On the Reaction of *N*-Vinyliminophosphoranes. Part 16.[1] A New Synthesis of 5*H*-Indeno[1,2-*b*]pyridines and 5*H*-Indeno[1,2-*b*]pyridin-5-ones

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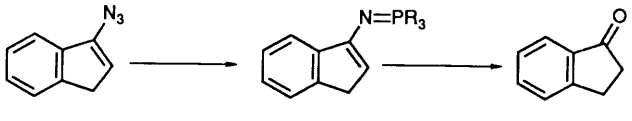
Thermal reaction of tributyl(inden-3-ylimino)phosphorane with α,β-unsaturated ketones and aldehydes led to a Michael-type C–C bond formation and subsequent aza-Wittig reaction to give 5*H*-indeno(1,2-*b*)pyridines in good to modest yield. The products were oxidized conveniently by chromium trioxide and t-butyl hydroperoxide to give 5*H*-indeno[1,2-*b*]pyridin-5-ones, including the 4-azafluorenone alkaloid onychine.

The 4-azafluorenone (5*H*-indeno[1,2-*b*]pyridin-5-one) alkaloids isolated from Annonaceae species comprise a small but biologically intriguing group of alkaloids. This class of alkaloids has been postulated to be derived from aporphine precursors.[2] Subsequent to the initial isolation and structural misassignment of onychine (4-methyl-5*H*-indeno[1,2-*b*]pyridin-5-one),[3] the structure of this alkaloid was confirmed by synthesis,[4–6] and the isolation[7–9] and synthesis of other 4-azafluorenones[8–10] have been explored. Several approaches have been developed for the synthesis of the 5*H*-indeno[1,2-*b*]pyridin-5-ones: oxidative thermal rearrangement of 2-indanone oxime *O*-allyl ethers, albeit in low yields;[4,9,11] direct cyclization of 2-aryl-3-methylpyridines to give 5*H*-indeno[1,2-*b*]pyridines followed by oxidation;[5,11] cyclization of 2-aryl-3-nicotinic acids by use of polyphosphoric acid.[6,8] Several other approaches have been studied.[12]

We have recently demonstrated the simple preparation of *N*-vinyliminophosphoranes, which were found to react with α-bromo ketones, α,β-unsaturated ketones, and activated tropones in an enamine-type alkylation (Michael addition) followed by aza-Wittig reaction to provide convenient routes to pyrroles,[13] pyridines,[14] [*n*](2,4)pyridinophanes,[15] and 1-azaazulenes.[16] As an extension of our studies on the synthetic utility of *N*-vinyliminophosphoranes, we have examined the reaction of tributyl(inden-3-ylimino)phosphorane **2b**[17] with α,β-unsaturated ketones and aldehydes to provide a convenient route to 5*H*-indeno[1,2-*b*]pyridines, which were conveniently oxidized to 5*H*-indeno[1,2-*b*]pyridin-5-ones, including the 4-azafluorenone alkaloid onychine **12e**. We describe here our results in detail.

Results and Discussion

The (inden-3-ylimino)triphenylphosphorane **2a** and tributyl(inden-3-ylimino)phosphorane **2b**[17] were easily prepared by Staudinger reaction of readily available 3-azidoindene **1**[18] with triphenylphosphine and tributylphosphine, respectively, in anhydrous solvent. The phosphoranes **2a** and **2b** were easily hydrolysed in acidic media to give indan-1-one **3** (Scheme 1).



1 **2a**; R = Ph, **b**; R = Bu **3**

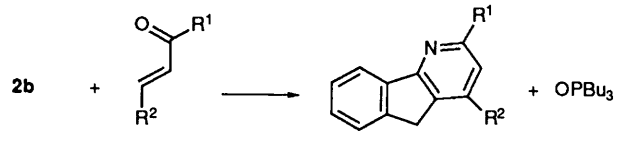
Scheme 1

The phosphorane **2a** is stable under work-up conditions and satisfactory physical data were obtained. On the other hand, the phosphorane **2b** was not stable under work-up conditions and satisfactory analytical data were not obtained. However, the acid hydrolysis and comparison of the assigned ^{1}H NMR data of compound **2b** with those of the triphenyl analogue **2a** clearly support the structure of compound **2b**. Since the phosphorane **2a** seemed to be less reactive as compared with the butyl analogue **2b**, the synthetic reactions were examined conveniently by using *in situ* butyl derivative **2b** in a one-pot procedure without isolation.[17]

