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New evidence on the structure of the product from the reaction of cyclic 2,4,6-trialkylphenylphosphine oxides with dimethyl acetylenedicarboxylate (DMAD); formed by an inverse Wittig reaction type protocol☆

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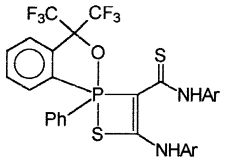
Abstract—New evidence based on spectroscopy, quantum chemical calculations and reactivity suggest that the spirocyclic oxaphosphetes (**5**) formed by the [2+2] cycloaddition of the title P-heterocycles (**4**) and DMAD are intermediates to afford a stabilised phosphonium ylide (**6**) existing as two conformers (**6A** and **B**). © 2002 Published by Elsevier Science Ltd.

1. Introduction

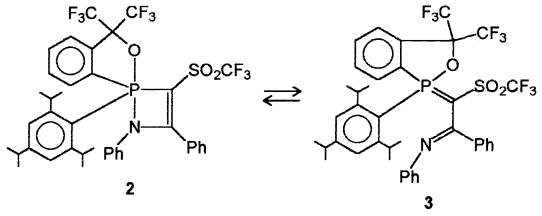
We have recently observed that a series of 2,4,6-triisopropylphenyl cyclic phosphine oxides enter into reaction with DMAD.[2] The example of a stable spirocyclic thiaphosphete (**1**) described recently by Kawashima and co-workers[3] together with the extensive ^{13}C and ^{1}H NMR spectral parameters including two-dimensional correlation diagrams encouraged us to assume the spirocyclic oxaphosphete structure.[2] However, we have never excluded the possibility of having ring-opened species as the stable products in hand.[4,5]



1

Ar = Ph, 1-Naphthyl

An analogous azaphosphete (**2**)[6] was found to equilibrate with the corresponding phosphorane/ylide (**3**) (Scheme 1). Variable temperature ^{31}P NMR spectroscopy suggested a significant contribution of the ring-opened species (**3**) at higher temperatures.[7]



2 **3**

Scheme 1.

2. Results and discussion

By now, it has become quite clear that the product from the reaction of P-trialkylphenyl cyclic phosphine oxides (**4**) and DMAD is stabilised phosphonium ylide **6** consisting of conformers **6A** and **B**, each represented by resonance structures **6-1**, **6-2**, **6-3** and **6-4** (Scheme 2).

Hence, the spirocyclic oxaphosphetes (**5**) formed by the [2+2] cycloaddition of the P═O group of **4** and the acetylene moiety of DMAD are only intermediates.

☆ See Ref. 1.

Keywords: phosphorus heterocycles; ylides; phosphoranes; theoretical studies.

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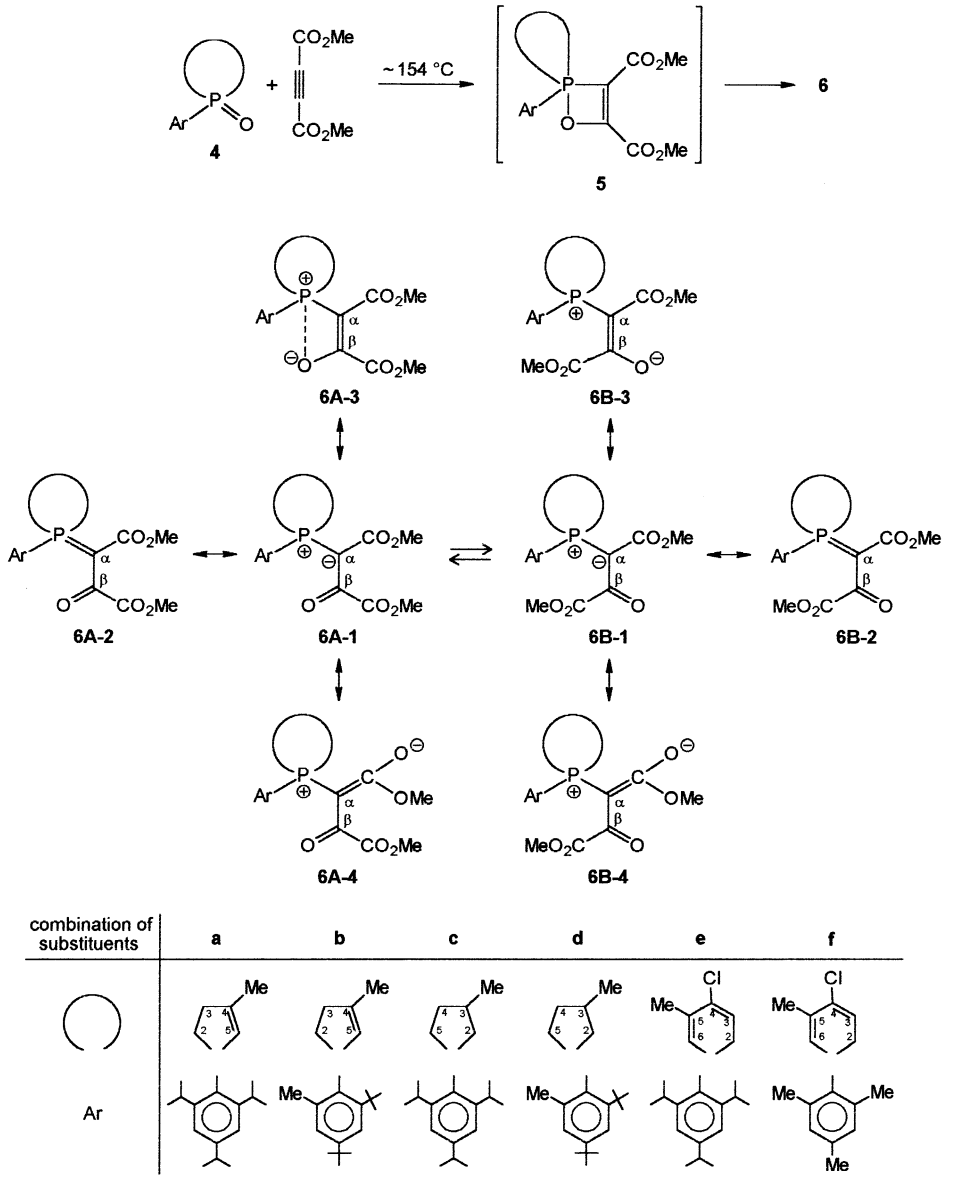


