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Synthesis of a Polycyclic π-Conjugated System Containing an Azulene Unit by the Flash Vacuum Pyrolytic Method. IV.[1)]

Synthesis and Properties of 1-Isopropylidene-1*H*- and 3-Isopropylidene-3*H*-cyclopent[*a*]azulene

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A new π-conjugated system, 1-isopropylidene-1*H*-cyclopent[*a*]azulene was synthesized by the base-catalyzed condensation of 1*H*-cyclopent[*a*]azulene with acetone. An isomeric 3-isopropylidene-3*H*-cyclopent[*a*]azulene was also synthesized by the reaction of 3*H*-cyclopent[*a*]azulen-3-one with dimethylketene. The condensation of fulvene did not perturb the properties of the azulene moiety as shown by the spectral data. The X-ray analysis of 3-isopropylidene-3*H*-cyclopent[*a*]azulene also indicated that this π-conjugated system was an azulene moiety slightly perturbed by the fused fulvene ring.

It is well known that a fulvene having electron donating groups at the 6-position is stabilized by the contribution of the 6π-electron system of its five-membered ring. Neuenschwander et al. showed that this π-delocalization reflects to the ^{1}H NMR H,H-coupling constants between protons on the five-membered ring of fulvene.[2)] The X-ray structural determinations of fulvene derivatives have also supported this observation.[3)]

Methylenecyclopent[*a*]azulenes which are formed by the condensation of fulvene with the five-membered ring of azulene have three possible isomers (Scheme 1). These new π-electron systems are attractive in the study of the chemistry of condensed aromatic compounds containing an azulene unit. New π-conjugated systems formed by the condensation of azulene with fulvene derivatives were synthesized by the reaction of cyclopent[*e*]azulenide with corresponding electrophilic reagents, and the details of their structures have been discussed.[4)]

We previously reported the syntheses of a new π-electron system, methyl 3-methylene-3*H*-cyclopent[*a*]-azulene-9-carboxylate (**B**) and related compounds by the condensation reaction of methyl 3*H*- cyclopent[*a*]azulene-9-carboxylate (**A**) with ketones.[5)] However, these compounds are not suitable for the study of the physical and chemical properties of the methylinecyclopent[*a*]azulene system because of large perturbations by the electron-withdrawing group at the 9-position. Unfortunately, many attempts to remove the electron-withdrawing methoxycarbonyl group of **B** to give 3-methylene-3*H*-cyclopent[*a*]azulene (**C**) were unsuccessful (Scheme 2).[5)]

In this paper, we wish to report the synthesis and the properties of two kinds of methylenecyclopent[*a*]-azulenes (**5** and **9**) having no substituent at the 9-position.[6,7)]

Results and Discussion

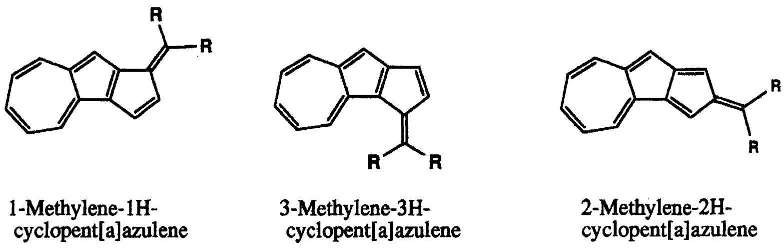
Synthesis of 1-Isopropylidene-1*H*-cyclopent[*a*]-azulene (5). Cyclopent[*a*]azulenes are adequate precursors for the synthesis of methylenecyclopent[*a*]-azulenes. Hafner et al. reported the syntheses of cyclopent[*a*]azulene by the thermal cyclization of 6-dimethylamino-1-(2,4,6-cycloheptatrienyl)fulvene[8)] but further reactions have not been reported yet. Recently, we reported the preparation of 1*H*- (**1**) and 3*H*-cyclopent[*a*]-azulene (**2**) from cycloadduct **3** in excellent yields by flash vacuum pyrolysis.[6)]

The mixture of **1** and **2** was easily anionized in tetrahydrofuran with methyllithium to give anion **4**. As expected, the condensation reaction of anion **4** with acetone gave 1-isopropylidene-1*H*-cyclopent[*a*]azulene (**5**) in a good yield. The formation of an isomeric 3-isopropylidene-3*H*-cyclopent[*a*]azulene was not observed (Scheme 3).

