Synthesis and reactivity of 3-(dialkylamino)allenyl phosphonium salts. PPh_3-mediated synthesis of pyrroles from propyne iminium triflates

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Dedicated to Professor Ernst Anders on the occasion of his 65th birthday

Abstract

The ambident cations of propyne iminium trifluoromethanesulfonates (triflates) **1** react with triphenyl- or tributylphosphane exclusively in a conjugate addition to form highly moisture-sensitive [3-(dialkylamino)allenyl]phosphonium triflates **2** and **4**. Allene **2f**, bearing a methyl group at the enamine α-position, rearranges to form (3-morpholinobuta-1,3-dienyl)phosphonium salt **3** under the reaction conditions. The rather electron-rich allenes are easily protonated by triflic acid to form dicationic 3-phosphonio-prop-2-ene iminium bis(triflates) **5**, one of which (**5a**) was characterized by X-ray crystal structure determination. Hydrolysis of the allenes yields (3-oxoprop-1-enyl)phosphonium triflates **6** ($-^+PPh_3$) or **8** ($-^+PBu_3$). Salts **6** can also be prepared by simultaneous addition of PPh_3 and triflic acid to acetylenic ketones. Salts **2** are converted thermally into 1,2,3,5-tetrasubstituted pyrroles **10**; this reaction can be used for a PPh_3-mediated conversion of propyne iminium salts **1** into pyrroles **10** without isolation of the allenylphosphonium salt intermediate.

Keywords: Aminoallenes, allenylphosphonium salts, vinylphosphonium salts, iminium salts, pyrroles, conjugate addition

Introduction

The conjugated π-system of acetylenic iminium (= propyne iminium) ions can accept nucleophiles at either the iminium carbon atom or the conjugate acetylenic position, resulting in the formation of propargylamines or aminoallenes, respectively.[1] Recently we have reported that propyne iminium triflates react with neutral phosphorus nucleophiles such as $Ph_2P–SiMe_3$ and Ph_2P-$OSiMe_3$ in a conjugate addition to form ultimately (dialkylamino)allenyl phosphanes and phosphanoxides, respectively.[2] Under thermal conditions, these aminoallenes are readily

transformed into highly substituted pyrroles with elimination of the P-containing substituent.[3] As a logical extension of this work, we have now investigated the use of triphenylphosphane and tributylphosphane for the same sequence of transformations. The results are reported in this paper.

Results and Discussion

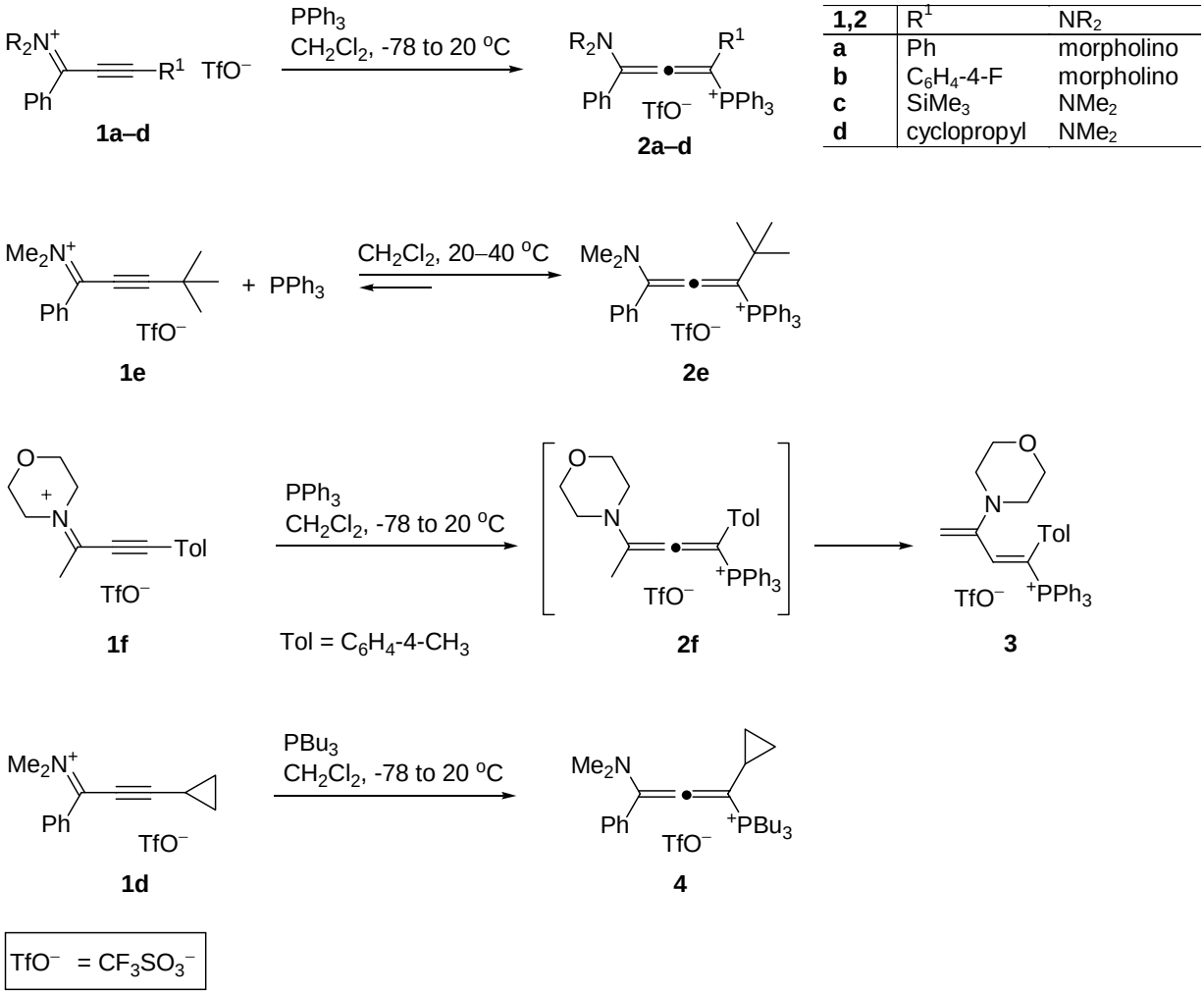
Propyne iminium triflates **1** can easily be prepared either from enaminoketones and triflic anhydride in two steps[4] or from alkynyl imines by *N*-methylation.[5,6] Reactions of salts **1a**–**f** with triphenylphosphane are shown in Scheme 1. In all cases, the phosphorus nucleophile underwent a conjugated addition to the iminium salt under very mild conditions, resulting in the formation of [3-(dialkylamino)allenyl]phosphonium triflates **2**. Solid salts **2a**–**d** could be isolated in good yields (Table 1). Due to the high moisture-sensitivity of these aminoallenes, it was not always possible to obtain a completely pure product; in particular, **2b** and (to a lesser extent) **2a** were contaminated with products of hydrolysis (vide infra). The higher hydrolytic stability of **2c** reflects our previous experience with 3-silyl-substituted aminoallenes.[7] Interestingly, the conversion of *tert*-butyl substituted propyne iminium salt **1e** into allene **2e** was not complete, and an equilibrium mixture was still present when two equivalents of PPh_3 were applied (**2e**:**1e** = 9:1 at 27 ^oC in dichloromethane). Obviously, severe steric interaction between the geminal *t*-Bu and PPh_3 substituents in **2e** enhances the reversibility of the reaction. However, this does not pave the way for nucleophilic addition of PPh_3 at the iminium carbon atom which, according to earlier calculations,[1] has both the higher positive charge density and the higher HOMO coefficient compared to the acetylenic β-C. Probably, the resulting propargylamine would also suffer from severe steric encumbrance around the propargyl position.

Allenylphosphonium salt **2f**, bearing a methyl group at the enamine α-position, could also not be isolated due to the expected[8] rapid isomerization into (3-morpholinobuta-1,3-dienyl)phosphonium triflate **3**. It should be noted that, in a similar manner, 3-CH substituted aminoallenes also isomerize by a 1,3-H shift to form 1-amino-1,3-dienes.[8] 3-Cyclopropyl-substituted aminoallene **2d**, however, does not undergo this isomerization, most likely because it would produce a highly strained methylenecyclopropane substructure.

Efforts to synthesize the PBu_3 analogues of allenylphosphonium salts **2** were less successful due to the extreme moisture-sensitivity of [3-(dialkylamino)allenyl]tributylphosphonium salts. Only the cyclopropyl-substituted salt **4** could be isolated, while the presence of hydrolysis products was observed already in the crude reaction mixtures resulting from the combination of iminium salts **1a,c** and PBu_3.

The somewhat higher hydrolytic stability of triphenylphosphonio as compared to tributylphosphonio substituted aminoallenes may be attributed to the higher acceptor character of the $^+PPh_3$ group. Weiss et al. have described the twofold donor-acceptor-substituted allene $(Me_2N)(Ph_3P^+)C{=}C{=}C(^+PPh_3)(NMe_2)$ $2I^-$ as an air-stable crystalline salt, and no tendency of

hydrolysis has been mentioned.[9] According to their MNDO calculations, the $^{+}PPh_3$ groups in this system act solely as σ, not as π acceptors.



