethoxyazulene derivatives (**26**) with phenylmagnesium bromide. In the case of **21**, an addition-type reaction proceeded and yielded 2-phenyl-derivative **22** and 4-phenyl derivative **23** together with **24** (run 15), and no substitution product was obtained. When **25** was treated with equimolar phenylmagnesium bromide, a yellow precipitate was produced. Decomposition of this complex by addition of methanol and dilute hydrochloric acid gave recovered **25** quantitatively (run 16). When diethyl 2,6-dimethoxyazulene-1,3-dicarboxylate (**26**) was treated with 3.5 molar equivalents of phenylmagnesium bromide, followed by hydrolysis and dehydrogenation with TCQ, only diethyl 6-methoxy-2-phenylazulene-1,3-dicarboxylate (**27**) was obtained in 85% yield (run 17) (Scheme 3).

The results showed that the displacement of 2-chloro-, 6-bromo- and 6-methoxy substituents did not occur and only the 2-methoxy substituent could be displaced. Such a difference in the reaction mechanism between 2-methoxy derivatives and



Scheme 3



Scheme 4

other azulenes towards Grignard reagents may be explained as follows. 1) The ethereal oxygen is much more strongly coordinated than the halogen atoms. Therefore, in the case of **15**, the Grignard reagent can easily attack at the 2-position to form a coordination complex in which the oxygen of the methoxy group at the 2-position is coordinated to the reagent, whereas in the case of **11** and **21**, the reagent can not attack at the 2-position or the 6-position because of the difficulty associated with formation of the coordination complex. 2) It seems that the electronic effects of the substituents also affect the reactivities of the azulenes. The seven-membered rings of **11** and **21** are activated to Grignard attack by the inductive effect of the halogen substituent, whereas **15** and **25** are deactivated by the mesomeric effect of the methoxy group. Therefore, with **25**, despite formation of the coordination complex, the substitution reaction did not occur. Furthermore, in the case of **25**, despite the use of excess phenylmagnesium bromide, only the substitution reaction took place at the 2-position.

Deesterification of the derived azulene derivatives could be carried out easily, e.g., 2,6-diphenylazulene (**28**) was obtained from **18a** in good yield. The reaction of azulenes with Grignard reagents is thought, therefore, to be a favorable method for synthesizing poly-substituted azulenes.

Reactions of **1** and **11** with phenyllithium and methyllithium gave similar results as for Grignard reagents and gave addition-oxidation products (run 18–21).

Like haloazulenes, 1-aza-analogues are known to react with some nucleophiles. In addition, it has been shown that the reaction of 2-chloro-1-azaazulenes<sup>10</sup> (**29**) and ethyl 2-chloro-1-azaazulene-3-carboxylate<sup>10</sup> (**33**) with the carbanion derived from active methylene compounds proceeds competitively to give the substitution product or addition product, and the reaction was highly influenced by the reaction conditions.<sup>28</sup> Furthermore, it is known that addition reactions occur with Grignard reagents 1,3-diazaazulene. Therefore, in the reaction of 2-chloro-1-azaazulenes with Grignard reagents, it would be interesting to determine which reaction, substitution or addition, occurs. For comparison of reactivity of the azulenes and 1-azaazulenes, we next examined the reaction of **29** and **33** with Grignard reagent (run 22 and 23). Treatment of **29** and **33** with phenylmagnesium bromide, under similar conditions to the azulenes, gave the corresponding 4-phenyl (**30** and **34**), 6-phenyl (**31** and **35**), and 8-phenyl derivatives (**32** and **36**), and the reactivities were determined as C-8 > C-4 > C-6 (Scheme 4). The preference for Grignard attack at the 8-position of 1-azaazulenes could be due to the coordination of the reagent with the ring nitrogen atom. Other Grignard reagents such as

styrylmagnesium bromide reacted with 1-azaazulenes to give similar results.<sup>29</sup>

On the contrary, treatment of 2-alkoxy-1-azaazulenes (**37** and **39**) with phenylmagnesium bromide gave 1-azaazulen-2(1*H*)-ones<sup>30</sup> (**38** and **40**) quantitatively (run 24 and 25). Obviously, cleavage of the *O*-alkyl bond must be assisted by the coordination of the reagent to the ring nitrogen atom as shown in **B**. When aryllithium was allowed to react with 6-bromo-2-ethoxy-1-azaazulene, exclusive formation of the corresponding 4-aryl derivative was noted.<sup>17</sup>

## Experimental

Melting points are uncorrected. <sup>1</sup>H NMR spectra (60 MHz) were recorded on a Hitachi Varian A-60 D spectrometer (60 MHz) and a Varian HA100 spectrometer (100 MHz) and <sup>13</sup>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. Electronic spectra were recorded with a Hitachi EPS-3 spectrophotometer. IR spectra were recorded for KBr pellets on a Shimadzu IR-27 infracord unless otherwise stated. Mass spectra were measured with a Hitachi RMU-6 mass spectrometer at 25 eV. Kieselgel 60 and Wako-gel C-200 were used for column chromatography.

### Reaction of diethyl azulene-1,3-dicarboxylates with Grignard reagents

**Typical procedure.** Under a nitrogen atmosphere, a solution of diethyl azulene-1,3-dicarboxylate<sup>22</sup> **1** (0.500 g, 1.84 mmol) in dry ether (30 ml) was added to an ether solution of phenylmagnesium bromide, produced from bromobenzene (0.720 g, 4.58 mmol) and magnesium metal (0.110 g, 4.58 mmol) in dry ether (30 ml), and stirred for 30 min at room temperature. The reaction mixture was cooled on an ice-bath, and then methanol (8 ml) and 2 M hydrochloric acid (5 ml) were added. The mixture was extracted with benzene, and the extract was washed with 2 M sodium hydroxide solution. TCQ (1.0 g) was added to the solution, and the mixture was stirred for 2 days at room temperature, then evaporated. The residue was purified by alumina column chromatography with chloroform as an eluant. The effluent was evaporated and the residue was chromatographed on silica gel. Elution with benzene gave diethyl 6-phenylazulene-1,3-dicarboxylate (**4a**) (0.008 g, 2%), diethyl 2-phenylazulene-1,3-dicarboxylate (**2a**) (0.077 g, 10%), and diethyl 4-phenylazulene-1,3-dicarboxylate (**3a**) (0.400 g, 70%).

