On the Reaction of *N*-Vinyliminophosphoranes. Part 11.[1] Convenient Synthesis of 9*H*-Cyclohepta[*b*]pyridines and Pyridotropones

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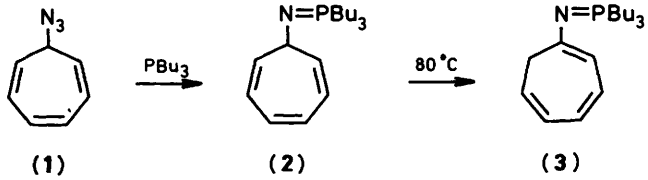
Thermal reaction of tributyl(cyclohepta-1,3,5-trienylimino)phosphorane with α,β-unsaturated ketones led to a Michael-type C–C bond formation and subsequent aza-Wittig reaction to give 9*H*-cyclohepta[*b*]pyridine derivatives in good yields. The 9*H*-cyclohepta[*b*]pyridine derivatives were oxidized conveniently by t-butyl hydroperoxide in the presence of catalytic chromium trioxide to give two or three isomers of the pyridotropones in good to moderate combined yields.

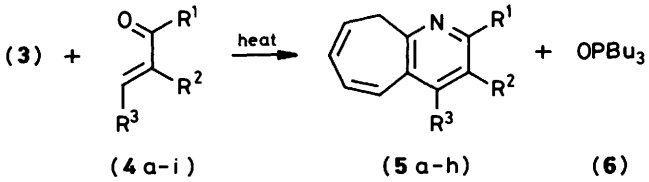
The convenient preparation of iminophosphoranes, from organic azides and tertiary phosphines (the Staudinger reaction),[2] and their synthetic utility have recently attracted considerable attention. The hydrolysis to amines or ketones,[3] and the oxidation to nitro compounds[4] are well recognized. The intermolecular[5] and intramolecular[6] aza-Wittig type reaction have high potential utility in the synthesis of nitrogen heterocycles. In connection with these studies, we have recently demonstrated the simple preparation of *N*-vinyliminophosphoranes,[7–11] which were found to react with α-bromo ketones.[8] α,β-unsaturated ketones,[9,10] and tropone derivatives[11] in an enamine alkylation process followed by aza-Witting reaction to provide convenient routes to pyrroles, pyridines, and 1-aza-azulenes. However, the potential value of the *N*-vinyliminophoranes bearing a cycloalkene residue on the nitrogen atom remains unexplored. As part of a series of studies on *N*-vinyliminophosphoranes, we have recently prepared tributyl(cyclohepta-1,3,5-trienylimino)phosphorane (**3**) in good yield *via* the Staudinger reaction of 7-azidocyclohepta-1,3,5-triene[12] and subsequent thermal hydrogen migration (Scheme 1).[13] The compound (**3**) reacted with α-bromoacetophenone derivatives to give 1-aza-azulene derivatives, albeit in low yields.[13]



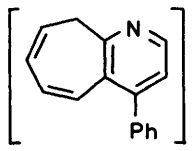
(1) (2) (3)

Scheme 1.

Recently, Jones and co-workers have reported the general preparation of the tropones annelated with benzene, furan, thiophene, and pyridine starting from the corresponding annelated cycloheptenones by bromination–dehydrobromination sequences, and they have investigated the chemical properties of these tropones.[14] Although pyridotropones have been prepared previously,[14,15] the multi-step preparative methods have accompanied modest overall yields. In addition, a few examples of cycloheptapyridines have been reported.[16] As an extension of our studies on the synthetic utility of (**3**), we have examined the reaction of (**3**) with α,β-unsaturated ketones to provide a convenient route to 9*H*-cyclohepta[*b*]pyridine derivatives, which were easily oxidized to give two or three isomers of the pyridotropone derivatives. We describe here the results in detail.



(4 a-i) (5 a-h) (6)



(5i)

a: R^1 = Ph, R^2 = R^3 = H
b: R^1 = Me, R^2 = R^3 = H
c: R^1 = Ph, R^2 = Me, R^3 = H
d: R^1 = Ph, R^2 = H, R^3 = Me
e: R^1 = Me, R^2 = H, R^3 = Ph
f: R^1 = Ph, R^2 = H, R^3 = Ph
g: R^1,R^2 = $-(CH_2)_3-$, R^3 = H
h: R^1,R^2 = $-(CH_2)_4-$, R^3 = H
i: R^1 = R^2 = H, R^3 = Ph

Scheme 2.

Results and Discussion

The thermal reactions of the iminophosphorane (**3**) with α,β-unsaturated ketones (**4a–i**) were examined in anhydrous solvent (benzene or toluene) in the presence of 5 mol% of Pd–C under reflux to give 9*H*-cyclohepta[*b*]pyridine derivatives (**5a–h**) and tributylphosphine oxide (**6**) (Scheme 2). The results are summarized in Table 1. The phosphorane (**3**) reacted rapidly with (**4a**) in benzene to give (**5a**) in good yield (entry 1). In the reaction of volatile (**4b**) with (**3**), an excess of (**4b**) was used to give a better yield of (**5b**). In the reaction of (**3**) with (**4c–f**), all of which are substituted on the double bond, use of 1 mol equiv. of (**3**) resulted in poor yields of (**5c–f**) even in refluxing toluene, and unchanged starting materials (**4c–f**) were recovered (entries 3–6). However, use of 2 mol equiv. of (**3**) gave better yields of (**5c–f**) (entries 7–10). The present reactions are quite general, and 2-methylenecycloalkanones (**4g, h**) were also treated with (**3**) to give the cycloalkeno[*b*]cyclohepta[*e*]pyridines (**5g, h**), albeit in modest yields (entries 11 and 12). On the other hand, the reaction of the aldehyde (**4i**) with (**3**) afforded (**5a**) instead of the expected (**5i**) (entry 13).

