Unexpected Generation and Rearrangement of Acetyl Benzotriazolyl Carbene

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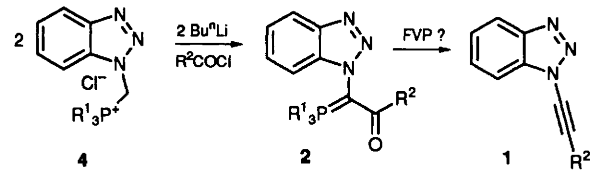
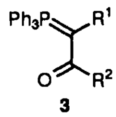
Flash vacuum pyrolysis of one example from a wide range of α-benzotriazolyl-β-oxo phosphorus ylides results in extrusion of Bu^n_3P to give 3-acetyl-1,2,4-benzotriazine and *o*-cyanoacetophenone, products apparently derived from rearrangement of the initially formed title carbene, and involving in the latter case a novel 1,3-acetyl migration process.

The benzotriazolyl group has emerged recently as a versatile auxiliary group for a wide variety of synthetic transformations,[1] but one group of compounds which has not been studied in this context is the *N*-alkynylbenzotriazoles **1**.We were interested to examine flash vacuum pyrolysis (FVP) of appropriately substituted β-oxo phosphorus ylides **2** as a route to these products, since pyrolytic extrusion of Ph_3PO from **3** has already allowed efficient access to substituted alkynes, $R^1C{\equiv}CR^2$ for R^1 = H or alkyl,[2] aryl[3,4] CN,[3,5] CO_2R,[3,6] COSMe,[7] Cl or Br,[8] SR,[9] SeAr,[10] OAr[11] and $PO(OPh)_2$.[12] It





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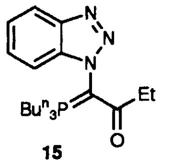

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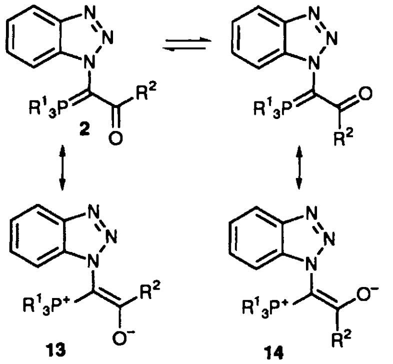
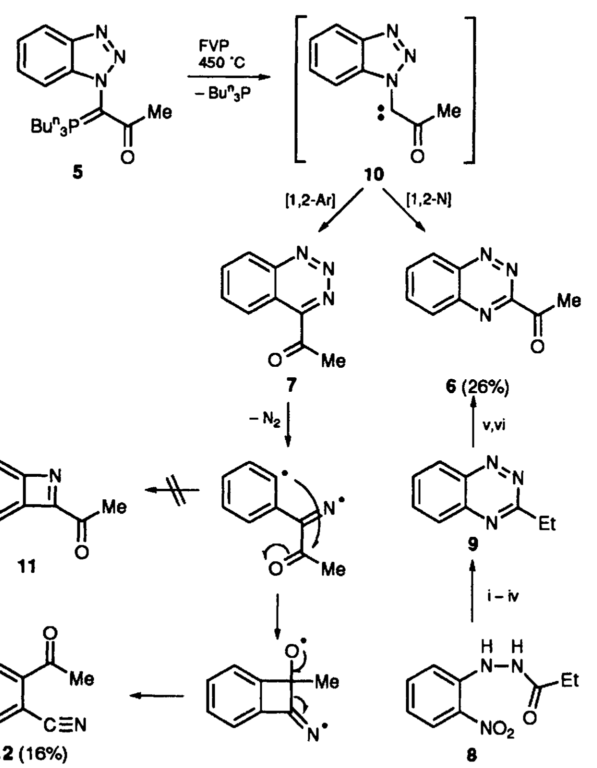


is noticeable that no nitrogen based group appears in this list and we were also aware of the thermal lability of the benzotriazole moiety[13] which raises interesting possibilities for the pyrolysis process. We report here that in one case the pyrolysis results in the quite unexpected extrusion of trialkylphosphine rather than the oxide. The products can be accounted for by rearrangement of the resulting novel carbene.

