# The reaction of 1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine 1-oxides with dimethyl acetylenedicarboxylate; a [4+2] or a [2+2] cycloaddition?

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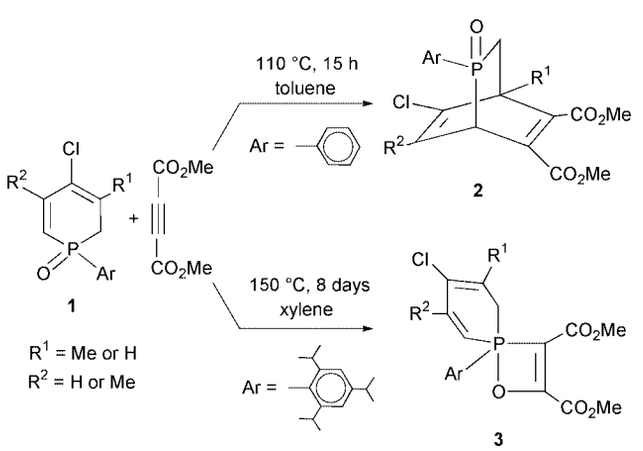
The reaction of dimethyl acetylenedicarboxylate (DMAD) with 3- and 5-methyl-1-aryl-1,2-dihydrophosphinine oxides (**6a** and **6b**, respectively) obtained by the two-step ring enlargement of 2,5-dihydro-1*H*-phosphole oxide **4** followed different routes. Isomer **6a** entered into a [4+2] cycloaddition with DMAD giving, although in low yield, phosphabicyclooctadiene **7**, while **6b** reacted with the acetylene moiety according to a recently discovered [2+2] protocol to afford spirocyclic oxaphosphete **8**. The reaction of isomers **6a** and **6b** with *N*-phenylmaleimide under forcing conditions furnished the expected Diels–Alder cycloadducts (**10a** and **10b**, respectively). Hence, depending on the reactant, isomer **6b** displayed a dual reactivity.

## Introduction

The 1,2-dihydrophosphinine oxides are excellent dienes in Diels–Alder reactions leading to 2-phosphabicyclo[2.2.2]octene derivatives[1–8] that are precursors of low-coordinate fragments, methylenephosphine oxides [YP(O)$CH_2$, Y = Ph, RO] useful in phosphorylations.[2–5,7–11] It was, however, surprising to find that whilst the reaction of the phenyldihydrophosphinine oxides (**1**, Ar = Ph) with dimethyl acetylenedicarboxylate (DMAD) afforded the phosphabicyclooctadiene oxides **2** expected,[2] the cycloaddition of the 2,4,6-triisopropylphenyl derivative (**1**, Ar = 2,4,6-triisopropylphenyl) with DMAD took place according to a [2+2] protocol to furnish spirocyclic oxaphosphate **3**[12,13] (Scheme 1). This was the first case in which the cycloaddition of the P=O group with an acetylene moiety had been observed to take place. The unusual reactivity of the P=O group that is obviously the consequence of the presence of the electron-releasing *P*-aryl substituent was investigated by semi-empirical calculations.[13] It is a challenge for us to explore the scope and limitations of this cycloaddition reaction giving an entry to valuable oxaphosphetes that are the unsaturated derivatives of the well-known Wittig intermediates, oxaphosphetanes.[14] In this paper, we discuss how the *P*-2,4,6-trimethylphenyl substituent affects the reactivity of the double-bond isomers of the dihydrophosphinine oxide in cycloaddition reactions.




