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Characterization of Azulenylphosphine Derivatives. Unexpected Debromination and Its Synthetic Utility in the Preparation of 2-Substituted Azulene

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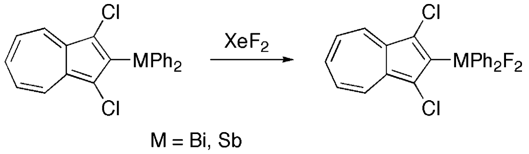
(1,3-Dihalo-2-azulenyl)diphenylphosphines **2** [halogen = Cl (**a**), Br (**b**)] and homologous bis(1,3-dihalo-2-azulenyl)phenylphosphines **4** have been synthesized, and the effect of the nonalternant azulenyl group on the reactivity and properties of these phosphines has been studied in comparison with that of the group 15 congeners. The electronic structure of the nonalternant conjugation is dramatically affected by the change in the valency at the phosphorus. Thus, oxidation of **2** and **4** with hydrogen peroxide proceeded with a dramatic color change from green to blue, giving the corresponding phosphine oxides **3** and **5**, respectively, in high yield. Similar color changes were observed when a solution of each phosphine, **2b** and **4b**, was left standing under ambient conditions, while **2a**, **4a**, and (2-azulenyl)diphenylphosphine (**7**) showed no such changes. (1-Bromo-2-azulenyl)diphenylphosphine oxide (**9**) was isolated from the solution of **2b**. This unexpected reaction was found to occur via electrophilic substitution at the five-membered ring through protonation. The bismuth and antimony congeners of **2b** showed no such reactivity, suggesting that the higher nucleophilicity of the phosphorus atom was the deciding factor. Such debromination of **2b** may be ascribed to the steric congestion around the bromine atom, which is inferred from the X-ray crystallographic study. The unexpected reaction was successfully applied to a convenient synthesis of 2-substituted azulene using triphenylphosphine as a reagent for debromination. The ^{13}C NMR study shows the enhanced π-polarization in the azulenyl group of the phosphine oxides compared to that of the parent phosphines, but the degree is not as marked as that observed in the bismuth and antimony systems. Comparison of the crystal structure of **3b** with that of **9** with respect to the intermolecular interaction between the azulenyl groups showed that the slight structural change in the nonalternant azulenyl group brings about a dramatic change in the packing. Thus, **3b** has head-to-tail $\pi-\pi$ stacking, but **9** forms a mutual halogen−hydrogen interaction of the bromine atom with a hydrogen atom of its positively charged seven-membered ring.

Introduction

Increasing attention has been focused on the construction of π-electron systems containing a main group metal center because of their interesting physical properties brought about by a change in its valency.[1] Recently, we have reported the first introduction of a nonalternant azulenyl group on a bismuth and an antimony center (Chart 1).[2] Since nonalternant conjugation shows high electron affinity, low ionization potential, and low aromatic resonance energy compared to those of alternant conjugation, slight structural modification of nonalternant molecules induces a significant change in the properties that are markedly different from those of alternant molecules.[3] Thus, oxidative fluorination of the tricoordinate bismuth and antimony metal centers markedly enhances the π-polarization in the azulenyl group, which is detected in solution by a color change as well as by changes in the spectroscopic characteristics. Furthermore, head-to-tail $\pi-\pi$ stacking arises in the crystal between the azulenyl

Chart 1



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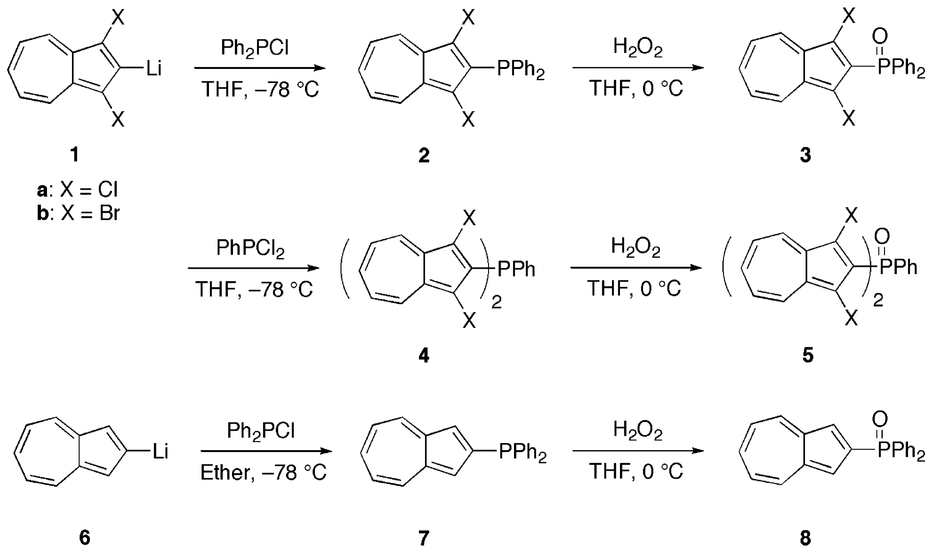
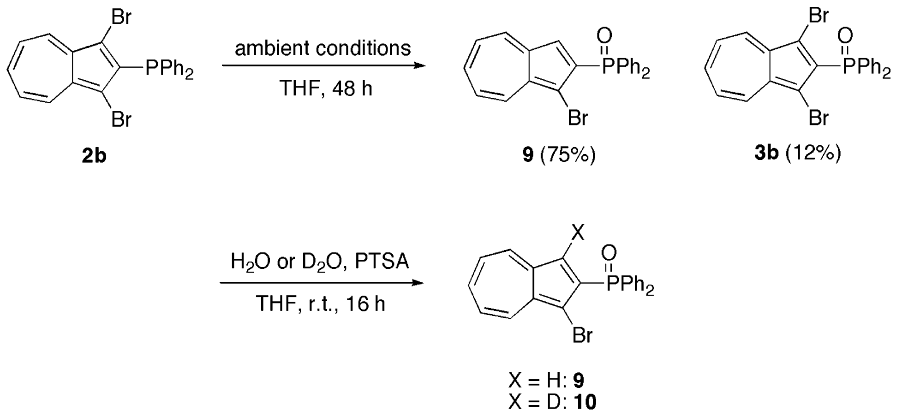
Scheme 1



