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Synthesis of the Spiro Derivatives of 1,2-Oxaphosphetes by [2+2] Cycloaddition of Cyclic 1-(2,4,6-Triisopropylphenyl)phosphine Oxides with Dimethyl Acetylenedicarboxylate†

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Abstract—Members of a new heterocyclic family, 1,2-oxaphosphetes were prepared by the unexpected [2+2] cycloaddition of the P═O group of 1-(2,4,6-triisopropylphenyl) P-heterocycles with the acetylene moiety of dimethyl acetylenedicarboxylate. The new oxaphosphetes are spiro derivatives of the starting heterocycles and exhibit a phosphorus atom with trigonal bipyramidal geometry. PM3 semiempirical calculations justified the novel reaction path and suggested a stepwise reaction mechanism.

Introduction

The 1,2-oxaphosphetanes are well known intermediates of the Wittig reaction.[1] No examples of the unsaturated derivatives, oxaphosphetes have, however, been described.

In this paper, we report our surprising findings on the easy construction of the oxaphosphete ring.

Results and Discussion

Searching for new synthetic methods in P-heterocyclic chemistry,[2–5] we found that the P═O group of cyclic phosphine oxides with a 2,4,6-trialkylphenyl substituent on the phosphorus atom underwent [2+2] cycloaddition with dimethyl acetylenedicarboxylate (DMAD) to afford oxaphosphete derivatives. Thus, the reaction of DMAD with 2,3-dihydrophosphole oxide **1**, tetrahydrophosphole oxides **4** and **6**, or 1,2-dihydrophosphinine oxide **8** at 150°C for 8 days furnished spiro derivatives **2**, **5**, **7** and **9**, respectively (Scheme 1). The similar reaction of 2,5-dihydrophosphole oxide **3**, that is the double-bond isomer 2,3-dihydro derivative **1**, also led to product **2**. In this case, the double-bond in the 2,5-dihydrophosphole moiety was isomerized to give the 2,3-dihydro hetero ring. 2,5-Dihydrophosphole oxides are known to undergo double-bond rearrangement on thermolysis.[6,7] Starting from the isomeric mixture of tetrahydrophosphole oxide **4**, obtained by the catalytic hydrogenation of dihydrophosphole oxide **3** (Scheme 2), the corresponding spiro compound (**5**) was also formed as a mixture of diastereomers (**5-1** and **5-2**). Tetrahydrophosphole oxide **6**, obtained by the hydrogenation of dihydrophosphinine oxide **10**, was also used as an isomeric mixture (**6-1**, **6-2** and **6-3**) (Scheme 3) to afford product **7** as the mixture of diastereomers (**7-1**, **7-2** and **7-3**). The reaction of isomer **6-3** separated from the hydrogenated mixture by repeated column chromatography led to a single isomer (**7-3**) of product **7**.

The oxaphosphetes (**2**, **5**, **7** and **9**) were obtained in 71–86% yields after column chromatography and were characterised by ^{31}P, ^{1}H and ^{13}C NMR, as well as IR data. The ^{13}C NMR spectral parameters were most useful in showing that the phosphorus atom in all of the products (**2**, **5**, **7** and **9**) must be in the pentavalent pentacoordinated state, i.e. four $^{1}J_{PC}$ couplings were found in each case. The assignments were confirmed by ^{13}C NMR spectra obtained by the Attached Proton Test technique and, in the case of compounds **2** and **9**, by two-dimensional correlation diagrams, such as HMQC and HMBC spectra. The elemental composition of the