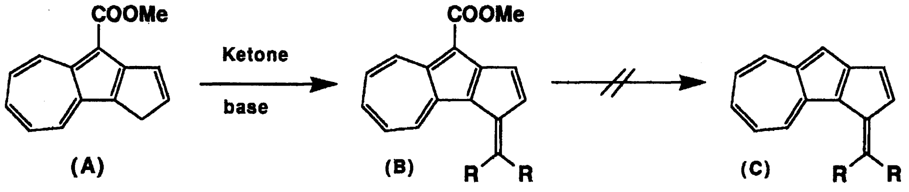
Synthesis of 3-Isopropylidene-3*H*-cyclopent[*a*]-azulene (9). It is already known that the cycloaddition reaction of di-substituted ketene with benzoquinone gives an exo-methylene compound via a β-lactone.[9)] Therefore, we applied this reaction to the synthesis of 3-isopropylidene-3*H*-cyclopent[*a*]azulene-3*H*-cyclopent[*a*]azulene (**9**). A desired precursor, 3*H*-cyclopent[*a*]azulen-3-one (**7**), was prepared from its adduct (**6**) by the application of flash vacuum pyrolysis.[7)] The reaction of **7** with dimethylketene generated from isobutyric anhydride[10)] gave **9** by [2+2] cycloaddition to form an adduct (**8**) which was subsequenly decarboxylated (Scheme 4).

Physical Properties of Isopropylidenecyclopent[*a*]azulenes 5 and 9. The ^{1}H and ^{13}C NMR spectral data of **5** and **9** are summarized in Table 1 together with those of azulene[12,13)] for comparison. The chemical shifts of the azulene moieties of **5** and **9** are little different from those of azulene itself, indicating no pertubation due to the condensation of 6,6-dimethylfulvene.

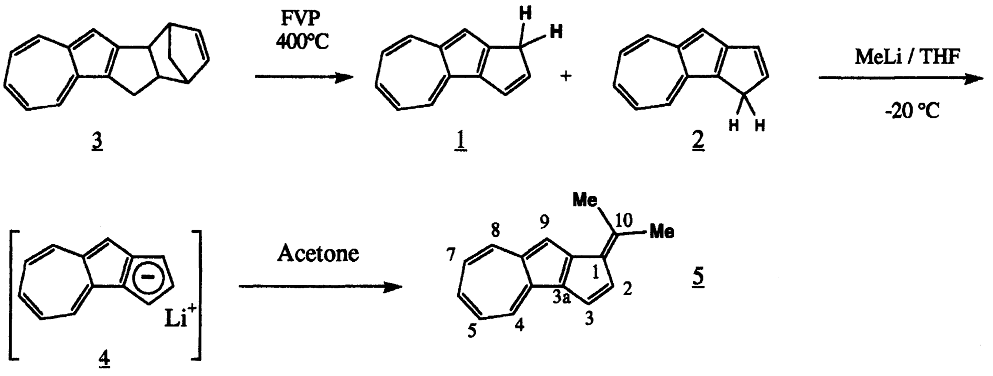
Bertelli and Crews have reported a difference in the coupling constants of the azulene moiety of benz[*a*]-azulene indicating the bond length alternation of its azulene part owing to the larger π-stabilization energy