Scheme 2



groups of the pentacoordinate difluoride through enhanced π-poralization. It is an important issue for us to know how the nonalternant ligand affects the structure and properties of organometallic compounds depending on the nature of the metal center and its valency. Despite the unique electronic structure of nonalternant conjugation, studies of the properties of organometallics bearing a nonalternant azulenyl group have been very limited.[2,4] We report here the first characterization of azulenylphosphorus compounds, the group 15 bismuth and antimony analogues.

Results and Discussion

Synthesis and Reactivities of Azulenylphosphines. 1,3-Dihalo-2-azulenyllithiums **1a** and **1b** were generated by deprotonation of 1,3-dihaloazulenes using lithium 2,2,6,6-tetramethylpiperidide (LTMP) (Scheme 1).[5] Initially, when **1a** was allowed to react with chlorodiphenylphosphine, the yield of **2a** was very low (22%).[5] It was greatly improved to 82% by adding dropwise a dilute solution of the chlorophosphine to **1a**. The reaction with the more reactive dichlorophenylphosphine gave the desired **4a** in 70% yield, but a reaction of **1a** with phosphorus trichloride gave only a tarry product mixture. Phosphines **2b** and **4b** were obtained from **1b** in similar manner (63 and 62% yields, respectively). The yields were lower compared to those of **2a** and **4a** due to their lower stability. Unsubstituted phosphine **7** was synthesized for comparison with **2**. The required 2-azulenyllithium **6** was prepared from 2-iodoazulene.[6] When **2**, **4**, and **7** were oxidized with hydrogen peroxide in THF, a dramatic color change from green to blue took place, and the corresponding phosphine oxides **3**, **5**, and **8**, respectively, were formed almost quantitatively. The change in color indicates that the change in the valency of the phosphorus center brings about a pronounced change in the conjugation of the nonalternant azulenyl group. A similar color change was observed when **2b** or **4b** was dissolved in THF and each solution was left standing in air for 48 h (Scheme 2). In contrast, phosphines **2a**, **4a**, and **7** were air-stable. Addition of hexane to a solution of **2b** in THF precipitated blue solids as the main product, the ^{1}H NMR spectrum of which was quite different from that of **3b**. This compound was shown by X-ray structure analysis to be the debrominated oxide **9**. From the filtrate, **3b** was obtained in 12% yield as a minor product. Oxides **3b** and **9** were stable and did not undergo any further reaction on standing in solution.

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Scheme 3

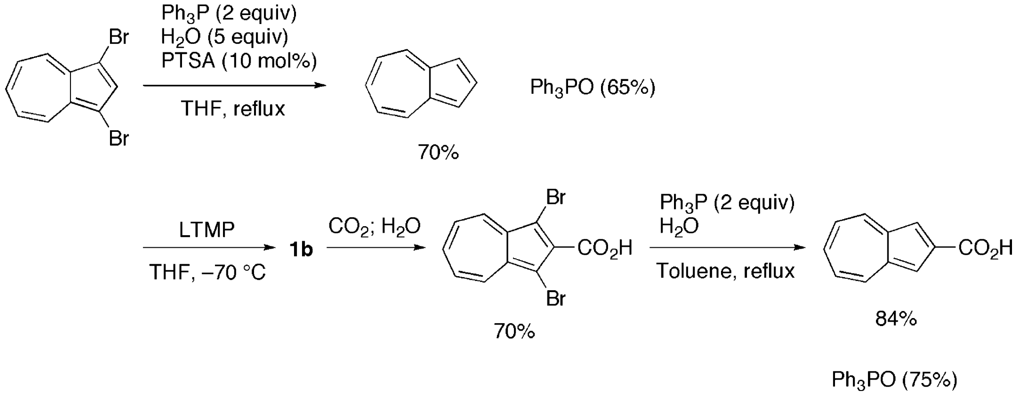
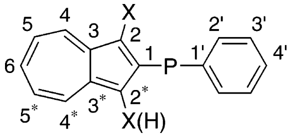


Table 1. ^{13}C and ^{31}P NMR Spectral Data (ppm) of Azulenyphosphines and Their Oxides in $CDCl_3$

