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Pyridinium Dichlorophosphinomethylides

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ABSTRACT: *Seven new pyridinium dichlorophosphinomethylides* **2** *have been obtained from dichlorophosphinylation of the pyridinium methylides generated in situ.* **2** *give 1,3-bis(alkoxycarbonyl)-2-phosphaindolizines* **4** *through 1,5-electrocyclization of the intermediate, bis(pyridinium ylidyl)phosphenium chloride* **3** *which is generated either from disproportionation of* **2** *or from the reaction of* **2** *with pyridinium methylide. Formation of* **3** *has been confirmed by carrying out a crossed reaction. 3-Substituted* **2** *forms* **4** *regiospecifically. Intramolecular 1,5-cyclocondensation of 2-methylpyridinium dichlorophosphinomethylide is preferred over its disproportionation.*
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INTRODUCTION

Pyridinium dichlorophosphinomethylide was first isolated as a stable intermediate in the synthesis of 2-phosphaindolizines from the [4 + 1]-cyclocondensation of 1,2-dialkylpyridinium bromide with phosphorus trichloride in the presence of triethylamine [1]. Later differently substituted pyridinium dichlorophosphinomethylides could be obtained from dichlorophosphinylation of the pyridinium methylides, generated in situ [2].

In view of the recently reported disproportionation and other properties of the triphenylphosphonium dihalophosphinomethylides [3–20] we investigated the behaviour of the 2-unsubstituted pyridinium dichlorophosphinomethylides and found that these compounds, on being left in a solution, gave 1,3-disubstituted-2-phosphaindolizines [21], formation of which could be explained on the basis of 1,5-electrocyclization of an intermediate, bis(pyridinium ylidyl)phosphenium chloride (**3**) formed from disproportionation of **2**, in analogy to that of the triphenylphosphonium dichlorophosphinomethylide [3]. The intermediate **3** could also be produced from the reaction of **2** with pyridinium methylide (**2′**), generated in situ leading to the development of a facile one-pot synthesis of 1,3-bis(alkoxycarbonyl)-2-phosphaindolizines **4** [21]. 1,3-Azaphospholo[5,1-*a*] isoquinolines have been prepared in a similar manner [22].

We have now studied intramolecular 1,5-cyclocondensation versus disproportionation of the 2-methylpyridinium dichlorophosphinomethylide and also the regioselectivity in 1,5-electrocyclization of the intermediate **3** formed from disproportionation of the unsymmetrically substituted pyridinium dichlorophosphinomethylides.

Recently, negative hyperconjugation has been detected in triphenylphosphonium di- and monochlorophosphinomethylides [5,7], which is related to that in vinylphosphines [23–25]. In view of the structural similarity of these compounds with the

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pyridinium dichlorophosphinomethylides, we have investigated the existence of this phenomenon in the latter by the semiempirical PM3 methods [26].

RESULTS AND DISCUSSION

Synthesis of Pyridinium Dichlorophosphinomethylides

N-(Alkoxycarbonylmethyl)pyridinium bromides (**1**) on reacting with phosphorus trichloride (1 equiv.) and triethylamine (2 equiv.) in toluene under nitrogen give pyridinium dichlorophosphinomethylides (**2**) (Scheme 1).

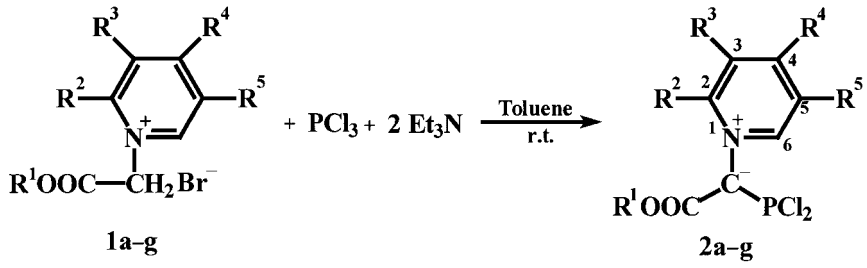
All the products are yellow, crystalline, sharp melting solids stable under a nitrogen atmosphere. The ^{31}P NMR signal of **2** appears in the range δ 145.6–149.6 ppm [2,21], which does not split under ^{1}H-coupled ^{31}P NMR mode, indicating the absence of any proton on the ylidic carbon. Physical and NMR data of **2** are given in Tables 1–3.