Table 1 Reaction of the phosphorane **2b** with α,β-unsaturated ketones **4a–d** and aldehydes **4e** and **f**

Entry	Substrate	Solvent	Reaction time (*t*/h)	Product (**5**) yield (%)
1	**4a**	PhMe	17	**5a** (80)
2	**4b**	PhH	4	**5b** (78)
3	**4c**	PhMe	20	**5c** (85)
4	**4d**	PhH	22	**5d** (84)
5	**4e**	PhMe	18	**5e** (49)
6	**4f**	PhH	9	**5f** (10), **5b** (30)

When a solution of 3-azidoindene **1** and tributylphosphine in anhydrous benzene or toluene was stirred at 0 °C, the reaction proceeded easily with complete disappearance of **1** within 30 min. To this reaction mixture were added an α,β-unsaturated ketone **4a–d** or an aldehyde **4e** or **4f** and 5 mol% of Pd–C, and the mixture was heated under reflux to give a 5*H*-indeno[1,2-*b*]pyridine derivative **5a–f** and tributylphosphine oxide (Scheme 2). The results are summarized in Table 1. In the case



4a – f **5a – f**

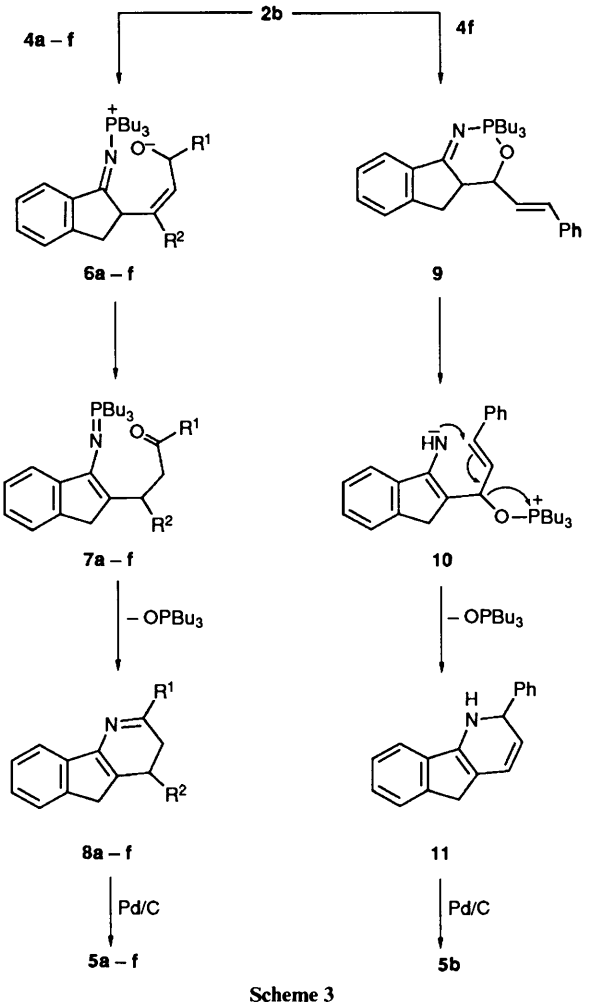
a; R^1 = Me, R^2 = H **b**; R^1 = Ph, R^2 = H
c; R^1 = Ph, R^2 = Ph **d**; R^1 = Me, R^2 = Ph
e; R^1 = H, R^2 = Me **f**; R^1 = H, R^2 = Ph

Scheme 2

of ketones **4a–d** (entries 1–4), products **5a–d** were obtained in good yield. In the case of aldehyde **4e**, on the other hand, 4-methyl-5*H*-indeno[1,2-*b*]pyridine **5e**, which is a precursor of onychine, was obtained in modest yield (entry 5). In contrast, the reaction with cinnamaldehyde **4f** resulted in the formation of two products, the expected 4-phenyl compound **5f** and unexpected 2-phenyl isomer **5b** in a modest combined yield (entry 6).

