Synthesis and Properties of Sterically-Protected 2-Azulenylphosphaethenes. II.[1] 2-(1-Azulenyl)- and 2-(2-Azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes

Tetsuya UENO,# Masafumi YASUNAMI, and Masaaki YOSHIFUJI*
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980-77
(Received February 14, 1994)

Several sterically-protected 2-(1-azulenyl)- and 2-(2-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes were synthesized as kinetically-stabilized crystalline compounds by the phospha-Peterson reaction of the corresponding 1- and 2-formylazulenes with lithium (2,4,6-tri-*t*-butylphenyl)trimethylsilylphosphide. On the basis of the ^{31}P NMR spectral data, the 1-azulenyl group is believed to be more electron-donating than the 2-azulenyl group. The bathochromic shift of the n–π^* transition of the 1-azulenyl derivatives relative to the parent azulene and *N*-(1-azulenylmethylene)-2,4,6-tri-*t*-butylaniline indicated that the 2-phosphaethenyl group has an electron-donating nature in contrast to the electron-withdrawing nature of the iminomethyl group.

Phosphaalkenes, one of the phosphorus analogs of alkenes, are of current interest because of their unusual structures and reactivity due to the low coordinated phosphorus–carbon double bond.[2] Soon after the breakthrough in the isolation of phosphaalkenes initiated by Becker,[3] the method of steric protection was introduced into the preparation of unstable phosphaalkenes by Bickelhaupt et al.[4] Since that time, various types of phosphaalkenes have been synthesized and characterized,[2] however, no phosphaethenes carrying an azulenyl group have yet been reported.

The parent phosphaethene (methylenephosphine), HP=CH_2,[5a] has a dipole moment of 0.869 D[5b] [1 D = 3.33564×10^{-30} Cm] and its negative end is postulated to be directed toward the carbon atom.[6] It is well-known that a non-benzenoid aromatic azulene (**3**), one of the structural isomers of naphthalene, has a dipole moment (0.796 D[7a]—1.08 D[7b]) with the negative end of the dipole directed toward the five-membered ring; furthermore, each position has a different electron density.[8] On the basis of these facts, the interaction between the azulene ring and the P=C double bond is expected to cause some interesting phenomena. The five positional isomers of 2-azulenylphosphaethenes (Chart 1) are expected to show different properties. Furthermore, *E*- and *Z*-isomers are possible for each positional isomer. The comparison of these isomers and *N*-(azulenylmethylene)anilines are basically important to clarify the properties of the low-coordinated P=C double bond.

In this paper, we wish to report the first synthesis of several 2-(1-azulenyl)- and 2-(2-azulenyl)-phosphaethenes kinetically stabilized by the 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated Ar) together with their spectral properties compared to *N*-(azulenylmethylene)anilines.[9]

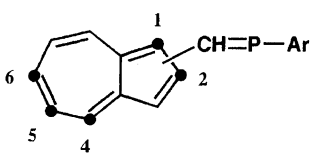


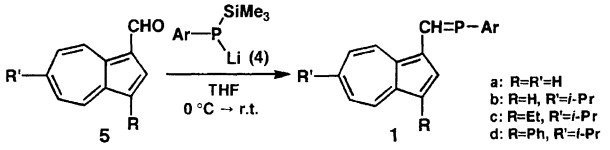
Chart 1.

#Fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

Results and Discussion

Synthesis of Sterically-Protected 2-Azulenylphosphaethenes. We have reported that the synthesis of 2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-phosphaethene was achieved by the phospha-Peterson reaction of benzaldehyde with lithium *t*-butyldimethylsilyl(2,4,6-tri-*t*-butylphenyl)phosphide.[10] Therefore, we applied this method to the synthesis of several sterically-protected 2-azulenylphosphaethenes. The starting material, 1-formylazulene (**5a**),[11] was synthesized from **3** by the Vilsmeier–Haack reaction. Other 1-formylazulenes (**5b**—**d**) were prepared from the corresponding azulenes by the same reaction. 2-Formylazulene (**6a**)[12] was synthesized by the reaction of 2*H*-cyclohepta[*b*]furan-2-one with 3,3-dimethoxy-2-(1-pyrrolidinyl)propene[13] followed by hydrolysis of the resulting 2-(dimethoxymethyl)azulene. 2-Formyl-6-isopropylazulene (**6b**) was prepared from 6-isopropyl-2*H*-cyclohepta[*b*]furan-2-one by the same method.

Synthesis of 2-(1-Azulenyl)phosphaethenes (1). 2-(1-Azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)-phosphaethene (**1a**) was synthesized by the reaction of **5a** with lithium (2,4,6-tri-*t*-butylphenyl)trimethylsilylphosphide (**4**)[14] in tetrahydrofuran (THF) under an argon atmosphere (Scheme 1) and the results are summarized in Table 1. The addition reaction of **4** to the formyl group started smoothly even at 0 °C but the formation of the P=C double bond appeared to begin on warming the reaction mixture to room temperature. The formation of the phosphaethene can be detected by



Scheme 1.

Table 1. 2-(1-Azulenyl)phosphaethenes **1**

Formylazulene	Phosphaethene			Yield/%[a]	Crystal form		Mp	^{31}P NMR[b]
		R	R′	(*E* : *Z*)	(solvent)		°C	δ ($^2J_{PH}$/Hz)
5a	**1a**	H	H	21	*E*: Green prisms	(AcOEt)	153.5—154.5	238.2 (24.5)
				(10 : 1)	*Z*: Green needles	(EtOH)	172—174	216.1 (34.9)
5b	**1b**	H	*i*-Pr	67	*E*: Green prisms	(AcOEt)	149.5—151	234.7 (24.4)
				(28 : 1)	*Z*: Green needles	(EtOH)	177.5—178.5	221.6 (35.9)
5c	**1c**	Et	*i*-Pr	50	*E*: Green prisms	(EtOH)	159.5—161.5	231.5 (24.4)
				(33 : 1)	*Z*: Green plates	(AcOEt)	183—184	210.4 (36.6)
5d	**1d**	Ph	*i*-Pr	59	*E*: Green prisms	(AcOEt)	167.5—169	237.2 (24.3)
				(22 : 1)	*Z*: Green prisms	(MeOH)	130—132	216.4 (36.9)

a) Isolated yield based on formylazulenes. The ratio of *E*: *Z* in parentheses was determined by the ^{31}P NMR of the crude reaction mixture. b) 81 MHz, in $CDCl_3$.