Scheme 1. Reactions of propyne iminium triflates with triphenyl- or tributylphosphane.

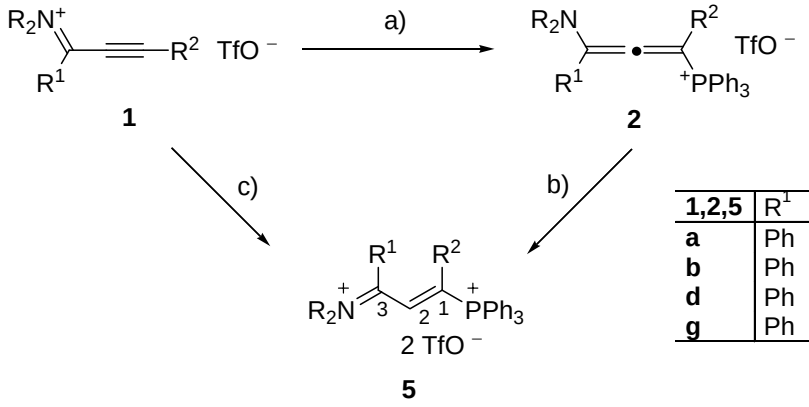
Some characteristic spectroscopic data of allenes **2** and **4** are given in Table 1. In the IR spectra, the C=C=C valence vibration appears as a weak absorption in the range 1886–1907 cm^{-1}. The ^{13}C NMR signal of the central allenic carbon atom in **2a**–**e** is observed in the δ range 215–233 ppm, corresponding to a low-field shift by about 19–26 ppm relative to the analogous aminoallenes where the $^{+}PPh_3$ substituent is replaced by a phenyl group.[7,8]

Table 1. Yields and characteristic IR and NMR data of allenes **2** and **4**

2	Yield (%)	IR,[a] ν (cm^{-1})	^{13}C NMR,[b] δ (ppm) (J(^{13}C,^{31}P) (Hz)) C=C=*C*–P	C=*C*=C–P	^{31}P NMR,[b] δ (ppm)
a	73	1895	100.04 (83.5)	221.00 (0)	18.92
b	[c]	1907	99.16 (83.9)	221.06 (5.3)	18.85
c	90	1886	94.06 (40.4)	232.94 (7.9)	15.36
d	92	1891	100.36 (80.5)	214.50 (5.9)	19.39
e	[d]	1892	105.80 (68.2)	219.55 (6.1)	17.28
4	87	1902	99.08 (76.8)	208.55 (4.4)	29.69

[a] KBr pellet or film (**4**). [b] In $CDCl_3$. [c] Not obtained in pure form. [d] Equilibrium mixture of **2e** with precursors.

Due to the enamine substructure, allenes **2** are readily protonated at the central allenic carbon atom to form the dicationic 3-(triphenylphosphonio)propenyl iminium bis(triflates) **5** (Scheme 2). In fact, salts **5** were occasionally found as by-products in the preparation of **2** from **1** when the latter were contaminated with traces of triflic acid. More conveniently than from allenes **2**, salts **5** can be prepared in one step from propyne iminium salts **1** by simultaneous or successive addition of PPh_3 and triflic acid at low temperature. While salts **5a,b,g** could be isolated in 72–94% yield, this was not the case for cyclopropyl-substituted salt **5d**. NMR spectra indicated that **5d** maintained a solution equilibrium with small amounts of allene **2d**, and a separation of the salts was not possible.



1,2,5	R^1	R^2	NR_2
a	Ph	Ph	morpholino
b	Ph	C_6H_4-4-F	morpholino
d	Ph	cyclopropyl	NMe_2
g	Ph	Ph	$N(CH_2Ph)_2$

Scheme 2. Conditions: a) PPh_3, CH_2Cl_2, -78→20 °C; b) HOTf, CH_2Cl_2, rt; c) PPh_3 (1 equiv.), HOTf (1 equiv.), CH_2Cl_2, -78→20 °C.

Characteristic NMR data of dicationic iminium salts **5** are given in Table 2. In all cases, only one diastereomer was detected and the magnitude of the ^3J(P,H) coupling constant of the olefinic proton signal suggested a *cis*-relationship,[10,11,13] i.e. the *E*-configuration at the olefinic bond. This conclusion was confirmed by an XRD analysis of **5a** (Figure 1). The torsion angles indicate

considerable steric strain in the cation, as the conjugated propene iminium backbone is far from planarity and significant deviation from coplanarity is also found around the C1=$N^+$and C2=C3 double bonds.

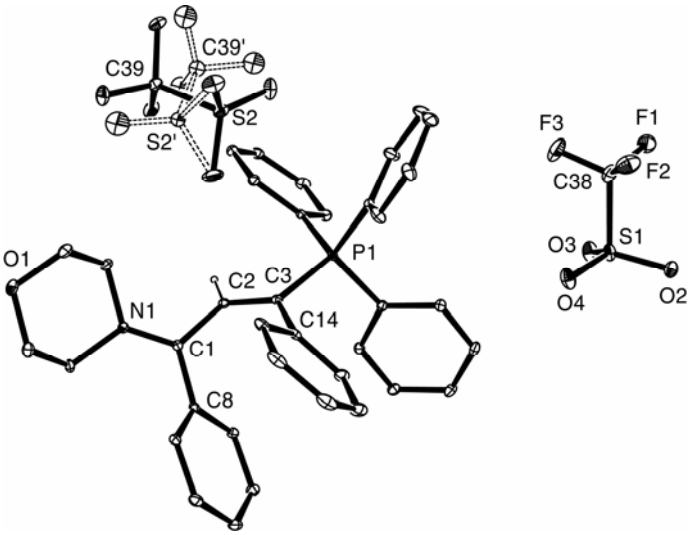


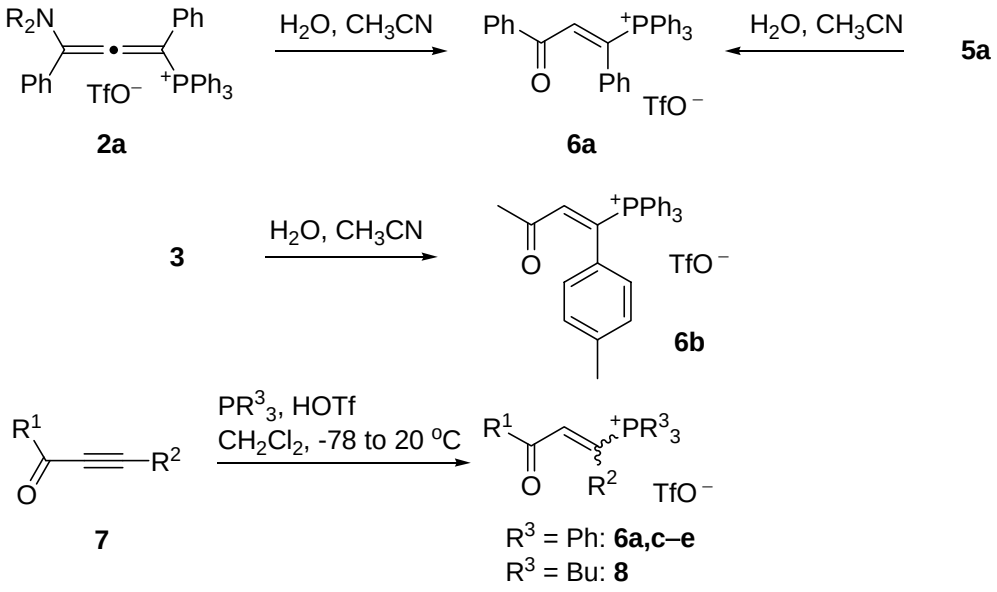
Figure 1. Solid-state structure of **5a**. Ellipsoids of thermal vibration are shown at the 20% probability level. Hydrogen atoms except 2-H are omitted. One of the two triflate anions is disordered over two positions. Selected bond lengths (Å) and angles (°): P1–C3 1.830(2), C1–C2 1.485(3), C2–C3 1.332(3), N1–C1 1.295(3); C3–C2–C1 123.5(2); C2–C3–P1 119.6(1), C2–C3–C14 122.8(2), N1–C1–C2 118.8(2), C8–C1–C2 118.6(2). Torsion angles (Å): N1–C1–C2–C3 138.1(2), C1–C2–C3–P1 171.2(1), C4–N1–C1–C2 -13.5(3), C7–N1–C1–C2 165.1(2).