The structure of each of the known compounds **5a–e**, but not that of compound **5f**, has been characterized by comparison of their physical data with those reported in the literature (see Experimental section). The structure of compound **5f** was assigned on the basis of elemental analyses of the picrate, and high-resolution mass, IR and ^{1}H NMR spectra. Comparison of the assigned ^{1}H NMR spectrum of compound **5f** with those of compounds **5a–e** easily revealed the structure of the former.

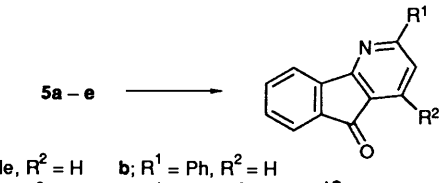
The formation of compounds **5a–f** is explained by the mechanism shown in Scheme 3. The initial step is the enamine-



Scheme 3

type alkylation (Michael addition) of substrate **2b** onto the β-carbon atom of enones **4a–f** to give intermediates **6a–f**, which undergo hydrogen migration to generate iminophosphoranes **7a–f**. Intramolecular aza-Wittig reaction then gives the dihydropyridines **8a–f**, which are dehydrogenated with Pd–C to give the 5*H*-indeno[1,2-*b*]pyridines **5a–f**. In the case of cinnamaldehyde **4f**, addition of the β-carbon atom of the phosphoranimine **2b** to the carbonyl carbon of aldehyde **4f** leading to the cyclic intermediate **9** occurs in addition to the Michael addition. We propose that the intermediate **9** then undergoes hydrogen migration and N–P bond cleavage to give the internal salt **10**, cyclization of which occurs to generate the dihydropyridine **11**, which is dehydrogenated with Pd–C to give compound **5b**. The Michael addition is frontier orbital controlled,[19] and is favoured with the ketones **4a–d** and aldehyde **4e**. In the case of cinnamaldehyde **4f**, however, the charge-controlled reaction or the lower steric hindrance of the formyl group in **4f** might cause the formation of the additional product **5b**. Results similar to the present case have been reported previously.[14,20]

Treatment of compounds **5a–e** with 10 mol% of CrO_3 and 7-fold excess of Bu^{t}OOH[21] in CH_2Cl_2 afforded 5*H*-indeno[1,2-*b*]pyridin-5-ones **12a–e** (Scheme 4, Table 2). In the



a; R^1 = Me, R^2 = H **b**; R^1 = Ph, R^2 = H
c; R^1 = Ph, R^2 = Ph **d**; R^1 = Me, R^2 = Ph
e; R^1 = H, R^2 = Me

Scheme 4 *Reagents:* CrO_3, Bu^{t}OOH

case of substrate **5e**, however, a modest yield of onychine **12e** was obtained. Even prolonged heating did not result in a high yield of onychine. Structural assignment of products **12a–e** was based on comparison of the physical data with those reported in the literature (see Experimental section).

Indene derivatives are widely available, hence the present methodology using tributyl(inden-3-ylimino)phosphorane can serve as a novel and convenient route to 5*H*-indeno[1,2-*b*]pyridine and 5*H*-indeno[1,2-*b*]pyridin-5-one derivatives.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Hitachi R-24 and Hitachi R-90H spectrometers and the chemical shifts are given relative to internal $SiMe_4$ standard. *J*-Values are given in Hz. High-resolution mass spectra were run on a JEOL DX-300 spectrometer. Microanalyses were performed at the Science and Engineering Research Laboratory of Waseda University. M.p.s were measured on a Büchi apparatus and are uncorrected.