Regioselectivity in 1,5-Electrocyclization

The 2:1 reaction of an *N*-(alkoxycarbonylmethyl) pyridinium bromide (**1**) and PCl_3 leads to the bis (pyridinium ylidyl)phosphenium salt (**3**) as an intermediate which undergoes intramolecular 1,5-electrocyclization to give a 1,3-bis(alkoxycarbonyl)-2-phosphaindolizine (**4**). Thus, from *N*-(alkoxycarbonylmethyl)-3-alkylpyridinium bromides (**1h–k**), 2-phosphaindolizines (**4h–k**) was formed through regiospecific 1,5-electrocyclization of the intermediate **3**, the less hindered position being preferred (Scheme 2).

The intermediate **3**, though, could not be isolated; its formation was proved unambiguously by carrying out a crossed reaction between **2a** and **2′b** or **2i** and **2′h** (Scheme 3) whereupon a mixture of four products **4a,b,l,n** or **4h,i,m,o**, as shown by ^{31}P- and ^{1}H NMR studies (Table 4), was obtained.

All the 2-phosphaindolizines isolated are yellow, crystalline solids. The physical and spectral data of 2-phosphaindolizines are given in Tables 1 and 4 respectively. The ^{31}P NMR chemical shift at δ 178.2–180.2 ppm is in the range characteristic for the two-coordinate, tervalent phosphorus in such system [1,21,27–30]. In the ^{1}H NMR spectrum two triplets (δ 1.1–1.4) and quartets (δ 4.3–4.4) for the two ethoxy groups in **4i** and **4k** and two singlets (δ 3.5–3.9) for the two methoxy groups in **4h** and **4j** confirm the presence of alkoxycarbonyl substitutents in 2-phosphaindolizines at both 1- and 3-positions. The assignment of ^{13}C NMR chemical shifts (Table 5) has been made on the basis of the literature reports [1,21,28]. C-1 and C-3 give a doublet each, due to coupling with phosphorus; the downfield doublet (δ 137.9–139.3; $^{1}J_{CP} = 48.5$–50.6 Hz) is assigned to C-3 due to a formal double bond [31]. In the mass spectrum of **4i** the molecular ion peak at *m/z* 307.8 forms the base peak. The initial fragmentation occurs at the ethoxycarbonyl groups which eliminate an ethoxy radical and CO or C_2H_4 and CO_2 molecules to generate the basic skeleton of 2-phosphaindolizine (*m/z* 235, 48%). The further fragmentation of the ring structure accompanies the loss of HCP molecule (*m/z* 191, 20%).



1 – 4	a	b	c	d	e	f	g	h	i	j	k
R^1	Me	Et	Me	Et	Me	Et	Me	Me	Et	Me	Et
R^2	H	H	H	H	H	H	Me	H	H	H	H
R^3	Me	Me	H	H	Me	Me	H	Et	Et	Bu	Bu
R^4	H	H	Me	Me	H	H	H	H	H	H	H
R^5	H	H	H	H	Me	Me	Et	H	H	H	H

SCHEME 1

TABLE 1 Physical Data of Compounds **2** and **4**

				Found % (Calcd.)		
	m.p. (°C)	*Yield (%)*	*Mol. Formula (mol. wt.)*	*C*	*H*	*N*
2a	74–76	66	$C_9H_{10}NO_2PCl_2$	–	–	–
			(266.1)	–	–	–
2b	78–80	78	$C_{10}H_{12}NO_2PCl_2$	–	–	–
			(280.1)	–	–	–
2c	80–82	18	$C_9H_{10}NO_2PCl_2$	–	–	–
			(266.1)	–	–	–
2d	78–80	45	$C_{10}H_{12}NO_2PCl_2$	–	–	–
			(280.1)	–	–	–
2e	78–80	71	$C_{10}H_{12}NO_2PCl_2$	–	–	–
			(280.1)	–	–	–
2f	65–68	79	$C_{11}H_{14}NO_2PCl_2$	–	–	–
			(294.1)	–	–	–
2g	75–78	80	$C_{12}H_{16}NO_2PCl_2$	–	–	–
			(308.1)	–	–	–
4h	119–120	50	$C_{13}H_{14}NO_4P$	51.0	5.8	3.9
			(279.2)	(50.7	6.1	3.5)
4i	67–69	49	$C_{15}H_{18}NO_4P$	–	–	–
			(307.2)	–	–	–
4j	64–65	57	$C_{15}H_{18}NO_4P$	58.4	6.2	5.3
			(307.2)	(58.7	5.9	5.6)
4k	62–64	62	$C_{17}H_{22}NO_4P$	60.7	6.9	4.1
			(335.3)	(60.9	6.6	4.2)