Table 2. Selected NMR data of 3-(triphenylphosphonio)propene iminium bis(triflates) **5** ($CDCl_3$, δ (ppm), *J* (Hz) in parentheses)[a]

5	R^1	R^2	NR_2	^{1}H NMR	^{13}C NMR: δ (*J*(P,C))			^{31}P NMR
				δ(2-H) (^{3}*J*(P,H))	C-1	C-2	C-3	
a	Ph	Ph	morpholino	7.93 (20.6)	175.82 (19.7)	142.09 (16.7)	144.54 (71.7)	26.90
b	Ph	C_6H_4-4-F	morpholino	8.00 (19.2)	176.98 (19.0)	144.87 (16.1)	144.01 (71.7)	25.36
d	Ph	cyclopropyl	NMe_2	7.45 (22.2)	175.74 (22.0)	144.29 (18.3)	142.49 (73.2)	25.65
g	Ph	Ph	$N(CH_2Ph)_2$	7.86 (20.2)	179.67 (19.8)	142.38 (16.8)	146.28 (70.3)	25.92

[a] ^{13}C assignments were established by HMBC and HSQC experiments.

Hydrolysis of (aminoallenyl)phosphonium salts **2** leads to (3-oxoprop-1-enyl)phosphonium triflates **6**, e.g. **2a** → **6a** (Scheme 3). Analogously, (3-morpholinobutadienyl)phosphonium salt **3** is hydrolyzed to form **6b**. In both cases, only the *E*-configuration at the olefinic bond was detected by NMR. The same products are obtained by hydrolysis of the dicationic iminium salts **5**. (3-Oxoprop-1-enyl)phosphonium salts can also be prepared from acetylenic ketones or esters, PPh_3, and mineral acids.[11,12] Accordingly, we have prepared vinylphosphonium triflates **6a,c,d,e** from the corresponding alkynones **7**, PPh_3 and HOTf. The reaction was also successful when PBu_3 was applied, furnishing salt **8** which was also prepared by in-situ hydrolysis of the allene formed from **1a** and PBu_3. In contrast to the hydrolysis of aminoallenes **2** and dicationic iminium salts **5**, the alkynone route provided either the *E* or the *Z* isomer or mixtures of both (Table 2). Similar observations were made when mineral acids rather than HOTf were used.[11,12] In the case of **6d**, the initial product was identified as *Z*-**6d** which underwent slow isomerization in solution to provide an *E*/*Z* mixture.



Scheme 3. See Table 3 for individual compounds.

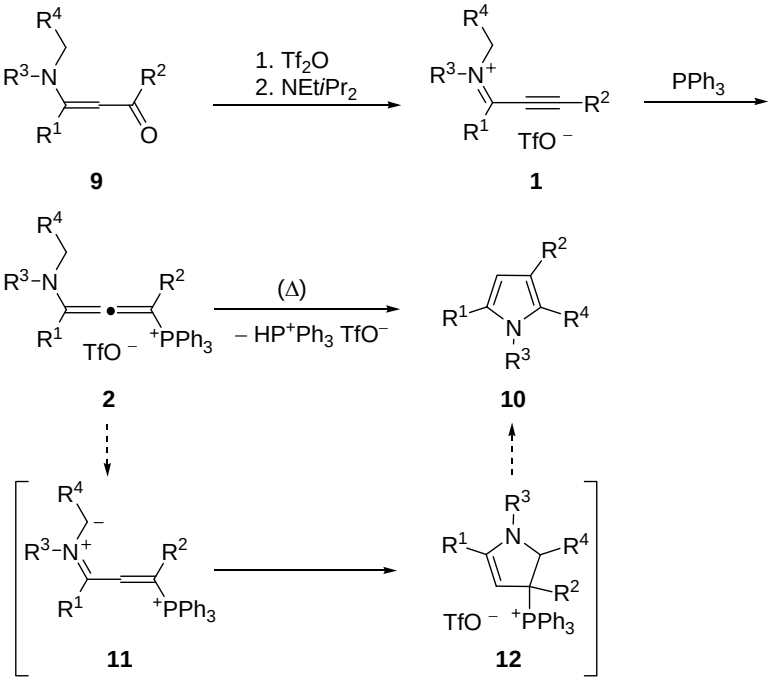
Table 3 lists some characteristic NMR data of vinylphosphonium salts **6** and **8**. In agreement with other authors,[10,11] the configurational assignment rests on the different magnitude of the vicinal P,H coupling at the olefinic bond, namely ^3J(P,H-*trans*) > ^3J(P,H-*cis*). Thus, the *Z*-configuration can be assigned to the isomer with the larger coupling constant (36–38 Hz vs. 20–23 Hz). Another reliable feature is the magnitude of the $^3J_{P,C\text{-}3}$ coupling constant at the propenylphosphonium moiety,[14] which for the present examples has values of ca. 16–18 Hz (*trans* coupling, *E*-isomer) and 4–5 Hz (*cis* coupling, *Z*-isomer).

Table 3. (3-Oxoprop-1-enyl)phosphonium salts prepared and selected NMR data ($CDCl_3$. δ (ppm, *J* (Hz))

Com-pound	R^1	R^2	Yield (%)	*E*:*Z* ratio	^{1}H NMR: δ, (*J*(P,H)) 2-H	^{13}C NMR: δ (*J*(P,C)) C-1	C-2	C-3
R^3 = Ph								
6a	Ph	Ph	81[a] 81[b]	100:0 7:93	*E*: [c] *Z*: 8.29 (37.3)	132.32 (71.4) 137.02 (71.0)	149.95 (8.7) 147.33 (6.1)	191.27 (17.8) 188.46 (4.2)
6b	Me	4-tolyl	70[d]	100:0	6.99 (22.2)	131.06 (70.6)	150.46 (8.7)	198.96 (18.2)
6c	C_6H_3-3,4-Cl_2	Ph	77[e]	0:100 (45:55[f])	*Z*: 8.26 (37.4) *E*: 7.45 (22.9)	139.59 (70.2)	146.52 (5.7)	[g]
6d	Ph	2-thienyl	86[e]	3:97	*Z*: 8.18 (36.3) *E*: 7.38 (22.0)	137.01 (70.6)	149.50 (5.7)	180.19 (5.3)
6e	C_6H_4-2-Br	C_6H_4-4-Cl	41[e]	90:10	*E*: 7.97 (21.1) *Z*: 8.39 (37.6)	131.64 (71.2)	148.80 (8.4)	187.74 (14.1)
R^3 = Bu								
8	Ph	Ph	41[h]	100:0	7.84 (19.7)	131.73 (65.1)	146.91 (7.3)	190.54 (16.1)

[a] From **2a**. [b] From **7a**. [c] Covered by phenyl protons. [d] From **3**. [e] From alkynone **7**. [f] After slow *Z*/*E* equilibration. [g] Not found. [h] From **1a**; alternatively from **7a** (yield n.d.).

The [3-(dialkylamino)allenyl]phosphonium salts **2** undergo a thermally induced transformation into pyrroles **10** (Scheme 4). In mechanistic terms, this reaction is likely to proceed via α,β-unsaturated azomethine ylides **11** which undergo a 1,5-cyclization to form dihydropyrroles **12**, followed by elimination of PPh_3 and triflic acid. The analogy to our previous synthesis[3] of pyrroles from (aminoallenyl)diphenylphosphanes or (aminoallenyl)diphenylphosphanoxides is obvious. Another pyrrole synthesis based on unsaturated azomethine ylide cyclization has been developed by Gupton et al. who generated the azomethine ylide intermediates from 3-chloropropene iminium or vinamidinium salts and (*N*-substituted) glycine esters.[15]



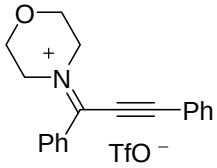
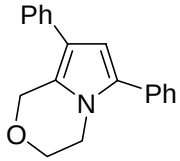
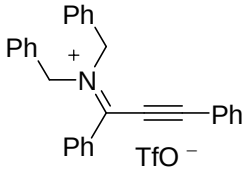
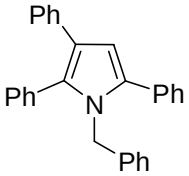
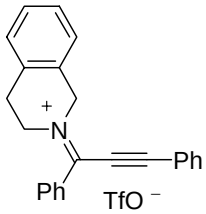
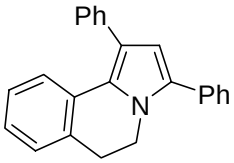
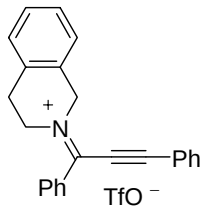
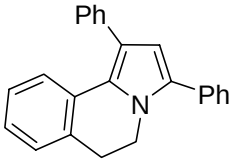
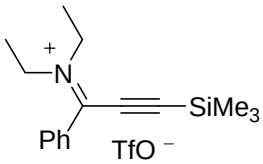
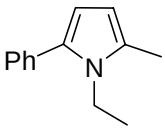
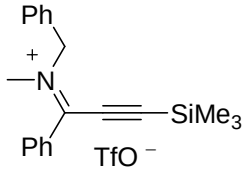
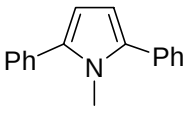
Scheme 4. Transformation of propyne iminium salts **1** into pyrroles **10**.

