A Study of the Reactions of *N*-Methylnitrilium Trifluoromethanesulfonate Salts with Benzylidenetriphenylphosphorane

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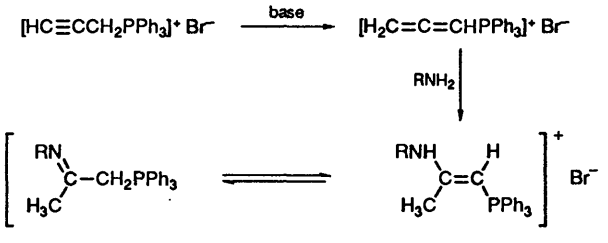
Reactions between the *N*-methylnitrilium trifluoromethanesulfonate salts $[RC{\equiv}NMe]^+ OTf^-$ (R = Ph, 2-MeC_6H_4, 4-MeC_6H_4, Me, Et, $PhCH_2$, Pr and Pr^i; OTf = CF_3SO_3) and benzylidenetriphenylphosphorane ($PhCH{=}PPh_3$) give, as the major product, the enaminophosphonium salts $[Ph_3PCPh{=}CRNHMe]^+ X^-$, where X = OTf or Br depending upon the reaction conditions and work-up procedure. Spectroscopic data and a single crystal X-ray structure determination on the compound $[Ph_3PCPh{=}CPr^iNHMe]^+ Br^-$ have shown that in all cases the major product has the *E* configuration about the C=C bond and the *Z* configuration about the C–N bond, but the other possible stereoisomers are also present in minor amounts. When R = Bu^t the product is the α-iminophosphonium salt $[Ph_3PCHPhCBu^t{=}NMe]^+ OTf^-$ and there was no evidence for the formation of an enaminophosphonium salt in this case.

Vinylphosphonium salts are versatile reagents which have been widely used in the synthesis of heterocyclic compounds.[1-7] Several methods are available for the preparation of simple vinylphosphonium salts including reaction between activated vinyl halides and phosphorus(III) nucleophiles;[8] nucleophilic attack of phosphines on alkynes;[9] isomerisation of alkylidenephosphoranes;[10,11] electrochemical oxidation of triphenylphosphine in the presence of alkenes;[12] and, more recently, the palladium-catalysed vinylation of triphenylphosphine using vinyl trifluoromethanesulfonate.[13] Reports of β-aminovinylphosphonium (enaminophosphonium) salts, however, are rare,[14] and the only synthesis which might be considered a general one is that by Schweizer[15] in which amines are caused to react with allenyltriphenylphosphonium bromide (prepared *in situ* from prop-2-ynyltriphenylphosphonium bromide and a base) (see Scheme 1). Even this method is restricted to the preparation of compounds having a 2-methyl substituent only. Enaminophosphonium salts have a rich chemistry and Schweizer has demonstrated their use in heterocyclic syntheses.[15,16] Furthermore, Yoshida[17,18] has shown that the phosphoranes $[Ph_3P{=}CHCR^2{=}NR^1]$ (R^1 = aryl; R^2 = Ph, OMe, SEt) react with aldehydes to generate α,β-unsaturated imines, and recently, Cristau and Gase[19] have described the preparation of the salt $[Ph_3PCH{=}CHNMe_2]Br$, which, in the presence of KOBu^t, undergoes normal Wittig reactions with aldehydes and ketones.



Scheme 1

We have recently described[20] a new synthesis of enaminophosphonium salts $[MeNHCR{=}C(CO_2Me)PPh_3]^+ OTf^-$ by reaction of *N*-methylnitrilium trifluoromethanesulfonate salts $[RC{\equiv}NMe]^+ OTf^-$ with the stabilised ylide, $MeO_2CCH{=}PPh_3$. These salts react rapidly with a base to form the corresponding phosphorane but, as might be expected, these are too stable to react with simple aldehydes. As an extension of this work we have now investigated the reaction of nitrilium salts with benzylidenetriphenylphosphorane in an effort to prepare enaminophosphonium salts which are potentially more useful in synthesis. This work is now described.

