Synthesis of Cyclopent[*a*]azulenes and 1(3)-Methylenecyclopent[*a*]azulene Derivatives Having an Electron Withdrawing Group at the 9-Position[1)]

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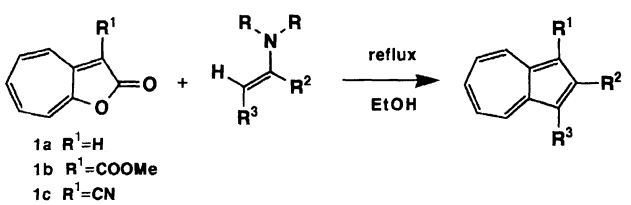
1*H*- and 3*H*-Cyclopent[*a*]azulenes having an electron withdrawing group, such as a methoxycarbonyl or a cyano group, at the 9-position were synthesized from their dihydro compounds by means of bromination with NBS and succeeding dehydrobromination by refluxing in chloroform. Base-catalyzed condensation of these cyclopent[*a*]azulenes with carbonyl compounds afforded 1-methylene-1*H*- and 3-methylene-3*H*-cyclopent[*a*]azulene derivatives having an electron withdrawing group at the 9-position. The physical properties of these methylenecyclopent[*a*]azulenes are also discussed.

New π-conjugated tricyclic systems formed by the condensation of an aromatic ring with the 1,2-position of the azulene ring are of current interest concerning their physical and chemical properties.[2)] Among these systems, 1*H*- and 3*H*- cyclopent[*a*]azulenes have been of interest due to their chemical properties, not only as new tricyclic π-conjugated systems, but also as versatile synthetic precursors. Hafner et al. have synthesized cyclopent[*a*]azulene by thermal pericyclic reactions of 6-dimethylamino-1-(2,4,6-cycloheptatrienyl)fulvene.[3)] Recently, we reported on the syntheses of 1*H*- and 3*H*-cyclopent[*a*]azulenes by the effective application of flash vacuum pyrolysis.[4)] These cyclopent[*a*]azulenes, however, are not suitable as synthetic precursors due to their instability and low reactivity. The introduction of an electron-withdrawing group at the 9-position is expected to be one method for the stabilization and activation of the methylene group of these cyclopent[*a*]-azulenes.

The present authors have found a useful synthetic method of azulenes by the reaction of 2*H*-cyclohepta[*b*]-furan-2-ones with enamines (Scheme 1).[5)] This method has been successfully used in our synthetic studies of polycyclic conjugated systems containing an azulene ring by the use of cycloalkanone enamines.[6)] In this azulene synthetic reaction, remarkable differences in the yields of the azulene derivatives were observed, depending on the substituent at the 3-position of 2*H*-cyclohepta[*b*]furan-2-one and the kind of the amine used in the enamine function. Thus, 2*H*-cyclohepta[*b*]furan-2-one (**1a**) gave azulene derivatives in excellent yields in reactions with pyrrolidine enamines. On the other hand, the reactions of the 3-methoxycarbonyl derivative **1b** with pyrrolidine enamines gave azulene derivatives in fairly low yield.



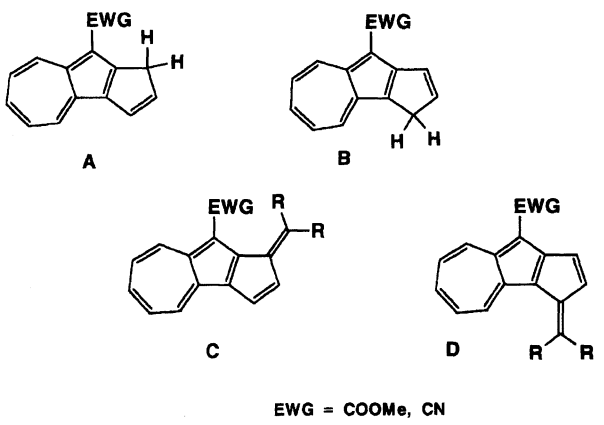
Scheme 1.

We report in this paper on the synthesis of methyl 2,3-dihydro-1*H*-cyclopent[*a*]azulene (**2**) in a specific high yield on the reaction of **1b** with 1-morpholinocyclopentene and its conversion to 1*H*- **A** and 3*H*-cyclopent[*a*]azulene **B** having an electron-withdrawing group (EWG) at the 9-position. Furthermore, the condensation reactions of these cyclopent[*a*]azulenes **A** and **B** with carbonyl compounds under mild basic conditions to give 1-methylene-1*H*- (**C**) and 3-methylene-3*H*-cyclopent[*a*]azulene derivatives (**D**) (Scheme 2) are also reported.

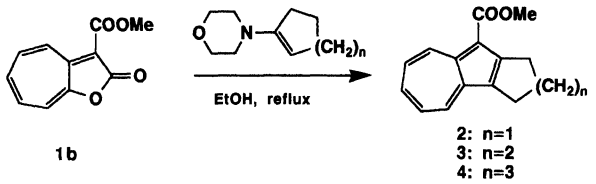
Results and Discussion

Synthesis of Appropriate Precursors of Cyclopent[*a*]azulenes Having an Electron-Withdrawing Group at the 9-Position. It has been established that the reactions of **1b** with pyrrolidine enamines give azulene derivatives in fairly low yields due to the formation of such by-products as the heptafulvene derivative **E**. Since the by-product seemed to be formed by an attack of a highly reactive pyrrolidine, which is formed in the reaction system, to the 8a-position, the reactions of **1b** with less-reactive morpholino enamines were investigaed (Scheme 3).

In spite of the low yields of the azulene derivatives on the reaction of **1b** with the morpholino enamines



Scheme 2.

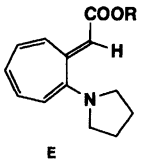


Scheme 3.

Table 1. Yields of Azulenes **2**, **3**, and **4** on the Reaction of **1b** with Cycloalkanone Morpholine Enamines

Enamine	React. time/h	Azulene deriv.	Yield/%
n=1	24	2	95
n=2	20	3	10
n=3	14	4	12

Note: The reactions of **1a** with cycloalkanone pyrrolidine enamines gave azulene derivatives in high yields in all cases.



derived from cyclohexanone or cycloheptanone, an appropriate precursor, methyl 2,3-dihydro-1*H*-cyclopent[*a*]azulene-9-carboxylate (**2**), of the titled compounds was synthesized in especially high yield by the reaction of **1b** with 1-morpholinocyclopentene in ethanol under refluxing as shown in Table 1.

A deuterio derivative **11D** was required for the structure determination of the 2*H*-cyclopent[*a*]azulene derivative **11**. A precursor **2D** deuterated at the 1-position (D-content 84.8%) was prepared by a treatment of **2** with sodium methoxide in methanol-*d*. The deuterium-incorporated position was determined by the oxidation of **2D** with DDQ[7] to give ketone **5D** (D-content 84%). Since the treatment of **2D** with 100% phosphoric acid, which was expected to form **6D**, gave 2,3-dihydro-1*H*-cyclopent[*a*]azulene (**6**) in 98% yield, the deuterio derivative **6D** (D-content 84%) was prepared by the reaction of **1a** with 1-morpholinocyclopentene in EtOD (Scheme 4). The ^{13}C NMR methylene carbon chemical shifts of **6** were assigned based on a comparison of the spectral data of **6** with those of **6D**.

