COMMUNICATION

Inverse Wittig reaction of oxaphosphetenes formed by the [2+2] cycloaddition of arylphosphine oxides and dimethyl acetylenedicarboxylate (DMAD)

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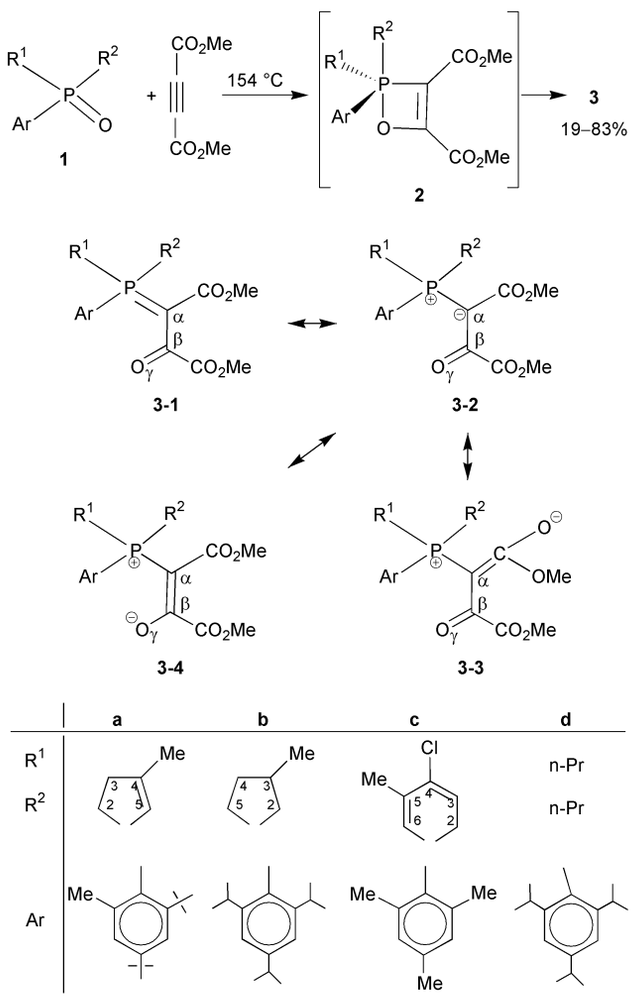
The intermediate oxaphosphetenes 2 formed by the novel cycloaddition of the P=O group of arylphosphine oxides 1 and the acetylene moiety of DMAD are stabilised by an inverse Wittig reaction to afford the corresponding stabilised phosphonium ylide 3.

We have recently reported that a series of 2,4,6-trialkylphenylphosphine oxides underwent a novel [2+2] cycloaddition with DMAD.[1] On the basis of analogies[2] and spectroscopic data, we thought first that the products were the oxaphosphetenes themselves formed by the cycloaddition of the P=O group and the acetylene moiety.[3] Later on, it was suggested, however, by the results of semiempirical calculations that the oxaphosphetene structure contains considerable ring strain.[4] HF/6-31G* *ab initio* calculations supported the conclusion that the four-membered species can be only intermediates.[5] The products of the reaction of the cyclic or acyclic trialkylphenylphosphine oxides **1a**–**d** with DMAD are now shown to be the stabilised ylides **3a**–**d** formed by the ring opening of intermediates **2a**–**d** (Scheme 1). In an extension of the reactants investigated, compounds **3a**–**d**, obtained in variable yields after chromatography, were characterised by ^{31}P, ^{13}C and ^{1}H NMR, as well as by their IR and mass spectroscopic data, including HRMS. The 16.7–43.6 range of the δ_P values unambiguously supported the phosphonium salt character of the product **3**, and hence the involvement of the resonance structures **3-2**, **3-3** and **3-4**. It is, however, clear from the IR spectra refined by derivation that a keto carbonyl moiety (at $\nu_{C=O} \approx 1663$ cm^{-1}) and two ester groups (at $\nu_{C=O} \approx 1713$ and 1761 cm^{-1}) are present in product **3** thus justifying the resonance structure **3-1**.

The optimised structure of product **3c** determined by HF/6-31G* calculation is shown in Fig. 1. It is worth noting that the P=C and the C=Oγ bonds are slightly elongated (1.690 and 1.234 Å, respectively,) while the Cα–Cβ bond is somewhat shortened (1.436 Å). The distance between the P1 and Oγ atoms is 2.87 Å.

The only criterion of the novel reaction is that the phosphorus atom should bear an electron-donating trialkylphenyl substituent. The presence of a 2,4,6-triisopropylphenyl group is the optimum in this respect; with 2,4-di-*tert*-butyl-6-methylphenyl, there is increased steric hindrance, while with 2,4,6-trimethylphenyl, the electron-releasing ability is lower, resulting in a decrease in the efficiency of the reaction.

Careful observation shows that the transformation **2**⟶**3** can be regarded as an intramolecular inverse Wittig reaction, as it formally involves the rupture of the P–O bond and the formation of a P=C and a C=O double bond. This kind of reaction has never been observed before since it would not be possible to generate a phosphetene intermediate *via* a Wittig reaction of an ylide with a carbonyl compound. Kano and Kawashima have described, however, a similar azaphosphete⟶phosphorane conversion.[6]



Scheme 1

It can be concluded that the novel reaction of trialkylphenylphosphine oxides (**1**) and DMAD, which is especially efficient with cyclic phosphine oxides (**1a**–**c**), gives an entry to transient oxaphosphetenes (**2**) that are stabilised by a retro Wittig type reaction to furnish the corresponding stabilised phosphonium ylides (**3**).