Results and Discussion

The study involved the reactions of benzylidenetriphenylphosphorane ($Ph_3P{=}CHPh$), generated *in situ* from benzyltriphenylphosphonium bromide or chloride and butyllithium in either benzene or ether, with the nitrilium salts in dichloromethane. The choice of solvents for the nitrilium salts is limited to the polar solvents nitromethane, acetonitrile and chlorinated solvents—they react with tetrahydrofuran and are insoluble in most other common solvents. Dichloromethane is not an ideal solvent for an ylide reaction, but in the majority of the reactions studied reaction between the ylide and the highly electrophilic nitrilium salt is so fast that the solvent does not appear to cause any complications. However, in those reactions which involved a hindered phosphorane and a nitrilium salt bearing a bulky substituent, reaction was slow and by-products arising from the solvent may be formed. In all the reactions with benzylidenetriphenylphosphorane the phosphonium salt, $[Ph_3CH_2Ph]^+X^-$ (X = Cl or Br), precipitated from solution during the reaction and the new enaminophosphonium salts **1a–e** could be isolated after treatment of a concentrate of the filtrate with ethyl acetate. In the majority of cases the enaminophosphonium salts were isolated as their trifluoromethanesulfonates, but compound **1e** was obtained as the bromide salt as in this reaction the lithium bromide formed during the preparation of the ylide was not removed prior to addition to the nitrilium salt. All the reactions gave, in addition, intractable oils which were inseparable complex mixtures of by-products.

The IR spectra of the compounds **1a–e** (Table 1) showed a medium-strong NH stretching vibration in the range 3240–3410 cm^{-1} and a C=C stretching vibration (strong–very strong) in the range 1540–1570 cm^{-1}. The ν(C=N) vibrations in these compounds were observed in the range 1450–1520 cm^{-1}, that is, to lower frequency than a normal imine C=N bond. In contrast, the IR spectrum of compound **1f** (Table 1) showed no bands in the NH or C=C stretching vibration regions but, instead, showed a band of medium intensity at 1660 cm^{-1} for ν(C=N) indicating that this compound has the α-iminophosphonium

Table 1 Microanalytical, m.p. and IR spectroscopic data for the compounds **1a–f**

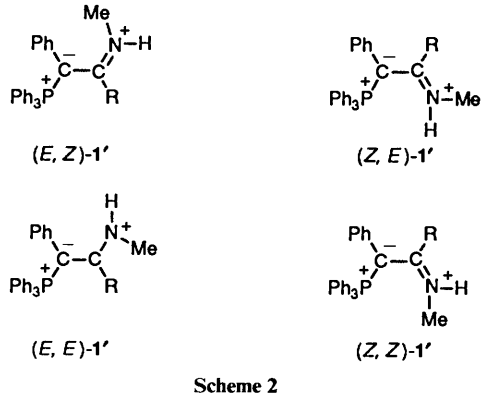
	X	M.p. (°C)	Microanalytical data (%)/ Found (Calc.) C	H	N	P	ν_{max}/cm^{-1} ν(N–H)	ν(C=N)	ν(C=C)
1a	OTf	150–152	65.4 (65.9)	4.6 (4.68)	1.8 (2.26)	5.1 (5.0)	3330s		1545vs
1b	OTf	171–173	66.2 (66.3)	5.0 (4.9)	2.1 (2.2)	4.9 (4.9)	3340s		1570vs
1c	OTf	204–206	62.2 (62.4)	4.0 (4.35)	2.4 (2.5)	5.5 (5.5)	3330s		1545vs
1d	OTf	146–149	63.4 (63.6)	5.3 (5.3)	2.4 (2.4)	5.3 (5.3)	3410s		1560vs
1e	Br	228–231	69.5 (69.8)	6.2 (6.0)	2.7 (2.7)		3240s		1540vs
1f	OTf	170–172	64.0 (64.1)	5.5 (5.5)	2.4 (2.34)	5.2 (5.2)		1660m	

salt structure. The ^{1}H NMR spectra of compounds **1a–e** showed a band in the range δ 4.5–6.3 for NH and a doublet at δ 2.2–2.9 (J 5–6 Hz) for the *N*-methyl protons. Interestingly, the spectrum of compound **1d** (R = Pr) showed two *N*-methyl resonances indicating that it is a mixture of isomers. The ^{1}H NMR spectrum of **1f** showed a sharp singlet at δ 2.9 for the *N*-methyl protons and a doublet (J_{P-H} 9 Hz) at δ 6.6 for the unique proton on the carbon atom adjacent to the phosphonium group, in agreement with the assigned α-iminophosphonium bromide structure. ^{1}H NMR spectroscopy is a fairly insensitive technique for the detection of minor isomers in the enaminophosphonium salts and the ^{31}P spectra (Table 2) are much more informative. It can be seen from the information presented in Table 2 that the enaminophosphonium salts **1a–e** all have a major band in the range +18.6 to +21.6 ppm and a minor band in the range +15.2 to +16.5 ppm. There is good spectroscopic and X-ray crystallographic evidence that these enaminophosphonium salts exist as a hybrid of the canonical forms **2** and **3** (see Fig. 1), and at room temperature in solution