Scheme 2.

Among the resonance structures, **6A-1** and **6B-1** are ylides, **6A-2** and **6B-2** are phosphoranes, **6A-3** and **6B-3** are enolates, while **6A-4** and **6B-4** are stabilised ylides. The novel reaction is quite general; both five-membered P-heterocycles, such as 2,3-dihydro-1*H*-phosphole 1-oxides (**4a** and **b**) or tetrahydro derivatives (**4c** and **d**), as well as six-membered species, like 1,2-dihydrophosphinine oxides (**4e** and **f**), can be the starting materials. The phosphorus atom may bear a 2,4,6-triisopropylphenyl, a 2,4-di-*tert*-butyl-6-methylphenyl, or a 2,4,6-trimethylphenyl substituent. For the above cases, products **6a–f** were obtained, respectively, in a pure form after column chromatography and identified by ^{31}P, ^{13}C and ^{1}H NMR, as well as FAB-MS spectroscopy. Starting from the diastereomeric mixture of tetrahydrophosphole oxides **4c** and **d**, the products (**6c** and **d**) were also formed as a mixture of isomers (**6c**$_1$/**6c**$_2$ or **6d**$_1$/**6d**$_2$, respectively). The δ_P values of 24–44 obtained for products **6a–f** supported the phosphonium salt character (hence **6-1**, **6-3** and **6-4**) of product **6**.[8] It has also been suggested for the ylide/phosphorane systems that the ylide component predominates.[9] The term phosphonium ylides for such systems has spread. No examples of oxaphosphetes are known, but, on the basis of the analogy of oxaphosphetanes with a five-coordinate phosphorus atom, they should have up-field δ_P shifts in the negative region.[10] The up-field δ_C shifts of 71.8–76.1 detected for the C_α carbon atom of products **6a–f** were in agreement with the enolate component (**6-3**). A detailed study of the IR spectra refined by differentiation revealed the presence of two ester carbonyls (at ca. 1722 and 1752 cm^{-1}) and that of a single keto carbonyl (at ca. 1665 cm^{-1}) in products **6**, as they are in resonance structures **6-1** and **6-2**. It can be seen that the ^{31}P and ^{13}C NMR, as well as the IR spectral parameters adequately confirm structure **6** involving four resonance structures.

PM3 semi-empirical calculations showed that the spirocyclic oxaphosphetes (**5**) are highly strained.[4] Attempts to

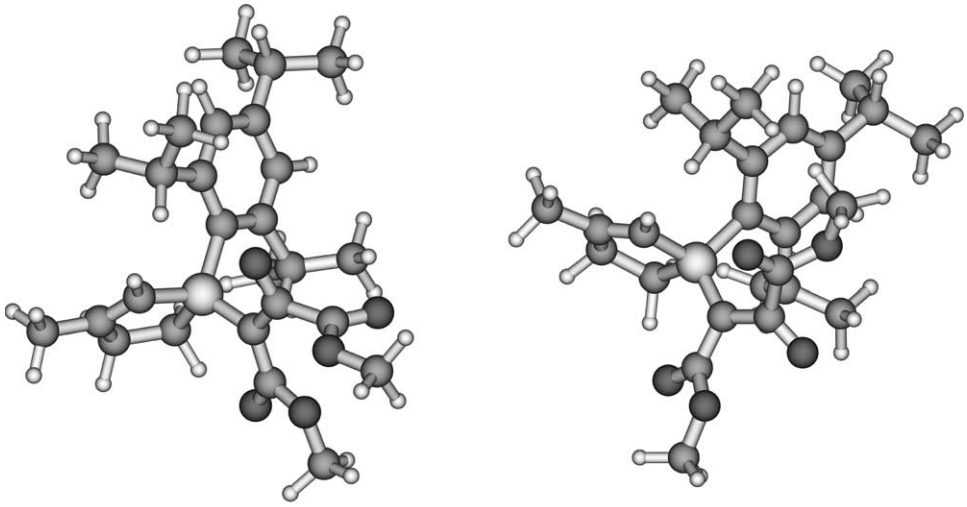
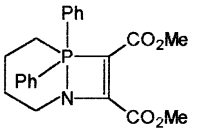