**Scheme 1**

## Results and discussion

The model compounds, the dihydrophosphinine oxides (**6a** and **6b**) were synthesised by the two-step ring enlargement of dihydrophosphole oxide **4**. According to our procedure elaborated for the ring expansion of other dihydrophosphole oxides,[15–17] dichlorocarbene generated in a liquid–liquid two-phase system was added onto the double bond of the starting compound **4**, resulting in the formation of 3-phosphabicyclo-[3.1.0]hexane 3-oxide **5** as a mixture of two diastereomers (**5a** and **5b**) (Scheme 2). The diastereomers **5a** and **5b** were separated by repeated column chromatography; stereostructure of the isomers **5a** and **5b** was substantiated on the basis of stereospecific $^3J_{PC}$ couplings[18,19] detected for C-6 of the adducts **5**. The $^3J_{PC}$ coupling of 8.4 Hz suggested the *trans* disposition of the *P*-aryl substituent and the dichlorocyclopropane ring (**5a**), while the value of 15.5 Hz confirmed structure **5b**. In the second step, the dichlorocyclopropane ring of adducts **5a** and **5b** was opened up thermally to afford dihydrophosphinine oxide **6** as an 80–20% mixture of double-bond isomers **6a** and **6b** (Scheme 2). All new compounds (**5a**, **5b**, **6a** and **6b**) were characterised by $^{31}P$, $^{13}C$ and $^1H$ NMR, as well as mass spectroscopic methods. The $^{13}C$ NMR assignments were confirmed by spectra obtained by the Attached Proton Test (APT) technique. The elemental composition was confirmed in all cases by high-resolution mass spectrometry (HR-MS).

In the first place, an 80–20% mixture of dihydrophosphinine oxides **6a** and **6b** was treated with DMAD in boiling toluene for

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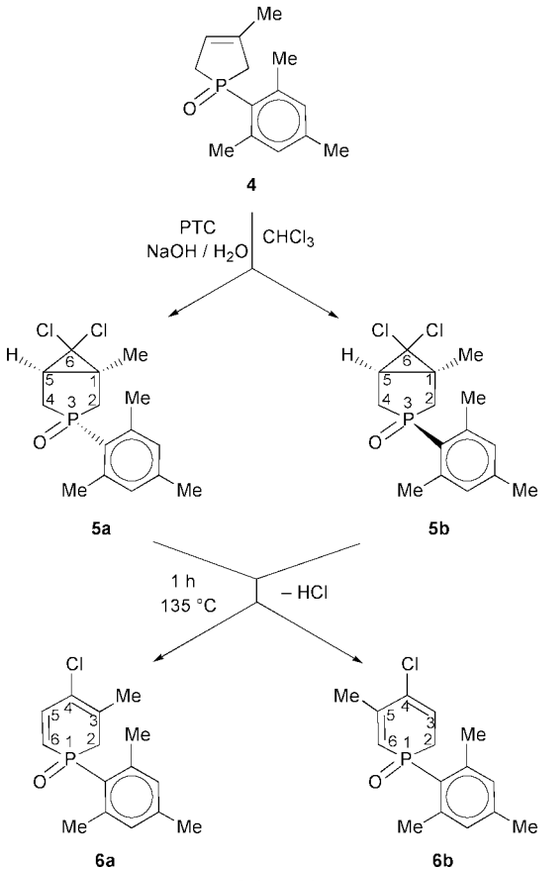
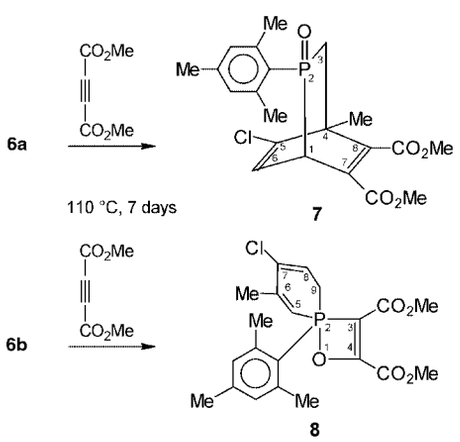



**Scheme 2**

7 days. $^{31}$P NMR spectroscopy of the crude mixture showed the presence of a major (89%) and a minor (11%) component at $\delta_P$ 26.3 and 41.9, respectively. After separation by repeated column chromatography, the species at $\delta_P$ 42.0 was assigned as the 2-phosphabicyclo[2.2.2]octa-5,7-diene **7**, while the component with $\delta_P$ 26.4 was identified as the spirocyclic oxaphosphete **8** (Scheme 3). The structure of the phosphabicyclooctadiene **7**