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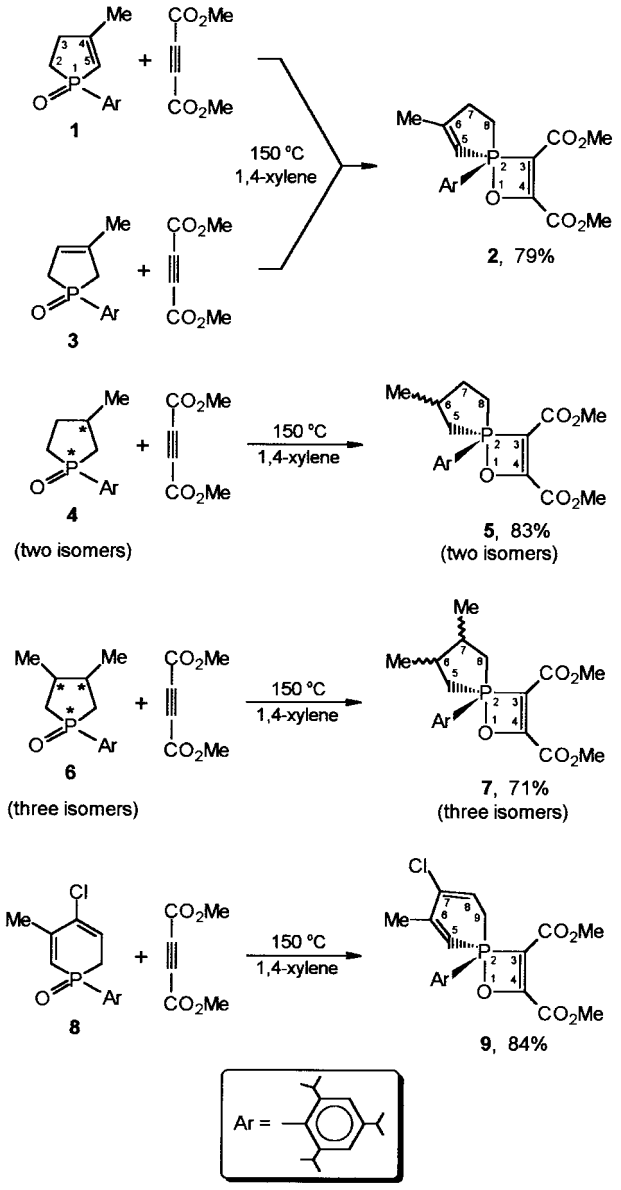
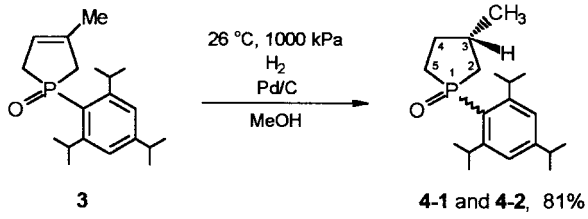


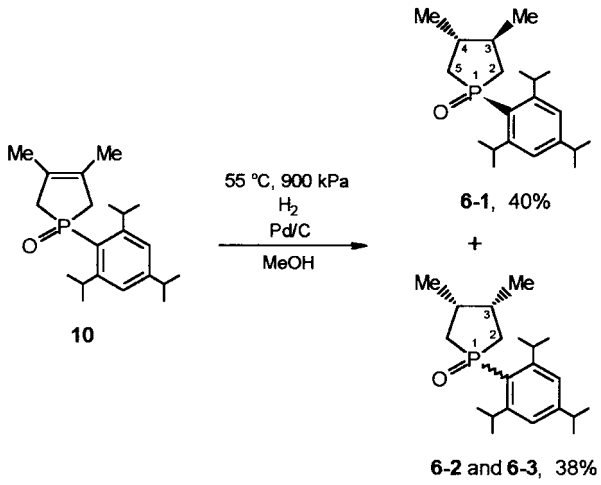
Scheme 1.

products (**2**, **5**, **7** and **9**) was supported by elemental analyses and by HRMS.

In the above structures with trigonal bipyramidal geometry at phosphorus (**2**, **5**, **7** and **9**), the oxygen atom must be in the apical position due to its electronegativity. The sterically demanding triisopropylphenyl substituent is preferably placed in the equatorial position to minimise the number of interactions with bonds at 90° during the pseudorotation



Scheme 2.



Scheme 3.

processes. Being small rings, the four- and five-membered ring may bridge one apical and one equatorial position per cycle, but the six-membered rings may also tend to prefer the apical–equatorial position to a diequatorial bridge. Considering backbonding, the sp^2 C(5) atom of products **2** and **9** should occupy the equatorial position, while the corresponding methylene moieties ($C(8)H_2$ and $C(9)H_2$, respectively) are, accordingly, placed in the apical position. It is noteworthy that, due to the rigid spiro ring system, the phosphorus atom of the oxaphosphetes (**2**, **5**, **7** and **9**) probably resists undergoing politopical rearrangements, consequently the products are racemates. This phenomenon will soon be explored. Simple pentacoordinated pentavalent P-species with five different substituents do not display optical activity due to the pseudorotations.[8] Heterocyclic systems containing the oxaphosphete moiety with a spiro phosphorus atom have not yet been published. A few examples of spirophosphoranes with the oxaphosphetane ring have, however, been described.[1,9]

This is the first case that the P=O group of phosphine oxides reacted with an acetylene moiety to afford the 1,2-oxaphosphete ring. As an analogous process, Japanese authors have recently described the interaction of azaylides (–P=N–) with DMAD to furnish 1,2-azaphosphetes as transient species.[10] Another valuable observation in this field is that the reaction of a phosphorus ylide with an isothiocyanate afforded the first example of a 1,2-thiaphosphete.[11]

The ability of the P=O group to react with DMAD is obviously the consequence of the presence of the electron releasing triisopropylphenyl substituent at the phosphorus atom, as the corresponding phenyl derivatives (**1′**, **3′**, **4′**, **6′** and **8′** containing a phenyl group instead of the triisopropylphenyl substituent) did not enter into [2+2] cycloaddition reaction with DMAD at 150°C.

