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Unexpected [2 + 2] cycloaddition between the P=O group of *P*-(2,4,6-triisopropylphenyl) P-heterocycles and dimethyl acetylenedicarboxylate

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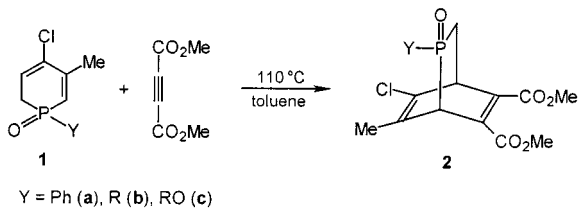
The reaction of 1-(2,4,6-triisopropylphenyl)-1,2-dihydrophosphinine 1-oxide 1d with dimethyl acetylenedicarboxylate (DMAD) affords, surprisingly, oxaphosphetene 3 instead of the expected Diels–Alder cycloadduct; the unusual reactivity of the trialkylphenylphosphine oxides towards DMAD seems to be of general value.

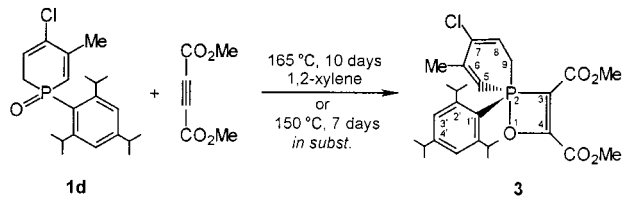
The 1,2-dihydrophosphinine 1-oxides (**1**) with phenyl, alkyl or alkoxy substituents on the phosphorus atom proved to be valuable starting materials in the synthesis of phosphabicyclo-[2.2.2]octadienes **2** that are precursors of low-coordinated fragments, methylenephosphine oxides ($YP(O)CH_2$) useful in the phosphorylation of nucleophiles.[1–4] The cycloadducts (**2**) are obtained by the Diels–Alder reaction of dihydrophosphinine oxides **1** and DMAD (Scheme 1).[1,4] Other dienophiles, such as maleic acid derivatives were also utilised in the synthesis of bridged phosphorus heterocycles.[5,6]



Scheme 1[1–4]

Recently, we have described the preparation of 1-(triisopropylphenyl)dihydrophosphinine oxide **1d** revealing unique properties due to the presence of the sterically demanding P-substituent.[7] We wished to utilise compound **1d** in the synthesis of *P*-(trialkylphenyl)phosphabicyclooctadiene **2d** (**2**, Y = 2,4,6-$Pr^i_3C_6H_2$) that seemed to be promising in the generation of a sterically hindered and hence a relatively stable methylenephosphine oxide (2,4,6-$Pr^i_3C_6H_2P(O)CH_2$).

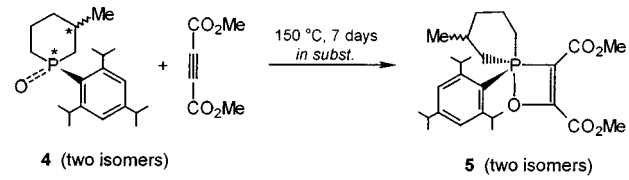
The reaction of **1d** and DMAD in 1,2-xylene at 165 °C (in a bomb) did not lead, however, to cycloadduct **2d**, instead oxaphosphete **3** isomeric with **2d** could be isolated in 76% yield after column chromatography (Scheme 2). Cycloadduct **2** could not be detected, not even in traces. Spiro derivative **3** exhibited a δ_P value of 24.0 ($CDCl_3$). Similar 1,2-oxaphosphetes have never been reported in the literature. The 1,2-oxaphosphetes are, however, well-known intermediates in the Wittig reaction.[8] The structure of product **3** was confirmed by ^{13}C and ^1H NMR,[9] as well as two-dimensional correlation diagrams, such as HMQC and HMPC spectra. Elemental composition of **3** was supported by HRMS.



Scheme 2

This is the first case in which the P=O group of a phosphine oxide reacted with DMAD to furnish the 1,2-oxaphosphete ring. Moreover, the [2+2] cycloaddition was fully selective and the dihydrophosphinine ring of starting material **1d** remained intact.