Preparation of Phosphoranes **2a** *and* **2b**.—A solution of azidoindene **1**[18] (391 mg, 2.5 mmol) and triphenylphosphine (622 mg, 2.5 mmol) in anhydrous benzene (7 cm^3) was stirred at room temperature for 1 h. After the benzene was evaporated off, the residue was crystallized from benzene–hexane to give *compound* **2a** as crystals, m.p. 126–127 °C; δ_H($CDCl_3$; 90 MHz) 3.10 (2 H, br s, 1-H), 4.79 (1 H, d, *J* 1.8, 2-H) and 7.00–7.90 (19 H, m, 4-, 5-, 6- and 7-H and Ph); δ_C($CDCl_3$; 22.6 MHz) 35.31 (1 C, s, C-1), 105.13 (1 C, d, J_{PC} 9.7, C-2), 118.94 (1 C, tert-C), 122.78 (1 C, d, J_{PC} 1.4, C-4), 123.76 (1 C, tert-C), 125.34 (1 C, tert-C), 128.21 (6 C, d, J_{PC} 12.4, Ph), 130.65 (3 C, d, J_{PC} 98.1, Ph), 131.35 (3 C, d, J_{PC} 2.8, Ph), 132.48 (6 C, d, J_{PC} 9.7, Ph), 143.42 (1 C, d, J_{PC} 1.4, C-7a), 147.14 (1 C, d, J_{PC} 23.5, C-3a) and 149.29 (1 C, d, J_{PC} 2.1, C-3); ν_{max}($CHCl_3$)/cm^{-1} 3060, 3002, 1597, 1562, 1446, 1349, 1309, 1266, 1141, 1108 and 980; *m/z* 392 (M + 1, 21), 391 (M$^+$, 75) and 183 (100%) (Found: M$^+$, 391.1485. $C_{27}H_{22}NP$ requires M, 391.1492).

A solution of the phosphorane **2b**[17] in $CDCl_3$ was prepared in a ^{1}H NMR tube and exhibited the following spectral data: δ_H($CDCl_3$; 60 MHz) 0.65–1.85 (27 H, m, Bu^t), 3.35 (2 H, br s, 1-H), 4.97 (1 H, br s, 2-H), 6.70–7.50 (3 H, m, 4-, 5- and 6-H), 7.72–7.98 (1 H, m, 7-H) (Found: M$^+$, 331.2421. Calc. for $C_{21}H_{34}NP$: M, 331.2421).

Hydrolysis of Phosphoranes **2a** *and* **2b**.—(*A*) A solution of compound **2a** (78 mg, 0.2 mmol) in ethanolic H_2SO_4 [0.5 mol dm^{-3}; water–EtOH (1:9)] (3 cm^3) was heated under reflux for 7 h. The reaction mixture was then neutralized with aq. $NaHCO_3$ and extracted with CH_2Cl_2. After the extract was dried over $MgSO_4$, CH_2Cl_2 was evaporated off and the resulting residue was separated by TLC on silica gel with hexane–AcOEt (3:1) as a developer to give indan-1-one **3** (16 mg, 61%) and triphenylphosphine oxide (50 mg, 95%).

(*B*) To a solution of the phosphorane **2b**, which was prepared

Table 2 Oxidation of compounds **5a–e** with CrO_3–Bu^{t}OOH

Entry	Substrate	Solvent	Reaction time (t/h)	Product yield (%)	Recovery of substrate **5** (%)
1	**5a**	CH_2ClCH_2Cl	3	62	13
2	**5b**	CH_2Cl_2	3	89	6
3	**5c**	CH_2Cl_2	22	88	8
4	**5d**	CH_2Cl_2	5	73	14
5	**5e**	CH_2Cl_2	8	33	36

by reaction of the azide **1** (32 mg, 0.2 mmol) and tributylphosphine (40 mg, 0.2 mmol) in benzene (2 cm^3) at room temperature, was added hydrochloric acid (2 mol dm^{-3}; 0.2 cm^3). Then the mixture was heated under reflux for 1 h. The reaction mixture was neutralized with aq. $NaHCO_3$, extracted with benzene, and the extract was dried over Na_2SO_4. After the benzene was evaporated off, the residue was separated by TLC on silica gel with hexane–AcOEt (3:1) as a developer to give the ketone **3** (17 mg, 65%) and tributylphosphine oxide (19 mg, 44%).