We plan to study the mechanism of the new [2+2] cycloaddition by ab initio calculations. Already the PM3 semiempirical calculations, particularly well suited to computation of phosphorus containing systems,[12,13] are promising in suggesting that the oxaphosphete ring is

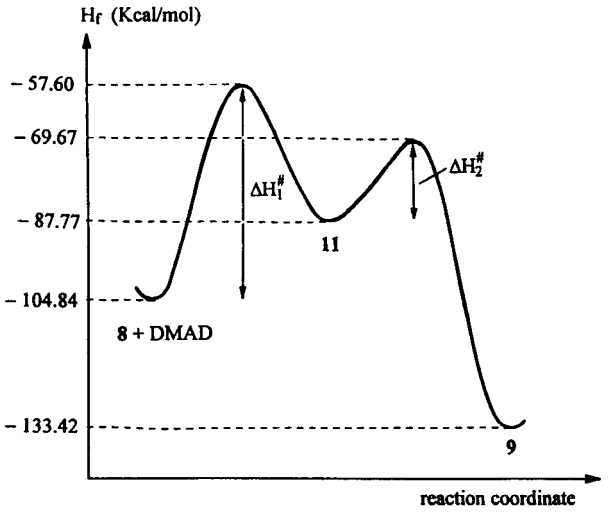
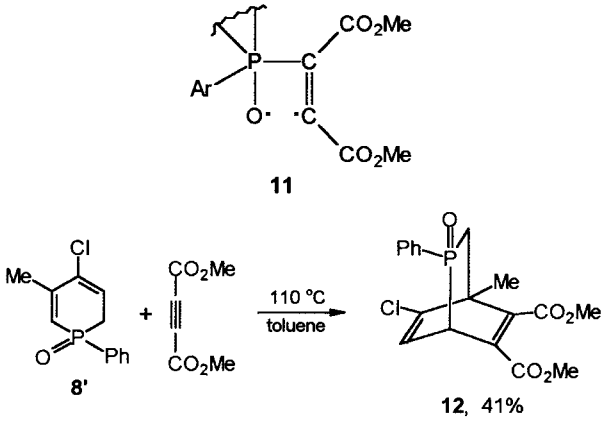


Figure 1. Energy profile in terms of heat of formation for the **8**+DMAD→**9** transformation calculated by the PM3 method.

constructed in a stepwise process through biradical intermediate **11** formed in the rate-determining step from the interaction of the phosphine oxide (**1**, **4**, **6** and **8**) and DMAD. Species **11** may be stabilised by fast recombination. The energy profile for the **8**→**9** transformation calculated on the basis of the values of heat of formation (H_f) for the starting materials (**8** and DMAD), intermediate **11**, product **9** and for the transient states leading to **11** and **9** is shown in Fig. 1. It can be seen that the enthalpy of activation for the rate-determining step is 47.24 Kcal/mol. The similar value for the cycloaddition of the phenyl-analogue (**8′** containing a phenyl group instead of the triisopropylphenyl substituent) was found to be 59.79 Kcal/mol, suggesting that the P-triisopropylphenyl compound (**8**) is more reactive in the [2+2] cycloaddition under discussion, than the P-phenyl counterpart ($\Delta\Delta H_f$=12.55 Kcal/mol). A recent study of ours on 1-(triisopropylphenyl)dihydrophosphinine oxide **8** revealed its unique properties that are the consequence of the presence of the sterically demanding P-substituent.[14] The steric bulk has a significant effect on the molecular geometry and hence on the electron distribution. The electron density, especially around the phosphorus atom, is also affected by the presence of the three electron releasing isopropyl groups in the aromatic ring.[14] It was also examined,



Scheme 4.[15]

why dihydrophosphinine oxide **8** did not react with DMAD in a [4+2] (Diels–Alder) fashion in a competitive way. It is recalled that the P-phenyl analogue (**8′**) easily underwent Diels–Alder cycloaddition with DMAD to afford phosphabicyclo[2.2.2]octadiene **12** (Scheme 4).[15] The comparative PM3 study on the [4+2] cycloaddition of dienes **8** and **8′** with DMAD suggested that the P-phenyl compound (**8′**) is much more reactive as compared to the triisopropylphenyl-derivative (**8**); the difference in the enthalpy of activation is as much as 11.93 Kcal/mol in favour of **8′**. It can be seen that the results of the PM3 calculations are in all aspects in accord with the preparative observations. Still, we wish to refine our results by extensive ab initio calculations. The scope and limitations of the above type [2+2] cycloaddition giving an entry to new oxaphosphetes will also be explored soon.