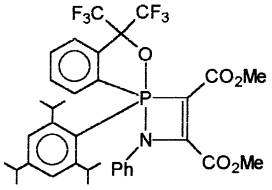
Figure 1. Perspective view of conformers **6Aa** and **6Ba** obtained by the PM3 semi-empirical calculation.

refine the structures (**5**) by HF/6-31G* ab initio calculations led to the ring-opened products **6**. For the **5e→6e** transformation, the enthalpy of activation was only 0.88 kJ mol^{-1}, while the enthalpy gain was 28.0 kJ mol^{-1} indicating the intermediacy of **5e**. It can be seen that the **5→6** transformation can be regarded as an intramolecular inverse Wittig reaction, formally involving the rupture of the P–O bond and the formation of a P═C and C═O double bond. This kind of reaction has never previously been observed.

A few azaphosphetes (**7** and **8**) have also been substantiated as intermediates by Japanese authors,[11,12] the latter (**8**) giving a stabilised phosphonium ylide by ring opening.[12]

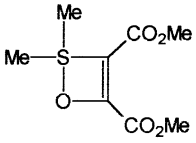


7[11]



8[12]

It is worth mentioning that the thio analogue of an oxaphosphete (**9**) was suggested to be an intermediate in the reaction of dimethylsulfoxide with DMAD affording a betaine type adduct, and after its reaction with a second unit of DMAD, furantetracarboxylic acid tetramethyl ester.[13]



9[13]

The structure of the products (**6a**–**g**) was evaluated by PM3 quantum chemical calculations.[14,15] These calculations suggested that the products (**6a**–**g**) can exist as two conformations. Conformer **6A**, where there may be a favourable interaction between the oppositely charged phosphorus and oxygen atoms in form **6A-3**, is favoured by ca. 21–46 kJ mol^{-1} as compared to conformer **6B**, where the P═C and the C═O moieties are nearly *trans* in form **6B-2** promoting an advantageous conjugation. In the lack of any stabilising interaction, the role of resonance structure **6B-3** is probably marginal. Anyhow, conformers **6A** and **6B** may be in an equilibrium at room temperature. The perspective views of compounds **6a**–**f** in the two stable conformations are shown in Figs. 1–6, respectively.

The relevant geometries for both conformers (**A** and **B**) of the stabilised phosphonium ylides **6a**–**f** are listed in Table 1. One can see that, in accordance with the electron delocalisation, the C_α–C_β bond is somewhat shortened. The shorter C_α–C_β bond in **6A** as compared to that in **6B** suggests the significance of resonance structure **6A-3** stabilised by an intermolecular ionic interaction. The length of the P═C bond is comparable with that reported for other stabilised phosphonium ylides.[16]

The samples of compounds **6a** and **c** were subjected to variable temperature ^{31}P NMR measurements in the range of +15 to −60°C, in $CDCl_3$. Practically, no change in the position of the chemical shifts (δ_P 39.0 and 32.7 (in the latter case for the major isomer)) could be observed suggesting the exclusive involvement of the ring-opened forms (**6**). There may, however, be an interaction between the oppositely charged phosphorus and the oxygen atoms of **6**, as can be seen in the enolate resonance structure (**6A-3**).

The stability of products **6a**–**f** also confirmed the ring-opened structure suggested. On standing at room temperature for months, the samples of **6a**–**f** remained unchanged. Attempts to effect the catalytic hydrogenation of compounds **6** were unsuccessful. Hydrogenation of a system stabilised by delocalisations may indeed be difficult. Finally, stabilised phosphonium ylides **6a** and **c** were tested in the Wittig reaction with benzaldehyde derivatives. These reactions attempted in boiling tetrahydrofuran or toluene or in ethyleneglycol dimethylether at 160°C using benzalde-