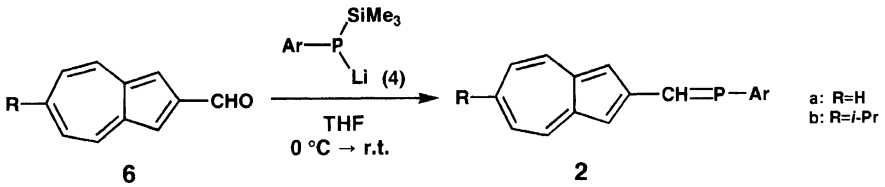
observation of the color change of the reaction mixture (from reddish brown to green). The ^{31}P NMR of the reaction mixture indicated that **1a** formed as a mixture of geometrical isomers. After chromatographic separation on a basic alumina column followed by further purification with a preparative HPLC column, **1a** was obtained in 21% yield as an isomeric mixture. The major product resonating at the lower field was assigned to the *E*-isomer according to the empirical *cis rule*,[15] *E*: *Z*=10 : 1. Recrystallization from ethyl acetate gave (*E*)-**1a** as green prisms. The other geometrical isomer, (*Z*)-**1a**, was isolated from the mother liquor as green needles by preparative HPLC separation followed by recrystallization from ethanol. The yield of **1** was improved by the introduction of an isopropyl group at the 6-position of the azulene ring. In fact, 1-formyl-6-isopropylazulene (**5b**) reacted with **4** even at 0 °C to give **1b** in 67% yield. The 6-isopropyl group may sterically protect the seven-membered ring from nucleophilic attack by **4**. Furthermore, its electron-donating effect cause a higher electron density at the oxygen atom of the phospha-Peterson reaction intermediate and facilitates the elimination of the trimethylsiloxy anion to form the P=C double bond. Other 2-(1-azulenyl)phosphaethenes carrying the 6-isopropyl group (**1c**—**d**) were also synthesized in higher yields than **1a**. X-Ray structure analysis was performed for the single crystal of (*E*)-**1b** and the result ensured that the assignment of the configuration around the P=C double bond was correct.[1]

Synthesis of 2-(2-Azulenyl)phosphaethenes (2). 2-Azulenyl derivatives (**2**) were obtained by a similar reaction of 2-formylazulenes (**6**) with **4** (Scheme 2) and the results are summarized in Table 2. In contrast to **1**, the *E*-isomer was formed as the sole product. The configuration around the double bond was assigned by the $^2J_{PH}$ value (ca. 25 Hz) in the ^{1}H and ^{31}P NMR analyses.[16] In general, the formyl group at the 2-position of the azulene ring is more reactive toward organolithium reagents than that at the 1-position, however, the yield of **2** was not high. The introduction of the 6-isopropyl group did not affect the yield of **2b**, either. These facts indicated that the electron-donating nature of the azulenyl group appears to play an important role in the formation of the P=C double bond.

Synthesis of *N*-(Azulenylmethylene)anilines. Nitrogen analogs of 2-azulenylphosphaethenes, *N*-(azulenylmethylene)anilines, were synthesized in order to obtain insight into the spectral character of these double bonds. The attempted preparation of an *N*-(1-azulenylmethylene)-2,4,6-tri-*t*-butylaniline (**9**) was not successful by the condensation reaction of **5a** with 2,4,6-tri-*t*-butylaniline (**7**) in the presence of diethyl ether–boron trifluoride (1/1).[17] However, the reaction of **5a** with lithium *N*-trimethylsilyl-2,4,6-tri-*t*-butylanilide (**8**) gave **9** in 75% yield as violet prisms (Scheme 3), whereas *N*-(2-azulenylmethylene)-2,4,6-tri-*t*-butylaniline (**10**) was synthesized by the acid catalyzed condensation of **6a** with **7** in refluxing benzene for 8 h in 36% yield as green needles (Scheme 4).

^{31}P NMR Spectra. The ^{31}P NMR spectra of all the new 2-azulenylphosphaethenes (Tables 1 and 2) were observed in the general region of the *C*-substituted phosphaethenes.[2] It should be noted that (*E*)-**1a** resonates at a higher field by 21.1 ppm than (*E*)-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (δ_P=259.3),[10] while (*E*)-**2a** resonates at a lower field by 20.5 ppm than the latter. The ^{31}P NMR chemical shift of (*E*)-**1a** is similar to that of 2-phenylphosphaethenes having a strong electron-donating group on the phenyl ring such as *p*-dimethylaminophenyl- ($\delta_P(E)$=253.5) and *p*-methoxyphenyl- ($\delta_P(E)$=243.0) phosphaethenes.[18] This high-field shift observed for **1a** indicates that the 1-azulenyl group is more electron-donating than the 2-azulenyl group as expected and also indicates that there is some contribution of canonical structure **1A** of the tropylium ion type causing a negative charge at the phosphorus atom (Scheme 5).

^{1}H NMR Spectra. ^{1}H NMR spectral data of **1**, **2**, **9**, and **10** together with **3** are summarized in Table 3. Assignments were confirmed by ^{1}H,^{1}H decoupling, ^{1}H,^{1}H-COSY, and/or NOE experiments. The expanded ^{1}H NMR spectra of (*E*)- and (*Z*)-**1b** are shown in Fig. 1. Both of the HC= protons of the 2-phosphaethenyl moieties resonate at the lowest field with a large $^2J_{PH}$ coupling constant. Both isomers have a general spectrum for azulene derivatives with a conjugating

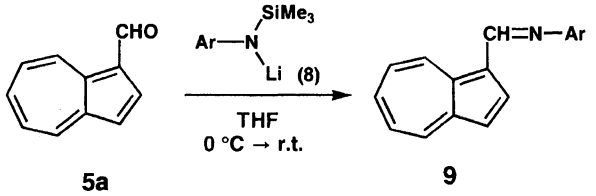


Scheme 2.

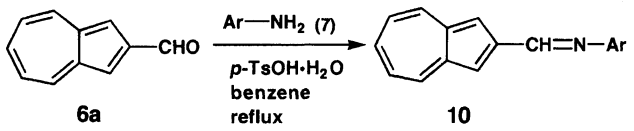
Table 2. 2-(2-Azulenyl)phosphaethenes **2**

Formyl azulene	Phosphaethene R		Yield/%[a]	Crystal form[b]	Mp °C	^{31}P NMR[c] δ ($^2J_{PH}$/Hz)
6a	**2a**	H	19	Green needles	230—231	279.8 (24.4)
6b	**2b**	*i*-Pr	22	Green needles	190—191	274.4 (24.8)

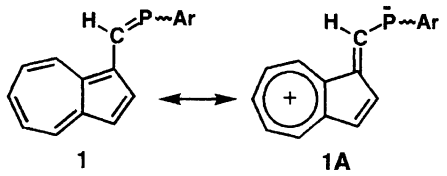
a) Isolated yield based on formylazulenes. b) Recrystallized from AcOEt. c) 81 MHz, in $CDCl_3$.



Scheme 3.



Scheme 4.



Scheme 5.

group at the 1-position, except for H-2. The significant high-field shift of the H-2 proton in (*Z*)-**1b** by 2.82 ppm from (*E*)-**1b** is believed to be caused by the shielding effect of the Ar aromatic ring. This shielding effect also affects the H-3 proton causing a high-field shift of the signal with a magnitude of 0.45 ppm from (*E*)-**1b**. These results and NOE experiments suggest that the conformers for both isomers in solution take the structure shown in Fig. 2.[19] Since the high-field shifts of the δ values of H-2 and the 3-substituent are also observed in other 1-azulenyl derivatives, **1a**, **c**, and **d** are estimated to take quite similar conformations in solution. It is noteworthy that long-range ^{31}P–^{1}H coupling were observed for **1** ($^4J_{PH}$ for H-2) and **2** ($^4J_{PH}$ for H-1 and H-3; $^6J_{PH}$ for H-4 and H-8).