Conclusion

The unexpected [2+2] cycloaddition of the P=O group of 1-(2,4,6-triisopropylphenyl) P-hetereocycles with the acetylene moiety of DMAD gives an easy access to spirocyclic oxaphosphete derivatives, a completely new family of P-heterocycles. Theoretical calculations justified the novel [2+2] protocol that seems to be of general value for P-(2,4,6-trialkylphenyl) phosphine oxides.

Experimental

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.

The starting P-heterocycles (**3** and **8**) were synthesised according to our earlier procedures.[14,16] 2,3-Dihydrophosphole oxide **1** was obtained by the isomerisation of starting material **3** (see below). Compounds **4** and **6** were prepared by the catalytic hydrogenation of unsaturated derivatives **3** and **10** respectively (see below). Column chromatography was performed on Merck Kieselgel 60 (70–230 mesh). Composition of the fractions collected was monitored by ^{31}P NMR and/or TLC. The oily products were kept at 40°C and 0.05 mmHg for 2 h to give samples suitable for elemental analysis.

All calculations were performed using MOPAC 6.0[17] on a SGI R8000 workstation. Based on our good experience,[16] PM3 semiempirical parametrisation[12] was used for geometry optimisations and for the location of transition states for the [2+2] cycloaddition and the Diels–Alder reaction. Full geometry optimisations have been carried out at the UHF level. Transition states were located by the linear synchronous transit method and characterised through the correct number of negative eigenvalues of the energy second derivative matrix. Transition states having only one negative eigenvalue were finally subjected to frequency calculation.

4-Methyl-1-(2,4,6-triisopropylphenyl-)2,3-dihydro-1H-phosphole 1-oxide 1. A mixture of 2,5-dihydrophophole oxide **3** (0.70 g, 2.20 mmol) and 6% aqueous sodium hydroxide (12 mL) was kept at 130°C in a sealed tube for 9 days. After adding the contents of the tube to water (50 mL), the pH was adjusted to 3 by the addition of conc. hydrochloric acid and the mixture was extracted with chloroform (2×40 mL). The organic phase was dried (Na_2SO_4) and the solvent evaporated. The residue so obtained was purified by column chromatography on silica gel using 3% methanol in chloroform as the eluant to give product **1** (0.57 g, 81%) as a colourless oil. ^{31}P NMR ($CDCl_3$) δ 61.8; ^{13}C NMR ($CDCl_3$) δ_C 20.7 (J_{PC}=17.0 Hz, C_4-*C*H_3), 23.5 (J_{PC}=1.6 Hz, CH(*C*H_3)$_3$), 24.3 (CH(*C*H_3)$_2$), 24.9 (CH(*C*H_3)$_2$), 30.9 (J_{PC}=69.4 Hz, C_2), 31.8 (J_{PC}=5.1 Hz, $CHMe_2$), 33.6 (J_{PC}=8.6 Hz, C_3), 34.0 ($CHMe_2$), 122.0 (J_{PC}=10.7 Hz, $C_{3'}$), 123.4 (J_{PC}=98.1 Hz, C_5), 129.4 (J_{PC}=100.6 Hz, $C_{1'}$), 151.2 (J_{PC}=10.7 Hz, $C_{2'}$), 151.5 ($C_{4'}$), 161.3 (J_{PC}=25.5 Hz, C_4); ^1H NMR ($CDCl_3$) (1.24 (d, J=7.1 Hz, 12H, CH(C*H*$_3$)$_2$), 1.32 (d, J=6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 2.02 (s, 3H, C_4–CH_3), 2.84–2.93 (m, 1H, $CHMe_2$), 3.55-3.65 (m, 2H, $CHMe_2$), 6.26 (d, J=24.9 Hz, 1H, C_5–H), 7.08 (s, 2H, ArH); MS, *m*/*z* (rel. int.) 318 (M^+ 100), 303 (M–Me, 96), 43 (Pr, 13); HRMS calcd for $C_{20}H_{31}OP$ 318.2113, found 318.2105. Anal. calcd for $C_{20}H_{31}OP$: C, 75.42; H, 9.83. Found: C, 75.63; H, 10.13.