Although another precursor, 9-cyano-2,3-dihydro-1*H*-cyclopent[*a*]azulene (**8**), has been synthesized by the reaction of 3-cyano-2*H*-cyclohepta[*b*]furan-2-one (**1c**) with 1-morpholinocyclopentene,[8] the synthetic method was not suitable for preparing the precursor **8** on a large scale, due to the tedious synthetic procedure of **1c**. Therefore, compound **8** was synthesized via an aldehyde **7** starting from the azulene **6**. Thus, 2,3-dihydro-1*H*-cyclopent[*a*]azulene (**6**) was converted to 9-formyl derivative **7** under Vilsmeier conditions. The treatment of **7** with hydroxylamine in refluxing acetic acid[9] gave the 9-cyano compound **8** (Scheme 5). This method is convenient for the synthesis of azulenes having a cyano group at the 1(3)-position.

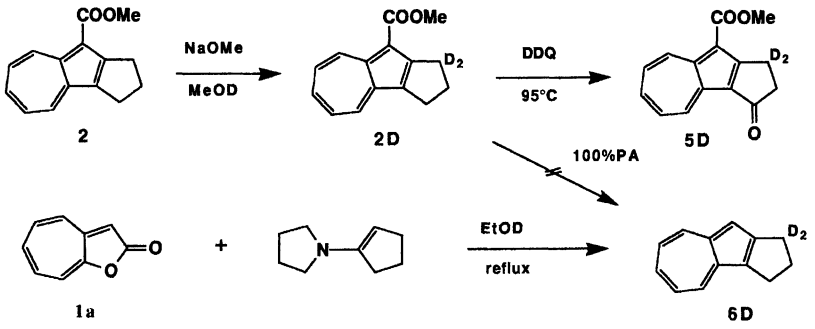
Synthesis of Methyl 3*H*-Cyclopent[*a*]azulene-9-carboxylate (11). Bromination of **2** with NBS in anhydrous chloroform at room temperature afforded dibromo compound **9** in 40% yield. The debromination of **9** with zinc powder in ethanol gave methyl 3*H*-cyclopent[*a*]azulene-9-carboxylate (**11**) in low yield. On the other hand, the bromination of **2** in anhydrous carbontetrachloride at 0 °C gave monobromide **10** in good yield. Although the dehydrobromination of **10** with various amines gave no desired product, heating a chloroform solution of **10** under refluxing afforded **11** in good yield. The structure of **11** was confirmed by the synthesis of a 1-deuterio compound **11D** using of **2D** as a starting material (Scheme 6). The 3*H*-isomer **11** was isomerized to 1*H*-isomer **14** by a treatment with triethylamine in benzene to give a mixture of **11** and **14** in a ratio of 7:13 (Scheme 7). All attempts to remove the methoxycarbonyl group of **11** were unsuccessful.

The bromination of the 9-cyano derivative **8** with NBS in carbon tetrachloride at room temperature gave monobromide **12**. Without purification, a subsequent dehydrobromination by refluxing of the chloroform solution of **12** afforded 9-cyano-3*H*-cyclopent[*a*]azulene (**13**) (Scheme 6).

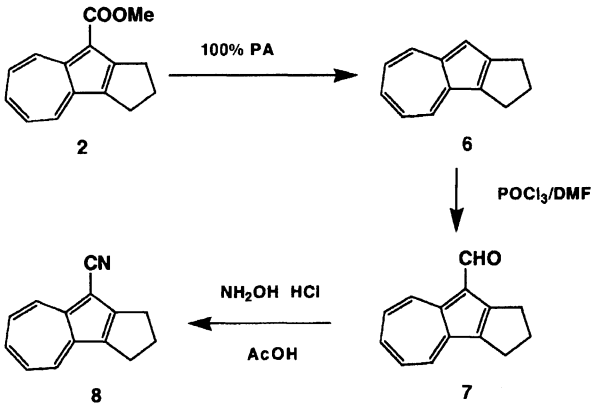
Condensation of 11 with Carbonyl Compounds to form 3-Methylene-3*H*- (15) and/or 1-Methylene-1*H*-cyclopent[*a*]azulene Derivatives (16). Although 3*H*-cyclopent[*a*]azulene could be deprotonated only by a treatment with a strong base, such as butyllithium in tetrahydrofuran,[4] 9-methoxycarbonyl-1*H*-cyclopent[*a*]azulene (**11**) having an electron-withdrawing group at the 9-position was easily deprotonated by treatment with an amine. Base-catalyzed condensation reactions of **11** with ketones and aldehydes were carried out by the addition of an amine to a solution of **11** in a corresponding ketone or aldehyde (Scheme 8) and the results are summarized in Table 2.

The condensation reaction of **11** with acetone in the presence of methylamine gave methyl 3-isopropylidene-3*H*-cyclopent[*a*]azulene-9-carboxylate (**15a**) in 47.4% yield as a single product. The structure of **15a** was confirmed by a spectral inspection, especially by observing of NOE on the ^{1}H NMR between H-4 and *syn*-Me at the 10-position (methylene carbon on 3-position). The reaction of **11** with diethyl ketone and cyclopentanone gave **15b** and **15c**, respectively. Interestingly, the reaction of **11** with acetophenone gave **15d** as a sole product. The structure of **15d** was determined on the basis of high-field shift of H-4, due to an anisotropy effect of the phenyl ring at the 10-position.

Condensation reactions of **11** with aldehydes occurred very easily. The reaction of **11** with isobutyraldehyde in the presence of propylamine in dioxane at room temperature gave condensation product **15e**



Scheme 4.



Scheme 5.

(31.6%) together with isomeric product **16e** (30.8%). The structures of **15e** and **16e** were confirmed by observing NOE on ^{1}H NMR between H-4 and H-10 (hydrogen on the methylene carbon at the 3-position) of **15e** and between COOMe and H-10 of **16e**, respectively. The *E*-configurations of the *exo*-cyclic double bond of **15e** and **16e** were surely determined by these NOE observations.

Methylenecyclopent[*a*]azulenes having one or two electron donating groups at the 10 position were also synthesized. The reaction of **11** with *N,N*-dimethylformamide diethylacetal (DMAA)[10] in DMF at 100 °C gave 1-[(*E*)-dimethylaminomethylene]-1*H*- (**15h**) and 3-[(*E*)-dimethylaminomethylene]-3*H*-cyclopent[*a*]azulene (**16h**). The structures of **15h** and **16h** were determined by the observing of NOE between H-4 and H-10 on **15h** and COOMe and H-10 on **16h**, respectively. The reaction of **11** with bis(dimethylamino)ethoxycarbonium tetrafluoroborate (DMFA)[11] gave methyl 3-[bis-(dimethylamino)methylene]-3*H*-cyclopent[*a*]azulene-9-carboxylate (**15g**) (Scheme 8).

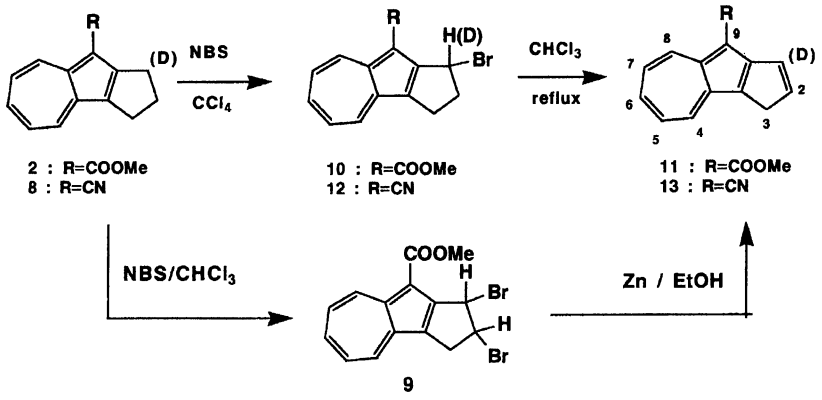
Condensation Reactions of 9-Cyano-3*H*-cyclopent[*a*]azulene (13) with Carbonyl Compounds. Because of the high reactivity of 9-cyano-3*H*-cyclopent-[*a*]azulene (**13**), the condensation reactions of **13** with carbonyl compounds were carried out in dioxane in the presence of propylamine. Although the 3-(1-ethylpropylidene) derivative **15b** was formed as a sole product in a condensation reaction of the methoxycarbonyl derivative **11** with diethyl ketone, the reaction of **13** with diethyl ketone gave **18b** (32%) as a major product together with an isomeric product **17b** (8.9%). The structure of **17b** was confirmed to be 9-cyano-3-(1-ethylpropylidene)-3*H*-cyclopent[*a*]azulene by observing NOE on ^{1}H NMR between the methyl signal (1.39 ppm) of the *syn*-ethyl group with H-4, and a comparison of the ultraviolet and visible spectra with that of **15b**. Therefore, the structure of another product **18b** was determined to be 9-cyano-1-(3-pentylidene)-1*H*-cyclopent[*a*]azulene. On the other hand, the reaction of **13** with acetone gave **18a** in 70.8% yield as a sole product. The structure of **18a** was confirmed by a spectral inspection, especially by a comparison of the ultraviolet and visible spectra with that of **18b**. The reactions of **13** with aldehydes did not give any identificable products.

