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Synthesis and Properties of Some Sterically Protected 2-(1- and 2-Azulenyl)-1-phosphaethenes

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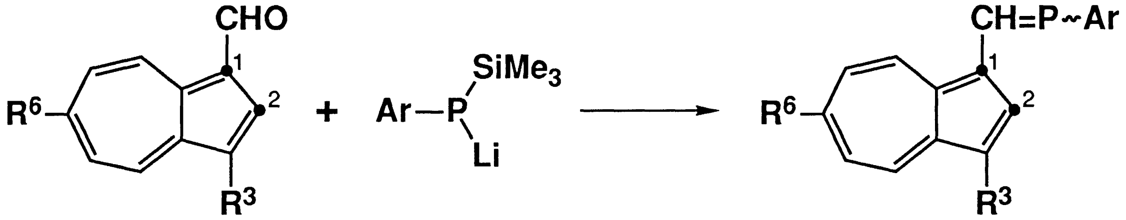
Some sterically protected 2-(1-azulenyl)- and 2-(2-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethenes were prepared from the corresponding silylphosphide and 1- and 2-formylazulenes by the phospha-Peterson reactions. The crystal structure of 2-(6-isopropyl-1-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene was determined by the X-ray analysis.

Great interest has been focused on the chemistry of low-coordinated phosphorus compounds because of their unusual properties and structures.1) Various types of phosphaethenes have been synthesized after the first report by Bickelhaupt *et al.* on the isolation of sterically protected 2,2-diphenyl-1-mesitylphosphaethene in 1978.2) However, no phosphaethenes carrying an azulenyl group3) have yet been reported so far. There can be expected 5 positional isomers for azulenylphosphaethenes on the azulene ring, *i.e.*, 1-, 2-, 4-, 5-, and 6-, with different electronic states. Furthermore, *E*- and *Z*- isomers are possible for each positional isomer and the comparison among these isomers is important to know the properties of phosphaethenes.

We wish to report here the first synthesis of several 2-(1-azulenyl)- and 2-(2-azulenyl)-1-phosphaethenes sterically stabilized with 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) together with the ^{31}P NMR spectral data. Furthermore, the X-ray analysis of (*E*)-2-(6-isopropyl-1-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**3b**) was carried out for the first time.



1 (1-formyl)
2 (2-formyl)

5
Ar = 2,4,6-$Bu^t{}_3C_6H_2$

3 (1-azulenyl)
4 (2-azulenyl)

Several novel phosphaethenes were synthesized by the phospha-Peterson reaction of the corresponding 1- and 2-formylazulenes4,5) with silylphosphide similarly to the previously reported method for the preparation of phosphaethenes.6,7) In a typical preparative experiment, to a stirred solution of 1-formylazulene (**1a**; 1.00 g, 6.40 mmol) in 15 ml of THF (tetrahydrofuran), was added a solution of lithium 2,4,6-tri-*t*-butylphenyltrimethylsilylphosphide (**5**; 1.1 mol equiv.) in THF (10 ml) at 0 °C under argon atmosphere, stirred for 30 min, and warmed to room temperature. After removal of the solvent, the reaction mixture was dissolved in benzene and passed through Celite. The filtrate was chromatographed on an alumina column twice and the

Table 1. Properties of Some (1- and 2-Azulenyl)-1-phosphaethenes **3** and **4**

R^3	R^6	Formyl-azulene	Phospha-ethene	Yield$^{a)}$ / %	Mp / °C$^{b)}$	^{31}P NMR / δ ($^2J_{PH}$ /Hz)$^{c)}$ *E*-Form	Z-Form
H	H	**1a**	**3a**	21 (20:1)	153–154	238.2 (24.5)	216.6 (37.7)
H	*i*-Pr	**1b**	**3b**	67 (28:1)	149–151	235.1 (24.4)	213.2 (35.9)
Et	*i*-Pr	**1c**	**3c**	50 (27:1)	159–161	232.4 (24.2)	211.7 (36.9)
Ph	*i*-Pr	**1d**	**3d**	59 (22:1)	167–169	237.2 (24.3)	216.4 (37.3)
H	H	**2a**	**4a**	19	230–231	279.8 (24.4)	—
H	*i*-Pr	**2b**	**4b**	22	190–191	274.4 (24.8)	—