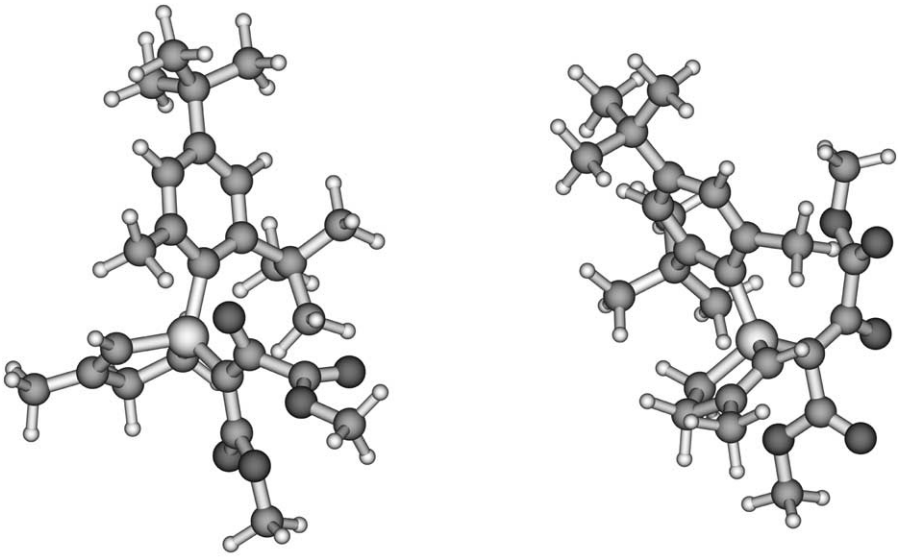


Figure 2. Perspective view of conformers **6Ab** and **6Bb** obtained by the PM3 semi-empirical calculation.

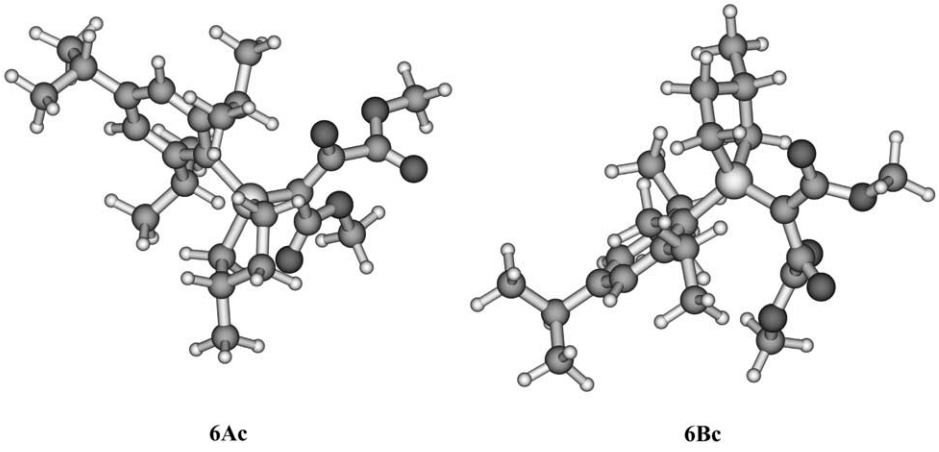


Figure 3. Perspective view of conformers **6Ac** and **6Bc** obtained by the PM3 semi-empirical calculation.

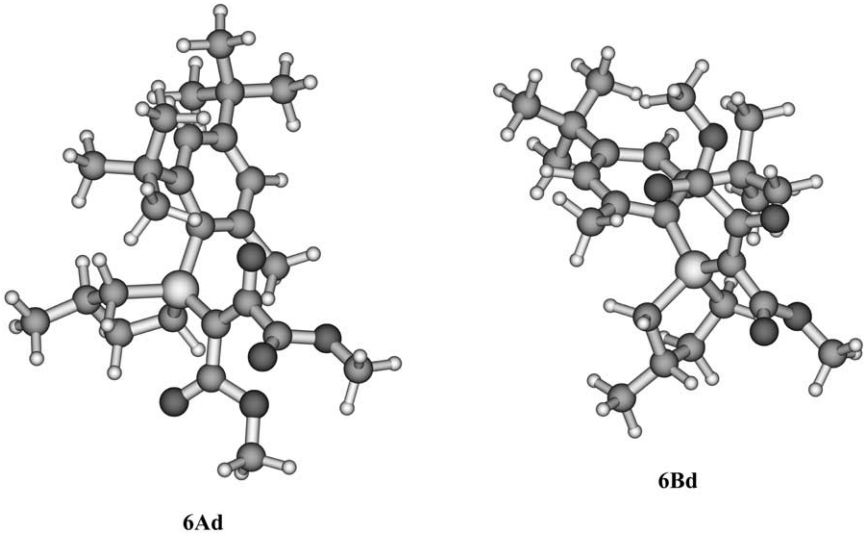


Figure 4. Perspective view of conformers **6Ad** and **6Bd** obtained by the PM3 semi-empirical calculation.