Examples of the PPh_3-modification of our previously developed pyrrole synthesis are given in Table 4. Given the notorious moisture-sensitivity of allenes **2**, we have usually refrained from their isolation and have performed the pyrrole synthesis directly from propyne iminium salts **1** via in-situ generated allenes **2** (Scheme 4). In some cases, we have gone one step further and have not even isolated the (also moisture-sensitive) iminium salts **1**; rather, the multi-step synthesis of pyrroles **10** from enaminoketones **9** has been performed in one pot without isolation of any reaction intermediates. Although the yields of pyrroles **10** were only moderate in most cases, we have not been able to isolate any other product; however, products from the hydrolysis of intermediate allenes (see above) could be detected by ^{1}H NMR septroscopy in most of the crude reaction mixtures.

It should be noted that not all examples in Table 4 represent an overall synthesis of pyrroles from enaminoketones. While propyne iminium salts **1a,g,h,i** are derived from enaminoketones, salts **1j,k** were obtained from alkynyl imines. Thus, pyrroles **10j,k** can be prepared in two steps from alkynyl imines. Recently, a direct Cu(I)-mediated conversion of alkynyl imines into pyrroles has been described; however, it is limited to substrates bearing a CH_2 group at the acetylenic bond.[16]

The results reported in Table 4 are commented as follows: a) Although PPh_3 seems to furnish somewhat lower yields in comparison to $Me_3SiO–PPh_2$/LiCl as activator,[3] (e.g. **10a**: 13 vs. 24%), it has the advantage of being the more convenient reagent. b) We have replaced triphenylphosphane by polymer-supported triphenylphosphane in the hope of facilitating the work-up of the product mixture. However, this led to reduced yields in all tested cases; furthermore, removal of the finely divided solid polymer by simple filtration was hardly possible and centrifugation was required. c) The 3-trimethylsilyl-substituted pyrroles expected from **1i** and **1j** could not be isolated, obviously because of rapid protiodesilylation by the HP^+Ph_3 cation formed in the reaction.

Table 4. Pyrroles **10** from propyne iminium salts **1**

Iminium salt **1**	Pyrrole **10**	Method[a]	Conditions for cyclization	Yield of **10** (%)
 **1a**	 **10a**	B	100 °C, 5 h	13
 **1g**	 **10g**	A	20 °C, 14 h	42
 **1h**	 **10h**	B	20 °C, 14 h	15
 **1i**	 **10i**	A	100 °C, 3 h	41
 **1j**	 **10j**	A	60 °C, 4 h	37[b]
 **1k**	 **10k**	A	60 °C, 4 h	77[b]

[a] Method A: from isolated iminium salt **1**. Method B: from iminium salt **1** generated in situ from corresponding enaminoketone **9**; overall yield is given. [b] The expected 3-$SiMe_3$ substituted pyrrole was not found.

In conclusion, we have prepared and characterized novel [3-(dialkylamino)allenyl]phosphonium triflates. These salts are readily protonated at the central allenic carbon atom, giving rise to dicationic 3-phosphonio-substituted propeniminium salts, and are hydrolyzed to form (3-oxoprop-1-ene)phosphonium salts. In a synthetically useful application, they occur as reaction intermediates in a PPh_3-mediated synthesis of 1,2,3,5- and 1,2,5-substituted pyrroles, including *a*-anellated pyrroles, from propyne iminium triflates.

Experimental Section

General Procedures. The following spectroscopic and analytical instruments were used. NMR: Bruker DRX 400 (^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz; ^{31}P: 161.98 MHz). The spectra were recorded in $CDCl_3$ solution if not stated otherwise. For ^{1}H spectra, TMS was used as internal standard. For ^{13}C NMR spectra, the solvent signal was used as internal standard [$\delta(CDCl_3)$ = 77.0, $\delta(CD_3CN)$ = 118.2]. Signal assigments for ^{13}C spectra are based on DEPT 135, gs-HMBC, gs-HSQC and gs-HMQC experiments. – IR: Perkin-Elmer 1310, Bruker Vector 22 FT-IR spectrophotometer. – Mass spectrometry: Finnigan MAT SSQ 7000 (EI spectra), Finnigan TSQ 7000 (FAB spectra; matrix: 3-nitrobenzyl alcohol), Bruker Daltonics Reflex III (MALDI-TOF). – X-ray diffraction: STOE IPDS. – Elemental analyses: Perkin-Elmer EA 2400 and Elementar Vario EL.

All reactions except hydrolysis reactions were performed in oven-dried glassware, in anhydrous solvents, and under an argon atmosphere. Propyne iminium triflates **1a,f**,[4] **1b**,[3] **1c,j,k**,[5] **1d,e**,[6] and **1g**[13] were prepared by published procedures.

[3-(Morpholin-4-yl)-1,3-diphenyl-propa-1,2-dienyl]triphenylphosphonium trifluoromethanesulfonate (2a). A solution of propyne iminium salt **1a** (0.47 g, 1.11 mmol) in dry CH_2Cl_2 (6 mL) was cooled at -78 ^{o}C and triphenylphosphane (0.29 g, 1.11 mmol) was added. The temperature was raised to 20 ^{o}C during 12 h. Small amounts of propene iminium bis(triflate) **5a** could be separated by addition of absolutely dry ether (5 mL) followed by scratching the flask wall with a metal spatula to induce crystallization and filtration under inert atmosphere. The desired product was precipitated from the solution by addition of more ether. The supernatant solution was removed with a pipette, and the solid residue was washed with abs. ether to leave highly moisture-sensitive pale-yellow allene **2a** (0.56 g, 73%), m.p. 81 °C (dec.). IR (KBr): 1895 (w), 1439 (m), 1270 (s), 1150 (s), 1030 (s) cm^{-1}. ^{1}H NMR: δ 2.48 (m, 2H, NCH), 2.70 (m, 2H, NCH), 3.62–3.65 (m, 4H, OCH_2), 7.03 (d, 2H), 7.18 (d, 2H), 7.27 (m, 3H), 7.36 (m, 3H), 7.54–7.69 (m, 12H), 7.83 (t, 3H, *p*-H of PPh_3). ^{13}C{^{1}H} NMR: δ 49.70 (NCH_2), 66.12 (OCH_2), 100.04 (d, $J_{P,C}$ = 83.5 Hz, C-1), 118.25 (d, $J_{P,C}$ = 86.9 Hz, PC_{Ph}), 127.25–135.42 (C_{Ph} and C-3), 221.00 (C-2). MS (FAB, 8 keV): *m*/*z* = 539 ([M]$^+$of cation).

[1-(4-Fluorophenyl)-3-(morpholin-4-yl)-3-phenylpropa-1,2-dienyl]triphenylphosphonium trifluoromethanesulfonate (2b). A solution of propyne iminium salt **1b** (0.44 g, 1.00 mmol) in

dry CH_2Cl_2 (10 mL) was cooled at -78 °C and triphenylphosphane (0.26 g, 1.00 mmol) was added. The temperature was raised to 20 °C during 12 h. After addition of absolutely dry ether (5 mL) followed by scratching the flask wall with a metal spatula to induce crystallization, a precipitate appeared. The supernatant solution was removed with a pipette, and the solid residue was washed with abs. ether to leave highly moisture-sensitive yellow allene **2b** contaminated with varying quantities of salt **5b** and [1-(4-fluorophenyl)-3-oxo-3-phenylprop-1-enyl]triphenylphosphonium triflate. IR (KBr): 1907 (vw), 1597 (m), 1506 (m), 1270 (s), 1223 (s), 1163 (s), 1151 (s), 1109 (s), 1031 (s) cm^{-1}. $^{13}C\{^1H\}$ NMR: δ 49.65 (NCH_2), 66.09 (OCH_2), 99.16 (d, $J_{P,C}$ = 83.9 Hz, C-1), 221.06 (d, $J_{P,C}$ = 5.3 Hz, C-2).

(3-Dimethylamino-3-phenyl-1-trimethylsilyl-propa-1,2-dienyl)triphenylphosphonium trifluoromethanesulfonate (2c). A solution of propyne iminium salt **1c** (0.38 g, 1.00 mmol) in dry CH_2Cl_2 (25 mL) was cooled at -78 °C and triphenylphosphane (0.26 g, 1.00 mmol) was added. The solution was brought to room temperature during 12 h, the solvent was removed at 0.01 mbar, and the remaining solid was washed with abs. ether to obtain a pale rose-colored moisture-sensitive powder (0.58 g, 90%), m.p. 111–112 °C. IR (KBr): 1886 (w), 1440 (m), 1274 (vs), 1146 (s), 1108 (m), 1032 (s) cm^{-1}. ^1H NMR: δ 0.09 (s, 9H, $SiMe_3$), 2.34 (s, 6H, NMe_2), 7.03–7.06 (m, 2H), 7.37 (d, 3H), 7.54–7.59 (m, 6H), 7.71–7.76 (m, 6H), 7.85–7.89 (t, 3H). $^{13}C\{^1H\}$ NMR: δ -0.05 (s, $SiMe_3$), 41.69 (NMe_2), 94.06 (d, $J_{P,C}$ = 40.4 Hz, C-1), 118.80 (d, $J_{P,C}$ = 86.7 Hz, PC_{Ph}), 120.77 (q, $^1J_{F,C}$ = 321.3 Hz, $CF_3SO_3^-$), 126.63 (d, $J_{P,C}$ = 3.0 Hz), 128.90 (s), 129.43 (s), 130.24 (d, $J_{P,C}$ = 12.8 Hz), 131.94 (d, $J_{P,C}$ = 5.1 Hz), 133.68 (d, $J_{P,C}$ = 8.9 Hz), 135.19 (d, $J_{P,C}$ = 3.0 Hz), 232.94 (d, $J_{P,C}$ = 7.9 Hz, C-2).