Table 1. Reaction of phosphorane (3) with α,β-unsaturated ketones (4a–i)

Entry	Ketone	Mol equiv. of (3)	Conditions: Solvent	Conditions: Reaction time (h)	Product yield (%) (5)	Recovery of (4) (%)
1	(4a)	1	PhH	2	(5a) 79	—
2	(4b)	$\frac{1}{3}$	PhH	24	(5b) 49	—
3	(4c)	1	Toluene	60	(5c) 59	11
4	(4d)	1	Toluene	24	(5d) 64	7
5	(4e)	1	Toluene	24	(5e) 48	19
6	(4f)	1	Toluene	24	(5f) 45	49
7	(4c)	2	Toluene	48	(5c) 66	—
8	(4d)	2	Toluene	24	(5d) 89	—
9	(4e)	2	Toluene	24	(5e) 61	—
10	(4f)	2	Toluene	24	(5f) 76	—
11	(4g)	1	Toluene	24	(5g) 31[a]	—
12[b]	(4h)	1	Toluene	24	(5h) 17	—
13	(4i)	2	Toluene	24	(5a) 21	—

[a] Yield was not decreased in the absence of Pd–C. [b] Reaction was carried out in the absence of Pd–C.

Table 2. Oxidation of cyclohepta[*b*]pyridines (5a, b, f) with CrO_3–t-BuOOH.

Entry	Starting (5)	Reaction time (h)	Product yield (%): (15)	(16)	(17)
1	(5a)	24	13	21	36
2	(5b)	24	18	44	0
3	(5f)	96	0	22	24

The structures of the new compounds (5a–h) were determined on the basis of elemental analyses and high-resolution mass, IR and ^{1}H NMR spectral data. Each of the ^{1}H NMR spectra of (5a–h) showed, besides signals for the substituted pyridine ring, five characteristic signals for the cycloheptatriene ring. The assignments of the signals are summarized in the Experimental section. Furthermore, the methylene signals (9-H) of (5a–h), already appearing at relatively low field, are shifted to much lower field compared to those for 5-H and 6-H in the pseudo-contact ^{1}H NMR spectrum obtained by using Eu(fod)$_3$. These facts are consistent with the view that (5a–h) are the 9*H*- rather than the 5*H*-isomers.

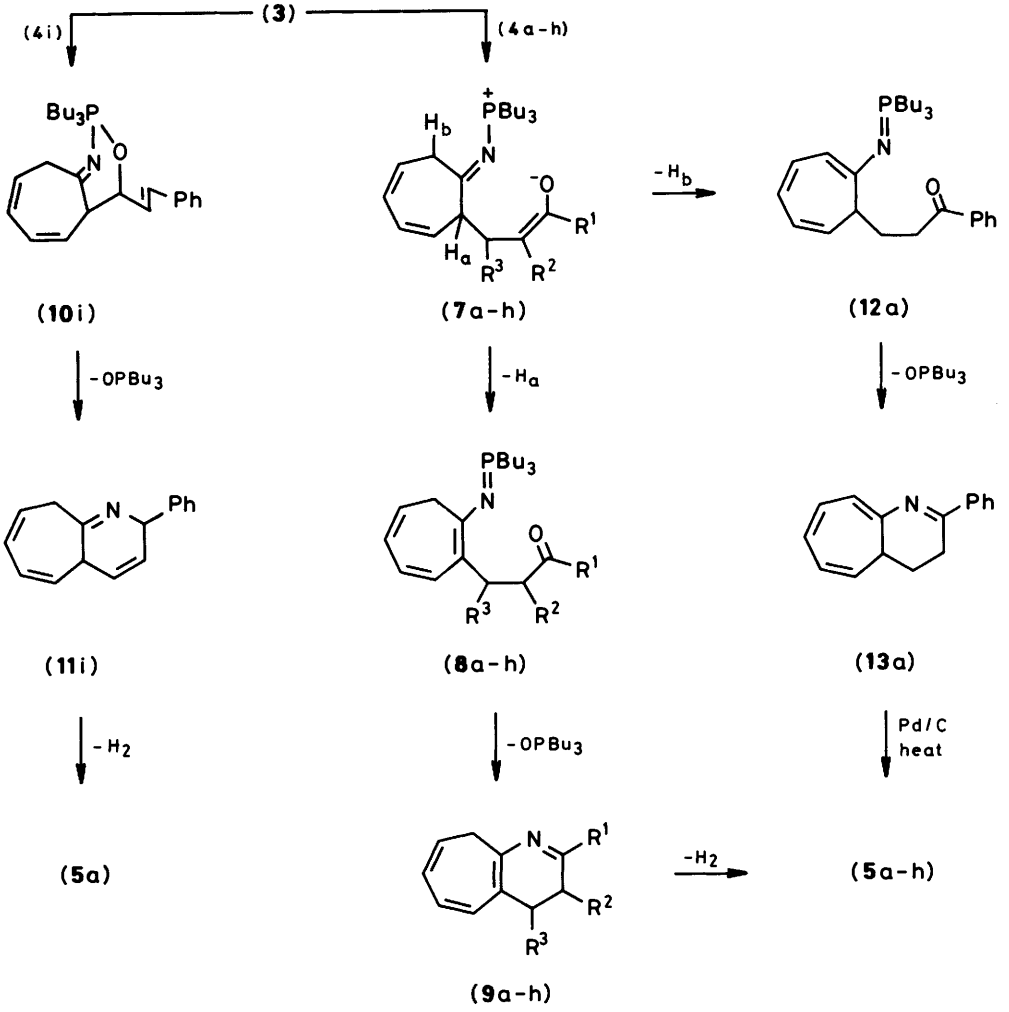
The formation of compounds (5a–h) is explained by the mechanism shown in Scheme 3.[9,10] The initial step is the enamine alkylation of the iminophosphoranes (3) onto the β-carbon of the enones (4a–h) to give the intermediates (7a–h), which undergo hydrogen (H_a) migration to give the imino-phosphoranes (8a–h). Intramolecular aza-Wittig reaction then gives the dihydropyridines (9a–h), which are dehydrogenated with Pd–C to give the 9*H*-cyclohepta[*b*]pyridines (5a–h). The iminophosphorane of type (8), which has a substituent at the 2-position, would be more stable than type (12), which has no substituent at the 2-position. Thus, the product (5a–h) could be derived from the intermediate (8).

