Tetrahedron Vol. 49, No. 23, pp. 5153-5168, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Reaction of Allyl Iminophosphoranes with Ketenes and Acyl Chlorides: One-Pot Preparation of 4-Pentenenitriles[1]

Pedro Molina*, Mateo Alajarín, Carmen López-Leonardo, and Julian Alcántara.

Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia,
Campus de Espinardo, E-30071 Murcia, Spain.

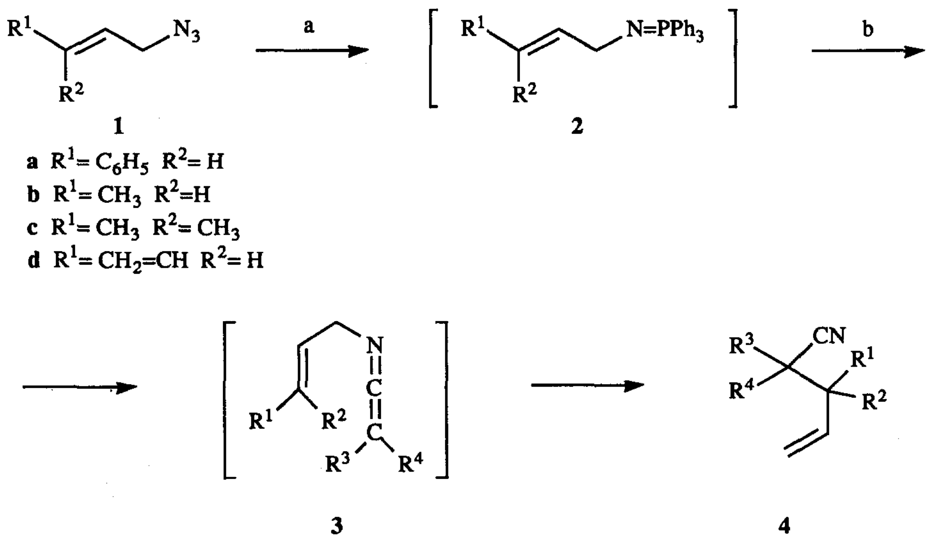
(*Received in UK* 12 *February* 1993)

Abstract: One-pot conversion of allyl azides into 4-pentenenitriles **4** is achieved by sequential treatment of allyl azides with triphenylphosphine and the corresponding ketene under mild and neutral conditions. On the other hand, allyl iminophosphoranes and related react with arylacetic acid chlorides to give unexpectedly the phosphonium salts **5** which by treatment with base and then heating lead to 4-pentenenitriles **9**.

One-flask multiple bond-forming reactions are powerful synthetic tools widely used in the convergent synthesis of complex molecules. In this context, in the last few years we have been developing novel cyclization methods based on consecutive processes involving unsaturated heterocumulenes as key intermediates which can undergo several kinds of heterocyclization reactions such as 6π-electrocyclization[2], intramolecular [4+2] Diels-Alder cycloaddition[3], and intramolecular amination[4]. We now report the iminophosphorane-mediated one-pot conversion of allyl azides into α-allylated nitriles based on a consecutive Staudinger reaction / aza Wittig-type reaction / 3-aza Claisen rearrangement process.

The starting azides **1a**[5], **1b**[6], **1c**[7], and **1d**[8] were prepared from the corresponding bromides and Amberlite IR-400 (N_3^- form)[9]. Allyl azides are known to equilibrate rapidly at room temperature by 1,3-rearrangement[10], so the purity of azides **1** used in this work ranged from 60% (**1b**) to ≥ 95% (**1d**) as determined by ^{1}H NMR. Staudinger reaction of azides **1** with triphenylphosphine in dry benzene led to the corresponding iminophosphoranes **2** which were used without purification for the next step. Aza Wittig-type reaction of iminophosphoranes **2** with disubstituted ketenes, prepared by dehydrochlorination of the corresponding 2,2-disubstituted acyl chlorides with triethylamine[11], in the same solvent at room temperature for a short period of time, yielded the corresponding nitriles **4** in moderate yields (41-60%). Considering the number of steps involved in this one-pot conversion, the yields obtained can by considered as very good. In general, this conversion proceeded without complications in a range of substrates.

Scheme 1 presents some of the 4-pentenenitriles **4** rendered readily available *via* this methodology. The ready availability of quaternary stereocenters *via* this conversion is shown in entries **4b**, **4c**, **4d**, and **4g**. A word about the diastereoselection of this reaction is relevant. Nitrile **4d** was obtained in 55% yield as a 10:1 mixture of diastereomers (by ^{1}H NMR); similarly nitrile **4b** was obtained in 48% yield as 2:1 mixture of diastereomers, whereas in the formation of **4c** diastereoselection was not observed.

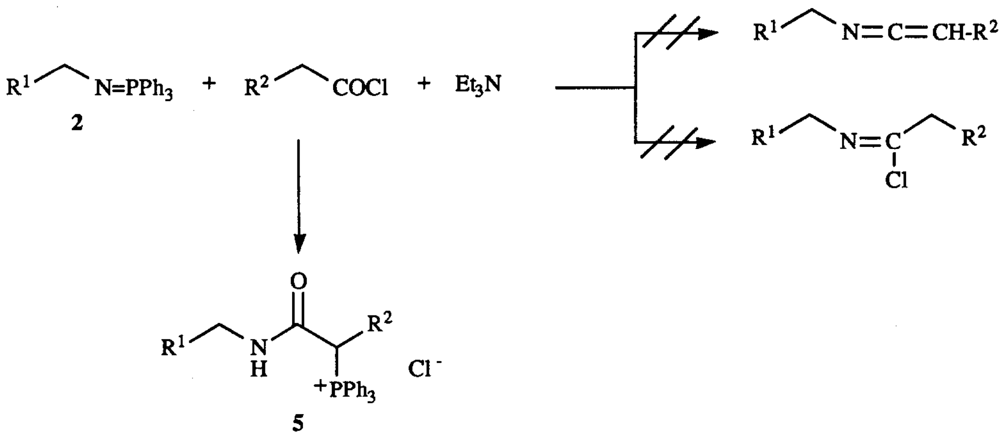


Reagents: a) PPh_3, C_6H_6, r.t.; b) $R^3R^4C{=}C{=}O$, C_6H_6, r.t.

Compound	R^1	R^2	R^3	R^4	Yield %
4a	C_6H_5	H	C_6H_5	C_6H_5	51
4b	C_6H_5	H	C_6H_5	C_2H_5	48
4c	C_6H_5	H	C_6H_5	4-$CH_3C_6H_4$	44
4d	CH_3	H	C_6H_5	C_2H_5	55
4e	CH_3	CH_3	C_6H_5	C_6H_5	47
4f	$CH_2{=}CH$	H	C_6H_5	C_6H_5	60
4g	$CH_2{=}CH$	H	C_6H_5	C_2H_5	41

Scheme 1

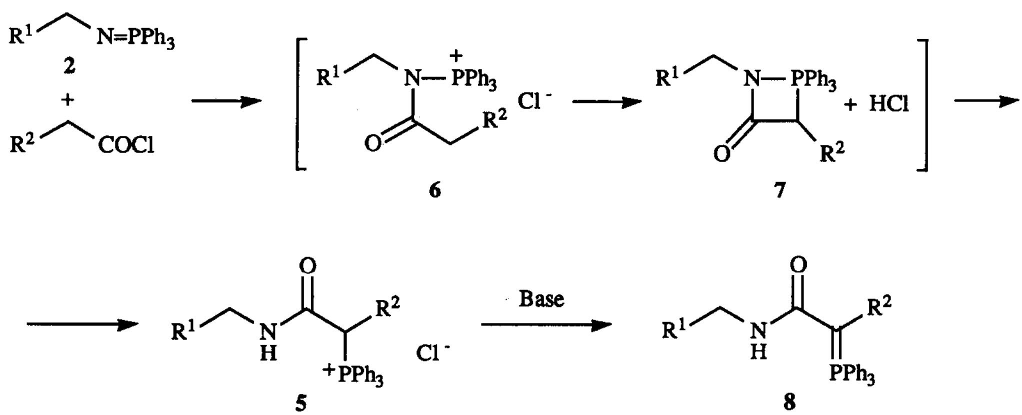
The conversion **2** → **4** can be rationalized in terms of an initial formation of a ketenimine **3** as highly reactive intermediate which cleanly undergoes a 3-aza-Claisen rearrangement to give **4**. In general, the conversion of ketenimines to nitriles is known to ocurr with varying degrees of ease and through competing reaction pathways depending on the nature of C- and N-substituents. Kinetic, stereochemical and trapping experiments involving N-(arylmethyl)diphenylketenimines have shown that the [1,3] nitrogen to carbon rearrangement proceeds *via* a free-radical mechanism[12]. Formulation of ketenimine 3 as intermediate is derived from the fact that iminophosphoranes react with ketenes to give ketenimines[13]. This sort of intermediate has also been postulated in the conversion of N-allyl amides into α-allylated nitriles[14].



Compound	R^1	R^2	Yield %
5a	$(CH_3)_2C$=CH	C_6H_5	37
5b	(E)-CH_2=CH-CH=CH	C_6H_5	66
5c	(E)-CH_2=CH-CH=CH	4-ClC_6H_4	25
5d	(E)-CH_2=CH-CH=CH	4-FC_6H_4	41
5e	(E)-C_6H_5-CH=CH	C_6H_5	67
5f	(E)-C_6H_5-CH=CH	4-ClC_6H_4	35
5g	(E)-C_6H_5-CH=CH	4-FC_6H_4	68
5h	CH≡C	C_6H_5	55
5i	C_6H_5	C_6H_5	51
5j	CH_3-CH_2-OCO	C_6H_5	97
5k	CH_2=CH$(CH_2)_2$	C_6H_5	33
5l	C_6H_5	CH_3	30

Scheme 2

Having established that the reaction of iminophosphoranes **2** with ketenes provides unsaturated nitriles under extremely mild conditions, we tried to expand the scope of this conversion by reaction of iminophosphoranes **2** with several substituted acetyl chlorides under ketene formation conditions. At first, it was reasonable to expect that iminophosphoranes **2** would react in an aza Wittig-type fashion either with the *in situ* formed ketene to give a ketenimine or directly with the acyl chloride to give the corresponding imidoyl chloride which by the action of triethylamine could lead to the intermediate ketenimine. However, the reaction unexpectedly led to the formation of phosphonium salts **5** (25-97%). It is noteworthy that in the absence of triethylamine the yields are similar to that with triethylamine. Examples in Scheme 2 suggest that this reaction seems to be quite general. The reaction with the iminophosphorane derived from (S)-1-phenylethylamine led to the corresponding phosphonium salt and no diastereoselection was observed.