(1-Cyclopropyl-3-dimethylamino-3-phenyl-propa-1,2-dienyl)triphenylphosphonium trifluoromethanesulfonate (2d). A preparation as described for **2c**, from propyne iminium salt **1d** (0.37 g, 1.00 mmol) and PPh_3 (0.26 g, 1.00 mmol), furnished a pale rose-colored moisture-sensitive powder (0.56 g, 92%), m.p. 105–106 °C (dark-red melt). IR (KBr): ν = 1891 (w), 1438 (m), 1269 (vs), 1147 (s), 1109 (s), 1032 (s) cm^{-1}. ^1H NMR: δ 0.86 (m, 1H, H_{cp}), 0.94 (m, 1H, H_{cp}), 1.08 (m, 2H, H_{cp}), 1.46 (m, 1H, H_{cp}), 2.34 (s, 6H, NMe_2), 6.99 (m, 2H), 7.31–7.87 (several m, 18H). $^{13}C\{^1H\}$ NMR: δ 10.11 (d, $J_{P,C}$ = 2.9 Hz, C_{cp}), 10.42 (d, $J_{P,C}$ = 2.9 Hz, C_{cp}), 13.02 (d, $J_{P,C}$ = 22.7 Hz, C_{cp}), 40.89 (s, NMe_2), 100.36 (d, $J_{P,C}$ = 80.5 Hz, C-1), 117.62 (d, $J_{P,C}$ = 86.4 Hz, PC_{Ph}), 120.56 (q, $^1J_{C,F}$ = 321.3 Hz, $CF_3SO_3^-$), 126.77 (d, J = 2.9 Hz), 128.49 (s), 129.39 (s), 129.99 (d, J = 12.4 Hz), 131.94 (d, J = 5.1 Hz), 133.52 (d, J = 10.3 Hz), 134.92 (d, J = 2.9 Hz), 136.46 (d, J = 13.2 Hz), 214.50 (d, $J_{P,C}$ = 5.9 Hz, C-2). MS (ESI, 3.2 kV): m/z = 460 ($[M]^+$ of cation).

(1-*tert*-Butyl-3-dimethylamino-3-phenyl-propa-1,2-dienyl)triphenylphosphonium trifluoromethanesulfonate (2e). A solution of salt propyne iminium salt **1e** (0.18 g, 0.50 mmol) in dry CH_2Cl_2 (5 mL) was placed in a Schlenk tube and triphenylphosphane (0.13 g, 0.50 mmol) was added. After heating at 40 °C for 1 h, the solvent was evaporated at 0.001 mbar. NMR analysis of the residue indicated the presence of **2e**, **1e**, and PPh_3 (**2e**:**1e** = 7:3 according to ^1H NMR in $CDCl_3$, 300 K). ^1H NMR: δ 1.17 (s, 9H, CMe_3), 2.41 (s, 6H, NMe_2), 6.98 (d, 2H, H_{Ph}). Selected IR and ^{13}C data of **2e**: Table 1.

[(*Z*)-3-(Morpholin-4-yl)-1-(4-tolyl)buta-1,3-dienyl]triphenylphosphonium trifluoromethanesulfonate (3). The preparation was carried out as described for **2b**, from propyne iminium triflate **1f** (0.47 g, 1.25 mmol) and triphenylphosphane (0.33 g, 1.25 mmol). A reddish solid was obtained which was washed with abs. ether, redissolved in the minimum amount of CH_2Cl_2, and precipitated again with abs. ether: rose-colored powder (0.40 g, 50%), m.p. 112–113 °C (dec.). IR (KBr): 3065 (w), 2956 (w), 2860 (w), 2818 (w), 1600 (m), 1441 (m-s), 1276 und 1256 (ss), 1147 (s), 1108 (s), 1029 (s), 638 (s) cm^{-1}. ^1H NMR: δ 2.32 (s, 3H, CH_3), 2.69 (virtual t, 4H, CH_2NCH_2), 3.34 (virtual t, 4H, CH_2OCH_2), 4.41 (s, 1H, 4-H^1), 4.45 (s, 1H, 4-H^2), 6.80 (t, 2H, H_{Ph}), 6.83 (d, 1H, $^3J_{P,H}$ = 28.3 Hz, 2-H), 7.05 (d, 2H, H_{Ph}), 7.49–7.87 (several m, 15H). $^{13}C\{^1H\}$ NMR: δ 20.82 (CH_3), 48.41 (NCH_2), 65.06 (OCH_2), 100.19 (C-4), 116.04 (d, $J_{P,C}$ = 88.1 Hz, PC_{Ph}), 123.38 (d, $J_{P,C}$ = 76.7 Hz, C-3), 127.72–138.79 (C_{Ph}), 149.03 (d, $J_{P,C}$ = 19.7 Hz, C-2), 149.83 (d, $J_{P,C}$ = 12.9 Hz, C_{Ph}). ^{31}P NMR: 27.12. MS (FAB, 8 keV): *m*/*z* = 490 $[M]^+$ of cation). Anal. Calcd for $C_{34}H_{33}F_3NO_4PS$ (639.67): C, 63.84; H, 5.20; H, 2.19; found: C, 63.81, H, 5.18, N, 2.17.

(1-Cyclopropyl-3-dimethylamino-3-phenyl-propa-1,2-dienyl)tributylphosphonium trifluoromethanesulfonate (4). A solution of propyne iminium salt **1d** (0.17 g, 0.50 mmol) in dry CH_2Cl_2 (15 mL) was cooled at -78 °C and tri-n-butylphosphane (0.12 mL, 0.50 mmol) was added. The temperature was raised to 20 °C during 12 h, and the solvent was removed at 0.001 mbar. The residue was washed with several portions of abs. ether to leave **4** as a yellow oil (0.24 g, 87%). IR (film): 1902 (w), 1466 (m), 1378 (m), 1264 (vs), 1151 (s), 1031 (s) cm^{-1}. ^1H NMR: δ 0.55–0.58 (m, 2H, H_{cp}), 0.80 (t, 9H, $3CH_3$), 0.85–1.03 (m, 2H, H_{cp}), 1.20–1.58 (m, 13H, $3\times(CH_2)_2$, $1H_{cp}$), 2.12–2.28 (m, 6H, $3\times PCH_2$), 2.46 (s, 6H, NMe_2), 7.21 (m, 2H), 7.31 (m, 3H). $^{13}C\{^1H\}$ NMR: δ 8.03 (d, $J_{P,C}$ = 2.2 Hz), 8.31 (d, $J_{P,C}$ = 2.9 Hz), 10.39 (d, $J_{P,C}$ = 19.8 Hz), 12.96, 18.79 (d, $J_{P,C}$ = 47.6 Hz), 23.32 (d, $J_{P,C}$ = 2.2 Hz), 23.42 (d, $J_{P,C}$ = 8.1 Hz), 99.08 (d, $J_{P,C}$ = 76.8 Hz, C-1), 120.64 (q, $J_{C,F}$ = 321.0 Hz, $CF_3SO_3^-$), 127.00 (d, $J_{P,C}$ = 2.2 Hz), 128.68, 129.31, 130.9, 132.97 (d, $J_{P,C}$ = 5.1 Hz), 135.30 (d, $J_{P,C}$ = 12.4 Hz), 208.55 (d, $J_{P,C}$ = 4.4 Hz, C-2).

General procedure for dicationic salts 5

A solution of propyne iminium salt **1** (0.50 mmol) in CH_2Cl_2 (10 mL) was cooled at –78 °C and PPh_3 (0.13 g, 0.50 mmol) was added in one portion. After stirring for 2 h at –78 °C, trifluoromethanesulfonic acid (0.04 ml, 0.50 mmol) was added and the mixture was allowed to warm to room temperature overnight. The solvent was evaporated at 0.001 mbar, and the solid residue was dissolved in CH_2Cl_2 and precipitated again with ether.