A total of over 20 ylides **2** were readily prepared in good yield by treating the known[14] phosphonium salts **4** (R = Bu^n, Ph) with butyllithium followed by the appropriate acid chloride (0.5 equiv.).[15] As expected the stabilised benzotriazolyl ylides **2**† are high-melting unreactive solids (δ_P + 22–24 for R = Bu^n and +16–18 for R = Ph).

When these were subjected to FVP in a conventional flow system (contact time ≈ 10 ms) at 450 °C for R^1 = Bu^n or 600 °C for R^1 = Ph, there was generally loss of both R^1_3PO and N_2 to give intractable products. However, in one case only, compound **5**, there was exclusive loss of Bu^n_3P to give two nitrogen-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 **7**. Since we had difficulty in reproducing the reported[16] synthesis of **6** a new route was devised as follows: *o*-nitrophenylhydrazine was converted to its hydrazide **8** with propionic acid; reduction of the nitro group, cyclisation and oxidation[17] gave 3-ethyl-1,2,4-benzotriazine **9**, and this was subjected to radical bromination with 1,3-bromo-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 **10** resulting from extrusion of Bu^n_3P. This intermediate might also undergo 1,2-migration of Ar to give **7**. The minor pyrolysis product isolated in 16% yield appeared to result from loss of N_2 from **7** *i.e.* to have the benzazete structure **11**, and pyrolysis of 1,2,3-benzotriazines is known to give benzazetes.[18] 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 *o*-cyanoacetophenone **12**, confirmed by comparison with the authentic material.[19] It seems most likely that this product is formed, as shown, by loss of N_2 from 1,2,3-benzotriazine **7** to give the aryl-iminyl diradical. Rather than cyclise to give the antiaromatic benzazete **11**, this appears to prefer to cyclise on to the carbonyl group to form a cyclobutane ring which then undergoes β-scission leading to **12**. Although pyrolysis of aromatic-fused 1,2,3-triazines sometimes gives the benzazetes,[18] other reactions of the initial aryl-iminyl diradicals have been observed before,[20] including one case of an apparent 1,3-H migration to give a nitrile.[21] Ring opening of the cyclobutaniminyl radical to generate a nitrile is also well precedented.[22]



Scheme 1 *Reagents*: i, H_2, Pd/C; ii, aq. HCl; iii, aq. KOH; iv, $K_3Fe(CN)_6$; v, 1,3-dibromo-5,5-dimethylhydantoin, AIBN (azoisobutyronitrile), CCl_4; vi, $NaHCO_3$, Me_2SO

The anomalous behaviour of **5** 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 known[23] and the extrusion from β-oxo ylides can be achieved photochemically.[24] It is, however, the discrepancy between the behaviour of **5** and all the other examples **2** studied which is most striking. We believe this to be owing to the relative importance of the (*Z*)- and (*E*)-phosphonium enolate forms **13** and **14** in the gas phase. The relatively bulky benzotriazolyl group means that, particularly for R^1 = Bu^n, the *Z*-form **13** is sterically crowded. It is only for R^2 = Me, however, that the alternative *E*-configuration **14** offers any advantage and **5** may exist in this form making the loss of Bu^n_3PO impossible. For larger alkyl groups such as R^2 = Et the *Z*-form is preferred and **15** loses exclusively Bu^n_3PO. This hypothesis was tested by X-ray structure determination of **5** and **15**[25] which clearly showed both compounds to exist in the *Z*-form in the solid state, their structures being almost superimposable. Nevertheless we believe that, in the absence of crystal-packing forces, **5** does exist mainly in the *E*-form, thus explaining its anomalous thermal behaviour.

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