TABLE 2 ^{31}P NMR and ^{1}H NMR Data of **2** in C_6D_6, δ (ppm), and J (Hz)

	2a	***2b***	***2c***	***2d***	***2e***	***2f***	***2g***[a]
^{31}P	145.6	145.9	149.1	149.6	146.1	146.7	148.8
2-H,6-H	7.69	7.77	7.92	7.99	7.92	7.71	8.06
^{3}J (H,H)	–	–	6.7	6.7			
3-H/5-H	5.85	5.89	6.01	6.06			6.05
^{3}J (H,H)	8.1	8.1	6.7	6.7			8.1
4-H	6.02	6.06			6.11	5.96	6.29
^{3}J (H,H)	8.1	8.1					8.1
3-CH_3	1.01	1.04			1.13	1.10	
4-CH_3			1.49	1.54			
5-CH_3					1.13	1.10	
OCH_3	3.37		3.80		3.52		3.39
OCH_2CH_3		4.00		4.42		4.03	
OCH_2CH_3		0.91		1.45		0.93	
^{3}J (H,H)		7.1		7.1		7.3	

[a]2-Me δ 2.07; 5-Et: CH_2 δ 1.53, ^{3}J (H,H) = 7.6 Hz; CH_3 δ 0.38, ^{3}J (H,H) = 7.6 Hz.

1,5-Electrocyclization versus Intramolecular Cyclocondensation

On addition of 5-ethyl-2-methylpyridinium methoxycarbonylmethylide (**2′g**), generated in situ in methylene chloride, to the solution of 5-ethyl-2-methylpyridinium dichlorophosphino-methoxycarbonylmethylide (**2g**) in toluene, 6-ethyl-3-methoxycarbonyl-2-phosphaindolizine (**5g**) [28] is formed exclusively showing the preference of intramolecular 1,5-cyclocondensation over disproportionation and 1,5-electrocyclization in a hindered position (Scheme 4).

A reaction of pyridinium dichlorophosphino-methoxycarbonylmethylide (**2p**) with 5-ethyl-2-methylpyridinium ethoxycarbonylmethylide (**2′q**) afforded a mixture of 2-phosphaindolizines (**4p**) and **5q**, no crossed product being formed in the reaction. The **4p** is formed from **2p** through disproportionation and 1,5-electrocyclization. The phosphorus trichloride liberated in this reaction reacts with **2′q** to give **5q** through the

TABLE 3 ^{13}C NMR Data of **1, 2** in $CDCl_3$, δ (ppm), and J (H_Z)

	1k[a]	***2a***	***2b***
C-2	145.8	147.9	148.1
C-3	143.3	136.5	136.7
C-4	143.8	141.2	141.6
C-5	127.1	124.5	124.8
C-6	145.5	145.2	145.4
OCH_2CH_3	60.5	–	59.2
OCH_2CH_3	13.8	–	15.1
OCH_3	–	50.2	–
NCH_2	62.9	–	–
CO	165.7	166.2	166.1
^2J (P,C)	–	34.8	–
3-CH_3	–	17.3	17.6
>C-PCl_2	–	98.2	99.0
^1J (P,C)	–	91.3	90.2

[a]3-Bu: α CH_2 δ 32.1; β CH_2 δ 32.0; γ CH_2 δ 21.8; CH_3 δ 13.5.

formation of **2q** followed by its intramolecular 1,5-cyclocondensation (Scheme 5).

EXPERIMENTAL

Solvents and commercial reagents were distilled and dried by common methods before use. Melting points were determined by the capillary method and are uncorrected. NMR spectra were recorded on a Bruker ARX 300 (^{31}P NMR at 121.5 MHz, ^1H NMR at 300 MHz, ^{13}C NMR at 75.5 MHz) spectrometer or a JEOL FX 90 Q (^{31}P NMR at 36.23 MHz, ^1H NMR at 89.55 MHz) spectrometer. The chemical shifts refer to 85% H_3PO_4 as an external reference for ^{31}P NMR and TMS as an internal reference for ^1H- and ^{13}C NMR. The EI Mass spectrum was recorded at 70 eV at room temperature on Varian CH7 mass spectrometer.