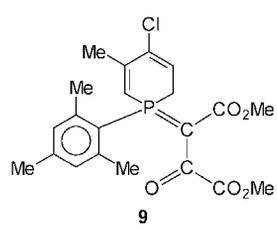



**Scheme 3** Non-systematic numbering for spiro-system **8**.

was confirmed by $^{31}$P and $^{1}$H NMR, as well as EI, including high-resolution electron impact (HR-EI) mass spectroscopy. The *P*-phenyl analogues described earlier exhibited $^{31}$P NMR chemical shifts in the range of 38.5–42.9.[2] The only olefinic signal, at $\delta_H$ 6.58 ($J_1 = J_2 = 6.2$ Hz), in the $^{1}$H NMR spectrum of **7** represented $C^6$–H. The mass spectroscopic fragmentation involving the loss of the bridging moiety was also characteristic of the earlier phosphabicyclooctadienes.[9] The structure of isomeric oxaphosphete **8** obtained in 86% yield was supported by $^{31}$P, $^{13}$C and $^{1}$H NMR, as well as fast-atom bombardment (FAB) mass spectroscopy. The $\delta_P$-value of 26.4 matched well the value of 24.0 reported for the *P*-2,4,6-triisopropylphenyl analogue.[13] The $^{13}$C NMR spectrum was convincing in revealing four $^{1}J_{PC}$ couplings (61.0–107.7 Hz) due to the pentavalent pentacoordinate phosphorus atom. The other spectral parameters of product **8** also showed close resemblance to those of other oxaphosphetes.[13] The elemental composition of compound **8** was confirmed by HR-MS.

It is an interesting and even surprising observation that the two double-bond isomers (**6a** and **6b**) display different reactivity in reaction with DMAD; isomer **6a** reacts in the usual [4+2] fashion, while the cycloaddition of isomer **6b** follows a [2+2] protocol. As a consequence of the steric hindrance due to the 2,4,6-trimethylphenyl group, the Diels–Alder reactivity of the 3-methyldihydrophosphinine oxide **6a** is suppressed. This is well demonstrated by the fact that, although phosphabicyclooctadiene **7** is derived from the major dihydrophosphinine isomer (**6a**), its yield was only 9%. At the same time, the electron distribution in the -MeCH=CH–P(O)- moiety of double-bond isomer **6b** enables the P=O group to take part in a [2+2] cycloaddition reaction. In the few examples of the [2+2] cycloadditions described, the critical role of the electron-releasing 2,4,6-triisopropylphenyl substituent was clearly established.[13] In dihydrophosphinine oxide **6b**, the electron-releasing ability of the trimethylphenyl ring needs to be completed by the effect of a conjugated methyl group to favour the [2+2] cycloaddition.

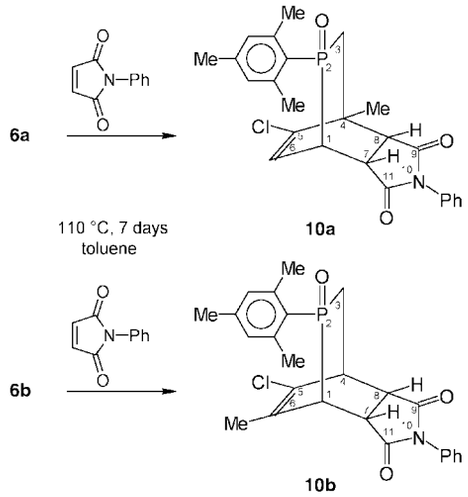
The formation of 2,4,6-trimethylphenyl derivative **8** is obviously an extension of the recently described reaction. Further work to utilise other phosphine oxides, as well as to carry out *ab initio* calculations to evaluate the mechanism, is in progress. The reactivity of the oxaphosphetes is also to be studied; the possibility for rearrangement of the oxaphosphetes to the corresponding phosphoranes (*i.e.*, **8** to **9**) will be explored.




**9**

Finally, we wished to test the [4+2] reactivity of dihydrophosphinine oxide isomers **6a** and **6b** in reaction with *N*-phenyl maleimide (NPMI). The diene components (**6a** and **6b**) were consumed only after a prolonged reaction time (7 days at 110 °C). Starting from the 4 : 1 mixture of isomers **6a** and **6b**, the expected phosphabicyclooctenes **10a** and **10b** were obtained in a 22 : 78% ratio after flash column chromatography (Scheme 4). As can be seen from the change in the isomeric ratio, the reactivity of the 3-methyldihydrophosphinine oxide **6a** is much more suppressed than that of the 5-methyl isomer **6b**. Much of **6a** may have undergone polymerisation as was suggested by the presence of the insoluble material formed. The Diels–Alder cycloadducts **10a** and **10b** obtained in 23% yield were characterised by $^{31}$P, $^{13}$C and $^{1}$H NMR, as well as mass spectroscopic methods. The $^{13}$C NMR assignment was confirmed by the APT technique. Spectral parameters of products **10a** and **10b** showed close resemblance to analogous derivatives described earlier.[7,8] The elemental composition of cycloadducts **10a** and **10b** was supported by HR-FAB.