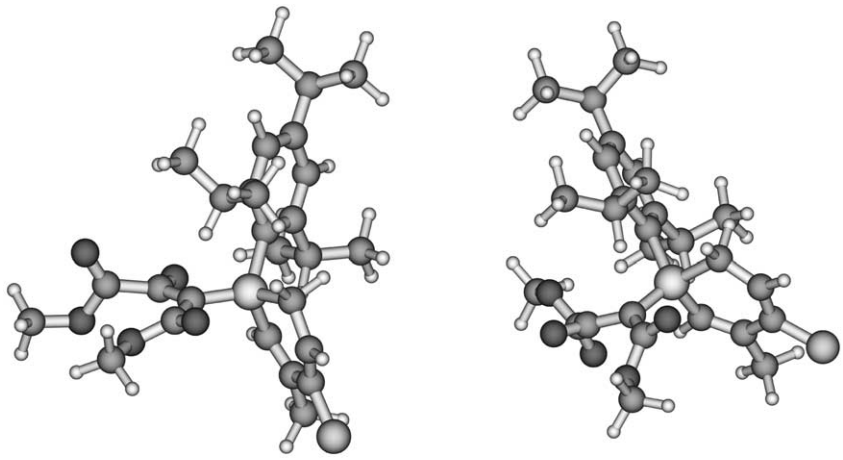


Figure 5. Perspective view of conformers **6Ae** and **6Be** obtained by the PM3 semi-empirical calculation.

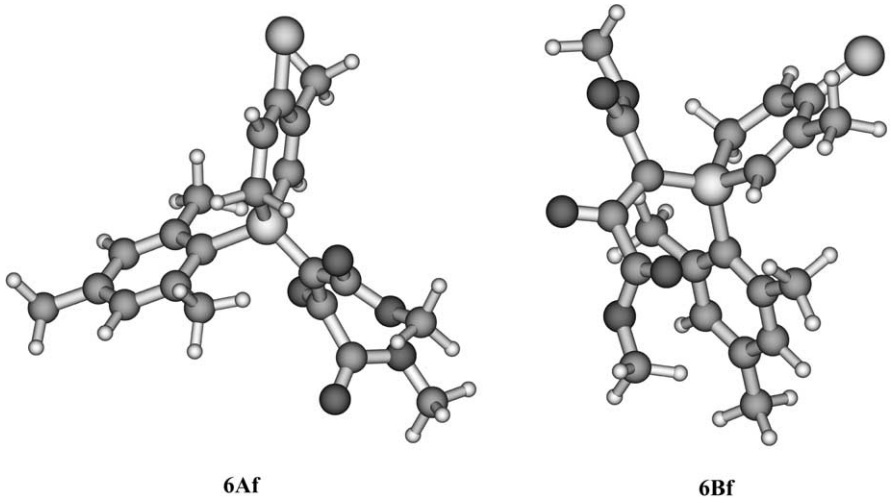


Figure 6. Perspective view of conformers **6Af** and **6Bf** obtained by the PM3 semi-empirical calculation.

Table 1. Relevant bond distances (Å), bond angles (°) and dihedral angles (°), as well as heat of formation values (kJ mol^{-1}) for the conformers (**A** and **B**) of products **6a–f** obtained by PM3 semi-empirical calculations

	P–C_2	P–C_5 or P–C_6	P–C_α	C_α–C_β	C_β–O	C_α–(C)O	C_β–(C)O	P–O distance	C_2–P–C_α	C_2–P–$C_{1'}$	C_5–P–C_α or C_6–P–C_α	C_5–P–$C_{1'}$ or C_6–P–C_1	P–C_α–C_β–O	H_f
6Aa	1.831	1.763	1.701	1.435	1.231	1.440	1.532	2.912	113.72	107.76	113.01	113.89	13.05	−788.77
6Ab	1.844	1.773	1.693	1.440	1.229	1.446	1.539	3.099	117.36	104.92	112.27	111.42	26.35	−737.35
6Ac	1.828	1.821	1.705	1.435	1.231	1.440	1.532	2.928	110.94	114.87	113.86	106.68	14.34	−872.91
6Ad	1.823	1.847	1.694	1.455	1.233	1.455	1.535	3.081	113.60	112.56	112.91	103.73	0.41	−821.12
6Ae	1.834	1.767	1.695	1.433	1.233	1.446	1.531	2.856	117.43	99.95	107.70	114.40	8.47	−701.82
6Af	1.824	1.755	1.706	1.436	1.231	1.439	1.533	2.913	112.24	105.63	110.16	111.70	12.70	−612.79
6Ba	1.827	1.765	1.678	1.450	1.215	1.448	1.548	3.854	114.98	107.48	113.20	113.03	−142.89	−769.12
6Bb	1.848	1.776	1.660	1.438	1.225	1.476	1.545	3.930	111.83	108.17	113.18	109.54	−164.01	−697.14
6Bc	1.833	1.820	1.683	1.449	1.220	1.450	1.547	3.868	111.07	115.12	114.19	107.13	−143.78	−851.88
6Bd	1.842	1.834	1.665	1.438	1.225	1.476	1.542	3.635	110.94	110.37	111.75	108.38	−163.12	−781.54
6Be	1.831	1.766	1.671	1.447	1.220	1.457	1.548	3.874	119.13	100.16	107.71	114.09	−152.97	−681.76
6Bf	1.832	1.757	1.665	1.442	1.222	1.468	1.546	3.904	111.84	105.41	110.81	110.70	−162.16	−566.60

hyde or 4-nitrobenzaldehyde were, however, unsuccessful, presumably due to the increased stability of the ylide/phosphorane (**6**).