2 **3**

Fig. 1

there is no rotation about either the C=C or C–N bonds. Consequently, four stereoisomers, *EZ*, *ZE*, *EE* and *ZZ*, are possible (see Scheme 2). A single crystal X-ray structure determination (Fig. 2) on the compound **1e** has shown that in the solid state it has the *E,Z* geometry. The carbon atom attached to the Ph_3P group is nominally sp^2 hybridised, and the C_α–C_β bond length (13.92 pm) is longer than a normal C=C double bond. The C_β–N bond length (13.43 pm) is longer than



Scheme 2

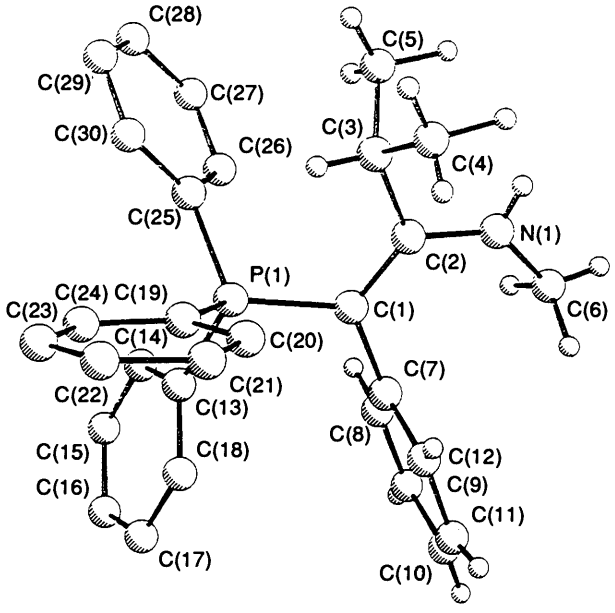


Fig. 2 X-Ray crystal structure of $[Ph_3PCPh{=}CPr^iNHMe]^+$ Br^- **1e** (the chloroform molecule, phenyl hydrogens and the Br^- counterion have been omitted for clarity)

a normal C=N bond. These data support the *E,Z*-betaine structure shown in Scheme 2. The structure is remarkably similar to that of the compound $[Ph_3PC(CO_2Me)CPr^iNH\text{-}Me]^+$ OTf^-, **1g** (see Fig. 3) whose preparation has been described previously.[20] In both cases the NHMe group is *trans* to the PPh_3 group and the C_α–C_β and C_β–N bond lengths in **1g** (14.40 and 13.00 pm, respectively) are similar to those for **1e** despite the change of the C-α substituent from a phenyl to an ester group. This implies that the nature of the substituent on the carbon atom α- to the phosphorus has little influence on the structure and that the major enaminophosphonium salts isolated in this work have the same *E,Z*-betaine structure.

From this analysis the ^{31}P NMR bands in the range +18.6 to +21.6 ppm are assigned to the *E,Z* isomer, while those at +15.2 to +16.5 ppm are possibly due to the *Z,E* or *Z,Z* isomer. It can be seen from Table 2 that the ^{31}P spectra of compounds **1d,e** show, in addition, a minor band at +29.4 and +26.6 ppm, respectively. Bands in this chemical-shift range are attributable (*vide infra*) to the presence of a small amount of the respective α-iminophosphonium salts. This is not apparent from the ^{1}H NMR spectrum as the concentration in each case was too low to be detected easily. However, support for the assignment comes from the ^{31}P NMR spectrum of **1f**, which, as noted previously, exists entirely as the α-iminophosphonium salt in