It can be seen that both double-bond isomers **6a** and **6b** could enter into a [4+2] cycloaddition with NPMI, which is a better dienophile than DMAD. These cycloadditions, especially that of isomer **6a**, were not, however, too efficient due to the steric hindrance brought about by the presence of the trimethylphenyl substituent.




**Scheme 4** Non-systematic numbering scheme for adducts **10a**, **10b**.

To summarise our results, the 3-methyl-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine oxide **6a** displays a suppressed [4+2] reactivity with both DMAD and NPMI. At the same time, the 5-methyl counterpart **6b** encounters a dual reactivity; a [2+2] cycloaddition was observed with DMAD, but the usual [4+2] reaction took place with NPMI.

## Experimental

The $^{31}$P, $^{13}$C and $^{1}$H NMR spectra were taken on a Bruker DRX-500 instrument operating at 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% $H_3PO_4$ or $SiMe_4$ (TMS). *J*-Values are given in Hz. Mass spectra were obtained on a MS-902 or on a ZAB-2SEQ spectrometer at 70 eV. The IR spectrum of compound **8** was measured on a Perkin-Elmer 1600 spectrometer with a Fourier transformer.

3-Methyl-1-(2,4,6-trimethylphenyl)-2,5-dihydro-1*H*-phosphole 1-oxide **4** was prepared from 1-chloro-3-methyl-2,5-dihydro-1*H*-phosphole[20] and 2,4,6-trimethylphenylmagnesium bromide followed by oxidation as described for the synthesis of other aryl-dihydrophosphole oxides.[21] $^{31}$P NMR ($CDCl_3$) $\delta$ 60.8; MS, *m/z* (rel. int.) 234 ($M^+$, 100%), 219 (M − 15, 32), 119 (Ar, 48).

### 6,6-Dichloro-1-methyl-3-(2,4,6-trimethylphenyl)-3-phosphabicyclo[3.1.0]hexane 3-oxides 5a and 5b

To a solution of 6.0 g (25.6 mmol) of dihydrophosphole **4** and 1.10 g (4.84 mmol) of benzyltriethylammonium chloride (TEBAC) in 120 ml of abs. chloroform was added dropwise a solution of 44 g (1.10 mol) of sodium hydroxide in 48 ml of water. The mixture was stirred and heated for 4 h. After filtration and separation, the organic phase was made up to its original volume and 1.10 g (4.84 mmol) of TEBAC was added. The reaction mixture was treated with a second portion of aq. sodium hydroxide as above. Flash column chromatography of the crude product obtained after evaporation of the organic phase (silica gel; 3% methanol in chloroform) afforded the product as a 72–28% mixture of isomers **5a** and **5b** in 84% yield. The isomers were separated by repeated column chromatography using the same adsorbent and eluant, as above.

**5a**: Yield 1.7 g (21%); $^{31}$P NMR ($CDCl_3$) $\delta$ 80.7; $^{13}$C NMR ($CDCl_3$) $\delta$ 20.9 ($C^{4'}$-Me), 21.9 ($J$ = 7.3, $C^1$-Me), 23.5 ($J$ = 3.4, $C^{2'}$-Me), 33.4 ($J$ = 64.5, $C^4$), 36.0 ($J$ = 9.5, $C^1$), 37.3 ($J$ = 7.6, $C^5$), 38.8 ($J$ = 64.5, $C^2$), 71.7 ($J$ = 8.4, $C^6$), 127.5 ($J$ = 85.9, $C^{1'}$), 131.1 ($J$ = 11.0, $C^{3'}$), 141.5 ($J$ = 10.7, $C^{2'}$), 141.6 ($J$ = 2.1, $C^{4'}$); $^{1}$H NMR ($CDCl_3$) $\delta$ 1.48 (s, 3H, $C^{4'}$-Me), 2.29 (s, 3H, $C^1$-Me), 2.57 (s, 6H, $C^{2'}$-Me); MS, *m/z* (rel. int.) 316 ($M^+$, 10%), 301 (M − 15, 6), 281 (M − 35, 100), 245 (281 − 36, 52), 165 (ArPO − H, 43), 119 (Ar, 30); HR-MS, $M^+_{found}$ = 316.0562. $C_{15}H_{19}Cl_2OP$ requires *M*, 316.0551 for the $^{35}$Cl isotopes.

