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Synthesis of a Polycyclic π-Conjugated System Containing an Azulene Unit by the Flash Vacuum Pyrolytic Method. II. Synthesis and Paratropic Properties of 3*H*-Cyclopent[*a*]azulen-3-one and Its Methyl Derivatives

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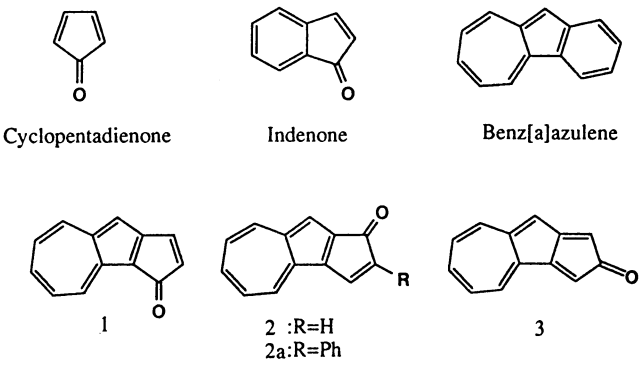
3*H*-Cyclopent[*a*]azulen-3-one and two methyl derivalives, which have a new tricyclic π-conjugated system, were synthesized starting from 9-methoxycarbonyl-1,2-dihydro-3*H*-cyclopent[*a*]azulen-3-one by the application of flash vacuum pyrolysis in the final step. All proton signals of these compounds were observed at higher fields than those of the referenced 1,2-dihydro compound, but there are no significant differences between the carbon magnetic resonances of 3*H*-cyclopent[*a*]azulen-3-ones and the reference compound. These high field shifts on ^{1}H NMR were appreciated in terms of an induced paramagnetic ring current caused by the contribution of a 12-π electron system in the periphery of this molecule. 3*H*-cyclopent[*a*]azulen-3-one was stable in the crystalline state, but gradually changed in solution to a hexacyclic compound by decarbonylative dimerization, while the 2-methyl derivative was very stable both in the crystalline state and in solution. Although the reaction of 3*H*-cyclopent[*a*]azulen-3-one with cyclopentadiene immediately gave a [4+2] cycloaddition product, the reaction with dimethyl acetylenedicarboxylate gave no products. These chemical behaviors are consistent with the results of Hückel molecular orbital calculations.

Cyclopentadienone, the smallest $4n+1$ annulenone, is known as an anti-aromatic compound owing to the contribution of a 4π electron system caused by polarization of its carbonyl group.[1] The IR spectrum of this highly reactive species has been measured for a sample deposited on a sodium chloride plate at −196 °C and shows the carbonyl stretching absorption at 1709 cm^{-1}.[2] The effects of condensation of aromatic compounds with a cyclopentadienone moiety have interested many researchers. For instance, the benzene ring proton magnetic resonances of indenone which consists of benzene and a cyclopentadienone moiety have shown to occurr up-field from those of indanone. The reasons for those proton paramagnetic shifts of indenone have not been clarified.[3]

Tricyclic π-conjugated systems which are formed by the condensation of an aromatic ring with the five-membered ring of azulene have been extensively investigated.[4-6] Bertelli et al. showed that the seven-membered ring of benz[*a*]azulene exhibits a clear bond length alternation caused by the difference of the aromatic stabilization energy between benzene and azulene.[4] Thus, the effect of the condensation of an anti-aromatic cyclopentadienone with azulene is extremely attractive. Three possible isomers of tricyclic systems which are formed by the condensation of cyclopentadienone with the five-membered ring of azulene are shown in Scheme 1. Among these isomers, the 2-phenyl derivative of **2a** has been synthesized, but its chemical properties have not been investigated in detail.[7]

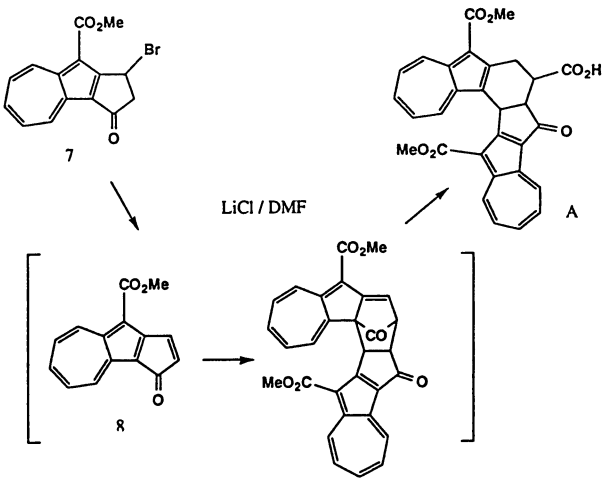
We have already reported an efficient synthesis of azulene by the reaction of 2*H*-cyclohepta[*b*]furan-2-ones with enamines.[8] This reaction occurs under mild conditions to give azulene derivatives in high yields.



Scheme 1.

Especially, 1,2-polymethyleneazulenes, which are difficult to obtain by other synthetic methods, could be easily synthesized by the reaction with enamines derived from cycloalkanones. By the use of 9-methoxycarbonyl-2,3-dihydro-1*H*-cyclopent[*a*]azulene, which was synthesized by this method, 3*H*-cyclopent[*a*]azulen-3-one (**1**), a new tricyclic π-conjugated system, and its methyl derivatives, (**31**) and (**32**), were synthesized.

In our previous work, the formation of 9-methoxycarbonyl-3*H*-cyclopent[*a*]azulen-3-one (**8**) as a considerably reactive intermediate was confirmed by the formation of **A** in the dehydrobromination reaction of a monobromo compound (**7**) (Scheme 2).[9] This result suggested that 3*H*-cyclopent[*a*]azulen-3-one (**1**) itself should also be a reactive compound. For the isolation of such a highly reactive species as **1**, we applied the flash vacuum pyrolytic (FVP) method to a precursor (**10**), the cyclopentadiene adduct of **1**. For detailed studies on the physical and chemical properties of this



Scheme 2.

new π-electron system, two methyl derivatives of **1** were also synthesized.[11]

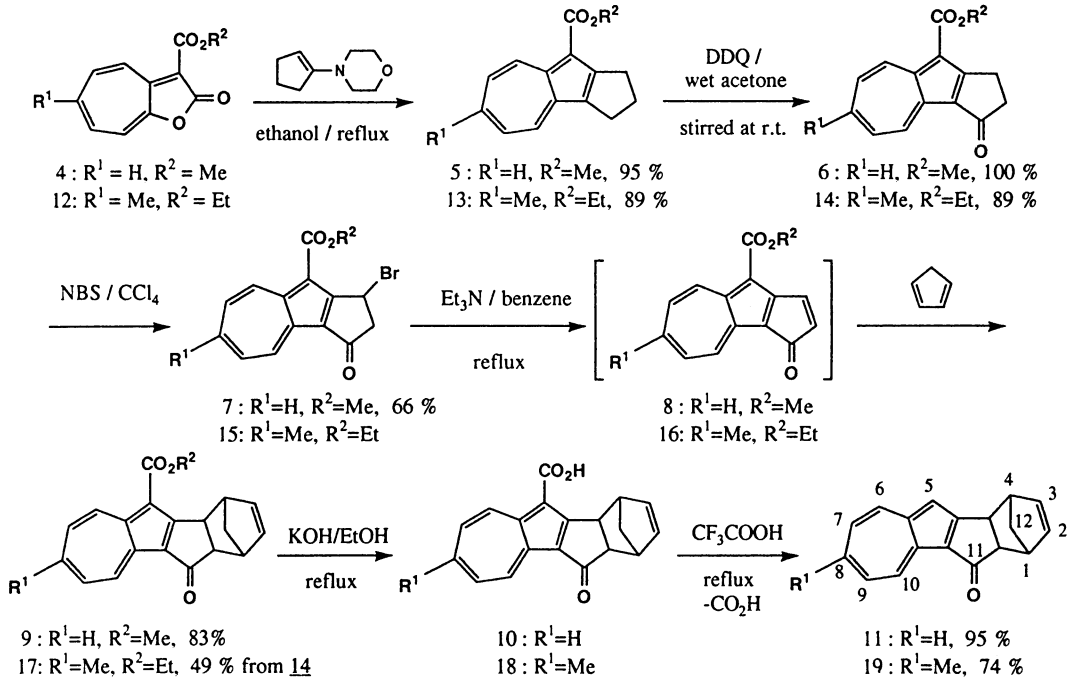
Results and Discussion

Synthesis of the Pyrolytic Precursor (11) of Flash Vacuum Pyrolysis. As described above, 3*H*-cyclopent[*a*]azulen-3-one (**1**) should be a very reactive compound. Flash vacuum pyrolysis is known to be an efficient method for isolation of highly reactive compounds.[10] Therefore, the FVP method was used in the final step of the synthesis of **1**. The cycloadduct (**11**) was prepared as a suitable precursor of FVP as shown in Scheme 3. The starting material, 9-methoxycarnonyl-2,3-dihydro-1*H*-cyclopent[*a*]azulene (**5**), was prepared by the reaction of 3-methoxycarbonyl-2*H*-cyclohepta-[*b*]furan-2-one (**4**) with 1-morpholinocyclopentene.[8] The dihydrocyclopent[*a*]azulene (**5**) was oxidized with DDQ in aqueous acetone to give a ketone (**6**).[12] Bromination of the ketone (**6**) with NBS afforded a monobromide (**7**). Dehydrobromination of **7** with triethylamine in the presence of cyclopentadiene gave a cycloadduct (**9**) by the trapping of generated 9-methoxycarbonyl-3*H*-cyclopent[*a*]azulen-3-one (**8**) with cyclopentadiene. The treatment of **9** with 100% phosphoric acid for demethoxycarbonylation to form **11** gave no identifiable products. However, the precursor (**11**) could be prepared by acid catalyzed decarboxylation of the carboxylic acid (**10**) which was obtained by the hydrolysis of **9**.