a) Isolated yield, base on formylazulenes. The ratio in parentheses denotes the molar ratio of *E* : *Z* according to the ^{31}P NMR of the crude reaction mixture but no Z-isomer was detected in the cases of **4a** and **4b**. b) Melting point of the *E*-isomer. c) Measured at 81 MHz in $CDCl_3$.

resulting green material was chromatographed on a preparative HPLC column (Merck, LiChroprep NH_2, B-column, hexane). 2-(1-Azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (**3a**) was obtained in 21% yield (0.56 g, 1.35 mmol). Recrystallization from ethyl acetate gave pure *E*-**3a**, as the major isomer of green prisms of mp 153 – 154 °C. In order to define the configuration around the P=C double bond, we applied the empirical *cis rule* which states that nuclei have a larger coupling to phosphorus, if they are cis relative to the phosphorus lone pair,$^{8)}$ and that the ^{31}P NMR chemical shifts of *Z* isomers appear in the higher field than those of *E*.$^{7a)}$ Table 1 shows some properties of phosphaethenes **3** and **4** carrying azulenyl group thus prepared.

In order to obtain insight into the ^{31}P NMR characters of the azulenylphosphaethenes, 1-naphthyl and 2-naphthyl (Np) derivatives were prepared according to the similar method from the corresponding naphthaldehydes. 1-NpCH=PAr: 62% yield (*E*:*Z*, 19:1; pale yellow), mp (*E*) 130 – 131 °C, $\delta_P(E)$ 263.8 ($^2J_{PH}$ 24.3 Hz), $\delta_P(Z)$ 249.1 (35.6 Hz). 2-NpCH=PAr: 37% yield (*E*:*Z*, 9:1; pale yellow), mp (*E*) 185 – 186 °C, $\delta_P(E)$ 261.5 ($^2J_{PH}$ 25.2 Hz), $\delta_P(Z)$ 243.5 (38.0 Hz). Chemical shifts of the naphthyl derivatives are similar to those for the phenyl derivatives; $\delta_P(E)$ 259.3 ($^2J_{PH}$ 26.9 Hz), $\delta_P(Z)$ 241.6 (39.1 Hz).$^{7a)}$ It should be noted here that 1-azulenylphosphaethenes **3a-d** resonate at higher field by 25 – 30 ppm in the ^{31}P NMR than the naphthyl or phenyl derivatives, while the 2-azulenyl derivative **4a,b** resonate at lower field by *ca.* 20 ppm, indicating that 1-azulenyl group is more electron donating than 2-azulenyl group owing to the existence of a canonical structure causing negative charge at the phosphorus atom.$^{9)}$

Furthermore, the structure of (*E*)-2-(6-isopropyl-1-azulenyl)-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**3b**) was unambiguously determined by the X-ray crystallographic analysis. Figure 1 depicts the ORTEP drawing$^{10)}$ of the molecular structure and Fig. 2 shows a stereoscopic view of the crystal structure of **3b**. Due to the strong intermolecular dipole interaction$^{3)}$ between the two azulene rings related by a center of symmetry, a dimer-like structure is formed in the crystal by the parallel overlapping stacks of the planar azulene rings within 0.034(4) Å. The stacking distance between the azulene rings of this centrosymmetric dimer is 3.502(2) Å with the shortest interatomic distance of 3.556(5) Å between C1 and C4' (Fig. 2).$^{11)}$ The Ar ring is only slightly deformed into a boat form,$^{12)}$ since the atoms C16, C17, C19, and C20 are coplanar within 0.007(3) Å and this plane makes angles of 5.8° and 1.3° with the planes (C15, C20, C16) and (C17, C18, C19), respectively. Dihedral angles ∠C1-C14-P-C15, −172.1(2)°, ∠C14-P-C15-C16, 84.4(2)°, and ∠P-C14-C1-C2, 12.7(4)° indicate that the azulene ring deviates considerably from the approximate mirror plane of Ar-P moiety which goes