As mentioned above, the methylene protons of 3*H*-cyclopent[*a*]azulenes having an electron-withdrawing group at the 9-position were easily deprotonated by amine to form cyclopent[*a*]azulenides which reacted with carbonyl compounds to give 1-methylene-1*H*- and/or 3-methylene-3*H*-cyclopent[*a*]azulene derivatives. The product ratio depended on both the steric bulkiness of the substituent at the 9-position and alkyl group of the carbonyl compounds.

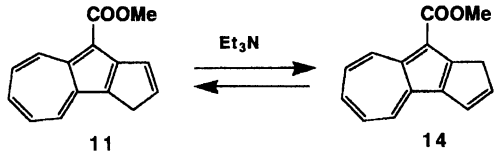
Characterization of 1-Methylene-1*H*- and 3-Methylene-3*H*-cyclopent[*a*]azulenes Having an Electron-Withdrawing Group at the 9-Position. Typical examples of the ultraviolet and visible absorption spectra of 1-methylene-1*H*- and 3-methylene-3*H*-cyclopent[*a*]azulene derivatives are shown in Fig. 1. The absorpion maxima of the isomeric compounds, **15e** and **16e**, are clearly different and the absorption maxima of **17b** and **18b** on the visible region are shifted to a longer wave length region by the electron-donating group at the 10-position (methylene carbon on the 3-position).

Benz[*a*]azulene (**19**) is known to exhibit a clear bond-length alternation in the seven-membered ring which is reflected by the vicinal coupling constants ($J_{8,9}=10.9$ Hz, $J_{5,6}=8.2$ Hz).[12] This bond-length alternation in the azulene ring could be ascribed to the larger aromatic stabilization energy of benzene than that of azulene.

^{1}H NMR spectral data of the 1- or 3- methylenecy-



Scheme 6.



Scheme 7.

clopent[*a*]azulene derivatives (**15**—**18**) prepared in this study are summarized in Table 3. The vicinal coupling constants $J_{4,5}$ are almost equal to $J_{7,8}$, indicating no bond-length alternation in the seven-membered ring of these compounds as shown in Fig. 2.

The contribution of ionic structures of 6-(dimethylamino)fulvene (**20**) and 1-(dimethylaminomethylene)-1*H*-indene (**21**) have been estimated by $\Delta G_c^{\ddagger}$ (free enthalpy of activation at coalescence temperature) of the C–NMe_2 bond rotation to be 56.1 and 43.5 kJ mol^{-1}, respectively.[13] Variable temperature ^{1}H NMR spectra of **15h** and **16h** were measured in a dichloromethane-d_2 solution. The two signals of the dimethylamino group of **15h** at −80 °C coalesced to one broad peak at −55.5 °C. On the basis of this coalesce temperature, $\Delta G_c^{\ddagger}$ for rotation of the C–NMe_2 group was estimated to be 46.0 kJ mol^{-1}. Similarly, the two signals of the dimethylamino group of **16h** coalesced at −32.6 °C, and $\Delta G_c^{\ddagger}$ was estimated to be 52.7 kJ mol^{-1} (Fig. 3). These results indicated that the contribution of the ionic structures of **15h′** and **16h′** is larger than that of **21** and less than that of **20**.

Experimental

General. The 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 a R-24B (^{1}H), and EM-360 (^{1}H), or a Varian XL-200 (^{1}H and ^{13}C), and the 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.

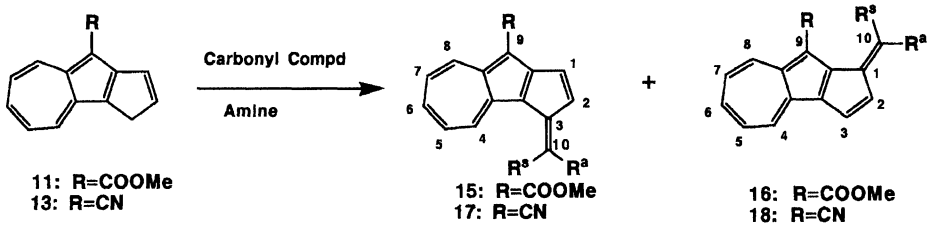
Synthesis of Methyl 2,3-Dihydro-1*H*-cyclopenta[*a*]azulene-9-carboxylate (2). 1-Morpholino-1-cyclopentene (75 g, 0.49 mol) was added to a solution of 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one (**1b**) (40 g, 0.2 mol) in anhydrous EtOH (800 ml) and the mixture was then heated under refluxing for 18 h. After being cooled to room temperature, the solvent was removed under reduced pressure and the residual oil was dissolved in benzene. The benzene solution was washed with water, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. After the residual oil was purified with a short silica-gel column, subsequent re-chromatography was applied with an alumina column to give **2** (40 g, 90% yield).

2: Dark violet prisms (hexane), mp 103—104 °C; UV (MeOH) 238 (log ε 4.29), 294 (4.68), 306.5 (4.74), 354 (3.65), 370 (3.78), 390 (3.81), and 542 nm (3.14); ^{1}H NMR (200 MHz, $CDCl_3$) δ=2.54 (2H, quint, J=7.0 Hz, H-2), 3.06 (2H, t, J=7.0 Hz, H-3), 3.31 (2H, t, J=7.0 Hz, H-1), 3.93 (s, COOMe), 7.29 (dd, J=10.0 and 10.0 Hz, H-5), 7.40 (dd, J=10.0 and 10.0 Hz, H-7), 7.62 (dd, J=10.0 and 10.0 Hz, H-6), 8.08 (d, J=10.0 Hz, H-4), and 9.43 (d, J=10.0 Hz, H-8); ^{13}C NMR (50 MHz, $CDCl_3$) δ=25.52 (t, C-2), 29.40 (t, C-3), 30.85 (t, C-1), 50.74 (s, COO<u>Me</u>), 109.35 (s, C-9), 125.59 (d, C-5), 127.09 (d, C-7), 133.90 (d, C-4), 135.11 (s, C-3a), 135.42 (d, C-8), 136.82 (d, C-6), 137.09 (s, C-3b), 146.05 (s, C-8a), 164.79 (s, C-9a), and 166.05 (s, <u>C</u>OOMe); Anal. ($C_{15}H_{14}O_2$), C, H.

Synthesis of Deuterio Compound (2D): Sodium methoxide (286 mg, 5.3 mmol) was added to a solution of **2** (1.2 g, 5.3 mmol) in MeOD (20 ml) and the solution was then refluxed for 4 h. After being cooled to room temperature, the residue obtained by removing the solvent was dissolved in benzene. The bezene solution was then passed through a short silica-gel column eluted with benzene to give **2D** (1.17 g, 96.4%). The D-content was determined to be 85.7% by ^{1}H NMR.