**2a:** Red prisms (from ethanol), 103–104.5 °C;  $\delta_{\text{H}}$  0.93 (6H, t, *J* 7.0), 4.18 (4H, q, *J* 7.0), 7.50 (5H, br s), 7.60–8.00 (3H, m) and 9.81 (2H, d, *J* 10.0);  $\delta_{\text{C}}$  13.95, 60.30, 117.54, 127.13, 127.27, 129.06, 130.70, 139.09, 139.35, 140.52, 143.18, 156.21 and 166.17;  $\nu_{\text{max}}/\text{cm}^{-1}$  1675 (C=O);  $\lambda_{\text{max}}$  (chloroform)/nm (log  $\epsilon$ ) 235 (4.55), 269 (4.43), 305 (4.65) and 520 (2.77) (Found: C, 75.9; H, 5.9. Calc. for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>: C, 75.8; H, 5.8%).

**3a:** Violet prisms (from ethanol), mp 113–114 °C;  $\delta_{\text{H}}$  1.08 (3H, t, *J* 7.0), 1.45 (3H, t, *J* 7.0), 3.70 (2H, q, *J* 7.0), 4.48 (2H, q, *J* 7.0), 7.40–8.00 (8H, m), 8.72 (1H, s) and 10.45 (1H, br d, *J* 10.0);  $\delta_{\text{C}}$  14.49, 14.94, 60.41, 61.13, 116.22, 122.23, 128.66, 128.87, 128.92, 129.19, 133.97, 138.91, 139.05, 139.72, 143.11, 144.04, 145.41, 153.41, 165.45 and 166.58;  $\nu_{\text{max}}/\text{cm}^{-1}$  1715 and 1686 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 237 (4.45), 265 (4.42), 308 (4.46) and 550 (2.97) (Found: C, 75.4; H, 5.6. Calc. for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>: C, 75.8; H, 5.8%).

**4a:** Red prisms (from ethanol), mp 148–150 °C;  $\delta_{\text{H}}$  1.48 (6H, t, *J* 7.3), 4.58 (4H, q, *J* 7.3), 7.40–7.80 (5H, m), 8.16 (2H, d, *J* 12.0), 8.90 (1H, s) and 9.97 (2H, br d, *J* 12.0);  $\delta_{\text{C}}$  14.98, 60.47, 116.82, 129.19, 129.35, 129.49, 131.29, 138.88, 143.14, 143.60, 143.95, 154.98 and 165.49;  $\nu_{\text{max}}/\text{cm}^{-1}$  1681 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 272 (4.35), 277 (4.36), 327 (4.72), 360 (4.27),

507 (2.84) and 542 (2.75) (Found: C, 75.9; H, 6.0. Calc. for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>: C, 75.8; H, 5.8%).

### Deesterification of diethyl 2-phenylazulene-1,3-dicarboxylate (**2a**)

a) A mixture of **2a** (0.050 g, 0.14 mmol) and 10% potassium hydroxide solution (6 ml, ethanol–water = 4:1) was refluxed for 0.5 h. To the reaction mixture water was added, then the mixture was neutralized with hydrochloric acid. The resultant precipitate was collected, dried, then sublimed at 250 °C under reduced pressure to give **5** (0.028 g, 96%).

b) A mixture of **2a** (0.100 g, 0.29 mmol) and 100% phosphoric acid (2 ml) was stirred overnight at room temperature. To the reaction mixture water was added. The mixture was extracted with chloroform, then the extract was washed with water, dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel. Elution with benzene gave **5**<sup>23,24</sup> (0.030 g, 51%) and ethyl 2-phenylazulene-1-carboxylate (**7**) (0.038 g, 48%).

**7:** Violet oil;  $\delta_{\text{H}}$  1.13 (3H, t, *J* 7.3), 4.40 (2H, q, *J* 7.3), 7.30–7.90 (9H, m), 8.50 (1H, br d, *J* 10.0) and 9.97 (1H, br d, *J* 10.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1688 (C=O) (Found: C, 75.9; H, 6.0. Calc. for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>: C, 75.8; H, 5.8%).

### Deesterification of diethyl 4-phenylazulene-1,3-dicarboxylate (**3a**)

A mixture of **3a** (0.100 g, 0.29 mmol) and 10% potassium hydroxide solution (8 ml, ethanol–water = 4:1) was refluxed for 2 h. To the reaction mixture water was added, then the mixture was neutralized with hydrochloric acid. The resultant precipitate was collected, then was sublimed at 250 °C under reduced pressure to give **6**<sup>12</sup> (0.050 g, 85%).

In a similar manner as above, we treated **1** and **11** with  $\alpha$ -naphthylmagnesium bromide, methylmagnesium iodide and *tert*-butylmagnesium bromide. Results are listed at Table 1.

**2b:** Red prisms (from ethanol), 95–98 °C;  $\delta_{\text{H}}$  0.30 (6H, t, *J* 7.3), 3.75 (4H, q, *J* 7.3), 7.30–8.20 (10H, m) and 9.93 (2H, br d, *J* 9.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1677 (C=O) (Found: C, 78.6; H, 5.4. Calc. for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>: C, 78.4; H, 5.6%).