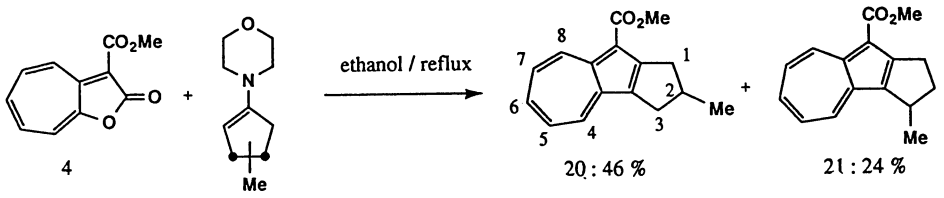
Synthesis of the Pyrolytic Precursor (19) of 6-Methyl-3*H*-cyclopent[*a*]azulen-3-one (31) and the Precursor (30) of 2-Methyl-3*H*-cyclopent[*a*]azulen-3-one (32). In order to investigate the magnetic tropicity of 3*H*-cyclopent[*a*]azulen-3-one (**1**), introduction of a methyl group to the seven-membered ring of **1** was desired. For this purpose, the precursor (**19**) for 6-methyl-3*H*-cyclopent-[*a*]azulen-3-one (**31**) was synthesized from 3-ethoxycarbonyl-6-methyl-2*H*-cyclohepta[*b*]furan-2-one (**12**) in a manner similar to the preparation of **19** (Scheme 3).

As described below, an intermolecular [4+2] cycloaddition reaction between two molecules of 3*H*-cyclopent[*a*]azulen-3-one (**1**) occurred readily in solution to give **33** via a dimer. To prevent its dimerization reaction by steric hindrance, 2-methyl-3*H*-cyclopent[*a*]-azulen-3-one (**32**) was synthesized as follows (Schemes 4, 5, 6).

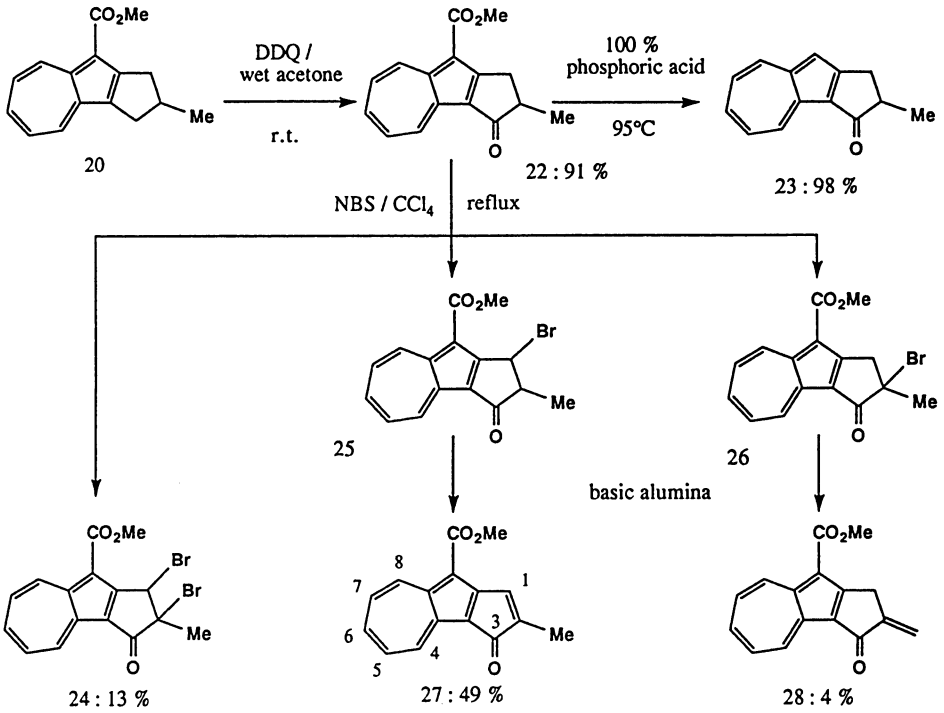
A mixture of 2-methyl- (**20**) and 3-methyl-9-methoxy-



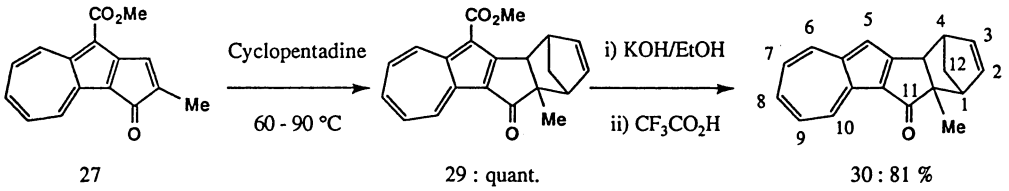
Scheme 3.



Scheme 4.



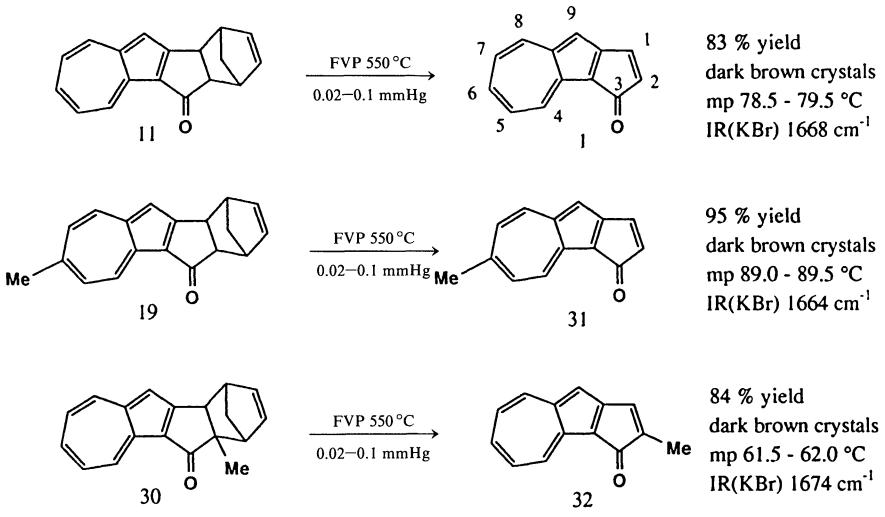
Scheme 5.