Reaction of 1a with 1-Pyrrolidino-1-cyclopentene in EtOD — Synthesis of 6D: After addition of 1-Pyrrolidino-1-cyclopentene (1.0 g, 6.84 mmol) to a solution of **1a** (300 mg, 2 mmol) in EtOD (5 ml), the solution was then heated under refluxing. After 3 h, *p*-toluenesulfonic acid (20 mg) was added and refluxed for an additional 30 min. The usual work up of the reaction mixture gave **6D** (188 mg, 54%), D-content 84%.

6D: Selected ^{13}C NMR (10 MHz, $CDCl_3$) δ=25.8 (t, C-2), 28.9 (t, C-3). The signal of C-1 observed at 30.4 ppm on



Scheme 8.

Table 2. Yields of 3-Methylene-3*H*- (**15**), (**17**), 1-Methylene-1*H*-cyclopent[*a*]azulene Derivatives (**16**), (**18**)

Substrate **11,13**	Carbonyl compd	Product R^s	Product R^a	3-Methylene- **15,17**	Yield (%)	1-Methylene- **16,18**	Yield (%)
11	Acetone	Me	Me	**15a**	47.4		
11	Diethylketone	Et	Et	**15b**	45.2		
11	Cyclopentanone	$(CH_2)_4$		**15c**	43.7		
11	Acetophenone	Ph	Me	**15d**	30.0		
11	Isobutyraldehyde	H	iPr	**15e**	31.6	**16e**	30.8
11	Benzaldehyde	H	Ph	**15f**	31.3	**16f**	27.0
11	DMAA	NMe_2	NMe_2	**15g**	43.1		
11	DMFA	H	NMe_2	**15h**	22.9	**16h**	30.6
13	Acetone	Me	Me			**18a**	70.8
13	Diethylketone	Et	Et	**17b**	8.9	**18b**	32.0

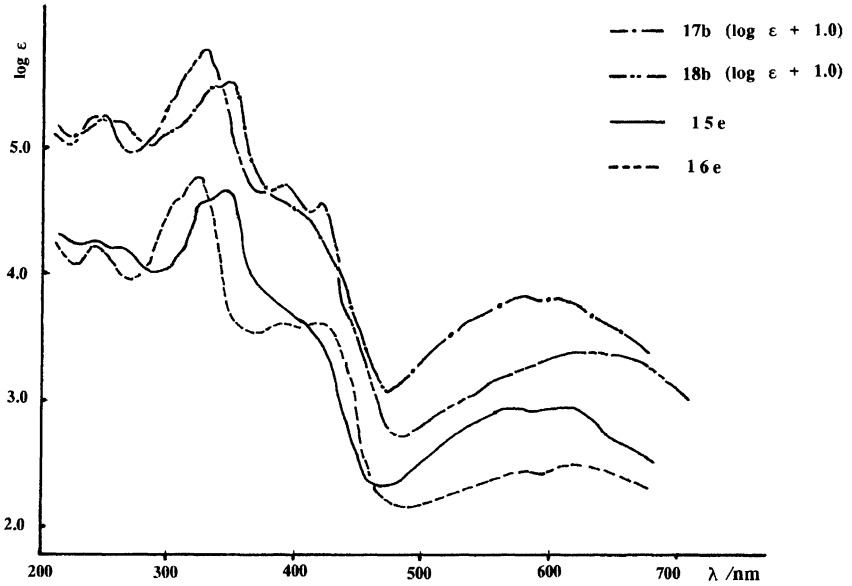


Fig. 1. Ultra violet and visible spectra of **15e**, **16e**, **17b**, and **18b** in MeOH.

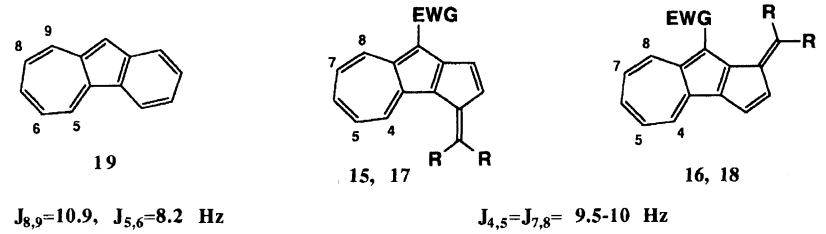


Fig. 2. Vicinal coupling constants of benz[*a*]azulene and methylenecyclopent[*a*]azulene derivatives **15**—**18**.

Table 3. ^{1}H NMR Spectral Data of Methyl 3-Methylene-3*H*- (**15**), 1-Methylene-1*H*-cyclopent[*a*]azulene-9-carboxylates (**16**), 9-Cyano-3-methylene-3*H*- (**17**), and 9-Cyano-1-methylene-1*H*-cyclopent[*a*]azulene Derivateves (**18**)

	H-1 (d)	H-2 (d)	H-3 (d)	H-4 (d)	H-5 (dd)	H-6 (dd)	H-7 (dd)	H-8 (d)	H-10 (bs)	Other Proton				
										CH_3,	CH_2,	$N(CH_3)_2$,	Ph	COOMe
15a	7.13	7.04		8.36		6.94—7.52		9.38		2.21		2.39		3.92
15b	7.25	7.16		8.39		7.08—7.65		9.46		1.23,	2.65	1.39,	2.88	3.95
15c	7.23	7.21		8.67	7.33	7.57	7.42	9.56		1.92		3.03		4.00
15d	7.23	7.23		6.28	6.51	7.13—7.32		9.33		2.55(Me)		7.37(Ph)		3.94
15e	7.22	7.18		8.45	7.23	7.52	7.24	9.43	6.63	1.23		3.13		3.96
15f	7.13—7.20			8.47		7.20—7.43		9.36	7.63			7.37(Ph)		3.93
15g	6.88	6.64		7.60	7.20	7.45	7.33	9.37		2.88(NMe_2)				3.90
15h	7.50	7.11		8.54	7.34	7.60	7.42	9.55	7.11	3.34(NMe_2)		3.97		3.97
16e		6.89	7.08	8.28	7.23	7.57	7.33	9.39	7.76	1.24		3.15		4.04
16f		7.07	7.16	8.22	7.20	7.55	7.32	9.37	8.84	7.32(*m*,*p*-Ph)		7.67(*o*-Ph)		4.07
16g		7.13	7.26	8.48	7.37	7.60	7.41	9.40	9.36	3.39(NMe_2)				4.04
17a		6.81	6.96	8.20	(7.26)	7.57	(7.26)	8.42		2.34		2.77		
17b	7.19	6.91		8.33		7.10—7.57		8.33		1.28,	2.68	1.42,	2.89	
18b		6.70	6.83	8.03	7.05	7.43	7.23	8.31		1.27,	2.64	1.35,	3.08	

Coupling constans: $J_{1,2}=J_{2,3}=5.0$ Hz and $J_{4,5}=J_{5,6}=J_{6,7}=J_{7,8}=9.5$—10.0 Hz.

