[2 + 2] Cycloaddition reaction of cycloheptatriene with dichloroketene. A novel and efficient synthetic strategy for the synthesis of 2-hydroxyazulene

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The reaction of cycloheptatriene with dichloroketene, generated by the treatment of trichloroacetyl chloride with activated zinc in dry diethyl ether, affords 9,9-dichlorobicyclo[5.2.0]nona-2,4-dien-8-one **2** as a major product together with 3′,3′,9,9-tetrachlorospiro(bicyclo[5.2.0]nona-2,4-diene-8,2′-oxetan)-4′-one **3**. Structure **3** is elucidated by the X-ray crystallographic analysis of its partially reduced product. Lactone **3** exhibits [1,5] hydrogen-migration in the seven-membered ring to give 3′,3′,9,9-tetrachlorospiro(bicyclo[5.2.0]nona-3,5-diene-8,2′-oxetan)-4′-one **7** without any decarbonylation. The reaction of **2** with diazomethane exhibits ring expansion of the four-membered ring to give 1,1-dichloro-3,3a,4,8a-tetrahydroazulen-2(1*H*)-one **8**. 2-Hydroxyazulene **9** is successfully derived by the reaction of **8** with lithium chloride in good yield. The reaction of **8** with triethylamine exhibits dehydrochlorination to give 3-chloro-8,8a-dihydroazulen-2(1*H*)-one **10** in high yield. *N*-(Azulen-2-yl)pyrrolidine is also derived from either **9** or **10** in good yield.

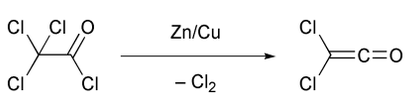
Introduction

Azulene ($C_{10}H_8$) is of great interest to many chemists due to its special carbon skeleton derived from sesquiterpenes as well as its beautiful blue color. Synthetic methods for azulenes have been extensively studied so far.[1] Ziegler and Hafner reported the synthesis of parent azulene using the reaction of Zincke's aldehyde with cyclopentadiene in 1955.[2] Nozoe *et al.* found the reaction of activated troponoids to give 1,2,3-trisubstituted azulenes.[3] Furthermore, Yasunami *et al.* developed a new synthetic method for various azulene derivatives by the reaction of 2*H*-cyclohepta[*b*]furan-2-ones with enamines.[4] These methods are highly efficient for the synthesis of azulenes. However, it could not be said that azulenes are readily available compounds even using these methods. If commercially available cycloheptatriene **1** could be utilized as a source for the seven-membered ring of azulenes, the strategy would become an efficient method for the synthesis of azulenes substituted on the five-membered ring.

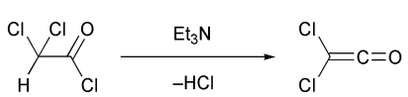
We considered that the [2 + 2] cycloadduct of **1** to ketenes could be easily transformed into azulene derivatives *via* ring-expansion reaction of its four-membered ring.[5] Therefore, we focused our attention on [2 + 2] cycloaddition reactions of **1** with ketenes in order to develop a new and efficient synthetic method for azulene derivatives. Since diphenylketene was synthesized and isolated by Staudinger in 1905,[6] reactions of varieties of ketenes with olefins and carbonyl compounds have appeared in the literature.[7] However, there are only two reports concerning the reaction of **1** with ketenes because of the low reactivity of their substrates.[8,9] We found the reaction conditions in which **1** reacted with dichloroketene to give a [2 + 2] cycloadduct in good yield. In this paper we report the reaction of **1** with the ketene and a new strategy for the synthesis of several azulene derivatives starting from the [2 + 2] cycloadduct.

Results and discussion

Dichloroketene is unstable and polymerizes readily.[10] However, it can be easily generated *in situ* by two methods [equations (1) and (2)]. The reactivity of **1** with the ketene significantly



(1)



(2)

depended on the preparation method and the solvents used. The ketene generated by the above two methods did not react with **1** in either dry hexane or dry benzene. When the ketene was generated by equation (2) in dry diethyl ether, the reaction also did not afford satisfactory results. However, we found that the ketene generated by equation (1) in dry diethyl ether reacted with **1** to give desired [2 + 2] cycloadduct, 9,9-dichlorobicyclo[5.2.0]nona-2,4-dien-8-one **2** in 58% yield together with 3′,3′,9,9-tetrachlorospiro(bicyclo[5.2.0]nona-2,4-diene-8,2′-oxetan)-4′-one **3**, (2%) (Scheme 1). GLC analysis exhibited the recovery of unchanged **1** (17%).The isolated yield of **3** was increased up to 12% by conducting the reaction at reflux temperature. Table 1 summarizes isolated and GLC yields of **2** and **3** under several conditions. Although crude **2** exhibited decomposition even at room temperature, it could be purified by molecular distillation at 90 °C (bath temp)/1.0 mmHg (1 mmHg = 133.322 Pa). Purified **2** was relatively stable at higher temperature. Even if purified **2** were heated without any solvent at 100 °C for 3 h, it could be recovered almost quantitatively.

