

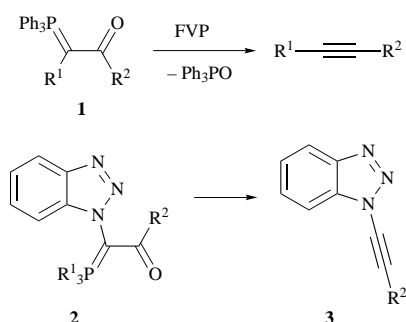
Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 11.¹ Unexpected generation and rearrangement of acetyl benzotriazolyl carbene

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Seventeen novel α -benzotriazolyl- β -oxo phosphorus ylides **2** have been prepared and characterised. Flash vacuum pyrolysis (FVP) of these generally leads to loss of both R^1_3PO and N_2 to give intractable products but, in one case, **2l**, extrusion of Bu_3P is observed to give 3-acetyl-1,2,4-benzotriazine **6** and 2'-cyanoacetophenone **7**, products apparently derived from rearrangement of the initially formed carbene **11**, and involving in the latter case a novel 1,3-acetyl migration process.

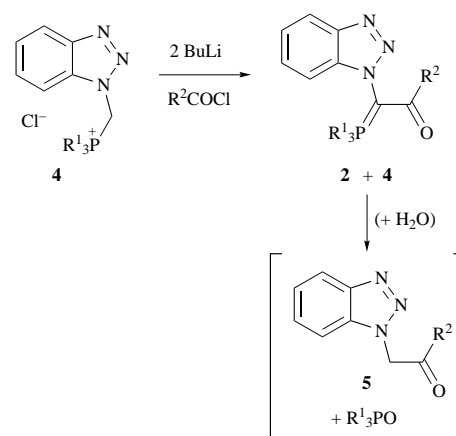
In previous parts of this series we have described the thermal extrusion of Ph_3PO from a variety of types of β -oxo phosphorus ylides **1** using flash vacuum pyrolysis (FVP) as a useful route to alkynes. The benzotriazolyl group has recently emerged as a versatile auxiliary group for a wide variety of synthetic transformations,² but one group of compounds which has not been studied in this context is the *N*-alkynylbenzotriazoles **3**.



We were interested to examine FVP of appropriately substituted β -oxo phosphorus ylides **2** as a route to these products, although, as far as we are aware, no example of the pyrolysis of **1** where R^1 is a nitrogen-based group has been reported. We were also aware of the thermal lability of the benzotriazole moiety³ which raises interesting possibilities for the pyrolysis process. We report here the preparation of a range of benzotriazolyl ylides **2** and their pyrolytic behaviour which, in one case, results in the quite unexpected extrusion of trialkylphosphine rather than the oxide. The products can be accounted for by rearrangement of the resulting novel carbene.⁴

Results and discussion

A total of 17 ylides **2** were readily prepared by treating the phosphonium salts **4** ($R^1 = Ph^5$ or Bu) with butyllithium followed by the appropriate acid chloride (0.5 equiv.). The reaction proceeds with transylidation to give the product and regenerate one equivalent of **4**.⁶ The stabilised benzotriazolyl ylides **2** were unreactive solids which showed ^{31}P NMR signals in the expected ranges (see Table 1). Their structure was further confirmed by the highly informative ^{13}C NMR spectra (Table 2), showing phosphorus coupling throughout the P-phenyl or butyl groups and through the ylide and carbonyl carbons to the first carbon atom of R^2 . The value of the one-bond coupling constant between phosphorus and the ylide carbon in these



compounds is anomalously high compared to the normal values of 100–120 Hz for β -oxo ylides. While satisfactory microanalytical data were obtained for some examples, this was not possible in other cases due to the ready hydrolysis of the compounds. For the ylide **2o** the resulting benzotriazolyl ketone **5** was isolated in pure form after storage under normal laboratory conditions for a period of weeks. We conclude that these ylides are less stabilised than is generally the case for **1** and are particularly susceptible to hydrolysis since the carbanion resulting from nucleophilic attack of water at phosphorus can be stabilised by the adjacent benzotriazolyl group. Despite this problem, the compounds obtained showed no significant impurity in their ^{31}P or ^{13}C NMR spectra and consisted overwhelmingly of the desired ylides.

When the ylides **2** were subjected to FVP in a conventional flow system (contact time ≈ 10 ms) at 450 °C for $R^1 = Bu$ or 600 °C for $R^1 = Ph$, the phosphine oxides R^1_3PO were generally formed, together with intractable products which are probably due to subsequent loss of N_2 and polymerisation of the resulting reactive intermediates. However in one case only, compound **2l**, there was exclusive loss of Bu_3P to give two nitrogen-

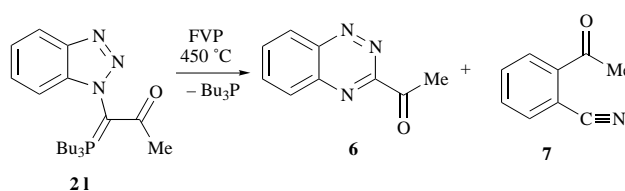


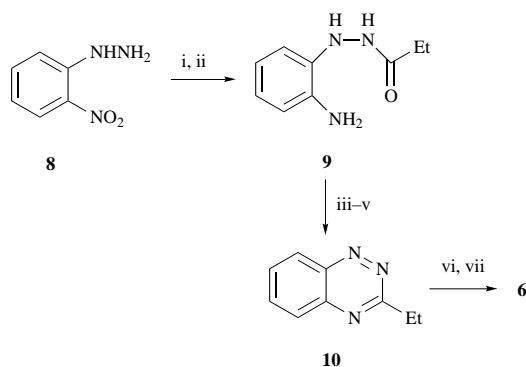
Table 1 Preparation of the benzotriazolyl ylides **2**