[(*E*)-1,3-Diphenyl-3-triphenylphosphonio-prop-2-enylidene]morpholinium bis(trifluoromethanesulfonate) (5a). Yellow crystals (0.32 g, 72%), m.p. 203 °C. IR (KBr): ν = 1611 (m), 1439 (m), 1255 (vs), 1152 (s), 1106 (s), 1027 (s) cm^{-1}. H NMR: δ 3.87 (pseudo-t, 2H, NCH_2), 3.89 (pseudo-t, 2H, NCH_2), 4.19 (pseudo-t, 2H, OCH_2), 4.31 (pseudo-t, 2H, OCH_2), 6.67–7.87 (several m, 25H, H_{Ph}), 7.97 (d, $^3J_{P,H}$ = 20.6 Hz, 1H, 2-H). $^{13}C\{^1H\}$ NMR: δ 54.75 (NCH_2), 55.11 (NCH_2), 64.01 (OCH_2), 64.76 (OCH_2), 114.81 (d, $^1J_{P,C}$ = 88.4 Hz, PC_{Ph}), 127.76–136.04 (C_{Ph}),

142.09 (d, $J_{P,C}$ = 16.7 Hz, C-2), 144.54 (d, $J_{P,C}$ = 71.7 Hz, C-3), 175.82 (d, $J_{P,C}$ = 19.7 Hz, C-1). MS (FAB, 8 keV): *m*/*z* = 539 ([M]$^+$ of cation). Anal. Calcd for $C_{39}H_{34}F_6NO_7PS_2$ (837.79): C, 55.91; H, 4.09; N, 1.67; found: C, 55.83; H, 4.00; N, 1.64.

[(*E*)-3-(4-Fluorophenyl)-1-phenyl-3-triphenylphosphonio-prop-2-enylidene]morpholinium bis(trifluoromethanesulfonate) (5b). After crystallization from CH_2Cl_2/ether, the product was washed with several portions of dry ether: yellow powder (0.32 g, 75%), mp. 221–223 °C. IR (KBr): 1626 (w), 1597 (w), 1504 (m), 1440 (m), 1269 (vs, broad), 1222 (s), 1164 (s), 1150 (s), 1110 (s), 1031 (s) cm^{-1}. ^{1}H NMR: δ 3.88–3.91 (m, 4H, CH_2NCH_2), 4.18 (pseudo-t, 2H, OCH_2), 4.31 (pseudo-t, 2H, OCH_2), 6.65 (t, 2H), 6.68–6.69 (m, 1H), 7.18–7.90 (several m, 21H), 8.00 (d, 1H, $^3J_{P,H}$ = 19.2 Hz, 2-H). ^{13}C{^{1}H} NMR (CD_3CN): δ 56.87 (NCH_2), 57.55 (NCH_2), 66.67 (OCH_2), 67.15 (OCH_2), 115.60 (d, $J_{P,C}$ = 88.6 Hz, PC_{Ph}), 117.55 (d, *J* = 22.7 Hz, C-2,4$_{F\text{-}Ph}$), 127.42 (d, *J* = 3.4 Hz, C-1$_{F\text{-}Ph}$), 130.06), 130.27 (meta-C_{Ph}), 131.02, 131.74 (d, $J_{P,C}$ = 13.2 Hz), 132.71 (d, *J* = 4.6 Hz, C-3,5$_{F\text{-}Ph}$), 134.59, 136.34 (d, $J_{P,C}$ = 10.3 Hz), 137.37 (d, $J_{P,C}$ = 2.9 Hz), 144.01 (d, $J_{P,C}$ = 71.7 Hz, C-3), 144.87 (d, $J_{P,C}$ = 16.1 Hz, C-2), 164.97 (d, $J_{F,C}$ = 254.0 Hz, C-4$_{F\text{-}Ph}$), 176.98 (d, $J_{P,C}$ = 19.0 Hz, C-1). MS (MALDI): *m*/*z* = 556 ([M–H]$^+$ of cation).

[(*E*)-3-Cyclopropyl-1-phenyl-3-triphenylphosphonio-prop-2-enylidene]dimethylammonium bis(trifluoromethanesulfonate) (5d). A mixture of **5d** and allene **2d** was obtained (**5d**:**2d** = 88:12 in $CDCl_3$ at 300 K) which could not be separated. Addition of HOTf to this mixture led to an increase of **5d** but full conversion was not achieved. NMR data of **5d**: ^{1}H NMR: δ 0.08–0.19 (m, 2H, H_{cp}), 0.20–0.24 (m, 2H, H_{cp}), 1.77–1.84 (m, 1H, H_{cp}), 3.64 (s, 3H, NCH_3), 3.69 (s, 3H, NCH_3), 7.45 (d, 1H, $^3J_{P,H}$ = 22.2 Hz, 2-H), 7.56–7.96 (m, H_{Ph}). ^{13}C{^{1}H} NMR: δ 10.30 (d, $J_{P,C}$ = 4.4 Hz, C_{cp}), 12.47 (C_{cp}) 15.12 (d, $J_{P,C}$ = 8.1 Hz, C_{cp}), 47.01/47.42 (NMe_2), 116.16 (d, $J_{P,C}$ = 86.4 Hz, PC_{Ph}), 120.73 (q, $J_{C,F}$ = 320.5 Hz, *C*$F_3SO_3^-$), 128.69–135.97 (C_{Ph}), 142.49 (d, $J_{P,C}$ = 73.2 Hz, C-3), 144.29 (d, $J_{P,C}$ = 18.3 Hz, C-2), 175.74 (d, $J_{P,C}$ = 22.0 Hz, C-1).

[(*E*)-1,3-Diphenyl-3-triphenylphosphonio-prop-2-enylidene]dibenzylammonium bis(trifluoromethanesulfonate (5g). Yellow crystals (0.89 g, 94%), m.p. 63–71 °C. IR (KBr): 1605 (m, br), 1441 (m), 1279/1256 (vs, br), 1224 (s), 1157 (s), 1106 (m), 1030 (vs) cm^{-1}. ^{1}H NMR: δ 5.11 (s, 2, NCH_2), 5.52 (s, 2H, NCH_2), 6.67–6.69 (m, 2H, H_{Ph}), 7.02–7.10 (m, 6H, H_{Ph}), 7.18–7.30 (m, 10 H_{Ph}), 7.56–7.66 (m, 14 H_{Ph}), 7.75–7.81 (m, 3H_{Ph}), 7.86 (d, $^3J_{P,H}$ = 20.2 Hz, 1H, 2-H). ^{13}C{^{1}H} NMR: δ 60.86 (2×NCH_2), 114.22 (d, $^1J_{P,C}$ = 88.6 Hz, PC_{Ph}), 120.41 (q, $J_{C,F}$ = 319.8 Hz, *C*$F_3SO_3^-$), 127.38–135.95 (C_{Ph}), 142.38 (d, $J_{P,C}$ = 16.8 Hz, C-2), 146.28 (d, $J_{P,C}$ = 70.3 Hz, C-3), 179.67 (d, $J_{P,C}$ = 19.8 Hz, C-1). MS (MALDI): *m*/*z* = 649.3 ([M]$^+$ of cation).

Hydrolysis of allene 2a. [(*E*)-3-Oxo-1,3-diphenyl-prop-1-enyl]triphenylphosphonium trifluoromethanesulfonate ((*E*)-6a). A solution of allene **2a** (0.21 g, 0.30 mmol) in acetonitrile (4 mL) containing a few drops of water was stirred for 24 h. The product was precipitated with ether (3×5 mL) and dried at 0.001 mbar. Yellow crystals (0.15 g, 81%), mp. 204–206 °C. IR (KBr): 1677 (m), 1483 (m), 1264 (vs), 1225 (s), 1145 (s), 1107 (m), 1030 (s) cm^{-1}. ^{1}H NMR: δ 6.81 (d, 2H, H_{Ph}), 7.00 (t, 2H, H_{Ph}), 7.12 (t, 1H, H_{Ph}), 7.36–7.45 (m, 3H_{Ph}, 2-H), 7.54–7.59 (several m, 17H). ^{13}C{^{1}H} NMR): δ 114.71 (d, $J_{P,C}$ = 88.4 Hz, PC_{Ph}), 128.76–135.96 (C_{Ph} and C-1), 149.95 (d, $^2J_{P,C}$ = 8.7 Hz, C-2), 191.27 (d, $^3J_{P,C}$ = 17.8 Hz, C-3). ^{31}P NMR: δ 26.27. MS

(FAB, 8 keV): m/z = 469 ($[M]^+$ of cation). Anal. Calcd for $C_{34}H_{26}F_3O_4PS$ (618.60): C, 66.01; H, 4.24; found: C, 65.94; H, 4.20.