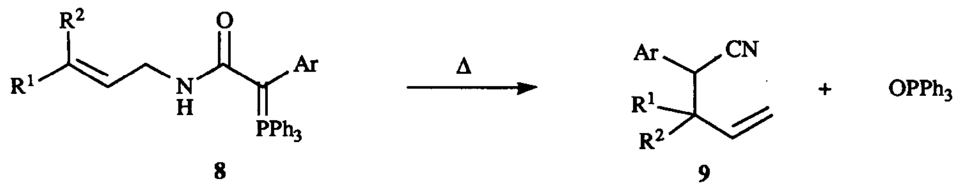


Compound	R^1	R^2	Yield %
8a	$(CH_3)_2C$=CH	C_6H_5	89
8b	(E)-CH_2=CH-CH=CH	C_6H_5	83
8c	(E)-CH_2=CH-CH=CH	4-ClC_6H_4	79
8d	(E)-CH_2=CH-CH=CH	4-FC_6H_4	75
8e	(E)-C_6H_5-CH=CH	C_6H_5	86
8f	(E)-C_6H_5-CH=CH	4-ClC_6H_4	70
8g	(E)-C_6H_5-CH=CH	4-FC_6H_4	84
8h	CH≡C	C_6H_5	80
8i	C_6H_5	C_6H_5	80
8j	CH_3-CH_2-OCO	C_6H_5	66
8k	CH_2=CH$(CH_2)_2$	C_6H_5	75

Scheme 3

The aza Wittig reaction between acyl chlorides and iminophosphoranes to give imidoyl chlorides is well-documented[15]. However no examples with the two components (iminophosphorane and acyl chloride) bearing hydrogen atoms at α position have been reported, to the best of our knowledge. A tentative mechanism for the conversion **2** → **5** can be rationalized in terms of an initial acylation to give an acylamino phosphonium salt **6** which undergoes cyclization to give a four-membered ring **7** and further P-N bond cleavage by the action of hydrogen chloride to give **5** (Scheme 3). This conversion formally is a [1,3] nitrogen to carbon rearrangement involving a triphenylphosphine moiety. To the best of our knowledge no reports dealing with such sort of rearrangement have been described and only a related process involving a [1,3] nitrogen to nitrogen triphenylphosphine migration has been reported[16].

The phosphonium salts **5** undergo deprotonation by the action of bases to give the α-carbamoyl phosphoranes **8** in good yields (66-89%) (Scheme 3). When compounds **8** were heated at temperatures slightly higher than their melting points (90-140 °C) triphenylphosphine oxide and the corresponding 4-pentenenitrile **9** were formed without diastereoselection (Scheme 4).

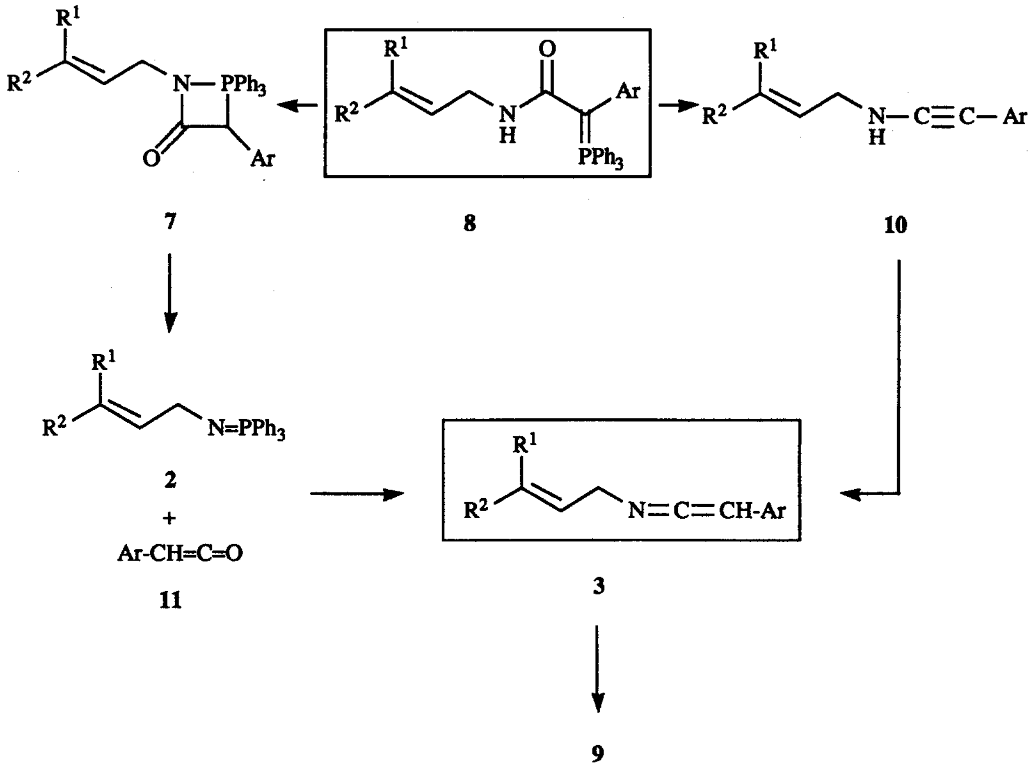


Compound	R^1	R^2	Ar	Δ °C	Yield %
9a	CH_3	CH_3	C_6H_5	140	55
9b	CH_2=CH	H	C_6H_5	130	57
9c	CH_2=CH	H	4-ClC_6H_4	115	29
9d	CH_2=CH	H	4-FC_6H_4	120	69
9e	C_6H_5	H	C_6H_5	125	60
9f	C_6H_5	H	4-ClC_6H_4	90	25
9g	C_6H_5	H	4-FC_6H_4	130	59

Scheme 4

We thought at first that the conversion **8** → **9** would involve thermal triphenylphosphine oxide extrusion to give an ynamine **10** which isomerizes to the more stable ketenimine **3** and eventually 3-aza-Claisen rearrangement to give **9**. Another acceptable pathway would involve the formation of the four membered ring **7** followed by [2+2] retrocycloaddition to give the iminophosphorane **2** and aryl ketene **11** which through an aza Wittig-type reaction yield the intermediate ketenimine **3** (Scheme 5).

Strong support for the latter pathway was provided by trapping of the intermediate ketene **11**. Thus, when compounds **8** were heated in the presence of p-toluidine or p-cresol, the final products were found to be the iminophosphorane **2** and the corresponding arylacetanilide or aryl arylacetic ester respectively.



Scheme 5

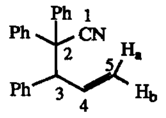
Experimental

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as films or Nujol emulsions on a Nicolet-5DX spectrophotometer. NMR spectra were recorded on a Bruker AC-200 (200 MHz) or a Varian Unity-300 (300 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

General Procedure for the Preparation of 4-Pentenenitriles 4.

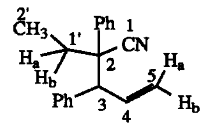
To a solution of triphenylphosphine (2.62 g, 1 mmol) in dry benzene (20 ml) was added dropwise a solution of the appropriate azide **1** (1 mmol) in the same solvent and the reaction mixture was stirred at 70 °C for 1 h. The solution was cooled at room temperature and the ketene (1 mmol) was added under nitrogen. The resultant solution was stirred at room temperature for 15 min, the solvent was then removed and the residual material was extracted with n-hexane (2 x 20 ml). The extracts were combined and concentrated to dryness, the crude product was chromatographed on silica gel column, eluting with n-hexane/ethyl acetate (9:1) to afford **4**.

4a: (51%), m.p. 129-130 °C (colourless prisms from n-hexane/ethyl acetate); (Found: C, 89.15; H, 6.12; N, 4.59.



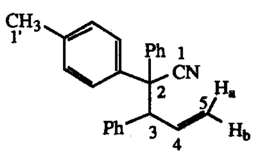
$C_{23}H_{19}N$ requires: C, 89.28; H, 6.19; N, 4.53); i.r. (Nujol) 2242, 1494 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 4.44 (d, 1H, J= 7.7 Hz, H-3), 5.10 (d, 1H, J= 17.1 Hz, H_a-5), 5.19 (d, 1H, J= 10.3 Hz, H_b-5), 6.30 (ddd, 1H, J= 7.7, 10.3, 17.1 Hz, H-4), 7.04-7.80 (m, 15H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 56.17 (C-3), 57.30 (C-2), 119.50 (C-5), 121.54 (C-1), 127.10 (C_p), 127.22 (C_m), 127.31 (C_p), 127.87 (C_p), 127.95 (C_m), 128.09 (C_o), 128.22 (C_o), 128.66 (C_m), 129.48 (C_o), 136.63 (C_i), 136.84 (C-4), 136.86 (C_i), 136.92 (C_i); m/z (%) 165 (20), 117 (100).

4b: (48%), colourless oil; (Found: C, 87.25; H, 7.40; N, 5.30. $C_{19}H_{19}N$ requires: C, 87.31; H, 7.33; N, 5.36); i.r.



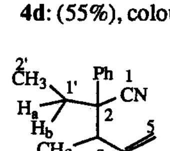
(film) 2236, 1494 cm^{-1}; ^{1}H n.m.r. (200 MHz, $CDCl_3$) mixture of diastereomers 2/1 δ 0.75 (t, 3H, J= 7.3 Hz, H-2'), 0.87 (t, 3H, J= 7.2 Hz, H-2'), 1.76 (dd, 1H, J= 7.3, 14.0 Hz, H_a-1'), 1.91 (dd, 1H, J= 7.3, 14.0 Hz, H_b-1'), 2.31 (dd, 1H, J= 7.2, 14.1 Hz, H_a-1'), 2.35 (dd, 1H, J= 7.2, 14.1 Hz, H_b-1'), 3.55 (d, 1H, J= 9.0 Hz, H-3), 3.64 (d, 1H, J= 8.8 Hz, H-3), 4.78 (dd, 1H, J= 1.4, 16.9 Hz, H_a-5), 4.99 (dd, 1H, J= 1.4, 10.3 Hz, H_b-5), 5.28 (dd, 1H, J= 1.4, 16.5 Hz, H_a-5), 5.30 (dd, 1H, J= 1.4, 10.5 Hz, H_b-5), 6.05 (ddd, 1H, J= 8.8, 10.3, 16.9 Hz, H-4), 6.39 (ddd, 1H, J= 9.0, 10.5, 16.5 Hz, H-4), 6.9-7.4 (m, 20 H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) mixture of diastereomers δ 9.64 (C-2'), 9.75 (C-2'), 31.30 (C-1'), 31.81 (C-1'), 51.86 (C-2), 53.69 (C-2), 59.81 (C-3), 60.50 (C-3), 118.74 (C-5), 118.99 (C-5), 121.41 (C-1), 121.48 (C-1), 127.03 (C_p), 127.57 (C_p), 127.71 (C_p), 127.84 (C_p), 127.07*, 127.16*, 128.03*, 128.41*, 128.58*, 128.65*, 128.67*, 129.28*, 136.10 (C_i), 136.67 (C-4), 136.67 (C_i), 138.55 (C-4), 138.97 (C_i), 139.10 (C_i). *Ortho and meta carbons of the phenyl groups; m/z (%) 261 (M^+, 5), 117 (100).