3-Methyl-1-(2,4,6-triisopropylphenyl-)2,3,4,5-tetrahydro-1H-phosphole 1-oxide 4. Dihydrophosphole oxide **3** (0.82 g, 2.58 mmol) in methanol (30 mL) was hydrogenated in the presence of 10% palladium on carbon (0.5 g) at 1000 kPa and 26°C until one equivalent of hydrogen was absorbed (ca 6 h). The suspension was filtered, the solvent evaporated and the residue purified by column chromatography on silica gel using 2% methanol in chloroform as the eluant to give 0.67 g (81%) of product **4** as a colourless oil consisting of 68% of the **4-1** isomer and 32% of the **4-2** isomer. The stereochemistry of isomers **4-1** and **4-2** was not determined. MS, *m*/*z* (rel. int.) 320 (M^+, 98), 305 (M−Me, 100), 277 (M−Pr, 28), 250 (ArPO, 12), 203 (Ar, 7); Anal. calcd for $C_{20}H_{33}OP$: C, 74.95; H, 10.4. Found: C, 75.30; H, 10.71; IR (film) 2960, 1603, 1463, 1166, 685 cm^{-1}.

4-1. ^{31}P NMR ($CDCl_3$) δ 60.6; ^{13}C NMR ($CDCl_3$) (21.2 (J_{PC}=10.9 Hz, C_3–Me), 23.8 (CH(*C*H_3)$_2$), 24.8 (CH(*C*H_3)$_2$), 25.4 (J_{PC}=2.7 Hz, CH(*C*H_3)$_2$), 32.4 (J_{PC}=4.7 Hz, $CHMe_2$), 32.8 (J_{PC}=6.3 Hz, C_4), 33.8 (J_{PC}=7.1 Hz, C_3), 34.3 ($CHMe_2$), 34.9 (J_{PC}=65.4 Hz, C_5), 42.0 (J_{PC}=66.6 Hz, C_2), 122.5 (J_{PC}=10.7 Hz, $C_{3'}$), 128.8 (J_{PC}=93.3 Hz, $C_{1'}$), 152.2 (J_{PC}=1.7 Hz, $C_{4'}$), 152.5 (J_{PC}=10.9 Hz, $C_{2'}$); ^1H NMR ($CDCl_3$) δ 1.21 (d, J=5.6 Hz, 3H, C_3–CH_3), 1.26 (d, J=6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.28 (d, J=6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, J=6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.84–2.94 (m, 1H, $CHMe_2$), 3.46–3.56 (m, 2H, $CHMe_2$), 7.08 (s, 2H, ArH).

4-2. ^{31}P NMR ($CDCl_3$) δ 59.9; ^{13}C NMR ($CDCl_3$) δ 21.3 (J_{PC}=15.0 Hz, C_3–Me), 23.8 (CH(*C*H_3)$_2$), 24.8 (CH(*C*H_3)$_2$), 25.4 (J_{PC}=2.7 Hz, CH(*C*H_3)$_2$), 32.3 (J_{PC}=3.7 Hz, $CHMe_2$), 32.6 (J_{PC}=5.1 Hz, C_4), 33.0 (J_{PC}=9.3 Hz, C_3), 34.3 ($CHMe_2$), 34.3 (J_{PC}=66.4 Hz, C_5), 42.5 (J_{PC}=64.5 Hz, C_2), 122.5 (J_{PC}=10.7 Hz, $C_{3'}$), 128.9 (J_{PC}=93.6 Hz, $C_{1'}$), 152.2 (J_{PC}=1.7 Hz, $C_{4'}$), 152.5 (J_{PC}=10.9 Hz, $C_{2'}$); ^1H NMR ($CDCl_3$) δ 1.15 (d, J=6.1 Hz, 3H, C_3–CH_3), 1.26 (d, J=6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.28 (d, J=6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, J=6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.84–2.94 (m, 1H, $CHMe_2$), 3.46–3.56 (m, 2H, $CHMe_2$), 7.08 (s, 2H, ArH).

3,4-Dimethyl-1-(2,4,6-triisopropylphenyl-)2,3,4,5-tetrahydro-1H-phosphole 1-oxides 6-1, 6-2 and 6-3. Dihydrophosphole oxide **10** (2.2 g, 6.62 mmol) in methanol (80 mL) was hydrogenated in the presence of 10% palladium on carbon (1.2 g) at 900 kPa and 55°C until one equivalent of hydrogen was consumed. The suspension was filtered, the solvent evaporated and the oily residue purified by column chromatography on silica gel using 2% methanol in chloroform as the eluant to afford 1.72 g (78%) of the oily product as the mixture of isomer **6-1** (51%), isomer **6-2** (27%) and isomer **6-3** (22%). The stereochemistry of isomers **6-2** and **6-3** was not determined. MS, *m*/*z* (rel. int.) 334 (M^+, 73), 319 (M−Me, 100), 291 (M−Pr+H, 46), 250 (ArPO, 16), 203 (Ar, 8); HRMS calcd for $C_{21}H_{35}OP$ 334.2426, found 334.2409; IR (film) 2959, 1602, 1461, 1169, 732 cm^{-1}. Repeated column chromatography of the isomeric mixture (as above) afforded isomer **6-3** in a pure form. The synthesis was repeated several times to collect 0.19 g of isomer **6-3**.