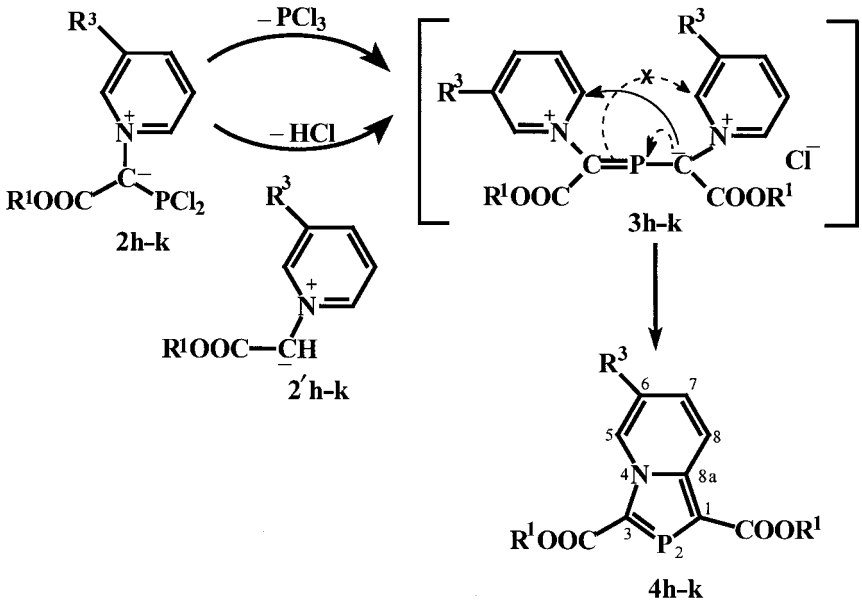
*N-Alkoxycarbonylmethylpyridinium Bromides (***1c,h–k***)*

To a solution of 3- or 4-alkylpyridine (5 mmol) in diethyl ether (40 ml) was added an equimolar amount of the alkyl bromoacetate with constant stirring. After stirring of the mixture for 5–12 days at room temperature (~25°C), white to cream colored solid formed was filtered off, washed with dry ether (2 × 25 ml) and dried under vacuum. In the case of **1k**, an oily layer separated which was dissolved in acetonitrile and added dropwise into diethyl ether (40 ml) with vigorous stirring, whereupon a cream solid separated. Salts **1a,b,d–g** were prepared according to the literature [21,28].

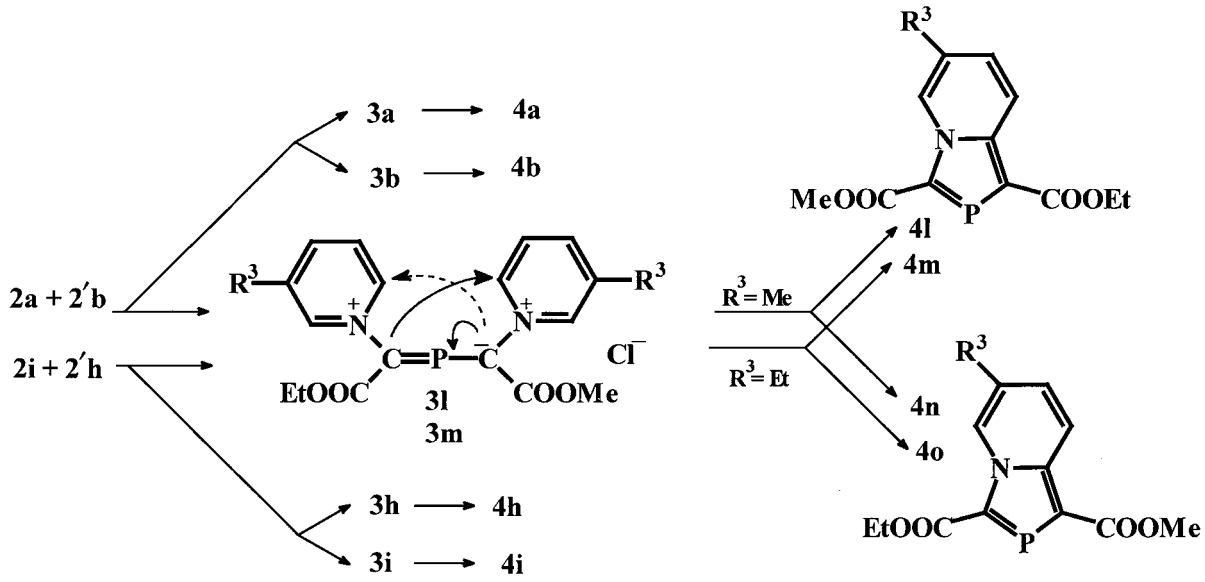
1c: Yield 80%, m.p. 160–162°C; ^1H NMR ($CDCl_3$): δ = 2.62 (s, 3H, 4-CH_3), 3.68 (s, 3H, OCH_3), 6.20 (s, 2H, NCH_2), 7. 80 (d, 2H, $^3J_{HH}$ = 6.6 Hz, 3-H, 5-H), 9.33 (d, 2H, $^3J_{HH}$ = 6.6 Hz, 2-H, 6-H).

