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Synthesis of a Polycyclic π-Conjugated System Containing an Azulene Unit by the Flash Vacuum Pyrolytic Method. I. Synthesis and Properties of Cyclopent[*a*]azulenes[1)]

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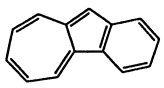
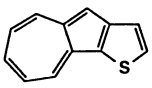
1*H*- and 3*H*-cyclopent[*a*]azulene were synthesized in excellent yields by applying flash vacuum pyrolysis. Their structures were clearly determined. A mixture of 1*H*- and 3*H*-cyclopent[*a*]azulene was completely anionized with methyllithium in THF, but 67% so in ether. Although 1*H*-cyclopent[*a*]azulene reacted with dichloroketene to give a [2+2] cycloadduct, 3*H*-cyclopent[*a*]azulene reacted with cyclopentadiene to give a [4+2] cycloadduct. These chemical behaviors were predictable according to HMO theory.

Tricyclic fused π-conjugated ring systems containing an azulene unit were well-investigated concerning their properties as well as the effect of condensation of the other ring on the chemical properties of the azulene unit.

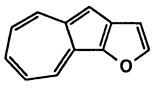
Among these compounds, benz[*a*]azulene, azuleno-[2,3-*b*]thiophene, and azuleno[2,3-*b*]furan etc., formed by the condensation of an aromatic ring with azulene, exhibited bond-length alternation on the seven-membered ring of their azulene parts. These properties are due to the larger stabilization energy of the fused ring than that of azulene.[2–4)]



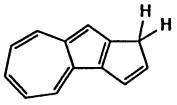
Benz[*a*]azulene



Thiophen[*a*]azulene



Furan[*a*]azulene



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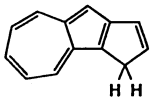

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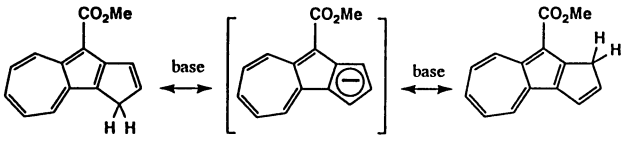
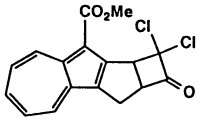
Cyclopent[*a*]azulenes (**1**) and (**2**) formed by the condensation of cyclopentadiene and azulene are fundamental compounds among cata-fused ring systems containing an azulene unit. They are also useful precursors for synthetic studies concerning new π-conjugated systems. We have recently prepared 9-methoxycarbonyl-3*H*-cyclopent[*a*]azulene (**3**) and investigated their reactions. Compound (**3**) was easily isomerized to 1*H*-isomer (**4**) with triethylamine, and each reacted with ketene to give [2+2] cycloadducts, (**5**) and (**6**). Furthermore, the base-catalyzed condensation reactions of **3** with the corresponding carbonyl compounds to form fused compounds azulene with fulvene. Unfortunately, removing the methoxycarbonyl groups of **3** to give **1** and **2** has not yet succeeded.[5)]



3 **7** **4**



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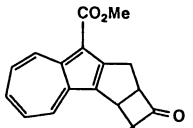

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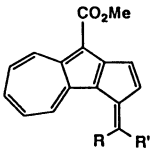
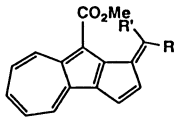
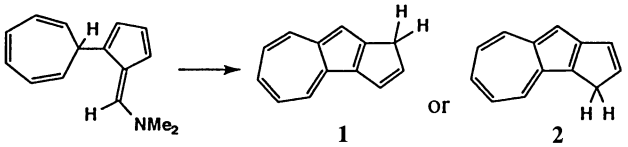


Fulven[1,2-*a*]azulene

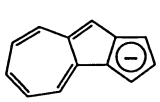


Fulven[2,1-*a*]azulene

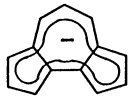
Hafner et al. have prepared cyclopent[*a*]azulene (**1**) by an elegant thermal pericyclic cyclization of 6-dimethylamino-1-(2,4,6-cycloheptatrienyl)fulvene, followed by the elimination of dimethylamine.[6)] Furthermore, they have succeeded in preparing cyclopent[*a*]azulenide (**A**) by treating the hydrocarbon with methyllithium in ether, and have discussed its electronic spectra. However, the structures of the hydrocarbon (**1**) and/or (**2**) have not yet been clarified.[6)]