6-1. ^{31}P NMR ($CDCl_3$) δ 52.9; ^{13}C NMR ($CDCl_3$) δ 19.0 (J_{PC}=17.7 Hz, C_3–Me[a]), 19.1 (J_{PC}=13.0 Hz, C_4–Me[a]), 23.7 (CH(*C*H_3)$_2$), 25.4 (CH(*C*H_3)$_2$), 32.3 (J_{PC}=5.0 Hz, $CHMe_2$), 34.2 ($CHMe_2$), 39.3 (J_{PC}=8.0 Hz, C_3^b), 40.0 (J_{PC}=5.3 Hz, C_4^b), 43.3 (J_{PC}=66.0 Hz, C_2^c), 43.6 (J_{PC}=66.4 Hz, C_5^c), 122.4 (J_{PC}=10.6 Hz, $C_{3'}$), 128.7 (J_{PC}=94.7 Hz, $C_{1'}$), 152.1 ($C_{4'}$), 152.4 (J_{PC}=11.0 Hz, $C_{2'}$); [a-c]tentative assignments.

6-2. ^{31}P NMR ($CDCl_3$) δ 61.0; ^{13}C NMR ($CDCl_3$) δ 15.9 (J_{PC}=7.5 Hz, C_3–Me), 23.7 (CH(*C*H_3)$_2$), 24.6 (CH(*C*H_3)$_2$), 32.5 (J_{PC}=5.1 Hz, $CHMe_2$), 34.2 ($CHMe_2$), 36.8 (J_{PC}=7.0 Hz, C_3), 40.8 (J_{PC}=65.2 Hz, C_2), 122.4 (J_{PC}=10.6 Hz, $C_{3'}$).

6-3. ^{31}P NMR ($CDCl_3$) δ 57.9; ^{13}C NMR ($CDCl_3$) δ 16.4 (J_{PC}=9.0 Hz, C_3–Me), 23.8 (CH(*C*H_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 32.6 (J_{PC}=5.4 Hz, $CHMe_2$), 34.3 ($CHMe_2$), 35.2 (J_{PC}=7.0 Hz, C_3), 40.6 (J_{PC}=65.5 Hz, C_2), 122.6 (J_{PC}=10.8 Hz, $C_{3'}$), 129.8 (J_{PC}=94.4 Hz, $C_{1'}$), 152.0 (J_{PC}=11.3 Hz, $C_{2'}$), 152.1 ($C_{4'}$); ^1H NMR ($CDCl_3$) δ 0.89 (d, J=6.5 Hz, 6H, C_3–CH_3), 1.25 (d, J=7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, J=6.5 Hz, 12H, CH(C*H*$_3$)$_2$), 2.84–2.92 (m, 1H, $CHMe_2$), 3.45–3.55 (m, 2H $CHMe_2$), 7.07 (s, 2H, ArH).

General method for the preparation of oxaphosphetes 2, 5, 7 and 9

A solution of P-heterocycle **1**, **4**, **6** or **8** (2.0 mmol) and DMAD (0.31 mL, 2.50 mmol) in dry 1,4-xylene (5 mL) was kept at 150°C for 8 days in a sealed tube. The volatile components were removed in vacuo, first at 20 mmHg and then at 0.2 mmHg. 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 (**2**, **5**, **7** and **9**) as pale brown oils.

3,4-Di(methoxycarbonyl)-6-methyl-2-(2′,4′,6′-triisopropylphenyl)-1,2-oxaphosphaspiro[3.4]octa-3,5-diene 2. Yield: 79%; ^{31}P NMR ($CDCl_3$) δ 39.5; ^{13}C NMR ($CDCl_3$) δ 20.7 (J_{PC}=18.0 Hz, C_6–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_8), 32.0 (J_{PC}=6.3 Hz, $CHMe_2$), 34.3 ($CHMe_2$), 35.7 (J_{PC}=6.8 Hz, C_7), 50.7 (CH_3O), 51.8 (CH_3O), 76.1 (J_{PC}=103.0 Hz, C_3), 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_6), 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_4); ^{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); HRMS calcd for $C_{26}H_{37}O_5P$ 460.2379, found 460.2381. Anal. calcd for $C_{26}H_{37}O_5P$: C, 67.79; H, 8.11. Found: C, 67.44; H, 8.33; IR (film) 2958, 1739, 1559, 1436, 1087, 773 cm^{-1}.

The reaction of dihydrophosphole oxide **3** with DMAD under the conditions provided in the General method also furnished product **2**. Yield: 86%; ^{31}P NMR ($CDCl_3$) δ 39.4.