The possibility of the hydrogen migration of H_b in (7b) to give the iminophosphorane (12a) was shown by using (4a). In the reaction of (3) with 2 mol equiv. of (4a) in the presence of Pd–C, 4,4a-dihydro-2-phenyl-3*H*-cyclohepta[*b*]pyridine (13a) was isolated in 54% yield, in addition to 14% of (5a). Since (13a) is unstable, decomposing gradually under recrystallization in benzene–hexane, satisfactory analytical data were not obtained. However, unequivocal structural elucidation was provided by 2D ^{1}H NMR as well as high resolution mass, IR, and ^{13}C NMR spectral data. Similarly, the reaction of (4a) with 1 mol equiv. of (3) in the presence of an excess of NEt_3 gave (13a) in 50% yield along with 32% of (5a). Thus, the phosphorane (3) itself or NEt_3 seems to act as a kinetic base to abstract H_b in (7a) to give (12a), the aza-Wittig reaction of which gives (13a). On treatment of (13a) with Pd–C in benzene under reflux, (5a) was obtained in 94% yield after prolonged heating for 10 h (*cf.* Table 1, entry 1). In the reaction of (4c–f) with 2 mol equiv. of (3), however, no dihydrocyclohepta[*b*]pyridine of type (13) was detected during the reaction. The detailed reason for this difference is unclear, and there is no evidence for even a partial intervention of an intermediate of type (12) in the formation of (5b–h).

On the other hand, compound (4i) did not undergo Michael addition. In this case, addition of the β-carbon of (3) to the carbonyl carbon of (4i) occurs to give (10i). It is proposed that the intermediate (10i) then undergoes elimination of tributylphosphine oxide (6) and concomitant cyclization to generate the intermediate (11i), which is dehydrogenated under the reaction conditions to give (5a). The Michael addition is frontier orbital controlled,[17] and is therefore favoured with (4a–h). However, compound (4i), which has no substituent on the carbonyl carbon atom, seems to follow the charge-controlled reaction to generate (10i). Results similar to the present case have been reported previously.[9]

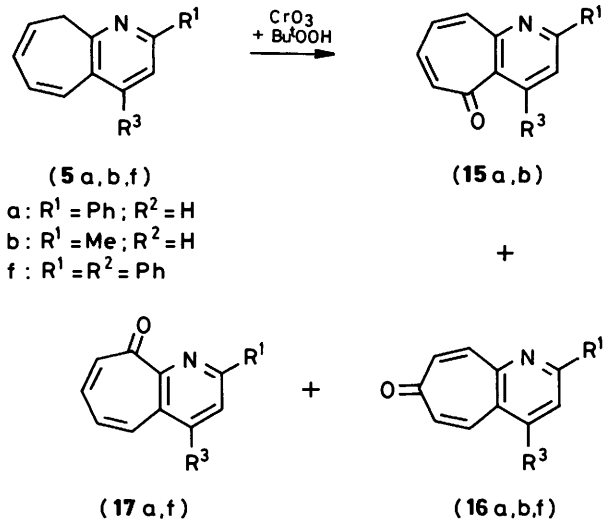
On treatment of (5b) with BuLi and followed by methyl iodide in tetrahydrofuran at −78 °C, alkylation occurred on the methyl group rather than on the cycloheptatriene ring to give 2-ethyl-9*H*-cyclohepta[*b*]pyridine (14) in 63% yield (Scheme 4). The lack of alkylation on the cycloheptatriene ring can be understood by the antiaromatic nature of the cycloheptatrienide anion.