General Procedure for the Reaction of Phosphorane **2b** *with* α,β-*Unsaturated Ketones* **4a–d** *and Aldehydes* **4e** *and* **4f**.—To a solution of 3-azidoindene[19] (188 mg, 1.2 mmol) in dry benzene or toluene (5 cm^3) was added tributylphosphine (202 mg, 1 mmol) and the mixture was stirred for 30 min at 0 °C to give compound **2b**. To this solution were added a ketone **4a–d** or aldehyde **4e** or **4f** (0.5 mmol) and 10% Pd/C (25 mg, 0.025 mmol of Pd) was added and the mixture was refluxed under nitrogen for the period indicated in Table 1. The reaction mixture was concentrated and the resulting residue was separated by TLC on silica gel with hexane–AcOEt (10:1) as developer to give the corresponding tricycle **5a–f**, along with tributylphosphine oxide (60–90%). The results are summarized in Table 1.

For 2-methyl-5*H*-indeno[1,2-*b*]pyridine **5a**: oil (lit.,[5] m.p. 27–30 °C); δ_H($CDCl_3$; 60 MHz) 2.56 (3 H, s, Me), 3.55 (2 H, s, 5-H), 6.81 (1 H, d, *J* 8.0, 3-H), 7.12–7.58 (3 H, m, 6-, 7- and 8-H), 7.80 (1 H, d, *J* 8.0, 4-H) and 8.17–8.37 (1 H, m, 9-H); ν_{max}($CHCl_3$)/cm^{-1} 3051, 2930, 1710, 1601, 1575, 1445, 1264 and 740.

For 2-phenyl-5*H*-indeno[1,2-*b*]pyridine **5b**: m.p. 119.4–120.5 °C (from EtOH) (lit.,[22] 126–128 °C); δ_H($CDCl_3$; 60 MHz) 3.80 (2 H, s, 5-H_2), 7.12–7.82 (8 H, m, 3-, 4-, 6-, 7- and 8-H and Ph) and 7.98–8.23 (3 H, m, 9-H and Ph); ν_{max}($CHCl_3$)/cm^{-1} 3012, 1601, 1570, 1475, 1424, 1415, 1189 and 1072.

For 2,4-diphenyl-5*H*-indeno[1,2-*b*]pyridine **5c**: m.p. 151.2–152.5 °C (from EtOH) (lit.,[11] 157.5–158 °C); δ_H($CDCl_3$; 60 MHz) 3.81 (2 H, s, 5-H_2), 7.06–7.64 (12 H, m, 3-, 6-, 7- and 8-H and Ph) and 7.92–8.24 (3 H, m, 9-H and Ph); ν_{max}($CHCl_3$)/cm^{-1} 2691, 1437, 1426, 1341, 1217 and 1028.

For 2-methyl-4-phenyl-5*H*-indeno[1,2-*b*]pyridine **5d**: m.p. 216–217.5 °C (from EtOH) (lit.,[23] 217–218 °C); δ_H($CDCl_3$; 60 MHz) 2.59 (3 H, s, Me), 3.68 (2 H, s, 5-H), 6.90 (1 H, s, 3-H), 7.10–7.57 (8 H, m, 6-, 7- and 8-H and Ph) and 7.95–8.19 (1 H, m, 9-H); ν_{max}($CHCl_3$)/cm^{-1} 2941, 1593, 1563, 1501, 1452, 1381, 1263, 1189, 1072 and 869.

For 4-methyl-5*H*-indeno[1,2-*b*]pyridine **5e**: m.p. 90.5–96 °C (from EtOH) (lit.,[5] 97–99 °C); δ_H($CDCl_3$; 60 MHz) 2.21 (3 H, s, Me), 3.47 (2 H, s, 5-H), 6.70 (1 H, d, *J* 5.6, 3-H), 7.16–7.48 (3 H, m, 6-, 7- and 8-H), 7.80–8.05 (1 H, m, 9-H) and 8.21 (1 H, d, *J* 5.6, 2-H); ν_{max}($CHCl_3$)/cm^{-1} 2954, 1601, 1455, 1384 and 1072.