	C1	C2	C3	C4	C5	C6	C1′	C2′	C3′	C4′	P
2a	138.2	120.6	133.5	135.3	123.9	140.9	134.5	133.7	128.4	128.8	−19.3
2b	*a*	110.5	136.6	137.0	124.6	140.7	134.3	133.7	128.4	128.8	−11.9
3a	131.5	118.8	133.7	138.0	124.6	143.2	132.4	131.9	128.5	132.1	22.8
3b	134.8	107.7	136.7	139.6	125.2	142.8	132.4	132.2	128.4	132.0	24.8
4a	137.0	120.0	133.3	134.9	123.9	140.5	131.1	135.2	128.2	129.5	−34.4
5a	131.8	118.5	133.7	138.0	124.5	143.0	131.5	132.4	128.5	132.5	13.6
5b	135.5	107.6	136.7	139.5	125.1	142.6	131.2	133.3	128.6	132.6	17.6
7	148.7	122.2	140.5	136.0	123.5	137.3	137.4	134.0	128.5	128.9	−14.2
8	140.4	122.0	140.2	139.9	124.1	140.3	133.5	131.8	128.3	131.7	24.7
9	138.0	106.5 124.4*	137.1 139.2*	139.5 141.2*	125.5 125.2*	142.4	131.7	132.5	129.0	132.5	24.2

[a] Owing to many impurities produced during the measurement, assignment of this signal failed.

Chart 2



The behavior of solutions of **4b** in air was complex and many products were formed.

It has been reported that triphenylphosphine attacks the bromine atom of 1,2-dibromo-1-nitro-2-phenylethane to generate an intermediate ion pair, which is hydrolyzed in protic solvent to give 1-bromo-2-nitro-1-phenylethane and triphenylphosphine oxide.[7] Since azulene undergoes electrophilic substitution preferentially at the 1- or 3-position of its negatively polarized five-membered ring through the generation of a tropylium cation intermediate, the formation of **9** through debromination of **2b** is considered to occur via protonation at this position and subsequent intramolecular nucleophilic attack of the phosphorus atom at the adjacent allylic bromine atom in the cationic intermediate. Actually, addition of water (5 equiv) and a catalytic amount of *p*-toluenesulfonic acid (PTSA) hydrate (10 mol %) to a THF solution of **2b** dramatically accelerated the formation of **9** (complete in 16 h; 80% yield) (Scheme 2). Furthermore, the use of D_2O in place of water gave a mixture of **9** and its deuterated congener **10** in 79% yield (**9**/**10** = 40:60). In both of these reactions, little oxide **3b** was formed. The fact that the yield of **9** was much higher than that of **3b** seems to show that the intramolecular debromination precedes the intermolecular one. This debromination is undoubtedly characteristic of azulenylphosphine **2b** and reflects the higher nucleophilicity of the phosphorus atom, since such a reaction is not observed in the bismuth and antimony congeners. The formation of **9** could be alternatively explained by acid-catalyzed addition of water to the five-membered ring of **2b** followed by rearrangement of geminal diphenylphosphinocarbinol thus formed to **9**. For comparison with the study of **2b**, 1,3-dibromoazulene was treated with triphenylphosphine (2 equiv) in the presence of water and the acid catalyst (Scheme 3). More forcing conditions were required for induction of the debromination. Thus, when the mixture was refluxed in THF for 48 h, azulene and triphenylphosphine oxide were formed in 70 and 65% yields, respectively, together with recovered 1,3-dibromoazulene (22%). The facile debromination of **2b** may be ascribed to the steric congestion around the bromine atom adjacent to the phosphinyl group and the proton at the 4-position of the seven-membered ring, which enhances the reactivity of the ipso carbon at the 1-position toward the electrophilic substitution.

Next, the synthetic utility of the debromination was examined. Thus, we were successful in a convenient synthesis of azulene-2-carboxylic acid[8] in high yield by debromination (Scheme 3). The reaction was complete without addition of an acid catalyst, suggesting that the carboxyl group plays the role as the catalyst. Since the synthesis of 2-substituted azulenes requires many steps by the conventional method,[8] this debromination is a very useful method for their easy access when combined with the lithiation of 1,3-dibromoazulene.

Spectroscopic Study. The ^{13}C NMR spectral data of azulenylphosphines (**2**, **4**, and **7**) and their oxides (**3**, **5**, and **8**) are shown in Table 1 and Chart 2. The signals due to the five-membered ring carbons (C1 and C2) of the oxides appeared more upfield, while those due to the seven-membered ring carbons (C4, C5, and C6) were observed more downfield, relative to the parent phosphines. In particular, the tendency of the downfield shift was marked in C4 and C6 rather than in C5. A similar change in the chemical shifts was observed in the phenyl group (the C1′ and C2′ signals more upfield and the C3′ and C4′ signals more downfield), but the extent was not as pronounced as seen in the azulenyl group. These findings are in accord with the observation in the homologous pentacoordinate (diaryl)azulenylbismuth difluorides and the antimony

Table 2. P−C Coupling Constants (Hz) of Azulenyphosphines and Their Oxides in $CDCl_3$

	C1	C2	C3	C4	C5	C6	C1′	C2′	C3′	C4′
2a	21.3	14.2	0	1.9	0	0	8.2	20.1	7.4	0
2b	*a*	17.0	2.7	1.5	0	0	7.3	20.0	6.9	0
3a	107.3	5.3	9.9	0	0	0	109.2	10.5	12.8	2.8
3b	106.5	6.9	10.4	0	0	0	109.0	10.4	12.7	2.9
4a	16.1	14.9	2.4	2.8	0	0	4.2	22.8	8.9	0
5a	112.2	5.5	10.4	0	0	0	115.2	7.3	13.6	0
5b	114.9	6.9	10.6	0	0	0	114.2	10.6	13.5	0
7	11.5	15.4	5.5	2.4	0	1.5	9.4	20.0	7.4	0
8	105.6	11.3	0	0	0	0	104.7	10.1	12.2	2.5
9	109.0	7.6	10.6	0	0	0	108.8	10.3	12.7	2.9
		11.1*	0*	0*	0*					

[a] Owing to many impurities produced during the measurement, assignment of this signal failed.