4c: (44%), colourless oil; (Found: C, 89.18; H, 6.43; N, 4.22. $C_{24}H_{21}N$ requires: C, 89.13; H, 6.54; N, 4.33); i.r.



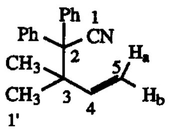
(film) 2236, 1495 cm^{-1}; ^{1}H n.m.r. (200 MHz, $CDCl_3$) mixture of diastereomers 1/1 δ 2.07 (s, 6H, H-1'), 4.43 (d, 2H, J= 8.1 Hz, H-3), 5.06 (dd, 1H, J= 1.0, 10.3 Hz, H_b-5), 5.14 (dd, 1H, J= 0.9, 17.0 Hz, H_a-5), 5.19 (dd, 1H, J= 1.0, 16.9 Hz, H_a-5), 5.24 (dd, 1H, J= 0.9, 10.4 Hz, H_b-5), 6.28 (ddd, 1H, J= 8.1, 10.4, 17.0 Hz, H-4), 6.32 (ddd, 1H, J= 8.1, 10.3, 16.9 Hz, H-4), 6.82-7.61 (m, 28H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) mixture of diastereomers δ 14.24 (C-1'), 14.28 (C-1'), 56.35 (C-3), 56.37 (C-3), 57.04 (C-2), 57.11 (C-2), 119.44 (C-5), 119.51 (C-5), 121.80 (C-1), 121.82 (C-1), 127.16*, 127.27*, 128.02*, 128.05*, 128.10*, 128.27*, 128.34*, 128.48*, 128.71*, 129.03*, 129.45*, 129.59*, 129.63*, 130.03*, 130.12*, 130.37*, 135.05 (C-4), 136.12 (C-4), 137.82 (C_i), 138.27 (C_i), 139.06 (C_i), 139.08 (C_i), 139.10 (C_i), 139.23 (C_i), 139.68 (C_i), 139.82 (C_i). *Ortho, meta and para carbons of the aryl groups; m/z (%) 165 (20), 117 (100).

4d: (55%), colourless oil; (Found: C, 84.25; H, 8.53; N, 7.11. $C_{14}H_{17}N$ requires: C, 84.37; H, 8.60; N, 7.03); i.r.

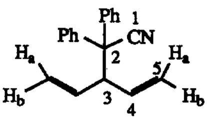


(film) 2236, 1494 cm^{-1}; ^{1}H n.m.r. (300 MHz, $CDCl_3$) mixture of diastereomers 10/1; major diastereomer δ 0.90 (t, 3H, J= 7.5 Hz, H-2'), 1.21 (d, 3H, J= 6.8 Hz, H-1"), 1.88 (dq, 1H, J= 7.5, 13.8 Hz, H_a-1'), 2.02 (dq, 1H, J= 7.5, 13.8 Hz, H_b-1'), 2.67 (dq, 1H, J= 6.8, 8.2 Hz, H-3), 4.87-5.54 (m, 3H, H-4 and H-5), 7.25-7.37 (m, 5H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) major diastereomer δ 9.70 (C-2'), 16.21 (C-1"), 32.83 (C-1'), 46.64 (C-3), 53.20 (C-2), 116.90 (C-5), 122.13 (C-1), 127.06*, 127.93*, 128.51*, 138.16 (C_i), 137.97 (C-4). *Ortho, meta and para carbons of the aryl group; m/z (%) 199 (M^+, 7), 117 (100).

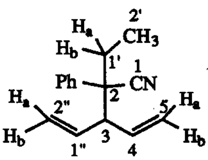
4e: (47%), colourless oil; (Found: C, 87.40; H, 7.25; N, 5.23. $C_{19}H_{19}N$ requires: C, 87.31; H, 7.33; N, 5.36); i.r. (film) 2236, 1494 cm^{-1}; ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 1.36 (s, 6H, H-1'), 5.19 (dd, 1H, J= 0.7, 10.8 Hz, H_b-5), 5.26 (dd, 1H, J= 0.7, 17.5 Hz, H_a-5), 6.07 (dd, 1H, J= 10.8, 17.5 Hz, H-4), 7.25-7.59 (m, 10H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 26.08 (C-1'), 43.69 (C-3), 60.67 (C-2), 113.80 (C-5), 123.02 (C-1), 127.69 (C_p), 128.04 (C_m), 129.59 (C_o),



138.34 (C_i), 143.81 (C-4); m/z (%) 149 (100), 117 (49).



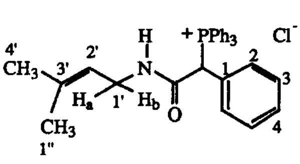
4f: (60%), colourless oil; (Found: C, 88.07; H, 6.54; N, 5.32. $C_{19}H_{17}N$ requires: C, 87.99; H, 6.61; N, 5.40); i.r. (film) 2236, 1494 cm^{-1}; ^1H n.m.r. (200 MHz, $CDCl_3$) δ 3.98 (t, 1H, J= 7.3 Hz, H-3), 5.11 (dd, 2H, J= 1.3, 17.0 Hz, H_a-5), 5.15 (dd, 2H, J= 1.3, 10.6 Hz, H_b-5), 5.86 (ddd, 2H, J= 7.3, 10.6, 17.0 Hz, H-4), 7.14-7.75 (m, 10H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 54.05 (C-3), 56.52 (C-2), 119.29 (C-5), 120.85 (C-1), 127.26 (C_o), 127.69 (C_p), 128.64 (C_m), 135.27 (C-4), 138.64 (C_i); m/z (%) 259 (M^+, 6), 165 (100).



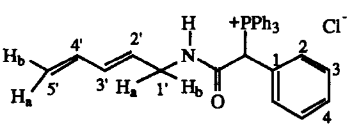
4g: (41%), colourless oil; (Found: C, 85.32; H, 8.02; N, 6.71. $C_{15}H_{17}N$ requires: C, 85.26; H, 8.11; N, 6.63); i.r. (film) 2236, 1494 cm^{-1}; ^1H n.m.r. (200 MHz, $CDCl_3$) δ 0.82 (t, 3H, 7.4 Hz, H-2'), 1.91 (dq, 1H, J= 7.4, 13.4 Hz, H_a-1'), 2.18 (dq, 1H, J= 7.4, 13.4 Hz, H_b-1'), 3.16 (dd, 1H, J= 7.4, 9.0 Hz, H-3), 4.92 (dd, 1H, J= 1.6, 16.8 Hz, H_a-5), 4.97 (dd, 1H, J= 1.6, 10.3 Hz, H_b-5), 5.22 (dd, 1H, J= 1.6, 17.0 Hz, H_a-2"), 5.28 (dd, 1H, J= 1.6, 10.4 Hz, H_b-2"), 5.58 (ddd, 1H, J= 7.4, 10.4, 17.0 Hz, H-1"), 5.93 (ddd, 1H, J= 9.0, 10.3, 16.8 Hz, H-4), 7.24-7.39 (m, 5H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 9.52 (C-2'), 31.44 (C-1'), 52.48 (C-2), 57.38 (C-3), 118.19 (C-5), 119.00 (C-2"), 121.01 (C-1), 126.93 (C_o), 127.74 (C_p), 128.65 (C_m), 135.18 (C-4), 135.59 (C-1"), 136.46 (C_i); m/z (%) 211 (M^+, 3), 67 (100).

General Procedure for the Preparation of Phosphonium Salts 5.

To a solution of the corresponding iminophosphorane **2** (4 mmol) in dry benzene (10 ml) at 5 °C was added dropwise the appropriate acyl chloride (4 mmol) in the same solvent (5 ml) under nitrogen. The reaction mixture was allowed to warm at room temperature and then stirred for 4 h. The precipitated solid was separated by filtration and recrystallized from benzene to give **5**.

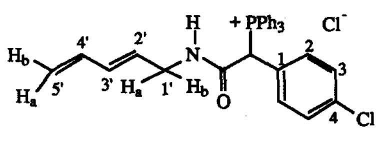


5a: (37%), m.p. 219-220 °C (colourless prisms from benzene); (Found: C, 74.32; H, 6.37; N, 2.85. $C_{31}H_{31}ClNOP$ requires: C, 74.47; H, 6.25; N, 2.80); i.r. (Nujol) 3200, 1665 cm^{-1}; ^1H n.m.r (200 MHz, $CDCl_3$) δ 1.54 (s, 3H, H-1"), 1.60 (s, 3H, H-4'), 3.59 (ddd, 1H, J= 4.3, 6.5, 14.8 Hz, H_a-1'), 3.75 (ddd, 1H, J= 5.5, 6.4, 14.8 Hz, H_b-1'), 5.01 (dd, 1H, J= 6.4, 6.5 Hz, H-2'), 7.1-7.9 (m, 20H, aryl), 8.00 (d, 1H, $^2J_{P-H}$= 12.6 Hz, CH-P), 9.81 (dd, 1H, J= 4.3, 5.5 Hz, NH); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 17.86 (C-1"), 25.39 (C-4'), 37.97 (C-1'), 47.65 (CH-P, ^1J= 50.8 Hz), 118.16 (C_i, ^1J= 85.5 Hz), 119.64 (C-2'), 128.60 (C-1, ^2J= 7.0 Hz), 128.65 (C-3, ^4J= 1.1 Hz), 128.91 (C-4, ^5J= 3.3 Hz), 129.69 (C_m, ^3J= 12.7 Hz), 131.00 (C-2, ^3J= 6.1 Hz), 134.47 (C_p, ^4J= 3.1 Hz), 134.72 (C_o, ^2J= 9.6 Hz), 135.02 (C-3'), 165.75 (CO, ^2J= 1.7 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.42; m/z (%) 278 (5), 118 (100).