K. Hafner **1** or **2** Z. Yoshida



Cyclopent[*a*]azulenide(*A*)



Cyclopent[*e*]azulenide(*E*)

Recently, Yoshida et al. reported on the synthesis of considerably stable cyclopent[*e*]azulenide (**E**) and demonstrated its peripheral 14 π-conjugated structure. Their estimation of the resonance energy of cyclopentazulenide has also indicated that the resonance energies of cyclopent[*e*]- and cyclopent[*f*]azulenide are larger than that of cyclopent[*a*]azulenide.[7] In this paper, we report on the successful synthesis of 1*H*-(**1**) and 3*H*-cyclopent[*a*]azulene (**2**) by the application of flash vacuum pyrolysis. A clear assignment of the structures and chemical properties of **1** and **2** are also described.

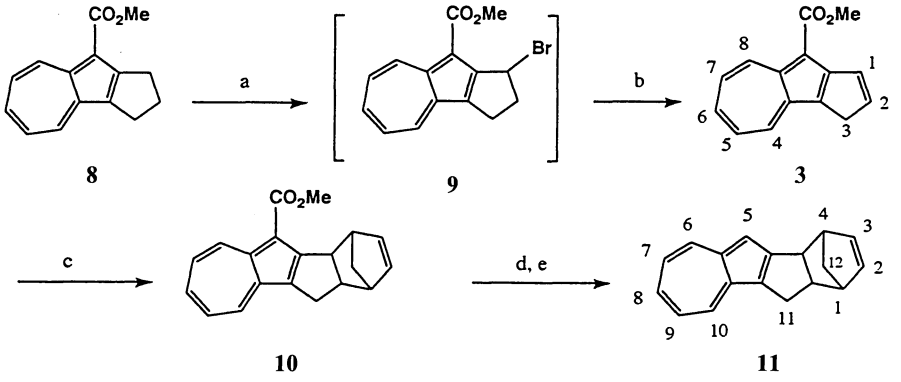
Results and Discussion

Synthesis of Pyrolytic Precursor (11). As described above, demethoxycarbonylation of 9-methoxycarbonyl-3*H*-cyclopent[*a*]azulene (**3**) with 100% phosphoric acid gave nothing identifiable. This result suggests the chemical or thermal instability of **1** and **2**. We then attempted to apply flash vacuum pyrolysis (FVP), which is very effective for the isolation of unstable compounds, in the final preparation step of cyclopent[*a*]azulenes.[8]

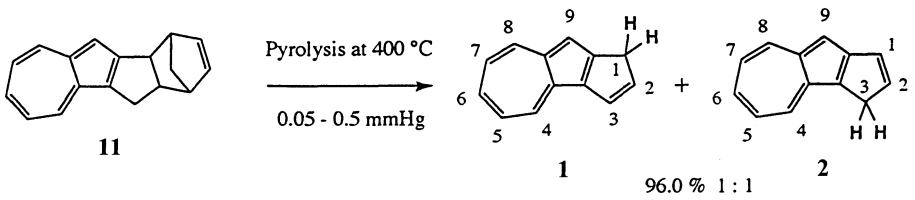
The adequate precursor selected for FVP was a pentacyclic compound (**11**), the preparation of which is given in Scheme 1. The starting material, 9-methoxycarbonyl-2,3-dihydro-1*H*-cyclopent[*a*]azulene (**8**), was prepared by reacting 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one with 1-morpholino-1-cyclopentene.[9] The bromination of **8** with NBS in carbon tetrachloride at 0 °C gave monobromide (**9**), which was used for the next reaction without purification because of its instability. The elimination of HBr from **9** was easily achieved under reflux in chloroform to give 9-methoxycarbonyl-3*H*-cyclopent[*a*]azulene (**3**) as violet crystals in good yield. A Diels–Alder reaction of **3** with cyclopentadiene gave **10**. The treatment of **10** with 100% phosphoric acid for the purpose of demethoxycarbonylation gave nothing identifiable. The hydrolysis of the methoxycarbonyl group of **1** followed by acid-catalyzed decarboxylation afforded the precursor (**11**) in excellent yield.