	R ¹	R ²	Yield (%)	δ _p		R ¹	R ²	Yield (%)	δ _p
a	Ph	Ph	20	17.4	j	Bu	Ph	57	23.3
b	Ph	Bu'	27	16.4	k	Bu	Bu'	56	22.1
c	Ph	Me	83	16.5	l	Bu	Me	69	22.1
d	Ph	4-MeOC ₆ H ₄	28	17.3	m	Bu	4-MeOC ₆ H ₄	89	23.0
e	Ph	4-ClC ₆ H ₄	96	17.8	n	Bu	4-ClC ₆ H ₄	66	23.7
f	Ph	4-MeC ₆ H ₄	78	17.4	o	Bu	4-MeC ₆ H ₄	77	23.2
g	Ph	4-O ₂ NC ₆ H ₄	78	18.0	p	Bu	4-O ₂ NC ₆ H ₄	95	24.4
h	Ph	2-MeOC ₆ H ₄	50	16.3	q	Bu	Et	12	22.4
i	Ph	2-MeSC ₆ H ₄	25	17.0					

Table 2 ¹³C NMR spectra [δ_C (J_{p-c})] of the benzotriazolyl ylides **2**

R ²	CO	P=C	P-phenyl or P-butyl				Benzotriazole signals	R ² signals	
			C-1	C-2	C-3	C-4			
2a	Ph	185.3 (17)	72.4 (126)	124.3 (92)	133.4 (10)	128.8 (12)	132.4 (2)	145.2 (quat.), 137.2 (quat.), 127.4, 123.2, 119.5, 110.2	139.3 (10), 129.4, 127.6 (2 C), 127.0 (2 C)
2b	Bu'	196.4 (15)	70.4 (138)	125.4 (92)	133.2 (10)	128.4 (12)	131.9 (2)	145.1 (quat.), 137.9 (quat.), 127.1, 123.1, 119.6, 111.0	40.7 (8), 27.8 (3 C)
2c	Me	189.9 (17)	71.0 (135)	124.2 (92)	133.4 (10)	128.8 (12)	132.5 (2)	145.3 (quat.), 136.9 (quat.), 127.4, 123.3, 119.7, 110.1	24.2 (8)
2d	4-MeOC ₆ H ₄	184.1 (17)	71.5 (137)	124.7 (92)	133.4 (10)	128.7 (12)	132.3 (2)	145.3 (quat.), 137.3 (quat.), 127.4, 123.2, 119.6, 110.4	160.6, 131.7 (10), 128.9 (2 C), 113.0 (2 C), 55.0
2e	4-ClC ₆ H ₄	184.0 (18)	72.6 (135)	124.1 (92)	133.4 (10)	128.8 (12)	132.5 (2)	145.3 (quat.), 137.2 (quat.), 127.6, 123.3, 119.7, 110.1	137.9 (10), 135.2, 128.5 (2 C), 127.9 (2 C)
2f	4-MeC ₆ H ₄	185.1 (18)	71.9 (137)	124.6 (92)	133.4 (10)	128.7 (12)	132.3 (2)	145.3 (quat.), 137.4 (quat.), 127.3, 123.2, 119.5, 110.4	139.4, 136.4 (10), 128.3 (2 C), 127.0 (2 C), 21.2
2g	4-O ₂ NC ₆ H ₄	183.4 (19)	74.0 (140)	123.5 (92)	133.4 (10)	129.0 (13)	132.9 (2)	145.3 (quat.), 137.1 (quat.), 127.8, 123.5, 119.9, 109.8	147.9, 145.9 (10), 127.9 (2 C), 123.0 (2 C)
2j	Ph	185.4 (16)	70.4 (127)	20.0 (54)	24.2 (4)	23.9 (15)	13.5	145.5 (quat.), 136.8 (quat.), 127.4, 123.5, 119.8, 110.3	139.8 (9), 128.9, 127.6 (2 C), 126.6 (2 C)
2k	Bu'	196.8 (15)	67.6 (129)	20.1 (55)	24.3 (4)	23.8 (15)	13.4	145.4 (quat.), 138.0 (quat.), 127.6, 123.6, 120.1, 110.9	40.7 (7), 28.0 (3 C)
2l	Me	189.2 (17)	69.4 (126)	19.8 (54)	24.0 (<2)	23.9 (16)	13.5	145.5 (quat.), 136.8 (quat.), 127.8, 123.8, 120.1, 110.2	23.4 (8)
2m	4-MeOC ₆ H ₄	184.3 (17)	69.4 (128)	20.1 (54)	24.2 (4)	23.9 (15)	13.5	145.5 (quat.), 136.9 (quat.), 127.5, 123.6, 119.8, 110.4	160.1, 132.3 (9), 128.3 (2 C), 112.9 (2 C), 55.0
2n	4-ClC ₆ H ₄	183.8 (17)	70.3 (126)	19.9 (54)	24.1 (4)	23.9 (15)	13.5	145.5 (quat.), 136.8 (quat.), 127.7, 123.7, 119.9, 110.1	138.3 (9), 134.7, 128.1 (2 C), 127.8
2p	4-O ₂ NC ₆ H ₄	182.9 (18)	71.7 (123)	19.8 (53)	24.1 (4)	23.9 (16)	13.4	145.5 (quat.), 136.6 (quat.), 128.0, 123.9, 120.1, 109.7	147.6, 146.4 (10), 127.5 (2 C), 122.9 (2 C)
2q	Et	193.1 (16)	69.6 (125)	19.9 (54)	24.0 (4)	23.8 (16)	13.4	145.5 (quat.), 136.9 (quat.), 127.8, 123.8, 120.2, 110.2	28.4 (7), 10.1

containing products. The major product, isolated in 26% yield after preparative TLC, appeared to be either 3-acetyl-1,2,4-benzotriazine **6** or the previously unknown isomeric 4-acetyl-1,2,3-benzotriazine **12**. Since we had difficulty in reproducing the reported⁷ synthesis of **6**, a new route was devised (Scheme 1). This involved the preparation of the previously unknown