^{13}C NMR Spectra. ^{13}C{^{1}H} NMR spectral data of **1**, **2**, **9**, and **10** together with **3** as a standard are summarized in Table 4 and substituent chemical shifts (SCS) are shown in Table 5. All carbons were assigned by ^{1}H,^{13}C-COSY and/or COLOC experiments. The values of J_{PC} were also useful for the assignment of the signals. The HC= carbon atoms of the 2-phosphaethenyl moieties resonate at a lower field with a large $^1J_{PC}$ coupling constant. The SCS values of (*E*)-**1a**, (*Z*)-**1a**, and **9** are the same in sign except for C-2; larger values were observed for C-1 and C-8a, but the substituent effects[8,21] of the three double bonds are not clear. The SCS values of each of the seven-membered ring carbons (C-4—C-8) of (*E*)-**2a** and **10** are opposite in sign. This suggests that the 2-phosphaethenyl group is electron-donating. Long-range ^{31}P–^{13}C couplings through three to seven bonds were observed for all carbons of the azulene ring indicating some conjugation between the azulene ring and the P=C double bond. Interestingly, nine-bond coupling (1.7 Hz) was observed for the isopropyl methyl carbon of (*E*)-**2b**.

UV-Visible Absorption Spectra. The UV-visible absorption spectra of (*E*)-**1a**, (*Z*)-**1a**, and **9** were taken in hexane (Fig. 3). The absorption profile shows that both isomers of **1a** exist as real azulene derivatives, thus the contribution of tropylium ion-type canonical structure **1A** is not so large. The visible absorption of (*E*)-**1a** is longer than that of (*Z*)-**1a** suggesting that the strain caused by the bulky Ar group is less in (*E*)-**1a** than in (*Z*)-**1a**. Since the values of the molar extinction coefficients of (*E*)-**1a** and (*Z*)-**1a** are almost the same, no coplanarity exists between the Ar benzene ring and the 2-phosphaethenyl moiety.[22] On the other hand, isoelectronic azomethine **9** shows a dissimilar spectrum. Plattner's rule[23] is a useful rule for the structural determination of azulenes: electron-donating groups on the 1-, 3-, 5-, and 7-positions are bathochromic, and electron-withdrawing groups are hypsochromic. A bathochromic shift in the visible region of **1a** from **3** (ca. 60 nm) shows that the 2-phosphaethenyl group has an electron-donating nature. The profiles of the π–π^* transition absorptions of **2a** and **10** in the UV-region (Fig. 4) are quite distinct from each other. The results

Table 3. ^{1}H NMR Data for **1**, **2**, **9**, **10**, and **3**[a)]

Compound	H-1	H-2	H-3 or R	H-4	H-5	H-6 or R′	H-7	H-8	CH=E[b)]	Ar
(*E*)-**1a**	—	8.46dd	7.37d	8.13d	7.02dd	7.44dd	6.99dd	8.25d	8.60d	1.39s, 1.56s
		(4.2, *3.5*)	(4.2)	(9.4)	(10.0, 9.4)	(10.0, 10.0)	(10.0, 9.9)	(9.9)	(*24.4*)	7.48s
(*Z*)-**1a**	—	5.60dd	6.91d	8.05dd	7.05ddd	7.49dd	7.14ddd	8.38d	8.44d	1.44s, 1.47d (*1.0*)
		(4.3, *3.1*)	(4.3)	(9.5, 0.5)	(10.0, 9.5, 2.3)	(10.0, 10.0)	(10.0, 9.5, 2.3)	(9.5)	(*35.2*)	7.53d (*1.2*)
(*E*)-**1b**	—	8.32dd	7.29d	8.07d	6.97d	1.30d (6.9)	6.98d	8.24d	8.58d	1.39s. 1.56s
		(4.2, *3.4*)	(4.2)	(10.0)	(10.0)	2.95sept (6.9)	(10.5)	(10.5)	(*24.4*)	7.48d (*1.1*)
(*Z*)-**1b**	—	5.50dd	6.84d	8.00d	7.01dd	1.31d (6.9)	7.10dd	8.32d	8.42d	1.44s, 1.47d (*0.6*)
		(4.4, *2.6*)	(4.4)	(9.9)	(9.9, 1.8)	2.99sept (6.9)	(10.3, 1.8)	(10.3)	(*35.8*)	7.52d (*1.0*)
(*E*)-**1c**	—	8.24d	1.42t (7.5)	7.98d	6.82dd	1.28d (6.9)	6.87d	8.07d	8.54d	1.39s, 1.56d (*0.4*)
		(*2.5*)	3.02q (7.5)	(9.7)	(9.7, 2.0)	2.91sept (6.9)	(10.3, 2.0)	(10.3)	(*24.4*)	7.45d (*1.1*)
(*Z*)-**1c**	—	5.65d	1.00t (7.5)	7.93d	6.94dd	1.29d (6.9)	6.97dd	8.24d	8.39d	1.43s, 1.47s
		(*2.8*)	2.66q (7.5)	(9.9)	(9.9, 2.1)	2.95sept (6.9)	(10.3, 2.1)	(10.3)	(*36.4*)	7.55d (*1.0*)
(*E*)-**1d**	—	8.42d	7.34dd (7.2, 2.2)	8.24d	6.93dd	1.28d (6.9)	6.93dd	8.26d	8.60d	1.39s, 1.57s
		(*2.7*)	7.46dd (7.8, 7.2)	(10.8)	(10.8, 1.8)	2.93sept (6.9)	(10.3, 1.8)	(10.3)	(*24.5*)	7.48d (*0.5*)
			7.61dd (7.8, 2.2)							
(*Z*)-**1d**	—	5.96d	7.18—7.40m	8.21d	6.98dd	1.30d (6.9)	7.08dd	8.34d	8.46d	1.26s, 1.50d (*0.8*)
		(*3.0*)		(10.2)	(10.2, 1.7)	2.98sept (6.9)	(10.4, 1.7)	(10.4)	(*35.6*)	7.50d (*1.1*)
(*E*)-**2a**	7.46d	—	7.46d	8.13dd	7.06dd	7.40dd	7.06dd	8.13dd	8.39d	1.37s, 1.55s
	(*2.7*)		(*2.7*)	(9.6, *2.3*)	(10.0, 6.9)	(10.0, 10.0)	(10.0, 9.6)	(9.6, *2.3*)	(*24.8*)	7.47s
(*E*)-**2b**	7.39d	—	7.39d	8.06dd	7.00d	1.31d (6.9)	7.00d	8.06dd	8.37d	1.37s, 1.53s
	(*2.2*)		(*2.2*)	(10.3, *2.2*)	(10.3)	2.98sept (6.9)	(10.3)	(10.3, *2.2*)	(*24.9*)	7.46d (*1.0*)
9	—	8.32d	7.44d	8.43d	7.33dd	7.72dd	7.39dd	9.42d	8.62s	1.37s, 7.39s
		(4.3)	(4.3)	(9.3)	(9.9, 9.3)	(9.9, 9.9)	(9.9, 9.7)	(9.7)		
10	7.77s	—	7.77s	8.38d	7.17dd	7.59dd	7.17dd	8.38d	8.48s	1.34s, 1.36s
				(9.3)	(9.8, 9.3)	(9.8, 9.8)	(9.8, 9.3)	(9.3)		7.37s
3	7.17	7.77	7.17	8.10	6.88	7.30	6.88	8.10	—	—