**3b:** Violet prisms (from ethanol), mp 135.5–136.5 °C;  $\delta_{\text{H}}$  0.52 (3H, t, *J* 7.3), 1.43 (3H, t, *J* 7.3), 2.40–3.00 (1H, m), 3.20–3.70 (1H, m), 4.44 (2H, q, *J* 7.3), 7.30–8.10 (10H, m), 8.53 (1H, s) and 9.99 (1H, br d, *J* 8.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1708 and 1688 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 237 (4.45), 265 (4.42), 308 (4.46) and 550 (2.97) (Found: C, 78.5; H, 5.5. Calc. for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>: C, 78.4; H, 5.6%).

**4b:** Red prisms (from ethanol), 103–104.5 °C;  $\delta_{\text{H}}$  1.46 (6H, t, *J* 7.1), 4.47 (4H, q, *J* 7.1), 7.20–8.10 (9H, m), 8.91 (1H, s) and 9.93 (2H, br d, *J* 9.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1680 (C=O);  $\lambda_{\text{max}}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 221 (4.98), 237 (4.62), 269 (4.44), 306 (4.69), 353 (4.38), 374 (4.27), 512 (2.83), 547 (2.75) and 595 (2.19) (Found: C, 78.3; H, 5.7. Calc. for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>: C, 78.4; H, 5.6%).

**2c:** Red prisms (from ethanol), 67–67.5 °C;  $\delta_{\text{H}}$  1.44 (6H, t, *J* 7.2), 2.96 (3H, s), 4.45 (4H, q, *J* 7.2), 7.30–7.70 (3H, m) and 9.37 (2H, d, *J* 10.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1669 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 238 (4.61), 269 (4.44), 296 (4.66), 307 (4.76), 346 (3.90), 355 (3.86), 373 (3.86) and 508 (2.65) (Found: C, 71.0; H, 6.2. Calc. for C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>: C, 71.3; H, 6.3%).

**3c:** Red prisms (from ethanol), mp 66–67.5 °C;  $\delta_{\text{H}}$  1.44 (6H, t, *J* 7.0), 3.03 (3H, s), 4.43 (4H, q, *J* 7.0), 7.40–7.80 (3H, m), 8.62 (1H, s) and 9.81 (1H, br d, *J* 11.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  (chloroform) 1715 and 1686 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 240 (4.45), 270 (4.42), 298 (4.65, sh), 305 (4.70), 342 (3.98), 372 (3.65), 424 (3.10), 515 (2.74) and 545 (2.36, sh) (Found: C, 71.2; H, 6.2. Calc. for C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>: C, 71.3; H, 6.3%).

**4c:** Red prisms (from ethanol), 168–169 °C;  $\delta_{\text{H}}$  1.47 (6H, t, *J* 7.0), 2.80 (3H, s), 4.48 (4H, q, *J* 7.0), 7.76 (2H, d, *J* 11.0), 8.90 (1H, s) and 9.81 (2H, d, *J* 10.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1675 (C=O);  $\lambda_{\text{max}}$

(cyclohexane)/nm (log  $\epsilon$ ) 234 (4.44), 270 (4.31), 292 (4.33), 298 (4.44), 303 (4.46), 308 (4.55), 336 (3.65), 343 (3.67), 366 (3.77), 378 (3.86), 465 (2.55), 500 (2.68) and 536 (2.60) (Found: C, 70.9; H, 6.4. Calc. for  $C_{17}H_{18}O_4$ : C, 71.3; H, 6.3%).

**8c:** Red prisms (from ethanol), 101–103 °C;  $\delta_H$  1.48 (3H, t,  $J$  7.0), 2.72 (3H, s), 4.52 (2H, q,  $J$  7.0), 7.50–8.10 (3H, m), 8.90 (1H, s) and 9.70–10.40 (2H, m);  $\nu_{max}/cm^{-1}$  1692 and 1645 (C=O);  $\lambda_{max}$  (cyclohexane)/nm (log  $\epsilon$ ) 239 (4.57), 278 (4.63), 288 (4.47), 295 (4.51), 300 (4.53), 305 (4.61), 333 (3.72), 373 (4.01), 383 (4.01), 487 (2.58), 515 (2.71) and 554 (2.64) (Found: C, 74.5; H, 5.9. Calc. for  $C_{15}H_{14}O_3$ : C, 74.4; H, 5.8%).

**3d:** Red oil;  $\delta_H$  0.63 (3H, t,  $J$  7.0), 1.40 (3H, t,  $J$  7.0), 1.58 (9H, s), 4.06 (2H, q,  $J$  7.0), 4.46 (2H, q,  $J$  7.0), 7.50–8.10 (3H, m), 8.77 (1H, s) and 9.83 (1H, br d,  $J$  10.0);  $\nu_{max}/cm^{-1}$  (chloroform) 1710 and 1680 (C=O) (Found: C, 72.8; H, 7.3. Calc. for  $C_{20}H_{24}O_4$ : C, 73.1; H, 7.4%).

**4d:** Red prisms (from ethanol), 100–101 °C;  $\delta_H$  1.31 (6H, t,  $J$  7.0), 1.52 (9H, s), 4.52 (4H, q,  $J$  7.0), 8.07 (2H, d,  $J$  11.0), 8.95 (1H, s) and 9.91 (2H, br d,  $J$  11.0);  $\delta_C$  14.99, 32.25, 39.43, 60.34, 116.10, 128.73, 129.26, 138.59, 143.18, 165.58 and 165.99;  $\nu_{max}/cm^{-1}$  1681 (C=O);  $\lambda_{max}$  (cyclohexane)/nm (log  $\epsilon$ ) 235 (4.61), 290 (4.53), 308 (4.78), 337 (3.40), 342 (3.90), 365 (3.99), 374 (4.06), 497 (2.83), 532 (2.76) and 580 (2.25) (Found: C, 73.2; H, 7.5. Calc. for  $C_{20}H_{24}O_4$ : C, 73.1; H, 7.4%).