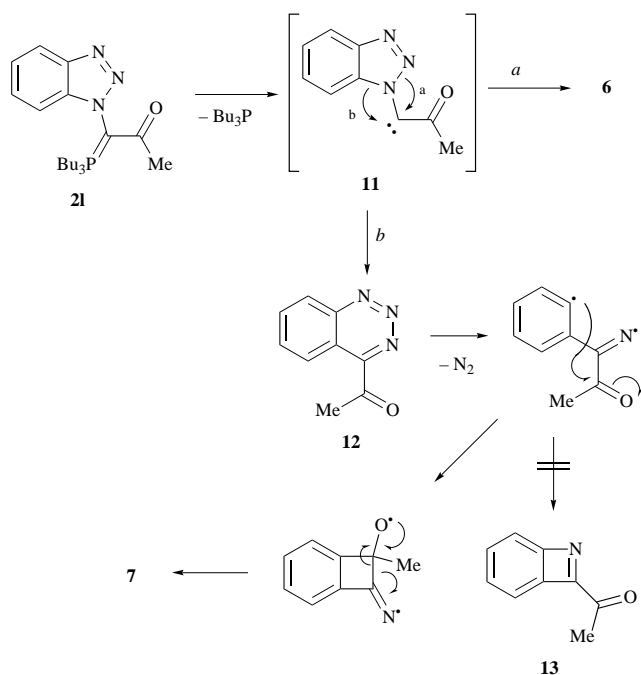


Scheme 1 Reagents: i, EtCO₂H, heat; ii, H₂, Pd/C; iii, 4 M HCl, heat; iv, aq. KOH; v, K₃Fe(CN)₆; vi, 1,3-dibromo-5,5-dimethylhydantoin, AIBN, CCl₄; vii, Me₂SO, NaHCO₃

3-ethyl-1,2,4-benzotriazine **10** from 2'-nitrophenylhydrazine **8** following the procedure reported for the 3-methyl compound.⁸

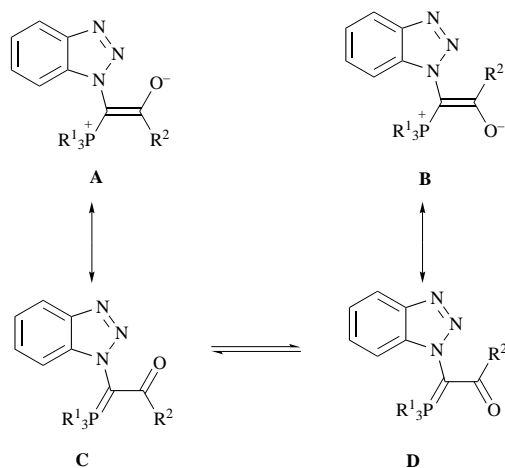
Thus, **8** was converted to its hydrazide with propionic acid and reduction of the nitro group by catalytic hydrogenation gave **9**. Cyclisation of this and oxidation⁸ gave **10**, which was then subjected to radical bromination with 1,3-dibromo-5,5-dimethylhydantoin and Kornblum oxidation to afford **6**, identical in all respects with the pyrolysis product.

The formation of **6** is readily explained by a 1,2-N migration in the carbene intermediate **11** resulting from extrusion of Bu₃P (Scheme 2). This intermediate might also undergo 1,2-migration of Ar to give **12**. The minor pyrolysis product isolated in 16% yield appeared to result from loss of N₂ from **12** *i.e.* to have the benzazete structure **13**, and pyrolysis of 1,2,3-benzotriazines is known to give benzazetes.⁹ However all the previous examples were highly reactive and, although the acetyl group might be expected to stabilise the structure to some extent, the compound seemed too unreactive towards cycloaddition and pyrolysis (unchanged on FVP at 850 °C) for this to be a realistic possibility. The observation of a weak IR absorption at 2220 cm⁻¹ led to the identification of the minor product as 2'-cyanoacetophenone **7**, confirmed by comparison with the authentic material.¹⁰ It seems most likely that this product is formed, as shown in Scheme 2, by loss of N₂ from the 1,2,3-benzotriazine **12** to give the aryl-iminyl diradical. Rather than cyclise to give the antiaromatic benzazete **13**, this appears to prefer to cyclise on to the carbonyl group to form a cyclobutane ring which then undergoes β-scission leading to **7**. Although



pyrolysis of aromatic-fused 1,2,3-triazines sometimes gives the benzazetes,⁹ other reactions of the initial aryl-iminyl diradicals have been observed before,¹¹ including one case of an apparent 1,3-H migration to give a nitrile.¹² Ring opening of the cyclobutaniminyl radical to generate a nitrile is also well preceded.¹³ An alternative possibility is that the rearrangement of carbene **11** takes place regioselectively to give **6** and that this then loses N_2 to some extent to give the diradical isomeric with that derived from **12** (Scheme 2). This could then rearrange by way of 2-isocyanoacetophenone to give **7**. This was discounted however, by FVP of **6** which, even at the higher temperature of 550 °C, led to recovery of unchanged starting material with no trace of **7**.