a) 200 MHz or 600 MHz, in $CDCl_3$, δ. The values in parentheses denote coupling constants in Hz. J_{PH} is printed in italics. The data of **3** are taken from Ref. 20. s: singlet, d: doublet, t: triplet, q: quartet, sept: septet. b) E=P for **1a**—**d** and **2a**—**b**; E=N for **9** and **10**.

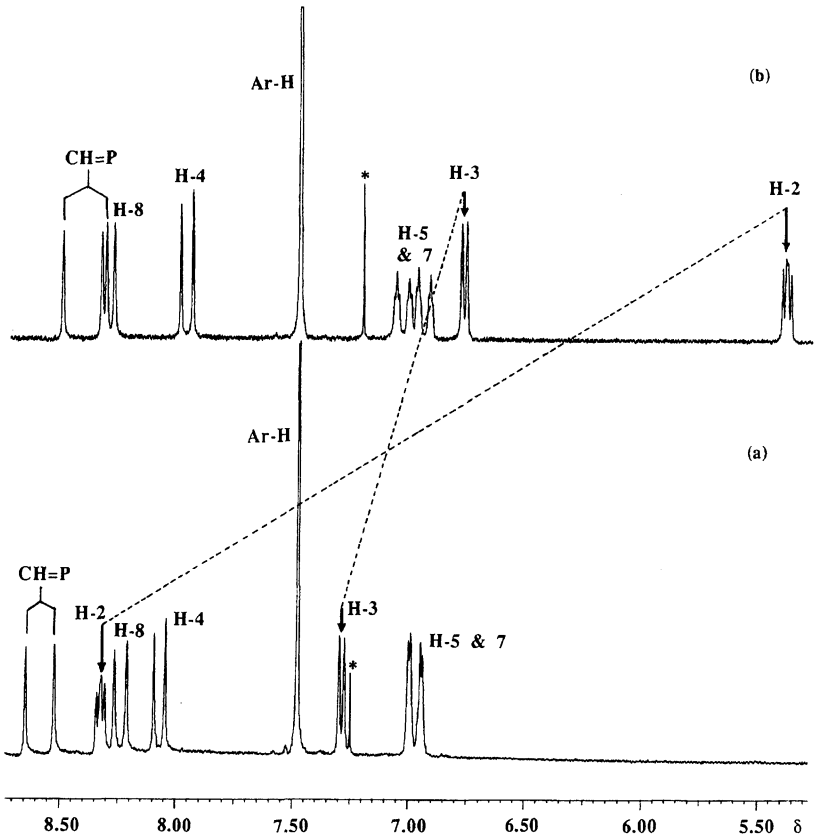


Fig. 1. Expanded 200 MHz ^{1}H NMR spectra in $CDCl_3$. (a): (*E*)-**1b**; (b): (*Z*)-**1b**. *: $CHCl_3$.

suggest that the bulky Ar group of the 2-phosphaethenyl moiety cause little perturbation of the coplanarity between the azulene ring and the P=C double bond due to its longer bond length than that of the N=C double

Table 4. $^{13}C\{^1H\}$ Data of **1**, **2**, **9**, **10**, and **3**[a)]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-3a	C-8a	CH=E[b)]	R	R′	Ar
(*E*)-**1a**	133.9	134.3	119.8	136.6	124.2	138.4	123.1	134.5	143.6	131.3	166.7	—	—	31.4, 33.9 (6.4), 35.0, 38.4 (0.5)
	(20.3)	(21.7)	(3.2)	(1.6)	(6.5)	(3.9)	(8.4)	(1.3)	(4.6)	(11.7)	(34.5)			121.7 (1.4), 140.5 (53.6)
														149.3, 154.3 (1.0)
(*Z*)-**1a**	130.0	138.6	119.9	136.4	124.6	138.0	123.5	133.2	141.5	134.9	152.9	—	—	31.5, 32.5 (7.3), 35.1, 38.2
	(28.3)	(8.9)	(3.8)	(3.3)	(6.4)	(3.9)	(7.6)	(5.2)	(3.7)	(17.4)	(46.3)			122.6 (0.7), 138.0 (61.9)
														150.8, 154.5
(*E*)-**1b**	132.9	133.3	119.5	136.4	123.1	160.5	122.8	134.2	142.3	131.2	167.1	—	24.1	31.5, 33.9 (7.0), 35.0, 38.4 (0.5)
	(19.8)	(21.0)	(3.2)	(1.5)	(6.6)	(3.8)	(8.3)	(1.9)	(4.7)	(11.4)	(34.6)		39.6	121.7 (1.3), 140.8 (53.6)
														149.2, 154.3 (1.0)
(*Z*)-**1b**	129.9	137.5	119.7	136.2	123.6	160.1	123.0	132.8	140.2	133.8	153.0	—	24.2	31.5, 32.5 (7.3), 35.1, 37.2 (1.0)
	(28.3)	(8.9)	(3.8)	(3.2)	(6.4)	(3.9)	(7.5)	(5.1)	(3.8)	(17.5)	(46.1)		39.6	122.6 (0.7), 138.1 (61.9)
														150.7, 154.2 (0.8)
(*E*)-**1c**	133.1	131.6	134.5	132.6	121.7	160.3	121.9	133.6	138.5	129.7	166.5	15.1	24.0	31.4, 33.9 (7.0), 35.0, 38.4 (0.5)
	(20.1)	(21.6)	(3.6)	(1.1)	(6.1)	(3.9)	(9.3)	(0.8)	(5.1)	(10.9)	(34.2)	20.1	39.4	121.6 , 140.9 (53.5)
														149.1, 154.3 (0.7)
(*Z*)-**1c**	128.7	136.9	134.6	132.7	122.3	159.8	122.1	132.2	136.0	134.2	152.1	15.8	24.1	31.5, 32.5 (7.3), 35.1, 38.3 (1.0)
	(28.8)	(9.0)	(4.2)	(3.6)	(7.5)	(4.4)	(8.6)	(5.4)	(4.6)	(18.1)	(46.2)	19.9	39.4	122.6 , 138.3 (62.7)
														150.4, 154.2 (1.0)
(*E*)-**1d**	134.2	132.9	132.6	134.6	123.5	161.3	122.8	135.5	137.8	130.0	166.5	126.6, 128.6	24.0	31.5, 34.0 (7.0), 35.0, 38.4
	(19.6)	(21.7)	(3.3)	(2.3)	(6.5)	(3.6)	(8.1)	(1.4)	(4.8)	(11.8)	(34.5)	129.7, 136.8	39.5	121.7 (1.2), 140.7 (53.6)
														149.3, 154.3 (0.9)
(*Z*)-**1d**	128.8	135.1	133.6	135.7	124.0	160.9	123.1	135.3	132.8	137.0	152.0	126.2, 128.4	24.1	31.3, 32.5 (7.2), 35.0, 38.3
	(28.3)	(9.6)	(4.9)	(4.0)	(6.5)	(3.9)	(7.5)	(4.0)	(3.9)	(19.6)	(46.3)	129.5, 138.5	39.5	122.6, 129.1 (57.6)
														150.7, 154.1
(*E*)-**2a**	115.2	149.9	115.2	135.2	124.0	135.8	124.0	135.2	141.4	141.4	170.2	—	—	31.4, 33.9 (6.2), 35.0, 38.3
	(21.6)	(14.0)	(21.6)	(7.7)	(4.3)	(7.3)	(4.3)	(7.7)	(2.4)	(2.4)	(34.0)			121.8, 139.4 (53.2), 149.8, 154.0
(*E*)-**2b**	114.9	148.8	114.9	135.1	123.3	158.0	123.3	135.1	140.0	140.0	170.6	24.2 (1.7)	—	31.4, 33.9 (7.0), 35.0, 38.3
	(21.7)	(13.9)	(21.7)	(7.9)	(5.2)	(8.2)	(5.2)	(7.9)	(4.0)	(4.0)	(33.8)	39.7		121.8 (1.3), 139.6 (53.7)
														149.7, 154.0 (1.0)
9	125.0	138.9	118.9	137.9	125.6	138.8	126.2	136.1	144.5	139.1	157.0	—	—	31.7, 31.7, 34.7, 36.0
														121.7, 138.9, 143.6, 151.8
10	117.8	144.2	117.8	139.8	121.7	138.7	121.7	139.8	141.0	141.0	159.2	—	—	31.7, 31.7, 34.8, 36.1
														123.9, 138.3, 138.3, 146.0
3	118.0	137.0	118.0	136.6	122.8	137.2	122.8	136.6	140.4	140.4	—	—	—	—