**12a:** Violet needles (from ethanol), mp 108–109 °C;  $\delta_H$  1.12 (3H, t,  $J$  7.0), 1.47 (3H, t,  $J$  7.0), 3.60 (2H, q,  $J$  7.0), 4.51 (2H, q,  $J$  7.0), 7.46 (5H, br s), 7.40–8.00 (3H, m) and 9.54–9.80 (1H, m);  $\delta_C$  14.27, 14.82, 61.04, 61.51, 114.49, 122.24, 128.61, 129.04, 129.07, 129.55, 134.32, 136.01, 138.58, 138.74, 141.21, 141.72, 143.69, 152.01, 164.75 and 165.51;  $\nu_{max}/cm^{-1}$  1718 and 1695 (C=O);  $\lambda_{max}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 238 (4.35), 269 (4.18), 300 (4.56), 309 (4.57), 355 (3.80), 530 (2.74) and 550 (2.74) (Found: C, 69.5; H, 5.0. Calc. for  $C_{22}H_{19}O_4Cl$ : C, 69.2; H, 5.0%).

**13a:** Red prisms (from ethanol), 138–139 °C;  $\delta_H$  1.49 (6H, t,  $J$  7.0), 4.53 (4H, q,  $J$  7.0), 7.40–7.80 (5H, m), 7.94 (2H, dd,  $J$  10.3 and 1.5) and 9.57 (2H, dd,  $J$  10.3 and 1.5);  $\delta_C$  14.99, 60.47, 116.82, 129.09, 129.35, 129.49, 131.29, 138.89, 143.14, 143.60, 143.95, 154.99 and 165.49;  $\nu_{max}/cm^{-1}$  1686 (C=O);  $\lambda_{max}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 237 (4.54), 270 (4.19), 325 (4.75), 366 (4.24), 502 (2.81) and 528 (2.77) (Found: C, 69.1; H, 5.1. Calc. for  $C_{22}H_{19}O_4Cl$ : C, 69.2; H, 5.0%).

**12b:** Red violet needles (from ethanol), mp 124–125 °C;  $\delta_H$  0.61 (3H, t,  $J$  7.1), 1.47 (3H, t,  $J$  7.1), 2.40–3.00 (1H, m), 3.20–3.80 (1H, m), 4.52 (2H, q,  $J$  7.1), 7.30–8.10 (10H, m) and 9.93 (1H, br d,  $J$  10.0);  $\nu_{max}/cm^{-1}$  1720 and 1683 (C=O);  $\lambda_{max}$  (chloroform)/nm (log  $\epsilon$ ) 300 (4.61), 310 (4.69), 335 (4.00, sh) and 542 (3.05) (Found: C, 72.4; H, 4.5. Calc. for  $C_{26}H_{21}O_4Cl$ : C, 72.1; H, 4.9%).

**13b:** Red needles (from ethanol), 143–145 °C;  $\delta_H$  1.50 (6H, t,  $J$  7.0), 4.57 (4H, q,  $J$  7.0), 7.40–8.20 (9H, m) and 9.77 (2H, br d,  $J$  12.0);  $\nu_{max}/cm^{-1}$  1678 (C=O);  $\lambda_{max}$  (chloroform)/nm (log  $\epsilon$ ) 265 (4.35), 309 (4.58), 350 (4.21), 375 (4.10) and 535 (2.82) (Found: C, 71.9; H, 5.1. Calc. for  $C_{26}H_{21}O_4Cl$ : C, 72.1; H, 4.9%).

**12c:** Red prisms (from ethanol), mp 79.5–81 °C;  $\delta_H$  1.44 (3H, t,  $J$  7.2), 1.46 (3H, t,  $J$  7.2), 2.90 (3H, s), 4.49 (2H, q,  $J$  7.2), 4.51 (2H, q,  $J$  7.2), 7.40–7.90 (3H, m) and 9.60 (1H, br d,  $J$  10.0);  $\nu_{max}/cm^{-1}$  (chloroform) 1723 and 1676 (C=O);  $\lambda_{max}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 240 (4.50), 296 (4.71), 305 (4.73), 353 (4.01), 370 (3.72), 508 (2.83), 533 (2.80) and 577 (2.44) (Found: C, 63.4; H, 5.3. Calc. for  $C_{17}H_{17}O_4Cl$ : C, 63.6; H, 5.3%).

**13c:** Red prisms (from ethanol), 57–61 °C;  $\delta_H$  1.48 (6H, t,  $J$  7.3), 2.80 (3H, s), 4.55 (4H, q,  $J$  7.3), 7.76 (2H, d,  $J$  11.0) and 9.81 (2H, d,  $J$  11.0);  $\nu_{max}/cm^{-1}$  1675 (C=O) (Found: C, 63.3; H, 5.2. Calc. for  $C_{17}H_{17}O_4Cl$ : C, 63.6; H, 5.3%).

**14c:** Red prisms (from cyclohexane), 88–90 °C;  $\delta_H$  1.47 (3H, t,  $J$  7.0), 2.74 (3H, s), 4.50 (2H, q,  $J$  7.0), 7.50–8.10 (3H, m) and 9.70–10.40 (2H, m);  $\nu_{max}/cm^{-1}$  1695 and 1645 (C=O) (Found: C, 65.3; H, 4.8. Calc. for  $C_{15}H_{13}O_3Cl$ : C, 65.1; H, 4.7%).