Table 2 ^{31}P and ^{13}C NMR spectroscopic data for the compounds **1a–f**

Compound	δ_P (%) (assignment)	$\delta_C(J_{P-C})$ C-1	C-2	NMe	*ipso*-C	Other characteristic bands
1a	+18.6 (92.7) (*E*,*Z*) +16.5 (7.5) (*Z*,*Z*?)	72.1 (*E*) (113)	167.0 (*E*) (22.0)	31.9 (*E*)	122.5 (*E*) (91.2)	133.6 (C_o10), 129.1 (C_m 13), 135.0 [C_p(2.7)]
1b	+19.5 (88.8) (*E*,*Z*) +15.7 (11.1) (*Z*,*Z*?)	76.9 (*E*) (116)	163.7 (*E*) (20.2) 166.0 (*Z*) (0.0)	31.4 (*E*) 31.5 (*Z*)	125.5 (*E*) (90.2) 118.5 (87.7)	36.9 (CH_2 4.8), 133.4 (C_o 9.8), 129.3 (C_m 13.2), 135.0 (C_p 3.5)
1c	+29.4 (12.0)* +19.9 (82.8) (*E*,*Z*) +18.2 (1.9) +15.2 (3.3 (*Z*,*Z*?)	74.1 (*E*) (117)	163.5 (*E*) (19.7)	30.8 (*E*)	122.2 (*E*) (90.2) 117.0 (86.5)	19.7 (Me 4), 30.4 (*48.5), 133.3 (C_o 9.5), 129.6 (C_m 12.2), 133.5 (C_p 3.5)
1d	+26.6 (2.2)* +19.6 (82.8) (*E*,*Z*) +15.3 (15.0) (*Z*,*Z*?)	74.0 (*E*) (124) 74.6 (*Z*) (93.6)	167.0 (*E*) (23.0) 168.1 (*Z*) (0.0)	31.0 (*E*) 31.3 (*Z*)	121.8 (*E*) (90.1) 119.1 (*Z*) (87.9)	13.1 (Me, *E*), 13.6 (Me, *Z*), 18.7 (CH_2, *E*) 20.5 (CH_2, *Z*), 21.3 (CH_2, *E*), 30.4 (*47.6), 32.7 (CH_2, *E* 8.2), 34.1 (CH_2, *Z*), 37.8(*), 116.1(*), 131.3 (C_o 10.1), (133.1 C_o 10), 129.2 (C_m 12.4), 129.7 (C_m 12.4), 133.3 (C_p 1.5), 13.9 (C_p 2.5), 133.6(*), 134.0(*)
1e	+21.6 (100) (*E*,*Z*)	70.3 (*E*) (112)	170.0 (*E*) (21.5)	30.6 (*E*)	116.8 (*E*) (89.2)	19.9 (Me), 36.6 (CH 6.8), 133.6 (C_o 10), 129.1 (C_m 13), 135.0 (C_p 2.7)
1f	+25.0 (100)*	59.2 (62.1)	174.3 (5.5)	38.0	121.6 (88.2)	28.2 (Me of Bu^t), 39.4 (C of Bu^t 4.6), 129.1 (C_m 12.5), 133.1 (C_p 2.8), 133.8 (C_o 8.6)

* Bands due to the α-iminophosphonium salt.