The anomalous behaviour of **21** demands some explanation since, as far as we are aware, this is the first instance of thermal extrusion of phosphine rather than phosphine oxide from a β -oxo phosphorus ylide. Thermal extrusion of phosphine from less well stabilised ylide types is known¹⁴ and the extrusion from β -oxo ylides can be achieved photochemically.¹⁵ It is, however, the discrepancy between the behaviour of **21** and all the other examples **2** studied which is most striking. It appeared that this might be due to the relative importance of the *E*- and *Z*-phosphonium enolate forms **A** and **B** in the gas phase. As shown in Scheme 3, the structure of β -oxo phosphorus ylides can be



represented by the four contributing forms **A–D** with the relative importance of each depending on the substituents present. The relatively bulky benzotriazolyl group means that, particularly for $R^1 = \text{Bu}$, the *Z*-form **B** is sterically crowded. It is only for $R^2 = \text{Me}$, however, that the alternative *E*-configuration **A** offers any advantage and **21** may exist in this form making the loss of Bu_3PO impossible. For larger R^2 groups the *Z*-form **B** may be preferred and this is likely to undergo exclusive loss of Bu_3PO .

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. Infrared spectra were recorded as Nujol mulls for solids and as thin films for liquids on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ^1H at 300 MHz and for ^{13}C at 75 MHz using a Bruker AM300 instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl_3 with internal Me_4Si as reference for ^1H and ^{13}C and external 85% H_3PO_4 as reference for ^{31}P . Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz. Mass spectra were obtained on an A. E. I./Kratos MS-50 spectrometer using electron impact at 70 eV unless otherwise indicated. Chemical ionisation (CI) spectra were obtained on a VG Autospec spectrometer using isobutane. Dry THF was freshly distilled from potassium benzophenone ketyl. Ether refers to diethyl ether.

(1-Benzotriazolylmethyl)triphenylphosphonium chloride **4a** was prepared by the literature method.⁵

(Benzotriazol-1-ylmethyl)tri-*n*-butylphosphonium chloride **4b**

A solution of 1-chloromethylbenzotriazole⁵ (20 g, 120 mmol) and tri-*n*-butylphosphine (30 g, 149 mmol) in toluene (150 cm^3) was heated under reflux for 18 h. The precipitate which formed on cooling was filtered off and dried to give **4b** (39.9 g, 90%) as colourless crystals, mp 138–140 °C (Found: C, 61.9; H, 9.2; N, 11.3. $\text{C}_{19}\text{H}_{33}\text{ClN}_3\text{P}$ requires C, 61.7; H, 9.0; N, 11.4%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1610, 1300, 1230, 1170, 1103, 1070, 978, 915, 850, 790, 775 and 732; δ_{H} 8.90 (1 H, m), 8.18 (1 H, m), 7.85–7.45 (2 H, m), 7.01 (2 H, d, *J* 7), 2.95–2.5 (6 H, m), 1.70–1.30 (12 H, m) and 0.86 (9 H, t, *J* 6); δ_{C} 145.3, 134.3, 129.4, 125.1, 119.5, 111.8, 40.0 (d, *J* 43), 23.9 (3 C, d, *J* 16), 23.6 (3 C, d, *J* 5), 18.4 (3 C, d, *J* 44) and 13.3 (3 C); δ_{P} +35.1.

Preparation of the benzotriazolyl ylides **2**

A suspension of the appropriate (benzotriazolylmethyl)phosphonium salt **4** (11.6 mmol) in dry THF (75 cm^3) was stirred at room temperature under N_2 while butyllithium in hexane (4.65 cm^3 of a 2.5 M solution, 11.6 mmol) was added by syringe. After 15 min a solution of the appropriate acid chloride (5.8 mmol) in dry THF (10 cm^3) was added dropwise. After stirring for 1 h, the mixture was added to water (250 cm^3). Extraction with ether–ethyl acetate (1 : 1) (3 \times 100 cm^3), drying and evaporation gave the crude product which was recrystallised from ethyl acetate–petroleum (bp 60–80 °C) (1 : 1).

(α -Benzotriazol-1-yl- α -benzoylmethylene)triphenylphosphorane **2a**. From **4a** and benzoyl chloride as yellow crystals (20%), mp 272–274 °C (Found: C, 77.5; H, 4.3; N, 8.4. $\text{C}_{32}\text{H}_{24}\text{N}_3\text{OP}$ requires C, 77.2; H, 4.9; N, 8.4%) (HRMS: Found $M^+ - N_2$, 469.1603. $\text{C}_{32}\text{H}_{24}\text{NOP}$ requires *M*, 469.1596); $\nu_{\text{max}}/\text{cm}^{-1}$ 1510, 1275, 1180, 1104, 1052, 1025, 995, 960, 745, 722 and 693; δ_{H} 7.9–7.0 (24 H, m); δ_{C} see Table 2; δ_{P} +17.4; *m/z* 469 ($M^+ - N_2$, 3%), 392 (2), 364 (8), 337 (3), 262 (100), 183 (50), 152 (10), 108 (28), 105 (45) and 77 (45).

(α -Benzotriazol-1-yl- α -trimethylacetylmethylene)triphenylphosphorane **2b**. From **4a** and trimethylacetyl chloride as yellow crystals (27%), mp 221–223 °C (Found: C, 74.9; H, 5.7; N, 8.8. $\text{C}_{30}\text{H}_{28}\text{N}_3\text{OP}$ requires C, 75.5; H, 5.9; N, 8.8%) (HRMS: Found $M^+ - N_2$, 449.1901. $\text{C}_{30}\text{H}_{28}\text{NOP}$ requires *M*, 449.1909); $\nu_{\text{max}}/\text{cm}^{-1}$

cm⁻¹ 1522, 1338, 1280, 1180, 1118, 1066, 1008, 756, 724 and 700; δ_{H} 7.8–7.15 (19 H, m) and 0.93 (9 H, s); δ_{C} see Table 2; δ_{P} +16.4; *m/z* 449 (M⁺ – N₂, 5%), 420 (3), 392 (32), 364 (24), 262 (50), 183 (48), 108 (22) and 57 (100).