Furthermore, treatment of (5a, b, f) with 10 mol% of CrO_3 and a 7-fold excess of Bu^{t}OOH in CH_2Cl_2[18] afforded two or three isomers of the pyridotropone derivatives (15), (16), and (17) in good combined yields (Scheme 5). The results are summarized in Table 2. The structures of compounds (15a, b), (16a, b, f), and (17a, f) were assigned on the basis of elemental analyses and high-resolution mass, IR, and ^{1}H NMR spectra. Comparison of the assigned ^{1}H NMR spectra of (15)–(17) with those of known pyridotropones[14,15] and benzotropones[19,20] easily revealed the structures. Although oxidation of the benzotropylium cation and benzocycloheptatrienes with Na_2O_2,[19] KO_2,[19] *m*-chloroperbenzoic acid,[19] and SeO_2[20] have been studied to give two or three isomers of benzotropones, the methodology using CrO_3–Bu^{t}OOH seems to be efficient for the oxidation of 9*H*-cyclohepta[*b*]pyridines.



Scheme 3.

Scheme 4.



Scheme 5.

The present reaction using *N*-(cyclohepta-1,3,5-trienyl-iminotributylphosphorane (**3**) can therefore serve as a convenient route to novel 9*H*-cyclohepta[*b*]pyridines and pyridotropone derivatives. The preparation and synthetic applications of *N*-cycloalkenyliminophosphorane are now underway.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Hitachi R-24, Hitachi R-90H and JEOL JNM-GSX400 spectrometers, and the chemical shifts are given relative to internal $SiMe_4$ standard. Mass spectral or high-resolution mass spectral studies were run on a Shimadzu GCMS-QP1000 or 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. The desired α,β-unsaturated ketones, phenyl vinyl ketone (**4a**),[21] phenyl isopropenyl ketone (**4c**),[22] crotonophenone (**4d**,[23] chalcone (**4f**),[24] 2-methylenecyclopentanone (**4g**),[22] and 2-methylenecyclohexanone (**4h**)[22] were prepared by the methods described in the literature.

General Procedure for the Reaction of Phosphorane (**3**) *with* α,β-*Unsaturated Ketones* (**4a–i**).—A solution of (**3**) (0.5 or 1.0

mmol), ketone (**4a–i**) (0.5 mmol), and 10% Pd–C (25 mg, 0.025 mmol of Pd) in anhydrous benzene or toluene (3 ml) was heated under reflux for the period indicated in Table 1. After the solvent had been evaporated, the residue was purified by TLC on silica gel with hexane–AcOEt (5:1) as eluant to give (**5a–h**). In the reaction of ketone (**4b**), a solution of (**3**) (154 mg, 0.5 mmol), (**4b**) (105 mg, 1.5 mmol), and 10% Pd–C (25 mg, 0.025 mmol of Pd) in anhydrous benzene (3 ml) was heated under reflux for 24 h to afford (**5b**) in 49% yield. The results are summarized in Table 1.

For 2-*phenyl*-9H-*cyclohepta*[b]*pyridine* (**5a**): oil; δ_H(CCl_4, 60 MHz) 3.29 (2 H, d, *J* 6.4 Hz, 9-H), 5.77 (1 H, dt, *J* 9.2, 6.4 Hz, 8-H), 6.05 (1 H, dd, *J* 9.2 and 4.7 Hz, 7-H), 6.45 (1 H, dd, *J* 11.2 and 4.7 Hz, 6-H), 6.82 (1 H, d, *J* 11.2 Hz, 5-H), 7.20–7.40 (3 H, m, ArH), 7.46 (2 H, s, 3-H and 4-H), and 7.84–8.05 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 592, 1 571, 1 531, 1 462, 1 447, and 1 427 cm^{-1}; *m/z* 219 (M^+, 100%) (Found: M^+, 219.1029. $C_{16}H_{13}N$ requires *M*, 219.1049). *Picrate*: m.p. 147–148 °C (from MeOH) (Found: C, 58.7; H, 3.45; N, 12.5. $C_{22}H_{16}N_4O_7$ requires C, 58.9; H, 3.6; N, 12.5%).

For 2-*methyl*-9H-*cyclohepta*[b]*pyridine* (**5b**): oil; δ_H(CCl_4, 60 MHz) 2.44 (3 H, s, Me), 3.15 (2 H, d, *J* 5.9 Hz, 9-H), 5.72 (1 H, dt, *J* 9.9 and 5.9 Hz, 8-H), 6.03 (1 H, dd, *J* 9.9 and 4.7 Hz, 7-H), 6.36 (1 H, dd, *J* 11.5 and 4.7 Hz, 6-H), 6.77 (1 H, d, *J* 11.5 Hz, 5-H), 6.84 (1 H, d, *J* 7.6 Hz, 3-H), and 7.31 (1 H, d, *J* 7.6 Hz, 4-H); ν_{max}($CHCl_3$) 1 594, 1 581, 1 548, 1 468, and 1 428 cm^{-1}; *m/z* 157 (M^+, 13%) and 156 (100) (Found: M^+, 157.0894. $C_{11}H_{11}N$ requires *M*, 157.0892). *Picrate*: m.p. 147–148 °C (from MeOH) (Found: C, 53.0; H, 3.55; N, 14.55. $C_{17}H_{14}N_4O_7$ requires C, 52.85; H, 3.65; N, 14.5%).