**12d:** Reddish violet oil;  $\delta_H$  1.30 (6H, t,  $J$  7.0), 1.50 (9H, s), 4.53 (4H, q,  $J$  7.0), 7.40–8.05 (3H, m) and 9.85 (1H, br d,  $J$  11.0);  $\nu_{max}/cm^{-1}$  (chloroform) 1710 and 1685 (C=O); 1,3,5-trinitrobenzoate complex of **12d**: reddish orange needles, mp 122–125 °C (Found: C, 54.6; H, 4.4; N, 7.6. Calc. for  $C_{26}H_{26}O_{10}N_3Cl$ : C, 54.2; H, 4.6; N, 7.3%).

**13d:** Red needles (from cyclohexane), mp 32–35 °C;  $\delta_H$  1.49 (6H, t,  $J$  7.0), 1.49 (9H, s), 4.53 (4H, q,  $J$  7.0), 7.94 (2H, dd,  $J$  10.5 and 1.0) and 9.91 (2H, dd,  $J$  10.5 and 1.0);  $\delta_C$  15.40, 32.69, 39.90, 61.49, 115.66, 129.80, 130.32, 138.06, 141.55, 165.42 and 166.00;  $\nu_{max}/cm^{-1}$  1681 (C=O);  $\lambda_{max}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 236 (4.54), 263 (4.30), 271 (4.38), 302 (4.71), 312 (4.79), 357 (4.00), 373 (3.73), 489 (2.79) and 507 (2.75); 1,3,5-trinitrobenzoate complex of **13d**: reddish orange needles, mp 142.5–143 °C (Found: C, 54.4; H, 4.5; N, 7.3. Calc. for  $C_{26}H_{26}O_{10}N_3Cl$ : C, 54.2; H, 4.6; N, 7.3%).

## Preparation and isolation of dihydroazulenes

Under a nitrogen atmosphere, a solution of **1** (1.000 g, 3.67 mmol) in dry ether (50 ml) was added to an ether solution of phenylmagnesium bromide, produced from bromobenzene (1.440 g, 9.17 mmol) and magnesium metal (0.223 g, 9.17 mmol) in dry ether (50 ml), and stirred for 30 min at room temperature. The reaction mixture was cooled on an ice-bath, and then methanol (8 ml) and 2 M hydrochloric acid (5 ml) was added. The mixture was extracted with ether, then the extract was washed with water, dried over sodium sulfate and evaporated. The residue was separated rapidly by silica gel (Wako-gel C-200) chromatography. Elution of benzene gave diethyl 4-phenyl-1,4-dihydroazulene-1,3-dicarboxylate (**10**) (0.900 g, 70%) and diethyl 2-phenyl-1,2-dihydroazulene-1,3-dicarboxylate (**9**) (0.210 g, 16%).

**9:** Yellow oil,  $\delta_H$  0.98 (3H, t,  $J$  7.0), 1.28 (3H, t,  $J$  7.0), 3.45 (1H, d,  $J$  3.6), 3.98 (2H, q,  $J$  7.0), 4.25 (2H, q,  $J$  7.0), 4.50 (1H, d,  $J$  3.6), 6.00–6.40 (4H, m), 7.13 (5H, br s) and 7.62 (1H, br d,  $J$  12.0);  $\nu_{max}/cm^{-1}$  (neat) 1736 and 1689 (C=O);  $\lambda_{max}$  (methanol)/nm (log  $\epsilon$ ) 365 (4.20) and 440 (3.38); Mass  $m/z$  350 ( $M^+$ ) (Found: C, 75.6; H, 6.4. Calc. for  $C_{22}H_{22}O_4$ : C, 75.4; H, 6.3%).

**10:** Yellow oil,  $\delta_H$  1.28 (3H, t,  $J$  7.0), 1.30 (3H, t,  $J$  7.0), 3.67 (1H, br s), 4.20 (1H, br s), 4.25 (2H, q,  $J$  7.0), 4.27 (2H, q,  $J$  7.0), 5.80–6.40 (3H, m), 6.90–7.30 (6H, m) and 7.50 (1H, br d,  $J$  12.0);  $\nu_{max}/cm^{-1}$  (neat) 1706 and 1695 (C=O);  $\lambda_{max}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 360 (3.94) and 402 (3.90); Mass  $m/z$  350 ( $M^+$ ) (Found: C, 75.7; H, 6.5. Calc. for  $C_{22}H_{22}O_4$ : C, 75.4; H, 6.3%).

## Dehydration of diethyl 2-phenyl-1,2-dihydroazulene-1,3-dicarboxylate (**9**)

A solution of **9** (0.042 g, 0.093 mmol) and TCQ (50 mg, 0.20 mmol) in benzene (10 ml) was refluxed for 1 h. The mixture was washed with 4% potassium hydroxide and water, dried over sodium sulfate, and evaporated. Chromatography of the residue on silica gel–benzene gave diethyl 2-phenylazulene-1,3-dicarboxylate **2a** (0.021 g, 50%).

## Dehydration of diethyl 4-phenyl-1,4-dihydroazulene-1,3-dicarboxylate (**10**)

A solution of **10** (0.200 g, 0.57 mmol) and TCQ (250 mg, 1.08 mmol) in xylene (8 ml) was refluxed for 2 h, then evaporated. Chromatography of the residue on alumina–benzene gave diethyl 4-phenylazulene-1,3-dicarboxylate (**3a**) (0.090 g, 36%).