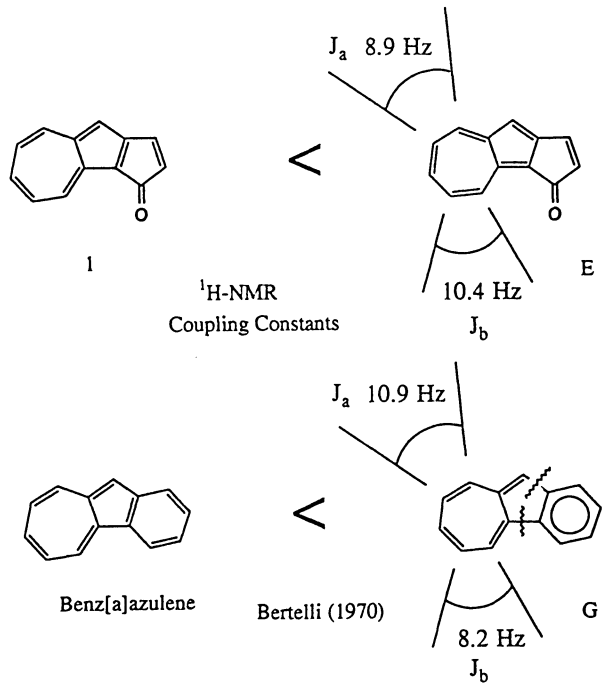
Scheme 6.

carbonyl-1,2-dihydro-3*H*-cyclopent[*a*]azulene (**21**), was synthesized by the reaction of **4** and the morpholine enamine derived from 3-methylcyclopentanone. The mixture of **20** and **21** could be separated by reversed-phase HPLC. The 2-methyl derivative (**20**) was oxidized with DDQ in aqueous acetone to give a ketone (**22**). Bromination of the ketone (**22**) with NBS afforded a mixture of a dibromide (**24**) (12.5% yield), the desired monobromide (**25**), and another monobromide (**26**). The dibromide (**24**) could be isolated from the mixture by chromatography on silica gel, but the separation of **25** and **26** was very difficult by column chromatography. Therefore, the elimination of HBr from **25** and **26** was carried out on a basic alumina column without separation to give to give 9-methoxycarbony-2-methyl-3*H*-cyclopent[*a*]azulen-3-one (**27**) and an exo-methylene derivative (**28**) in 49% and 4.4% yields respectively, from **22**, (Scheme 5). In contrast to the considerably reactive **1**, the 2-methyl derivative (**27**) was quite stable both in the crystalline state and in solution. Since direct demethoxycarbonylation of **27** could not be achieved, the methoxycarbonyl derivative (**27**) was taken to cycloadduct (**30**) via **29** by the same procedure used for the preparation of **11** (Scheme 6).

Flash Vacuum Pyrolysis of (11), (19), and (3). Synthesis of 3*H*-Cyclopent[*a*]azulen-3-ones (1), (31), and



Scheme 7.



Scheme 8.

(32). The pyrolytic apparatus is described in the experimental section.[13] The sample tube was heated by an air bath at 170 °C at 0.02—0.1 mmHg (1 mmHg= 133.322 Pa). The precursor (**11**) was sublimed into the pyrolytic silica tube (heated to 550 °C) and the pyrolisate was collected as dark red crystals on the cold finger cooled by dry ice-methanol. These crystals were purified on a short silica-gel column. Careful removal of the solvent avoiding dimerization gave 3H-cyclopent-[*a*]azulen-3-one (**1**) in an 83.4% yield. Pyrolysis of **19** and **30** in the same manner gave 6-methyl-(**31**) (95.0% yield) and 2-methyl-3*H*-cyclopent[*a*]azulen-3-one(**32**) (85.0% yield), respectively (Scheme 7).

Characterization of the 3*H*-Cyclopent[*a*]azulen-3-ones. The electronic properties of **1**, **31**, and **32** were investigated by their NMR spectral data. The chemical properties of these compounds were also examined by their reactions and HMO calculations.

1) The Vicinal Coupling Constants on the Seven-Membered Ring of the 3*H*-Cyclopent[*a*]azulen-3-ones: Benz[*a*]azulene is known to exhibit a clear bond length alternation in the seven-membered ring which is reflected by the vicinal coupling constants (J_a=10.9 Hz, J_b=8.2 Hz). This bond length alternation in the azulene part could be ascribed to the larger aromatic stabilization energy of benzene than that of azulene (see G in Scheme 8). In contrast to benz[*a*]azulene, J_b (10.5 Hz) is larger than J_a (9.0 Hz) in **1**. This difference in coupling constants reflects a bond length alternation which is caused by the contribution of the structure E to avoid an unstable anti-aromatic cyclopentadienone partial structure (Scheme 8). Similar coupling constant differences were also observed on the azulene rings of 2-methyl- (**32**) and 6-methyl (**31**) derivatives.

2) The NMR Chemical Shifts of the 3*H*-Cyclopent-[*a*]azulen-3-ones: Lacy et al. reported the upfield shifts of aromatic protons of indenone relative to those of indanone, but the reasons for this paramagnetic shifts of indenone have not been clarified.[3] The ^{1}H and ^{13}C NMR spectral data of **1**, **31**, and **32** are shown in Tables 1 and 2 together with their 1,2-dihydro derivatives **34**, **35**, and **23**.

All the proton magnetic resonances of the azulene part of **1** occur upfield by 0.31—0.68 ppm compared to those of **34**. On the other hand, there are no significant differences between the carbon magnetic resonances of **1** and **34**. The high field shifts of these protons could be caused by an increase in the electron density on the carbons of the azulene part of **1**. But the ^{13}C NMR spectral data indicate that the distribution of electron density on the azulene part of **1** is similar to that of **34**.

Table 1. ^{1}H NMR Spectral Data and Chemical Shift Differences of the 3*H*-Cyclopent-[*a*]azulen-3-ones and Their Dihydro Derivatives (in $CDCl_3$)

Compd	**1**	**34**	Δδ	**31**	**35**	Δδ	**32**	**23**	Δδ
H-4	8.23	8.91	−0.68	8.08	8.75	−0.67	8.13	8.87	−0.74
H-5	7.07	7.38	−0.31	6.98	7.30	−0.32	7.02	7.31	−0.29
H-6	7.29	7.69	−0.40	—	—	—	7.22	7.62	−0.40
H-7	7.05	7.43	−0.38	6.98	7.30	−0.32	7.02	7.36	−0.34
H-8	7.85	8.32	−0.47	7.72	8.18	−0.46	7.72	8.25	−0.53
H-9	6.70	7.04	−0.34	6.60	6.96	−0.36	6.55	6.97	−0.42
av	7.37	7.80	−0.43	7.27	7.70	−0.43	7.28	7.73	−0.45

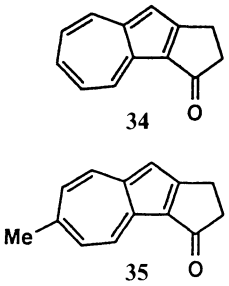
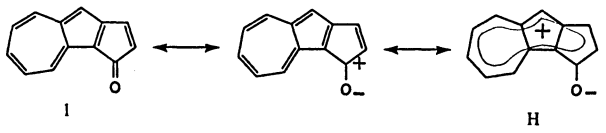
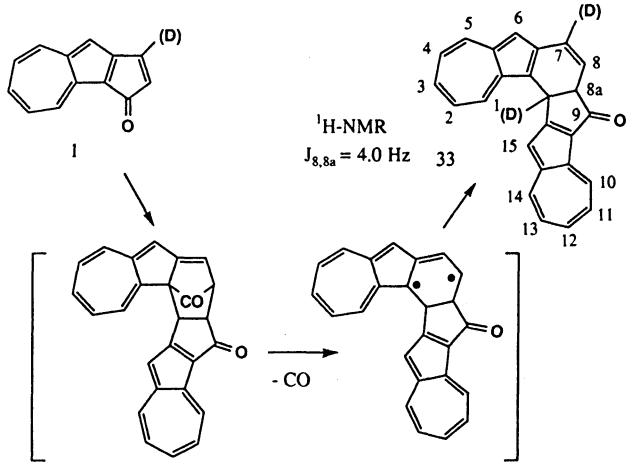


Table 2. ^{13}C NMR Spectral Data and Chemical Shift Differences of the 3*H*-Cyclopent[*a*]azulen-3-ones and Their Dihydro Derivatives

Compd	**1**	**34**	Δδ	**31**	**35**	Δδ	**32**	**23**	Δδ
C-4	133.21	134.78	−1.57	132.42	133.90	−1.48	132.45	134.69	−2.24
C-5	129.11	127.99	1.12	129.43	129.43	0.00	129.15	127.75	1.40
C-6	137.04	138.12	−1.08	—	—	—	135.38	137.92	−2.54
C-7	129.98	128.69	1.29	132.16	130.01	2.15	129.88	128.51	1.37
C-8	136.68	137.96	−1.28	136.09	136.92	−0.83	135.19	137.71	−2.52
C-9	113.17	112.11	1.06	113.22	112.18	1.04	111.87	112.34	−0.47
av	129.87	129.94	−0.05	128.66	128.49	0.17	128.99	129.82	−0.83



Scheme 9.



Scheme 10.

Therefore, the upfield shifts of proton magnetic resonances of **1** should reflect the contribution of a shielding effect by an induced paramagnetic ring current originating from the peripheral 12 π electron framework such as **H** (Scheme 9). Furthermore, all the proton magnetic resonances of 6-methyl-(**31**) and 2-methyl-3*H*-cyclopent[*a*]azulen-3-one (**32**) also moved upfield in comparison with that of reference dihydro compounds and **35** and **23**, respectively.