For 3-*methyl*-2-*phenyl*-9H-*cyclohepta*[b]*pyridine* (**5c**): oil; δ_H(CCl_4, 60 MHz) 2.30 (3 H, s, Me), 3.25 (2 H, d, *J* 5.9 Hz, 9-H), 5.78 (1 H, dt, *J* 10.2 and 5.9 Hz, 8-H), 6.07 (1 H, dd, *J* 10.2 and 5.0 Hz, 7-H), 6.45 (1 H, dd, *J* 11.0 and 5.0 Hz, 6-H), 6.81 (1 H, d, *J* 11.0 Hz, 5-H), and 7.10–7.60 (6 H, m, 4-H and ArH); ν_{max}($CHCl_3$) 1 593, 1 535, 1 449, and 1 428 cm^{-1}; *m/z* 233 (M^+, 58%) and 232 (100) (Found: M^+, 233.1199. $C_{17}H_{15}N$ requires *M*, 233.1206). *Picrate*: m.p. 155 °C (from MeOH) (Found: C, 59.5; H, 3.9; N, 11.8. $C_{23}H_{18}N_4O_7$ requires C, 59.7; H, 3.9; N, 12.1%).

For 4-*methyl*-2-*phenyl*-9H-*cyclohepta*[b]*pyridine* (**5d**): oil; δ_H(CCl_4, 60 MHz) 2.35 (3 H, s, Me), 3.24 (2 H, d, *J* 6.0 Hz, 9-H), 5.82 (1 H, dt, *J* 9.5 and 6.0 Hz, 8-H), 6.07 (1 H, dd, *J* 9.5 and 4.9 Hz, 7-H), 6.50 (1 H, dd, *J* 11.5 and 4.9 Hz, 6-H), 6.97 (1 H, d, *J* 11.5 Hz, 5-H), 7.22–7.45 (4 H, m, 3-H and ArH), and 7.87–8.09 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 596, 1 565, 1 539, 1 458, and 1 449 cm^{-1}; *m/z* 233 (M^+, 100%) (Found: M^+, 233.1204. $C_{17}H_{15}N$ requires *M*, 233.1206). *Picrate*: m.p. 157–158 °C (from MeOH) (Found: C, 59.7; H, 3.85; N, 12.2. $C_{23}H_{18}N_4O_7$ requires C, 59.7; 3.9; N, 12.1%).

For 2-*methyl*-4-*phenyl*-9H-*cyclohepta*[b]*pyridine* (**5e**): oil; δ_H(CCl_4, 60 MHz) 2.46 (3 H, s, Me), 3.18 (2 H, d, *J* 6.1 Hz, 9-H), 5.82 (1 H, dt, *J* 9.8 and 6.1 Hz, 8-H), 6.08 (1 H, dd, *J* 9.8 and 5.0 Hz, 7-H), 6.40 (1 H, dd, *J* 11.5 and 5.0 Hz, 6-H), 6.75 (1 H, d, *J* 11.5 Hz, 5-H), 6.82 (1 H, s, 3-H), and 7.25 (5 H, s, ArH); ν_{max}($CHCl_3$) 1 595, 1 566, 1 532, 1 495, and 1 445 cm^{-1}; *m/z* 233 (M^+, 100%) (Found: M^+, 233.1208. $C_{17}H_{15}N$ requires *M*, 233.1206). *Picrate*: m.p. 177–178 °C (from MeOH) (Found: C, 59.55; H, 3.8; N, 12.2. $C_{23}H_{18}N_4O_7$ requires C, 59.7; H, 3.9; N, 12.1%).

For 2,4-*diphenyl*-9H-*cyclohepta*[b]*pyridine* (**5f**): m.p. 110 °C (from EtOH); δ_H(CCl_4, 60 MHz) 3.42 (2 H, d, *J* 6.0 Hz, 9-H), 5.93 (1 H, dt, *J* 9.9 and 6.0 Hz, 8-H), 6.20 (1 H, dd, *J* 9.9 and 4.5 Hz, 7-H), 6.48 (1 H, dd, *J* 12.1 and 4.5 Hz, 6-H), 6.83 (1 H, d, *J* 12.1 Hz, 5-H), 7.30–7.55 (8 H, m, ArH), 7.55 (1 H, s, 3-H), and 7.95–8.15 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 592, 1 562, 1 527, 1 495, and 1 444 cm^{-1}; *m/z* 295 (M^+, 100%) (Found: M^+, 295.1342; C, 89.5; H, 5.9; N, 4.7%. $C_{22}H_{17}N$ requires *M*, 295.1362; C, 89.5; H, 5.8; N, 4.7%).