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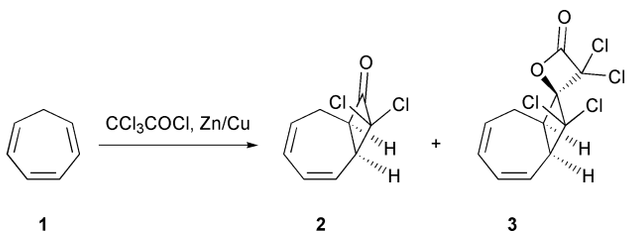
Table 1 Reaction of **1** with dichloroketene

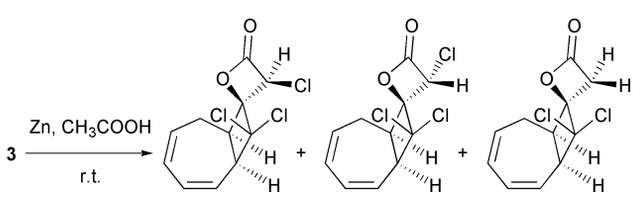
Conditions		Yield (%)[a]		
Temp.	CCl_3COCl (eq.)	**2**	**3**	recovered **1**
r.t.	2	58 (59)	2 (3)	(17)
Reflux	2	(37)	(13)	(8)
Reflux	4	9 (12)	12 (14)	(0)

[a] Yields of **2** and **3** were calculated on the basis of **1**. GLC yields are shown in parentheses.



Scheme 1

The structure of **3** suggests that it was produced by the reaction of **2** with another molecule of dichloroketene. Indeed further reaction of isolated **2** with the ketene generated under similar reaction conditions afforded **3**, although the yield was poor (4%). The rather low yield of **3** results from the significant decomposition of **2** under the reaction conditions. Determination of the stereochemistry of **3** could not be achieved from the spectroscopic data above; also, suitable crystals for X-ray crystallographic analysis were not obtained for this compound. Therefore, compound **3** was partially reduced by zinc in acetic acid to give (1*RS*,7*SR*,2′*RS*,3′*RS*)-3′,9,9-trichlorospiro-,(1*RS*,7*SR*,2′*RS*,3′*SR*)-3′,9,9-trichlorospiro-, and 9,9-dichlorospiro-(bicyclo[5.2.0]nona-2,4-diene-8,2′-oxetan)-4′-ones **4**, **5** and **6** in 40, 12 and 14% yield, respectively (Scheme 2). Suitable crystals



Scheme 2

for X-ray crystallographic analysis were obtained from the major product **4**. Thus, the relative structure of **4** was established, as shown in Fig. 1. Consequently, the stereochemistry of **3** was elucidated as shown in Scheme 1.

β-Lactones frequently show decarboxylation, *e.g.*, the [2 + 2] cycloadduct obtained by the reaction of cyclopentanone with dichloroketene exhibits decarboxylation even at 120–150 °C.[11] However, **3** did not show any decarboxylation even on heating to above 200 °C without any solvent. Instead of the decarboxylation reaction, **3** exhibited intramolecular [1,5] hydrogen-migration in the seven-membered ring at above 115 °C to afford 3′,3′,9,9-tetrachlorospiro(bicyclo[5.2.0]nona-3,5-diene-8,2′-oxetan)-4′-one **7**. This rearrangement reached equilibrium in a ratio of **3** : **7** = 1 : 4.5 at 200 °C after 7 h (Scheme 3).

The four-membered cyclobutanone ring of **2** could be expanded regioselectively to give 1,1-dichloro-3,3a,4,8a-tetrahydroazulen-2(1*H*)-one **8** by the reaction with diazomethane in 85% yield (Scheme 4). The ring-expansion reaction would become a key step for the synthesis of azulene derivatives using the adduct **2**, although **8** was relatively unstable even at room temperature.

Table 2 Effect of lithium reagent on the dehydrochlorination of **8**

	Conditions		Yield (%)	
Entry	Reagent	Time (*t*/h)	**9**	**10**
1		18	2	21
2	LiCl	6	73	
3	Li_2CO_3	12	41	
4	$LiCl–Li_2CO_3$	12	66	
5	LiBr	6	46	