Flash Vacuum Pyrolysis of the Precursor (11). Preparation of 1*H*-(1) and 3*H*-Cyclopent[*a*]azulene (2). The used pyrolytic apparatus was described in the experimental section.[9] The sample tube was heated by an air bath at 150 °C, the system was then reduced at a pressure of 0.05—0.5 mmHg (1 mmHg=133.322 Pa). The precursor (**11**) sublimed through a pyrolytic silica tube (heated 400 °C) to give pyrolysates as blue crystals on a cold finger cooled with dry ice–methanol. These crystals were collected with a small amount of hexane. Careful removal of the solvent gave a mixture of 1*H*-(**1**) and 3*H*-cyclopent[*a*]azulene (**2**) in quantitative yield from the cycloadduc (**11**).

Characterization of Cyclopent[*a*]azulenes. Separating the mixture of **1** and **2** into each components by the usual column chromatography or HPLC methods was very difficult. However, since the 1*H*-isomer (**1**) was fairly unstable on a silica-gel column, the 3*H*-isomer (**2**) could be obtained in pure form by column chromatography of the mixture on a silica-gel column eluted with benzene.



Scheme 1. a) NBS/CCl_4, stirred at 0 °C; b) reflux in $CHCl_3$, 86.5% from **8**; c) heat at 60—90 °C, quant; d) KOH/EtOH, reflux; e) CCl_3CO_2H/benzene, reflux, 97.1% from **10**.



Scheme 2.

Table 1. ^1H and ^{13}C NMR (CD_2Cl_2, 200 MHz) δ/ppm, J in Hz

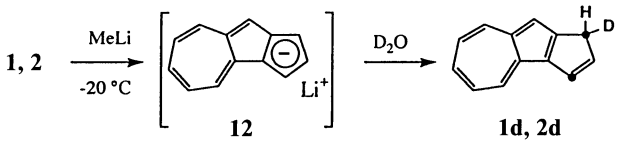
Position	1	2	Azulene[a)]
H-1	3.39(dd, J=2.0,2.0)	7.06(dt, J=5.5,2.0)	
H-2	6.56(dt, J=5.5,2.0)	6.90(dt, J=5.5,2.0)	7.77(H-2)
H-3	7.19(dtd, J=5.5,2.0,0.9)	3.46(dd, J=2.0,2.0)	
H-4	8.17(dd, J=9.5,1.0)	8.18(dd, J=9.5,1.0)	8.10($J_{4,5}$=9.5)
H-5	6.98(dd, J=9.5,9.5)	7.07(dd, J=9.5,9.5)	6.88($J_{5,6}$=10.0)
H-6	7.44(dddd, J=9.5,9.5,1.0,1.0)	7.42(dddd, J=9.5,9.5,1.0,1.0)	7.30
H-7	7.00(dd, J=9.5,9.5)	7.08(dd, J=9.5,9.5)	6.88
H-8	8.26(bd, J=9.5)	8.22(dd, J=9.5,1.0)	8.10
H-9	7.26(bs)	7.17(s)	7.17(H-1,3)
C-1	34.7	122.2	
C-2	134.7	143.2	136.9
C-3	122.5	33.2	
C-4	133.3	131.8	136.4
C-5	121.3	123.0	122.6
C-6	136.4	135.0	136.9
C-7	126.9	129.2	122.6
C-8	135.7	135.3	136.4
C-9	111.3	106.9	118.1(C-1)

a) ^1H NMR from Ref. 1, ^{13}C NMR from Ref. 10.

The NMR spectral data for **1** was obtained from the spectrum of a mixture of **1** and **2**, except for the signals corresponding to isolated **2**. The spectral data of **1** and **2** are summarized in Table 1. The ^{13}C NMR chemical shift values of the methylene groups were observed at 33.2 and 34.7 ppm. The signal at higher field was assigned to the methylene group of **2** since C-3 of **2** is adjoined to the highest electron density position in azulene. ^1H NMR integration of these methylene signals of **1** and **2** were used to determined the ratio of the mixture of **1** and **2** generated by flash vacuum pyrolysis. (**1**:**2**=1:1) The ^1H NMR H,H-coupling constant between H-3 and H-9 of **1** was observed ($J_{3,9}$=0.9 Hz). The ^1H and ^{13}C NMR spectra of **1** and **2** showed the usual chemical shifts, compared to azulene itself indicating a slight perturbation of condensed cyclopentadiene to the azulene part of **1** and **2**.

Cyclopent[*a*]azulenide (12). To estimate the reaction conditions for the preparation of cyclopent[*a*]-azulenide (**12**), deuterium incorporation at the methylene position of **1** and **2** was investigated in ether and THF, as is shown in Scheme 3. Methyllithium was added to the solution of the mixture in a corresponding solvent, and the solution was maintained at −20 °C under nitrogen. After 1 or 2 h, deuterium oxide was added to quench the anion. The ratio of deuterated compounds was determined by ^1H NMR integration of the methylene groups. The results summarized in Table 2 indicate that the anionization reaction was achieved completely in THF, but only 67% so in ether.