Hydrolysis of aminodiene 3. [(*E*)-3-Oxo-1-(4-tolyl)-but-1-enyl]triphenylphosphonium trifluoromethanesulfonate ((*E*)-6b). A solution of **3** (1.60 g, 2.50 mmol) in acetonitrile (10 mL) containing a few drops of water was stirred for 24 h. The solvent was replaced by CH_2Cl_2 and ether was added to obtain a precipitate which was isolated and dried at 0.001 mbar/20 °C. Yellow-brownish solid (0.99 g, 70%), m.p. 180–181 °C. IR (KBr): 1707 (m), 1438 (m), 1266 (vs), 1151 (m), 1105 (m), 1032 (s) cm^{-1}. ^1H NMR: δ 2.06 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 6.83/7.08 (AA'BB', 4H, tolyl), 6.99 (d, 1H, $^3J_{P,H}$ = 22.2 Hz, 2-H), 7.52–7.57 (m, 6H, H_{PPh3}), 7.69–7.74 (m, 6H, H_{PPh3}), 7.87 (t, 3H, H_{PPh3}). $^{13}C\{^1H\}$ NMR: δ 21.27 (d, $J_{P,C}$ = 1.1 Hz, tolyl-CH_3), 30.60 (d, $J_{P,C}$ = 2.3 Hz, C-4), 115.68 (d, $J_{P,C}$ = 88.1 Hz, PC_{Ph}), 127.25–135.83 (6 d), 131.08 (d, J = 70.6 Hz, C-1), 140.80 (d, $J_{P,C}$ = 2.7 Hz), 150.46 (d, $J_{P,C}$ = 8.7 Hz, C-2), 198.96 (d, $J_{P,C}$ = 18.2 Hz, C-3). ^{31}P NMR: δ 26.57. MS (FAB, 8 keV): m/z = 421 ($[M]^+$ of cation). Anal. Calcd for $C_{30}H_{26}F_3O_4PS$ (570.56): C, 63.15; H, 4.59; found: C, 62.80; H, 4.53.

General procedure for reaction of alkynones 7 with PPh_3 and HOTf

A solution of alkynone **7** (1.00 mmol) in CH_2Cl_2 (3 mL) was cooled at -78 °C, and PPh_3 (0.26 g, 1.00 mmol) and trifluoromethanesulfonic acid (0.09 mL, 1.00 mmol) were added successively. The mixture was brought to room temperature while stirring overnight and then ether was added to obtain a precipitate of the propenylphosphonium salt which was pure by NMR spectroscopy.

[(*E*/*Z*)-3-Oxo-1,3-diphenyl-prop-1-enyl]triphenylphosphonium trifluoromethanesulfonate ((*E*/*Z*)-6a). Light-yellow solid (0.50 g, 81%), mixture of diastereomers, *E*:*Z* = 7:93 (^1H NMR), m.p. 164–165 °C. NMR data attributable to (*Z*)-**6a** (see above for data of (*E*)-**6a**): ^1H NMR: δ 7.14–7.26 (m, 5H), 7.44 (t, 2H), 7.49–7.67 (m, 16H), 7.74 (dd, 2H), 8.29 (d, $^3J_{P,H}$ = 37.3 Hz, 2-H). $^{13}C\{^1H\}$ NMR): δ = 117.99 (d, $J_{P,C}$ = 90.3 Hz, PC_{Ph}), 128.78–137.42 (C_{Ph}) 137.02 (d, $J_{C,P}$ = 71.0 Hz, C-1), 147.33 (d, $J_{P,C}$ = 6.1 Hz, C-2), 188.46 (d, $J_{P,C}$ = 4.2 Hz, C-3). ^{31}P NMR: δ 25.94. MS (FAB, 8 keV): m/z = 469 ($[M]^+$ of cation).

[3-(3,4-Dichlorophenyl)-3-oxo-1-phenyl-prop-1-enyl]triphenylphosphonium trifluoromethanesulfonate (6c). Following the general procedure, (*Z*)-**6c** was isolated as a yellow solid (0.52 g, 77%), m.p. 180–182 °C. IR (KBr): 1674 (m), 1583 (m), 1442 (m), 1389 (m), 1274/1255 (vs), 1154 (s), 1107 (m), 1029 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.18–7.23 (m, 5H), 7.51–7.59 (m, 7H), 7.61–7.68 (m, 10H), 7.94 (dd, 1H), 8.26 (d, $^3J_{P,H}$ = 37.4 Hz, 2-H). $^{13}C\{^1H\}$ NMR: δ 118.10 (d, $J_{P,C}$ = 90.7 Hz, PC_{Ph}), 129.11–134.67 (C_{aryl}), 139.59 (d, $J_{P,C}$ = 70.2 Hz, C-1), 146.52 (d, $J_{P,C}$ = 5.7 Hz, C-2), C-3 not found. ^{31}P NMR: δ 25.89. MS (FAB, 8 keV): m/z = 537 ($[M\text{-}H]^+$ of cation). In $CDCl_3$ solution, (*Z*)-**6c** is slowly transformed into a diastereomeric mixture, *E*:*Z* = 45:55. NMR data of (*E*)-**6c**: ^1H NMR: δ 7.45 (d, $J_{P,H}$ = 22.9 Hz, 2-H). ^{31}P NMR: δ 26.33. Anal. Calcd for $C_{34}H_{24}Cl_2F_3O_4PS_2$ (687.49): C, 59.40; H, 3.52; found: C, 59.42; H, 3.65.

[(*E*,*Z*)-3-Oxo-3-phenyl-1-(thiophen-2-yl)prop-1-enyl]triphenylphosphonium trifluoromethanesulfonate ((*E*,*Z*)-6d). Light-brown solid (0.54 g, 86%), m.p. 215–216 °C;

mixture of diasteromers, *E*:*Z* = 3:97 (^{1}H NMR). IR (KBr): 1629 (s), 1441 (m), 1416 (s), 1263 (vs), 1154 (m), 1107 (m), 1030 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$), *Z*-isomer: δ 7.07–7.18 (m, 6H), 7.44–7.49 (m, 6H), 7.53–7.62 (m, 9H), 7.65 (dd, 1H), 8.03 (dd, 1H), 8.18 (d, $^3J_{P,H}$ = 36.3 Hz, 2-H); *E*-isomer: δ 7.38 (d, $^3J_{P,H}$) = 22.0 Hz). $^{13}C\{^1H\}$ NMR, *Z*-isomer: δ 115.55 (d, $^1J_{P,C}$ = 90.7 Hz, PC_{Ph}), 128.74–137.60 ($C_{Ph,}$ C_{thie}), 137.01 (d, $J_{P,C}$ = 70.6 Hz, C-1), 146.50 (d, $J_{P,C}$ = 5.7 Hz, C-2), 180.19 (d, $J_{P,C}$ = 5.3 Hz, C-3). ^{31}P NMR: δ 26.32 (*Z*), 26.70 (*E*). MS (FAB, 8 keV): *m*/*z* = 475 ($[M]^+$ of cation). Anal. Calcd for $C_{32}H_{24}F_3O_4PS_2$ (624.63): C, 61.53; H, 3.87; found: C, 61.41; H, 3.69.

[(*E*/*Z*)-3-(2-Bromophenyl)-1-(4-chlorophenyl)-3-oxo-prop-1-enyl]triphenylphosphonium trifluoromethanesulfonate (6e). Off-white solid (0.30 g, 41%), mixture of diastereomers, *E*:*Z* = 90:10 (^{1}H NMR), m.p. 209–215 °C (dec.). IR (KBr): 1673 (s), 1587 (m), 1440 (m), 1269/1262 (vs), 1141 (s), 1105 (s), 1030 (s) cm^{-1}. ^{1}H NMR, *E*-isomer: δ 7.05–7.08 (m, 1H), 7.22–7.28 (m, 2H), 7.36–7.38 (m, 1H), 7.47–7.50 (m, 2H), 7.54–7.67 (m, 6H), 7.73–7.78 (m, 6H), 7.85–7.92 (m, 5H), 7.97 (d, $^3J_{P,H}$ = 21.1 Hz, 2-H); *Z*-isomer: δ 8.39 (d, $^3J_{P,H}$ = 37.6 Hz, 2-H). $^{13}C\{^1H\}$ NMR, *E*-isomer: δ 115.34 (d, $J_{P,C}$ = 88.4 Hz, PC_{Ph}), 128.05–136.22 (C_{aryl}), 131.64 (d, $J_{P,H}$ = 71.2 Hz, C-1), 148.80 (d, $J_{P,C}$ = 8.4 Hz, C-2), 187.74 (d, $J_{C,P}$ = 14.1 Hz, C-3). ^{31}P NMR: δ 25.68 (*Z*), 26.42 (*E*). MS (FAB, 8 keV): *m*/*z* = 583 $[M]^+$ of cation). Anal. Calcd for $C_{34}H_{24}BrClF_3O_4PS_2$ (731.94): C, 55.79; H, 3.30; found: C, 55.26; H, 3.30.