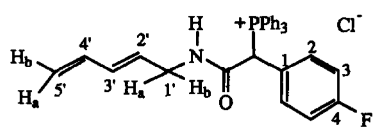


5b: (66%), m.p. 95-97 °C (colourless prisms from benzene); (Found: C, 74.65; H, 5.81; N, 2.93. $C_{31}H_{29}ClNOP$ requires: C, 74.77; H, 5.87; N, 2.81); i.r. (Nujol) 3211, 1670 cm^{-1}; ^1H n.m.r (200 MHz, $CDCl_3$) δ 3.66 (ddd, 1H, J= 5.2, 6.2, 15.4 Hz, H_a-1'), 3.84 (ddd, 1H, J= 6.0, 6.1, 15.4 Hz, H_b-1'), 4.96 (dd, 1H, J= 1.7, 9.3 Hz, H_b-5'), 5.03 (dd, 1H, J= 1.7, 12.2 Hz, H_a-5'), 5.47 (ddd, 1H, J= 6.0, 6.2, 15.4 Hz, H-2'), 5.93-6.26 (m, 2H, H-3' and H-4'), 7.06-7.70 (m, 20H, aryl), 8.00 (d, 1H, $^{2}J_{P-H}$= 12.5 Hz, CH-P), 10.00 (dd, 1H, J= 5.2, 6.1 Hz, NH); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 41.17 (C-1'), 47.88 (CH-P, ^{1}J= 51.0 Hz), 116.78 (C-5'), 118.1 (C_i, ^{1}J= 85.4 Hz), 128.55 (C-1, ^{2}J= 7.0 Hz), 128.64 (C-3, ^{4}J= 1.2 Hz), 128.69 (C-2'), 128.98 (C-4, ^{5}J= 3.3 Hz), 129.73 (C_m, ^{3}J= 12.7 Hz), 130.99 (C-2, ^{3}J= 6.1 Hz), 132.24 (C-3'), 134.54 (C_p, ^{4}J= 4.5 Hz), 134.64 (C_o, ^{2}J= 9.8 Hz), 136.23 (C-4'), 166.70 (CO, ^{2}J= 2.0 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.23; m/z (%) 278 (19), 51 (100).

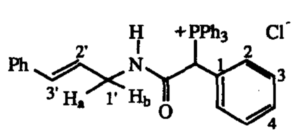
5c: (25%), m.p. 108-110 °C (brown prisms from benzene); (Found: C, 69.80; H, 5.27; N, 2.74. $C_{31}H_{28}Cl_2NOP$ requires: C, 69.93; H, 5.30; N, 2.63); i.r. (Nujol) 3126, 1670 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.66 (ddd, 1H, J= 4.9, 6.0, 15.6 Hz, H_a-1'), 3.83 (ddd, 1H, J= 6.0, 6.1, 15.6 Hz, H_b-1'), 4.99 (d, 1H, J= 10.1 Hz, H_b-5'), 5.05 (d, 1H, J= 16.9 Hz, H_a-5'), 5.47 (ddd, 1H, J= 6.0, 6.1, 15.1 Hz, H-2'), 5.97-6.23 (m, 2H, H-3', H-4'), 7.13-7.93 (m, 19H, aryl), 8.15 (d, 1H, $^{2}J_{P-H}$= 12.7, CH-P), 9.99 (dd, 1H, J= 4.9, 6.0 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.26 (C-1'), 46.94 (CH-P, ^{1}J= 51.4 Hz), 116.95 (C-5'), 117.80 (C_i, ^{1}J= 85.6 Hz), 127.22 (C-1, ^{2}J= 7.1 Hz), 128.49 (C-2'), 128.91 (C-3, ^{4}J= 2.5 Hz), 129.90 (C_m, ^{3}J= 12.6 Hz), 132.39 (C-2, ^{3}J= 6.0 Hz), 132.48 (C-3'), 134.69 (C_o, ^{2}J= 9.6 Hz), 134.74 (C_p, ^{4}J= 2.5 Hz), 135.36 (C-4, ^{5}J= 4.1 Hz) , 136.21 (C-4'), 165.79 (CO, ^{2}J= 1.5 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.18; m/z (%) 278 (7), 77 (100).



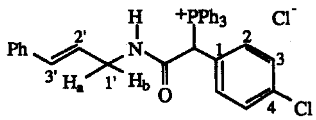
5d: (41%), m.p. 98-99 °C (brown prisms from benzene); (Found: C, 72.20; H, 5.53; N, 2.60.$C_{31}H_{28}ClFNOP$ requires: C, 72.16; H, 5.47; N, 2.71); i.r. (Nujol) 3200, 1670 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.65 (ddd, 1H, J= 4.8, 6.1, 15.8 Hz, H_a-1'), 3.85 (ddd, 1H, J= 6.0, 6.2, 15.8 Hz, H_b-1'), 4.98 (d, 1H, J= 11.4 Hz, H_b-5'), 5.03 (d, 1H, J= 17.6 Hz, H_a-5'), 5.48 (ddd, 1H, J= 4.8, 6.2, 15.0 Hz, H-2'), 5.98-6.23 (m, 2H, H-3' and H-4'), 6.85 (t, 2H, $^{3}J_{F-H}$= 8.4 Hz, H-3), 7.31-7.93 (m, 17H, aryl), 8.05 (d, 1H, $^{2}J_{P-H}$= 12.6 Hz, CH-P), 10.02 (dd, 1H, J= 6.0, 6.1 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 40.70 (C-1'), 46.42 (CH-P, $^{1}J_{C-P}$= 51.4 Hz), 115.28 (C-3, $^{4}J_{C-P}$= 2.5 Hz, $^{2}J_{C-F}$= 21.7 Hz), 116.50 (C-5'), 117.27 (C_i, $^{1}J_{C-P}$= 85.6 Hz), 124.04 (C-1, $^{2}J_{C-P}$= 6.1 Hz, $^{4}J_{C-F}$= 3.0 Hz), 128.14 (C-2'), 129.47 (C_m, $^{3}J_{C-P}$= 12.6 Hz), 131.91 (C-3'), 132.47 (C-2, $^{3}J_{C-P}$= 6.0 Hz, $^{3}J_{C-F}$= 8.1 Hz), 134.18 (C_o, $^{2}J_{C-P}$= 9.5 Hz), 134.37 (C_p, $^{4}J_{C-P}$= 3.0 Hz), 135.75 (C-4'), 162.55 (C-4, $^{5}J_{C-P}$= 3.5 Hz, $^{1}J_{C-F}$= 249.8 Hz), 165.50 (CO); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 22.08 (d, $^{6}J_{P-F}$=5.5 Hz); m/z (%) 278 (41), 277 (100).



5e: (67%), m.p. 120-121 °C (colourless needles from benzene); (Found: C, 76.61; H, 5.78; N, 2.60. $C_{35}H_{31}ClNOP$ requires: C, 76.70; H, 5.70; N, 2.56); i.r. (Nujol) 3199, 1676 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 3.72 (ddd, 1H, J= 4.8, 5.9, 15.4 Hz, H_a-1'), 3.96 (ddd, 1H, J= 6.0, 6.2, 15.4 Hz, H_b-1'), 5.96 (ddd, 1H, J= 5.9, 6.0, 15.9 Hz, H-2'), 6.38 (d, 1H, J= 15.9 Hz, H-3'), 7.11-7.92 (m, 25H, aryl), 7.99 (d, 1H, $^{2}J_{P-H}$= 12.6 Hz, CH-P), 10.12 (dd, 1H, J= 4.8, 6.2 Hz, NH) ; ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 41.37 (C-1'), 47.77 (CH-P, ^{1}J= 51.2 Hz), 117.75 (C_i, ^{1}J= 85.5 Hz), 124.53 (C_p), 126.11 (C_o), 127.02 (C-2'), 127.98 (C_m), 128.40 (C-1, ^{2}J= 6.9 Hz), 128.49 (C-3, ^{4}J= 2.8 Hz), 128.84 (C-4, ^{5}J= 3.2 Hz), 129.53 (C_m, ^{3}J= 12.6 Hz), 130.77 (C-2, ^{3}J= 6.1 Hz), 131.31 (C-3'), 134.37 (C_p, ^{4}J= 2.7 Hz), 134.43 (C_o, ^{2}J= 9.7 Hz), 136.50 (C_i), 165.85 (CO, ^{2}J= 1.8 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.37; m/z (%) 278 (8), 117 (100).

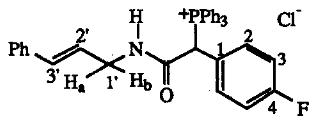


5f: (35%), m.p. 220-222 °C (colourless needles from benzene); (Found: C, 72.02; H, 5.24; N, 2.12. $C_{35}H_{30}Cl_2NOP$ requires: C, 72.17; H, 5.19; N, 2.40); i.r. (Nujol) 3200, 1676 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.75 (ddd, 1H, J= 5.1, 6.0, 15.5 Hz, H_a-1'), 3.96 (ddd, 1H, J= 5.9, 6.1, 15.5 Hz, H_b-1'), 5.95 (ddd, 1H, J= 6.0, 6.1, 15.9 Hz, H-2'), 6.37

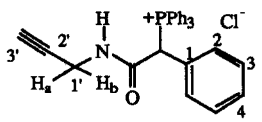


(d, 1H, J= 15.9, H-3'), 7.11-7.91 (m, 24H, aryl), 8.09 (d, 1H, $^2J_{P-H}$= 12.7 Hz, CH-P), 10.09 (dd, 1H, J= 5.1, 5.9 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.60 (C-1'), 47.08 (CH-P, ^1J= 50.9 Hz), 117.67 (C_i, ^1J= 85.6 Hz), 124.49 (C-2'), 126.29* (C_o), 127.16* (C_m), 127.21 (C-1, ^2J= 6.6 Hz), 127.22 (C_p), 128.82 (C-3, ^4J= 2.0 Hz), 129.77 (C_m, ^3J= 12.6 Hz), 131.70 (C-3'), 132.29 (C-2, ^3J= 6.1 Hz), 134.58 (C_o, ^2J= 10.0 Hz), 134.65 (C_p, ^4J= 2.0 Hz), 135.30 (C-4, ^5J= 4.0 Hz), 136.61 (C_i), 165.72 (CO, ^2J= 1.0 Hz). *Interchangeable; ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.20; m/z (%) 278 (15), 183 (100).

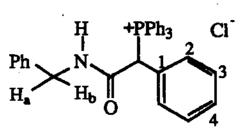
5g: (68%), m.p. 122-123 °C (colourless prisms from benzene); (Found: C, 74.18; H, 5.41; N, 2.44. $C_{35}H_{30}ClFNOP$ requires: C, 74.27; H, 5.34; N, 2.47); i.r. (Nujol) 3200, 1678 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.75 (ddd, 1H, J= 5.1, 6.1, 15.3 Hz, H_a-1'), 3.97 (ddd, 1H, J= 6.1, 6.4, 15.3 Hz, H_b-1'), 5.96 (dt, 1H, J= 6.1, 15.9 Hz, H-2'), 6.40 (d, 1H, J= 15.9 Hz, H-3'), 6.86 (t, 2H, $^3J_{F-H}$= 8.6 Hz, H-3), 7.18-7.91 (m, 22H, aryl), 8.11 (d, 1H, $^2J_{P-H}$= 15.9 Hz, CH-P), 10.10 (dd, 1H, J= 5.1, 6.4 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.66 (C-1'), 47.02 (CH-P, $^1J_{C-P}$= 51.4 Hz), 115.35 (C-3, $^4J_{C-P}$= 2.0 Hz, $^2J_{C-F}$= 21.2 Hz), 117.84 (C_i, $^1J_{C-P}$= 85.6 Hz), 124.47 (C-1, $^2J_{C-P}$= 6.6 Hz, $^4J_{C-F}$= 3.5 Hz), 124.62 (C-2'), 126.36* (C_o), 127.26 (C_p), 128.21* (C_m), 129.81 (C_m, $^3J_{C-P}$= 12.6 Hz), 131.76 (C-3'), 132.92 (C-2, $^3J_{C-P}$= 6.1 Hz, $^3J_{C-F}$= 8.0 Hz), 134.65 (C_p, ^4J= 3.0 Hz), 134.66 (C_o, $^2J_{C-P}$= 9.5 Hz), 136.72 (C_i), 163.04 (C-4, $^5J_{C-P}$= 3.5 Hz, $^1J_{C-F}$= 249.7 Hz), 165.98 (CO). *Interchageable; ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.33 (d, $^6J_{P-F}$= 5.5 Hz); m/z (%) 278 (10), 117 (100).