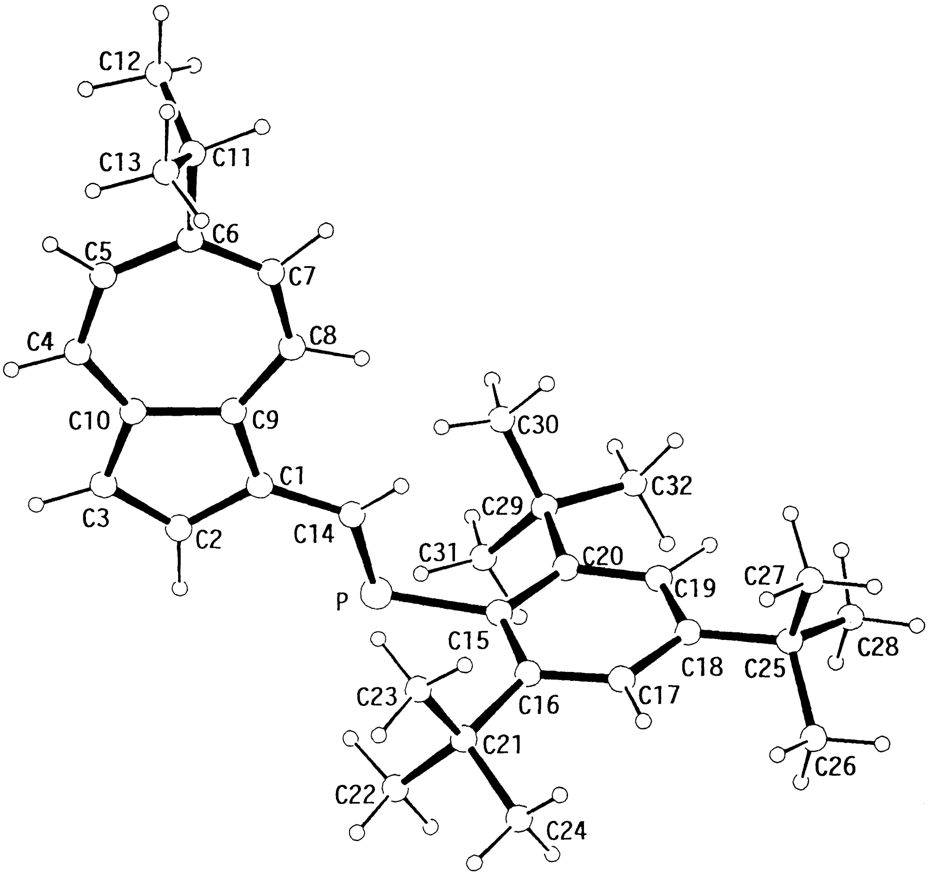


Fig. 1. Molecular structure of **3b** showing the atomic labelling scheme. Selected bond lengths and angles: P–C14, 1.666(3); C1–C14, 1.444(3); P–C15, 1.850(2); C1–C2, 1.418(4); C2–C3, 1.367(4); C3–C10, 1.411(5); C9–C10, 1.470(3); C1–C9, 1.409(4) Å; ∠P-C14-C1, 123.7(2); ∠C15-P-C14, 102.9(1); ∠C2-C1-C9, 107.1(2); ∠C2-C1-C14, 125.0(3); ∠C9-C1-C14, 127.9(3)°.