a) 50 MHz or 150 MHz, in $CDCl_3$, δ. The values in parentheses denote J_{PC} in Hz. The data of **3** are taken from Ref. 21.
b) E=P for **1a**—**d** and **2a**—**b**; E=N for **9** and **10**.

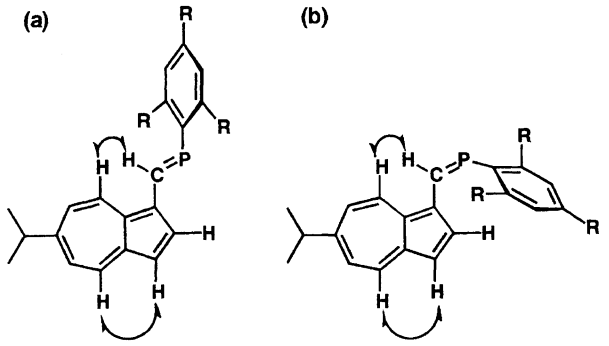


Fig. 2. Proposed structures and NOE correlations.
(a): (*E*)-**1b**; (b): (*Z*)-**1b**. R=*t*-Bu.

bond.[24)]

In conclusion, we have applied the phospha-Peterson reaction to synthesize some sterically-protected 2-(1-azulenyl)- and 2-(2-azulenyl)phosphaethenes from the corresponding formylazulenes with lithium silylphosphide. The δ values in the ^{31}P NMR analyses are diagnostic of the electron-donating nature of the azulenyl group. On the basis of ^{13}C NMR and UV-visible absorption spectra, the 2-phosphaethenyl group is electron-donating whereas the iminomethyl group is electron-withdrawing.

We are currently investigating the preparation of the other three positional isomers and the reaction of the P=C double bond. The synthesis of 1,3-bis(2-phosphaethenyl)azulenes is also in progress.

Experimental

General. Melting points were determined with a Yanagimoto micro melting point apparatus MP-J3 and are not corrected. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200P or Bruker AM600 spectrometer, and chemical shifts are given in δ relative to internal tetramethylsilane. ^{31}P NMR spectra were obtained with a Bruker AC200P spectrometer, and chemical shifts are given in δ relative to external 85% H_3PO_4. Mass spectra were recorded on a JEOL HX-110 or Hitachi M-2500S mass spectrometer. FT-IR and UV-visible absorption spectra were taken on a Horiba FT-300 and a Hitachi U-3210 spectrometer, respectively. Analytical HPLC characterization was carried out on a Nacalai COSMOSIL 5C18-AR column (4.6×150 mm, acetonitrile, at 254 nm). A Merck LiChroprep NH_2 column (25×310 mm, hexane) was used for normal-phase preparative HPLC. A YMC S-50 ODS column (20×300 mm, acetonitrile) was utilized for reversed-phase preparative HPLC.

Table 5. ^{13}C NMR SCS Values of **1a**, **2a**, **9**, and **10**[a)]

	(*E*)-**1a**	(*Z*)-**1a**	**9**	(*E*)-**2a**	**10**
C-1	+15.9	+12.0	+7.0	−2.8	−0.2
C-2	−2.7	−3.7	+1.9	+12.9	+7.2
C-3	+1.8	+1.9	+0.9	−2.8	−0.2
C-4	0.0	+2.0	+1.3	−1.4	+3.2
C-5	+1.4	+1.8	+2.8	+1.2	−1.1
C-6	+1.2	+0.8	+1.6	−1.4	+1.5
C-7	+0.3	+0.7	+3.4	+1.2	−1.1
C-8	−2.1	−0.2	−0.5	−1.4	+3.2
C-3a	+3.5	+1.4	+4.4	+1.3	+0.9
C-8a	−8.8	−5.2	−1.0	+1.3	+0.9

a) The negative sign denotes a high-field shift from the corresponding values for **3**.