[(*E*)-3-Oxo-1,3-diphenyl-prop-1-enyl]tributylphosphonium trifluoromethanesulfonate (8). A brown oil separated after addition of ether from which yellow crystals were obtained after several weeks. The supernatant solution was removed with a pipette, and the crystals were washed with ether and dried. **Alternative synthesis.** A solution of propyne iminium salt **1a** (1.06 g, 2.50 mmol) in dry CH_2Cl_2 (20 mL) was cooled and tributylphosphane (0.62 mL, 2.50 mmol) was added. The solution was allowed to warm to room temperature overnight and concentrated to a volume of 10 mL. Ether and a few drops of water were added and the mixture was set aside until yellow crystals had formed which were isolated as described above (0.57 g, 41%). M.p. 121–123 °C. ^{1}H NMR: δ 0.96 (t, 9H, 3×CH_3), 1.54 (broadened "s", 12H, 3×$(CH_2)_2$), 2.40–2.52 (m, 6H, 3×PCH_2), 7.10 (m, 2H), 7.35–7.37 (m, 3H), 7.46 (t, 2H), 7.57 (t, 1H), 7.84 (d, $^3J_{P,H}$ = 19.7 Hz, 1H, 2-H), 7.92 (d, *J* = 7.4 Hz, 2H, H_{Ph}). $^{13}C\{^1H\}$ NMR: δ 13.32 (CH_3), 18.88 (d, $J_{P,C}$ = 46.8 Hz, PCH_2), 23.72 (d, $J_{P,C}$ = 4.4 Hz, CH_2), 23.72 (d, $J_{P,C}$ = 6.6 Hz, CH_2), 128.42–131.20 (C_{Ph}), 131.73 (d, $J_{P,C}$ = 65.1 Hz, C-1), 134.57, 135.32 (d, $J_{P,C}$ = 2.2 Hz, C_{Ph}), 146.91 (d, $J_{P,C}$ = 7.3 Hz, C-2), 190.54 (d, $J_{P,C}$ = 16.1 Hz, C-3). ^{31}P NMR: δ 32.10. MS (GC-EI): *m*/*z* = 409 ($[M]^+$ of cation). The salt could not be obtained in analytically pure form (^{1}H NMR: small impurity signals at δ 0.80–1.65).

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a) From a propyne iminium triflate 1 (method A). A solution of **1** (2.5 mmol) in dry CH_2Cl_2 (15 mL) was cooled at –78 °C and triphenylphosphane (0.66 g, 2.5 mmol) was added. After complete dissolution of the phosphane, the solution was brought to room temp. overnight. Eventually, the mixture was then heated at the temperature given in Table 4. It was then shaken

vigorously with 1% aq. H_2O_2 (20 mL) followed by aq. Na_2CO_3, and dried (Na_2SO_4). The solvent was removed and the residue was subjected to column chromatography (silica gel 0.063–0.2 mm, elution with mixtures of cyclohexane/ethyl acetate).

b) From an enaminoketone 9 (method B). A solution of triflic anhydride (0.42 ml, 2.5 mmol) in dry CH_2Cl_2 (15 mL) was placed in a 50 mL Schlenk flask and cooled at –78 °C. An enaminoketone **9** (2.5 mmol) was added and after its complete dissolution, the cooling bath was removed and the mixture was allowed to warm up to room temp. within 15 min. It was then cooled again to –78 °C and ethyldiisopropylamine (0.42 ml, 2.5 mmol) was added. The reaction mixture was brought back to room temp. within 15 min to allow the formation of propyne iminium salt **1**, then cooled back to –78 °C. Triphenylphosphane (0.66 g, 2.5 mmol) was added and the mixture was brought to room temp. overnight. The further procedure was the same as in method A (see above).

3,4-Dihydro-6,8-diphenyl-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (10a). Prepared from enaminoketone **9a** (0.73 g, 2.5 mmol), method B, recrystallization from ether. Yield: 0.09 g (13%). M.p. 153–155 °C (lit.[3]: 154–155 °C). NMR data agree with the reported ones.[3]

1-Benzyl-2,3,5-triphenylpyrrole (10g). Prepared from salt **1g** (1.07 g, 2.00 mmol), method A, recrystallization from ether; yield: 0.32 g, 42%. M.p. 167–168 °C (lit.[17]: 165–167 °C). ^{1}H NMR agrees with lit.[17] ^{13}C NMR: δ 48.41 (N*C*H$_2$), 109.47 (C-4), 123.23–139.08 (C_{Ph}, $C_{pyrrole}$). Anal. Calcd for $C_{29}H_{23}N$ (385.50): C, 90.35; H, 6.01; N, 3.63; found: C, 90.28, H, 6.11, N, 3.68.

5,6-Dihydro-1,3-diphenylpyrrolo[2,1-*a*]isoquinoline (10h). From enaminoketone **9h** (0.85 g, 2.5 mmol), method B; recrystallization from ether. Yield: 0.12 g (15%). M.p. 170 °C. ^{1}H NMR: δ 3.03 (t, 2H, aryl–CH$_2$), 4.12 (t, 2H, NCH$_2$), 6.37 (s, 1H, 2-H), 6.99–7.09 (m, 2H) 7.19–7.54 (m, 12H). ^{13}C NMR: δ 30.38 (C-6), 42.43 (C-5), 111.07 (C-2), 122.82 (C-1), 124.49 (C-10), 125.59 (C-8), 125.80, 126.20, 126.54 (C-9), 127.01, 127.65 (C-7), 128.43, 128.45, 128.73, 128.99, 130.02 (C-10a), 132.42, 132.49 (C-6a), 133.52, 137.38 (C-3). Anal. Calcd for $C_{24}H_{19}N$ (321.41): C, 89.68; H, 5.96; N, 4.36; found: C, 89.62; H, 5.96; N, 4.20.

1,3-Diphenyl-5*H*-pyrrolo[2,1-*a*]isoindole (10i). A solution of iminium salt **1i** (0.57 g, 1.25 mmol), triphenylphosphane (0.33 g, 1.25 mmol), and ethyldiisopropylamine (0.21 ml, 1.25 mmol) in dry CH_2Cl_2 (6 mL) was placed in a thick-walled Schlenk tube and heated at 100 °C for 3 h. Workup was done as described for method A. Recrystallization from ether, fine needles (0.16 g, 41%). M.p. 162–163 °C (lit.[3]: 162 °C). NMR data agree with the reported ones.[3] Anal. Calcd for $C_{23}H_{17}N$ (307.39): C, 89.87; H, 5.57, N, 4.56; found: C, 89.88; H, 5.50; N, 4.45.

1-Ethyl-2-methyl-5-phenylpyrrole (10j). A solution of iminium salt **1j** (0.85 g, 2.5 mmol) and triphenylphosphane (0.66 g, 2.5 mmol) in dry CH_3CN (10 mL) was placed in a thick-walled Schlenk tube and heated at 60 °C for 4 h. After cooling, the solvent was removed at 0.001 mbar, and the residual oil was subjected to Kugelrohr distillation at 110 °C (oven temp.)/0.001 mbar (lit.[18]: b.p. 125–130 °C/3 Torr) to leave a colorless oil which was sensitive to air-oxidation (indicated by a color change from colorless to rose) and was therefore stored under argon at –18 °C. Yield: 0.17 g (37%). ^{1}H NMR data agree with lit.[18] ^{13}C NMR: δ 12.55 (CH_3), 16.39 (CH_2CH_3), 38.79 (CH_2CH_3), 106.74 (C-4), 107.77 (C-3), 126.60–134.35 (C_{Ph}, C-2, C-5).

1-Methyl-2,5-diphenylpyrrole (10k). Iminium salt **1k** (0.23 g, 0.50 mmol), triphenylphosphane (0.13 g, 0.50 mmol) and CH_2Cl_2 (10 mL) were placed in a thick-walled Schlenk tube and were heated at 60 °C for 4 h. After cooling, the resulting dark-brown solution was washed with 1% aq. H_2O_2 (10 mL) and satd. aq. sodium bicarbonate. After drying (Na_2SO_4), the solvent was evaporated and the residue was recrystallized from ether to furnish white crystals (0.09 g, 77%), m.p. 199–200 °C (lit.[19a]: 200–202°C; lit.[19b]: 197–199 °C). ^{1}H NMR and ^{13}C NMR data agree with lit.[19b] Anal. Calcd for $C_{17}H_{15}N$ (233.31): C, 87.52; H, 6.48; N, 6.00; found: C, 87.86; H, 6.84; N, 6.17.

X-Ray crystal structure determination for 5a. Crystals were obtained from acetonitrile solution. *Crystal data*: $C_{39}H_{34}F_6NO_7PS_2$, M = 837.76, monoclinic, space group $P2_1/n$; a = 9.840(2), b = 20.463(4), c = 19.230(3) Å, α =90, β = 99.37(2), γ = 90°; V = 3820.4(11) Å^3, Z = 4, D_c = 1.457 g cm^{-3}. *Data collection*: crystal size 0.31×0.23×0.15 mm, 29866 reflection data in the range θ = 1.99–25.97°, 7230 independent reflections (R_{int} = 0.0639). *Structure refinement*: 7230 data, 534 parameters; the final R indices were R_1 = 0.0254, wR_2 = 0.0545; residual electron density between 0.32 and –0.30 e A^{-3}. The structures were solved with direct methods and refined by a full-matrix least-squares method (SHELX-97[20]). Hydrogen atoms were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure; atom H2 was refined isotropically. Molecule plot: ORTEP-3.[21] CCDC-626101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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References and Footnotes

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