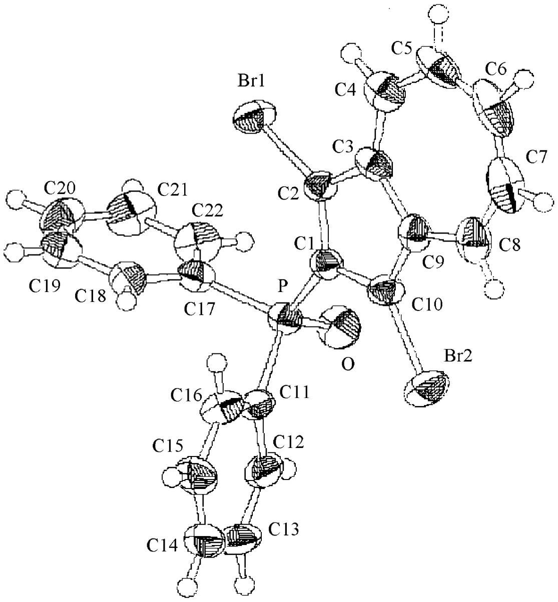


Figure 1. ORTEP drawing of **3b** showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

congeners.[2] Thus, the change in the valency of the metal center enhances the π-polarization in the nonalternant azulenyl group rather than in the alternant phenyl group. The upfield shift of the ipso carbons attached to the tetracoordinate phosphorus atom of the phosphine oxides is attributed to the π-inductive effect[9] induced by the electronic fields of its positively polarized phosphorus atom. The π-polarization in the azulenyl group seems to be more pronounced in the previous bismuth and antimony systems compared to the phosphorus system since the sum of the differences in the chemical shifts between **2a** and **3a** with respect to the C1 and C2 carbons (ΔC1 + 2ΔC2 = −10.23 ppm) is smaller than those of the bismuth (−18.62 ppm) and antimony (−12.58 ppm).

It is known that the ^{31}P NMR signal due to the phosphorus atom of *p*-substituted triarylphosphines is shifted upfield with increasing electron-donating nature of the aryl group and that the coupling constant $^1J_{PC}$ increases with increasing electron-withdrawing nature of the substituent.[10] The ^{31}P NMR study of the azulenylphosphorus compounds provided useful information about the electronic effect of the azulenyl group on the phosphorus atom. The $^1J_{PC}$ value of C1 in **2a** (21.3) is much larger than that in **7** (11.5), indicating the inductive polarization of the phosphorus−carbon bond (Table 2). The upfield shift of the phosphorus signal of **2a** (δ_p −19.30) relative to **7** (δ_p −14.18) does not correspond to the electron donation of the 1,3-dichloro-2-azulenyl group toward the phosphorus atom (Table 1), since the azulenyl group is shown to act as an electron-withdrawing group. The upfield shift in **2a** is, hence, attributed to the anisotropic effect of the chlorine atoms adjacent to the phosphorus atom. A clear additivity of chemical shifts was observed between triphenylphosphine (δ_p −4.86), **2a** and **4a** (δ_p −34.40) with respect to the replacement of the phenyl group by the azulenyl group. This shows the close proximity of the phosphorus atom to the halogen atoms. A similar additivity was seen between **3a**, **5a**, and triphenylphosphine oxide (δ_p 29.65).

Comparison of azulenylphosphine **2a** with its oxide **3a** by UV/vis absorption spectrum showed that the absorbance (ϵ) of the longer wavelength absorption band (λ_{max} = ca. 664 nm) due to the charge transfer absorption of the azulene nucleus is

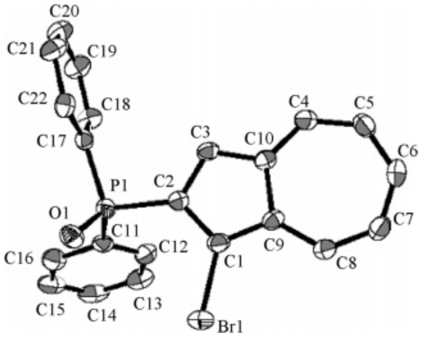


Figure 2. ORTEP drawing of **9** showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3b and 9