**5b**: Yield 0.65 g (8%); $^{31}$P NMR ($CDCl_3$) $\delta$ 79.1; $^{13}$C NMR ($CDCl_3$) $\delta$ 20.6 ($C^{4'}$-Me), 21.2 ($J$ = 5.0, $C^1$-Me), 23.0 ($J$ = 3.7, $C^{2'}$-Me), 34.0 ($J$ = 66.7, $C^4$), 35.8 ($J$ = 8.4, $C^1$), 36.3 ($J$ = 7.1, $C^5$), 40.1 ($J$ = 66.8, $C^2$), 72.2 ($J$ = 15.5, $C^6$), 128.6 ($J$ = 89.3, $C^{1'}$), 129.8 ($J$ = 10.8, $C^{3'}$), 139.7 ($J$ = 10.2, $C^{2'}$), 141.1 ($J$ = 1.6, $C^{4'}$); $^{1}$H NMR ($CDCl_3$) $\delta$ 1.75 (s, 3H, $C^{4'}$-Me), 2.28 (s, 3H, $C^1$-Me), 2.55 (s, 6H, $C^{2'}$-Me); MS, *m/z* (rel. int.) 316 ($M^+$, 19%), 301 (M − 15, 21), 281 (M − 35, 90), 245 (281 − 36, 100), 165 (ArPO − H, 39), 119 (Ar, 33); HR-MS, $M^+_{found}$ = 316.0559. $C_{15}H_{19}Cl_2OP$ requires *M*, 316.0551 for the $^{35}$Cl isotopes.

### 4-Chloro-3- and -5-methyl-1-(2,4,6-trimethylphenyl)-1,2-dihydrophosphinine 1-oxides 6a and 6b

A sample of 0.71 g (2.24 mmol) of dichlorocarbene adduct **5a** was heated at 135 °C in a vial for 1 h until the evolvement of hydrochloric acid ceased. The crude product so obtained was purified by column chromatography (as above) to give 0.35 g (56%) of the product as an 80–20% mixture of double-bond isomers **6a** and **6b**. A similar result was obtained by thermolysis of the 72–28% mixture of **5a** and **5b**. MS, *m/z* (rel. int.) 280 ($M^+$, 82%), 245 (M − 35, 100), 119 (Ar, 24); HR-MS, $M^+_{found}$ = 280.0798. $C_{15}H_{18}ClOP$ requires *M*, 280.0784 for the $^{35}$Cl isotope.

**6a**: $^{31}$P NMR ($CDCl_3$) $\delta$ 18.8; $^{13}$C NMR ($CDCl_3$) $\delta$ 21.0 ($C^{4'}$-Me), 23.3 ($C^{2'}$-Me), 23.5 ($J$ = 4.8, $C^3$-Me), 37.5 ($J$ = 68.8, $C^2$), 121.7 ($J$ = 91.8, $C^6$), 124.0 ($J$ = 20.2, $C^3$), 124.7 ($J$ = 104.9, $C^{1'}$), 131.2 ($J$ = 11.8, $C^{3'}$), 131.5 ($J$ = 9.6, $C^4$), 140.6 ($C^5$), 142.0 ($C^{4'}$), 142.9 ($J$ = 10.8, $C^{2'}$); $^{1}$H NMR ($CDCl_3$) $\delta$ 2.10 (s, 3H, $C^3$-Me), 2.30 (s, 3H, $C^{4'}$-Me), 2.51 (s, 6H, $C^{2'}$-Me), 6.36 (dd, $^2J_{PH}$ = $^3J_{HH}$ = 12.8, 1H, $C^6$-H), 6.79 (dd, $^3J_{PH}$ = 34.9, $^3J_{HH}$ = 12.8, 1H, $C^5$-H).