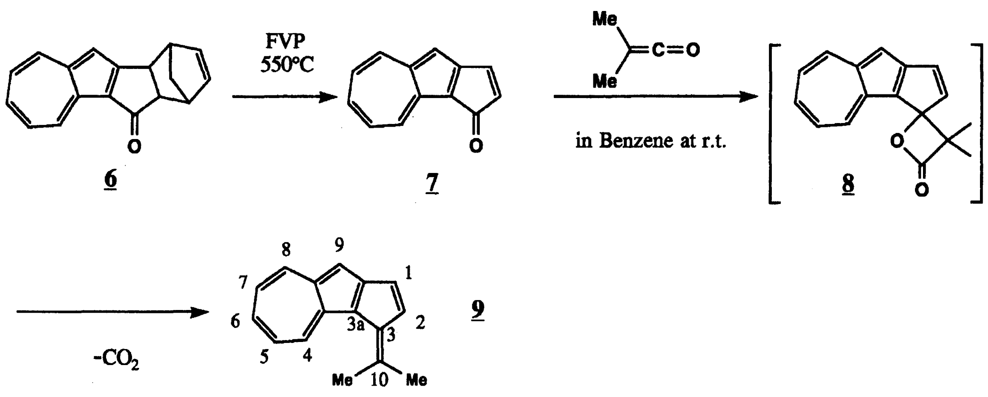
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

of benzene than that of azulene.[11] The coupling constant between H-7 and H-8 of **5** is slightly larger than that between H-4 and H-5 in contrast to **9**. This coupling constant difference is so small as to indicate the existence of bond length alternation.

X-Ray Analysis of 3-Isopropylidene-3*H*-cyclopent[*a*]azulene (9). For the structural information of these conjugated systems, X-ray structure analysis

Table 1. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) of **5**, **9**, and Azulene

	Position	4	5	6	7	8	9	
^{1}H	**5**$^{a)}$	8.02	6.89	7.30	6.91	8.08	7.22	$J_{4,5}$=9.5, $J_{7,8}$=10.0 (Hz)
	9$^{b)}$	8.61	7.10	7.42	7.11	8.19	7.21	$J_{4,5}$=10.3, $J_{7,8}$=9.6 (Hz)
	Azulene$^{c)}$	8.10	6.88	7.30	6.88	8.10	7.17	$J_{4,5}$=$J_{7,8}$=9.5 (Hz)
	Position	4	5	6	7	8	9	
^{13}C	**5**$^{a)}$	132.33	121.19	135.08	122.01	134.76	111.19	
	9$^{b)}$	132.52	122.40	134.52	123.37	134.45	109.30	
	Azulene$^{d)}$	136.40	122.60	136.90	122.60	136.40	118.10	

a) In $CDCl_3$, b) In CCl_4, locked by internal $CDCl_3$, c) From Ref. 11, d) From Ref. 12.

of **5** was more desirable than **9** because **5** shows no steric hindrance. However, suitable single crystals of **5** could not be obtained, while single crystals of **9** were easily obtained by recrystallization from hexane. The X-ray experimental data of **9** is shown in Table 2 and the structural results are shown in Fig. 1, Tables 3 and 4. As for the molecular planarity, three carbons (C1, C2, and C3) in the fulvene part keep a planarity with the azulene moiety, but the methylene part (C10, C11, and C12) is out of this plane markedly as indicated by the largest torsion angles of 16.3° for C3b–C3a–C3–10. This bending is clearly due to the steric interaction between H14 and C12, which reflects also on the bond angles around the C3 atom (C3a–C3–C10=130.5° vs. C2–C3–C10=121.8°). The bond lengths in the azulene moiety of **9** indicate a 10π peripheral structure, being almost the same as those of azulene molecules.

In conclusion, we believe that the condensation of azulene with fulvene at the five-membered ring did not give enhanced delocalization in the π-electron system and the azulene ring was slightly perturbed by the fulvene ring.