3,4-Di(methoxycarbonyl)-6-methyl-2-(2′,4′,6′-triisopropylphenyl)-1,2-oxaphosphaspiro[3.4]oct-3-ene (5). The starting tetrahydrophosphole oxide (**4**) was used as a 68–32% mixture of two diastereomers (**4-1** and **4-2**). Yield: 83%; isomeric composition: 67% of **5-1** and 33% of **5-2**; HRMS (FAB) calcd for $C_{26}H_{40}O_5P$ 463.2613, found 463.2633. Anal. calcd for $C_{26}H_{39}O_5P$: C, 67.50; H, 8.52. Found: C, 67.17; H, 8.88; IR (film) 2957, 1738, 1556, 1434, 1078, 731 cm^{-1}.

5-1. ^{31}P NMR ($CDCl_3$) δ 32.7; ^{13}C NMR ($CDCl_3$) δ 20.0 (J_{PC}=11.7 Hz, C_6–Me), 23.6 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 31.9 (J_{PC}=54.4 Hz, C_8), 31.9 (J_{PC}=5.7 Hz, $CHMe_2$), 33.6 (J_{PC}=6.2 Hz, C_7), 34.1 ($CHMe_2$), 34.2 (J_{PC}=55.5 Hz, C_5), 34.6 (J_{PC}=6.1 Hz, C_6), 50.6 (MeO), 51.6 (MeO), 73.2 (J_{PC}=98.1 Hz, C_3), 120.9 (J_{PC}=85.6 Hz, $C_{1'}$), 123.3 (J_{PC}=11.6 Hz, $C_{3'}$), 152.8 (J_{PC}=2.8 Hz, $C_{4'}$), 153.5 (J_{PC}=11.1 Hz, $C_{2'}$), 167.2 (J_{PC}=14.0 Hz, C=O), 167.9 (J_{PC}=14.6 Hz, C=O), 183.1 (J_{PC}=6.2 Hz, C_4); ^{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).

5-2. ^{31}P NMR ($CDCl_3$) δ 32.0; ^{13}C NMR ($CDCl_3$) δ 20.5 (J_{PC}=15.8 Hz, C_6–Me), 23.6 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 27.2 (J_{PC}=55.2 Hz, C_8), 31.8 (J_{PC}=6.5 Hz, $CHMe_2$), 32.5 (J_{PC}=3.7 Hz, C_7), 33.6 (J_{PC}=10.9 Hz, C_6), 34.1 ($CHMe_2$), 38.7 (J_{PC}=56.1 Hz, C_5), 50.6 (MeO), 51.6 (MeO), 72.9 (J_{PC}=98.3 Hz, C_3), 120.8 (J_{PC}=86.0 Hz, $C_{1'}$), 123.4 (J_{PC}=11.1 Hz, $C_{3'}$), 152.8 (J_{PC}=2.8 Hz, $C_{4'}$), 153.5 (J_{PC}=11.1 Hz, $C_{2'}$), 167.2 (J_{PC}=14.3 Hz, C=O), 167.9 (J_{PC}=14.6 Hz, C=O), 183.1 (J_{PC}=6.2 Hz, C_4); ^{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).

3,4-Di(methoxycarbonyl)-6,7-dimethyl-2-(2′,4′,6′-triisopropylphenyl)-1,2-oxaphosphaspiro(3.4(oct-3-ene (7). The starting tetrahydrophosphole oxide (**6**) was used as a 51-27-22% mixture of three diastereomers (**6-1**, **6-2** and **6-3**). Yield: 71%; isomeric composition: 57% of **7-1**, 23% of **7-2** and 18% of **7-3**; HRMS (FAB) calcd for $C_{27}H_{42}O_5P$ 477.2770, found 477.2769; IR (film) 2957, 1739, 1556, 1435, 1084, 753 cm^{-1}.

7-1. ^{31}P NMR ($CDCl_3$) δ 23.9; ^{13}C NMR ($CDCl_3$) δ 18.2 (J_{PC}=13.4 Hz, C_6–Me[a]), 18.3 (J_{PC}=19.3 Hz, C_7–Me[a]), 24.1 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 31.8 (J_{PC}=8.1 Hz, $CHMe_2$), 34.1 ($CHMe_2$), 35.0 (J_{PC}=54.6 Hz, C_5^b), 40.1 (J_{PC}=55.8 Hz, C_8^b), 40.2 (J_{PC}=8.5 Hz, C_6^c), 40.6 (J_{PC}=4.3 Hz, C_7^c), 50.6 (MeO), 51.6 (MeO), 73.3 (J_{PC}=98.6 Hz, C_4), 120.9 (J_{PC}=85.9 Hz, $C_{1'}$), 123.3 (J_{PC}=(10 $C_{3'}$), 152.8 ($C_{4'}$), 153.5 (J_{PC}=11.0 Hz, $C_{2'}$), 167.2 (J_{PC}=14.6 Hz, C=O), 167.9 (J_{PC}=14.8 Hz, C=O), 183.1 (C_4); [a–c] tentative assignments.