1h: Yield 95%, m.p. 48–50°C; ^1H NMR ($CDCl_3$): δ = 1.27 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_3), 2.77 (q, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3), 3.68 (s, 3H, OCH_3), 6.20 (s, 2H, NCH_2), 7.98 (dd, 1H, $^3J_{HH}$ = 7.8, 6.9 Hz, 5-H), 8.29 (d, 1H, $^3J_{HH}$ = 7.8 Hz, 4-H), 9.32 (s, 1H, 2-H), 9.46 (d, 1H, $^3J_{HH}$ = 6.9 Hz, 6-H).

1i: Yield 86%, m.p. 58–60°C; ^1H NMR ($CDCl_3$): δ = 1.20 (t, 3H, $^3J_{HH}$ = 6.9 Hz, CH_2CH_3), 1.27 (t, 3H,



SCHEME 2



SCHEME 3

$^3J_{HH}$ = 7.60 Hz, OCH_2CH_3), 2.88 (q, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2CH_3), 4.15 (q, 2H, $^3J_{HH}$ = 7.6 Hz, OCH_2CH_3), 6.23 (s, 2H, NCH_2), 7.91 (dd, 1H, $^3J_{HH}$ = 7.8, 6.9 Hz, 5-H), 8.25 (d, 1H, $^3J_{HH}$ = 7.8 Hz, 4-H), 9.18 (s, 1H, 2-H), 9.30 (d, 1H, $^3J_{HH}$ = 6.9 Hz, 6-H).

1j: Yield 94%, m.p. 66–68°C. Anal. calcd. for $C_{12}H_{18}NO_2Br$ (288.1): C, 50.0; H, 6.3; N, 4.9. Found C, 49.8; H, 6.1; N, 5.1. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.20–1.89 (unresolved m, 4H, β-, γ-CH_2), 2.79 (t, 2H, $^3J_{HH}$ = 7.6 Hz, α-CH_2), 3.68 (s, 3H, OCH_3), 6.23 (s, 2H, NCH_2), 7.92 (dd, 1H, $^3J_{HH}$ = 7.6, 6.2 Hz, 5-H), 8.23 (d, 1H, $^3J_{HH}$ = 7.6 Hz, 4-H), 9.31 (merged s and d, 2H, $^3J_{HH}$ = 6.2 Hz, 2-, 6-H).

TABLE 4 ^{31}P NMR and ^{1}H NMR Data of **4** in $CDCl_3$ and of Mixture **4p** and **5q** in C_6D_6, δ (ppm), and J (H_Z)

	4h	***4i***	***4j***[a]	***4k***[b]	***4a,b,l,n***	***4h,i,m,o***	***4p***[c]	***5q***[d]
^{31}P	178.9	178.8	178.2	178.7	178.9 (29%) 178.7 (13%) 178.5 (21%) 178.4 (37%)	179.1 (21%) 178.9 (43%) 178.8 (16%) 178.6 (20%)	180.2	162.7
5-H	9.78	9.76	9.80	9.85	9.38	9.76	9.36	9.50
7-H	8.62	8.60	8.83	8.86	8.40	8.61	6.24	6.53
^3J (7H,8H)	9.2	9.2	9.3	9.2	10.7	9.1	8.3	8.5
8-H	7.31	7.29	6.66	6.65	6.24	7.30	8.41	6.04
^4J (P,H)	1.6	1.9	1.7	1.6		2.2		
1,3-OCH_3	3.93 3.94		3.52 3.62		3.23 3.32	3.92 3.93	3.19 3.28	
1,3-OCH_2		4.38 4.40		4.17 4.25	3.88 3.96	4.39 4.40		3.93
1,3-OCH_2CH_3		1.41 1.42		1.06 1.14	0.81 0.85	1.41 1.42		0.85
^3J (H,H)		7.1		7.1	7.3	7.1		7.2
6-Et/Me								
CH_2	2.74	2.72				2.72		1.88
CH_3	1.33	1.25			1.42	1.32		0.65
^3J (H,H)	7.5	7.5				7.5		7.2