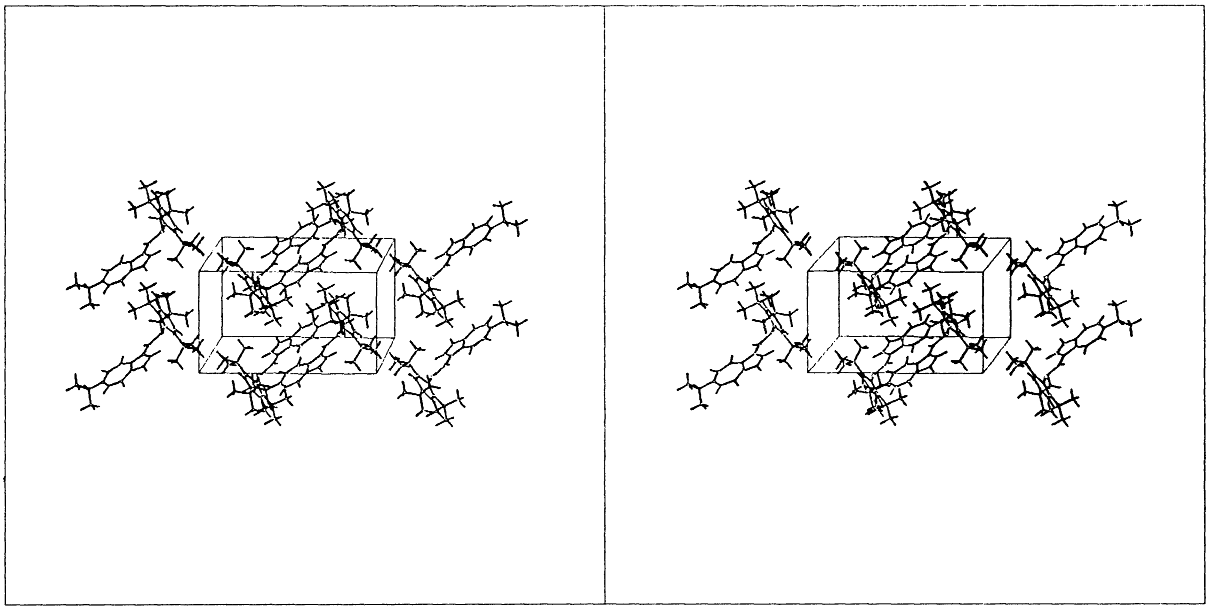


Fig. 2. Stereoscopic view of the crystal structure of **3b**; *c* is vertical, *b* is horizontal, and *a* is out of the plane of the paper.

through C15 and C18 and is perpendicular to the benzene ring, probably due to the intermolecular interaction of the azulene rings. The azulene ring makes an angle of 19.3° with the plane (C1, C14, P, C15), indicating that the coplanarity of azulenyl group and CH=P is not ideal. It should be noted here that C1–C14 (1.444(3) Å) is shorter than the corresponding bond length of C–Ph (1.464(8) Å) for ArP=C(H)Ph,[7b)] indicating some dipolar contribution of a tropylium phosphide type in **3b** as has also been suggested from the upfield shift in ^{31}P NMR.

X-Ray analysis of **3b** is as follows:[13)] $C_{32}H_{43}P$, $M = 458.67$, triclinic, recrystallized from ethanol, space group, $P\bar{1}$, $a = 10.186(2)$, $b = 16.317(4)$, $c = 9.392(2)$ Å, $\alpha = 90.40(2)$, $\beta = 108.91(2)$, $\gamma = 103.20(2)°$, $U = 1432.2(6)$ Å^3, $Z = 2$, $Dc = 1.064$ g cm^{-3}, $\mu = 0.11$ mm^{-1}. 4926 Reflections with $2\theta \leq 50°$ were recorded on a four circle diffractometer using graphite-monochromated Mo-$K\alpha$ radiation. Of these, 3547 [with $I > 3\sigma(I)$] were judged as observed. The structure was solved using SHELX.[14)] All hydrogen atoms could be located on a difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to $R = 0.057$ and $R_w = 0.064$.[15)]

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