3b		9	
P−C(1)	1.806(7)	P(1)−C(2)	1.787(3)
P−C(11)	1.802(7)	P(1)−C(11)	1.812(4)
P−C(17)	1.821(8)	P(1)−C(17)	1.796(4)
P−O	1.480(5)	P(1)−O(1)	1.482(3)
C(2)−Br(1)	1.886(7)	C(1)−Br(1)	1.880(4)
C(10)−Br(2)	1.890(7)		
C(1)−C(2)	1.407(9)	C(2)−C(1)	1.413(5)
C(2)−C(3)	1.412(10)	C(1)−C(9)	1.394(5)
C(3)−C(4)	1.39(1)	C(9)−C(8)	1.393(5)
C(3)−C(9)	1.47(1)	C(9)−C(10)	1.479(5)
C(4)−C(5)	1.39(1)	C(8)−C(7)	1.376(5)
C(5)−C(6)	1.39(1)	C(7)−C(6)	1.396(8)
C(6)−C(7)	1.38(1)	C(6)−C(5)	1.376(6)
C(7)−C(8)	1.38(1)	C(5)−C(4)	1.388(5)
C(8)−C(9)	1.40(1)	C(4)−C(10)	1.374(5)
C(9)−C(10)	1.389(10)	C(10)−C(3)	1.39(5)
C(1)−C(10)	1.41(9)	C(3)−C(2)	1.395(5)
C(1)−P−C(11)	104.6(3)	C(2)−P(1)−C(11)	105.3(2)
C(1)−P−C(17)	110.8(3)	C(2)−P(1)−C(17)	102.7(2)
C(11)−P−C(17)	104.3(3)	C(11)−P(1)−C(17)	107.4(2)
O−P−C(1)	111.2(3)	O(1)−P(1)−C(2)	114.8(2)
O−P−C(11)	114.4(3)	O(1)−P(1)−C(11)	113.0(2)
O−P−C(17)	111.1(3)	O(1)−P(1)−C(17)	112.8(2)
Br(1)−C(2)−C(1)	127.0(5)	Br(1)−C(1)−C(2)	124.6(3)
Br(2)−C(10)−C(1)	125.3(5)		
C(2)−C(1)−P−C(17)	−27.9(8)	C(11)−P(1)−C(2)−C(1)	−71.4(4)
O−P−C(1)−C(2)	96.1(7)	O(1)−P(1)−C(2)−C(1)	53.5(4)

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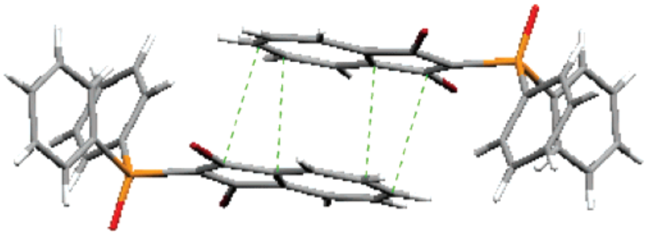

Figure 3. Head-to-tail $\pi-\pi$ interaction in **3b**.

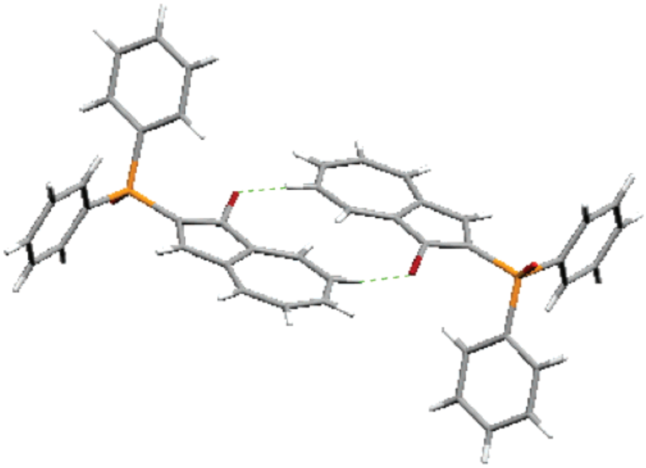

Figure 4. Intermolecular CH---Br interaction in **9**.

larger in **3a** (550) than that in **2a** (460). This tendency was commonly observed through the comparison of the phosphine oxides with the parent phosphines, as seen in the bismuth and antimony counterparts.[2] This ensures the enhanced π-polarization of the azulene nucleus in the higher oxidation state of the phosphorus center.

X-ray Crystallographic Study of Azulenylphosphine Oxides 3b and 9. The molecular structures of **3b** and **9** are shown in Figures 1 and 2, respectively. An outstanding feature is the bond angles around the phosphorus center of **3b** (Table 3). The C(1)−P−C(17) bond angle [110.8(3)°] is much larger than those of C(1)−P−C(11) and C(11)−P−C(17), indicating the steric congestion around the Br(1) atom. In contrast, **9** does not show this tendency around the phosphorus atom due to replacement of the bromine atom by the proton at the C3 atom. The bond angle of Br(1)−C(1)−C(2) in **9** [124.6(3)°] is smaller than that of Br(1)−C(2)−C(1) in **3b** [127.0(5)°]. Although the molecular structure of **2b** is not clarified, such steric congestion as observed in **3b** may arise in **2b** as well and facilitate its debromination.

It should be stressed that the intermolecular interaction between the azulenyl groups in **3b** is quite different from that in **9**. Oxide **3b** forms head-to-tail $\pi-\pi$ stacking (Figure 3). On the other hand, **9** forms a mutual halogen−hydrogen interaction of the bromine atom with the hydrogen atom attached to the 7-position of its positively charged seven-membered ring (Figure 4). Such a dramatic difference between **3b** and **9** seems to show the electronic structure of the nonalternant conjugation that is easily affected by the slight structural change. Bond alternation appears in the seven-membered ring of **9** compared to that of **3b**, although the tendency is not marked.