Chemical Properties of Isopropylidenecyclopent[*a*]azulenes 5 and 9. A nucleophilic attack on pentafulvene is generally known to occur at the 6-position. From this point of view, a nucleophilic reaction of **5** and **9** was examined. As shown in Scheme 5, the reaction of **5** with methyllithium in tetrahydrofuran gave 1-*t*-butyl-3*H*-cyclopent[*a*]azulene (**11**) via anion **10**. This chemical behavior indicated that the fulvene moiety of **5** maintained the characteristic chemical properties of fulvene. On the other hand, a similar reaction of **9** with methyllithium gave an unidentifiable complex mixture. This result could be explained by the low reactivity of the methylene carbon of **9** owing to its adjacent position to the electron-rich position of the azulene ring.

Tables of atomic coordinates, temperature factors, bond lengths, bond angles, and the F_o-F_c list are kept as Document No. 9050 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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 a JNM-GX-400(^{1}H) or Varian XL-200(^{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.

1-Isopropylidene-1*H*-cyclopent[*a*]azulene (5). Methyllithium (1 M solution (1 M=1 mol dm^{-3}) in ether, 0.7 ml, 0.7 mmol) was added to a solution of a mixture of 1*H*-(**1**) and 3*H*-cyclopent[*a*]azulene (**2**) (60 mg, 0.36 mmol) in dry THF (6 ml) at −20°C with stirring. The color of the solution immediately changed from blue to red. After stirring for 1 h, acetone (1 ml) was added to this solution and the mixture was warmed to room temperature. The color of the reaction mixture gradually changed from red to green. After additional stirring for 2 h, the lithium hydroxide formed was filtered off and the filtrate was evaporated to dryness under reduced pressure. Chromatography of the resulting oil on a reversed-phase column (RP-18, Merck) with acetonitrile – water (7 : 3) gave 1-isopropylidene-1*H*-cyclopent[*a*]azulene (**5**) (50 mg, 67.4%)

5: Light-green crystals, mp 111.5—112.5° C; UV (MeOH) 226 (log ε 4.22), 283 (sh, 4.26), 296 (sh 4.44), 307.5 (4.65), 319.5 (4.89), 390.5 (3.72), 416 (3.60), 604 (2.45), and 654 nm (2.50); IR (KBr) 1625, 1365, 850, 765, and 725 cm^{-1}; ^{1}H NMR (200 MHz in CD_2Cl_2) δ=2.30 (s, Me-anti), 2.46 (s, Me-syn), 6.86 (d, J=5.5 Hz, H-2), 6.99 (dd, J=10.0 and 10.0 Hz, H-5), 7.02 (dd, J=9.2 Hz, H-7), 7.09 (dd, J=5.5 and 1.0 Hz, H-3), 7.38 (broad s, H-9), 7.41 (dddd, J=10.0, 9.2, 1.0, and 1.0 Hz, H-6), and 8.16 (dd, J=9.2 and 1.0 Hz, H-4), 8.16 (d, J=10.0 Hz, H-8); ^{13}C NMR (CCl_4, 50 MHz) δ=22.85 (q, Me), 111.19 (s, C-9), 121.19 (d, C-5), 122.01 (d, C-7), 123.79 (d, C-3), 126.63 (s), 127.88 (d, C-2), 132.33 (d, C-4), 134.08 (s), 134.76 (d, C-8), 135.08 (d, C-6), 138.35 (s), 140.17 (s), 146.82 (s), and 149.68 (s); MS m/z 206 (M^{+}, 100 %). Found: C, 93.68; H, 6.95%. Calcd for $C_{16}H_{14}$: C, 93.26; H, 6.84%.

Synthesis of 3-Isopropylidene-3*H*-Cyclopent[*a*]azulene (9). To a solution of 3*H*-cyclopent[*a*]azulen-3-one (**7**) (100 mg, 0.56 mmol) in benzene (4 ml) was added dimethylketene derived from isobutyric anhydride (3 ml) by flash vacuum pyrolysis, and the mixture was stirred at room temperature for 21 h. After removal of the solvent to dryness under reduced pressure, chromatographic purification of the residual oil on an alumina column eluted with hexane gave 3-isopropylidene-3*H*-cyclopent[*a*]azulene (**9**) (52 mg, 45.4%).