For 1,2,3,5-*tetrahydrocyclopenta*[b]*cyclohepta*[e]*pyridine* (**5g**): oil; δ_H($CDCl_3$, 90 MHz) 2.12 (2 H, quint, *J* 7.7 Hz, 2-H), 2.92 (2 H, t, *J* 7.7 Hz, 1-H), 3.00 (2 H, t, *J* 7.7 Hz, 3-H), 3.23 (2 H, d, *J* 6.6 Hz, 5-H), 5.83 (1 H, dt, *J* 9.9 and 6.6 Hz, 6-H), 6.13 (1 H, dd, *J* 9.9 and 5.1 Hz, 7-H), 6.51 (1 H, dd, *J* 11.2 and 5.1 Hz, 8-H), 6.91 (1 H, d, *J* 11.2 Hz, 9-H), and 7.44 (1 H, s, 10-H); ν_{max}($CHCl_3$) 1 603, 1 585, 1 545, 1 456, and 1 421 cm^{-1}; *m/z* 183 (M^+, 10%) and 57 (100) (Found: M^+, 183.1044. $C_{13}H_{13}N$ requires *M*, 183.1049). *Picrate*: m.p. 160–161 °C (from MeOH) (Found: C, 55.1; H, 3.9; N, 13.25. $C_{19}H_{16}N_4O_7$ requires C, 55.3; H, 3.9; N, 13.6%).

For 1,2,3,4-*tetrahydro*-6H-*cyclohepta*[b]*quinoline* (**5h**): oil; δ_H(CCl_4, 60 MHz) 1.70–2.00 (4 H, m, 2-H and 3-H), 2.60–3.00 (4 H, m, 1-H and 4-H), 3.14 (2 H, d, *J* 6.2 Hz, 6-H), 5.74 (1 H, dt, *J* 10.2 and 6.2 Hz, 7-H), 6.00 (1 H, dd, *J* 10.2 and 5.0 Hz, 8-H), 6.37 (1 H, dd, *J* 11.3 and 5.0 Hz, 9-H), 6.75 (1 H, d, *J* 11.3 Hz, 10-H), and 7.11 (1 H, s, 11-H); ν_{max}($CHCl_3$) 1 591, 1 542, 1 452, 1 435, and 1 423 cm^{-1}; *m/z* 197 (M^+, 100%) (Found: M^+, 197.1209. $C_{14}H_{15}N$ requires *M*, 197.1206). *Picrate*: m.p. 160 °C (from MeOH) (Found: C, 56.2; H, 4.15; N, 13.2. $C_{20}H_{18}N_4O_7$ requires C, 56.3; H, 4.3; N, 13.1%).

Reaction of the Phosphorane (**3**) *with Ketone* (**4a**) *in the Presence of* Pd–C.—A solution of (**3**) (614 mg, 2.0 mmol), (**4a**) (132 mg, 1.0 mmol), and 10% Pd–C (50 mg, 0.05 mmol of Pd) in anhydrous benzene (5 ml) was heated under reflux for 2.5 h. The reaction mixture was then chromatographed on silica gel. The fractions eluted with benzene–EtOAc (10:1) were concentrated and then crystallized from hexane to give (**13a**) (47 mg, 21%). The filtrate contained a mixture of (**5a**) (31 mg, 14%) and (**13a**) (72 mg, 33%) in a ratio of 1:2.3, as determined by the ^1H NMR spectrum.

For 4,4a-*dihydro*-2-*phenyl*-3H-*cyclohepta*[b]*pyridine* (**13a**): m.p. 83–85 °C (from benzene–hexane); δ_H($CDCl_3$, 400 MHz) 1.85 (1 H, tdd, *J* 12.8, 5.5, and 4.0 Hz, 4-H), 1.91 (1 H, m, 4a-H), 2.16 (1 H, dm, *J* 12.8 Hz, 4-H), 2.31 (1 H, ddd, *J* 16.9, 12.8, and 5.0 Hz, 3-H), 3.13 (1 H, dm, *J* 16.9 Hz, 3-H), 5.58 (1 H, dd, *J* 9.5 and 5.5 Hz, 5-H), 6.32 (1 H, dd, *J* 9.5 and 5.5 Hz, 6-H), 6.62 (1 H, d, *J* 6.6 Hz, 9-H), 6.67 (1 H, dd, *J* 11.0 and 5.5 Hz, 7-H), 6.76 (1 H, dd, *J* 11.0 and 6.6 Hz, 8-H), 7.39–7.42 (3 H, m, ArH), and 7.93–7.95 (2 H, m, ArH); δ_C($CDCl_3$, 100.40 MHz) 23.28, 23.64, 33.64, 33.82, 121.37, 122.48, 126.40, 126.56, 128.40, 129.39, 130.13, 130.15, 136.30, 139.13, and 165.60; ν_{max}($CHCl_3$) 3 010, 1 603, 1 556, 1 446, 1 385, 1 346, and 1 340 cm^{-1}; *m/z* 219 (M^+, 26%) and 57 (100) (Found: M^+, 221.1191. $C_{16}H_{15}N$ requires *M*, 221.1206).

Reaction of Phosphorane (**3**) *with Ketone* (**4a**) *in the Presence of Triethylamine*.—A solution of (**3**) (307 mg, 1.0 mmol), (**4a**) (132 mg, 1.0 mmol), and Et_3N (303 mg, 3.0 mmol) in anhydrous benzene (3 ml) was heated under reflux for 45 min. The reaction mixture was then chromatographed on silica gel, and the fractions eluted with benzene were concentrated and then crystallized from hexane to give (**13a**) (42 mg, 19%). The filtrate contained a mixture of (**5a**) (70 mg, 32%) and (**13a**) (68 mg, 31%) in a ratio of 1:0.96, as determined by the ^1H NMR spectrum.