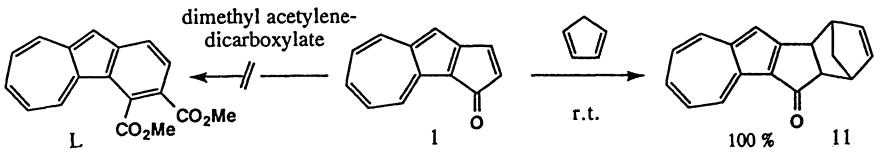
The ^{1}H NMR chemical shift of the methyl group of **31** is observed significantly upfield by 0.18 ppm in comparison with that of **35**, but ^{13}C NMR chemical shift values of the methyl groups of **31** and **35** are again almost the same. These results confirm the existence of an induced paramagnetic ring current in the periphery of the 3*H*-cyclopent[*a*]azulen-3-ones.

The Chemical Behaviors of 3*H*-Cyclopent[*a*]azulen-3-ones (1), (31), and (32). 1) Dimerization of 3*H*-Cyclopent[*a*]azulen-3-one (1): 3*H*-Cyclopent[*a*]azulen-3-ones **1**, **31**, and **32**, were stable in the crystalline state. Although the parent compound (**1**) was stable enough in solution for measurement of its spectra, a new compound (**33**) precipitated as dark brown crystals on prolonged standing of the $CDCl_3$ solution for NMR measurement. The compound (**33**) is proposed to form by an intermolecular [4+2] cycloaddition reaction followed by decarbonylation (Scheme 10).

For the determination of the regio-selectivity of this cycloaddition reaction, the deuterio derivative (**1D**) was prepared from **5D**[14] by the same procedure as that used for the preparation of **1**. On standing of a solution of 1-deuterio-3*H*-cyclopent[*a*]azulen-3-one (**1D**) in deuteriochloroform, compound **33D** was obtained in a quantitative yield. Since the vicinal H,H-coupling constant between H-8 and H-8a ($J_{8,8a}$=4.0 Hz) remained unchanged, the regioselectivity of the dimerization of **1** was determined as shown in Scheme 10.

On the contrary, the 2-methyl derivative (**32**) was quite stable even in solution because of the steric hindrance induced by the methyl group at the 2 position.

2) The Diels-Alder Reaction of 1: The reaction of **1**



Scheme 11.

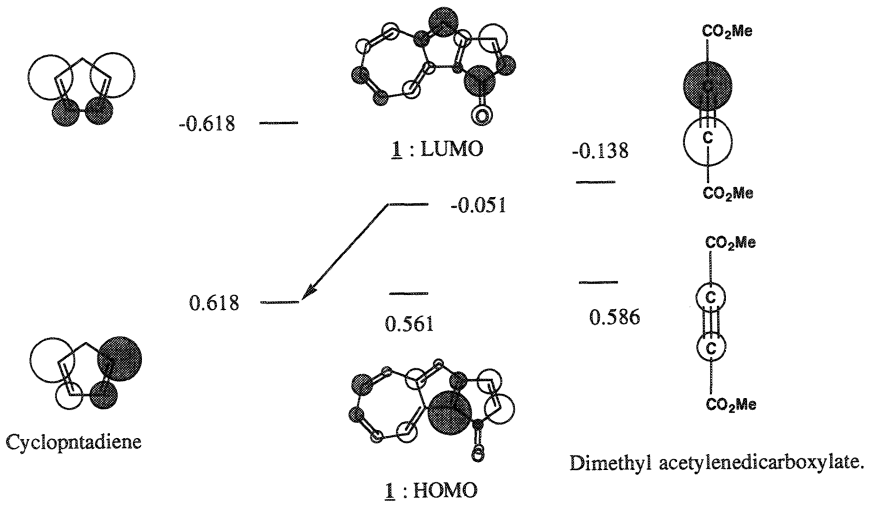


Fig. 1. HMO Calculations of **1**, cyclopentadiene, and dimethyl acetylenedicarboxylate.

with freshly distilled cyclopentadiene as a solvent immediately gave the cycloadduct (**11**) in a quantitative yield. The attempted reaction of **1** with dimethyl acetylenedicarboxylate in expectation of the formation of a benz[*a*]azulene derivative (**L**) gave only a dimerization product (**33**) (Scheme 11). These chemical behaviors, as well as the decarbonylative dimerization of **1** to give **33** as described above, are consistent with the results of the Hückel molecular orbital calculations shown in Fig. 1. The LUMO energy level of **1** is relatively low. Because the energy gap between HOMO of cyclopentadiene and LUMO of **1** is quite small, the Diels–Alder reaction of **1** with cyclopentadiene was easily achieved. The energy gap between LUMO of dimethyl acetylenedicarboxylate and HOMO of **1** is much larger than the energy gap between HOMO and LUMO of **1**. Thus, **1** barely reacted with dimethyl acetylenedicarboxylate, but the intermolecular cycloaddition reaction occurred easily.

Experimental

General. Melting points were determined with a Yamato Model-MP21 melting point apparatus. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. NMR spectra were recorded on an R-24B (^{1}H), 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 Hitachi Model 260-30, Hitachi Model 323, and Hitachi M-50 spectrometers, respectively.

Pyrolytic Apparatus and Procedure. The apparatus used for the pyrolytic synthesis consisted of an empty horizonal tube (30 by 1.5 cm o.d.) with small protrusions in the middle of the tube and heated at 550 °C over 25 cm with an external electric furnace. The outlet of the pyrolysis tube was directly attached to a cold finger (dry ice–methanol). The part 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 (about 100 °C) with a ribbon heater. The pressure was measured with a manometer attached to the exit of the cold finger. A thermocouple for measurement of pyrolytic temperature was placed in the middle of the heat zone. The precursor to be pyrolyzed was sublimed into the heated tube from a sample tube heated at 170 °C with an air bath. The pyrolytic products were collected on the cold finger. After the completion of sublimation of the precursor 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 in a small amount of benzene and the solution was purified over a short silica-gel column with benzene. The eluants were not permitted to stand at room temperature to avoid dimerization of pyrolytic products. Further details will be described below.

Preparation of Monobromide 7. *N*-bromosuccinimide (1.63 g, 9.16 mmol) was added to a solution of **6** (1.0 g, 4.16 mmol) in carbon tetrachloride (150 ml) and the solution was refluxed for 11 h. After being cooled to room temperature, the succinimide formed was removed by filtration. The filtrate was concentrated under reduced pressure, and purified on a silica-gel column eluted with chloroform to give **7** (0.88 g, 66.1%)

followed by the recovered substrate (**6**) (0.27 g, 26.6%).

7: Red micro-crystals (from benzene); mp 160—162 °C. UV (MeOH) 240 (log ε 4.40), 285 (sh, 4.50), 300 (sh, 4.59), 310.5 (4.70), 345 (3.78), 365 (sh, 3.86), 380 (4.02), and 488 nm (2.85); IR (KBr) 1688 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=3.33 (dd, *J*=18.0 and 2.0 Hz, H-2), 3.70 (dd, *J*=18.0 and 6.0 Hz, H-2), 4.00 (s, OMe), 5.89 (dd, *J*=6.0 and 2.0 Hz, H-1), 7.53—8.23 (m, H-5,6, and 7), 9.12 (d, *J*=10 Hz, H-4), and 9.76 (d, *J*=10 Hz, H-8); MS *m/z* 320 (M^++2, 13.0%), 318 (M^+, 13.0%), and 239 (M^+−Br, 100%). Found: C, 56.34; H, 3.63%. Calcd for $C_{15}H_{11}O_3Br$: C, 56.45; H, 3.47%.

Preparation of 9. Triethylamine (0.63 g, 6.26 mmol) and freshly distilled cyclopentadiene (0.41 g, 6.26 mmol) as a trapping reagent were added to a solution of **7** (1.0 g, 3.13 mmol) in benzene (100 ml) and the solution was refluxed for 4 h. After being cooled to room temperature, the solvent was removed under reduced pressure, and the residual oil was purified on a silica-gel column eluted with benzene to give **9** (0.80 g, 83.4%).

9: Reddish-orange prisms (from MeOH); mp 193.5—195.0 °C. UV (MeOH) 241 (log ε 4.54), 278 (4.53), 302 (sh, 4.60), 314 (4.73), 350 (sh, 3.84), 372 (sh, 3.93), 386 (4.10), and 475 nm (2.71); IR (KBr) 1690 and 1666 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ=1.80 (m, H-12), 3.42 (m, H-1), 3.46—3.58 (m, H-4 and 11a), 4.02 (s, OMe), 4.16 (dd, *J*=6.0 and 4.0 Hz, H-4a), 5.48 (dd, *J*=6.0 and 2.0 Hz, H-3), 5.96 (dd, *J*=6.0 and 2.0 Hz, H-2), 7.66—8.03 (m, H-7, 8, and 9), 9.06 (dd, *J*=9.0 and 1.0 Hz, H-10), and 9.73 (dd, *J*=9.0 and 1.0 Hz, H-6); MS *m/z* 304 (M^+, 21.1%) and 238 ($M^+-C_5H_6$, 100%). Found: C, 79.17; H, 5.16%. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30%.