3. Experimental

3.1. General

The ^{31}P, ^{13}C and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The couplings are given in Hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument at 70 eV.

3.2. General method for the preparation of products 6a–f

P-heterocycle **4a**–**f** (2.0 mmol) and DMAD (4.0 ml, 32.5 mmol) was kept at 154°C for 8 days (**4a**,**c** and **e**) or 14 days (**4b**,**d** and **f**) in a sealed tube. The excess of the reagent was removed in vacuo. The residue so obtained was purified by flash chromatography on silica gel using 3% methanol in chloroform as the eluant. The main fraction was refined by a second chromatography using the same type of absorbent and eluant to give the products (**6a**–**f**) as pale brown oils.

3.2.1. Compound 6a. Yield: 79%; ^{31}P NMR ($CDCl_3$) δ 39.5; ^{13}C NMR ($CDCl_3$) δ 20.7 (J_{PC}=18.0 Hz, C_4–Me), 23.7 (J_{PC}=3.7 Hz, CH(CH_3)$_2$), 23.8 (CH(CH_3)$_2$), 25.5 (CH(CH_3)$_2$), 26.0 (J_{PC}=59.2 Hz, C_2), 32.0 (J_{PC}=6.3 Hz, $CHMe_2$), 34.3 ($CHMe_2$), 35.7 (J_{PC}=6.8 Hz, C_3), 50.7 (CH_3O), 51.8 (CH_3O), 76.1 (J_{PC}=103.0 Hz, C_α), 116.3 (J_{PC}=88.6 Hz, C_5), 122.8 (J_{PC}=93.7 Hz, $C_{1'}$), 123.2 (J_{PC}=11.3 Hz, $C_{3'}$), 152.7 ($C_{2'}$), 152.8 ($C_{4'}$), 164.0 (J_{PC}=23.0 Hz, C_4), 167.0 (J_{PC}=14.3 Hz, C=O), 168.1 (J_{PC}=15.4 Hz, C=O), 182.5 (J_{PC}=6.2 Hz, C_β); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, J=6.5 Hz, 6H, CH(CH_3)$_2$), 1.24 (d, J=7.0 Hz, 6H, CH(CH_3)$_2$), 1.34 (d, J=6.5 Hz, 6H, CH(CH_3)$_2$), 2.04 (s, 3H, C_6–CH_3), 2.27–2.37 (m, 1H, CH), 2.60–2.71 (m, 1H, CH), 2.83–2.93 (m, 2H, $CHMe_2$, CH), 3.49–3.60 (m) and 3.55 (s) overlapped, total int. 5H ($CHMe_2$, OCH_3), 3.78 (s, 3H, OCH_3), 3.85–3.96 (m, 1H, CH), 6.26 (d, J=27.5 Hz, 1H, C_5-H), 7.08 (s, 2H, ArH); M^+_{found}=460.2381, $C_{26}H_{37}O_5P$ requires 460.2379; IR (film) 1754, 1715, 1669 cm^{-1}.

3.2.2. Compound 6b. Yield: 35%; ^{31}P NMR ($CDCl_3$) δ 43.6; ^{13}C NMR ($CDCl_3$) δ 20.7 (J=18.1 Hz, C_4–Me), 24.5 (J=7.2 Hz, $C_{6'}$–Me), 27.7 (J=62.2 Hz, C_2), 31.0 (C(CH_3)$_3$), 33.6 (C(CH_3)$_3$), 36.3 (J=6.4 Hz, C_3), 50.2 (MeO), 51.7 (MeO), 72.2 (J=100.4 Hz, C_α), 115.1 (J=89.7 Hz, C_5), 123.1 (J=11.3 Hz, $C_{3'}$*), 124.3 (J=87.4 Hz, $C_{1'}$), 127.0 (J=11.1 Hz, $C_{5'}$*), 142.3 (J=10.0 Hz, $C_{6'}$), 153.0 ($C_{4'}$), 153.4 (J=7.4 Hz, $C_{2'}$), 164.8 (J=16.6 Hz, C_4), 167.1 (J=12.9 Hz, C=O), 168.1 (J=14.4 Hz, C=O), 183.6 (J=7.0 Hz, C_β), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 5.98 (d, J=28.0 Hz, C_5–H); HR-FAB, $(M+H)^+_{found}$=461.2445, $C_{26}H_{38}O_5P$ requires 461.2457; IR (film) 1756, 1714, 1666 cm^{-1}.