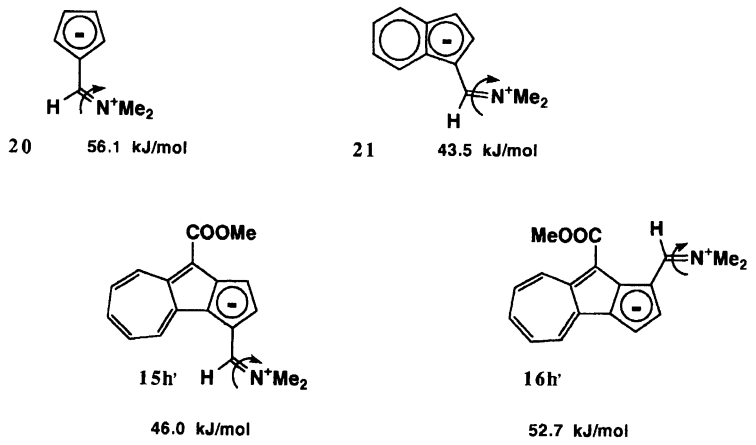


Fig. 3. Free enthalpy of activation at coalescence temperature ($\Delta G_c^{\ddagger}$) of methylenecyclopent[*a*]azulene derivatives, **15h**, **16h** and Reference Compounds **20** and **21**.

6 disappeared.

DDQ Oxidation of 2D: DDQ (1.11 g, 4.86 mmol) was added under stirring to a solution of **2D** (500 mg, 2.20 mmol) in 10% aqueous acetone (30 ml) and the mixture was stirred for 1 h. The precipitates of DDQH were collected by filtration and then washed with benzene. The filtrate and washings were combined and passed through a short alumina column to give **5D** (408 mg, 76.9%), D-contents 83%.

5D: ^{1}H NMR (60 MHz, $CDCl_3$) δ=2.95 (2H, t, J=2.0 Hz, H-2), 3.93 (s, COOMe), 7.47—8.17 (3H, m, H-5,6,7), 9.04 (dm, J=9.0 Hz, H-4), and 9.67 (dm, J=9.0 Hz, H-8).

Synthesis of 9-Formyl-2,3-dihydro-1*H*-cyclopent-[*a*]azulene (7). A mixture of **2** (3.5 g, 15.6 mmol) in 100% phosphoric acid (60 ml) was heated at 90—95 °C in a water-bath for 15 min. After being cooled to room temperature, the reaction mixture was poured into water (300 ml) and the aqueous solution was extracted with benzene. The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The residual oil was chromatographed with a silica-gel column eluted with benzene to give 2,3-dihydro-1*H*-cyclopent[*a*]azulene (**6**) (2.5 g, 98% yield).

6: ^{13}C NMR (10 MHz, $CDCl_3$) δ=25.8 (t, C-2), 28.9 (t, C-3), 30.4 (t, C-1), 110.0 (d, C-9), 121.3 (d, C-5), 122.3 (d, C-7), 130.9 (s, C-3a), 132.8 (d, C-4 or 8), 134.4 (d, C-8. or 4), 135.4 (d, C-6), 137.8 (s, C-3b), 145.8 (s, C-8a), and 160.9 (s, C-9a).

A solution of Vilsmeier reagent prepared by the addition of phosphoryl chloride (7.1 g) in DMF (25 ml) was dropwise added to a solution of **6** (2.5 g, 14.9 mmol) in DMF (25 ml) under ice cooling. After stirring for 3 h, the reaction mixture was poured into ice-water, it was then made basic by adding a potassium hydroxide solution, and extracted with benzene. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residue was purified with a silica-gel column eluted with benzene to give the formyl derivative **7** (3.04 g, 100% yield).

7: Violet plates (cyclohexane), mp 80—82.5 °C; UV (MeOH) 215.5 (log ε 4.34), 272.5 (4.08), 304 (4.50 sh), 318

(4.60), 380 (3.80 sh), 397 (3.87), and 529 nm (2.81); IR (KBr) 2940, 2730, 1649, 1472, 1431, 1404, 1390, 1310, 985, and 750 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=2.53 (2H, m, H-2), 2.97 (2H, t, J=6.0 Hz, H-3), 3.25 (2H, t, J=6.0 Hz, H-1), 7.15—7.47 (2H, m, H-5,7), 7.57 (1H, dd, J=9.0 and 9.0 Hz, H-6), 7.98 (1H, d, J=9.0 Hz, H-4), 9.10 (1H, d, J=9.0, H-8), and 10.25 (1H, s, CHO); Mass (25 eV, 80 °C) m/z 196 (M^+, 100%); Anal. Found: C, 85.78; H, 6.22%. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.12%.

Synthesis of 9-Cyano-2,3-dihydro-1*H*-cyclopent[*a*]-azulene (8). Hydroxylamine hyrdochloride (1.22 g, 10.2 mmol) and sodium acetate (1.4 g, 17.5 mmol) were added to a solution of the formyl derivative **7** (2.0 g, 10.2 mmol) in acetic acid (200 ml), and the mixture was then refluxed for 5 h. After being cooled to room temperature, precipitated sodium chloride was filtered off. The filtrate was diluted with water and extracted with benzene. After the benzene solution was washed with sodium hydrogencarbonate solution and dried over sodium sulfate, the solvent was removed under reduced pressure. The residue was purified with a silica-gel column eluted with benzene to give the cyano compound **8** (1.14 g, 59% yield). Recrystallization from ethyl acetate gave violet prisms.

8: Dark violet prisms (AcOEt); mp 126—127 °C; UV (MeOH) 236 ($\log\varepsilon$ 4.28), 291 (4.70), 303 (4.74), 360 (3.73), 379 (3.73), 548 (2.71), and 586 nm (2.69); IR (KBr) 2196, 1470, 1460, 1403, 1400, 1310, and 750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 2.60 (2H, quint, J=7.0 Hz, H-2), 3.08 (2H, t, J=7.0 Hz, H-3), 3.22 (2H, t, J=7.0 Hz, H-1), 7.34 (dd, J=10.0 and 10.0 Hz, H-5), 7.39 (dd, J=10.0 and 10.0 Hz, H-7), 7.68 (dd, J=10.0 and 10.0 Hz, H-6), 8.11 (d, J=10.0 Hz, H-4), and 8.41 (d, J=10.0 Hz, H-8); ^{13}C NMR (50 MHz, $CDCl_3$) 25.72 (t, C-2), 28.55 (t, C-3), 29.76 (t, C-1), 89.96 (s, CN), 117.34 (s, C-9), 126.12 (d, C-5, 7), 133.73 (s, C-3a), 134.18 (d, C-8), 134.66 (d, C-4), 137.75 (d, C-6), 138.83 (s, C-3b), 148.62 (s, C-8a), and 163.65 (s, C-9a); Mass (25 eV, 80 °C) m/z 193 (M^+, 100%); Anal. Found: C, 86.95; H, 5.69; N, 7.13%. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25%.

Reaction of 2 with *N*-Bromosuccinimide. a) Formation of the Dibromo Compound (9) in Chloroform: NBS (3.46 g, 19.4 mmol) was added to a solution of **2** (2.0 g, 8.84 mmol) in anhydrous chloroform (20 ml) and the mixture was then stirred at room temperature for 2.5 h. After confirmation in the absence of the substrate by TLC, precipitated succinimide was filtered off and the filtrate was evaporated under reduced pressure to give dark violet crystals. Chromatography of the crystals with a silica-gel column eluted with benzene gave the dibromo compound (**9**) (1.51 g, 44.6%).