Synthesis of the Pyrolytic Precursor (11) of 3*H*-Cyclopent[*a*]azulen-3-one (1). A solution of **9** (3 g, 9.9 mmol) in 10% KOH solution in aqueous ethanol (EtOH 240 ml, H_2O 160 ml, KOH 40 g) was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was poured into water, and acidified with 6 M HCl (1 M=1 mol dm^{-3}). The precipitates of the carboxylic acid formed were collected by filtration and dried under reduced pressure to give **10** (2.72 g, 9.4 mmol, 94.7% yield) as reddish-orange crystals. The carboxylic acid (**10**) was dissolved in trifluoroacetic acid (40 ml) and the solution was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was diluted with water, and the solution was extracted with benzene. The benzene layer was then dried, concentrated under reduced pressure, and purified on a short silica-gel column to give the cycloadduct (**11**) (2.31 g, 9.4 mmol, 94.7% yield based on **9**).

11: Dark red prisms (from MeOH); mp 163.5—164 °C. UV (MeOH) 235 (sh, log ε 4.16), 299 (sh, 4.61), 311.5 (4.71), 355.5 (3.79), 369.5 (3.95), 389 (4.05), 507 (2.72), and 551 nm (sh, 2.58); IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz), δ=1.76 (ddd, *J*=8.0, 1.5, and 1.5 Hz, H-12), 1.84 (ddd, *J*=8.0, 1.5, and 1.5, H-12), 3.32 (m, H-1 and 4), 3.52 (dd, *J*=6.0 and 4.8 Hz, H-11a), 3.95 (dd, *J*=6.0 and 4.8 Hz, H-4a), 5.40 (dd, *J*=6.0 and 3.0 Hz, H-2), 5.88 (dd, *J*=6.0 and 3.0 Hz, H-3), 7.00 (s, H-5), 7.37 (ddd, *J*=9.5, 9.5, and 1.5 Hz, H-7), 7.42 (ddd, *J*=9.5, 9.5, and 12.5 Hz, H-9), 7.63 (dd, *J*=9.5 and 9.5 Hz, H-8), 8.27 (d, *J*=9.5 Hz, H-6), and 8.82 (d, *J*=9.5 Hz, H-10); MS *m/z* 247 (M^++1, 7.8%), 254 (M^+, 20.6%), and 180 ($M^+-C_5H_6$, 100%). Found: C, 87.48; H, 5.80%. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73%.

Preparation of Methyl 6-Methyl-2,3-dihydro-1*H*-cyclopent[*a*]azulene-9-carboxylate (13). 1-morpholinocyclopentene (25.0 g, 163.0 mmol) was added to a solution of **4** (12.6 g, 54.2 mmol) in ethanol (270 ml) and the solution was refluxed for 19 h. After being cooled to room temperature, the solvent was removed under reduced pressure, and the resulting oil was purified on a silica-gel column eluted with benzene to give **13** (12.3 g, 89.3%).

13: Violet needles (from cyclohexane); mp 88.5—89.0 °C; UV (MeOH) 237.5 (log ε 4.44), 299 (4.89), 312 (4.95), 355 (3.89), 372 (3.96), 393 (3.96), 530 (2.93), and 560 nm (sh, 2.86); IR(KBr) 1673 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.37 (t, *J*=7.0 Hz, $-OCH_2C\underline{H}_3$), 2.25—2.60 (m, H-2), 2.55 (s, Me-6), 2.93 (t, *J*=6.8 Hz, H-3), 3.17 (t, *J*=6.8 Hz, H-1), 4.29 (q, *J*=7.0 Hz, $-OC\underline{H}_2CH_3$), 6.93 (d, *J*=10.0 Hz, H-5), 7.10 (d, *J*=10.0 Hz, H-7), 7.67 (d, *J*=10.0 Hz, H-4), and 9.10 (d,*J*=10.0 Hz, H-8). MS *m/z* 255 (M^++1, 11.0%) and 254 (M^+, 100.0%). Found: C, 80.36; H, 7.21%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

Preparation of Ketone (14). DDQ (6.0 g, 26.4 mmol) was added to a solution of **13** (3.0 g, 11.8 mmol) in aqueous acetone (H_2O 15 ml, acetone 135 ml) and the mixture was stirred at room temperature for 15 min. After removing the solvent under reduced pressure, dioxane was added to the residue, and precipitated DDQH was removed by filtration. The filtrate was concentrated under reduced pressure, and benzene was added to the residue. A further crop of precipitated DDQH was filtered off. After removing the solvent, the resulting oil was purified on an alumina column eluted with benzene to give ketone **14** (2.8 g, 88.5,%).

14: Light orange needle (from ethyl acetate); mp 171.5—172.5 °C. UV (MeOH) 237 (log ε 4.35), 273 (4.46), 303 (sh, 4.58), 315 (4.72), 345 (sh, 3.87), 370 (sh, 3.87), 384 (4.01), and 460 nm (2.89); IR (KBr) 1702 and 1675 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.43 (t, *J*=7.0 Hz, $OCH_2C\underline{H}_3$), 2.75 (s, Me-6), 2.97 (m, H-2), 3.37 (m, H-1), 4.40 (q, *J*=7.0 Hz, $OC\underline{H}_2CH_3$), 7.53 (d, *J*=10.8 Hz, H-5), 7.60 (d, *J*=10.8 Hz, H-7), 8.83 (d, *J*=10.8 Hz, H-4), and 9.47 (d, *J*=10.8 Hz, H-8); MS *m/z* 269 (M^++1, 13.9%) and 268 (M^+, 100%). Found: C, 76.23; H, 6.22%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

Synthesis of Precursor 17. *N*-bromosuccinimide (1.75 g, 9.8 mmol) was added to a solution of **14** (1.2 g, 4.5 mmol) in carbon tetrachloride (165 ml) and the solution was refluxed for 8 h. After being cooled to room temperature, precipitated succinimide was removed by filtration, and the filtrate was concentrated under reduced pressure. The purification of the residual oil on a short silica-gel column eluted with chloroform gave a crude monobromide (**15**) which was used for the succeeding reaction without further purification.

Trietliylamine (1.3 g, 12.9 mmol) and freshly distilled cyclopentadiene (2.0 g, 25.6 mmol) as a trapping reagent was added to a solution of the monobromide (**15**) in benzene (150 ml) and the mixture was refluxed for 1 h. After being cooled to room temperature, the solvent was removed under reduced pressure and the resulting oil was purified on a silica-gel column eluted with benzene–ethyl acetate (5 : 1) to give **17** (730.0 mg, 49.1% from **14**).

17: Red prisms (from benzene); mp 191.5 °C; UV (MeOH) 237.5 (log ε 4.42), 278 (4.42), 318 (4.68), 350 (sh, 3.86), 370 (sh, 3.82), 392 (4.01), and 462 nm (2.86); IR (KBr) 1694 and 1664 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.50 (t, *J*=7.2 Hz, $OCH_2C\underline{H}_3$), 1.80 (m, H-12), 2.72 (s, Me-8), 3.31—3.53 (m, H-1,4, and 11a), 4.12 (dd, *J*=4.8 and 4.8 Hz, H-4a), 4.47 (q, *J*=7.2 Hz, $OC\underline{H}_2CH_3$), 5.43 (dd, *J*=6.0 and 3.0 Hz, H-20), 5.90 (dd, *J*=6.0 and 2.0 Hz, H-3), 7.50 (d, *J*=10.8 Hz, H-9), 7.59 (d,

J=10.8 Hz, H-7,8), 8.79 (d, J=10.8 Hz, H-1), and 9.47 (d, J=10.8 Hz, H-6); MS m/z 332 (M^+, 23.6%), 266 ($M^+ - C_5H_6$, 100%). Found: C, 79.49; H, 6.07%. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06%.

Synthesis of Pyrolytic Precursor 19. A solution of **17** (550 mg, 1.7 mmol) in 10% KOH in aqueous ethanol (ethanol 36 ml, H_2O 24 ml, KOH 6 g) was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was poured into water. After acidification with 6 M HCl, the carboxylic acid precipitates were collected by filtration. After drying under reduced pressure, the carboxylic acid was dissolved in trifluoroacetic acid (10 ml) and the solution was refluxed for 1.5 h. After cooling to room temperature, the reaction mixture was diluted with water, extracted by chloroform and the organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Purification of the resulting oil on a silica-gel column eluted with 10 : 1 benzene–ethyl acetate gave **19** (321.0 mg, 74.4% from **17**).