In conclusion, this study not only showed that the difference in the electronic structure between the group 15 metal centers clearly appears in the properties of the respective congeners by utilizing the unique nature of the nonalternant azulenyl ligand, but also develops a new convenient route for the synthesis of 2-substituted azulene based on the nucleophilicity of triphenylphosphine.

Experimental Section

General Comments. All reactions were carried out under argon unless otherwise noted. THF was distilled from sodium benzophenone ketyl under argon before use. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400S spectrometer with TMS as an internal standard. ^{31}P NMR spectra were measured in $CDCl_3$ on a Bruker Avance 400S spectrometer with 85% H_3PO_4 as an internal standard. IR spectra were obtained as KBr pellets on a Nicolet Impact 410 spectrophotometer. UV/vis spectra were measured in $CHCl_3$ by means of a Shimadzu UV-1600PC spectrophotometer.

Generation of Azulenyllithium 1 and the Reaction with Chlorodiphenylphosphine or Dichlorophenylphosphine. General Procedure. A typical example is exemplified by the reaction of **1a** with chlorodiphenylphosphine. To a solution of lithium 2,2,6,6-tetramethylpiperidide (ca. 1.2 mmol) prepared from 2,2,6,6-tetramethylpiperidine (1.2 mmol) and *n*-BuLi (1.2 mmol) in THF (5 mL) at −70 °C was added a solution of 1,3-dichloroazulene (1.0 mmol) in THF (3 mL) at the same temperature. The color of the solution immediately turned from blue to dark green, showing the generation of **1a**. To this solution thus obtained was added a solution of chlorodiphenylphosphine (1.0 mmol) in THF (20 mL), and the resulting solution was stirred for 5 min. The reaction was quenched at −70 °C with brine (10 mL), and the mixture was extracted with ether (7 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on a silica gel column with hexane−AcOEt (4:1) to give crude **2a**. Recrystallization from THF−hexane (4:1) gave the pure product.

(1,3-Dichloro-2-azulenyl)diphenylphosphine (2a): green solid; yield 82%; mp 150−152 °C; ^{1}H NMR δ 7.16 (2H, t, *J* 10.0, AzH), 7.32−7.38 (6H, m, PhH), 7.41−7.47 (4H, m, PhH), 7.62 (1H, t, *J* 9.9, AzH), 8.31 (2H, d, *J* 9.4, AzH); UV/vis λ_{max}/nm (ϵ) 240 (20 690), 303 (32 150), 350 (sh, 5730), 357 (5980), 373 (3160), 665 (460); ^{31}P NMR δ −19.30 (triplet-like, *J* 7.8). Anal. Calcd for $C_{22}H_{15}Cl_2P$: C, 69.31; H, 3.97. Found: C, 69.63; H, 4.17.

Bis(1,3-dichloro-2-azulenyl)phenylphosphine (4a): green solid; yield 70%; mp 237−239 °C; ^{1}H NMR δ 7.16 (4H, t, *J* 9.8, AzH), 7.34 (2H, m, PhH), 7.40 (1H, m, PhH), 7.58−7.63 (4H, m, AzH, PhH), 8.28 (4H, d, *J* 10.1, AzH); UV/vis λ_{max}/nm (ϵ) 242 (41 030), 302 (72 780), 337 (52 160), 410 (12 660), 665 (1100); ^{31}P NMR δ −34.40 (triplet-like, *J* 7.9). Anal. Calcd for $C_{26}H_{15}Cl_4P$: C, 62.43; H, 3.02. Found: C, 62.80; H, 3.19.

(1,3-Dibromo-2-azulenyl)diphenylphosphine (2b). The reaction was quenched at −70 °C with brine (10 mL), and the mixture was extracted immediately with ether (7 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed immediately on a silica gel column with hexane−AcOEt (4:1) to give crude **2b** containing a small amount of **9**. Recrystallization from THF−hexane (4:1) failed due to the gradual change of **2b** to **9**. Green solid; yield 63%; mp 120−122 °C; ^{1}H NMR δ 7.25 (2H, t, *J* 10.0, AzH), 7.33−7.38 (6H, m, PhH), 7.42−7.47 (4H, m, PhH), 7.64 (1H, t, *J* 9.8, AzH), 8.33 (2H, d, *J* 9.5, AzH); ^{31}P NMR δ −11.86 (triplet-like, *J* 9.0). Due to the poor stability of this compound, the elemental analysis was given up.

Bis(1,3-dibromo-2-azulenyl)phenylphosphine (4b). The reaction was quenched at −70 °C with brine (10 mL), and the mixture was extracted immediately with ether (7 mL × 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed immediately on a silica gel column with hexane−AcOEt (4:1) to give crude **4b**. Recrystallization from THF−hexane (4:1) failed due to the gradual formation of many products. Green solid; yield 62%; mp 190−192 °C; ^{1}H NMR δ 7.25 (4H, t, *J* 9.8, AzH), 7.34 (2H, m, PhH), 7.42 (1H, m, PhH), 7.57−7.66 (4H, m, AzH, PhH), 8.31 (4H, d, *J* 10.0, AzH); ^{31}P NMR δ −20.65 (triplet-like, *J* 9.0). Due to the poor stability of this compound, the elemental analysis was given up.