## Reaction of diethyl 2-methoxyazulene-1,3-dicarboxylate (**15**) with Grignard reagents

**Typical procedure.** a) Under a nitrogen atmosphere, a solution of **15** (1.000 g, 3.31 mmol) in dry ether (30 ml) was added to an ether solution of phenylmagnesium bromide, produced

from bromobenzene (0.800 g, 5.10 mmol) and magnesium metal (0.120 g, 4.94 mmol) in dry ether (50 ml), at  $-20^{\circ}\text{C}$ , and then stirred for 30 min at room temperature. To the reaction mixture, methanol (8 ml) and 2 M hydrochloric acid (5 ml) were added. The mixture was extracted with benzene, then the extract was evaporated. The residue was chromatographed on silica gel. Elution with benzene gave diethyl 2-phenylazulene-1,3-dicarboxylate (**2a**) (0.826 g, 72%). Elution with chloroform gave diethyl 2-hydroxyazulene-1,3-dicarboxylate<sup>9</sup> (**16**) (0.241 g, 22%).

b) Under a nitrogen atmosphere, a solution of **15** (1.000 g, 3.31 mmol) in dry ether (30 ml) was added to an ether solution of phenylmagnesium bromide, produced from bromobenzene (1.820 g, 11.6 mmol) and magnesium metal (0.282 g, 11.6 mmol) in dry ether (50 ml), and stirred for 30 min at room temperature. The reaction mixture was cooled on ice-bath, and then methanol (15 ml) and 2 M hydrochloric acid (10 ml) were added. The mixture was extracted with benzene, then the extract was washed with 2 M sodium hydroxide solution. TCQ (2.0 g) was added to the solution, and stirred for 2 days at room temperature. The mixture was evaporated, and the residue was purified by alumina column chromatography with chloroform as an eluant. The effluent was evaporated and the residue was chromatographed on silica gel. Elution with benzene gave diethyl 2,6-diphenylazulene-1,3-dicarboxylate (**18a**) (0.065 g, 5%) and diethyl 2,4-diphenylazulene-1,3-dicarboxylate (**17a**) (0.645 g, 46%).

**17a**: Violet prisms (from ethanol), mp 113–114.5  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  0.75 (3H, t, *J* 7.3), 0.94 (3H, t, *J* 7.3), 3.34 (2H, q, *J* 7.3), 4.15 (2H, q, *J* 7.3), 7.36 (5H, br s), 7.40–7.90 (8H, m) and 9.78 (1H, dd, *J* 10.5 and 2.5);  $\nu_{\text{max}}/\text{cm}^{-1}$  1716 and 1681 (C=O);  $\lambda_{\text{max}}$  (2,2,4-trimethylpentane)/nm (log  $\epsilon$ ) 231 (4.40), 272 (4.31), 314 (4.60), 355 (3.96), 538 (2.89), 565 (2.89) and 615 (2.53) (Found: C, 78.9; H, 5.8. Calc. for  $\text{C}_{28}\text{H}_{24}\text{O}_4$ : C, 79.2; H, 5.7%).

**18a**: Red prisms (from ethanol), mp 188–189  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  0.93 (6H, t, *J* 7.3), 4.09 (4H, q, *J* 7.3), 7.37 (5H, br s), 7.40–7.80 (5H, m), 7.93 (2H, dd, *J* 10.5 and 1.0) and 9.81 (2H, dd, *J* 10.5 and 1.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1673 (C=O);  $\lambda_{\text{max}}$  (chloroform)/nm (log  $\epsilon$ ) 260 (4.01), 278 (4.14), 332 (4.73), 368 (4.19) and 507 (2.79) (Found: C, 79.0; H, 5.7. Calc. for  $\text{C}_{28}\text{H}_{24}\text{O}_4$ : C, 79.2; H, 5.7%).

In a similar manner, reactions of **2a**, **2c**, **21**, **25** and **26** with some Grignard reagents were performed (Table 1).

**19a**: Red prisms (from ethanol), mp 178–180  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  0.93 (6H, t, *J* 7.2), 4.11 (4H, q, *J* 7.2), 7.40 (5H, br s), 7.30–8.20 (7H, m), 9.55–9.85 (1H, m) and 9.99 (1H, d, *J* 2.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1685 (C=O) (Found: C, 79.0; H, 5.8. Calc. for  $\text{C}_{28}\text{H}_{24}\text{O}_4$ : C, 79.2; H, 5.7%).

**17c**: Violet prisms (from ethanol), mp 109.5–110.5  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  1.08 (3H, t, *J* 7.1), 1.46 (3H, t, *J* 7.1), 2.78 (3H, s), 3.52 (2H, q, *J* 7.1), 4.49 (2H, q, *J* 7.1), 7.48 (5H, br s), 7.30–7.70 (3H, m) and 9.62–9.87 (1H, m);  $\nu_{\text{max}}/\text{cm}^{-1}$  1698 and 1684 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 236 (4.30), 270 (4.30), 295 (4.43, sh), 309 (4.52), 357 (3.77), 378 (3.55), 540 (2.81) and 610 (2.33, sh) (Found: C, 75.9; H, 6.2. Calc. for  $\text{C}_{23}\text{H}_{22}\text{O}_4$ : C, 76.2; H, 6.1%).

**19c**: Red prisms (from ethanol), mp 95–96  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  1.49 (6H, t, *J* 7.3), 3.10 (3H, s), 4.55 (4H, q, *J* 7.3), 7.30–8.20 (7H, m), 9.53 (1H, d, *J* 10.5) and 9.91 (1H, d, *J* 10.5);  $\nu_{\text{max}}/\text{cm}^{-1}$  1685 (C=O) (Found: C, 76.0; H, 5.8. Calc. for  $\text{C}_{23}\text{H}_{22}\text{O}_4$ : C, 76.2; H, 6.1%).

**22**: Red prisms (from ethanol), mp 185–187  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  0.90 (6H, t, *J* 7.0), 4.07 (4H, q, *J* 7.0), 7.28 (5H, br s), 7.93 (2H, d, *J* 11.4) and 9.25 (2H, d, *J* 11.4);  $\nu_{\text{max}}/\text{cm}^{-1}$  1672 (C=O) (Found: C, 61.8; H, 4.6. Calc. for  $\text{C}_{21}\text{H}_{19}\text{O}_4\text{Br}$ : C, 61.7; H, 4.5%).