19: Red prisms (from benzene–cyclohexane=1 : 1); mp 146.5—147.0 °C; UV (MeOH) 217 (log ε 4.40), 235 (sh, 4.17), 305 (4.71), 317 (4.81), 355 (3.77), 372 (3.96), 393 (4.03), and 495 nm (2.87); IR (KBr) 1661 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ=1.67 (broad s, H-12), 3.00—3.37 (m, H-1,4, and 11a), 3.75 (m, H-4a), 5.27 (dd, J=6.0 and 3.0 Hz, H-2), 5.78 (dd J=6.0 and 3.0 Hz, H-3), 6.73 (s, H-5), 7.03 (d, J=10.0 Hz, H-7 and 9), 7.93 (d, J=10.0 Hz, H-6), and 8.47 (d, J=10.0 Hz, H-10); MS m/z 260 (M^+, 14.9%) and 194 ($M^+ - C_5H_6$, 100%). Found: C, 87.48; H, 6.43%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20%.

Synthesis of Methyl 2-Methyl- (20) and 3-Methyl-2,3-dihydro-1*H*-cyclopent[*a*]azulene-9-carboxylate (21). 1-morpholino-3-methylcyclopentene (24.6 g, 0.147 mol) was added to a solution of **4** (30.0 g, 0.147 mol) in ethanol (600 ml) and the solution was refluxed for 87 h. After being cooled to room temperature, the solvent was removed under reduced pressure. Purification of the resulting oil on a silica-gel column eluted with benzene gave a mixture of **20** and **21** (11 : 21 by HPLC analysis, total 24.8 g, 70.2%). The components were separated on an ODS column, (Merck, RP-18, Gross B) eluted with 70 : 30 acetonitrile–H_2O to give **20** and **21**.

20: Violet crystal (from hexane); mp 60 °C; UV (MeOH) 237 (log ε 4.30), 294.2 (4.65), 307 (4.70), 338 (sh, 3.52), 353 (3.65), 369.5 (3.79), 389.5 (3.81), 545 (2.74), and 586 nm (sh, 2.64); IR (KBr) 1682 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.27 (d, J=6.2 Hz, Me), 2.53—3.53 (m, H-1,2, and 3), 3.90 (s, OMe), 7.18 (dd, J=9.3 and 9.3 Hz, H-5), 7.30 (dd, J=9.3 and 9.3 Hz, H-5), 7.30 (dd J=9.3 and 9.3 Hz, H-7), 7.53 (dd, J=9.3 and 9.3 Hz, H-6), 7.97 (d, J=9.3 Hz, H-4), and 9.30 (d, J=9.3 Hz, H-8); MS m/z 241 (M^+ +1, 54.9%) and 240 (M^+, 100%). Found: C, 79.75; H, 6.70%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.70%.

21: Violet crystals (from hexane); mp 42.0—43.0 °C; UV (MeOH) 237.5 (log ε 4.46), 294 (4.59), 307 (4.65), 352 (3.54), 367 (3.67), 387 (3.69), and 535 nm (2.58); IR (KBr) 1682 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.40 (d, J=6.8 Hz, Me), 2.07 (m, H-3), 3.17—3.73 (m, H-1 and 2), 3.90 (s, OMe), 7.17 (dd, J=9.3 and 9.3 Hz, H-5), 7.31 (dd, J=9.3 and 9.3 Hz, H-7), 7.53 (dd, J=9.3 and 9.3 Hz, H-6), 8.11 (d, J=9.3 Hz, H-4), and 9.33 (d J=9.3 Hz, H-8); MS m/z 240 (M^+, 38.5%) and 240 (M^+ −Me, 100%). Found: C, 79.32; H, 6.80%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.70%.

Synthesis of Ketone 22. DDQ (2.2 g, 9.69 mmol) was added to a solution of **20** (1 g, 4.12 mmol) in aqueous acetone (H_2O 5 ml, acetone 45 ml) and the resulting mixture was stirred at room temperature for 15 min. The reaction mixture was concentrated under reduced pressure and benzene was added to the residue. Precipitated DDQH was removed by filtration and the solvent was removed under reduced pressure. Purification of the resulting oil on an alumina column eluted with chloroform gave **22** (0.95 g, 90.8%).

22: Red prisms (from ethyl acetate); mp 138.5—139.0; °C; UV (MeOH) 238.5 (log ε 4.55), 273.5 (4.49), 294 (sh, 4.46), 298 (sh, 4.54), 310 (4.69), 368 (3.94), 382 (4.06), and 472 nm (2.77); IR (KBr) 1693 and 1678 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.41 (d, J=7.4 Hz, Me), 3.02 (dd, J=20.0 and 3.2 Hz, H-1), 3.05 (m, H-2), 3.73 (dd, J=20.0 and 7.8 Hz, H-1), 3.95 (s, OMe), 7.56—7.82 (m, H-5 and 7), 7.88 (dddd, J=9.3, 9.3, 1.8, and 1.8 Hz, H-6), 9.03 (dd, J=9.3 and 1.8 Hz, H-4), and 9.94 (dd, J=9.3 and 1.8 Hz, H-8); MS m/z 255 (M^+ +1, 12.3%), 254 (M^+, 100%), and 239 (M^+ −Me, 60.6%). Found: C, 75.58; H, 5.65%. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%.

Synthesis of 9-Methoxycarbonyl-2-methyl-3*H*-cyclopent[*a*]-azulen-3-one (27). *N*-bromosuccinimide (1.12 g, 6.30 mmol) was added to a solution of **22** (800 mg, 3.15 mmol) in carbon tetrachloride (110 ml) and the mixture was refluxed for 14 h. After being cooled to room temperature, the solvent was removed under reduced pressure. Purification of the resulting oil on a silica-gel column eluted with chloroform gave dibromide **24** (162.0 mg, 12.5%) followed by a mixture of monobromides **25** and **26**. After removing the solvent under reduced pressure, the resulting oil was adsorbed on a basic alumina column for dehydrobromination of **25** and **26**. After standing for 2 h, the mixture of **25** and **26** was eluted with 1 : 1 benzene–ethyl acetate. After removing the solvent, the resulting oil was purified on an ODS column (Merck, RP-18, Gross B) eluted with acetonitrile–H_2O (7 : 3) to give an exo-methylene compound **28** (35.0 mg, 4.4%) followed by **27** (387.0 mg, 49%).

24: Orange crystals; mp 158.0—159.5 °C; UV (MeOH) 232.5 (log ε 3.98), 314 (4.26), 369 (3.51), 384 (3.54), 445 (2.56), 483 (2.56), 516 (2.54), 558 (2.43), and 607 nm (2.20); IR (KBr) 1710 and 1694 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=2.25 (s, Me), 4.02 (s, OMe), 6.29 (s, H-1), 7.72 (ddd, J=9.6, 9.6, and 2.2 Hz, H-5 or 7), 7.79 (ddd J=9.6, 9.6, and 2.2 Hz, H-7 or 5), 8.00 (dddd J=9.6, 9.6, 2.2, and 2.2 Hz, H-6), 9.08 (dd, J=9.6 and 2.2 Hz, H-4), and 9.74 (dd, J=9.6 and 2.2 Hz, H-8); MS m/z 412 (M^+, 0.9%) and 252 ($M^+ - Br_2$, 100%). Found: C 46.64; H, 3.01%. Calcd for $C_{16}H_{12}O_3Br_2$: C, 46.64; H, 2.94%.

27: Reddish-violet needles (from benzene); mp 170.5—170.8 °C; UV (MeOH), 230 (log ε 4.20), 263 (4.17), 311 (sh, 4.64), 325 (4.74), 440 (sh, 3.04), 485 (2.89), 522 (2.99), and 560 nm (2.98); IR (KBr) 1707 and 1688 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.94 (d, J=1.8 Hz, Me), 3.88 (s, OMe), 7.17 (q J=1.8 Hz, H-1), 7.13—7.33 (m, H-5, 6, and 7), 8.17 (d, J=10.0 Hz, H-4), and 8.97 (d, J=8.5 Hz, H-8); MS m/z 253 (M^+ +1, 22.5%), 252 (M^+, 100%), and 237 (M^+ −Me, 29.4%). Found: C, 76.31; H, 5.02%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79%.

28: Red crystals; mp 173.5—174.0 °C; UV (MeOH) 239 (log 4.39), 288.5 (4.51), 310 (sh, 4.51), 319 (4.60), 380 (4.07), 394 (4.18), and 464 nm (2.91); IR (KBr) 1706 and 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=3.94 (s, OMe), 4.01 (m, H-1), 5.53 (m, H-a), 6.22 (m, H-b), 7.58—7.83 (m, H-5 and 7), 7.93 (dd, J=9.6 and 9.6 Hz, H-6), 9.10 (d, J=9.6 Hz, H-4), and 9.63 (d, J=9.6 Hz, H-8); MS m/z 253 (M^+ +1, 14.0%), 252 (M^+, 100%). Found: C, 75.74; H, 4.84%. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79%.