3.2.3. Compound 6c. The starting tetrahydrophosphole oxide (**4c**) was used as a 68:32% mixture of two diastereomers (**4c**-**1** and **4c**-**2**). Yield: 83%; isomeric composition: 67% of **6c**-**1** and 33% of **6c**-**2**; $(M+H)^+_{found}$=463.2633, $C_{26}H_{40}O_5P$ requires 463.2613; IR (film) 1739, 1666 cm^{-1}.

Compound 6c-1. ^{31}P NMR ($CDCl_3$) δ 32.7; ^{13}C NMR ($CDCl_3$) δ 20.0 (J=11.7 Hz, C_3–Me), 23.6 (CH(CH_3)$_2$), 24.2 (CH(CH_3)$_2$), 25.2 (CH(CH_3)$_2$), 31.9 (J=54.4 Hz, C_5), 31.9 (J=5.7 Hz, $CHMe_2$), 33.6 (J=6.2 Hz, C_4), 34.1 ($CHMe_2$), 34.2 (J=55.5 Hz, C_2), 34.6 (J=6.1 Hz, C_3), 50.6 (MeO), 51.6 (MeO), 73.2 (J=98.1 Hz, C_α), 120.9 (J=85.6 Hz, $C_{1'}$), 123.3 (J=11.6 Hz, $C_{3'}$), 152.8 (J=2.8 Hz, $C_{4'}$), 153.5 (J=11.1 Hz, $C_{2'}$), 167.2 (J=14.0 Hz, C=O), 167.9 (J=14.6 Hz, C=O), 183.1 (J=6.2 Hz, C_β); ^{1}H NMR ($CDCl_3$) δ 1.22 (d, J=7.1 Hz, 3H, C_6–CH_3), 1.23 (d, J=6.9 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, J=7.1 Hz, 6H, CH(CH_3)$_2$), 1.32 (d, J=6.6 Hz, 6H, CH(CH_3)$_2$), 2.84–2.93 (m, 1H, $CHMe_2$), 3.48–3.58 (m, 2H, $CHMe_2$), 3.59 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 7.09 (s, 2H, ArH).

Compound 6c-2. ^{31}P NMR ($CDCl_3$) δ 32.0; ^{13}C NMR ($CDCl_3$) δ 20.5 (J=15.8 Hz, C_3–Me), 23.6 (CH(CH_3)$_2$), 24.3 (CH(CH_3)$_2$), 25.2 (CH(CH_3)$_2$), 27.2 (J=55.2 Hz, C_5), 31.8 (J=6.5 Hz, $CHMe_2$), 32.5 (J=3.7 Hz, C_4), 33.6 (J=10.9 Hz, C_3), 34.1 ($CHMe_2$), 38.7 (J=56.1 Hz, C_2), 50.6 (MeO), 51.6 (MeO), 72.9 (J=98.3 Hz, C_α), 120.8 (J=86.0 Hz, $C_{1'}$), 123.4 (J=11.1 Hz, $C_{3'}$), 152.8 (J=2.8 Hz, $C_{4'}$), 153.5 (J=11.1 Hz, $C_{2'}$), 167.2 (J=14.3 Hz, C=O), 167.9 (J=14.6 Hz, C=O), 183.1 (J=6.2 Hz, C_β); ^{1}H NMR ($CDCl_3$) δ 1.16 (d, J=7.0 Hz, 3H, C_6–CH_3), 1.24 (d, J=6.4 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, J=7.1 Hz, 6H, CH(CH_3)$_2$), 1.32 (d, J=6.6 Hz, 6H, CH(CH_3)$_2$), 2.84–2.93 (m, 1H, $CHMe_2$), 3.48–3.58 (m, 2H, $CHMe_2$), 3.60 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 7.10 (s, 2H, ArH).

3.2.4. Compound 6d. The starting tetrahydrophosphole oxide (**4d**) was used as a 59:41% mixture of two diastereomers (**4d**-**1** and **4d**-**2**). Yield: 44%; isomeric composition 58% of **6d**-**1** and 42% of **6d**-**2**; $(M+H)^+_{found}$=463.2588, $C_{26}H_{40}O_5P$ requires 463.2613; IR (film) 1763, 1714, 1669 cm^{-1}.

Compound 6d-1. ^{31}P NMR ($CDCl_3$) δ 38.5; ^{13}C NMR ($CDCl_3$) δ 19.6 (J=16.8 Hz, C_3–Me), 24.9 (J=6.7 Hz, $C_{6'}$–Me), 30.7 (C(CH_3)$_3$), 33.0 (C(CH_3)$_3$), 33.4 (J=4.0 Hz, C_4), 33.7 (J=61.7 Hz, C_5), 34.7 (J=9.4 Hz, C_3), 35.1 (J=57.9 Hz, C_2), 50.0 (MeO), 51.4 (MeO), 72.2 (J=95.5 Hz, C_α), 121.7 (J=83.8 Hz, $C_{1'}$), 124.5 (J=12.0 Hz, $C_{5'}$[a]), 126.1 (J=10.0 Hz, $C_{3'}$[a]), 142.8 (J=8.3 Hz, $C_{6'}$), 152.5 (J=2.5 Hz, $C_{4'}$), 154.4 (J=7.5 Hz, $C_{2'}$), 166.9 (J=13.2 Hz, C=O), 167.8 (J=14.1 Hz, C=O), 183.3 (J=7.4 Hz, C_β).