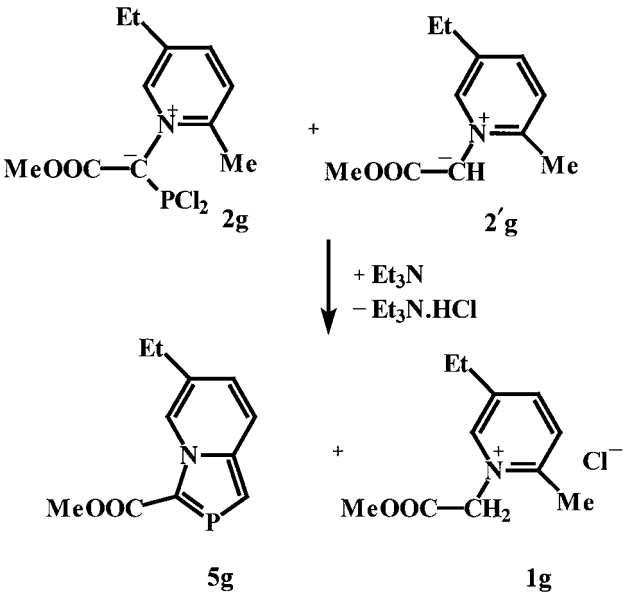
[a]6-Bu: α CH_2 δ 2.18, ^3J (H,H) = 7.7 Hz; β CH_2 δ 1.27, ^3J (H,H) = 7.2 Hz; γ CH_2 δ 1.21 (m); CH_3 δ 0.79, ^3J (H,H) = 7.3 Hz.
[b]6-Bu: α CH_2 δ 2.16, ^3J (H,H) = 7.5 Hz; β CH_2 δ 1.59, ^3J (H,H) = 7.6 Hz; γ CH_2 δ 1.06–1.14 (m); CH_3 δ 0.79, ^3J (H,H) = 7.2 Hz.
[c]6-H δ 5.83, ^3J (6H,5H) = 6.9 Hz, ^3J (6H,7H) = 7.2 Hz.
[d]1-H δ 6.93, ^2J (P,H) = 34.4 Hz.

TABLE 5 ^{13}C NMR Data of **4** in $CDCl_3$, δ (ppm), and J (H_Z)

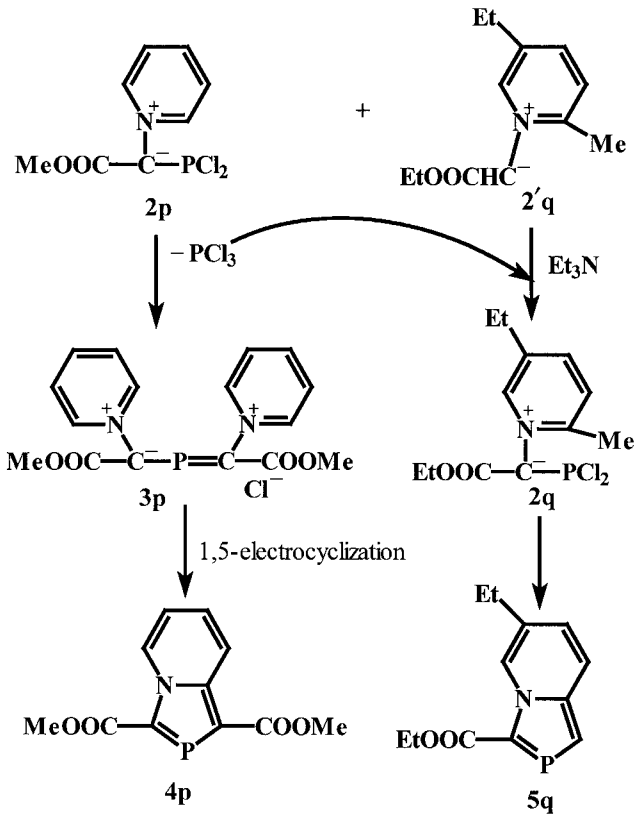
	4h [a]	***4i*** [b]	***4j*** [c]	***4k*** [d]
C-1	125.3	125.6	124.1	124.5
^1J (P,C)	41.2	40.6	40.5	40.1
C-3	138.6	139.3	138.2	137.9
^1J(P,C)	50.6	49.4	48.5	50.2
C-5	131.4	131.2	129.1	128.9
^3J (P,C)	2.5	2.2	2.4	2.2
C-6	119.2	119.2	118.1	118.1
^4J (P,C)	3.1	3.5	3.6	3.6
C-7	128.6	128.4	127.9	127.7
C-8	126.8	126.8	126.3	126.2
^3J (P,C)	3.1	2.4	2.7	2.2
C-8a	146.0	145.9	144.8	144.8
^2J (P,C)	7.5	7.5	8.0	7.4
1,3-OEt/OMe				
CH_2		60.3		59.3
		60.6		59.6
CH_3	51.5	14.3	50.5	13.3
	51.7	14.4	50.7	13.4
1-CO	164.1	163.7	163.1	162.6
^2J (P,C)	19.6	19.6	19.8	19.8
3-CO	166.5	166.2	165.4	165.0
^2J (P,C)	21.0	20.3	21.7	21.0