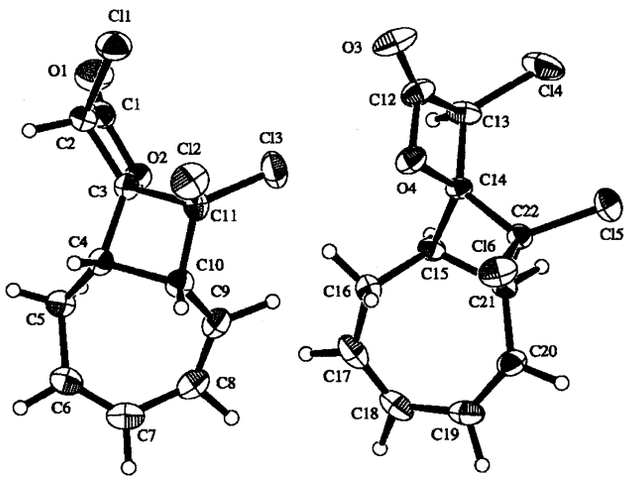
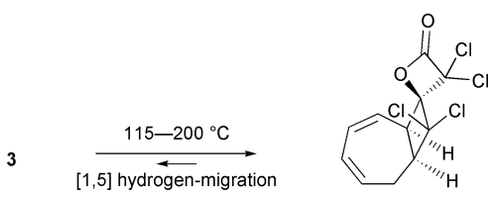
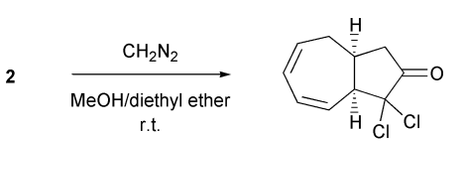


Fig. 1 ORTEP drawing of two independent molecules of **4** in the crystalline state along with the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The two molecules exhibit slight differences in their conformations.

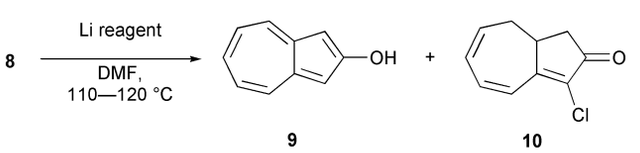


Scheme 3



Scheme 4

2-Hydroxyazulene **9**[12] was successfully synthesized by the reaction of **8** with lithium chloride, lithium bromide and/or lithium carbonate in DMF (Scheme 5). Table 2 displays the



Scheme 5

results of the reaction of **8** with lithium reagents under several conditions. Lithium reagents were essential for this reaction. Heating of **8** alone in DMF for 18 h resulted in the formation of **9** and 3-chloro-8,8a-dihydroazulen-2(1*H*)-one **10** in only

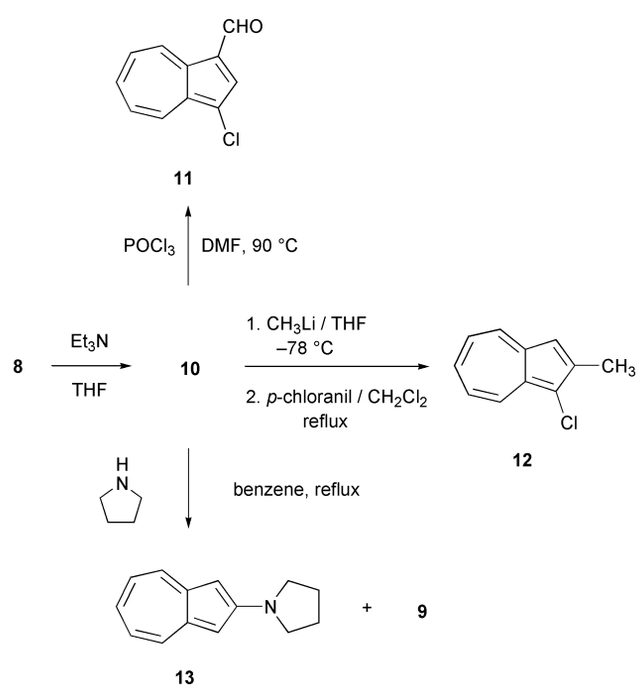
Table 3 Dehydrochlorination of **8** under acidic and basic conditions

Entry	Conditions	Yield (%) of **15**
1	1,4-Dioxane	0[a]
2	30% H_2SO_4–1,4-dioxane	43
3	5 M HCl–1,4-dioxane	61
4	DMSO	86
5	Et_3N–THF	95

[a] Starting material **13** was recovered (41%).

2 and 21% yield, respectively (entry 1). The reaction of **8** with LiCl at 110–120 °C for 6 h gave the desired **9** in 73% yield (entry 2). In the case of the reaction of **8** with LiCl–Li_2CO_3 or Li_2CO_3 in DMF, a prolonged reaction time was necessary to complete the reaction (entries 3 and 4). Lithium bromide also could serve as a reagent for this reaction (entry 5). A plausible reaction pathway for the formation of **9** was assumed to proceed *via* **10**. Indeed the reaction of **10** with LiCl under similar reaction conditions afforded **9** in 75% yield. In the present method, **9** can be prepared in 3 steps starting from the commercially available **1**. Using the previously reported method, 5 steps are necessary for the synthesis of **9** starting from commercially unavailable 2-substituted tropone derivatives.[12]

Compound **10** was obtained by the reaction of **8** with triethylamine in THF at room temperature in almost quantitative yield. The dehydrochlorination reaction also occurred either under acidic conditions or in DMSO. The results of the reaction under basic and acidic conditions are summarized in Table 3. Compound **10** was more stable than **8** and could be also utilized for the synthesis of azulene derivatives. 3-Chloroazulene-1-carbaldehyde[14] **11** was obtained by the Vilsmeier reaction of **10** in 54% yield. 1-Chloro-2-methylazulene **12** was obtained by the reaction of **10** with methyllithium followed by oxidation with *p*-chloranil in 31% yield. In addition, *N*-(azulen-2-yl)pyrrolidine[15] **13** was obtained by the reaction of **10** with pyrrolidine in refluxing benzene in 47% yield together with **9** (7%), which could be assumed to be an intermediate of this reaction (Scheme 6). The reaction of **9** with pyrrolidine under similar reaction conditions also afforded **13**, in 75% yield.