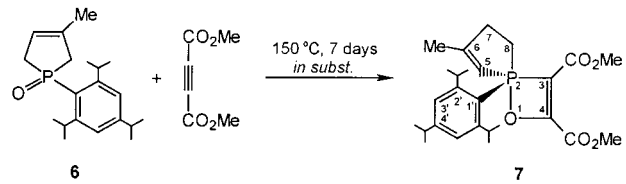
We wished to evaluate if the above [2+2] cycloaddition is of general value for P-heterocycles with a *P*-triisopropylphenyl substituent. Hexahydrophosphinine oxide **4** obtained from **1d** by catalytic hydrogenation was reacted with DMAD at 150 °C in the absence of any solvent, to give oxaphosphete **5** in 58% yield after chromatography (Scheme 3). Starting from the 63–37% diastereoisomeric mixture of **4**, product **5** was also formed as a mixture of two isomers.[10]



Scheme 3

Finally, it was examined if a P-heterocycle with a five-membered ring can be involved in the above type [2 + 2] cycloaddition. The interaction of 1-(triisopropylphenyl)dihydrophosphole oxide **6** and DMAD at 150 °C led again to the corresponding oxaphosphete (**7**). In this case the double-bond of the 2,5-dihydrophosphole moiety was, however, isomerised to afford the 2,3-dihydro hetero ring (Scheme 4). 2,5-Dihydrophospholes are known to undergo double-bond rearrangement on thermal treatment.[11] Product **7** was isolated in 83% yield in a clean reaction. The structure of spiro derivatives **5** and **7**[12] was confirmed by NMR and MS.

It is worth mentioning that the *P*-phenyl analogues of hexahydrophosphinine **4** and dihydrophosphole **6** did not enter into reaction with DMAD at 150–165 °C. This means that the electron-releasing ability of the triisopropylphenyl ring may be responsible for the new type of reactivity of the P=O group.



Scheme 4

To summarise our findings, it can be concluded that the reaction of DMAD with 5- and 6-membered P-heterocycles bearing a triisopropylphenyl substituent on the phosphorus atom affords the corresponding spiro derivative of 1,2-oxaphosphete. This type of [2+2] cycloaddition between the P=O group of tertiary phosphine oxides and the acetylene moiety of DMAD has not been observed previously and is, obviously, the consequence of the presence of the triisopropylphenyl substituent at the phosphorus atom. The reaction under discussion may be of general value and hence the cycloaddition of acyclic trialkylphenylphosphine oxides with DMAD may represent a new entry into the synthesis of *P*-aryl oxaphosphetes.

Future work will be directed towards the possible extension and the theoretical evaluation of the P=O + -C≡C- [2 + 2] cycloaddition reaction.

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Notes and references

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9 *Selected data* for **3**: $\delta_C(CDCl_3)$ 16.2 (J_{PC} 17.5, C^6–Me), 23.5 (J_{PC} 8.7, *o*-CH(*C*H$_3$)$_2$), 25.3 (*p*-CH(*C*H$_3$)$_2$), 30.0 (J_{PC} 62.8, C^9), 31.8 (J_{PC} 6.7, *o*-*C*HMe$_2$), 34.0 (*p*-*C*HMe$_2$), 50.6 (CH$_3$O), 51.5 (CH$_3$O), 74.4 (J_{PC} 107.4, C^3), 119.3 (J_{PC} 13.7, C^8), 121.6 (J_{PC} 94.3, C$^{1'}$), 122.5 (J_{PC} 85.0, C^5), 123.2 (J_{PC} 11.9, C$^{3'}$), 140.0 (J_{PC} 14.1, C^7), 152.7 (J_{PC} 11.3, C$^{2'}$), 153.0 (C$^{4'}$), 155.4 (J_{PC} 14.8, C^6), 166.4 (J_{PC} 14.8, C=O), 167.5 (J_{PC} 15.6, C=O), 182.4 (J_{PC} 6.1, C^4)
10 *Selected data* for **5**-**1**: $\delta_P(CDCl_3)$ 23.9 (69%), **5**-**2**: $\delta_P(CDCl_3)$ 29.1 (31%).
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12 *Selected data* for **7**: $\delta_P(CDCl_3)$ 39.5; $\delta_C(CDCl_3)$ 20.7 (J_{PC} 18.0, C^6-Me), 23.8 (J_{PC} 5.9, *o*-CH(*C*H$_3$)$_2$), 25.5 (*p*-CH(*C*H$_3$)$_2$), 26.0 (J_{PC} 59.2, C^8), 32.0 (J_{PC} 6.3, *o*-*C*HMe$_2$), 34.3 (*p*-*C*HMe$_2$), 35.7 (J_{PC} 6.8, C^7), 50.7 (CH$_3$O), 51.8 (CH$_3$O), 76.1 (J_{PC} 103.0, C^3), 116.3 (J_{PC} 88.6, C^5), 122.8 (J_{PC} 93.7, C$^{1'}$), 123.2 (J_{PC} 11.3, C$^{3'}$), 152.7 (C$^{2'}$), 152.8 (C$^{4'}$), 164.0 (J_{PC} 23.0, C^6), 167.0 (J_{PC} 14.3, C=O), 168.1 (J_{PC} 15.4, C=O), 182.5 (J_{PC} 6.2, C^4).

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