Cycloaddition Reaction of 1 and 2. The periselectivity of the cycloaddition reactions of **1** and **2** with ketene and cyclopentadiene were investigated. The HMO calculations of **1**, **2**, dichloroketene, and cyclopentadiene were carried out, and the results are given in Fig. 1.



Scheme 3.

Table 2. Anionization Reaction of **1** and **2**

Solvent	Reaction time/h	D_2O/mol equiv	D content/%
Ether	1.0	2.0	37
Ether	2.0	2.0	67
THF	1.0	2.5	100

a) A Cycloaddition Reaction of 1 and 2 with Dichloroketene. An electron-deficient ketene generally reacted as an electrophile with cyclopentadiene to give a [2+2] cycloadduct.[11,12] Therefore, the interactions of LUMO(ketene)-HOMO(**1**) and LUMO(ketene)-HOMO(**2**) could control this [2+2] cycloaddition reaction. The HMO calculations, as shown in Fig. 1, indicated only that the interaction of LUMO(ketene)-HOMO(**2**) is symmetry allowed.

The cycloaddition reaction was achieved as shown in Scheme 4. Dichloroketene generated in situ reacted with only **1** to give the [2+2] cycloadduct (**13**). We have already demonstrated that demethoxycarbonylation of **6** with 100% phosphoric acid also gave **13**. Both spectral data of **13** were identified between each other, and the structure of **13** was confirmed.[13]

b) Cycloaddition Reaction of 1 and 2 with Cyclopentadiene. The cycloaddition reaction of **1** and **2** with cyclopentadiene (CPD) gave the [4+2] cycloadducts, **11** and **14**, as shown in Scheme 4. Separating of the

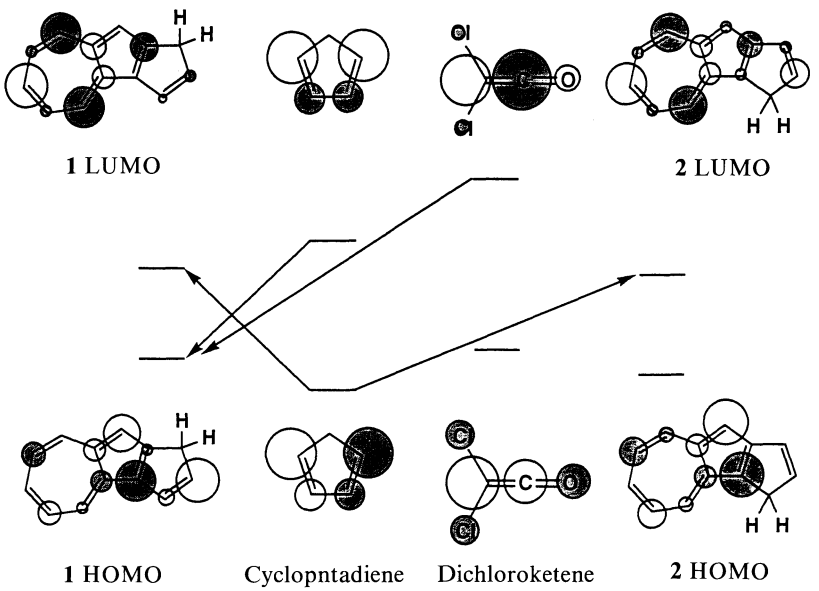
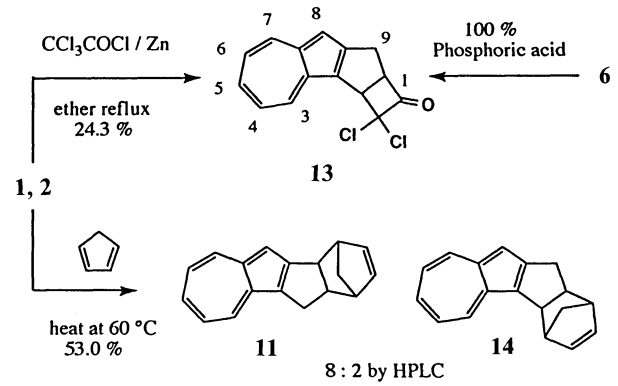


Fig. 1. HMO calculations of **1**, **2**, Dichloroketene, and cyclopentadiene.