(α -Benzotriazol-1-yl- α -acetylmethylene)triphenylphosphorane 2c. From **4a** and acetyl chloride as yellow crystals (83%), mp 216–218 °C (Found: C, 74.8; H, 5.0; N, 9.6. C₂₇H₂₂N₃O₂P requires C, 74.5; H, 5.1; N, 9.6%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1542, 1362, 1330, 1278, 1183, 1108, 1056, 1002, 752, 720 and 700; δ_{H} 7.95–7.15 (19 H, m) and 1.75 (3 H, s); δ_{C} see Table 2; δ_{P} +16.5; *m/z* 434 (M⁺ – 1, 1%), 407 (M⁺ – N₂, 6), 392 (6), 364 (21), 337 (3), 262 (88), 222 (15), 185 (40), 183 (100), 152 (15) and 108 (32).

(α -Benzotriazol-1-yl- α -(4-methoxybenzoyl)methylene)triphenylphosphorane 2d. From **4a** and 4-methoxybenzoyl chloride as yellow crystals (28%), mp 217–220 °C (Found: C, 75.5; H, 4.9; N, 8.05. C₃₃H₂₆N₃O₂P requires C, 75.1; H, 5.0; N, 8.0%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1605, 1350, 1300, 1255, 1180, 1110, 1052, 1027, 850, 758, 727 and 700; δ_{H} 7.90–7.10 (21 H, m), 6.53 (2 H, half AB pattern, *J* 9) and 3.63 (3 H, s); δ_{C} see Table 2; δ_{P} +17.3; *m/z* 499 (M⁺ – N₂, 2%), 364 (4), 314 (2), 277 (8), 262 (100), 183 (45), 135 (48) and 108 (26).

(α -Benzotriazol-1-yl- α -(4-chlorobenzoyl)methylene)triphenylphosphorane 2e. From **4a** and 4-chlorobenzoyl chloride as yellow crystals (96%), mp 250–253 °C (Found: C, 71.7; H, 4.2; N, 7.8. C₃₂H₂₃ClN₃O₂P requires C, 72.2; H, 4.4; N, 7.9%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1580, 1534, 1446, 1347, 1280, 1140, 1110, 1060, 1024, 1002, 967, 862, 757, 723 and 700; δ_{H} 7.85–7.15 (21 H, m) and 6.97 (2 H, half AB pattern, *J* 10); δ_{C} see Table 2; δ_{P} +17.8; *m/z* 503 (³⁵Cl-M⁺ – N₂, 0.5%), 392 (0.3), 364 (8), 318 (4), 277 (5), 262 (100), 183 (72), 139 (43) and 108 (35).

(α -Benzotriazol-1-yl- α -(4-methylbenzoyl)methylene)triphenylphosphorane 2f. From **4a** and 4-methylbenzoyl chloride as yellow crystals (78%), mp 273–276 °C (Found: C, 77.7; H, 5.1; N, 8.2. C₃₃H₂₆N₃O₂P requires C, 77.5; H, 5.1; N, 8.2%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1523, 1447, 1347, 1280, 1182, 1108, 1060, 837, 755, 726 and 700; δ_{H} 7.85–7.1 (21 H, m), 6.85 (2 H, half AB pattern, *J* 9) and 2.11 (3 H, s); δ_{C} see Table 2; δ_{P} +17.4; *m/z* 483 (M⁺ – N₂, 3%), 454 (1), 364 (10), 337 (2), 298 (5), 262 (100), 183 (38), 119 (40), 108 (20) and 91 (24).

(α -Benzotriazol-1-yl- α -(4-nitrobenzoyl)methylene)triphenylphosphorane 2g. From **4a** and 4-nitrobenzoyl chloride as yellow crystals (78%), mp 258–262 °C (Found: C, 70.4; H, 4.0; N, 10.1. C₃₂H₂₃N₄O₃P requires C, 70.8; H, 4.3; N, 10.3%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1548, 1520, 1448, 1346, 1280, 1140, 1110, 1060, 882, 868, 758, 733 and 702; δ_{H} 7.95–7.2 (23 H, m); δ_{C} see Table 2; δ_{P} +18.0; *m/z* 514 (M⁺ – N₂, 0.5%), 364 (8), 329 (4), 277 (20), 262 (100), 183 (62) and 108 (68).

(α -Benzotriazol-1-yl- α -(2-methoxybenzoyl)methylene)triphenylphosphorane 2h. From **4a** and 2-methoxybenzoyl chloride as yellow crystals (50%), mp 182–184 °C (Found: C, 74.5; H, 4.8; N, 7.9. C₃₃H₂₆N₃O₂P requires C, 75.1; H, 5.0; N, 8.0%) (HRMS: Found M⁺ – N₂, 499.1697. C₃₃H₂₆N₃O₂P requires *M*, 499.1701); $\nu_{\text{max}}/\text{cm}^{-1}$ 1528, 1442, 1360, 1282, 1247, 1140, 1108, 1054, 750, 720 and 700; δ_{H} 7.95–7.10 (19 H, m), 7.0–6.45 (4 H, m) and 3.66 (3 H, s); δ_{P} +16.3; *m/z* 499 (M⁺ – N₂, 1%), 468 (3), 364 (7), 262 (100), 183 (33), 135 (38) and 108 (18).

(α -Benzotriazol-1-yl- α -(2-methylsulfanylbenzoyl)methylene)triphenylphosphorane 2i. From **4a** and 2-methylsulfanylbenzoyl chloride as yellow crystals (25%), mp 214–216 °C (Found: C, 72.4; H, 4.4; N, 7.7. C₃₃H₂₆N₃OPS requires C, 72.9; H, 4.8; N, 7.7%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1534, 1342, 1280, 1110, 1058, 967, 752, 728 and 698; δ_{H} 7.95–7.10 (19 H, m), 7.0–6.55 (4 H, m) and 2.44 (3 H, s); δ_{P} +17.0; *m/z* 468 (M⁺ – N₂ – SMe, 2%), 364 (4), 330 (1), 277 (8), 262 (100), 238 (4), 183 (54), 151 (32) and 108 (38).