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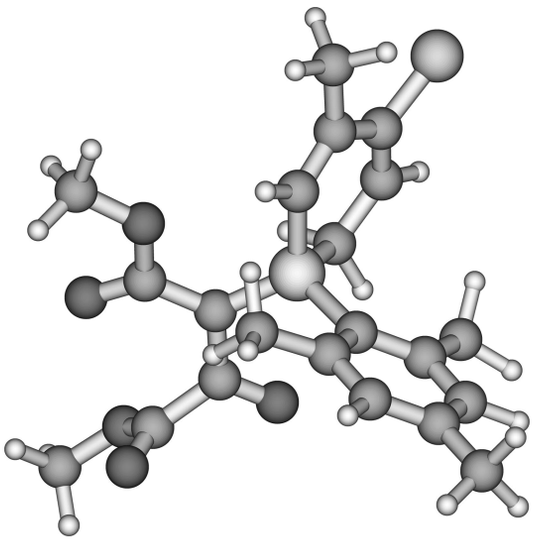

Fig. 1 Perspective view of **3c**. Selected bond lengths/Å: P1–Cα 1.690, Cα–Cβ 1.436, Cβ–Oγ 1.234, P1–C6 1.768, C6–C5 1.340, C5–C4 1.463, C4–C3 1.344, C3–C2 1.471, C2–P1 1.834, P1–C1′ 1.827.

Experimental

General method for the synthesis of compounds 3a–d

A mixture of the phosphine oxide **1a**–**d** (2.0 mmol) and DMAD (4.0 ml, 32.5 mmol) was kept at 154 °C for 8–14 days in a sealed tube. The excess of the reagent was removed *in vacuo*. The residue thus obtained was purified by repeated column chromatography (3% methanol in chloroform, silica gel) to give the products **3a**–**d** as oils.

Compound 3a. 14 days, 25%; δ_P ($CDCl_3$) 43.6; δ_C ($CDCl_3$) 20.7 (J = 18.1, C4–Me), 24.5 (J = 7.2, C6′–Me), 27.7 (J = 62.2, C2), 31.0 ($C(CH_3)_3$), 33.6 ($C(CH_3)_3$), 36.3 (J = 6.4, C3), 50.2 (MeO), 51.7 (MeO), 72.2 (J = 100.4, Cα), 115.1 (J = 89.7, C5), 123.1 (J = 11.3, C3′*), 124.3 (J = 87.4, C1′), 127.0 (J = 11.1, C5′*), 142.3 (J = 10.0, C6′), 153.0 (C4′), 153.4 (J = 7.4, C2′), 164.8 (J = 16.6, C4), 167.1 (J = 12.9, C=O), 168.1 (J = 14.4, C=O), 183.6 (J = 7.0, Cβ) (* assignments may be exchanged); IR (film) 1669, 1714, 1763 cm^{-1}; $(M + H)^+_{found}$ = 461.2445, $C_{26}H_{38}O_5P$ requires 461.2457.

Compound 3b. 8 days, 83%; δ_P ($CDCl_3$) 32.7 (major isomer); δ_C ($CDCl_3$) 20.0 (J = 11.7, C3–Me), 23.6 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 31.9 (J = 54.4, C5), 31.9 (J = 5.7, $CHMe_2$), 33.6 (J = 6.2, C4), 34.1 ($CHMe_2$), 34.2 (J = 55.5, C2), 34.6 (J = 6.1, C3), 50.6 (MeO), 51.6 (MeO), 73.2 (J = 98.1, Cα), 120.9 (J = 85.6, C1′), 123.3 (J = 11.6, C3′), 152.8 (J = 2.8, C4′), 153.5 (J = 11.1, C2′), 167.2 (J = 14.0, C=O), 167.9 (J = 14.6, C=O), 183.1 (J = 6.2, Cβ); IR (film) 1671, 1715, 1754 cm^{-1}; $(M + H)^+_{found}$ = 463.2633, $C_{26}H_{40}O_5P$ requires 463.2613.

Compound 3c. 14 days, 36%; δ_P ($CDCl_3$) 26.4; δ_C ($CDCl_3$) 16.7 (J = 17.8, C5–Me), 21.2 (C4′–Me), 23.1 (J = 5.8, C2′–Me), 28.6 (J = 61.0, C2), 51.0 (MeO), 51.9 (MeO), 73.9 (J = 107.7, Cα), 119.9 (J = 14.0, C3), 122.1 (J = 93.2, C1′), 122.8 (J = 84.8, C6), 131.1 (J = 12.1, C3′), 140.3 (J = 13.9, C4), 142.0 (J = 11.0, C2′), 142.7 (C4′), 155.3 (J = 14.3, C5), 167.0 (J = 14.6, C=O), 167.7 (J = 15.8, C=O), 182.9 (J = 6.2, Cβ); IR (film) 1648, 1711, 1767 cm^{-1}; $(M + H)^+_{found}$ = 423.1060, $C_{21}H_{25}ClO_5P$ requires 423.1128 for the ^{35}Cl isotope.

Compound 3d. 14 days, 19%; δ_P ($CDCl_3$) 22.9; IR (film) 1664, 1712, 1763 cm^{-1}; $(M + H)^+_{found}$ = 479.2800, $C_{24}H_{44}O_5P$ requires 479.2926.

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