Scheme 4.

mixture of **11** and **14** was very difficult. The ^{1}H NMR spectra of this mixture indicated the existence of **14**, as is shown in Fig. 2. The ratio of **11** and **14** was determined by reversed-phase HPLC (**11** : **14**=8 : 2). As shown in Fig. 1, the interaction of LUMO(**2**)–HOMO(CPD) controlled the usual Diels–Alder reaction to give **11**. The Diels–Alder reaction which controlled by the interaction of HOMO(**1**)–LUMO(CPD) was an inverse electron demand type. On the other hand, although the reaction controlled by the interaction of LUMO(**1**)–HOMO(CPD) was usual Diels–Alder type, coefficients on C-2 and C-3 of LUMO(**1**) were very small. Though both the interactions of HOMO(**1**)–LUMO(CPD) and

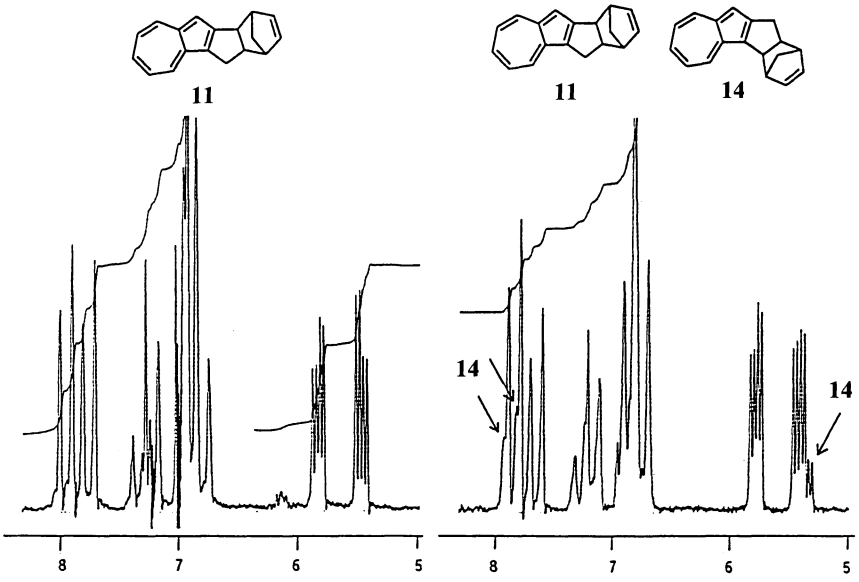


Fig. 2. ^{1}H NMR (90 MHz in CCl_4) of **11** and **14**, δ/ppm.

LUMO(**1**)–HOMO(CPD) could control the cycloaddition reaction to give **14**, no reasonable reactivity could be expected in the case of this cycloaddition reaction. Actually, as described above, although the reaction of a mixture of **1** and **2** with cyclopentadiene mainly gave **11**, it also gave a fair amount of **14**.

Experimental

General. Melting points were determined with a melting point apparatus, Yamato Model-MP21. Microanalysis were performed at Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. NMR spectra were recorded on an EM-390(^{1}H) or Varian XL-200(^{1}H & ^{13}C), and chemical shift values are given in δ/ppm relative to internal tetramethylsilane. Infrared, ultraviolet, and mass spectra were recorded on a Hitachi Model 260-30, a Hitachi Model 323, and Hitachi M-50, respectively.

Pyrolytic Apparatus and Procedure. The apparatus used in the pyrolytic synthesis comprised an empty horizontal tube (30 by 1.5 cm o.d.) with a small protrusions in the middle of the tube, and it was heated at 400 °C over 25 cm with an external electric furnance. The outlet of the pyrolysis tube was directly attached to a cold finger cooled by dry ice–methanol. The portion from the end of the heat zone to the cold finger and the outside of the cold finger where pyrolytic products were collected was heated at about 100 °C with a ribbon heater. The pressure was measured with a manometer attached to the exit of the cold finger. The temperature was measured with a thermocouple placed in the middle of the heat zone. The precursor in a sample tube, heated with an air bath at 150 °C, was sublimed into the heated tube and pyrolyzed. The pyrolytic products were collected on the cold finger. After the completion of precursor sublimation in the sample tube, the refrigerant was removed and the cold finger was warmed to room temperature. The products on the surface of the cold finger were dissolved with a small amount of hexane and the solution was carefully removed. Further details are described below.