7-2. ^{31}P NMR ($CDCl_3$) δ 32.5; ^{13}C NMR ($CDCl_3$) δ 15.0 (J_{PC}=7.9 Hz, C_6–Me), 23.5 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 31.8 (J_{PC}=6.1 Hz, $CHMe_2$), 34.1 ($CHMe_2$), 35.0 (J_{PC}=54.6 Hz, C_5), 38.1 (J_{PC}=6.1 Hz, C_6), 50.6 (MeO), 51.6 (MeO), 72.8 (J_{PC}=98.4 Hz, C_4), 121.3 (J_{PC}=85.7 Hz, $C_{1'}$), 123.4 (J_{PC}=11.7 Hz, $C_{3'}$), 152.8 ($C_{4'}$), 153.2 (J_{PC}=11.1 Hz, $C_{2'}$), 167.3 (J_{PC}=14.5 Hz, C=O), 167.9 (J_{PC}=14.8 Hz, C=O), 183.0 (C_4).

7-3. ^{31}P NMR ($CDCl_3$) δ 29.0; ^{13}C NMR ($CDCl_3$) δ 16.2 (J_{PC}=10.5 Hz, C_6–Me), 23.5 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 31.8 (J_{PC}=6.1 Hz, $CHMe_2$), 34.1 ($CHMe_2$), 35.0 (J_{PC}=54.6 Hz, C_5), 35.6 (J_{PC}=6.7 Hz, C_6), 50.6 (MeO), 51.6 (MeO), 72.8 (J_{PC}=98.4 Hz, C_4), 121.3 (J_{PC}=85.7 Hz, $C_{1'}$), 123.4 (J_{PC}=11.7 Hz, $C_{3'}$), 152.8 ($C_{4'}$), 153.3 (J_{PC}=11.1 Hz, $C_{2'}$), 167.3 (J_{PC}=14.5 Hz, C=O), 167.9 (J_{PC}=14.8 Hz, C=O), 183.1 (C_4); ^{1}H NMR ($CDCl_3$) δ 0.96 (d, J=6.5 Hz, 6H, C–CH_3), 1.25 (d, J=7.0 Hz, 6H, $CH(CH_3)_2$), 1.28 (d, J=6.5 Hz, 12H, $CH(CH_3)_2$), 2.84–2.94 (m, 1H, $CHMe_2$), 3.47-3.58 (m, 2H, $CHMe_2$), 3.59 (s, OCH_3), 3.77 (s, OCH_3), 7.10 (s, 2H, ArH).

7-3 was also prepared from isomer **6-3** separated by repeated column chromatography in a pure form (^{31}P NMR ($CDCl_3$) δ 29.1).

7-Chloro-3,4-di(methoxycarbonyl)-6-methyl-2-(2′,4′,6′-triisopropylphenyl)-1,2-oxaphosphaspiro[3.5]nona-3,5,7,-triene (9). Yield: 84%; ^{31}P NMR ($CDCl_3$) δ 24.0; ^{13}C NMR ($CDCl_3$) δ 16.2 (J_{PC}=17.5 Hz, C_6(Me), 23.6 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 30.0 (J_{PC}=62.8 Hz, C_9), 31.8 (J_{PC}=6.7 Hz, $CHMe_2$), 34.0 ($CHMe_2$), 50.6 (CH_3O), 51.5 (CH_3O), 74.4 (J_{PC}=107.4 Hz, C_3), 119.3 (J_{PC}=13.7 Hz, C_8), 121.6 (J_{PC}=94.3 Hz, $C_{1'}$), 122.5 (J_{PC}=85.0 Hz, C_5), 123.2 (J_{PC}=

11.9 Hz, $C_{3'}$), 140.0 (J_{PC}=14.1 Hz, C_7), 152.7 (J_{PC}=11.3 Hz, $C_{2'}$), 153.0 ($C_{4'}$), 155.4 (J_{PC}=14.8 Hz, C_6), 166.4 (J_{PC}=14.8 Hz, C=O), 167.5 (J_{PC}=15.6 Hz, C=O), 182.4 (J_{PC}=6.1 Hz, C_4); ^{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); HRMS calcd for $C_{27}H_{36}^{35}ClO_5P$ 506.1989, found 506.1941. Anal. calcd for $C_{27}H_{36}ClO_5P$: C, 63.95; H, 7.17. Found: C, 64.20; H, 7.34; IR (film) 2956, 1731, 1556, 1434, 1088, 755 cm^{-1}.

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