9: Dark blue needles(hexane); mp 81.0—82.5°C; UV (MeOH) 229.5 (log ε 4.28), 260 (4.38), 295 (sh, 4.16), 323.5

Table 2. Details of X-Ray Analysis

Molecular formula	$C_{16}H_{14}$
Molecular weight	206.29
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell constants	a=20.202(2), b=6.322(1), c=8.996(2) /Å α=90.0, β=90.16(3), γ=90.0°, V=1148.9(8) $Å^3$
Z value	4
D_{calcd}	1.192 g cm^{-3}
μ(Mo $K\alpha$)	0.62 cm^{-1}
Crystal size	0.2×0.2×0.25 mm
Deffractometer	Rigaku Denki AFC5PR
Radiation	Mo $K\alpha$ (λ=0.70926 Å) Graphite monochrometer, rotaing anode (45 kV, 200 mA)
Temperature	13°C
2θ range	5—55°
Scan mode, speed	$2\theta/\theta$, 4° min^{-1} (in ω)
Scan width	1.2+0.35tanθ
No. of unique reflections	1526
No. of used reflections	1440 ($>3\sigma(F_o)$)
Data collection	Lorenz and polation effects, no absorption, no extinction
Structure analysis	Direct method
Structure refinement	Block-diagonal least-squares method
Temperature factor	Anisotropic (C), isotropic (H), found from D-Fourier map
Standard deviations	0.003—0.004 Å(C–C)
$R\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0485
$R_w[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0390, Weighting scheme = $w = 1/\sigma^2(F_o)$

Atomic scattering factors were applied from "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. VI, p. 72. All calculations were performed by the ACOS2000 computer at Tohoku University using the applied library program UNICS III (T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem.*) and Rantan 81 direct method program (Y. Jia-zing, *Acta Crystallogr., Sect. A*, **34**, 642 (1981); Y. Jia-xing, *ibid.*, **39**, 35 (1983) with some modifications.

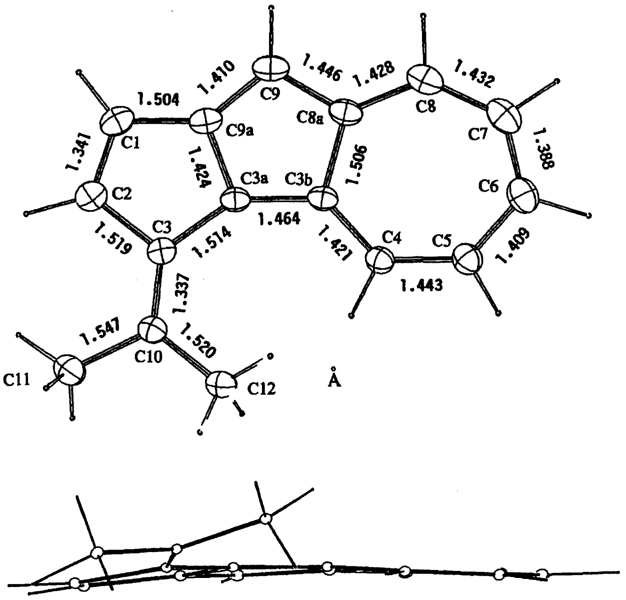


Fig. 1. ORTEP drawings of **9**. Top and side view.