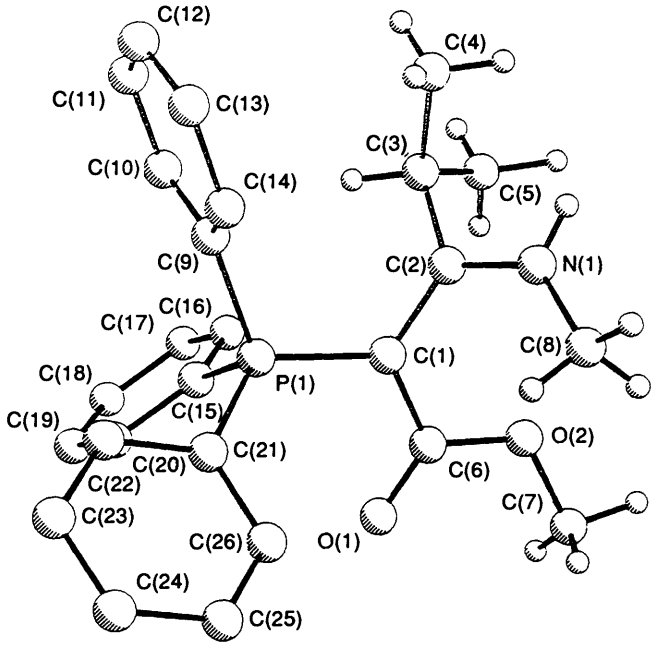


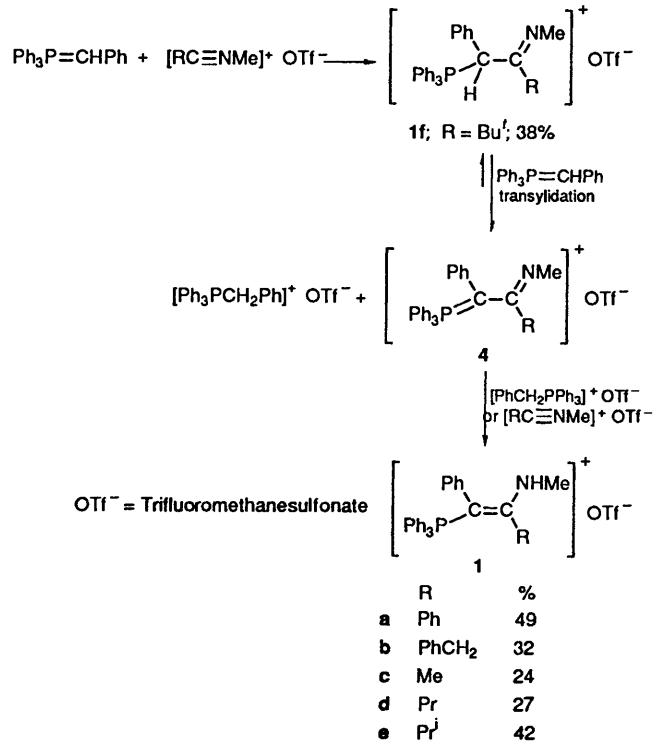
Fig. 3 X-Ray crystal structure of $[Ph_3PC(CO_2Me)=CPr^iNHMe]^+$ $[CF_3SO_3]^-$ (the counterion has been omitted for clarity)

solution. This has a ^{31}P resonance at +25.0 ppm and this is significantly higher than that for an enaminophosphonium salt, as expected for a P atom attached to an sp^3 atom.[15,21,22]

In the ^{13}C NMR spectra (Table 2) the C-1 resonance for the enaminophosphonium salts appear in the range δ 70.9–76.9 and the P–C coupling constants are large (93.4 to 124.4 Hz). In contrast, the C-1 resonance for the imine tautomer **1f** appears at δ 59.2 and the P–C coupling constant is reduced to 62.1 Hz. In agreement with previous observations made by Schweizer,[15,21] for the compounds **1a–f** the *ipso* carbon of the PPh_3 group has a chemical shift in the range δ 122.2–125.5 and $J_{P\ C}$ is large (89.2–91.2 Hz). The corresponding values for the tautomer **1f** are slightly lower (δ 121.6, J_{P-C} 88.2 Hz). The P–C coupling to C-2 is also diagnostic and can help in structure elucidation. For the major *E*-isomers of the compounds **1a–e** J_{P-C} is in the range 19.7–23 Hz, while the *Z* isomers have a coupling constant of 0–6 Hz. For the imine **1f** the coupling to C-2 is also small (5.5 Hz).

Mechanistically, this reaction between benzylidenetriphenylphosphorane and nitrilium triflate salts can be understood in terms of initial formation of an α-iminophosphonium salt intermediate (see Scheme 3), which then undergoes a transylidation reaction with another molecule of the phosphorane to give the intermediate **4** with formation of benzyltriphenylphosphonium triflate. Protonation of **4** then occurs mainly at nitrogen, rather than carbon, to give the isolated products **1a–e**. It would appear that when R is bulky, *e.g.* Bu^t then the transylidation reaction cannot occur for steric reasons and the product is the α-iminophosphonium salt **1f**. Although the isolated yields of these products are low the maximum yield expected on the basis of a 1:1 stoichiometry is 50%. We have tried to optimise the yields from some of these reactions by using a 2:1 ratio of ylide to nitrilium salt and carrying the reaction out at lower temperatures, but this did not lead to any significant improvement in most cases.