[a] 6-Et: CH_3 δ 14.8, CH_2 δ 26.0.
[b] 6-Et: CH_3 δ 14.8, CH_2 δ 26.0.
[c] 6-Bu: α CH_2 δ 31.5; β CH_2 δ 21.2; γ CH_2 δ 21.1; CH_3 δ 12.7.
[d] 6-Bu: α CH_2 δ 31.5; β CH_2 δ 21.2; γ CH_2 δ 21.0; CH_3 δ 12.8.

1k: Yield 42%, m.p. 53–55°C. Anal. calcd. for $C_{13}H_{20}NO_2Br$ (302.2): C, 51.6; H, 6.7; N, 4.6. Found C, 51.4; H, 6.7; N, 4.7. ^1H NMR ($CDCl_3$): $\delta = 0.94$ (t, 3H, $^3J_{HH} = 7.3$ Hz, CH_3), 1.27 (t, 3H, $^3J_{HH} = 7.1$ Hz, OCH_2CH_3), 1.41 (sext., 2H, $^3J_{HH} = 7.4$ Hz, γ-CH_2), 1.73 (quint., 2H, $^3J_{HH} = 7.6$ Hz, β-CH_2), 2.9 (t, 2H, $^3J_{HH} = 7.7$ Hz, α-CH_2), 4.28 (q, 2H, $^3J_{HH} = 7.1$ Hz, CH_2CH_3), 6.31 (s, 2H, NCH_2), 8.06 (t, 1H, $^3J_{HH} = 7.5$ Hz, 5-H), 8.34 (d, 1H, $^3J_{HH} = 7.8$ Hz, 4-H), 9.42 (unresolved broad signal, 2H, 2–, 6-H).



SCHEME 4



SCHEME 5

*Pyridinium Dichlorophosphinomethylides (**2a–g**)*

N-Alkylpyridinium bromide **2** (10 mmol) was suspended in toluene (35 ml) and triethylamine (2.01 g, 20 mmol) was added slowly with stirring at room temperature whereupon a light yellow colour developed. After stirring the reaction mixture for 10–15 min, a solution of phosphorus trichloride (1.36 g, 10 mmol) in toluene (10 ml) was added slowly with continuous stirring. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After 5–6 h, of stirring of the mixture, the ^{31}P NMR signal of phosphorus trichloride at δ 220 disappeared completely and a new signal appeared at $\delta \sim 145$. The reaction mixture was filtered and the residue washed with toluene (3 × 5 ml). In the case of **2g**, the solvent was removed in vacuo and the residue was extracted with diethyl ether (3 × 50 ml). Combined ether

extracts or toluene filtrates were concentrated to about 10–15 ml and left in a refrigerator whereupon a yellow or orange coloured solid deposited which was separated and dried in vacuo.

*2-Phosphaindolizines (**4h–k**)*

N-(Alkoxycarbonylmethyl)-3-alkylpyridinium bromide (**1h–k**) (2 mmol) was suspended in methylene chloride (40 ml) under nitrogen followed by addition of triethylamine (4 mmol) with constant stirring. After the colour changed to orangish yellow, a solution of phosphorus trichloride (1 mmol) in methylene chloride (20 ml) was added dropwise with stirring. Stirring was continued for 5–20 h till the reaction was complete, as indicated by ^{31}P NMR spectroscopy. The solvent was removed thereafter under reduced pressure and the residue extracted with diethyl ether (3 × 50 ml). Combined extracts were concentrated to one third of its volume and left in a refrigerator whereupon a yellow–orange solid (**4**) deposited which was separated and dried in vacuo.