Scheme 6

Conclusions

We have found that cycloheptatriene **1** reacts with dichloroketene, generated by reaction of trichloroacetyl chloride with zinc in diethyl ether, to give a [2 + 2] cycloadduct **2**, which is utilized for the synthesis of several azulene derivatives, *i.e.*, 2-hydroxyazulene **9**, 3-chloroazulene-1-carbaldehyde **11**, 1-chloro-2-methylazulene **12** and *N*-(azulen-2-yl)pyrrolidine **13**. This is a new short-step strategy for the synthesis of azulene derivatives starting from commercially available **1**. Synthetic application using this strategy for the synthesis of other azulene derivatives is under study in our laboratory.

Experimental

General

Mps were determined on a Yanagimoto micro melting-point apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR (^{13}C NMR) spectra were recorded on a JEOL GSX 400 at 400 MHz (100 MHz), a JEOL A500 at 500 MHz (125 MHz), a Bruker AM 600, or a JEOL Lambda 600 spectrometer at 600 MHz (150 MHz). *J*-Values are given in Hz. Gel-permeation chromatography (GPC) was performed on a TSKgel G2000H_6. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

9,9-Dichlorobicyclo[5.2.0]nona-2,4-dien-8-one 2. A solution of trichloroacetyl chloride (22.0 g, 121 mmol) in dry diethyl ether (200 cm^3) was added dropwise at room temperature to a mixture of activated zinc powder (11.6 g, 177 mg-atom) and **1** (5.54 g, 60.1 mmol) in the same solvent (200 cm^3) over a period of 2 h. After stirring of the mixture at the same temperature for another 2 h, residual zinc powder was removed by filtration. The filtrate was washed successively with water and 5% aq. $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by molecular distillation at 90 °C (bath temp)/1.0 mmHg to afford **2** (7.04 g, 58%) as a pale yellow oil and **3** (402 mg, 2%) as colorless crystals.

For **2**: (Found: C, 53.1; H, 4.2. Calc. for $C_9H_8Cl_2O$: C, 53.2; H, 4.0%); λ_{max} (MeOH)/nm 241 (log ε 3.66); ν_{max} (neat)/cm^{-1} 1809 (C=O); δ_H (600 MHz; $CDCl_3$) 6.24 (dd, *J* 11.8 and 3.0, 2-H), 6.01 (m, 4-H and 5-H), 5.94 (ddt, *J* 11.8, 5.5 and 1.5, 3-H), 4.05 (ddd, *J* 12.4, 11.4 and 4.0, 7-H), 3.74 (dtd, *J* 11.4, 3.0 and 1.5, 1-H), 2.64 (dddd, *J* 13.9, 12.4, 5.9 and 2.2, 6-*endo*-H) and 2.55 (ddd, *J* 13.9, 7.7 and 4.0, 6-*exo*-H); δ_C (150 MHz; $CDCl_3$) 196.0 (C-8), 131.5 (C-4 or C-5), 129.1 (C-2), 128.7 (C-3), 128.6 (C-5 or C-4), 91.2 (C-9), 66.0 (C-7), 51.2 (C-1) and 27.8 (C-6); *m*/*z* (EI) 201.9949 (M^+. $C_9H_8Cl_2O$ requires *M*, 201.9952), 139 (98%), 103 (100), 91 (70) and 51 (32).

For **3**: mp 101–102 °C (Found: C, 42.2; H, 2.6; Cl, 45.2. Calc. for $C_{11}H_8Cl_4O_2$: C, 42.1; H, 2.6; Cl, 45.2%); λ_{max} (CH_3CN)/nm 245 (log ε 3.65); ν_{max} (KBr disk)/cm^{-1} 1864 (C=O); δ_H (600 MHz; $CDCl_3$) 6.27 (dd, *J* 11.0 and 2.6, 2-H), 6.15 (ddd, *J* 10.4, 7.9 and 5.5, 5-H), 5.99 (dddd, *J* 11.0, 4.3, 3.3 and 1.0, 3-H), 5.95 (dddd, *J* 10.4, 4.3, 2.3 and 0.5, 4-H), 4.23 (ddd, *J* 12.8, 10.2 and 5.9, 7-H), 3.61 (dddd, *J* 10.2, 3.3, 2.6 and 0.5, 1-H), 2.68 (tddd, *J* 12.8, 5.5, 2.3 and 1.0, 6-*endo*-H) and 2.03 (ddd, *J* 12.8, 7.9 and 5.9, 6-*exo*-H); δ_C (150 MHz; $CDCl_3$) 159.1 (C-4′), 130.8 (C-5), 130.5 (C-4), 129.1 (C-2 and C-3), 94.8 (C-8), 84.1 (C-9), 80.7 (C-3′), 54.7 (C-7), 52.9 (C-1) and 22.6 (C-6); *m*/*z* (EI) 312 (M^+, 6%) and 92 (100).