A question still remains as to when and how protonation of intermediate **4** occurs. By monitoring the reaction by TLC it has been established that both the benzylphosphonium salt and the enaminophosphonium salt are formed in the reaction mixture shortly after mixing of the reactants. This indicates that both the transylidation and the protonation occur during the reaction and the protonation does not happen during the work-up procedure. One obvious proton source is the nitrilium salt and abstraction of the α-hydrogens would lead to a ketenimine intermediate. This is expected to be unstable and could be the part-source of the complex oily by-products which are always found in these reactions. It is noticeable that a significantly higher yield of product is obtained when R = Ph and there are no abstractable α-hydrogens. The nitrilium salt $[Bu^tC{\equiv}NMe]^+$ OTf^- is slightly anomalous in this respect, but, as outlined above, other factors such as steric requirements play a role. In an attempt to demonstrate experimentally that ketenimines may be generated under these conditions the reaction between $[Ph_2CHC{\equiv}NMe]^+$



	R	%
a	Ph	49
b	$PhCH_2$	32
c	Me	24
d	Pr	27
e	Pr^i	42

Scheme 3

OTf^- and benzylidenetriphenylphosphorane was investigated. The nitrilium salt was prepared in the usual way by the reaction of neat methyl trifluoromethanesulfonate with diphenylacetonitrile at 70 °C to give a brown semisolid product, which showed a $C\equiv N^+$ stretching vibration in the IR spectrum at 2390 cm^{-1} [*cf.* nitrile ν(C≡N) 2300 cm^{-1}] and on treatment with water it was hydrolysed quantitatively to *N*-methyldiphenylacetamide [ν(C=O) 1680 cm^{-1}]. Addition of a solution of the nitrilium triflate salt in dry dichloromethane to a solution of the ylide in dry ether gave immediate precipitation of the phosphonium salt $[Ph_2CHPPh_3]^+$ OTf^- and a yellow oil, which showed a strong, sharp band in the IR spectrum at 2020 cm^{-1} characteristic of a ketenimine [ν(C=C=N) 2000–2050 cm^{-1}].[23,24] This band persisted in the sample for more than 3 days. The ^{13}C NMR spectrum of the oil showed a quaternary C atom at δ 187.1 which is consistent with that expected for the α-C atom of a ketenimine [δ 186.6–195.5].[25,26] Despite good evidence that the expected ketenimine had been formed it was not possible to isolate it pure as the reaction is not a clean one. The ^{31}P NMR spectrum showed more than 30 peaks and TLC indicated that it was a complex mixture.

Experimental

Methyl trifluoromethanesulfonate was freshly prepared before each reaction from dimethyl sulfate and trifluoromethanesulfonic acid and was distilled immediately before use.[20] The *N*-methylnitrilium salts were prepared by addition of the nitrile (1 equiv.) to methyl trifluoromethanesulfonate (1 equiv.) under argon as described previously.[20] Benzylidenetriphenylphosphorane was prepared by the addition of butyllithium (1 equiv.) to benzyltriphenylphosphonium chloride, bromide or iodide (1 equiv.) under nitrogen or argon and was used without further purification.[27] All reactions were carried out in flame-dried apparatus under an atmosphere of dry argon, and dichloromethane and nitromethane were purified and dried by established procedures.[28]

IR spectra were recorded on a Perkin-Elmer model PE 298; ^1H and ^{13}C NMR spectra on an XL300 spectrometer, while ^{31}P spectra were recorded on a WP80 spectrometer operating at 32.4 MHz.

Crystallography.—Crystal data and refinement details for $[Ph_3PC(CO_2Me)=CPr^iNHMe]^+$ $[CF_3SO_3]^-$ and $[Ph_3PCPh=CPr^iNHMe]^+$ Br^- are presented in Table 3. Both compounds were mounted on glass fibres. All measurements were performed on a Enraf-Nonius CAD-4 diffractometer employing graphite monochromated Mo-Kα radiation (θ = 0.710 69 Å) and $\omega/2\theta$ scans. The structures were solved by direct methods using SHELX86[29] and refined by blocked-matrix least-squares based on *F* using SHELX76.[30] Non-hydrogen atoms were refined anisotropically and hydrogens isotropically. The absolute configuration of **1g** was determined by allowing η (multiplier of the imaginary anomalous component of the scattering factor) to refine.[31] An η value of 0.7(2) confirmed that the correct enantiomer had been chosen. Disordered chloroform of crystallisation (0.94 molecules) in $[Ph_3PCPh=CPr^iNHMe]^+$ Br^- was subjected to constrained refinement. The main solvent site contained 0.60 of a chloroform molecule, which shared one chlorine atom, Cl (1s), with a further 0.26 of a molecule and another chlorine, Cl (2s), is shared with another 0.08 of a molecule of chloroform. Neutral atom scattering factors were used throughout.[33]

The crystallographic detail (fractional atomic coordinates, bond lengths and angles and thermal parameters) are available on request from the Cambridge Crystallographic Data Centre.