*Reaction of Pyridinium Dichlorophosphino-alkoxycarbonylmethylide (**2a/2i**) with Pyridinium Alkoxycarbonylmethylide (**2′b/2′h**)*

To a well stirred suspension of *N*-(methoxycarbonylmethyl)pyridinium bromide (**1a**) (2.09 g, 9 mmol) in toluene (30 ml) was added triethylamine (1.81 g, 18 mmol), followed by dropwise addition of a solution of phosphorus trichloride (1.22 g, 9.0 mmol) in toluene in about 1.5 h. The reaction mixture was allowed to stir overnight at room temperature; a ^{31}P NMR signal at δ 147.6 indicated the formation of the pyridinium dichlorophosphinomethoxycarbonylmethylide (**2a**). To it was added a solution of **2′b** generated in situ by the addition of triethylamine (1.81 g, 18 mmol) to *N*-(ethoxycarbonylmethyl)pyridinium bromide (**1b**) (2.20 g, 9 mmol) in methylene chloride (20 ml). The reaction mixture was stirred at r.t. for 3 h. The ^{31}P NMR signal of the ylide at δ 147.6 was replaced by the signals at δ 181.4 and 181.9, observed by use of a JEOL FX 90 Q spectrometer, which were resolved into four signals in $CDCl_3$ on a Bruker ARX 300 instrument (Table 4). The reaction mixture was thereafter dried completely in vacuo and the residue was extracted with diethyl ether (3 × 50 ml). All the ether extracts were combined, concentrated to about 15 ml and kept in a refrigerator. Fine yellow crystals deposited which were filtered off and dried in vacuo. The ^{31}P-, ^{1}H- and ^{13}C NMR studies indicated the product to be a mixture of four 2-phosphaindolizines (**4a,b,l,n**). Likewise a reaction of **2i** with **2′h** afforded a mixture of **4h,i,m,o**.

*Reaction of 5-Ethyl-2-Methylpyridinium Dichlorophosphino-Methoxycarbonylmethylide (**2g**) with 5-Ethyl-2-Methylpyridinium Methoxycarbonylmethylide (**2′g**)*

A solution of **2g** (1.18 g, 4 mmol; δ ^{31}P = 150.2) in toluene (20 ml) was added dropwise to a solution of **2′g** generated in situ from the reaction of **1g** (1.10 g, 4 mmol) with triethylamine (0.81 g, 8 mmol) in methylene chloride (20 ml). After stirring of the mixture at room temperature for 3 h, only one signal at δ 163.5 was observed in ^{31}P NMR spectrum of the reaction mixture. ^{31}P- and ^{1}H NMR studies of the isolated product, obtained by extracting the reaction mixture with diethyl ether, indicated it to be **5g** [28].

*Reaction of Pyridinium Dichlorophosphino-Methoxycarbonylmethylide (**2p**) with 5-Ethyl-2-Methylpyridinium Ethoxycarbonylmethylide (**2′q**)*

A solution of **2p** (δ ^{31}P = 147.3) in toluene (30 ml) was generated from the reaction of *N*-(methoxycarbonylmethyl)pyridinium bromide (2.14 g, 9 mmol) with triethylamine (1.86 g, 18 mmol) and phosphorus trichloride (1.26 g, 9 mmol) at room temperature. To this was added a suspension of *N*-(ethoxycarbonylmethyl)-5-ethyl-2-methylpyridinium bromide (2.65 g, 9 mmol) in methylene chloride (20 ml) containing triethylamine (1.86 g, 18 mmol). The reaction mixture was stirred at room temperature overnight. The ^{31}P NMR of the reaction mixture indicated the disappearance of the signal of **2p** (δ 147.3) and the appearance of two signals at δ 162.7 and 180.2. The reaction mixture was dried in vacuo. The residue was extracted with diethyl ether (3 × 50 ml). All the ether extracts were combined, concentrated to about 15 ml and kept in a refrigerator. Yellow solid deposited, was filtered off, and dried in vacuo. The ^{31}P- and ^{1}H NMR studies indicated it to be a mixture of **4p** and **5q**.

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