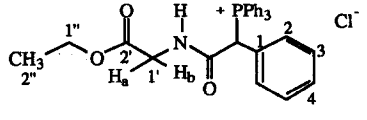
5h: (55%), m.p. 175-178 °C (brown prisms from benzene); (Found: C, 74.07; H, 5.43; N, 2.85. $C_{29}H_{25}ClNOP$ requires: C, 74.12; H, 5.36; N, 2.98); i.r. (Nujol) 3120, 1676 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 2.00 (dd, 1H, J= 2.3, 2.6 Hz, H-3'), 3.75 (ddd, 1H, J= 2.6, 5.0, 17.5 Hz, H_a-1'), 3.92 (ddd, 1H, J= 2.3, 6.0, 17.5 Hz, H_b-1'), 7.12-8.00 (m, 20H, aryl), 8.01 (d, 1H, $^2J_{P-H}$= 12.6 Hz, CH-P), 10.28 (dd, 1H, J= 5.0, 6.0 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 29.28 (C-1', ^4J= 1.5 Hz), 47.72 (CH-P, ^1J= 51.4 Hz), 70.84 (C-3'), 78.63 (C-2'), 118.05 (C_i, ^1J= 85.6 Hz), 128.20 (C-1, ^2J= 9.0 Hz), 128.73 (C-3, ^4J= 2.5 Hz), 129.13 (C-4, ^5J= 3.0 Hz), 129.84 (C_m, ^3J= 12.6 Hz), 131.12 (C-2, ^3J= 6.1 Hz), 134.62 (C_p, ^4J= 3.0 Hz), 134.75 (C_o, ^2J= 10.1 Hz), 166.23 (CO, ^2J= 1.5 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.66; m/z (%) 278 (20), 183 (100).



5i: (51%), m.p. 207-208 °C (colourless needles from benzene); (Found: C, 75.85; H, 5.49; N, 2.61. $C_{33}H_{29}ClNOP$ requires: C, 75.93; H, 5.60; N, 2.68); i.r. (Nujol) 3199, 1676 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 4.14 (dd, 1H, J= 5.0, 15.0 Hz, H_a), 4.43 (dd, 1H, J= 7.1, 15.0 Hz, H_b), 7.16-7.66 (m, 25H, aryl), 7.98 (d, 1H, $^2J_{P-H}$= 12.5 Hz, CH-P), 10.37 (dd, 1H, J= 5.0, 7.1 Hz, NH) ; ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 43.35 (CH_2), 47.74 (CH-P, ^1J= 51.4 Hz), 117.82 (C_i, ^1J= 85.6 Hz), 126.58 (C_p), 127.54 (C_o), 128.04 (C_m), 128.44 (C-1, ^2J= 6.8 Hz), 128.55 (C-3, ^4J= 2.6 Hz), 128.92 (C-4, ^5J= 3.3 Hz), 129.58 (C_m, ^3J= 12.6 Hz), 130.90 (C-2, ^3J= 6.1 Hz), 134.23 (C_p, ^4J= 2.1 Hz), 134.48 (C_o, ^2J= 9.8 Hz), 137.69 (C_i), 165.93 (CO, ^2J= 1.7 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 19.94; m/z (%) 278 (9), 91 (100).

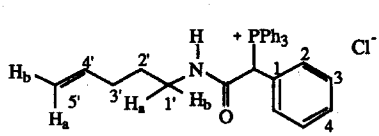


5j: (97%), m.p. 190-191 °C (colourless prisms from benzene); (Found: C, 70.00; H, 5.91; N, 2.84. $C_{30}H_{29}ClNO_3P$ requires: C, 69.56; H, 5.64; N, 2.70); i.r. (Nujol) 3182, 1750, 1676 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 1.06 (t, 3H, J= 7.1 Hz, H-2"), 3.80 (dd, 1H, J= 5.6, 17.5 Hz, H_a-1'), 3.89 (dd, 1H, J= 6.3, 17.5 Hz, H_b-1'), 4.00 (q, 2H, J= 7.1 Hz, H-1"), 7.11-7.90 (m, 20H, aryl), 8.06 (d, 1H, $^2J_{P-H}$= 12.5

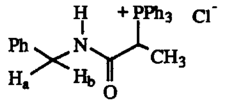


Hz, CH-P), 10.24 (dd, 1H, J= 5.6, 6.3 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 13.80 (C-2"), 41.49 (C-1'), 47.14 (CH-P, ^{1}J= 51.9 Hz), 60.69 (C-1"), 117.90 (C_i, ^{1}J= 85.6 Hz), 128.10 (C-1, ^{2}J= 6.6 Hz), 128.52 (C-3, ^{4}J= 2.5 Hz), 128.99 (C-4, ^{5}J= 3.3 Hz), 129.70 (C_m, ^{3}J= 12.6 Hz), 131.07 (C-2, ^{3}J= 5.5 Hz), 134.49 (C_p, ^{4}J= 4.0 Hz), 134.59 (C_o, ^{2}J= 10.1 Hz), 166.81 (CO, ^{2}J= 1.5 Hz), 168.20 (C-2'); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 24.11; m/z (%) 278 (12), 69 (100).

5k: (33%), m.p. 91-92 °C (colourless prisms from benzene); (Found: C, 74.37; H, 6.20; N, 2.75. $C_{31}H_{31}ClNOP$ requires: C, 74.47; H, 6.25; N, 2.80); i.r. (Nujol) 3200, 1676 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 1.48 (dt, 2H, J= 7.0, 7.5 Hz, H-2'), 1.97 (dt, 2H, J= 6.0, 7.5 Hz, H-3'), 3.00 (ddt, 1H, J= 5.3, 7.0, 13.4 Hz, H_a-1'), 3.21 (ddt, 1H, J= 5.3, 7.0, 13.4 Hz, H_b-1'), 4.87 (dd, 1H, J= 1.3, 10.1 Hz, H_b-5'), 4.92 (dd, 1H, J= 1.3, 15.8 Hz, H_a-5'), 5.68 (ddd, 1H, 6.0, 10.1, 15.8 Hz, H-4'), 7.12-7.90 (m, 20H, aryl), 7.95 (d, 1H, $^2J_{P-H}$= 12.8 Hz, CH-P), 9.89 (t, 1H, J= 5.3 Hz, NH) ; ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 27.84 (C-2'), 30.98 (C-3'), 39.38 (C-1'), 47.91 (CH-P, ^{1}J= 51.4 Hz), 114.80 (C-5'), 118.11 (C_i, ^{1}J= 85.1 Hz), 128.62 (C-1, ^{2}J= 5.5 Hz), 128.64 (C-3, ^{4}J= 3.0 Hz), 128.93 (C-4, ^{5}J= 3.5 Hz), 129.70 (C_m, ^{3}J= 13.1 Hz), 130.93 (C-2, ^{3}J= 6.0 Hz), 134.50 (C_p, ^{4}J= 3.0 Hz), 134.65 (C_o, ^{2}J= 9.5 Hz), 137.64 (C-4'), 165.94 (CO, ^{2}J= 1.5 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 22.91; m/z (%) 278 (42), 277 (100).



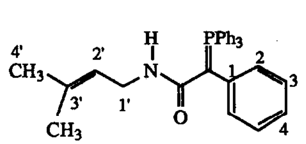
5l: (30%), m.p. 96-98 °C (colourless prisms from benzene); (Found: C, 73.00; H, 5.87; N, 3.15. $C_{28}H_{27}ClNOP$ requires: C, 73.12; H, 5.92; N, 3.05); i.r. (Nujol) 3200, 1676 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 1.68 (dd, 3H, J= 7.0 Hz, $^3J_{P-H}$= 19.4 Hz, CH_3), 4.18 (dd, 1H, J= 5.6, 14.8 Hz, H_a), 4.37 (dd, 1H, J= 6.6, 14.8 Hz, H_b), 6.31 (dq, 1H, J= 7.0 Hz, $^2J_{P-H}$= 11.9 Hz, CH-P), 7.19-7.89 (m, 20H, aryl), 10.36 (dd, 1H, J= 5.6, 6.6 Hz, NH) ; ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 14.83 (CH_3, ^{2}J= 3.9 Hz), 34.41 (CH-P, ^{1}J= 52.3 Hz), 43.14 (CH_2), 117.54 (C_i, ^{1}J= 85.8 Hz), 127.65* (C_o), 128.05* (C_m), 128.19 (C_p), 129.76 (C_m, ^{3}J= 12.6 Hz), 133.97 (C_o, ^{2}J= 9.8 Hz), 134.47 (C_p, ^{4}J= 3.0 Hz), 137.70 (C_i), 167.70 (CO, ^{2}J= 2.5 Hz). *Interchangeable; ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 27.04; m/z (%) 278 (22), 183 (100).



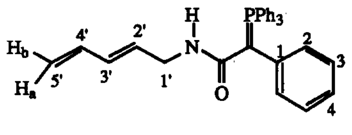
General Procedure for the Preparation of Phosphoranes 8.

To a solution of sodium carbonate (10 g, 94.3 mmol) in water (100 ml) was added the corresponding phosphonium salt **5** (2.5 mmol). The resultant suspension was stirred at room temperature for 24 h. The solid was filtered, washed with water (20 ml), and air-dried. The solid was treated with benzene (20 ml) and filtered. The filtrate was concentrated to dryness and the residual material **8** was used without further purification in the next step.

8a: (89%), m.p. 122-124 °C (yellow solid); i.r. (Nujol) 3432, 1562 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 1.57 (s, 3H, H-1"), 1.64 (s, 3H, H-4'), 3.75 (dd, 2H, J= 4.5, 6.7 Hz, H-1'), 4.64 (t, 1H, J= 4.5 Hz, NH), 5.14 (t, 1H, J= 6.7 Hz, H-2'), 6.88-7.71 (m, 20H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 17.88 (C-1"), 25.67 (C-4'), 37.83 (C-1', ^{4}J= 2.1 Hz), 49.34 (C=P, ^{1}J= 134.9 Hz), 123.23 (C-2'), 124.61 (C-4, ^{5}J= 2.1 Hz), 127.92 (C-3, ^{4}J= 1.3 Hz), 128.16 (C_m, ^{3}J= 12.6 Hz), 129.11 (C_i, ^{1}J= 91.0 Hz), 131.00 (C_p, ^{4}J= 2.9 Hz), 133.48 (C-3'), 133.73 (C_o, ^{2}J= 9.3 Hz), 135.28 (C-2, ^{3}J= 4.3 Hz), 138.66 (C-1, ^{2}J= 12.8 Hz), 171.01 (CO, ^{2}J= 12.7 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 15.94; m/z (%) 278 (8), 51 (100).