Partial reduction of 3. Zinc powder (660 mg, 10.1 mg-atom) was added at room temperature to a solution of **3** (320 mg, 1.02 mmol) in acetic acid (10 cm^3). After stirring of the mixture for

1 min at the same temperature, residual zinc powder was removed by filtration. The filtrate was washed successively with water and 5% aq. $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by medium-pressure liquid chromatography on silica gel with ethyl acetate–hexane (1 : 4) to afford **4** (114 mg, 40%) as colorless prisms, **5** (36 mg, 12%) as colorless crystals, and **6** (36 mg, 14%) as colorless crystals.

For **4**: mp 97–98 °C (Found: C, 47.4; H, 3.5. Calc. for $C_{11}H_9Cl_3O_2$: C, 47.3; H, 3.25%); λ_{max} (CH_3CN)/nm 242 (log ε 3.72); ν_{max} (KBr disk)/cm^{-1} 1862 (C=O); δ_H (500 MHz; $CDCl_3$) 6.03 (m, 2-H, 3-H and 4-H), 5.91 (m, 5-H), 5.63 (s, 3′-H), 3.66 (ddd, *J* 13.5, 10.0 and 3.5, 7-H), 3.54 (d, *J* 10.0, 1-H), 2.88 (tdd, *J* 13.5, 4.5 and 2.5, 6-*endo*-H) and 2.30 (ddd, *J* 13.5, 8.0 and 3.5, 6-*exo*-H); δ_C (150 MHz; $CDCl_3$) 161.5 (C-4′), 131.1 (C-4), 128.9 (C-2), 128.4 (C-5), 128.0 (C-3), 89.4 (C-8), 87.6 (C-9), 60.4 (C-3′), 52.7 (C-1), 47.1 (C-7) and 25.8 (C-6); *m*/*z* (EI) 278 (M^+, 13%) and 92 (100).

For **5**: mp 57–58 °C (Found: C, 47.2; H, 3.3. Calc. for $C_{11}H_9Cl_3O_2$: C, 47.3; H, 3.25%); λ_{max} (CH_3CN)/nm 242 (log ε 3.80); ν_{max} (KBr disk)/cm^{-1} 1844 (C=O); δ_H (500 MHz; $CDCl_3$) 6.23 (dd, *J* 11.3 and 2.9, 2-H), 6.09 (ddd, *J* 10.5, 7.8 and 5.4, 5-H), 5.98 (ddd, *J* 11.3, 4.6 and 2.9, 3-H), 5.93 (ddd, *J* 10.5, 4.6 and 2.2, 4-H), 5.05 (s, 3′-H), 3.88 (ddd, *J* 13.5, 10.0 and 5.4, 7-H), 3.66 (d, *J* 10.0, 1-H), 2.78 (tdd, *J* 13.5, 5.4 and 2.2, 6-*endo*-H) and 2.06 (ddd, *J* 13.5, 7.8 and 5.4, 6-*exo*-H); δ_C (150 MHz; $CDCl_3$) 162.2 (C-4′), 130.7 (C-4), 130.0 (C-2), 129.1 (C-5), 128.7 (C-3), 87.8 (C-8), 86.2 (C-9), 59.7 (C-3′), 54.5 (C-1), 54.4 (C-7) and 23.8 (C-6); *m*/*z* (EI) 278 (M^+, 0.9%) and 92 (100).

For **6**: mp 101 °C (Found: C, 53.7; H, 4.1; Cl, 28.6. Calc. for $C_{11}H_{10}Cl_2O_2$: C, 53.9; H, 4.1; Cl, 28.9%); λ_{max} (CH_3CN)/nm 242 (log ε 3.78); ν_{max} (KBr disk)/cm^{-1} 1883 (C=O); δ_H (600 MHz; $CDCl_3$) 6.05 (dd, *J* 11.8 and 2.7, 2-H), 6.00 (ddd, *J* 11.8, 5.3 and 2.5, 3-H), 5.99 (ddd, *J* 10.2, 5.3 and 4.8, 4-H), 5.88 (m, 5-H), 4.09 (d, *J* 16.7, 3′-*endo*-H), 3.60 (ddd, *J* 9.8, 2.7 and 2.5, 1-H), 3.42 (d, *J* 16.7, 3′-*exo*-H), 3.31 (ddd, *J* 13.8, 9.8 and 3.6, 7-H), 2.91 (dddd, *J* 13.8, 13.8, 4.8 and 2.3, 6-*endo*-H) and 2.38 (ddd, *J* 13.8, 8.3 and 3.6, 6-*exo*-H); δ_C (150 MHz; $CDCl_3$) 164.6 (C-4′), 131.2 (C-2), 128.6 (C-3), 128.2 (C-4 and C-5), 90.8 (C-8), 82.7 (C-9), 52.5 (C-1), 52.0 (C-7), 47.0 (C-3′) and 26.5 (C-6); *m*/*z* (EI) 244 (M^+, 9%), 139 (40), 103 (38) and 92 (100).