For 4-*phenyl*-5H-*indeno*[1,2-b]*pyridine* **5f**: δ_H($CDCl_3$; 90 MHz) 3.79 (2 H, br s, 5-H), 7.01 (1 H, d, *J* 5.1, 3-H), 7.26–7.64 (8 H, m, 6-, 7- and 8-H and Ph), 8.05–8.15 (1 H, m, 9-H) and 8.47 (1 H, d, *J* 5.1, 1-H); ν_{max}($CHCl_3$)/cm^{-1} 2892, 1566, 1445, 1334, 1157, 1075 and 823 (Found: M^+, 243.1046. $C_{18}H_{13}N$ requires M, 243.1049). *Picrate*: m.p. 207–208 °C (Found: C, 61.1; H, 3.75; N, 11.95. $C_{24}H_{16}N_4O_7$ requires C, 61.0; H, 3.4; N, 11.9%).

General Procedure for the Oxidation of Indenopyridines **5a–e** *with* CrO_3–Bu^{t}OOH.—A solution of indenopyridine (0.5 mmol), CrO_3 (5 mg, 0.05 mmol) and Bu^{t}OOH (3.5 mmol) in anhydrous CH_2Cl_2 or CH_2ClCH_2Cl (3 cm^3) was stirred under reflux for the period indicated in Table 2. After the reaction mixture had been washed with water, the extract was dried over Na_2SO_4 and then concentrated. The residue was separated by TLC on silica gel with hexane–AcOEt (2:1) or CH_2Cl_2 as developer to give 5*H*-indeno[1,2-*b*]pyridin-5-ones **12a–e**. The results are summarized in Table 2.

For 2-methyl-5*H*-indeno[1,2-*b*]pyridin-5-one **12a**: m.p. 116–118 °C (from EtOH) (lit.,[5] 104–105 °C); δ_H($CDCl_3$; 60 MHz) 2.55 (3 H, s, Me), 7.06 (1 H, d, *J* 7.4, 3-H) and 7.23–7.91 (5 H, m, 4-, 6-, 7-, 8- and 9-H); ν_{max}($CHCl_3$)/cm^{-1} 2972, 1716, 1580, 1419, 1257, 1174 and 1099.

For 2-Phenyl-5*H*-indeno[1,2-*b*]pyridin-5-one **12b**: m.p. 146–147.5 °C (from EtOH) (lit.,[24] 146–147 °C); δ_H($CDCl_3$; 60 MHz) 7.09–8.19 (11 H, m); ν_{max}($CHCl_3$)/cm^{-1} 2993, 1716, 1575, 1416, 1263, 1101 and 917.

For 2,4-diphenyl-5*H*-indeno[1,2-*b*]pyridin-5-one **12c**: m.p. 162.5–163.5 °C (from EtOH) (lit.,[11] 163–164.5 °C); δ_H($CDCl_3$; 60 MHz) 7.19–7.71 (12 H, m, 3-, 7-, 8- and 9-H and Ph) and 7.79–8.24 (3 H, m, 6-H and Ph); ν_{max}($CHCl_3$)/cm^{-1} 3002, 1708, 1550, 1363, 1270 and 928.

For 2-methyl-4-phenyl-5*H*-indeno[1,2-*b*]]pyridin-5-one **12d**: m.p. 115.5–116.7 °C (from EtOH) (lit.,[23] 119–120 °C); δ_H($CDCl_3$; 60 MHz) 2.59 (3 H, s, Me), 6.89 (1 H, s, 3-H) and 7.20–7.94 (9 H, m, 6-, 7-, 8- and 9-H and Ph); ν_{max}($CHCl_3$)/cm^{-1} 3001, 1715, 1593, 1550, 1378, 1273, 1172 and 891.

For 4-methyl-5*H*-indeno[1,2-*b*]pyridin-5-one **12e**: m.p. 125–127 °C (from EtOH) (lit.,[5] 134–135 °C); δ_H($CDCl_3$; 60 MHz) 2.53 (3 H, s, Me), 6.70 (1 H, d, *J* 5.8, 3-H), 6.99–7.91 (4 H, m, 6-, 7-, 8- and 9-H) and 8.29 (1 H, d, *J* 5.8, 2-H); ν_{max}($CHCl_3$)/cm^{-1} 2933, 1703, 1601, 1566 and 918.

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