Generation of Azulenyllithium 6 and the Reaction with Chlorodiphenylphosphine. To a solution of 2-iodoazulene[8] (1.0 mmol) in ether (10 mL) was added *n*-BuLi (1.2 mmol) at −78 °C, and the mixture was stirred for 30 min. A solution of chlorodiphenylphosphine (1.0 mmol) in ether (20 mL) was added dropwise. The reaction mixture was allowed to react at that temperature for 30 min and then allowed to warm to room temperature to react for 2 h. The reaction was then quenched with water, and the resulting mixture was dried with Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel with hexane−AcOEt (1:1) to afford **7**.

(2-Azulenyl)diphenylphosphine (7): blue solid; yield 56%; mp 133−135 °C; ^{1}H NMR δ 7.15 (2H, t, *J* 9.8, AzH), 7.22 (2H, d, J_{PH} 2.4, AzH), 7.35−7.38 (6H, m, PhH), 7.44−7.48 (4H, m, PhH), 7.54 (1H, t, *J* 10.0, AzH), 8.19 (2H, d, *J* 9.6, AzH); ^{31}P NMR δ −14.18 (s). Anal. Calcd for $C_{22}H_{17}P$: C, 84.60; H, 5.49. Found: C, 84.83; H, 5.20.

Oxidation of Azulenylphosphines with H_2O_2. General Procedure. A typical example is exemplified by the reaction of **2a**. To a solution of **2a** (1.0 mmol) in THF (10 mL) was added aqueous 30% H_2O_2 (1.2 mmol) at 0 °C, and the mixture was stirred for 3 h, during which time the temperature was raised to ambient. The reaction was quenched with H_2O, and the mixture was extracted with chloroform (7 mL × 3). Evaporation of the resulting extracts gave a residue, which was crystallized from THF−hexane (4:1) to give **3a**.

(1,3-Dichloro-2-azulenyl)diphenylphosphine oxide (3a): blue solid; yield 96%; mp 208−210 °C; ^{1}H NMR δ 7.18 (2H, t, *J* 10.0, AzH), 7.44−7.48 (4H, m, PhH), 7.53−7.57 (2H, m, PhH), 7.69 (1H, t, *J* 9.9, AzH), 7.75 (4H, m, PhH), 8.39 (2H, d, *J* 9.7, AzH); UV/vis λ_{max}/nm (ϵ) 241 (22 300), 303 (41 160), 312 (37 040), 358 (6620), 374 (3550), 665 (550); ^{31}P NMR δ 22.75 (quintet-like, *J* 12.2); IR/cm^{-1} ν 1580, 1439, 1276, 1186, 1116, 1014. Anal. Calcd for $C_{22}H_{15}Cl_2PO$: C, 66.52; H, 3.81. Found: C, 66.76; H, 3.81.

Bis(1,3-dichloro-2-azulenyl)phenylphosphine oxide (5a): blue solid; yield 95%; mp 295−298 °C; ^{1}H NMR δ 7.17 (4H, t, *J* 9.9, AzH), 7.46−7.51 (2H, m, PhH), 7.58 (1H, t, *J* 6.9, PhH), 7.68 (2H, t, *J* 9.8, AzH), 7.94 (2H, dd, J_{PH} 13.7, J_{HH} 7.3, PhH), 8.39 (4H, d, *J* 9.7, AzH); UV/vis λ_{max}/nm (ϵ) 242 (41 220), 308 (78 770), 318 (92 180), 361 (18 770), 374 (6770), 664 (1280); ^{31}P NMR δ 13.60 (triplet-like, *J* 13.9); IR/cm^{-1} ν 1579, 1398, 1273, 1199, 1019. Anal. Calcd for $C_{26}H_{15}Cl_4PO$: C, 60.50; H, 2.93. Found: C, 60.39; H, 3.03.

(1,3-Dibromo-2-azulenyl)diphenylphosphine oxide (3b): blue solid; yield 93%; mp 214−216 °C; ^{1}H NMR δ 7.25 (2H, t, *J* 10.0, AzH), 7.42−7.47 (4H, m, PhH), 7.52−7.55 (2H, m, PhH), 7.68 (1H, t, *J* 9.9, AzH), 7.72−7.77 (4H, m, PhH), 8.40 (2H, d, *J* 9.8, AzH); UV/vis λ_{max}/nm (ϵ) 241 (23 290), 305 (36 430), 315 (36290), 359 (6240), 375 (3760), 665 (550); ^{31}P NMR δ 24.82 (quintet-like, *J* 12.1); IR/cm^{-1} ν 1580, 1439, 1276, 1186, 1116, 1013. Anal. Calcd for $C_{22}H_{15}Br_2PO$: C, 54.35; H, 3.11. Found: C, 54.36; H, 3.09.

Bis(1,3-Dibromo-2-azulenyl)phenylphosphine oxide (5b): blue solid; yield 92%; mp 230−233 °C; ^{1}H NMR δ 7.29 (4H, t, *J* 10.1, AzH), 7.47−7.51 (2H, m, PhH), 7.59 (1H, t, *J* 6.9, PhH), 7.73 (2H, t, *J* 9.8, AzH), 7.96 (2H, dd, J_{PH} 13.3, J_{HH} 7.6, PhH), 8.46 (4H, d, *J* 9.8, AzH); UV/vis λ_{max}/nm (ϵ) 244 (43 820), 277 (sh, 77 100), 321 (92 860), 363 (sh, 18 490), 376 (sh, 7030), 662 (1280); ^{31}P NMR δ 17.02 (triplet-like, *J* 13.1); IR/cm^{-1} ν 1574, 1458, 1393, 1260, 1199, 1109, 985. Anal. Calcd for $C_{26}H_{15}Br_4PO$: C, 45.00; H, 2.18. Found: C, 45.23; H, 2.13.