3′,3′,9,9-Tetrachlorospiro(bicyclo[5.2.0]nona-3,5-diene-8,2′-oxetan)-4′-one 7. Lactone **3** (238 mg, 0.758 mmol) was heated at 130 °C for 12 h under an N_2 atmosphere. The reaction mixture was chromatographed by a short column on Florisil® with CH_2Cl_2 and purified by GPC with $CHCl_3$ to afford **7** (153 mg, 64%) as colorless crystals and recovered **3** (24 mg, 10%).

For **7**: mp 57 °C (Found: C, 42.1; H, 2.55; Cl, 45.2. Calc. for $C_{11}H_8Cl_4O_2$: C, 42.1; H, 2.6; Cl, 45.2%); λ_{max} (CH_3CN)/nm 243 (log ε 3.77); ν_{max} (KBr disk)/cm^{-1} 1862 (C=O); δ_H (600 MHz; $CDCl_3$) 6.02 (ddd, *J* 11.8, 5.7 and 2.7, 5-H), 5.96 (ddd, *J* 10.6, 8.5 and 4.8, 3-H), 5.88 (ddt, *J* 10.6, 5.7 and 1.3, 4-H), 5.69 (dd, *J* 11.8 and 3.3, 6-H), 4.20 (ddd, *J* 8.8, 3.3 and 2.7, 7-H), 3.39 (ddd, *J* 12.7, 8.8 and 3.9, 1-H), 2.58 (dddd, *J* 14.3, 12.7, 4.8 and 1.3, 2-*endo*-H) and 2.54 (ddd, *J* 14.3, 8.5 and 3.9, 2-*exo*-H); δ_C (150 MHz; $CDCl_3$) 159.4 (C-4′), 130.2 (C-5), 129.7 (C-3), 128.1 (C-4), 125.3 (C-6), 96.6 (C-8), 84.3 (C-9), 81.0 (C-3′), 59.8 (C-1), 44.2 (C-7) and 28.3 (C-2); *m*/*z* (EI) 312 (M^+, 16%) and 91 (100).

1,1-Dichloro-3,3a,4,8a-tetrahydroazulen-2(1*H*)-one 8. To a solution of **2** (938 mg, 4.62 mmol) in methanol (3 cm^3) and diethyl ether (30 cm^3) was added a solution of diazomethane (12 mmol) in the same solvent (12 cm^3) at room temperature. After stirring of the mixture for 30 min, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **8** (856 mg, 85%) as colorless crystals, mp 49–50 °C (Found: C, 55.4; H, 4.5. Calc. for $C_{10}H_{10}Cl_2O$: C, 55.3; H, 4.6%); λ_{max} (MeOH)/nm 240 (log ε 3.82); ν_{max} (KBr disk)/cm^{-1} 1759 (C=O); δ_H (600 MHz; $CDCl_3$) 6.12 (ddd, *J* 5.9 and 2.5, 7-H), 6.03 (dd, *J* 12.1 and 4.1, 8-H), 5.96 (m, 5-H and 6-H), 3.54 (m, 8a-H), 2.98 (m, 3a-H), 2.77 (dd, *J* 19.7 and 9.0, 3-*endo*-H), 2.65 (ddd, *J* 15.2, 10.8 and 4.8, 4-*endo*-H), 2.50 (dd, *J* 19.7 and 6.2, 3-*exo*-H) and 2.34 (ddd, *J* 15.2, 6.8 and 2.5, 4-*exo*-H); δ_C (150 MHz; $CDCl_3$) 201.6 (C-2), 132.5 (C-5), 129.0 (C-7), 127.2 (C-6 and C-8), 87.0 (C-1), 56.6 (C-8a), 39.2 (C-3a), 38.7 (C-3) and 32.0 (C-4); *m*/*z* (EI) 216 (M^+, 27%), 180 (93), 152 (35), 138 (54), 117 (100) and 91 (48).

2-Hydroxyazulene 9. A solution of **8** (435 mg, 2.00 mmol) in DMF (3 cm^3) was added at 110–120 °C to a solution of lithium chloride (856 mg, 20.2 mmol) in DMF (40 cm^3). After stirring of the mixture at the same temperature for 6 h, the reaction mixture was poured into water. The resulting mixture was acidified with 2 M hydrochloric acid and extracted with toluene. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate–hexane (1 : 4) to afford **9** (211 mg, 73%) as red plates, mp 115–116 °C (lit.,[12b] 116–117 °C).