Preparation of 9-Methoxycarbonyl-3*H*-cyclopent[*a*]azulene (3). A solution of 9-methoxycarbonyl-2,3-dihydro-1*H*-cyclopent[*a*]azulene (**8**) (3.0 g, 13.3 mmol) in carbon tetrachloride (250 ml) was cooled to 0 °C. To this solution was added *N*-bromosuccinimide (2.6 g, 14.6 mmol) and the mixture was stirred vigorously at 0 °C for 3 h. Succinimide formed during the reaction was removed by filtration, the filtrate was then concentrated under reduced pressure. The resulting oil containing monobromide (**9**) was immediately dissolved in chloroform (300 ml) and the solution was refluxed under nitrogen for 2 h. After being cooled to room temperature, the reaction mixture was washed with water, dried over magnesium sulfate and concentrated under reduced pressure. Chromatography of the residue on a silica-gel column eluted with benzene gave **3** (2.58 g, 86.5%).

3: Violet microneedles (cyclohexane); mp 91.0—92.0 °C; UV(MeOH) 234(log ε 4.06), 241.5(4.08), 275(4.00), 285(4.08), 315(4.65), 327(4.64), 367(3.79), 386(3.67), 546(2.81), and 576 nm(2.78); IR(KBr) 1675 cm^{-1} (este C=O); ^{1}H NMR (90 MHz, in $CDCl_3$) δ=3.46(dd, *J*=2.0 and 2.0 Hz, H-3), 3.94(s, OMe), 6.97(dt, *J*=5.0 and 2.0 Hz, H-2), 7.11—7.70(m, H-1, 5, 6, and 7), 8.20(d, *J*=9.0 Hz, H-4), and 9.50(d, *J*=9.0 Hz, H-8); MS *m*/*z* 224(M^+ 53%). Elemental Anal. Found: C, 79.77; H, 5.47%. Calcd for $C_{15}H_{12}O$: C, 80.34; H, 5.39%.

Preparation of the Methoxycarbonyl Derivative of Cycloadduct (10). The Cycloaddition Reaction of 3 with Cyclopentadiene: After 9-Methoxycarbonyl-3*H*-cyclopent-[*a*]azulene (**3**): (2.0 g, 8.9 mmol) was dissolved in freshly distilled cyclopentadiene (100 ml), the solution was heated at 50 °C for 5 h. Then, after being heated at 90 °C for an additional 1 h and being cooled to room temperature, the reaction mixture was charged on a silica-gel column and eluted with hexane in order to remove cyclopentadiene and its dimer. Further elution with benzene gave **10** (2.6 g, 100% yield).

10: Dark violet prisms (hexane); mp 130.5 °C; UV(MeOH) 240(log ε 4.27), 298.5(4.68), 310.5(4.74), 372(3.78), 392(3.81), 550(2.78), and 586 nm (2.71); IR ($CHCl_3$) 1680 cm^{-1} (ester C=O); ^{1}H NMR (90 MHz, in $CDCl_3$) δ=1.53(m, H-12), 2.37(dd, *J*=17.0 and 3.0 Hz, H-11), 2.90(dd, *J*=17.0 and 9.0 Hz, H-11), 3.30(m, H-1 and 4), 3.37(m, H-11a), 3.90(s, OMe), 4.00(m, H-4a), 5.50(dd, *J*=6.0 and 3.0 Hz, H-2), 5.83(dd, *J*=6.0 and 3.0 Hz, H-3), 6.90—7.45(m, H-7, 8, and 9), 7.82(d, *J*=9.0 Hz, H-10), and 9.33(d, *J*=9.0 Hz, H-6); MS *m*/*z* 290(M^+ 29.1%). Elemental Anal. Found: C, 82.64; H, 6.32%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

Preparation of the Pyrolytic Precursor (11). Removal of the Methoxycarbonyl Group of 10: Compound **10** (4.5 g, 15.5 mmol) was dissolved in a 10% KOH solution in aqueous ethanol (EtOH 300 ml, H_2O 200 ml, KOH 50 g), the solution was then refluxed for 3.5 h. After being cooled to room temperature, the reaction mixture was poured into water and acidified with 6 M HCl to pH 3 (1 M=1 mol dm^{-3}). The precipitates of carboxylic acid were collected by filtration and dried under reduced pressure to constant weight to give a carboxylic acid as light purple crystals.

To a solution of this carboxylic acid in benzene (150 ml) was added trichloroacetic acid (0.5 g, 3.1 mmol), the mixture was refluxed for 3.5 h. After being cooled to room temperature, the reaction mixture was chromatographed on a silica-gel column to give the precursor (**11**) (3.27 g, 97.1% yield based on **10**).