(2-Azulenyl)diphenylphosphine oxide (8): blue solid; yield 58%; mp 148−150 °C; ^{1}H NMR δ 7.21 (2H, t, *J* 9.9, AzH), 7.43−7.47 (4H, m, PhH), 7.51−7.55 (2H, m, PhH), 7.57 (2H, d, J_{PH} 5.0, AzH), 7.68 (1H, t, *J* 10.1, AzH), 7.71−7.77 (4H, m, PhH), 8.37 (2H, d, *J* 9.6, AzH); UV/vis λ_{max}/nm (ϵ) 241 (20 030), 287 (62 790), 297 (68 330), 330 (5960), 345 (7800), 640 (560); ^{31}P NMR δ 24.68 (s); IR/cm^{-1} ν 1578, 1436, 1189, 1118. Anal. Calcd for $C_{22}H_{17}PO$: C, 80.48; H, 5.22. Found: C, 80.25; H, 5.53.

Table 4. Selected Crystallographic Data for 3b and 9

	3b	**9**
empirical formula	$C_{22}H_{15}Br_2OP$	$C_{22}H_{16}BrOP$
fw	486.14	407.25
cryst syst	monoclinic	monoclinic
a (Å)	6.707(6)	9.984(5)
b (Å)	31.633(7)	9.519(5)
c (Å)	9.144(3)	18.881(10)
β (deg)	101.34(4)	95.740(2)
V (Å^3)	1902(1)	1785.5(16)
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
Z	4	4
D_{calc} (g cm^{-3})	1.697	1.515
F_{000}	960.00	824.00
μ(Mo Kα) (cm^{-1})	43.67	24.05
temp (K)	298	173
$2\theta_{max}$ (deg)	55.0	57.4
no. of rflns measd		
total; unique	4822; 4720	15 194; 4546
no. of observns	4365 ($I > 2.0\sigma(I)$)	4072 ($I > 2.0\sigma(I)$)
no. of variables	236	227
R indices	$R = 0.114^a$	$R = 0.091^a$
	$R_w = 0.196^b$	$R_1 = 0.046^c$
	$R_1 = 0.060^c$	$wR_2 = 0.110^d$
goodness of fit indicator	0.95	0.955
max. shift/error in final cycle	0.000	0.000
max. and min. peaks in final diff map (e$^-$/Å^3)	1.14; −1.61	0.79; −0.49

[a] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(F_o^2)$. [c] $R_1 = \Sigma||F_o| - |F_c||/|\Sigma|F_o|$. [d] $wR_2 = R_w$.

(1-Bromo-2-azulenyl)diphenylphosphine oxide (9): blue solid; yield 75%; mp 224−226 °C; ^{1}H NMR δ 7.23 (1H, t, *J* 9.7, AzH), 7.29 (1H, t, *J* 9.9, AzH), 7.35 (1H, d, J_{PH} 5.9, AzH), 7.46−7.50 (4H, m, PhH), 7.55−7.59 (2H, m, PhH), 7.70−7.76 (5H, m, AzH, PhH), 8.25 (1H, d, *J* 9.3, AzH), 8.44 (1H, d, *J* 9.9, AzH); UV/vis λ_{max}/nm (ϵ) 240 (25 620), 295 (56 800), 305 (60 240), 338 (sh, 5930), 352 (8410), 664 (550); ^{31}P NMR δ 24.24 (singlet-like); IR/cm^{-1} ν 1575, 1434, 1300, 1195, 1120, 963. Anal. Calcd for $C_{22}H_{16}BrPO$: C, 64.88; H, 3.96. Found: C, 65.17; H, 3.89.

Debromination of 1,3-Dibromoazulene-2-carboxylic Acid. A mixture containing 1,3-dibromoazulene-2-carboxylic acid (1 mmol), triphenylphosphine (2 mmol), and water (5 mmol) was heated in toluene at 90 °C for 48 h. After addition of water, the resulting mixture was extracted with ether (10 mL × 3) and the combined extracts were concentrated to leave a residue, which was purified by column chromatography on silica gel with hexane−AcOEt (1:1) to afford azulene-2-carboxylic acid in 84% yield together with triphenylphosphine oxide (75%).

Azulene-2-carboxylic acid: green solid; mp 200−203 °C, dec (lit.[8] 200−203 °C, dec).

X-ray Crystallography. All measuements were made on a Rigaku AFC5R or AFC8 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a rotating anode generator (Table 4). The data were collected by using the $\omega-2\theta$ scan technique. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods[11] and expanded using Fourier techniques.[12] The non-hydrogen atoms were

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refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in F_{calc};[14] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[15] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[16] All calculations were performed using the teXsan[17] crystallographic software package of Molecular Structure Corporation or using the Crystal Structure[18,19] crystallographic software package.

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Supporting Information Available: Crystal data for compounds **3b** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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