Cycloaddition Reaction of 27 with Cyclopentadiene.

Preparation of 29: 9-Methoxycarbonyl-2-methyl-3*H*-cyclopent[*a*]azulen-3-one (**27**) (170.0 mg, 0.68 mmol) was dissolved in freshly distilled cyclopentadiene (18 ml) and the mixture was heated at 60 °C for 12 h. After being cooled to room temperature, the reaction mixture was charged on a silica-gel column and eluted with hexane to remove cyclopentadiene. Elution with ethyl acetate gave the adduct **29** (214.5 mg, 100%).

29: Red needles (from cyclohexane); mp 159.5—161.0 °C; UV (MeOH) 238 (log ε 4.25), 285 (sh, 4.38), 302.5 (sh, 4.48), 312 (4.59), 347 (sh, 3.71), 367 (sh, 3.74), 383 (3.91), and 485 nm (2.76); IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.47 (s, Me), 1.78 (ddd, *J*=8.3, 1.5, and 1.5 Hz, H-12), 2.01 (bd, *J*=8.3 Hz, H-12), 2.80 (m, H-1), 3.38 (m, H-4), 3.67 (d, *J*=4.5 Hz, H-4a), 3.93 (s, OMe), 5.29 (dd, *J*=6.0 and 3.0 Hz, H-3), 5.93 (dd, *J*=6.0 and 3.0 Hz, H-2), 7.47—7.79 (m, H-7, 8, and 9), 8.92 (dd, *J*=9.6 and 1.5 Hz, H-10), and 9.58 (dd, *J*=9.6 and 1.5 Hz, H-6); MS *m/z* 318 (M^+, 5.8%) and 252 ($M^+ - C_5H_6$, 100%).

Synthesis of the Pyrolytic Precursor (30): A Cycloadduct of 2-Methyl-3*H*-cyclopent[*a*]azulen-3-one (32). The ester **29** (214.5 mg, 6.8 mmol) was dissolved in 10% KOH in aqueous ethanol (EtOH 15 ml, 10 ml, KOH 4 g) and the solution was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was poured into water and acidified with 6 M HCl. The precipitated carboxylic acid was collected by filtration. After drying under reduced pressure, the carboxylic acid was dissolved in trifluoroacetic acid (5 ml) and the solution was refluxed for 1 h. The reaction mixture was cooled to room temperature, diluted with water, extracted with benzene, and the organic layer was dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the residual oil was purified on a silica-gel column eluted with benzene to give **30** (142.0 mg, 80.9%).

30: Reddish-violet plates (from cyclohexane); mp 95.0—96.5 °C; UV (MeOH) 220 (sh, log ε 4.23), 235 (sh, 4.12), 300 (4.58), 312 (4.68), 350 (3.76), 370 (3.90), 389 (4.00), and 510 nm (2.72); IR (neat) 1670 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.54 (s, Me), 1.83 (d, *J*=7.5 Hz, H-12), 2.00 (d, *J*=7.5 Hz, H-12), 2.87 (m, H-1), 3.22 (m, H-4), 3.56 (d, *J*=4.2 Hz, H-4a), 5.33 (dd, *J*=6.0 and 3.0 Hz, H-3), 6.00 (dd, *J*=6.0 and 3.0 Hz, H-2), 7.00 (s, H-5), 7.40 (ddd, *J*=9.8, 9.8, and 1.5 Hz, H-9), 7.44 (ddd, *J*=9.8, 9.8, and 1.5 Hz, H-7), 7.65 (dd, *J*=9.8 and 9.8 Hz, H-8), 8.28 (d, *J*=9.8 Hz, H-6), and 8.84 (d, *J*=9.8 Hz, H-10); MS *m/z* 260 (M^+, 5%) and 194 ($M^+ - C_5H_6$, 100%). Found: C, 87.25; H, 6.31%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20%.

Preparation of 3*H*-Cyclopent[*a*]azulen-3-one (1): Flash Vacuum Pyrolysis of 11. Flash vacuum pyrolysis was achieved as described above. The cycloadduct **11** (100 mg, 0.41 mmol) was pyrolyzed at 550 °C (0.02—0.10 mmHg, 170 °C preheat) and the products were collected on the cold finger (−78 °C, dry ice-methanol) as brown crystals. After being warmed to room temperature, the crystals on the cold finger were dissolved in a small amount of benzene. The immediate purification of the resulting benzene solution on a silica-gel column eluted with benzene gave **1** (61.0 mg, 83.4%).

1: Dark brown crystals; mp 78.5—79.5 °C; UV (MeOH) 223.5 (log ε 4.24), 252 (4.26), 304 (4.49), 313.5 (4.58), 352 (sh, 4.06), 372 (3.91), 546 (2.93), 582 (2.94), and 633 nm (2.71); IR (KBr) 1668 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=6.03 (d, *J*=5.8 Hz, H-2), 6.70 (s, H-9), 7.05 (dd, *J*=10.2 and 9.0 Hz, H-7), 7.07 (dd, *J*=10.2 and 9.0, and 1.0 Hz, H-5), 7.27 (d, *J*=5.8 Hz, H-1), 7.29 (broad dd, H-6), 7.85 (d, *J*=9.0 Hz, H-8), and 8.23 (d, *J*=10.2 Hz, H-4); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=113.17 (d, C-9), 123.36 (s), 129.11 (d, C-5), 129.98 (d, C-7), 133.21 (d, C-4), 135.56 (s), 136.68 (d, C-8), 137.04 (d, C-6), 139.91 (d, C-2), 141.22 (d, C-1), 152.91 (s), 158.69 (s), and 191.19 (s); MS *m/z* 181 (M^+ +1, 47%), 180 (M^+, 100%), and 152 ($M^+ - CO$, 79%). Found: C, 86.50; H, 4.75%. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.47%.

Synthesis of 6-Methyl-3*H*-cyclopent[*a*]azulen-3-one (31). Flash Vacuum Pyrolysis of 19: Cycloadduct **19** (55.0 mg, 0.21 mmol) was pyrolyzed at 550 °C (0.02—0.20 mmHg, 170 °C preheat) and the products were collected on the cold finger (at −78 °C, dry ice-methanol) as brown crystals. After being warmed to room temperature, the crystals on the cold finger were dissolved in a small amount of benzene. Chromatography of the resulting solution on a silica-gel column with benzene gave 6-methyl-3*H*-cyclopent[*a*]azulen-3-one (**31**) (39.0 mg, 95.0%).

31: Dark violet crystals; mp 89.0—89.5 °C; UV (MeOH) 250 (log ε 4.45), 307 (sh, 4.58), 317 (4.69), 420 (3.32), 535 (3.07), 572 (3.01), and 620 nm (2.90); IR (KBr) 1664 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=2.48 (s, Me), 5.97 (d, *J*=5.7 Hz, H-2), 6.60 (s, H-9), 6.98 (broad d, H-5 and 7), 7.20 (d, *J*=5.7 Hz, H-2), 7.72 (d, *J*=9.5 Hz, H-8), and 8.08 (d, *J*=10.9 Hz, H-4); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=27.72(q, Me), 113.22 (d, C-9), 123.33 (s), 129.43 (d, C-5), 132.16 (d, C-7), 132.42 (d, C-4), 134.61 (s), 136.09 (d, C-8), 139.15 (d, C-2), 141.18 (d, C-1), 148.85 (d, C-6), 151.03 (s), 157.39 (s), and 191.35 (s); MS *m/z* 195 (M^+ +1, 7.1%) and 194(M^+, 100%). Found: C, 86.09; H, 5.28%. Calcd for $C_{14}H_{10}O$: C, 86.58; H, 5.19%.

Synthesis of 2-Methyl-3*H*-cyclopent[*a*]azulen-3-one (32). Flash Vacuum Pyrolysis of 30: Pyrolysis of **30** (50 mg, 0.19 mmol) by the same procedure used for **11** gave **32** (31.0 mg, 84.1%).