3-Chloro-8,8a-dihydroazulen-2(1*H*)-one 10. A solution of **8** (218 mg, 1.00 mmol) and triethylamine (209 mg, 2.07 mmol) in THF (30 cm^3) was stirred at room temperature for 9 h. The precipitated ammonium salt was removed by filtration. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **10** (171 mg, 95%) as pale yellow needles, mp 76 °C (Found: C, 66.3; H, 5.0; Cl, 19.9. Calc. for $C_{10}H_9ClO$: C, 66.5; H, 5.0; Cl, 19.6%); λ_{max} (MeOH)/nm 231 (log ε 4.00) and 333 (4.17); ν_{max} (KBr disk)/cm^{-1} 1703 (C=O); δ_H (600 MHz; $CDCl_3$) 6.79 (d, *J* 11.6, 4-H), 6.42 (dd, *J* 11.6 and 7.2, 5-H), 6.26 (ddd, *J* 11.6, 8.6 and 3.4, 7-H), 6.12 (ddd, *J* 11.6, 7.2 and 2.8, 6-H), 3.05 (dddd, *J* 13.5, 6.9, 3.7 and 2.5, 8a-H), 2.93 (dd, *J* 18.3 and 6.9, 1-*endo*-H), 2.64 (ddd, *J* 16.9, 8.6 and 2.5, 8-*exo*-H), 2.35 (ddd, *J* 16.9, 13.5 and 3.4, 8-*endo*-H) and 2.14 (dd, *J* 18.3 and 3.7, 1-*exo*-H); δ_C (150 MHz; $CDCl_3$) 198.8 (C-2), 164.8 (C-3a), 136.6 (C-7), 135.6 (C-5), 129.2 (C-3), 126.9 (C-6), 123.4 (C-4), 40.7 (C-1), 36.9 (C-8a) and 33.4 (C-8); *m*/*z* (EI) 180 (M^+, 86%), 138 (57) and 117 (100).

3-Chloroazulene-1-carbaldehyde 11. Phosphoryl trichloride (468 mg, 3.05 mmol) was added at room temperature to a solution of **10** (182 mg, 1.01 mmol) in DMF (10 cm^3). The resulting mixture was stirred at 90 °C for 3 h. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate–hexane (1 : 4) to afford **11**[14] (104 mg, 54%) as purple needles, mp 117–118 °C; λ_{max} (CH_2Cl_2)/nm 212 (log ε 4.25), 238 (4.28), 271 (4.09), 310 (4.51), 384 (3.92) and 549 (2.69); ν_{max} (KBr disk)/cm^{-1} 1655 (C=O); δ_H (500 MHz; $CDCl_3$) 10.28 (s, 1-CHO), 9.53 (d, *J* 9.8, 4-H), 8.57 (d, *J* 9.9, 8-H), 8.13 (s, 2-H), 7.90 (dd, *J* 10.1 and 9.6, 6-H), 7.62 (t, *J* 10.1 and 9.8, 5-H) and 7.59 (t, *J* 9.9 and 9.6, 7-H); δ_C (100 MHz; $CDCl_3$) 185.5 (1-CHO), 141.1 (C-6), 139.5 (C-3a), 139.1 (C-2), 138.9 (C-8a), 138.3 (C-4), 136.8 (C-8), 129.9 (C-5), 128.4 (C-7), 123.5 (C-3) and 118.5 (C-1); *m*/*z* (EI) 190 (M^+, 90%) and 126 (43).

1-Chloro-2-methylazulene 12. A solution of methyllithium in diethyl ether (2.0 cm^3, 2.2 mmol) was added at −78 °C under an N_2 atmosphere to a solution of **10** (182 mg, 1.01 mmol) in THF (30 cm^3) over a period of 5 min. After stirring of the mixture at the same temperature for 4 h, the mixture was warmed to room temperature and stirred for another 30 min. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was washed with water, dried over $MgSO_4$, and

concentrated under reduced pressure. *p*-Chloranil (748 mg, 3.04 mmol) and CH_2Cl_2 (30 cm^3) were added to the residue, and the mixture was refluxed for 3 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **12** (55 mg, 31%) as blue needles, mp 61 °C (Found: C, 74.6; H, 5.3; Cl, 20.2. Calc. for $C_{11}H_9Cl$: C, 74.8; H, 5.1; Cl, 20.1%); λ_{max} (CH_2Cl_2)/nm 284 (log ε 4.60), 290 (4.62), 352 (3.57) and 588 (2.25); ν_{max} (KBr disk)/cm^{-1} 1576, 1495, 1401, 1051, 871 and 731; δ_H (400 MHz; $CDCl_3$) 8.23 (d, *J* 9.8, 8-H), 8.21 (d, *J* 9.3, 4-H), 7.54 (dd, *J* 10.2 and 9.3, 6-H), 7.19 (dd, *J* 9.8 and 9.3, 7-H), 7.17 (s, 3-H), 7.14 (dd, *J* 10.2 and 9.3, 5-H) and 2.62 (s, 2-Me); δ_C (100 MHz; $CDCl_3$) 145.9 (C-2), 138.5 (C-3a), 136.9 (C-6), 135.2 (C-4), 133.7 (C-8a), 132.3 (C-8), 123.5 (C-5), 123.0 (C-7), 116.4 (C-1), 115.9 (C-3) and 14.6 (2-Me); *m*/*z* (EI) 176 (M^+, 100%) and 141 (45).