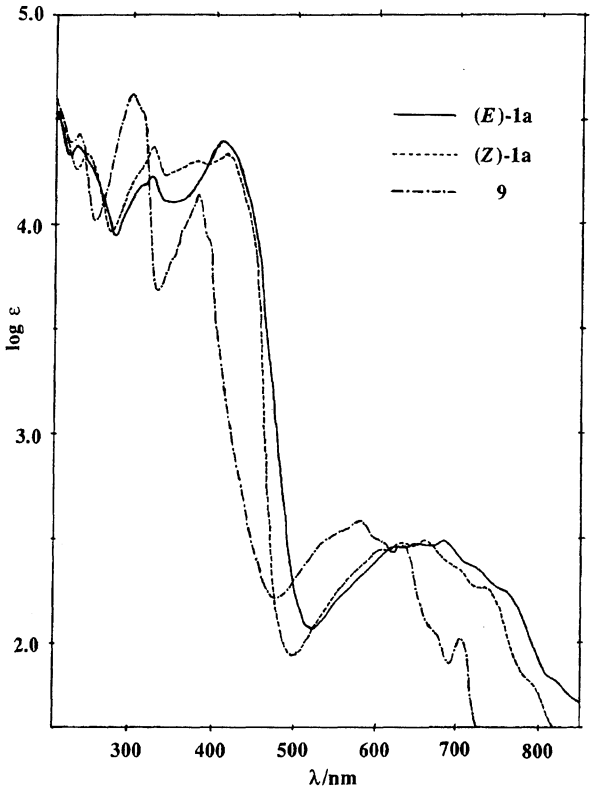


Fig. 3. UV-visible absorption spectra of (*E*)- and (*Z*)-**1a** and **9** in hexane.

Sumitomo alumina (KCG-30) and Merck silica gel (Cat. No. 7734) were used for column chromatography without pretreatment. TLC analysis was carried out on Merck Aluminiumoxid 60 F_{254} plates. THF was distilled from sodium benzophenone ketyl under argon. Chlorotrimethylsilane was distilled from CaH_2 under nitrogen. All reactions were carried out under an argon atmosphere except for the synthesis of **6b**.

Synthesis of 2-Formyl-6-isopropylazulene (6b). An anhydrous ethanol solution (200 mL) of 6-isopropyl-2*H*-cyclohepta[*b*]furan-2-one (6.9 g, 37 mmol) and 3,3-dimethoxy-2-(1-pyrrolidinyl)propene (19.0 g, 111 mmol) was heated under reflux for 5 h. After being cooled to room temperature, the solution was concentrated under reduced pressure. The residue was poured into water (500 mL) and extracted with benzene (150 mL) three times. The organic layer was washed with water and then with sat. NaCl, dried over $MgSO_4$, and the solvent was removed. The residue was chromatographed on a silica-gel column (100 g, 35×215 mm, benzene) to give a crude product. The crude product was purified by re-chromatography on an alumina column (100 g, 35×105 mm, benzene) to give 2-(dimethoxymethyl)-6-isopropylazulene (**11**) as a violet oil (2.3 g, 9.5 mmol, 26%). To a stirred ethanol solution (200 mL) of **11** (2.3 g, 9.5 mmol) was added water (20 mL) and *p*-toluenesulfonic acid monohydrate (0.3 g). After being stirred for 20 min at room temperature, the solution was poured into water (500 mL) and the aqueous solution was extracted with benzene (150 mL) three times. The organic layer was washed with water and then with sat. NaCl, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica-gel column (100 g, 35×220 mm, benzene) to give **6b** (1.5 g, 7.5 mmol, 78%).

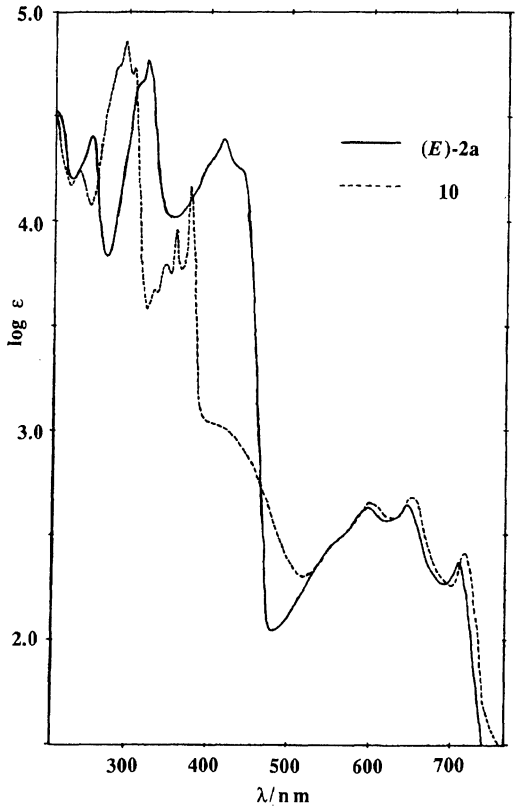


Fig. 4. UV-visible absorption spectra of (*E*)-**2a** and **10** in hexane.

6b: Green scales (cyclohexane), mp 90—91 °C; ^1H NMR (200 MHz, $CDCl_3$) δ=1.35 (6H, d, J=6.9 Hz, CH$\underline{Me}_2$), 3.06 (1H, sept, J=6.9 Hz, C$\underline{H}$Me$_2$), 7.14 (2H, d, J=10.6 Hz, H-5 and H-7), 7.67 (2H, s, H-1 and H-3), 8.38 (2H, d, J=10.6 Hz, H-4 and H-8), and 10.38 (1H, s, CHO); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=24.1 (CH$\underline{Me}_2$), 40.2 (C$\underline{H}$Me$_2$), 118.3 (C-1 and C-3), 123.8 (C-5 and C-7), 139.2 (C-3a and C-8a), 141.7 (C-4 and C-8), 143.6 (C-2), 164.6 (C-6), and 190.4 (CHO); UV-visible (hexane) 240 (log ε, 4.13), 267 (sh, 4.31), 278 (sh, 4.59), 290 (4.82), 301 (4.74), 326 (sh, 3.50), 343 (3.75), 351 (3.80), 361 (3.74), 368 (3.89), 553 (sh, 2.43), 598 (2.68), 620 (2.63), 647 (2.72), and 716 (2.46) nm; IR (KBr) 2966, 2933, 2789, 2710, 1684 ($\nu_{C=O}$), 1581, 1473, 1414, 1402, 1363, 1311,

1244, 1163, 1119, 1041, 978, 845, 810, 762, and 607 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 198 (M^+, 100), 183 (13), 155 (14), 153 (10), and 141 (5). Found: C, 84.56; H, 7.17%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

General Procedure for the Synthesis of 2-Azulenylphosphaethenes. To a stirred solution of formylazulene in 15 mL of THF was added a solution of **4**[11] (1.1 mol equiv) in THF (15 mL) at 0 °C over a period of 5 min. The reaction mixture was gradually warmed to room temperature. After 30 min, the end of the reaction was determined by reversed-phase HPLC analysis or TLC. At the end of the reaction, a small amount of methanol was added to the reaction mixture to destroy the excess organolithium reagent. After removal of the solvent, the reaction mixture was dissolved in hexane/benzene (10:1, v/v) and insoluble materials were removed with a Celite column. The filtrate was chromatographed on alumina (150 g, 36×150 mm, hexane/benzene 10:1 to 1:1). The green fraction was then chromatographed on a normal-phase HPLC and the desired 2-azulenylphosphaethene was obtained as an isomeric mixture. Recrystallization of the mixture gave the major *E*-isomer as green crystals. The minor *Z*-isomer was obtained by separation of the filtrate by normal-phase preparative HPLC followed by recrystallization. The *Z*-isomer was eluted first except for **1c**.