(α -Benzotriazol-1-yl- α -benzoylmethylene)tri-*n*-butylphosphorane 2j. From **4b** and benzoyl chloride as a colourless oil (57%) (correct elemental analysis could not be obtained owing to ready hydrolysis to give **5**); $\nu_{\text{max}}/\text{cm}^{-1}$ 1602, 1588, 1500, 1460, 1360, 1276, 1232, 1160, 1096, 1002, 970, 912, 810, 758, 724 and 698; δ_{H} 8.1–7.85 (1 H, m), 7.55–6.9 (8 H, m), 2.3–1.9 (6 H, m),

1.8–1.2 (12 H, m) and 0.87 (9 H, t, *J* 6); δ_{C} see Table 2; δ_{P} +23.3; *m/z* (M⁺ 437 not apparent), 218 (Bu₃PO, 6%), 189 (38), 161 (18), 147 (22), 134 (20), 120 (32), 105 (24), 92 (100) and 78 (68).

(α -Benzotriazol-1-yl- α -trimethylacetylmethylene)tri-*n*-butylphosphorane 2k. From **4b** and trimethylacetyl chloride as colourless crystals (56%), mp 71–73 °C (HRMS: Found M⁺ – N₂, 389.2857. C₂₄H₄₀NOP requires *M*, 389.2848); $\nu_{\text{max}}/\text{cm}^{-1}$ 1608, 1415, 1342, 1280, 1215, 1170, 1097, 1050, 1003, 962, 920, 808, 788, 756 and 725; δ_{H} 8.06 (1 H, d, *J* 8), 7.52 (2 H, m), 7.35 (1 H, m), 1.9–1.75 (6 H, m), 1.55–1.4 (6 H, m), 1.4–1.25 (6 H, m), 0.85 (9 H, t, *J* 7) and 0.83 (9 H, s); δ_{C} see Table 2; δ_{P} +22.1; *m/z* 416 (M⁺ – H, 1%), 389 (M⁺ – N₂, 10), 374 (5), 360 (8), 332 (100), 304 (12), 248 (20), 201 (40), 189 (32) and 92 (75).

(α -Benzotriazol-1-yl- α -acetylmethylene)tri-*n*-butylphosphorane 2l. From **4b** and acetyl chloride as colourless crystals (69%), mp 77–79 °C (HRMS: Found M + H⁺, 376.2522. C₂₁H₃₄N₃O₂P requires *M*, 376.2518); $\nu_{\text{max}}/\text{cm}^{-1}$ 1538, 1278, 1236, 1160, 1100, 1060, 1028, 1010, 910, 818, 756 and 735; δ_{H} 8.1–8.0 (1 H, m), 7.6–7.35 (3 H, m), 2.0–1.85 (6 H, m), 1.58 (3 H, s), 1.6–1.3 (12 H, m) and 0.87 (9 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +22.1; *m/z* (CI) 376 (M + H⁺, 100%), 347 (25), 203 (25) and 146 (6).

(α -Benzotriazol-1-yl- α -(4-methoxybenzoyl)methylene)tri-*n*-butylphosphorane 2m. From **4b** and 4-methoxybenzoyl chloride as colourless crystals (89%), mp 132–134 °C $\nu_{\text{max}}/\text{cm}^{-1}$ 1602, 1588, 1430, 1360, 1248, 1180, 1060, 1034, 970, 917, 848, 782, 765, 732 and 700; δ_{H} 8.05–7.85 (1 H, m), 7.4–7.15 (3 H, m), 7.10 and 6.48 (4 H, AB pattern, *J* 9), 3.56 (3 H, s), 2.25–1.8 (6 H, m), 1.6–1.3 (12 H, m) and 0.87 (9 H, t, *J* 7); δ_{C} see Table 2; δ_{P} +23.0; *m/z* (M⁺ 467 not apparent), 218 (Bu₃PO, 6%), 189 (35), 162 (19), 147 (20), 134 (21), 120 (34), 92 (100) and 78 (64).

(α -Benzotriazol-1-yl- α -(4-chlorobenzoyl)methylene)tri-*n*-butylphosphorane 2n. From **4b** and 4-chlorobenzoyl chloride as colourless crystals (66%), mp 152–154 °C (Found: C, 66.4; H, 7.6; N, 9.0. C₂₆H₃₅ClN₃O₂P requires C, 66.2; H, 7.5; N, 8.9%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1580, 1278, 1095, 1058, 1018, 970, 918, 843, 818, 778, 754 and 688; δ_{H} 8.1–7.9 (1 H, m), 7.5–7.2 (3 H, m), 7.16 and 6.95 (4 H, AB pattern, *J* 9), 2.25–1.8 (6 H, m), 1.7–1.2 (12 H, m) and 0.87 (9 H, t, *J* 6); δ_{C} see Table 2; δ_{P} +23.7; *m/z* 472 (³⁵Cl-M⁺ + 1, 0.5%), 443 (M⁺ – N₂, 8), 414 (15), 304 (5), 248 (8), 202 (72), 173 (48), 146 (82), 118 (54), 104 (54) and 76 (100).

(α -Benzotriazol-1-yl- α -(4-methylbenzoyl)methylene)tri-*n*-butylphosphorane 2o. From **4b** and 4-methylbenzoyl chloride as colourless crystals (77%) (correct elemental analysis could not be obtained owing to ready hydrolysis to give **5**); $\nu_{\text{max}}/\text{cm}^{-1}$ 1612, 1580, 1278, 1238, 1168, 1098, 1060, 976, 913, 820, 754, 732 and 700; δ_{H} 8.1–7.9 (1 H, m), 7.5–7.2 (3 H, m), 7.05 and 6.76 (4 H, AB pattern, *J* 9), 2.25–1.8 (6 H, m), 2.09 (3 H, s), 1.7–1.2 (12 H, m) and 0.88 (9 H, t, *J* 6); δ_{P} +23.2; *m/z* (M⁺ 451 not apparent), 218 (Bu₃PO, 3%), 189 (33), 161 (18), 147 (24), 134 (18), 120 (38), 92 (100) and 78 (64).