Typical Procedure for the Reactions of Benzylidenetriphenylphosphorane with Nitrilium Trifluoromethanesulfonate Salts.—(i) *In benzene–dichloromethane* (*Method A*). A solution of the phosphorane (13.09 g, 37.2 mmol) in dry benzene (150 cm^3) was added gently through a cannular over 10 min to a stirred solution of the nitrilium salt (18.6 mmol) in dichloromethane (20 cm^3) at room temperature. This resulted in precipitation of the phosphonium salt and a colour change from pale yellow to orange. The mixture was stirred for 24 h at room temperature before removal of the solvent under reduced pressure to give an orange oil. The oil was redissolved in dichloromethane (15 cm^3) and washed with diethyl ether (120 cm^3) to give benzyltriphenylphosphonium trifluoromethanesulfonate, which was filtered off. Concentration of the oil, addition of dichloromethane (15 cm^3), followed by ethyl acetate until the solution became turbid gave crystals of the enamino(triphenyl)phosphonium salt. This could be recrystallised from dichloromethane–diethyl ether (1:4). Using this procedure the following compounds were prepared.

2-Methylamino-1,2-diphenylvinyl(triphenyl)phosphonium trifluoromethanesulfonate **1a**. This compound was obtained as a pale yellow crystalline solid (5.2 g, 8.4 mmol, 49%); δ_H($CDCl_3$, TMS ext. ref.) 2.2 (3 H, d, *J* 6, NH*Me*), 5.25 (1 H, m, NH by D_2O shake), 6.7–7.1 (5 H, m, Ph) and 7.2–7.7 (15 H, m, Ph_3P).

2-Methylamino-1,3-diphenylprop-1-enyl(triphenyl)phosphonium trifluoromethanesulfonate **1b**. This compound was prepared as a pale yellow, crystalline solid (7.1 g, 11.2 mmol, 32%); δ_H($CDCl_3$, TMS ext. ref.) 2.8 (3 H, d, *J* 6, NH*Me* of major isomer), 3.8 (2 H, s, CH_2), 5.5 (1 H, Br, NH), 6.8 (2 H, d, *J* 7, H_o), 7.1–7.25 (3 H, m, H_m and H_p) and 7.35–7.7 (15 H, m, Ph_3P). A brown oil (8.35 g) was also isolated from this reaction.

(ii) *In diethyl ether–dichloromethane* (*Method B*). The phosphorane (17.68 mmol) in anhydrous diethyl ether (120 cm^3) was added over 10 min to a stirred solution of the *N*-methylnitrilium trifluoromethanesulfonate (8.84 mmol) in dichloromethane (35 cm^3) to give the phosphonium salt as a pale yellow precipitate. The mixture was stirred for a further 24 h before removal of the

Table 3 Crystal data and details of refinement

Compound	**1g**	**1e**
Formula	$C_{26}H_{29}NO_2P^+ CF_3SO_3^-$	$C_{30}H_{31}NP^+ Br^- \cdot 0.94 CHCl_3$
M	567.56	628.67
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
a/Å	9.567(2)	10.399(2)
b/Å	11.004(2)	11.742(4)
c/Å	13.391(2)	26.264(8)
β/°	101.35(2)	98.58(3)
U/Å^3	1382.2	3170.9
Z	2	4
D_c/g cm^{-3}	1.36	1.31
$F(000)$	592	1287.3
μ/cm^{-1}	1.86	1.54
Crystal size (mm)	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.2
Scan speed (°/min^{-1})	0.2–5.0	0.6–5.0
Scan range (°)	0.80 + 0.35 tanθ	0.60 + 0.35 tanθ
Maximum 2θ/°	50	50
Total data measured *	2722	11 361
No. of unique reflections	2447	5045
No. of observed reflections [$F_o > 3\sigma(F_o)$]	2359	5045
No. of parameters	460	530
ρ_{min},ρ_{max}/e Å^{-3}	−0.3, 0.3	−0.6, 0.5
Maximum least-squares shift-to-error ratio	0.03	0.10
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.000 12	0.001
Final R	0.038	0.068
Final R'	0.047	0.062