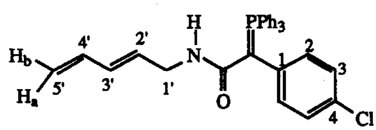


8b: (83%), m.p. 114-115 °C (brown solid); i.r. (Nujol) 3350, 1562 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 3.84 (t, 2H, J= 5.9 Hz, H-1'), 4.80 (t, 1H, J= 5.9 Hz, NH), 4.98 (d, 1H, J= 9.7 Hz, H_b-5'), 5.11 (d, 1H, J= 16.3 Hz, H_a-5'), 5.70 (dt, 1H, J= 5.9, 14.9 Hz, H-2'), 6.03-6.40 (m, 2H, H-3' and H-4'), 6.92-7.71 (m, 20H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 42.24 (C-1', ^{4}J= 2.1 Hz), 49.57 (C=P, ^{1}J= 134.4 Hz), 115.65 (C-5'), 124.89 (C-4, ^{5}J= 1.5 Hz), 128.00 (C-

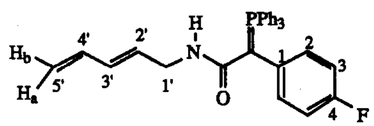


3, ^4J= 1.3 Hz), 128.21 (C_m, ^3J= 12.1 Hz), 128.36 (C-2'), 128.81 (C_i, ^1J= 91.3 Hz), 131.06 (C_p, ^4J= 2.7 Hz), 131.96 (C-3'), 133.66 (C_o, ^2J= 9.6 Hz), 135.32 (C-2, ^3J= 4.2 Hz), 136.91 (C-4'), 138.35 (C-1, ^2J= 12.8 Hz), 170.54 (CO, ^2J= 11.8 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.24; m/z (%) 278 (44), 277 (100).

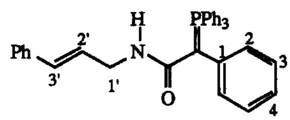
8c: (79%), m.p. 84-86 °C (brown solid); i.r. (Nujol) 3216, 1559 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.82 (dd, 2H, J= 5.4, 5.6 Hz, H-1'), 4.72 (t, 1H, J= 5.4 Hz, NH), 5.01 (d, 1H, J= 10.0 Hz, H_b-5'), 5.12 (d, 1H, J= 16.6 Hz, H_a-5'), 5.69 (dt, 1H, J= 5.6, 14.9 Hz, H-2'), 6.05-6.30 (m, 2H, H-3' and H-4'), 6.96-7.69 (m, 19H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.28 (C-1'), 48.85 (C=P, ^1J= 135.5 Hz), 115.94 (C-5'), 128.37 (C_m, ^3J= 12.1 Hz), 128.43 (C_i, ^1J= 91.7 Hz), 128.60 (C-2'), 131.06 (C_p, ^4J= 2.5 Hz), 131.31 (C-3, ^4J= 2.5 Hz), 131.98 (C-4, ^5J= 3.5 Hz), 132.01 (C-3'), 133.62 (C_o, ^2J= 9.5 Hz), 136.34 (C-2, ^3J= 4.5 Hz), 136.81 (C-4'), 137.02 (C-1, ^2J= 12.6 Hz), 170.43 (CO, ^2J= 11.0 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.27; m/z (%) 278 (41), 67 (100).



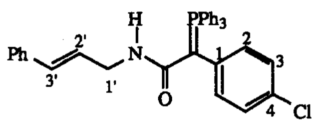
8d: (75%), m.p. 91-93 °C (yellow solid); i.r. (Nujol) 3455, 1559 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.84 (dd, 2H, J= 5.1, 5.3 Hz, H-1'), 4.65 (t, 1H, J= 5.3 Hz, NH), 4.99 (d, 1H, J= 10.1 Hz, H_b-5'), 5.12 (d, 1H, J= 16.9 Hz, H_a-5'), 5.70 (dt, 1H, J= 5.1, 15.2 Hz, H-2'), 6.06-6.34 (m, 2H, H-3' and H-4'), 6.69 (t, 2H, $^3J_{F-H}$= 8.1 Hz, H-3), 7.00-7.58 (m, 17H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.27 (C-1'), 48.28 (C=P, $^1J_{C-P}$= 135.5 Hz), 114.79 (C-3, $^4J_{C-P}$= 1.0 Hz, $^2J_{C-F}$= 21.5 Hz), 115.79 (C-5'), 128.28 (C_m, $^3J_{C-P}$= 12.1 Hz), 128.57 (C-2'), 128.58 (C_i, $^1J_{C-P}$= 91.2 Hz), 131.18 (C_p, $^4J_{C-P}$= 2.1 Hz), 132.00 (C-3'), 133.67 (C_o, $^2J_{C-P}$= 9.5 Hz), 134.13 (C-1, $^2J_{C-P}$= 12.6 Hz, $^4J_{C-F}$= 2.0 Hz), 136.84 (C-4'), 136.93 (C-2, $^3J_{C-P}$= 4.3 Hz, $^3J_{C-F}$= 7.8 Hz), 160.76 (C-4, $^5J_{C-P}$= 2.0 Hz, $^1J_{C-F}$= 245.2 Hz), 170.68 (CO, $^2J_{C-P}$= 12.1 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.43 (d, $^6J_{P-F}$= 3.7 Hz); m/z (%) 278 (20), 117 (100).



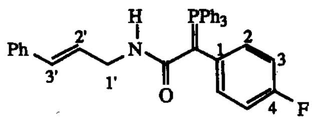
8e: (86%), m.p. 105-106 °C (yellow solid); i.r. (Nujol) 3426, 1563 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.95 (dd, 2H, J= 5.6, 5.9 Hz, H-1'), 4.88 (t, 1H, J= 5.9 Hz, NH), 6.21 (dt, 1H, J= 5.6, 15.9 Hz, H-2'), 6.43 (d, 1H, J= 15.9 Hz, H-3'), 6.93-7.63 (m, 25H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.68 (C-1', ^4J= 7.8 Hz), 49.65 (C=P, ^1J= 138.0 Hz), 124.86 (C-4, ^5J= 1.5 Hz), 126.21* (C_o), 126.99 (C_p), 128.01 (C-3, ^4J= 1.1 Hz), 128.18 (C_i, ^1J= 90.1 Hz), 128.19 (C_m, ^3J= 12.1 Hz), 128.40* (C_m), 129.30 (C-2'), 129.55 (C-3'), 131.04 (C_p, ^4J= 3.0 Hz), 133.63 (C_o, ^2J= 9.6 Hz), 135.31 (C-2, ^3J= 4.1 Hz), 137.43 (C_i), 138.34 (C-1, ^2J= 12.6 Hz), 170.71 (CO, ^2J= 12.2 Hz). *Interchangeable; ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.31; m/z (%) 278 (14), 117 (100).



8f: (70%), m.p. 43-45 °C (yellow solid); i.r. (Nujol) 3217, 1557 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.96 (t, 2H, J= 6.0 Hz, H-1'), 4.80 (br s, 1H, NH), 6.19 (dt, 1H, J= 6.0, 15.6 Hz, H-2'), 6.42 (d, 1H, J= 15.6 Hz, H-3'), 7.00-7.28 (m, 24H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.79 (C-1', ^4J= 1.5 Hz), 48.94 (C=P, ^1J= 135.9 Hz), 126.24* (C_o), 126.25* (C_m), 127.13 (C_p), 128.36 (C_m, ^3J= 12.6 Hz), 128.41 (C_i, ^1J= 83.1 Hz), 129.87 (C-2'), 131.44 (C-3'), 131.95 (C-4, ^5J= 3.0 Hz), 131.98 (C_p, ^4J= 1.5 Hz), 132.05 (C-3, ^4J= 1.5 Hz), 133.61 (C_o, ^2J= 9.1 Hz), 136.63 (C-2, ^3J= 2.0 Hz), 137.00 (C-1, ^2J= 12.0 Hz), 137.29 (C_i), 170.71 (CO, ^2J= 11.1 Hz). *Interchangeable; ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.32; m/z (%) 278 (5), 117 (100).

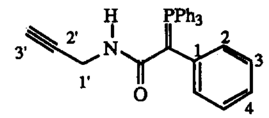


8g: (84%), m.p. 108-110 °C (yellow solid); i.r. (Nujol) 3216, 1566 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 3.95 (dd,

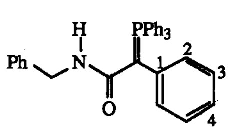


2H, J= 5.3, 5.7 Hz, H-1'), 4.73 (t, 1H, J= 5.7 Hz, NH), 6.21 (dt, 1H, J= 5.3, 15.8 Hz, H-2'), 6.43 (d, 1H, J= 15.8 Hz, H-3'), 6.70 (t, 2H, $^{3}J_{F-H}$= 8.5 Hz, H-3), 7.02 (t, 2H, $^{4}J_{F-H}$= 6.2 Hz, H-2), 7.18-7.69 (m, 20H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 41.80 (C-1', $^{4}J_{C-P}$= 2.0 Hz), 48.45 (C=P, $^{1}J_{C-P}$= 134.96 Hz), 114.84 (C-3, $^{4}J_{C-P}$= 0.5 Hz, $^{2}J_{C-F}$= 20.2 Hz), 126.24* (C_o), 127.10 (C_p), 128.31 (C_m, $^{3}J_{C-P}$= 12.1 Hz), 128.58* (C_m), 129.00 (C_i, $^{1}J_{C-P}$= 92.1 Hz), 129.14 (C-2'), 129.76 (C-3'), 131.22 (C_p, $^{4}J_{C-P}$= 2.5 Hz), 133.07 (C_o, $^{2}J_{C-P}$= 9.6 Hz), 134.04 (C-1, $^{2}J_{C-P}$= 12.1 Hz, $^{4}J_{C-F}$= 3.0 Hz), 137.06 (C-2, $^{3}J_{C-P}$= 4.0 Hz, $^{3}J_{C-F}$= 7.6 Hz), 137.37 (C_i), 160.81 (C-4, $^{5}J_{C-P}$= 2.3 Hz, $^{1}J_{C-F}$= 245.1 Hz), 170.79 (CO, $^{2}J_{C-P}$= 11.6 Hz). *Interchangeable; ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.51 (d, $^{6}J_{P-F}$= 3.7 Hz); m/z (%) 278 (43), 277 (100).