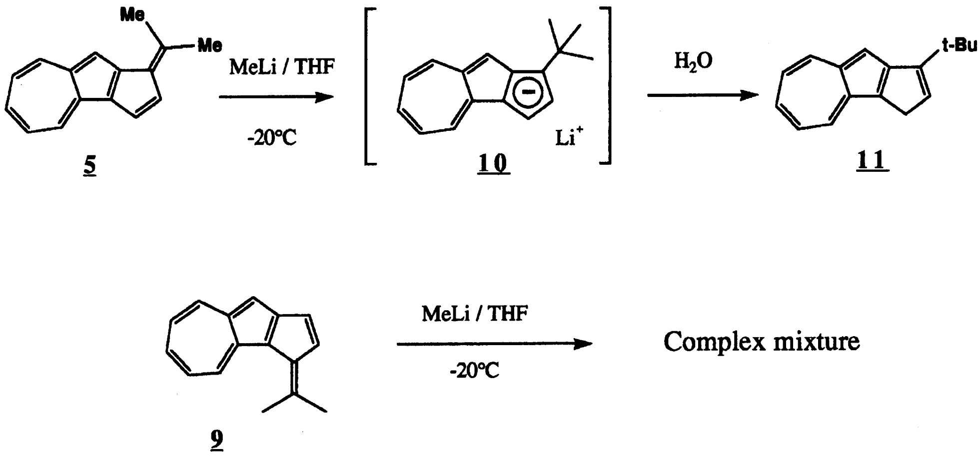
Table 3. Atomic Coordinates of Non-Hydrogen Atoms

N	Atom	x	y	z	B
1	C1	0.5793	0.3308	0.6543	6.41
2	C2	0.5436	0.1538	0.6716	5.99
3	C3	0.5728	0.0271	0.7995	4.94
4	C3a	0.6342	0.1426	0.8517	4.67
5	C3b	0.6932	0.1345	0.9466	4.68
6	C4	0.7188	−0.0293	1.0383	5.16
7	C5	0.7780	−0.0423	1.1280	6.11
8	C6	0.8291	0.1058	1.1512	7.13
9	C7	0.8346	0.3041	1.0864	7.66
10	C8	0.7907	0.4049	0.9830	6.81
11	C8a	0.7296	0.3383	0.9181	5.60
12	C9	0.6917	0.4492	0.8060	6.32
13	C9a	0.6356	0.3302	0.7641	5.47
14	C10	0.5417	−0.1410	0.8564	5.02
15	C11	0.5653	−0.2465	0.9989	5.50
16	C12	0.4782	−0.2312	0.7839	6.44

(4.50), 333.8 (4.57), 378 (sh, 3.77), 396 (sh, 3.59), 608 (2.93), and 630 nm (2.88); IR (KBr) 3010, 2920, 1620, 1380, 1365, 1360, 1125, and 850 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 2.19 (s, Me-anti), 2.61 (s, Me-syn), 6.91 (d, J=5.5 Hz, H-1), 7.10 (dd, J=10.3 and 10.0 Hz, H-5), 7.11 (dd, J=10.0 and 9.6 Hz, H-7), 7.21 (bs, H-9), 7.26 (d, J=5.5 Hz, H-2), 7.42 (dddd, J=10.0, 10.0, 1.0, and 1.0 Hz, H-6), 8.19 (d, J=9.6 and 1.0 Hz, H-8), and 8.61 (bd, J=10.3 Hz, H-4); ^{13}C NMR (50 MHz, $CDCl_3$) δ=24.1 (q), 26.5 (q), 109.3 (d, C-9), 122.4 (d, C-5), 123.4 (d, C-7), 123.8 (d, C-1), 129.9 (s), 130.0 (s), 132.5 (d, C-4), 134.4 (d, C-6), 134.5 (d, C-8), 135.1 (s), 137.0 (s), 137.6 (d, C-2), 147.3 (s), and 159.2(s); Mass m/z (25 eV, 80°C) 206 (M^+, 100%); Anal. ($C_{16}H_{14}$) C, H.