Dehydrogenation of (**13a**) *with* Pd–C.—A solution of (**13a**) (20 mg, 0.09 mmol) and 10% Pd–C (5 mg, 0.005 mmol of Pd) in anhydrous benzene (2 ml) under reflux for 20 h. After chromatography of the reaction mixture on silica gel, the fractions eluted with benzene gave (**5a**) (18.6 mg, 94%).

Methylation of 2-*Methyl*-9H-*cyclohepta*[b]*pyridine* (**5b**).—To a solution of (**5b**) (83 mg, 0.52 mmol) in anhydrous tetrahydrofuran (3 ml) at −78 °C was added butyl-lithium (0.42 ml; 1.26M in hexane, 0.53 mmol). After stirring for 10 min at −78 °C, MeI (230 mg, 1.6 mmol) was added, and the solution

was stirred for a further 1 h at −78 °C and then for 1 h at room temperature. The reaction mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and evaporated. The residue was separated by TLC on silica gel using hexane–EtOAc (5:1) as developer to give 2-*ethyl*-9H-*cyclohepta*[b]*pyridine* (**14**) (56 mg, 63%) as an oil; δ_H(CCl_4, 60 MHz) 1.26 (3 H, t, *J* 7.4 Hz, Me), 2.73 (2 H, q, *J* 7.4 Hz, CH_2Me), 3.18 (2 H, d, *J* 6.2 Hz, 9-H), 5.75 (1 H, dt, *J* 10.0 and 6.2 Hz, 8-H), 6.02 (1 H, dd, *J* 10.0 and 5.0 Hz, 7-H), 6.40 (1 H, dd, *J* 11.0 and 5.0 Hz, 6-H), 6.80 (1 H, d, *J* 11.0 Hz, 5-H), 6.84 (1 H, d, *J* 8.0 Hz, 3-H), and 7.34 (1 H, d, *J* 8.0 Hz, 4-H); ν_{max}($CHCl_3$) 1 595, 1 579, 1 545, 1 470, and 1 428 cm^{-1}; *m/z* 171 (M^+, 31%) and 91 (100) (Found: M^+, 171.1036. $C_{12}H_{13}N$ requires *M*, 171.1049). *Picrate*: m.p. 129–130 °C (from MeOH) (Found: C, 54.1; H, 4.0; N, 14.0. $C_{18}H_{16}N_4O_7$ requires C, 54.0; H, 4.0; N, 14.0%).

General Procedure for the Oxidation of (**5a**, **b**, **f**) *with* CrO_3–Bu^tOOH.—A solution of (**5**) (0.5 mmol), anhydrous CrO_3 (5 mg, 0.05 mmol), and Bu^tOOH (3.5 mmol) in anhydrous CH_2Cl_2 (3 ml) was stirred at room temperature for a period indicated in Table 2. The reaction mixture was washed with water, and the organic layer was dried over Na_2SO_4 and concentrated. The residue was separated by TLC on silica gel, using hexane–EtOAc (2:1) as developer, to give the pyridotropones (**15a**, **b**), (**16a**, **b**, **f**), and (**17a**, **f**). The results are summarized in Table 2.

For 2-*phenyl*-5H-*cyclohepta*[b]*pyridin*-5-*one* (**15a**): m.p. 77–79 °C (from MeOH); δ_H($CDCl_3$, 90 MHz) 6.76–6.95 (1 H, m, 8-H), 6.95–7.13 (2 H, m, 6-H and 7-H), 7.40–7.60 (3 H, m, ArH), 7.79 (1 H, d, *J* 10.8 Hz, 9-H), 7.99 (1 H, d, *J* 8.6 Hz, 3-H), 8.10–8.25 (2 H, m, ArH), and 8.82 (1 H, d, *J* 8.6 Hz, 4-H); ν_{max}($CHCl_3$) 1 645, 1 589, 1 577, 1 458, 1 351, and 828 cm^{-1}; *m/z* 233 (M^+, 19%) and 204 (100) (Found: M^+, 233.0846. $C_{16}H_{11}NO$ requires *M*, 233.0841). *Picrate*: m.p. 101–102 °C (from MeOH) (Found: C, 57.4; H, 3.1; N, 11.9. $C_{22}H_{14}N_4O_8$ requires C, 57.15; H, 3.05; N, 12.1%).

For 2-*phenyl*-7H-*cyclohepta*[b]*pyridin*-7-*one* (**16a**): m.p. 141 °C (from EtOH); δ_H($CDCl_3$, 90 MHz) 6.86 (1 H, d, *J* 12.3 and 2.4 Hz, 6-H), 7.04 (1 H, dd, *J* 12.3 and 2.4 Hz, 8-H), 7.41 (1 H, d, *J* 12.3 Hz, 5-H), 7.40–7.60 (3 H, m, ArH), 7.93 (1 H, d, *J* 12.3 Hz, 9-H), 7.90–8.00 (2 H, br s, 3-H and 4-H), and 8.05–8.20 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 632, 1 589, 1 580, 1 535, 1 262, and 872 cm^{-1}; *m/z* 233 (M^+, 28%) 102 (100) (Found: M^+, 233.0829; C, 82.3; H, 4.8; N, 5.8%. $C_{16}H_{11}NO$ requires *M*, 233.0841; C, 82.4; H, 4.75; N, 6.0%).