9: Dark violet prisms (benzene–hexane), mp 135—137 °C; UV (MeOH) 239 ($\log\varepsilon$ 4.29), 308 (4.69), 348 (3.83), 361 (3.82), 380 (3.86), and 550 nm (2.91); IR (KBr) 2940, 1684, 1530, 1440, 1402, 1390, 1300, 1218, 1192, 1078, 1040, 728, 704, and 610 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ=3.43 (d, J=18 Hz, H-3), 3.95 (dd, J=18 and 5 Hz, H-3), 3.97 (3H, s, OMe), 5.25 (d, J=5 Hz, H-2), 6.02 (s, H-1), 7.23—7.88 (3H, m, H-5, 6, and 7), 8.22 (br. d, J=10 Hz, H-4), and 9.61 (br. d, J=10 Hz, H-8); Mass m/z 384 (M^+, 100%).

b) Reaction in Chloroform: Isolation of the Monobromo Compound (10): NBS (94.4 mg, 0.53 mmol) was added to a solution of **2** (100 mg, 0.44 mmol) in anhydrous chloroform (6 ml) and the mixture was then stirred under room temperature for 2 h. After removing precipitates of succinimide by filtration, the filtrate was evaporated under reduced pressure to give dark violet crystals. The chromatography of the crystals with a silica-gel column eluted with benzene gave dibromide **9** (29.5 mg, 17.4%) on the first fraction, cyclopent[*a*]azulene derivative **11** (10.5 mg, 10.6%) on the second fraction, and the monobromide **10** (16 mg, 12%) on the third fraction as unstable dark violet crystals.

10: ^1H NMR (60 MHz, $CDCl_3$) 2.53—3.38 (4H, m, H-2,3), 3.97 (s, COOMe), 5.65 (1H, H-1), 7.10—7.85 (3H, m, H-5,6,7), 8.10 (br. d, J=10.0 Hz, H-4), 9.28 (br. d, J=10.0 Hz, H-8).

c) Synthesis of Methyl 3*H*-cyclopent[*a*]azulene-9-carboxylate (11): NBS (2.6 g 14.6 mmol) was added to a solution of **2** (3.0 g, 13.3 mmol) in anhydrous CCl_4 (250 ml) and the mixture was stirred vigorously at 0 °C for 3 h. After confirming the absence of the substrate by HPLC, precipitated succinimide was filtered off, and the filtrate was then evaporated under reduced pressure to give crude monobromide (**10**) as dark violet crystals.

The crystals were dissolved in anhydrous chloroform (300 ml) and the solution was refluxed under N_2 atmosphere for 2 h. After being cooled to room temperature, the reaction mixture was washed with water and dried over anhydrous $MgSO_4$.

Chromatography of the residual oil obtained by removing the solvent under reduced pressure with a silica-gel column eluted with benzene gave **11** (2.58 g, 86.5%) as violet crystals.

11: Violet micro needles (hexane), mp 94.5—95 °C; UV (MeOH) 234 ($\log\varepsilon$ 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) 2950, 1675, 1535, 1440, 1405, 1395, 1375, 1300, 1185, 1095, 1080, 945, 780, 720, and 662 cm^{-1}; Mass m/z 244 (M^+, 100%); Anal. ($C_{15}H_{12}O_2$) C, H.

d) Synthesis the Deuterated Compound (11D) by the Reaction of 2D with NBS: The reaction of **2D** (300 mg, 1.3 mmol, D-content 74.4%) with NBS (260 mg, 1.4 mmol) in CCl_4 (25 ml) and the same treatment as the procedure described in c) gave **11D** (200 mg, 82%, D-content 100%) as dark violet crystals.

11D: Selected ^1H NMR (60 MHz, $CDCl_3$) 3.22 (2H, d, J=2.0 Hz, H-3), 6.82 (t, J=2.0 Hz, H-2).

Debromination of the Dibromo Compound (9): Zinc powder (76.6 mg) was added to a solution of **9** (300 mg, 0.78 mmol) in EtOH (20 ml) and the mixture was stirred at 30—40 °C for 5 h. After the precipitates were filtered off, the filtrate was evaporated under reduced pressure. Chromatography of the residual crystals with a silica-gel column eluted with benzene gave **11** (132 mg 85.6%) as violet microneedles. Product **11** was identified with the sample obtained above.

Preparation of 9-Cyano-3*H*-cyclopent[*a*]azulene (13). NBS (170 mg, 0.96 mmol) was added to a solution of the cyano compound **8** (150 mg, 0.78 mmol) in anhydrous CCl_4 (16 ml) and the mixture was then stirred for 37.5 h. The precipitates of succinimide were filtered off and the filtrate was evaporated under reduced pressure. The residue was dissolved in anhydrous chloroform and the solution was heated under refluxing for 16 h. The reaction mixture was

then cooled to room temperature, was washed with water and dried over sodium sulfate. The residual oil obtained by removing of the solvent was chromatographed with a silica-gel column eluted with benzene to give **13** (83 mg, 56%).

13: Violet prisms (MeOH), mp 97—98.5 °C; UV (MeOH) 232 ($\log\varepsilon$ 4.15), 236 (4.16), 309 (4.66), 320.5 (4.64), 362 (3.83), 380 (3.77), 400 (3.42), 552 (2.83), and 586 nm (2.81); IR (KBr) 2194, 1440, 1425, 1390, 1380, 1330, 795, and 740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=3.43 (2H, dd, J=2.5 and 1.5 Hz, H-3), 6.92—7.20 (4H, m, H-1,2,5,7), 7.57 (m, H-6), 8.11 (dd, J=9.5, 2.5 Hz, H-4), and 8.40 (dd, J=9.5, 1.5 Hz, H-8); Mass (25 eV, 80 °C) m/z 193 (M^++2, 9.1%), 192 (M^++1, 13.2%), and 191 (M^+, 100%); Anal. ($C_{14}H_9N$) C, H.

Reaction of 11 with Acetone. Synthesis of Methyl 3-Isopropylidene-3*H*-cyclopent[*a*]azulene-9-carboxylate (15a): An aqueous methylamine 30% solution (2 ml) was dropwise added to a solution of **11** (80 mg, 0.357 mmol) in acetone (6 ml) under stirring at room temperature. After stirring for 6 h, the solvent was removed under reduced pressure and the residue was dissolved in benzene, washed with water, and dried over sodium sulfate. Chromatography of the residual oil obtained by removing the solvent under reduced pressure on a silica-gel column eluted with benzene gave **15a** (44.7 mg, 47.4% yield).

15a: Greenish violet needles (MeOH), mp 129—129.5 °C; UV (MeOH) 214 ($\log\varepsilon$ 4.36), 246 (4.33), 265 (4.25), 300 (4.20)sh, 333 (4.65)sh, 344 (4.70), 388 (3.80)sh, 410 (3.66)sh, 566 (2.93), and 598 nm (2.91); IR (KBr) 2950, 1685, 1622, 1538, 1440, 1402, 1385, 1198, 1125, 1092, 1052, 848, 800, 750, 718, and 696 cm^{-1}; Mass (25 eV, 90 °C) m/z 264 (M^+, 100%), 249 (M^+−Me, 31.4%), and 233 (M^+−OMe, 34.3%). Anal. Found: C, 81.60; H, 6.20%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

Reaction of 11 with Diethyl Ketone. Synthesis of Methyl 3-(1-Ethylpropylidene)-3*H*-cyclopent[*a*]azulene-9-carboxylate (15b): An aqueous methylamine 30% solution (2 ml) was added to a solution of **11** (100 mg, 4.46 mmol) in diethylketone (6 ml) under stirring at room temperature. After stirring for 9 h, the solvent was removed under reduced pressure. The residue was dissolved in benzene, washed with saturated sodium chloride solution, and dried over sodium sulfate. After removing the solvent under reduced pressure, the residual oil was chromatographed with a silica-gel column eluted with benzene to give **15b** (59 mg, 45.2% yield).

15b: Dark green solid; UV (MeOH) 247 ($\log\varepsilon$ 4.38), 265 (4.30), 287.5 (4.23), 300 (sh, 4.27), 335 (4.66), 346 (4.71), 390 (sh, 3.94), 410 (sh, 3.69), 566 (3.00), and 600 nm (2.98); IR (KBr) 2980, 2885, 1693, 1539, 1442, 1405, 1205, 1097, and 808 cm^{-1}; Mass (25 eV, 80 °C) 292 (M^+, 100%), 277 (M^+−Me, 32.5%), and 263 (M^+−Et, 80%). Anal. ($C_{20}H_{20}O_2$) C, H.