11: Blue plates (ethanol); mp 102.0—102.5 °C; UV(MeOH) 241(log ε 4.15), 281.5(4.70), 289.5(4.73), 305(3.94), 323(sh, 3.32), 337.5(3.55), 353(3.67), 366(sh, 2.79), 590(2.48), and 634 nm (2.42); IR (KBr) 2964, 2925, 2900, 1570, 1480, 1440, 1395, 1342, 1300, 795, and 730 cm^{-1}; ^{1}H NMR (90 MHz, in $CDCl_3$) δ=1.50(ddd, *J*=8.0, 1.5, and 1.5 Hz, H-12), 1.63(ddd, *J*=8.0, 1.5, and 1.5 Hz, H-12), 2.53(dd, *J*=17.0 and 3.0 Hz, H-11), 3.00(dd, *J*=17.0 and 9.0 Hz, H-11), 3.10(m, H-1 and 4), 3.43(dddd, *J*=9.0, 9.0, 3.0, and 3.0 Hz, H-11a), 3.89(dd, *J*=9.0 and 4.2 Hz, H-4a), 5.50(dd, *J*=6.0 and 3.0 Hz, H-2), 5.87(dd, *J*=6.0 and 3.0 Hz, H-3), 6.87(dd, *J*=9.0 and 9.0 Hz, H-7 and 9), 6.93(s, H-5), 7.27(dd, *J*=9.0 and 9.0 Hz, H-8), 7.78(d, *J*=9.0 Hz, H-10), and 7.97(d, *J*=9.0 Hz, H-6); MS *m*/*z* 232(M^+ 29.3%) and 166($M^+-C_5H_6$, 100%). Elemental Anal. Found: C, 92.83; H, 7.23%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%.

Flash Vacuum Pyrolysis of the Precursor (11). Preparation 1*H*- (1) and 3*H*-Cyclopent[*a*]azulene (2): Flash vacuum pyrolysis of **11** was achieved using the apparatus described above. The precursor (**11**) (200 mg, 0.86 mmol) was pyrolyzed at 400 °C (0.05—0.10 mmHg, 150 °C preheat) and the products were deposited on tha cold finger (−78 °C, dry ice–methanol) as blue crystals. The cold finger was warmed to room temperature and the crystals were swept with a small amount of hexane. Carefully removing the solvent under reduced pressure gave a mixture of 1*H*- (**1**) and 3*H*-

cyclopent[*a*]azulene (**2**) (137 mg, 96.0% yield).

1: Blue crystals; ^{1}H NMR (200 MHz, in CD_2Cl_2) δ= 3.39(dd, J=2.0 and 2.0 Hz, H-1), 6.56(dt, J=5.5 and 2.0 Hz, H-2), 6.98(dd, J=9.5 and 9.5 Hz, H-5), 7.00(dd, J=9.5 and 9.5 Hz, H-7), 7.19(dtd, J=5.5, 2.0, and 0.9 Hz, H-3), 7.26(broad s, H-9), 7.44(dddd, J=9.5, 9.5, 1.0, and 1.0 Hz, H-6), 8.17(dd, J=9.5 and 1.0 Hz, H-4), and 8.26(broad d, J=9.5 Hz, H-8); ^{13}C NMR (50 MHz, in CD_2Cl_2) δ=34.7(t, C-1), 111.3(d, C-9), 121.3(d, C-5), 122.5(d, C-3), 126.9(d, C-7), 126.9(s), 133.3(d, C-4), 134.7(d, C-2), 135.7(d, C-8), 136.4(d, C-6), 140.8(s), 146.1(s), and 159.0(s).