32: Dark brown needles (from benzene); mp 61.5—62.0 °C; UV (MeOH) 224 (log ε 4.31), 254 (4.26), 260 (4.26), 306 (4.54), 318 (4.65), 4.20 (sh, 3.15), 539 (2.92), 577 (2.91), and 630 nm (2.69); IR (KBr) 1674 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.91 (d, *J*=1.5 Hz, Me), 6.55 (s, H-9), 6.87 (q, *J*=1.5 Hz, H-1), 7.02 (broad dd, H-5 and 7), 7.22 (broad dd, H-6), 7.72 (d, *J*=9.8 Hz, H-8), and 8.13 (d, *J*=10.5 Hz, H-4); ^{13}C NMR ($CDCl_3$, 50 MHz), δ=11.54 (q, Me), 111.87 (d, C-9), 123.98 (s), 129.15 (d, C-5), 129.88 (d, C-7), 132.45 (d, C-4), 135.19 (d, C-8), 135.38 (d, C-6), 135.67 (s), 136.03 (d, C-1), 150.52 (s), 153.61 (s), 158.75 (s), and 191.02 (s); MS *m/z* 195 (M^+ +1, 9.6%) and 194 (M^+, 100%). Found: C, 86.66; H, 5.43%. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19%.

Dimerization of 1 to Give 33. A solution of **1** in benzene was left standing at room temperature. After 24 h, precipitates were collected to give **33** as dark brown crystals in a quantitative yield.

33: Dark brown crystals; mp 203 °C (decomposed); UV ($CHCl_3$) 299 (log ε 4.78), 319 (4.81), 371.5 (4.15), 388 (4.21), 402.5 (4.09), 516 (3.78), 551 (3.74), 594 (3.62), and 644 nm (sh, 3.51); IR (KBr) 1668 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ=4.42 (ddd, *J*=8.6, 4.0, and 3.0 Hz, H-8a), 5.63 (d, *J*=8.6 Hz, H-15b), 6.64 (dd, *J*=10.0 and 4.0 Hz, H-8), 6.85 (dd, *J*=10.0 and 3.0 Hz, H-7), 7.13 (broad s, H-6 and 15), 7.14 (dd, *J*=9.8 and 9.8 Hz, H-4), 7.28 (dd, *J*=9.8 and 9.8 Hz, H-2), 7.46 (dd, *J*=9.8 and 9.8 Hz, H-13), 7.56 (dd, *J*=9.8 and 9.8 Hz, H-3), 7.58 (dd, *J*=9.8 and 9.8 Hz, H-11), 7.79 (dd *J*=9.8 and 9.8 Hz, H-12), 8.17 (d, *J*=9.8 Hz, H-5), 8.33 (d, *J*=9.8 Hz, H-14), 8.64 (d, *J*=9.8 Hz, H-1), and 9.08 (d, *J*=9.8 Hz, H-10); MS *m/z* 333

(M^+ +1, 12.8%) and 332 (M^+, 100%). Found: C, 89.66; H, 4.71%. Calcd for $C_{25}H_{16}O$: C, 90.34; H, 4.85%.

Cycloaddition Reaction of 1 with Cyclopentadiene. A solution of **1** (20 mg, 0.11 mmol) in freshly distilled cyclopentadiene (5 ml) was stirred at room temperature for a few minutes. After being charged on a silica-gel column and eluted with hexane to remove excess cyclopentadiene, elution with benzene–ethyl acetate (1 : 1) gave cycloadduct **11** in a quantitative yield.

Synthesis of 2,3-Dihydro-3*H*-cyclopent[*a*]azulen-3-one (34). The ketone **6** (1.2 g, 5 mmol) was dissolved in 100% phosphoric acid and the mixture was heated at 95 °C for 1 h. After being cooled to room temperature, the reaction mixture was poured into water, extracted with chloroform and the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed and the residual oil was purified on a neutral alumina column eluted with chloroform to give crude **34**. Re-chromatography of the crude **34** on a silica-gel column eluted with benzene gave **34** (1.64 g, 4.5 mmol, 90%).

34: Red crystals (from ethyl acetate); mp 143.0—144.5 °C; UV (MeOH) 217 (log ε 4.27), 232 (4.20), 295.5 (4.55), 308.5 (4.60), 352 (3.69), 366 (3.89), 386 (3.99), and 504 nm (2.63); IR (KBr) 1664 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ=3.01 (2H, m, H-2), 3.27 (2H, m, H-1), 7.04 (s, H-9), 7.38 (ddd, J=9.3, 9.3, and 1.5 Hz, H-5), 7.43 (ddd, J=9.3, 9.3, and 1.5 Hz, H-7), 7.69 (dd, J=9.3, 9.3 Hz, H-6), 8.32 (d, J=9.3 Hz, H-8), 8.91 (d, J=9.3 Hz, H-4); ^{13}C NMR (50 MHz, $CDCl_3$) δ=23.73 (t, C-1), 42.37 (t, C-2), 112.11 (d, C-9), 127.99 (d, C-5), 128.69 (d, C-7), 129.54 (s), 134.78 (d, C-4), 134.78 (s), 137.96 (d, C-8), 138.12 (d, C-6), 150.12 (s), 172.94 (s), and 200.26 (s); MS m/z 183 (M^+ +1, 13.6%) and 182 (M^+, 100%). Found: C, 85.66; H, 5.50%. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53%.

Synthesis of 1,2-Dihydro-6-methyl-3*H*-cyclopent[*a*]azulen-3-one (35). A mixture of **14** (250 mg, 0.93 mmol) in 100% phosphoric acid (15 ml) was heated at 95 °C for 40 min. After being cooled to room temperature, the reaction mixture was poured into water, extracted with chloroform, and the organic layer was dried on magnesium sulfate. The solvent was removed and the residual oil was purified on a neutral alumina column eluted with chloroform to give crude **35**. Re-chromatography of the crude **35** on a silica-gel column eluted with benzene gave **35** (180.0 mg, 98.7%).

35: Red plates (from benzene); mp 141.5 °C; UV (MeOH) 235 (log ε 4.20), 302.5 (4.66), 312.5 (4.86), 352 (3.78), 368 (sh, 3.91), 389 (3.97), and 490 nm (2.83); IR (KBr) 1667 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=2.66 (s, Me), 2.97 (m, H-2), 3.23 (m, H-1), 6.96 (s, H-9), 7.30 (d, J=9.8 Hz, H-5 and 7), 8.18 (d, J=9.8 Hz, H-8), and 8.75 (d, J=9.8 Hz, H-4); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=23.53 (t, C-1), 28.02 (q, Me), 42.36 (t, C-2), 112.18 (d, C-9), 128.26 (s), 129.43 (d, C-5), 130.01 (d, C-7), 133.19 (s), 133.90 (d, C-4), 136.92 (d, C-8), 148.86 (s), 150.26 (s), 171.46 (s), 200.10 (s); MS m/z 197 (M^+ +1, 8.6%) and 196 (M^+, 100%). Found: C, 85.93; H, 6.15%. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16%.

Synthesis of 2-Methyl-1,2-dihydro-3*H*-cyclopent[*a*]azulen-3-one (23). A mixture of **22** (100 mg, 0.4 mmol) and 5 ml of 100% phosphoric acid was heated at 95 °C for 1 h. After being cooled to room temperature, the reaction mixture was poured into water, extracted with chloroform and the organic layer was dried on magnesium sulfate. The solvent was removed and the resulting oil was purified on an alumina column eluted with chloroform to give crude **23**. Re-chromatography of the crude **23** on a silica gel column eluted with benzene gave **23** (75.0 mg, 98.0%).

23: Red needles (from cyclohexane); mp 68.5—69.5 °C; UV (MeOH) 215 (log ε 4.23), 233 (4.25), 296 (4.63), 308 (4.72), 352 (3.76), 367 (3.95), 387 (4.05), and 506 (2.72); IR (KBr) 1667 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz), δ=1.38 (d, J=7.2 Hz, Me), 2.80 (dd, J=17.4 and 3.6 Hz, H-1), 3.03 (qdd, J=7.2, 6.6, and 3.6 Hz, H-2), 3.50 (dd, J=17.4 and 3.6 Hz, H-1), 6.97 (s, H-9), 7.31 (ddd, J=9.6, 9.6, and 1.5 Hz, H-5), 7.36 (ddd, J=9.6, 9.6, and 1.5 Hz, H-7), 7.62 (dd, J=9.6 and 9.6 Hz, H-6), 8.25 (broad d, J=9.6 Hz, H-8), and 8.87 (broad d, J=9.6 Hz, H-4); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=17.18 (t, C-1), 32.68 (q, Me), 48.13 (t, C-2), 112.33 (d, C-9), 127.75 (d, C-5), 128.51 (d, C-7), 128.68 (s), 134.69 (d, C-4), 135.07 (s), 137.71 (d, C-8), 137.92 (d, C-6), 150.29 (s), 170.82 (s), 202.76 (s); MS m/z 197 (M^+ +1, 4.4%), 196 (M^+, 92.0%), and 181 (M^+ −Me, 100%). Found: C, 85.44; H, 6.14%. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16%.

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