Compound 6d-2. ^{31}P NMR ($CDCl_3$) δ 38.3; ^{13}C NMR ($CDCl_3$) δ 20.0 (J=12.5 Hz, C_3–Me), 24.8 (J=6.8 Hz, $C_{6'}$–Me), 29.2 (J=57.2 Hz, C_5), 30.7 (C(CH_3)$_3$), 33.0 (C(CH_3)$_3$), 33.6 (J=6.6 Hz, C_4), 34.1 (J=7.7 Hz, C_3), 39.7 (J=58.3 Hz, C_2), 50.0 (MeO), 51.4 (MeO), 71.8 (J=95.8 Hz, C_α), 122.1 (J=83.9 Hz, $C_{1'}$), 124.5 (J=12.1 Hz, $C_{5'}$[b]), 126.1 (J=10.0 Hz, $C_{3'}$[b]), 142.9 (J=7.7 Hz, $C_{6'}$), 152.5 (J=3.1 Hz, $C_{4'}$), 154.4 (J=7.5 Hz,

$C_{2'}$), 167.0 (J=13.2 Hz, C=O), 167.8 (J=14.1 Hz, C=O), 183.2 (J=7.3 Hz, C_β), [a,b]may be reversed.

3.2.5. Compound 6e. Yield: 84%; ^{31}P NMR ($CDCl_3$) δ 24.0; ^{13}C NMR ($CDCl_3$) δ 16.2 (J=17.5 Hz, C_5–Me), 23.6 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 30.0 (J=62.8 Hz, C_2), 31.8 (J=6.7 Hz, $CHMe_2$), 34.0 ($CHMe_2$), 50.6 (CH_3O), 51.5 (CH_3O), 74.4 (J=107.4 Hz, C_α), 119.3 (J=13.7 Hz, C_3), 121.6 (J=94.3 Hz, $C_{1'}$), 122.5 (J=85.0 Hz, C_6), 123.2 (J=11.9 Hz, $C_{3'}$), 140.0 (J=14.1 Hz, C_4), 152.7 (J=11.3 Hz, $C_{2'}$), 153.0 ($C_{4'}$), 155.4 (J=14.8 Hz, C_5), 166.4 (J=14.8 Hz, C=O), 167.5 (J=15.6 Hz, C=O), 182.4 (J=6.1 Hz, C_β); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, J=6.6 Hz, 6H, $CH(CH_3)_2$), 1.24 (d, J=6.9 Hz, 6H, $CH(CH_3)_2$), 1.39 (d, J=6.5 Hz, 6H, $CH(CH_3)_2$), 2.10 (s, 3H, C_6–CH_3), 2.84–2.93 (m, 1H, $CHMe_2$), 3.08 (dd, J_1=18.5 Hz, J_2=9.0 Hz, 1H, C_9–H), 3.51–3.59 (m, 2H, $CHMe_2$), 3.60 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.93 (dd, J_1=17.9 Hz, J_2=14.8 Hz, 1H, C_9–H), 6.50 (s, 1H, C_8–H), 6.64 (d, J=23.3 Hz, 1H, C_5–H), 7.09 (s, 2H, ArH); M^+_{found}=506.1941, $C_{27}H_{36}{}^{35}ClO_5P$ requires 506.1989 for the ^{35}Cl isotope; IR (film) 1736, 1669 cm^{-1}.

3.2.6. Compound 6f. Yield: 86%; ^{31}P NMR ($CDCl_3$) δ 26.4; ^{13}C NMR ($CDCl_3$) δ 16.7 (J=17.8 Hz, C_5–Me), 21.2 ($C_{4'}$–Me), 23.1 (J=5.8 Hz, $C_{2'}$–Me), 28.6 (J=61.0 Hz, C_2), 51.0 (MeO), 51.9 (MeO), 73.9 (J=107.7 Hz, C_α), 119.9 (J=14.0 Hz, C_3), 122.1 (J=93.2 Hz, $C_{1'}$), 122.8 (J=84.8 Hz, C_6), 131.1 (J=12.1 Hz, $C_{3'}$), 140.3 (J=13.9 Hz, C_4), 142.0 (J=11.0 Hz, $C_{2'}$), 142.7 ($C_{4'}$), 155.3 (J=14.3 Hz, C_5), 167.0 (J=14.6 Hz, C=O), 167.7 (J=15.8 Hz, C=O), 182.9 (J=6.2 Hz, C_β); $(M+H)^+_{found}$=423.1060, $C_{21}H_{25}ClO_5P$ requires 423.1128 for the ^{35}Cl isotope; IR (film) 1765, 1715, 1648 cm^{-1}.

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