Recrystallisation of a sample of this ylide after prolonged storage gave the hydrolysis product 2-(benzotriazol-1-yl)-4'-methylacetophenone **5** (R² = 4-MeC₆H₄) as colourless crystals, mp 134–136 °C (Found: C, 72.0; H, 5.4; N, 16.5. C₁₅H₁₃N₃O requires C, 71.7; H, 5.2; N, 16.7%); δ_{H} 8.15–7.9 (3 H, m), 7.5–7.3 (5 H, m), 6.10 (2 H, s) and 2.48 (3 H, s); δ_{C} 190.0 (CO), 146.0, 145.6, 133.8, 131.6 (all quat.), 129.8 (2 C), 128.3 (2 C), 127.7, 123.9, 120.0, 109.6 (all CH), 53.7 (CH₂) and 21.8 (CH₃).

(α -Benzotriazol-1-yl- α -(4-nitrobenzoyl)methylene)tri-*n*-butylphosphorane 2p. From **4b** and 4-nitrobenzoyl chloride as orange crystals (95%), mp 140–142 °C (Found: C, 65.2; H, 7.3; N, 11.6. C₂₆H₃₅N₄O₃P requires C, 64.7; H, 7.3; N, 11.6%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1606, 1520, 1356, 1280, 1060, 1006, 969, 909, 870, 820, 770 and 732; δ_{H} 8.1–7.9 (1 H, m), 7.85 and 7.32 (4 H, AB pattern, *J* 9), 7.5–7.2 (3 H, m), 2.25–1.8 (6 H, m), 1.7–1.2 (12 H, m) and 0.88 (9 H, t, *J* 6); δ_{C} see Table 2; δ_{P} +24.4; *m/z* 482 (M⁺, 2%), 434 (4), 396 (3), 304 (4), 248 (6), 202 (38), 173 (37), 146 (46), 118 (36), 104 (55), 76 (100) and 61 (58).

(α -Benzotriazol-1-yl- α -propionylmethylene)tri-*n*-butylphosphorane 2q. From **4b** and propionyl chloride as colourless crystals (12%), mp 83–85 °C (HRMS: Found $M + H^+$, 390.2677. $C_{22}H_{36}N_3OP$ requires M , 390.2674); $\nu_{\max}/\text{cm}^{-1}$ 1530, 1277, 1180, 1098, 1054, 1008, 975, 920, 810, 756 and 732; δ_{H} 8.2–8.1 (1 H, m), 7.65–7.45 (3 H, m), 2.46 (2 H, q of d, J 7, 1), 2.1–1.8 (6 H, m), 1.6–1.35 (12 H, m), 1.19 (3 H, t, J 7) and 0.88 (9 H, t, J 6); δ_{C} see Table 2; δ_{P} +22.4; m/z (EI) 361 ($M^+ - N_2$, 5%), 360 (5), 332 (12), 304 (4), 248 (4), 228 (15), 218 (5), 202 (5), 189 (35), 162 (21), 148 (24) and 92 (100); m/z (CI) 390 ($M + H^+$, 100%), 361 (17), 219 (68), 203 (27), 190 (20) and 120 (23).

Flash vacuum pyrolysis (FVP) of the ylide 2l

The apparatus used was as described previously.¹⁶ The pyrolysis was conducted at a pressure in the range 10^{-3} – 10^{-2} Torr and was complete within 1 h. Under these conditions the contact time in the hot zone was estimated to be ≈ 10 ms.

Pyrolysis of the ylide **2l** (1.27 g) at 450 °C gave a yellow solid. The only phosphorus compound present was shown by ³¹P NMR to be Bu_3P (δ_{P} –31). Chromatography on silica using ether followed by preparative TLC on silica using first ether and then CH_2Cl_2 led to isolation of two compounds: 2'-cyanoacetophenone **7** (16%); $\nu_{\max}/\text{cm}^{-1}$ 2224, 1693, 1592, 1571, 1486, 1359, 1296, 1070 and 960; δ_{H} 8.0–7.9 (1 H, m), 7.85–7.8 (1 H, m), 7.75–7.6 (2 H, m) and 2.71 (3 H, s); δ_{C} 196.1 (quat.), 139.8 (quat.), 135.3 (CH), 132.6 (CH), 132.5 (CH), 129.9 (CH), 118.1 (quat.), 111.0 (quat.) and 27.9 (CH_3); m/z 145 (M^+ , 28%), 130 (100), 102 (50), 76 (20) and 75 (27); and 3-acetyl-1,2,4-benzotriazine **6** (26%) (HRMS: Found M^+ , 173.0582. $\text{C}_9\text{H}_7\text{N}_3\text{O}$ requires M , 173.0589); $\nu_{\max}/\text{cm}^{-1}$ 1716, 1605, 1565, 1473, 1398, 1360, 1138 and 1052; δ_{H} 8.7–8.6 (1 H, m), 8.35–8.25 (1 H, m), 8.2–8.0 (2 H, m) and 3.07 (3 H, s); δ_{C} 196.5 (quat.), 154.9 (quat.), 147.6 (quat.), 140.4 (quat.), 136.3 (CH), 132.9 (CH), 129.9 (CH), 129.4 (CH) and 27.3 (CH_3); m/z 173 (M^+ , 12%), 145 (35), 130 (10), 103 (100), 84 (20) and 77 (50).

Authentic preparation of 3-acetyl-1,2,4-benzotriazine 6

The preparation of 3-ethyl-1,2,4-benzotriazine **10** was based on the literature method⁸ for the 3-methyl analogue.