**23**: Red prisms (from ethanol), mp 188–189  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  1.07 (3H, t, *J* 7.3), 1.44 (3H, t, *J* 7.1), 3.65 (2H, q, *J* 7.3), 4.44 (2H, q, *J* 7.1), 7.53 (5H, br s), 7.94 (H, d, *J* 10.3), 8.03 (1H, s), 8.63 (1H, s) and 9.68 (1H, d, *J* 10.3);  $\nu_{\text{max}}/\text{cm}^{-1}$  1705 and 1697 (C=O) (Found: C, 61.9; H, 4.5. Calc. for  $\text{C}_{21}\text{H}_{19}\text{O}_4\text{Br}$ : C, 61.7; H, 4.5%).

**24**: Red plates (from ethanol), mp 201.5–202.5  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  0.93 (3H, t, *J* 7.2), 1.29 (3H, t, *J* 7.2), 3.24 (2H, q, *J* 7.2), 4.35 (2H, q, *J* 7.2), 7.48 (5H, br s), 7.45–8.05 (2H, m) and 9.10 (1H, d,

*J* 11.5);  $\nu_{\text{max}}/\text{cm}^{-1}$  3250 (OH), 1728, 1688 and 1668 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 242 (4.55), 268 (4.52), 306 (4.85, sh), 316 (4.85), 358 (4.17, sh), 518 (2.80) and 542 (2.78, sh) (Found: C, 46.7; H, 2.7. Calc. for  $\text{C}_{28}\text{H}_{19}\text{O}_6\text{Cl}_4\text{Br}$ : C, 47.0; H, 2.9%).

**27**: Orange needles (from ethanol), mp 126–127  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  0.91 (6H, t, *J* 7.1), 4.02 (3H, s), 4.11 (4H, q, *J* 7.1), 7.29 (2H, dm, *J* 12.0), 7.38 (5H, br s) and 9.54 (2H, dm, *J* 12.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  1668 (C=O);  $\lambda_{\text{max}}$  (cyclohexane)/nm (log  $\epsilon$ ) 234 (4.32), 265 (4.22, sh), 273 (4.30), 313 (4.69, sh), 325 (4.77), 353 (4.05), 362 (4.04), 380 (3.70), 470 (2.87) and 495 (2.80, sh) (Found: C, 73.2; H, 5.9. Calc. for  $\text{C}_{23}\text{H}_{22}\text{O}_5$ : C, 72.7; H, 5.9%).

#### Deesterification of diethyl 2,6-diphenylazulene-1,3-dicarboxylate (**18a**)

A mixture of **18a** (0.030 g, 0.071 mmol) and 100% phosphoric acid (2 ml) was heated at 100  $^{\circ}\text{C}$  for 1 h. To the reaction mixture water was added. The mixture was extracted with chloroform, then the extract was washed with water, dried over sodium sulfate and evaporated. The residue was chromatographed on alumina. Elution with benzene gave 2,6-diphenylazulene **28** (0.016 g, 81%).

**28**: Blue needles (from ethanol), mp 212–213.5  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  7.30–8.00 (12H, m), 8.43 (2H, d, *J* 10.0) and 9.20 (2H, d, *J* 10.0);  $\nu_{\text{max}}/\text{cm}^{-1}$  760, 694 and 685 (phenyl);  $\lambda_{\text{max}}$  (chloroform)/nm (log  $\epsilon$ ) 319 (4.89), 366 (3.90), 380 (4.00), 395 (4.08), 580 (2.60), 623 (2.60) and 680 (2.27) (Found: C, 93.5; H, 5.9. Calc. for  $\text{C}_{22}\text{H}_{16}$ : C, 93.3; H, 5.7%).

#### Reaction of diethyl azulene-1,3-dicarboxylates with phenyl and methyl lithium

**Typical procedure.** Under a nitrogen atmosphere, a solution of diethyl azulene-1,3-dicarboxylate **1** (0.200 g, 0.73 mmol) in dry ether (30 ml) was added to an ether solution of phenyllithium, produced from bromobenzene (0.344 g, 2.19 mmol) and lithium metal (0.030 g, 4.33 mmol) in dry ether (30 ml), and stirred for 30 min at room temperature. The reaction mixture was cooled on an ice-bath, and then methanol (8 ml) was added. TCQ (0.500 g) was added to the solution, and the solution was stirred overnight at room temperature. The solution was washed with 4% potassium hydroxide and water, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel. Elution with benzene gave diethyl 6-phenylazulene-1,3-dicarboxylate (**4a**) (0.003 g, 2%), diethyl 2-phenylazulene-1,3-dicarboxylate (**2a**) (0.028 g, 10%), and diethyl 4-phenylazulene-1,3-dicarboxylate (**3a**) (0.190 g, 70%).

In a similar manner, we treated **1** and **11** with phenyllithium and methyl lithium. Results are listed in Table 1.

#### Reaction of 2-chloro-1-azaazulenes with Grignard reagents

**Typical procedure.** Under a nitrogen atmosphere, a solution of 2-chloro-1-azaazulene (**29**) (1.000 g, 6.12 mmol) in dry THF (30 ml) was added to a solution of phenylmagnesium bromide, produced from bromobenzene (2.400 g, 15.30 mmol) and magnesium metal (0.372 g, 15.30 mmol) in dry THF (30 ml), and stirred for 30 min at room temperature. The reaction mixture was cooled on an ice-bath, and then methanol (8 ml) and 2 M hydrochloric acid (6 ml) were added. To the mixture water (150 ml) was added, and the mixture was extracted with chloroform. To the extract TCQ (2.00 g) was added, and the mixture was stirred for 3 h at room temperature, then evaporated. The residue was subjected to alumina column chromatography with chloroform as an eluant. The effluent was evaporated and the residue was chromatographed on silica gel. Elution with benzene gave 2-chloro-8-phenyl-1-azaazulene (**32**) (1.285 g, 88%), 2-chloro-6-phenyl-1-azaazulene (**31**) (0.050 g, 3%), and 2-chloro-4-phenyl-1-azaazulene (**30**) (0.057 g, 4%).