precipitate by filtration and concentration of the filtrate to give an oil. This was dissolved in the minimum amount of dichloromethane and ethyl acetate was added until turbidity was achieved. After some time the aminovinylphosphonium salt crystallised out and this was recrystallised as described above.

2-*Methylamino*-1-*phenylprop*-1-*enyl*(*triphenyl*)*phosphonium trifluoromethanesulfonate* **1c**. Reaction between *N*-methylacetonitrilium trifluoromethanesulfonate (3.63 g, 17.7 mmol) in dichloromethane (20 cm^3) and the phosphorane (12.46 g, 35.4 mmol) in diethyl ether (150 cm^3) gave **1c** as a yellow solid (2.4 g, 4.3 mmol, 24%); δ_H($CDCl_3$, TMS ext. ref.) 1.6 (3 H, s, =CMe), 2.7 (3 H, d, J 5, NH*Me*) 4.9 (1 H, br, NH), 6.8 (2 H, d, H_o), 6.9–7.0 (3 H, m, H_m and H_p), 7.3–7.5 (15 H, m, Ph_3P). An oil (6.36 g), which was a complex mixture of products by TLC, was also formed in this reaction.

2-*Methylamino*-1-*phenylpent*-1-*enyl*(*triphenyl*)*phosphonium trifluoromethanesulfonate* **1d**. This compound was isolated from the reaction between benzyltriphenylphosphonium chloride (6.32 g, 17.68 mmol) and *N*-methylbutyronitrilium trifluoromethanesulfonate (2.06 g, 8.84 mmol) as a pale yellow solid (1.4 g, 2.39 mmol, 27%); δ_H($CDCl_3$, 300 MHz, TMS int. ref.) 0.2 (3 H, t, J 7, CH_3), 1.4–1.5 (sextet, 2 H, J 7, CH_2), 2.2 (2 H, t, J 7, CH_2C=), 2.9 (3 H, d, J 5, CH_3NH), 5.1 (1 H, br, NH) and 6.9–7.8 (15 H, m, Ph_3P).

3-*Methyl*-2-*methylamino*-1-*phenylbut*-1-*enyl*(*triphenyl*)*phosphonium bromide* **1e**. This compound was isolated as a white crystalline solid (0.82 g, 1.8 mmol, 42%) from the reaction of benzyltriphenylphosphonium bromide (6.46 mmol) in diethyl ether (150 cm^3) and *N*-methylisopropionitrilium trifluoromethanesulfonate (1.51 g, 6.46 mmol) in dichloromethane (30 cm^3); δ_H($CDCl_3$, 220 MHz, TMS ext. ref.) 0.9 (6 H, d, J 7, CH_3), 1.9 (septet, 1 H, $CHMe_2$), 2.4 (3 H, d, J 5, CH_3N), 6.3 (1 H, br, NH), 6.9–7.1 (5 H, m, Ph) and 7.3–7.7 (15 H, m, Ph_3P).

3,3-*Dimethyl*-2-*methylimino*-1-*phenylbut*-1-*enyl*(*triphenyl*)-*phosphonium trifluoromethanesulfonate* **1f**. This compound was isolated as a pale yellow, crystalline solid (1.2 g, 2.0 mmol, 38%) from the reaction of the phosphorane (10.6 mmol) and *N*-methyltrimethylacetonitrilium trifluoromethanesulfonate (1.31 g, 5.3 mmol); δ_H($CDCl_3$, 220 MHz, TMS ext. ref.) 1.0 (9 H, s, Me_3C), 2.9 (3 H, s, CH_3N), 6.6 (1 H, d, J_{P-H} 9, CH), 6.85 (2 H, d, J 7, H_o), 7.0 (2 H, t, H_m), 7.1 (1 H, m, H_p) and 7.3–7.5 (15 H, m, Ph_3P). An uncharacterised oil (2.87 g) was also isolated from this reaction.

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