(a) Preparation of *N*-(2-nitrophenyl)-*N'*-propionylhydrazine. A solution of 2'-nitrophenylhydrazine **8** (5.0 g, 32.7 mmol) in propionic acid (25 cm^3 , excess) was heated under reflux for 5 h and evaporated. Ether (10 cm^3) was added to the residue and the solid filtered off to give the crude *tiile* hydrazide (5.16 g, 76%) as brown crystals, mp 120–122 °C; δ_{H} 8.9 (2 H, br s), 8.2–8.0 (1 H, m), 7.6–7.3 (1 H, m), 7.0–6.7 (2 H, m), 2.30 (2 H, q, J 7) and 1.16 (3 H, t, J 7).

(b) Preparation of *N*-(2-aminophenyl)-*N'*-propionylhydrazine 9 and cyclisation to 3-ethyl-1,2,4-benzotriazine 10. A solution of the above nitro compound (3.0 g, 14.4 mmol) in ethanol (300 cm^3) was hydrogenated at atmospheric pressure in the presence of 5% Pd/C catalyst. Absorption of hydrogen was complete after 20 min and the solution was filtered through Celite and evaporated. The crude amino compound was dissolved directly in 4 M HCl (20 cm^3) and heated at 95 °C in a water bath for 5 min. A solution of KOH (18.0 g, 320 mmol) in water (80 cm^3) was then added and the mixture stirred for 5 min, after which a solution of potassium ferricyanide (16.0 g, 59 mmol) in water (80 cm^3) was added and the mixture stirred vigorously for a further 30 min. The resulting dark mixture was extracted with toluene (3 \times 50 cm^3) which was dried and evaporated to give a dark oil. Kugelrohr distillation afforded 3-ethyl-1,2,4-benzotriazine **10** (1.0 g, 44%) as a bright yellow oil, bp (oven temp.) 165–170 °C/20 mmHg (HRMS: Found M^+ , 159.0801. $\text{C}_9\text{H}_9\text{N}_3$ requires M , 159.0796); δ_{H} 8.75–8.6 (1 H, m), 8.2–7.85 (3 H, m), 3.52 (2 H, q, J 7) and 1.60 (3 H, t, J 7); δ_{C} 167.3, 146.2, 140.9 (all quat.), 135.3, 129.8, 129.5, 128.5 (all CH), 31.1 (CH_2) and 12.9 (CH_3); m/z 159 (M^+ , 2%), 131 ($M^+ - N_2$, 85), 130 (100), 103 (46), 76 (63) and 50 (68).

Conversion of 3-ethyl-1,2,4-benzotriazine 10 into 3-acetyl-1,2,4-benzotriazine 6. A solution of **10** (0.59 g, 3.7 mmol), 1,3-dibromo-5,5-dimethylhydantoin (0.55 g, 1.9 mmol) and AIBN (50 mg) in tetrachloromethane (25 cm^3) was heated under reflux for 12 h. The dimethylhydantoin was filtered off and the filtrate evaporated to give the crude 3-(1-bromoethyl)-1,2,4-benzotriazine as a severely irritant brown oil, δ_{H} 8.6–8.5 (1 H, m), 8.15–7.85 (3 H, m), 5.82 (1 H, q, J 7) and 2.34 (3 H, d, J 7); δ_{C} 164.9, 146.5, 140.6 (all quat.), 135.9, 131.2, 129.5, 128.9 (all CH), 46.6 (CH) and 23.4 (CH_3).

Without further purification, this product was added to Me_2SO (25 cm^3) containing sodium hydrogen carbonate (0.34 g, 4.0 mmol) and the mixture heated at 100 °C in a fume cupboard for 3 h. The mixture was then added to water (100 cm^3) and extracted with ether (3 \times 50 cm^3). The ethereal extracts were washed well with water (10 \times 25 cm^3), dried and evaporated. The residue was purified by preparative TLC on silica using ether (R_{F} 0.3) to give 3-acetyl-1,2,4-benzotriazine **6** (0.48 g, 75%) as colourless crystals, mp 120–123 °C (lit.,⁷ 121.5–122.5 °C) (HRMS: Found M^+ , 173.0593. $\text{C}_9\text{H}_7\text{N}_3\text{O}$ requires M , 173.0589); $\nu_{\max}/\text{cm}^{-1}$ 1705, 1600, 1170, 1135, 1122, 1058, 953, 792, 770 and 722; δ_{H} 8.7–8.6 (1 H, m), 8.35–8.25 (1 H, m), 8.2–8.0 (2 H, m) and 3.10 (3 H, s); δ_{C} 196.7 (CO), 155.1, 147.8, 140.7 (all quat.), 136.5, 133.0, 130.1, 129.6 (all CH) and 27.6 (CH_3); m/z 173 (M^+ , 4%), 145 (30), 130 (3), 103 (82), 76 (48), 50 (24) and 43 (100).

FVP of 3-acetyl-1,2,4-benzotriazine 6

Pyrolysis of **6** (30 mg) at 550 °C gave a yellow solid at the furnace exit which proved to be unchanged **6**; δ_{H} as above, with no trace of **7** present.

Authentic preparation of 2'-cyanoacetophenone 7

This was prepared according to the literature method,¹⁰ involving reaction of 2'-bromoacetophenone with cuprous cyanide in dry pyridine. Sublimation of the product at 140–150 °C/0.1 mmHg gave colourless crystals (30%), mp 45–46 °C (lit.,¹⁰ 48 °C); δ_{H} 8.1–8.0 (1 H, m), 7.9–7.65 (3 H, m) and 2.71 (3 H, s); δ_{C} 196.2 (CO), 139.5 (C-1), 135.3 (C-4), 132.8 (C-5), 132.6 (C-3), 130.1 (C-6), 118.2 (CN), 110.7 (C-2) and 27.7 (Me).

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