For 2-*phenyl*-9H-*cyclohepta*[b]*pyridin*-9-*one* (**17a**): oil; δ_H($CDCl_3$, 90 MHz) 6.60–6.90 (1 H, m, 6-H), 7.02–7.35 (3 H, m, 5-H, 7-H, and 8-H), 7.40–7.60 (3 H, m, ArH), 8.04 (2 H, s, 3-H and 4-H), and 8.10–8.30 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 645, 1 615, 1 595, 1 566, 1 472, 1 452, 1 317, 1 178, and 847 cm^{-1}; *m/z* 233 (M^+, 32%) and 204 (100) (Found: M^+, 233.0838. $C_{16}H_{11}NO$ requires *M*, 233.0841). *Picrate*: m.p. 154–155 °C (from EtOH) (Found: C, 57.25; H, 3.0; N, 12.0. $C_{22}H_{14}N_4O_8$ requires C, 57.15; H, 3.05; N, 12.1%).

For 2-*methyl*-5H-*cyclohepta*[b]*pyridin*-5-*one* (**15b**): oil; δ_H($CDCl_3$, 90 MHz) 2.70 (3 H, s, Me), 6.91 (1 H, ddd, *J* 10.6, 7.6, and 2.9 Hz, 8-H), 6.95–7.10 (2 H, m, 6-H and 7-H), 7.39 (1 H, d, *J* 8.4 Hz, 3-H), 7.62 (1 H, d, *J* 10.6 Hz, 9-H), and 8.64 (1 H, d, *J* 8.4 Hz, 4-H); ν_{max}($CHCl_3$) 1 642, 1 588, 1 462, 1 347, and 814 cm^{-1}; *m/z* 171 (M^+, 29%) and 143 (100) (Found: M^+, 171.0659. $C_{11}H_9NO$ requires *M*, 171.0685). *Picrate*: m.p. 164 °C (from MeOH) (Found: C, 50.65; H, 2.9; N, 14.0. $C_{17}H_{12}N_4O_8$ requires C, 51.0; H, 3.0; N, 14.0%).

For 2-*methyl*-7H-*cyclohepta*[b]*pyridin*-7-*one* (**16b**): m.p. 119–120 °C (from cyclohexane); δ_H($CDCl_3$, 90 MHz) 2.68 (3 H, s, Me), 6.82 (1 H, dd, *J* 12.5 and 2.6 Hz, 6-H), 6.97 (1 H, dd, *J* 12.5 and 2.6 Hz, 8-H), 7.34 (1 H, d, *J* 7.9 Hz, 3-H), 7.36 (1 H, d, *J* 12.5 Hz, 5-H), 7.76 (1 H, d, *J* 12.5 Hz, 9-H), and 7.85 (1 H, d, *J* 7.9 Hz, 4-H); ν_{max}($CHCl_3$) 1 636, 1 587, 1 541, 1 243, and 870 cm^{-1}; *m/z* 171 (M^+, 29%) and 143 (100) (Found: M^+, 171.0669; C, 76.8; H, 5.3; N, 8.1%. $C_{11}H_9NO$ requires *M*, 171.0685; C, 77.2; H, 5.3; N, 8.2%).

For 2,4-*diphenyl*-7H-*cyclohepta*[b]*pyridin*-7-*one* (**16f**): m.p. 166–167 °C (from EtOH); δ_H($CDCl_3$, 90 MHz) 6.72 (1 H, dd, *J* 13.0 and 2.4 Hz, 6-H), 7.05 (1 H, dd, *J* 13.0 and 2.4 Hz, 8-H), 7.30–7.60 (8 H, m, ArH), 7.55 (1 H, d, *J* 13.0 Hz, 5-H), 7.84 (1 H, s, 3-H), 8.05 (1 H, d, *J* 13.0 Hz, 9-H), and 8.07–8.21 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 636, 1 592, 1 574, 1 498, and 1 370 cm^{-1}; *m/z* 309 (M^+, 24%) and 280 (100) (Found: M^+, 309.1142; C, 85.15; H, 4.9; N, 4.1%. $C_{22}H_{15}NO$ requires *M*, 309.1155; C, 85.4; H, 4.9; N, 4.5%).

For 2,4-*diphenyl*-9H-*cyclohepta*[b]*pyridin*-9-*one* (**17f**): m.p. 165–166 °C (from EtOH); δ_H($CDCl_3$, 90 MHz) 6.60–6.90 (1 H, m, 6-H), 7.10–7.30 (3 H, m, 5-H, 7-H, and 8-H), 7.30–7.75 (8 H, m, ArH), 7.96 (1 H, s, 3-H), and 8.25–8.40 (2 H, m, ArH); ν_{max}($CHCl_3$) 1 642, 1 622, 1 591, 1 553, 1 357, and 908 cm^{-1}; *m/z* 309 (M^+, 31%) and 280 (100) (Found: M^+, 309.1159; C, 85.0; H, 4.9; N, 4.4%. $C_{22}H_{15}NO$ requires *M*, 309.1155; C, 85.4; H, 4.9; N, 4.5%).

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