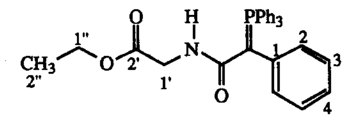
8h: (80%), m.p. 106-108 °C (brown solid); i.r. (Nujol) 3437, 1555 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 2.09 (t, 1H, J= 2.4 Hz, H-3'), 3.98 (dd, 2H, J= 2.4, 5.4 Hz, H-1'), 4.82 (t, 1H, J= 5.4 Hz, NH), 6.94-7.71 (m, 20H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 29.42 (C-1', ^{4}J= 2.0 Hz), 50.11 (C=P, ^{1}J= 132.5 Hz), 69.68 (C-3'), 82.77 (C-2'), 125.62 (C-4, ^{5}J= 1.0 Hz), 128.06 (C-3, ^{4}J= 0.7 Hz), 128.27 (C_m, ^{3}J= 12.1 Hz), 128.49 (C_i, ^{1}J= 91.2 Hz), 131.18 (C_p, ^{4}J= 2.5 Hz), 133.71 (C_o, ^{2}J= 9.6 Hz), 135.82 (C-2, ^{3}J= 4.6 Hz), 138.00 (C-1, ^{2}J= 12.5 Hz), 170.32 (CO, ^{2}J= 12.1 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 16.74; m/z (%) 278 (19), 149 (100).



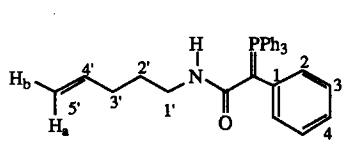
8i: (80%), m.p. 98-100 °C (brown solid); i.r. (Nujol) 3432, 1562 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 4.38 (d, 2H, J= 6.0 Hz, CH_2), 5.10 (t, 1H, J= 6.0 Hz, NH), 6.92-7.67 (m, 25H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 43.47 (CH_2, ^{4}J= 2.0 Hz), 49.76 (C=P, ^{1}J= 134.3 Hz), 124.82 (C-4, ^{5}J= 2.1 Hz), 126.32 (C_p), 127.36 (C_o), 127.95 (C-3, ^{4}J= 1.6 Hz), 128.06 (C_m), 128.18 (C_m, ^{3}J= 12.1 Hz), 128.83 (C_i, ^{1}J= 91.0 Hz), 131.05 (C_p, ^{4}J= 2.9 Hz), 133.65 (C_o, ^{2}J= 9.5 Hz), 135.20 (C-2, ^{3}J= 4.4 Hz), 138.23 (C-1, ^{2}J= 12.4 Hz), 141.76 (C_i), 170.72 (CO, ^{2}J= 11.6 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 17.94; m/z (%) 278 (45), 277 (100).



8j: (66%), m.p. 115-117 °C (brown solid); i.r. (Nujol) 3454, 1755, 1568 cm^{-1}; ^{1}H n.m.r (200 MHz, $CDCl_3$) δ 1.23 (t, 3H, J= 7.1 Hz, H-2"), 3.94 (d, 2H, J= 6.0 Hz, H-1'), 4.14 (q, 2H, J= 7.1 Hz, H-1"), 5.14 (t, 1H, J= 6.0 Hz, NH), 6.93-7.62 (m, 20H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 14.19 (C-2"), 41.91 (C-1', ^{4}J= 2.0 Hz), 49.88 (C=P, ^{1}J= 133.6 Hz), 60.55 (C-1"), 124.97 (C-4, ^{5}J= 2.2 Hz), 128.01 (C-3, ^{4}J= 1.4 Hz), 128.23 (C_m, ^{3}J= 12.1 Hz), 128.37 (C_i, ^{1}J= 91.3 Hz), 131.11 (C_p, ^{4}J= 2.9 Hz), 133.64 (C_o, ^{2}J= 9.6 Hz), 135.30 (C-2, ^{3}J= 4.2 Hz), 136.89 (C-1, ^{2}J= 12.1 Hz), 170.84 (CO, ^{2}J= 11.8 Hz), 172.28 (C-2'); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 14.31; m/z (%) 278 (43), 277 (100).

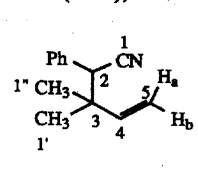


8k: (75%), m.p. 72-74 °C (yellow solid); i.r. (Nujol) 3441, 1562 cm^{-1}; ^{1}H n.m.r (300 MHz, $CDCl_3$) δ 1.49 (q, 2H, J= 7.0 Hz, H-2'), 2.04 (dt, 2H, J= 6.6, 7.0 Hz, H-3'), 3.17 (dt, 2H, J= 6.0, 7.0 Hz, H-1'), 4.76 (t, 1H, J= 6.0 Hz, NH), 4.88 (dd, 1H, J= 1.3, 10.1 Hz, H_b-5'), 4.94 (dd, 1H, J= 1.3, 17.1 Hz, H_a-5'), 5.78 (ddd, 1H, J= 6.6, 10.1, 17.1 Hz, H-4'), 6.93-7.04 (m, 20H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 30.22 (C-2'), 31.41 (C-3'), 39.22 (C-1', ^{4}J= 1.5 Hz), 49.36 (C=P, ^{1}J= 136.5 Hz), 114.28 (C-5'), 124.76 (C-4, ^{5}J= 2.0 Hz), 128.01 (C-3, ^{4}J= 1.0 Hz), 128.24 (C_m, ^{3}J= 12.1 Hz), 129.10 (C_i, ^{1}J= 91.7 Hz), 131.04 (C_p, ^{4}J= 3.0 Hz), 133.73 (C_o, ^{2}J= 9.6 Hz), 135.37 (C-2, ^{3}J= 4.6 Hz), 138.82 (C-1, ^{2}J= 12.0 Hz), 138.84 (C-4'), 171.06 (CO, ^{2}J= 11.6 Hz); ^{31}P n.m.r (125 MHz, $CDCl_3$) δ 15.90; m/z (%) 278 (46), 277 (100).

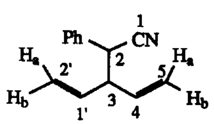


General Procedure for the Preparation of 4-Pentenenitriles 9.

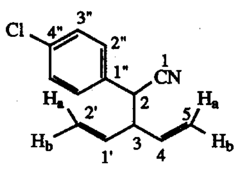
The phosphorane **8** (1 mmol) was heated under nitrogen at a temperature slightly above its melting point (90-140 °C) (Scheme 4) for 10 min. After cooling the residual product was chromatographed on silica gel colunm, eluting with n-hexane/ethyl acetate (9:1) to give **9**.



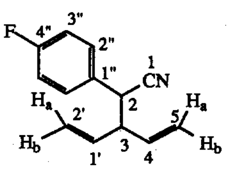
9a: (55%), colourless oil; (Found: C, 84.15; H, 8.05; N, 7.61. $C_{13}H_{15}N$ requires: C, 84.28; H, 8.16; N, 7.56); i.r. (Nujol) 2237, 1495 cm^{-1}; ^1H n.m.r (200 MHz, $CDCl_3$) δ 1.13 (s, 3H, H-1'), 1.14 (s, 3H, H-1"), 3.62 (s, 1H, H-2), 5.00 (d, 1H, J= 17.4 Hz, H_a-5), 5.10 (d, 1H, J= 10.7 Hz, H_b-5), 5.85 (dd, 1H, J= 10.7, 17.4 Hz, H-4), 7.22-7.35 (m, 5H, aryl); ^{13}C n.m.r. (50 MHz, $CDCl_3$) δ 24.47 (C-1'), 24.88 (C-1"), 40.47 (C-3), 49.04 (C-2), 114.42 (C-5), 119.97 (C-1), 128.18 (C_p), 128.20 (C_o), 129.52 (C_m), 132.80 (C_i), 143.06 (C-4); m/z (%) 182 (6), 117 (100).



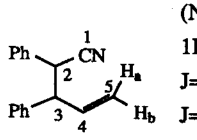
9b: (57%), colourless oil; (Found: C, 85.13; H, 7.22; N, 7.58. $C_{13}H_{13}N$ requires: C, 85.21; H, 7.15; N, 7.64); i.r. (Nujol) 2242, 1494 cm^{-1}; ^1H n.m.r (300 MHz, $CDCl_3$) δ 3.21 (dt, 1H, J= 6.4, 7.3 Hz, H-3), 3.90 (d, 1H, J= 6.4 Hz, H-2), 5.03-5.22 (m, 4H, H_a-5, H_b-5, H_a-2' and H_b-2'), 5.80 (ddd, 1H, J= 7.3, 10.3, 17.0 Hz, H-1'), 5.82 (ddd, 1H, J= 7.3, 10.3, 17.0 Hz, H-4), 7.26-7.40 (m, 5H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 42.92 (C-2), 52.44 (C-3), 118.26 (C-5), 119.05 (C-2'), 119.38 (C-1), 128.27 (C_p), 128.32* (C_o), 128.84* (C_m), 133.66 (C_i), 134.83 (C-4), 136.02 (C-1'). *Interchangeable; m/z (%) 183 (M^+, 6), 67 (100).



9c: (29%), colourless oil; (Found: C, 71.62; H, 5.50; N, 6.49. $C_{13}H_{12}ClN$ requires: C, 71.72; H, 5.56; N, 6.43); i.r. (Nujol) 2243, 1495 cm^{-1}; ^1H n.m.r (300 MHz, $CDCl_3$) δ 3.18 (dt, 1H, J= 6.1, 7.3 Hz, H-3), 3.87 (d, 1H, J= 6.1, H-2), 5.06 (dd, 1H, J= 1.2, 17.1 Hz, H_a-5), 5.15 (dd, 1H, J= 1.2, 17.1 Hz, H_a-2'), 5.20 (dd, 1H, J= 1.2, 10.3 Hz, H_b-5), 5.21 (dd, 1H, J= 1.2, 10.3 Hz, H_b-2'), 5.78 (ddd, 1H, J= 7.3, 10.3, 17.1 Hz, H-4), 5.80 (ddd, 1H, J= 7.3, 10.3, 17.1 Hz, H-1') 7.21-7.37 (m, 4H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 42.39 (C-2), 52.40 (C-3), 118.55 (C-5), 118.89 (C-1), 119.33 (C-2'), 125.22 (C-4"), 129.07* (C-2"), 129.66* (C-3"), 132.23 (C-1"), 134.54 (C-4), 135.70 (C-1'). *Interchangeable; m/z (%) 217 (M^+, 11), 67 (100).