**30**: Reddish orange needles (from hexane), 120–121  $^{\circ}\text{C}$ ;  $\delta_{\text{H}}$  6.97 (1H, s), 7.40–7.60 (5H, m), 7.64–7.98 (3H, m) and 8.59

(1H, dm,  $J$  9.0);  $\nu_{\max}/\text{cm}^{-1}$  798, 775, 745 and 695 (phenyl);  $\lambda_{\max}$  (methanol)/nm (log  $\epsilon$ ) 228 (3.76), 275 (4.68), 308 (3.73, sh), 337 (3.75) and 470 (3.37) (Found: C, 75.4; H, 4.2; N, 5.7. Calc. for  $\text{C}_{15}\text{H}_{10}\text{NCl}$ : C, 75.2; H, 4.3; N, 5.7%).

**31:** Reddish orange prisms (from hexane), mp 137.5–138.5 °C;  $\delta_{\text{H}}$  7.17 (1H, s), 7.40–7.70 (5H, m), 7.81 (1H, dd,  $J$  10.8 and 1.8), 7.92 (1H, dd,  $J$  10.2 and 1.8), 8.40 (1H, d,  $J$  10.8) and 8.55 (1H, d,  $J$  10.2);  $\nu_{\max}/\text{cm}^{-1}$  847, 775, 760 and 698 (phenyl);  $\lambda_{\max}$  (methanol)/nm (log  $\epsilon$ ) 226 (3.24), 273 (4.58), 307 (4.39), 346 (4.12), 361 (4.15) and 576 (3.36) (Found: C, 75.6; H, 4.2; N, 5.8. Calc. for  $\text{C}_{15}\text{H}_{10}\text{NCl}$ : C, 75.2; H, 4.3; N, 5.7%).

**32:** Reddish orange needles (from cyclohexane), 123–124 °C;  $\delta_{\text{H}}$  7.18 (1H, s), 7.30–7.90 (8H, m) and 8.40 (1H, d,  $J$  9.7);  $\nu_{\max}/\text{cm}^{-1}$  797, 747, 732 and 690 (phenyl);  $\lambda_{\max}$  (methanol)/nm (log  $\epsilon$ ) 223 (3.80), 268 (4.51), 292 (4.24), 338 (3.74) and 468 (3.44) (Found: C, 75.5; H, 4.1; N, 5.9. Calc. for  $\text{C}_{15}\text{H}_{10}\text{NCl}$ : C, 75.2; H, 4.3; N, 5.7%).

In a similar manner, we treated ethyl 1-azaazulene-3-carboxylate (**33**) with phenylmagnesium bromide. Results are listed in Table 1.

**34:** Orange prisms (from hexane), 115.5–116.5 °C;  $\delta_{\text{H}}$  1.06 (3H, t,  $J$  7.0), 3.59 (2H, q,  $J$  7.0), 7.43 (5H, m), 7.60–8.03 (3H, m) and 865 (1H, d,  $J$  10.0);  $\nu_{\max}/\text{cm}^{-1}$  1703 (C=O), 790, 755, 742 and 700 (phenyl);  $\lambda_{\max}$  (methanol)/nm (log  $\epsilon$ ) 230 (4.32), 283 (4.68), 337 (3.89) and 468 (3.44) (Found: C, 69.9; H, 4.5; N, 4.5. Calc. for  $\text{C}_{18}\text{H}_{14}\text{NOCl}$ : C, 70.0; H, 4.5; N, 4.5%).

**35:** Yellow needles (from hexane), mp 167–169 °C;  $\delta_{\text{H}}$  1.50 (3H, t,  $J$  7.2), 4.49 (2H, q,  $J$  7.2), 7.40–7.65 (5H, m), 8.13 (2H, dd,  $J$  10.3 and 1.5), 8.19 (1H, dd,  $J$  10.3 and 1.5) and 9.55 (1H, dd,  $J$  10.3 and 1.5);  $\nu_{\max}/\text{cm}^{-1}$  1680 (C=O), 852, 770, 743 and 685 (phenyl);  $\lambda_{\max}$  (methanol)/nm (log  $\epsilon$ ) 283 (4.49, sh), 298 (4.55), 313 (4.57), 345 (4.34), 361 (4.36) and 443 (3.34) (Found: C, 69.8; H, 4.4; N, 4.5. Calc. for  $\text{C}_{18}\text{H}_{14}\text{NOCl}$ : C, 70.0; H, 4.5; N, 4.5%).

**36:** Yellow needles (from cyclohexane), 154–155.5 °C;  $\delta_{\text{H}}$  1.47 (3H, t,  $J$  7.0), 4.46 (2H, q,  $J$  7.0), 7.36–8.06 (8H, m) and 9.58 (1H, dm,  $J$  9.5);  $\nu_{\max}/\text{cm}^{-1}$  1684 (C=O), 797, 765, 747 and 692 (phenyl);  $\lambda_{\max}$  (methanol)/nm (log  $\epsilon$ ) 279 (4.56), 300 (4.42, sh), 338 (4.01, sh) and 447 (3.20) (Found: C, 69.7; H, 4.5; N, 4.6. Calc. for  $\text{C}_{18}\text{H}_{14}\text{NOCl}$ : C, 70.0; H, 4.5; N, 4.5%).

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