(*E*)- and (*Z*)-2-(1-Azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes (1a). The reaction of 1-formylazulene (**5a** 1.00 g, 6.40 mmol) and **4** gave **1a** in 21% yield (0.56 g, 1.35 mmol). The *E*-isomer (0.43 g) was obtained by recrystallization from ethyl acetate and the *Z*-isomer (6 mg) was separated from the filtrate.

(*E*)-1a: Green prisms (AcOEt), mp 153.5—154.5 °C; UV-visible (hexane) 236 (log ε, 4.38), 309 (sh, 4.19), 325 (4.23), 411 (4.40), 618 (2.47), 648 (2.49), 682 (2.49), 721 (sh, 2.36), and 762 (sh, 2.24) nm; IR (KBr) 2952, 2902, 2864, 1593, 1566, 1545, 1531, 1479, 1454, 1412, 1392, 1360, 1286, 1238, 1213, 1180, 1126, 877, 816, 775, 739, and 714 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 416 (M^+, 86), 275 (26), 141 (100), and 57 (6). Found: C, 83.39; H, 8.99%. Calcd for $C_{29}H_{37}P$: C, 83.61; H, 8.95%.

(*Z*)-1a: Green needles (EtOH), mp 172—174 °C; UV-visible (hexane) 249 (log ε, 4.31), 308 (sh, 4.23), 325 (4.35), 361 (sh, 4.25), 382 (4.28), 421 (4.29), 603 (2.45), 632 (2.48), 664 (2.49), 704 (sh, 2.35), and 740 (2.25) nm; IR (KBr) 2952, 2902, 2866, 1593, 1570, 1479, 1454, 1415, 1394, 1360, 1290, 1240, 1211, 1128, 1049, 904, 877, 854, 775, 760, and 733 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 416 (M^+, 38), 275 (12), 141 (100), and 57 (4).

(*E*)- and (*Z*)-2-(6-Isopropyl-1-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes (1b). The reaction of 1-formyl-6-isopropylazulene (**5b**, 0.86 g, 4.4 mmol) and **4** gave **1b** in 67% yield (1.34 g, 2.92 mmol).

(*E*)-1b: Green prisms (AcOEt), mp 149.5—151 °C; UV-visible (hexane) 245 (log ε, 4.35), 260 (sh, 4.26), 308 (sh, 4.21), 322 (4.26), 355 (sh, 4.17), 419 (4.41), 599 (sh, 2.50), 613 (2.52), 660 (2.54), 742 (2.26), and 807 (sh, 1.68) nm; IR (KBr) 2964, 2904, 2866, 1581, 1572, 1479, 1462, 1437, 1421, 1400, 1360, 1288, 1238, 1213, 877, 837, 810, 721, and 702 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 458 (M^+, 100), 275 (29), 183 (84), and 57(8). Found: C, 83.68; H, 9.20%. Calcd for $C_{32}H_{43}P$: C, 83.80; H, 9.45%.

(*Z*)-1b: Green needles (EtOH), mp 177.5—178.5 °C; UV-visible (hexane) 248 (log ε, 4.17), 298 (sh, 4.04), 312 (sh, 4.14), 330 (4.24), 384 (4.15), 420 (4.21) 449 (sh, 3.90), 566 (sh, 2.31), 590 (2.40), 617 (2.43), 645 (2.44), 680 (sh, 2.32), and 720 (2.19) nm; IR (KBr) 2958, 2902, 2866, 1589, 1572, 1477, 1458, 1442, 1417, 1402, 1392, 1360, 1294, 1242, 1213, 1205, 1190, 876, 864, 849, 839, 806, 775, and 760 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 458 (M^+, 78), 275 (29), 183 (100), and 57(6).

(*E*)- and (*Z*)-2-(3-Ethyl-6-isopropyl-1-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes (1c). The reaction of 3-ethyl-1-formyl-6-isopropylazulene (**5c**, 1.00 g, 4.42 mmol) and **4** gave **1c** in 50% yield (1.07 g, 2.20 mmol).

(*E*)-1c: Green prisms (EtOH), mp 159.5—161.5 °C; UV-visible (hexane) 240 (log ε, 4.42), 263 (sh, 4.28), 319 (sh, 4.28), 335 (4.32), 431 (4.48), 617 (2.50), 654 (2.53), 678 (2.55), 728 (sh, 2.40), and 765 (sh, 2.28) nm; IR (KBr) 2960, 2927, 2904, 2866, 1593, 1572, 1477, 1462, 1429, 1408, 1392, 1360, 1298, 1240, 1174, 876, 868, 831, and 816 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 486 (M^+, 100), 275 (23), 211 (62), and 57 (5). Found: C, 84.13; H, 9.62%. Calcd for $C_{34}H_{47}P$: C, 83.90; H, 9.73%.

(*Z*)-1c: Green plates (AcOEt), mp 183—184 °C; UV-visible (hexane) 214 (log ε, 4.50), 249 (4.32), 300 (sh, 4.23), 312 (sh, 4.28), 335 (4.41), 428 (4.41), 611 (2.56), 636 (2.58), 663 (2.59), 704 (sh, 2.46), and 734 (sh, 2.38), nm; IR (KBr) 2962, 2935, 2927, 2902, 2866, 1591, 1570, 1477, 1460, 1427, 1408, 1390, 1360, 1304, 1238, 1211, 1186, 877, and 808 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 486 (M^+, 54), 275 (27), 211 (100), and 57 (33).

(*E*)- and (*Z*)-2-(6-Isopropyl-3-phenyl-1-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes (1d). The reaction of 1-formyl-6-isopropyl-3-phenylazulene (**5d**, 1.00 g, 3.63 mmol) and **4** gave **1d** in 59% yield (1.15 g, 2.15 mmol).

(*E*)-1d: Green prisms (AcOEt), mp 167.5—169 °C; UV-visible (hexane) 243 (log ε, 4.46), 279 (sh, 4.30), 304 (4.35), 337 (4.42), 427 (4.39), 613 (sh, 2.50), 670 (2.55), and 752 (sh, 2.29) nm; IR (KBr) 2962, 2904, 2868, 1653, 1570, 1525, 1481, 1462, 1431, 1392, 1362, 1238, 1201, 1190, 1126, 1043, 1024, 943, 926, 876, 829, 766, and 700 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 534 (M^+, 63), 275 (27), 259 (100), and 57 (24). Found: C, 85.57; H, 8.67%. Calcd for $C_{38}H_{47}P$: C, 85.35; H, 8.86%.

(*Z*)-1d: Green prisms (MeOH), mp 130—132 °C; UV-visible (hexane) 242 (log ε, 4.39), 289 (sh, 4.31), 300 (4.36), 322 (sh, 4.35), 337 (4.43), 406 (sh, 4.25), 428 (4.28), 575 (sh, 2.45), 599 (sh, 2.53), 630 (2.55), 657 (2.57), 694 (sh, 2.44), and 735 (sh, 2.31) nm; IR (KBr) 2964, 2902, 2866, 1572, 1525, 1477, 1460, 1431, 1392, 1379, 1360, 1315, 1240, 1207, 1126, 1055, 1041, 1028, 922, 879, 833, 804, 768, 702, and 652 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 534 (M^+, 68), 275 (16), and 259 (100).