Preparation of Methyl 3-Cyclopentylidene-3*H*-cyclopent[*a*]azulene-9-carboxylate (15c). Propylamine (1 g, 16.9 mmol) was added to a solution of **11** (190 mg, 0.85 mmol) in dioxane (1.5 ml) in the presence of cyclopentanone (900 mg, 9.5 mmol) under stirring at room temperature. After stirring for 3 h, benzene was added to the reaction mixture. The solution was then washed with water and dried over sodium sulfate. After removing the solvent under reduced pressure, the residual oil was chromatographed with a silica-gel column eluted with benzene to give **15c** (144.3 mg, 58.1%).

15c: Dark green crystals, mp 162.5 °C; UV (MeOH) 249 ($\log\varepsilon$ 4.38), 265 (4.30), 334 (4.67), 346 (4.73), 390 (sh, 3.80), 410 (sh, 3.64), 570 (2.97), and 606 nm (2.96); IR ($CHCl_3$) 3000, 2950, 2870, 1680, 1630, 1590, 1530, 1438, 1400, 1380, 1110, and 1040 cm^{-1}; ^{13}C NMR (50 MHz, $CDCl_3$) 26.19 (t, CH_2), 27.12 (t, CH_2), 34.43 (t, CH_2), 36.81 (t, CH_2), 50.88 (q, COOMe), 106.49 (s, C-9), 125.10 (d, C-1), 126.15 (d, C-5), 127.36 (s, C-3), 127.65 (c, C-7), 130.56 (s, C-10), 133.50 (d, C-4), 133.67 (s. C-3a), 135.05 (d, C-8), 135.83 (d, C-6), 139.63 (d, C-2), 147.15 (s, C-3b), 152.12 (s, C-8a), 160.91 (s, C-9a), and 166.06 (s, COOMe); Mass (25 eV, 80 °C) m/z 290 (M^+, 100%). Anal. ($C_{20}H_{18}O_2$) C, H.

Reaction of 11 with Acetophenone. Synthesis of Methyl 3-(1-Phenylethylidene)-3*H*-cyclopent[*a*]-azulene-9-carboxylate (15d). A 30% methylamine solution (0.25 ml) was added to a solution of **11** (100 mg, 0.446 mmol) in acetophenone (0.25 ml) under stirring at room temperature. After stirring for 9.5 h, benzene was added to the reaction mixture, washed with saturated sodium chloride solution three times, and dried over sodium sulfate. After removing the solvent under reduced pressure, a small amount of acetonitrile was added to the residual oil and separated crystals were collected by filtration. The crystals was chromatographed on a silica-gel column eluted with benzene to give **15d** (27.5 mg, 20% yield).

15d: Greenish violet needles, mp 144.5—145 °C; UV (MeOH) 266.5 ($\log\varepsilon$ 4.45), 346 (4.53), 570 (3.06), and 600 nm (3.06); IR (KBr) 2955, 1678, 1533, 1400, 1385, 1308, 1235, 1208, 1143, 1093, 808, 775, and 704 cm^{-1}; Mass (25 eV, 80 °C) 326 (M^+, 100%); Anal. ($C_{23}H_{18}O_2$) C, H.

Reaction of 11 with Isobutyraldehyde. Synthesis of Methyl 1-Isobutylidene-1*H*- (16e) and Methyl 3-Isobutylidene-3*H*-cyclopenta[*a*]azulene-9-carboxylate (15e): Propylamine (355 mg, 6 mmol) was added to a solution of **11** (63.7 mg, 0.3 mmol) and isobutyraldehyde (216.3 mg, 3 mmol) in dioxane (3 ml) under stirring at room temperature. After stirring for 5 h, benzene was added to the reaction mixture and the solution was washed with water, dried over sodium sulfate, and the solvent was removed under reduced pressure. Chromatography of the residual oil with a silica-gel column eluted with benzene gave **16e** (26.4 mg, 31.6%) in the first fraction and **15e** (17.4 mg, 20.8%) in the second fraction.

15e: Dark green oil; UV (MeOH) 240 ($\log\varepsilon$ 4.30), 263 (4.25), 330 (4.65), 342 (4.71), 570 (2.95), 607 nm (2.93); IR (neat) 3025, 2970, 1695, 1640, 1540, 1480, 1440, 1400, 1395, 1310, 1240, 1218, 1180, 1110, 860, 850, 780, 770, 740, 720, and 700 cm^{-1}; ^{13}C NMR (50 MHz, $CDCl_3$) δ=23.66 (q, $CHMe_2$), 30.09 (d, $CHMe_2$), 50.91 (q, COOMe), 106.45 (s, C-9), 126.99 (c, C-5), 127,48 (s, C-3), 128.26 (d, C-7), 128.75 (d, C-2), 132.27 (c, C-4), 133.77 (s, C-3a or 3b), 134.98 (s, C-3b or 3a), 135.90 (d, C-8), 136.27 (d, C-6), 136.41 (d, C-1), 140.83 (d, C-10), 147.99 (s, C-8a), 160.70 (s, C-9a), and 165.87 (s, COOMe); Mass (25 eV, 80 °C) m/z 278 (M^+, 100%). Anal ($C_{19}H_{18}O_2$) C, H.

16e: Green oil; UV (MeOH) 243 ($\log\varepsilon$ 4.28), 310 (sh, 4.62), 319 (4.81), 398 (3.64), 414 (3.64), 574 (2.46), and 614 nm (2.49); IR (neat) 2960, 2950, 1690, 1630, 1440, 1410, 1395, 1360, 1235, 1210, 1160, 1110, 1100, 1080, 840, 770, 740, and 680 cm^{-1}; ^{13}C NMR (50 MHz, $CDCl_3$) δ=23.30

(q, $CHMe_2$), 30.43 (d, $CHMe_2$), 50.97 (q, COOMe), 109.87 (s, C-9), 124.03 (d, C-3), 125.73 (d, C-5), 126.96 (d, C-7), 127.70 (d, C-2), 130.73 (s, C-3a), 133.98 (d, C-4), 135.22 (s, C-3B), 137.28 (d, C-8), 137.46 (d, C-6), 138.52 (s, C-3b), 146.26 (s, C-8a), 150.11 (d, C-10), 151.84 (s, C-9a), and 166.18 (s, COOMe); Mass (25 eV, 80 °C) m/z 278 (M^+, 100%). Anal. ($C_{19}H_{18}O_2$) C, H.

Reaction of 11 with Benzaldehyde. Synthesis of Methyl 3-[(*E*)-Benzylidene]-3*H*- (15f) and Methyl 1[(*E*)- Benzylidene]-1*H*-cyclopent[*a*]azulene-9-carboxylate (16f): Propylamine (709 mg, 12 mmol) was added to a solution of **11** (67.3 mg, 0.3 mmol) and benzaldehyde (637 mg, 6 mmol) in dioxane (1 ml) under stirring at room temperature. After stirring for 1.5 h, a sodium hydrogensulfite solution was added to the reaction mixture. The precipitates of the benzaldehyde hydrogensulfite adduct were filtered and washed with benzene. The filtrate and benzene washings were combined, washed with water and dried over sodium sulfate. The residual oil obtained by removing of the solvent was chromatographed with a silica-gel column eluted with benzene to give **16f** (25.4 mg, 27%) in the first fraction and **15f** (29.3 mg, 31.3%) in the second fraction.