2: Blue crystals; mp 90.0—90.5 °C; UV(hexane) 221.5 (log ε 4.16), 246(4.03), 283(sh, 4.58), 293.2(4.71), 302(4.65), 323.9(3.86), 341(3.53), 357(3.69), 372(3.83), 391(3.96), 550(sh, 2.39), 590(2.51), 620(sh, 2.46), and 640 nm (2.48); IR (KBr) 3090, 3060, 3020, 2890, 1575, 1565, 1390, 1355, 910, 795, 730, and 660 cm^{-1}; ^{1}H NMR (200 MHz, in CD_2Cl_2) δ=3.46(dd, J=2.0 and 2.0 Hz, H-3), 6.90(dt, J=5.5 and 2.0 Hz, H-2), 7.06(dt, J=5.5 and 2.0 Hz, H-1), 7.07(dd, J=9.5 and 9.5 Hz, H-5), 7.08(dd, J=9.5 and 9.5 Hz, H-7), 7.17(s, H-9), 7.42(dddd, J=9.5, 9.5, 1.0, and 1.0 Hz, H-6), 8.18(dd, J=9.5 and 1.0 Hz, H-4), and 8.22(dd, J=9.5 and 1.0 Hz, H-8); ^{13}C NMR (50 MHz, in CD_2Cl_2) δ=33.2(t, C-3), 106.9(d, C-9), 122.2(d, C-1), 123.0(d, C-5), 129.2(d, C-7), 130.3(s), 131.8(d C-4), 135.0(d, C-6), 135.3(d, C-8), 136.1(s), 143.2(d, C-2), 147.0(s), and 160.4(s); MS m/z 166(M^+, 63.1%) and 165(M^+-H, 100%); Elemental Anal. Found: C, 93.95; H, 6.12%, Calcd for $C_{13}H_{10}$: C, 93.94; H, 6.06%

Anionization and Deuteriation Reaction of 1 and 2. 1) Reaction of 1 in THF: To a solution of **1** and **2** (34.0 mg, 0.2 mmol) in dry THF was added methyllithium (1 M ether soln, 0.2 ml, 0.2 mmol) at −20 °C. The solution changed immediately from blue to red. After stirring for 1 h at −20 °C, heavy water (9 ml, 0.5 mmol) was added to the solution. The solution changed to blue again. The formed lithium hydroxide was filtered off, and the solvent was removed under reduced pressure to give a mixture of **1d** and **2d** in quantitative yield.

2) Reaction of 1 in Ether. An anionization reaction in ether was achieved by the same procedure applied for anionization in THF. The solution soon changed from blue to green after the addition of methyl lithium.

Cycloaddition Reaction of 1 and 2 with Dichloroketene. To a solution of **1** and **2** (100 mg, 0.60 mmol) and zinc (400 mg, 6.1 mmol) in dry ether (30 ml) was added dropwise a solution of trichloroacetyl chloride (200 mg, 1.1 mmol) in dry ether (30 ml) dropwise for 45 min. The mixture was refluxed for 2 h and then cooled to room temperature. Zinc was removed by filtration, and the filtrate was concentrated under reduced pressure. Chromatography of the resulting oil on a silica-gel column eluted with benzene gave a crude adduct (**13**). Further purification of crude **13** on reversed-phase column chromatography with acetonitrile–water (7:3) gave **13** (43.5 mg, 24.3%).

13: Violet microneedles (cyclohexane); mp 157.0—157.5 °C; UV(MeOH) 235(log ε 4.22), 280.8(4.71), 288.5(4.72), 303.8(4.05), 334(3.59), 347.5(3.75), 364.5(3.43), 565(2.44), and 606 nm (sh, 2.36); IR (KBr) 1800 cm^{-1}(CO); ^{1}H NMR (90 MHz, in $CDCl_3$) δ=3.20(dd, J=17.9 and 7.5 Hz, H-9), 3.56(d, J=17.9 Hz, H-9), 4.75(broad d, J=7.1 Hz, H-2a), 4.86(broad dd, J=7.5 and 7.1 Hz, H-9a), 6.99(s, H-8), 7.05—7.33(m, H-4 and 6), 7.54(broad dd, J=9.0 and 9.0 Hz, H-5), 8.14(d, J=9.2 Hz, H-7), and 8.24(d, J=9.2 Hz, H-3); MS m/z 280(M^+, 2.9%), 278(M^+, 12.4%), and 276(M^+, 20.6%). Elemental Anal. Found: C, 65.05; H, 3.83%. Calcd for $C_{15}H_{10}OCl_2$: C, 65.01; H, 3.64%.

Cycloadditon Reaction of 1 and 2 with Cyclopentadiene. A solution of the mixture of **1** and **2** (114 mg, 0.7 mmol) in freshly distilled cyclopentadiene (15 ml) was heated at 60 °C for 9 h. After being cooled to room temperature, the reaction mixture was charged on a silica-gel column and eluted with hexane to remove cyclopentadiene and its dimer. Further elution with benzene gave the mixture of cycloadduct (**11**) and (**14**) (85 mg, 53.0% yield, **11**:**14**=8:2). The ratio of **11** and **14** was determined by reversed-phase HPLC with acetonitrile–water 7:3.

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