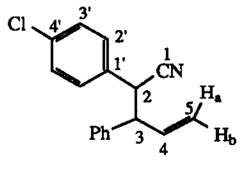
9d: (69%), colourless oil; (Found: C, 77.48; H, 6.16; N, 6.90. $C_{13}H_{12}FN$ requires: C, 77.59; H, 6.01; N, 6.96); i.r. (Nujol) 2243, 1512 cm^{-1}; ^1H n.m.r (300 MHz, $CDCl_3$) δ 3.18 (dt, 1H, J= 6.1, 7.3 Hz, H-3), 3.88 (d, 1H, J= 6.1 Hz, H-2), 5.06 (dd, 1H, J= 1.2, 17.1 Hz, H_a-5), 5.14 (dd, 1H, J= 1.2, 17.1 Hz, H_a-2'), 5.20 (dd, 1H, J= 1.2, 10.3 Hz, H_b-5), 5.21 (dd, 1H, J= 1.2, 10.3 Hz, H_b-2'), 5.78 (ddd, 1H, J= 7.3, 10.3, 17.1 Hz, H-4), 5.80 (ddd, 1H, J= 7.3, 10.3, 17.1 Hz, H-1') 7.02-7.28 (m, 4H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) δ 42.19 (C-2), 52.50 (C-3), 115.82 (C-3", $^2J_{C-F}$= 21.7 Hz), 118.41 (C-5), 119.15 (C-1), 119.17 (C-2'), 129.54 (C-1", $^4J_{C-F}$= 3.5 Hz), 130.00 (C-2", $^3J_{C-F}$= 8.1 Hz), 134.67 (C-4), 135.78 (C-1'), 162.54 (C-4", $^1J_{C-F}$= 247.7 Hz); m/z (%) 201 (M^+, 5), 67 (100).



9e: (60%), colourless oil; (Found: C, 87.43; H, 6.53; N, 5.92. $C_{17}H_{15}N$ requires: C, 87.52; H, 6.48; N, 6.00); i.r. (Nujol) 2237, 1497 cm^{-1}; ^1H n.m.r (300 MHz, $CDCl_3$) mixture of diastereomers 1/1 δ 3.69 (t, 1H, J= 7.7 Hz, H-3), 3.73 (t, 1H, J= 7.5 Hz, H-3), 4.06 (d, 1H, J= 7.7 Hz, H-2), 4.14 (d, 1H, J= 7.5 Hz, H-2), 5.11 (d, 2H, J= 17.1 Hz, H_a-5), 5.17 (d, 1H, J= 10.3 Hz, H_b-5), 5.25 (d, 1H, J= 10.3 Hz, H_b-5), 6.05 (ddd, 1H, J= 7.5, 10.3, 17.1 Hz, H-4), 6.23 (ddd, 1H, J= 7.7, 10.3, 17.1 Hz, H-4), 7.09-7.30 (m, 20H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) mixture of diastereomers δ

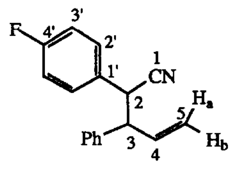
43.93 (C-2), 44.26 (C-2), 54.53 (C-3), 57.17 (C-3), 118.17 (C-5), 119.06 (C-5), 119.58 (C-1), 119.70 (C-1), 127.46 (C_p), 127.66 (C_p), 127.92*, 128.09 (C_p), 128.16*, 128.20 (C_p), 128.38*, 128.42*, 128.58*, 128.66*, 128.68*, 128.72*, 133.80 (C_i), 134.16 (C_i), 135.78 (C-4), 136.60 (C-4), 138.64 (C_i), 139.47 (C_i). *Ortho and meta carbons of the phenyl groups; m/z (%) 129 (14), 117 (100).

9f: (25%), colourless oil; (Found: C, 76.35; H, 5.22; N, 5.30. $C_{17}H_{14}ClN$ requires: C, 76.26; H, 5.27; N, 5.23);



i.r. (Nujol) 2243, 1495 cm^{-1}; ^1H n.m.r (300 MHz, $CDCl_3$) mixture of diastereomers 1/1 δ 3.65 (t, 1H, J= 8.1 Hz, H-3), 3.70 (t, 1H, J= 7.0 Hz, H-3), 4.05 (d, 1H, J= 8.1 Hz, H-2), 4.13 (d, 1H, J= 7.0 Hz, H-2), 5.10 (dd, 1H, J= 1.3, 17.0 Hz, H_a-5), 5.17 (dd, 1H, J= 1.3, 17.0 Hz, H_a-5), 5.21 (dd, 1H, J= 1.3, 10.3 Hz, H_b-5), 5.28 (dd, 1H, J= 1.3, 10.3, H_b-5), 6.04 (ddd, 1H, J= 7.0, 10.3, 17.0 Hz, H-4), 6.21 (ddd, 1H, J= 8.1, 10.3, 17.0 Hz, H-4), 7.01-7.70 (m, 18H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) mixture of diastereomers δ 43.47 (C-2), 43.77 (C-2), 54.52 (C-3), 55.23 (C-3), 118.62 (C-5), 119.24 (C-1), 119.39 (C-1), 119.41 (C-5), 127.73 (C_p), 127.91 (C_p), 127.96*, 128.46*, 128.78*, 128.93*, 128.94*, 128.96*, 129.58*, 129.80*, 132.37 (C-4'), 132.75 (C-4'), 134.22 (C-1'), 134.35 (C-1'), 135.59 (C-4), 136.28 (C-4), 138.31 (C_i), 139.11 (C_i). *Ortho and meta carbons of the aryl groups; m/z (%) 267 (M^+, 6), 117 (100).

9g: (59%), colourless oil; (Found: C, 81.18; H, 5.69; N, 5.65. $C_{17}H_{14}FN$ requires: C, 81.25; H, 5.62; N, 5.57);



i.r. (Nujol) 2243, 1510 cm^{-1}; ^1H n.m.r (300 MHz, $CDCl_3$) mixture of diastereomers 1/1 δ 3.65 (t, 1H, J= 7.5 Hz, H-3), 3.70 (t, 1H, J= 7.1 Hz, H-3), 4.04 (d, 1H, J= 7.5 Hz, H-2), 4.13 (d, 1H, J= 7.1 Hz, H-2), 5.08 (d, 1H, J= 17.0 Hz, H_a-5), 5.13 (d, 1H, J= 17.0 Hz, H_a-5), 5.18 (d, 1H, J= 10.3 Hz, H_b-5), 5.25 (d, 1H, J= 10.3, H_b-5), 6.04 (ddd, 1H, J= 7.1, 10.3, 17.0 Hz, H-4), 6.21 (ddd, 1H, J= 7.5, 10.3, 17.0 Hz, H-4), 6.90-7.28 (m, 18H, aryl); ^{13}C n.m.r. (75 MHz, $CDCl_3$) mixture of diastereomers δ 43.20 (C-2), 43.49 (C-2), 54.56 (C-3), 55.29 (C-3), 115.66 (C-3', $^2J_{C-F}$= 21.7 Hz), 115.64 (C-3', $^2J_{C-F}$= 21.7 Hz), 118.40 (C-5), 119.18 (C-5), 119.41 (C-1), 119.58 (C-1), 127.56 (C_p), 127.77 (C_p), 127.90*, 128.38*, 128.65*, 128.78*, 129.63 (C-1', $^4J_{C-F}$= 3.5 Hz), 129.87 (C-2', $^3J_{C-F}$= 8.8 Hz), 129.93 (C-1', $^4J_{C-F}$= 3.5 Hz), 130.08 (C-2', $^3J_{C-F}$= 8.1 Hz), 135.69 (C-4), 136.33 (C-4), 138.40 (C_i), 139.14 (C_i), 162.34 (C-4', $^1J_{C-F}$= 247.3 Hz), 162.45 (C-4', $^1J_{C-F}$= 247.3 Hz). *Ortho and meta carbons of the phenyl groups; m/z (%) 134 (15), 117 (100).

Acknowledgements: We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (Project Number PB89-0436). One of us (C. L. L.) also thanks to the Ministerio de Educación y Ciencia for a postdoctoral fellowship.

REFERENCES.

1. For a preliminary communication of a part of this work see Molina, P.; Alajarín, M.; López-Leonardo, C. *Tetrahedron Lett.* **1991**, *32*, 4041.
2. Molina, P.; Vilaplana, M. J.; Pastor, A. *Synlett.* **1992**, 873; Molina, P.; Lorenzo, A.; Aller, E. *Tetrahedron* **1992**, *48*, 4601; Molina, P.; Fresneda, P. M.; Cánovas, M. *Tetrahedron Lett.* **1992**, *33*, 2891; Molina, P.; Arques, A.; Vinader, M. V.; Becher, J.; Brondum, K. *J. Org. Chem.* **1988**, *53*, 4654.
3. Molina, P.; Alajarín, M.; Vidal, A.; Sánchez-Andrada, P. *J. Org. Chem.* **1992**, *57*, 929; Molina, P.; Alajarín, M.;

Vidal, A. *J. Org. Chem.* **1992**, *57*, 6703; Molina, P.; Alajarín, M.; Vidal, A. *J. Chem. Soc. Chem. Commun.* **1990**, 1277.

4. Molina, P.; Fresneda, P. M.; Almendros, P. *Tetrahedron Lett.* **1992**, *33*, 4491; Molina, P.; Vilaplana, M. J.; Pérez, J.; *Tetrahedron* **1990**, *46*, 7855; Molina, P.; Alajarín, M.; Vidal, A. *Tetrahedron* **1989**, *45*, 4286.
5. Balderman, D.; Kalir, A. *Synthesis* **1978**, 24.
6. Banert, K. *Chem. Ber.* **1985**, *118*, 1564.
7. Nishiyama, K.; Karigomi, H. *Chem. Lett.* **1982**, 1477.
8. Grieco, P. A.; Galatsis, P.; Spohn, R. F. *Tetrahedron* **1986**, *42*, 2847.
9. Hassner, A.; Stern, M. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 478.
10. Gagneux, A.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5956.
11. Brady, W. T.; Dorsey, E. D.; Parry, F. H. *J. Org. Chem.* **1969**, *34*, 2846.
12. Clarke, L. F.; Hegarty, A. F.; O'Neill, P. *J. Org. Chem.* **1992**, *57*, 362; Singer, L. A.; Lee, K. W. *J. Chem. Soc. Chem. Commun.* **1974**, 962; Lee, K. W.; Horowitz, N.; Ware, J.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2622.
13. Lee, K. W.; Singer, L. A. *J. Org. Chem.* **1974**, *39*, 3780.
14. Brannock, K. C.; Burpitt, R. *J. Org. Chem.* **1965**, *30*, 2564; Walters, M. A.; McDonough, C. S.; Brown, P. S.; Hoem, A. B. *Tetrahedron Lett.* **1991**, *32*, 179.
15. Zbiral, E.; Bauer, E. *Phosphorus* **1972**, *2*, 35.
16. Molina, P.; Alajarín, M.; López-Leonardo, C.; Claramunt, R. M.; Foces-Foces, M. C.; Cano, F. H.; Catalán, J.; de Paz, J. L. G.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 355.