15f: Dark green needles (MeOH), mp 112.5—114 °C; UV (MeOH) 263 ($\log\varepsilon$ 4.26), 361 (4.57), 578 (3.12), and 612 nm (3.12); IR ($CHCl_3$) 3010, 2950, 1685, 1530, 1438, 1405, 1395, 1380, 1125, and 1095 cm^{-1}; Mass (25 eV, 80 °C) m/z 312 (M^+, 100%); Anal. ($C_{22}H_{16}O_2$) C, H.

16f: Green solid, UV ($CHCl_3$) 344.5 ($\log\varepsilon$ 4.65), 430 (sh, 3.66), 578 (sh, 2.85), 612 (2.89), and 670 nm (sh, 2.68); IR (KBr) 2950, 1684, 1608, 1573, 1440, 1382, 1206, 1125, 840, 770, 740, and 700 cm^{-1}; Mass (25 eV, 120 °C) m/z 312 (M^+, 100%). Anal. ($C_{22}H_{16}O_2$) C, H.

Reaction of 11 with Dimethylformamide Dimethylacetal. Formation of Methyl 3(*E*)-Dimethylaminomethylidene-3*H*- (15h) and Methyl 1(*E*)-Dimethylaminomethylidene-1*H*-cyclopent[*a*]azulene-9-carboxylate (16h): After *N,N*-dimethylformamide diethylacetal (215 mg, 1.46 mmol) was added to a solution of **11** (236 mg, 1.05 mmol) in dimethylformamide (6 ml) at 100 °C and the mixture was heated for 15 min. After being cooled to room temperature, benzene was added to the reaction mixture, washed with saturated sodium chloride solution, and dried over sodium sulfate. The solvent was removed under reduced pressure. Chromatography of the residual oil with an alumina column eluted with benzene gave **15h** (90.1 mg, 30.6%). Further elution with chloroform gave **16h** (67.4 mg, 22.9%).

15h: Green prisms (AcOEt), mp 206—208 °C; UV (MeOH) 220 ($\log\varepsilon$ 4.37), 259 (4.37), 291 (4.38), 322.5 (4.23), 398 (4.58), 450 (3.93), 470 (sh, 3.86), 580 (sh, 3.07), 630 (3.20), and 670 nm (3.13); IR (KBr) 2950, 1692, 1625, 1570, 1534, 1512, 1459, 1408, 1373, 1203, 1121, 1099, and 792 cm^{-1}; Mass (25 eV, 120 °C) m/z 279 (M^+, 100%). Anal. ($C_{18}H_{17}O_2N$) C, H, N.

16h: Greenish brown crystals, mp 180—181 °C; UV (MeOH) 222 ($\log\varepsilon$ 4.19), 256.5 (4.24), 300 (4.45), 371 (4.66), 444 (sh, 3.86), 580 (2.72), and 625 nm (2.66); IR (KBr) 1658, 1592, 1440, 1422, 1358, 1303, 1207, 1122, 1085, 850, 773, and 725 cm^{-1}; Mass (25 eV, 80 °C) m/z 279 (M^+, 100%). Anal. ($C_{18}H_{17}O_2N$) C, H, N.

Synthesis of Methyl 3-[Bisdimethylaminomethylene]-3*H*-cyclopent[*a*]azulene-9-carboxylate (15g). An LDA solution which was prepared by a treatment of diisoprolylamine (15 ml) with a butyllithium 1 M solution (1 M=1 mol dm^{-3}) (1.5 ml) was added to a solution of **11** (400 mg, 1.78 mmol) in THF (30 ml) with a double-ended needle at −78 °C. After stirring for 1 h, bis(dimethylamino)ethoxycarbonium tetrafluoroborate (600 mg, 2.59 mmol) was added to the above solution and stirred for 1 h at −78 °C. After being warmed to room temperature, the reaction mixture was stirred for an additional 3 h. The solvent was removed under reduced pressure, and chromatography of the residue with an alumina column eluted with benzene gave recovered **11** (140 mg, 35%). Further elution with benzene-ethyl acetate (8:2) gave **15g** (248 mg, 43.1%).

15g: Light brown oil; UV (MeOH) 237 ($\log\varepsilon$ 4.34), 295 (4.35), 325 (sh, 4.16), 374 (4.30), 408 (4.44), 476 (3.78), and 648 nm (3.12); ^{13}C NMR (50 MHz, $CDCl_3$) δ=41.50 (m, NMe), 50.75 (q, COOMe), 98.68 (s, C-9), 105.60 (s, C-3), 109.03 (d, C-1), 124.25 (d, C-5), 125.21 (d, C-7), 129.06 (s, C-3a), 129.18 (d, C-4), 132.47 (d, C-8), 132.69 (d, C-6), 133.50 (s, C-9a), 136.81 (d, C-2), 145.41 (s, C-3a or 8a), 152.33 (s, C-8a or 3a), 163.24 (s, C-10), and 167.28 (s, COOMe); MS m/z 322 (M^+, 100%). Anal. ($C_{20}H_{22}N_2O_2$) C, H, N.

Reaction of 13 with Acetone. Formation of 9-Cyano-1-isopropylidene-1*H*-cyclopent[*a*]azulene (17a): After propylamine (300 mg, 5.1 mmol) was added to a solution of **13** (99 mg, 0.52 mmol) and acetone (300 mg, 5.2 mmol) in dioxane (5 ml), the mixture was stirred at room temperature. After 30 min, the reaction mixture was diluted with benzene, washed with water, and dried over anhydrous sodium sulfate. The residue obtained by removing of the solvent was chromatographed with a silica-gel column to give **17a** (85.2 mg, 70.8%).

17a: Light green needles (benzene), mp 158.5—160 °C; UV (MeOH), 245 ($\log\varepsilon$ 4.29), 325 (4.80), 385 (3.72), 422 (3.60), and 630 nm (2.30); IR (KBr) 2192, 1633, 1570, 1440, 1410, 1375, 1285, 840, and 740 cm^{-1}; Mass (25 eV, 80 °C) m/z 232 (M^++1, 21.2%), 231 (M^+, 100%), and 216 (M^+−CN, 40.7%). Anal. ($C_{17}H_{13}N$) C, H, N.

Reaction of 13 with Diethyl Ketone. Formation of 9-Cyano-1-(1-ethylpropylidene)-1*H*- (18b) and 9-Cyano-3-(1-ethylpropylidene)-3*H*-cyclopent[*a*]azulene (17b): Propylamine (250 mg, 4.24 mmol) was added to a solution of **13** (83 mg, 0.44 mmol) in diethyl ketone (5 ml) under stirring at room temperature. After stirring for 30 min, the reaction mixture was diluted with benzene, washed with water, and dried over sodium sulfate. The residue obtained by removing of the solvent was chromatographed with a silica-gel column eluted with benzene to give **18b** (36 mg, 32%) in the first fraction and **17b** (10 mg, 8.9%) in the second fraction.

17b: Dark blue crystals, mp 77.5—79 °C; UV (MeOH) 245.5 ($\log\varepsilon$ 4.24), 262 (4.18), 331 (4.51), 345 (4.53), 386 (sh, 3.56), and 575 nm (2.80); IR (CCl_4) 2970, 2205, 1404, 1255, and 872 cm^{-1}; Mass (25 eV, 120 °C), m/z 259 (M^+, 92.6%) and 230 (M^+−Et, 100%). Anal. ($C_{19}H_{17}N$) C, H, N.

18b: Light brown crystals, mp 88.5—89 °C; UV (MeOH) 247 ($\log\varepsilon$ 4.26), 328 (4.80), 387 (3.72), 398 (sh, 3.70), 423 (3.58), and 630 nm (2.39); IR ($CHCl_3$) 3000, 2195, 1595, 1530, 1455, 1435, and 1400 cm^{-1}; Mass (25 eV, 160 °C) m/z 259 (M^+, 100%). Anal. ($C_{19}H_{17}N$) C, H, N.

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