Table 4. Bond Lengths and Angles of **9**

List of distances (Å)					
C1–C2	1.341(4)	C10–C11	1.520(4)	C9–C9a	1.410(4)
C2–C3	1.519(4)	C1–C9a	1.504(4)	C10–C12	1.547(4)
C3–C10	1.377(3)	C3a–C3b	1.464(3)	C3–C3a	1.514(3)
C3b–C4	1.421(3)	C3b–C8a	1.506(3)	C3a–C9a	1.424(3)
C6–C7	1.388(5)	C5–C6	1.409(4)	C4–C5	1.443(4)
C8a– C9	1.446(4)	C8–C8a	1.428(4)	C7–C8	1.432(4)
List of angles (degrees)					
C2–C1–C9a	109.1(2)	C7–C8–C8a	131.8(2)	C1–C9a–C9	141.2(2)
C1–C2–C3	108.6(2)	C3b–C8a–C8	127.2(2)	C3–C10–C12	121.4(2)
C2–C3–C3a	107.2(2)	C8a–C9–C9a	110.5(2)	C3a–C3–C10	130.5(2)
C3–C3a–C3b	146.0(2)	C1–C9a–C3a	110.4(2)	C3b–C3a–C9a	109.5(2)
C3a–C3b–C4	146.0(2)	C3–C10–C11	121.7(2)	C4–C3b–C8a	123.0(2)
C3b–C4–C5	131.2(2)	C2–C3–C10	121.8(2)	C8–C8a–C9	126.7(2)
C4–C5–C6	130.8(2)	C3–C3a–C9a	104.3(2)	C3a–C9a–C9	108.3(2)
C5–C6–C7	130.6(3)	C3a–C3b–C8a	105.5(2)	C11–C10–C12	116.8(2)
C6–C7–C8	128.7(3)	C3b–C8a–C9	106.0(2)		



Scheme 5.

X-Ray Crystallographic Analysis of 9. Experimental details are summarized in Table 3.

The Reaction of 5 with Methyllithium. 1-Isopropylidene-1*H*-cyclopent[*a*]azulene (**5**) (80 mg, 0.39 mmol) was dissolved in THF (10 ml) and the solution was cooled to −20°C under N_2. Methyllithium (0.8 ml of a 1 M solution in ether, 0.8 mmol) was added to this solution. The color of the reaction mixture changed immediately from blue to red. After stirring for 1 h at −20°C, a small amount of water was added to the mixture. The color of the reaction mixture changed to blue again. The reaction mixture was warmed to room temperature and the lithium hydroxide formed was removed by filtration. The filtrate was concentrated to dryness under reduced pressure. Chromatography of the resulting oil on a reversed-phase column (RP-18, Merck) eluted with acetonitrile–water(7 : 3) gave 1-*t*-butyl-1*H*-cyclopent[*a*]azulene (**11**) (13.5 mg, 15.6 %).

11: Blue crystals; mp 70.5—71.0°C; UV (MeOH) 220 (log ε 4.26), 238 (4.25), 296 (4.72), 306.8 (4.70), 326 (3.88), 346.5 (3.61), 362 (3.72), 379 (3.86), 398 (3.89), 546 (2.72), 590 (2.80), and 640 nm (2.78); ^{1}H NMR (90 MHz, in $CDCl_3$) δ=1.41 (s, *t*-Bu), 3.33 (d, J=2.1 Hz, H-3), 6.33 (t, J=2.1 Hz, H-2), 6.89 (dd, J=9.6 and 9.6 Hz, H-5), 6.92 (dd, J=9.6 and 9.6 Hz, H-7), 7.07 (s, H-9), 7.29 (dddd, J=9.6, 9.6, 1.2, and 1.2 Hz, H-6), and 8.01 (broad d, J=9.6 Hz, H-4 and 8); MS m/z 223 (M^++1, 3.9%), 222 (M^+, 29.4 %), 165 (M^+ − *t*-Bu, 100%). Anal. ($C_{13}H_{18}$) C, H.

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