(*E*)-2-(2-Azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)-phosphaethene (2a). The reaction of 2-formylazulene (**6a**, 0.76 g, 4.9 mmol) with **4** gave (*E*)-**2a** (0.39 g, 0.94 mmol, 19%). After washing with hexane, pure (*E*)-**2a** (0.31 g) was obtained by recrystallization from ethyl acetate.

(*E*)-2a: Green needles (AcOEt), mp 230—231 °C; UV-visible (hexane) 254 (log ε, 4.41), 306 (sh, 4.61), 321 (4.76), 393 (sh, 4.27), 415 (4.40), 440 (sh, 4.22), 552 (sh, 2.45), 598 (2.63), 650 (2.63), and 712 (2.35) nm; IR (KBr) 2958, 2902, 2862, 1591, 1570, 1468, 1404, 1390, 1362, 1294, 1238, 1211, 1200, 1184, 876, 837, 804, 760, 723, 648, 633, and 580 cm^{-1};

MS (DEI, 70 eV) *m/z* (rel intensity) 416 (M^+, 23), 360 (34), 275 (100), 155 (15), 142 (27), and 57 (25). Found: C, 82.60; H, 9.07%. Calcd for $C_{29}H_{37}P$: C, 83.61; H, 8.95%. Found: *m/z* 416.2625. Calcd for $C_{29}H_{37}P$: M, 416.2633.

(*E*)-2-(6-Isopropyl-2-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (2b). The reaction of 2-formyl-6-isopropylazulene (**6b**, 0.80 g, 4.0 mmol) with **4** gave (*E*)-**2b** (0.40 g, 0.87 mmol, 22%).

(*E*)-2b: Green needles (AcOEt), mp 190—191 °C; UV-visible (hexane) 237 (sh, $\log\varepsilon$, 4.32), 258 (4.41), 309 (sh, 4.67), 322 (4.84), 398 (sh, 4.38), 418 (4.50), 445 (sh, 4.30), 544 (sh, 2.50), 586 (2.67), 632 (2.68), and 692 (2.36) nm; IR (KBr) 2960, 2900, 2868, 1576, 1475, 1464, 1412, 1394, 1362, 1240, 1213, 877, and 834 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 458 (M^+, 22), 401 (71), 275 (100), 183 (55), and 57 (59). Found: C, 82.98; H, 9.63%. Calcd for $C_{32}H_{43}P$: C, 83.80; H, 9.45%. Found: *m/z* 458.3099. Calcd for $C_{32}H_{43}P$: M, 458.3102.

***N*-(1-Azulenylmethylene)-2,4,6-tri-*t*-butylaniline (9).** a) The benzene solution (10 mL) of **5a** (0.20 g, 1.3 mmol) with 2,4,6-tri-*t*-butylaniline (**7**) (0.41 g, 1.6 mmol) and diethyl ether—trifluoroborane (1/1) (0.03 mL) was heated under reflux for 3 h. No identical products were detected by ether HPLC or TLC analysis, and 0.19 g of **7** was recovered. b) Lithium *N*-trimethylsilyl-2,4,6-tri-*t*-butylanilide (**8**) was prepared from **7** by a method similar to that used in the case of **4**. The reaction of **5a** (1.00 g, 6.40 mmol) with **8** (1.1 equiv) was carried out in THF at 0 °C for 30 min. After removal of the solvent, the reaction mixture was chromatographed on a silica-gel column (150 g, 36×150 mm, hexane/benzene (10:1, v/v)). Crude **9** was washed with acetonitrile to remove the recovered **7**, then the filtrate was subjected to chromatographic separation on a reversed-phase preparative HPLC column. Finally, 1.62 g of **9** was obtained (4.77 mmol, 75%).

9: Violet prisms (hexane), mp 170—171 °C; UV-visible (hexane) 239 ($\log\varepsilon$, 4.43), 303 (4.62), 315 (sh, 4.53), 362 (sh, 3.98), 380 (4.14), 396 (sh, 3.90), 538 (sh, 2.49), 557 (sh, 2.53), 582 (2.58), 610 (sh, 2.48), 633 (2.47), 674 (2.06), and 705 (2.03) nm; IR (KBr) 2956, 2906, 2866, 1608 ($\nu_{C=N}$), 1592, 1576, 1500, 1477, 1464, 1454, 1437, 1414, 1392, 1360, 1346, 1327, 1286, 1267, I213, 1197, 1119, 889, 877, 850, 781, 756, and 740 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 399 (M^+, 100), 384 (47), 141 (22), and 57 (5). Found: C, 87.12; H, 9.54; N, 3.50%. Calcd for $C_{29}H_{37}N$: C, 87.16; H, 9.33; N, 3.51%.

***N*-(2-Azulenylmethylene)-2,4,6-tri-*t*-butylaniline (10).** A benzene solution (10 mL) of **6a** (0.20 g, 1.3 mmol), **7** (0.67 g, 2.6 mmol), and *p*-toluenesulfonic acid monohydrate (0.02 g) was heated under reflux for 8 h. The water formed during the reaction was removed by azeotropic distillation following passage over MS4A. After removal of the solvent, the reaction mixture was chromatographed on a silica-gel column (20 g, 25×150 mm, hexane/benzene (1:1, v/v)). Crude **10** was washed with acetonitrile to remove recovered **7**, then the filtrate was subjected to chromatographic separation on a reversed-phase preparative HPLC column. Finally, 0.185 g of **10** was obtained (0.46 mmol, 36%).

10: Green needles (AcOEt), mp 179—179.5 °C; UV-visible (hexane) 238 ($\log\varepsilon$, 4.26), 279 (sh, 4.69), 292 (4.87), 304 (4.73), 331 (3.68), 345 (3.80), 357 (3.97), 375 (4.18), 419 (sh, 3.01), 539 (sh, 2.37), 598 (2.66), 649 (2.69), and 716 (2.42) nm; IR (KBr) 3012, 2985, 2962, 2947, 2906, 2868, 1626 ($\nu_{C=N}$), 1585, 1572, 1477, 1450, 1427, 1404, 1390, 1362, 1271, 1217, 1196, 1132, 1119, 891, 877, 837, 820, and 729 cm^{-1}; MS (DEI, 70 eV) *m/z* (rel intensity) 399 (M^+, 100), 384 (62), 342 (8), and 57 (4). Found: C, 86.96; H, 9.48; N, 3.47%. Calcd for $C_{29}H_{37}N$: C, 87.16; H, 9.33; N, 3.51%.

This work was supported in part by Grants-in-Aid for Scientific Research Nos. 05640586 and 00000627 from the Ministry of Education, Science and Culture. We thank Shin-Etsu Chemical Co., Ltd. and Takasago International Corp. for donating chemicals.

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