***N*-(Azulen-2-yl)pyrrolidine 13.** A solution of **9** (76 mg, 0.53 mmol) and pyrrolidine (80 mg, 1.1 mmol) in benzene (30 cm^3) was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **13** (77 mg, 75%) as an orange powder, mp 117–118 °C (lit.,[15] 114–115 °C).

X-Ray crystallographic data for 4†. Data and diffraction parameters were obtained for a crystal with dimension 0.05 × 0.10 × 0.20 mm using a Rigaku/MSC mercury CCD diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) at 20 °C. Crystal system: monoclinic. Space group: $P2_1/a$. Unit-cell dimensions: a = 9.751(1), b = 18.486(1), c = 14.7287(6) Å, β = 115.7591(4)°, V = 2391.1(3) $Å^3$, Z = 8. D_{calc} = 1.553 g cm^{-3}; μ (Mo-Kα) = 7.45 cm^{-1}; F (000) = 1136. 2θ-Range for data collection = 0.0–55.0°. Number of measured reflections = 20 686. Independent reflections = 5258 (R_{int} = 0.028). Final R = 0.041, R_w = 0.042 for 2442 observed reflections [$I_0 > 2\sigma(I_0)$]. Parameters = 289. GOF = 0.94. $\Delta\rho_{max}$ and $\Delta\rho_{min}$ are 0.21 and −0.22 e $Å^{-3}$, respectively. Refinement method: full-matrix least-squares. All calculations were performed using software package of Molecular Structure Corporation (Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1999).

† CCDC reference number(s) 164081. See http://www.rsc.org/suppdata/p1/b1/b104164a/ for crystallographic files in .cif or other electronic format.

References

1 K.-P. Zeller, in Houben-Weyl, *Methoden der Organischen Chemie*, ed. E. Müller, Georg Thieme Verlag, Stuttgart, 1985, vol. 5, Part 2c, p. 127.
2 (*a*) K. Ziegler and K. Hafner, *Angew. Chem.*, 1955, **67**, 310; (*b*) K. Hafner, *Angew. Chem.*, 1955, **67**, 301; (*c*) K. Hafner and H. Kaiser, *Justus Liebigs Ann. Chem.*, 1958, **618**, 140.
3 T. Nozoe, S. Matsumura, Y. Yurase and S. Seto, *Chem. Ind. (London)*, 1955, 1257.
4 (*a*) P. W. Yang, M. Yasunami and K. Takase, *Tetrahedron Lett.*, 1971, 4275; (*b*) M. Yasunami, A. Chen, P. W. Yang and K. Takase, *Chem. Lett.*, 1980, 579; (*c*) M. Yasunami, S. Miyoshi, N. Kanegae and K. Takase, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 892.
5 A. E. Greene and J.-P. Deprés, *J. Am. Chem. Soc.*, 1979, **101**, 4003.
6 H. Staudinger, *Ber. Dtsch. Chem. Ges.*, 1905, **38**, 1735.
7 (*a*) W. T. Brady, *Tetrahedron*, 1981, **37**, 2949; (*b*) T. T. Tidwell, *Acc. Chem. Res.*, 1990, **23**, 273; (*c*) J. A. Hyatt, *Org. React. (N.Y.)*, 1994, **45**, 159.
8 C. Falshaw, A. Lakoues and G. Taylor, *J. Chem. Res. (S)*, 1985, 106.
9 D. C. England and C. G. Krespan, *J. Org. Chem.*, 1970, **35**, 3300.
10 W. T. Brady and O. H. Waters, *J. Org. Chem.*, 1967, **32**, 3703.
11 (*a*) W. T. Brady and A. D. Patel, *Synthesis*, 1972, 565; (*b*) H. W. Moor, F. Mercer, D. Kunert and P. Albaugh, *J. Am. Chem. Soc.*, 1979, **101**, 5435.
12 (*a*) T. Nozoe, K. Takase and N. Shimazaki, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 1644; (*b*) K. Takase, T. Asao and T. Nozoe, *Chem. Commun.*, 1968, 368.
13 N. Morita, M. Kudo, R. Yokoyama and S. Ito, *Heterocycles*, 2001, **54**, 679.
14 V. A. Nefedov, *Zh. Org. Khim.*, 1973, **9**, 783 (*Chem. Abstr.*, 1973, **79**, 418486).
15 M. Nitta and T. Takayasu, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1325.