**6b**: $^{31}$P NMR ($CDCl_3$) $\delta$ 17.5; $^{13}$C NMR ($CDCl_3$) $\delta$ 21.0 ($C^{4'}$-Me), 23.3 ($C^{2'}$-Me), 25.1 ($J$ = 13.2, $C^5$-Me), 31.9 ($J$ = 68.7, $C^2$), 121.3 ($J$ = 95.4, $C^6$), 123.8 ($J$ = 10.1, $C^3$), 145.8 ($C^5$).

### Cycloaddition of dihydrophosphinine oxides 6a and 6b with DMAD

The solution of 0.46 g (1.64 mmol) of the 4 : 1 isomeric mixture of dihydrophosphinine oxides **6a** and **6b** and 0.25 ml (2.03 mmol) of DMAD in 6 ml of toluene was stirred at the boiling point for 7 days. The crude mixture obtained after evaporation of the volatile components *in vacuo* was refined by flash column chromatography (silica gel; 3% methanol in chloroform). $^{31}$P NMR showed the presence of 89% of **8** and 11% of **7**. The components were separated by repeated column chromatography using the adsorbent and the eluant as above to give 0.12 g (86% based on **6b**) of oxaphosphete **8** and 0.05 g (9% based on **6a**) of phosphabicyclooctadiene **7**. The purity of the latter species (**7**) was 95% according to NMR.

**8**: $^{31}$P NMR ($CDCl_3$) $\delta$ 26.4; $^{13}$C NMR ($CDCl_3$)† $\delta$ 16.7 ($J$ = 17.8, $C^6$-Me), 21.2 ($C^{4'}$-Me), 23.1 ($J$ = 5.8, $C^{2'}$-Me), 28.6 ($J$ = 61.0, $C^9$), 51.0 (MeO), 51.9 (MeO), 73.9 ($J$ = 107.7, $C^3$), 119.9 ($J$ = 14.0, $C^8$), 122.1 ($J$ = 93.2, $C^{1'}$), 122.8 ($J$ = 84.8, $C^5$), 131.1 ($J$ = 12.1, $C^{3'}$), 140.3 ($J$ = 13.9, $C^7$), 142.0 ($J$ = 11.0, $C^{2'}$), 142.7 ($C^{4'}$), 155.3 ($J$ = 14.3, $C^6$), 167.0 ($J$ = 14.6, C=O), 167.7 ($J$ = 15.8, C=O), 182.9 ($J$ = 6.2, $C^4$); $^{1}$H NMR ($CDCl_3$) $\delta$ 2.12 (s, 3H, $C^6$-Me), 2.27 (s, 3H, $C^{4'}$-Me), 2.59 (s, 6H, $C^{2'}$-Me), 3.05 (dd, $J_1$ = 18.0, $J_2$ = 9.8, 1H, $C^9$-H), 3.60 (s, 3H, OMe), 3.79 (s, 3H, OMe), 5.03 (dd, $J_1$ = 18.4, $J_2$ = 13.0, 1H, $C^9$-H), 6.51 (s, 1H, $C^8$-H), 6.66 (d, $J$ = 22.9, 1H, $C^5$-H), 6.90 (s, 2H, ArH); IR (film) 2952, 1731, 1445, 1083, 756 cm$^{-1}$; FAB, 423 (M + H); HR-FAB, $(M + H)^+_{found}$ = 423.1060. $C_{21}H_{25}ClO_5P$ requires *m/z*, 423.1128 for the $^{35}$Cl isotope.

**7**: $^{31}$P NMR ($CDCl_3$) $\delta$ 42.0; $^{1}$H NMR ($CDCl_3$) $\delta$ 6.58 (d,

† Non-systematic numbering scheme.

$J_1 = J_2 = 6.2$, $C^6$-H); MS, *m/z* (rel. int.) 422 ($M^+$, 2%), 211 [M − MeO − ArP(O)$CH_2$, 100]; HR-FAB, $(M + H)^+_{found}$ = 423.1089. $C_{21}H_{25}ClO_5P$ requires *m/z*, 423.1128 for the $^{35}Cl$ isotope.

### Cycloaddition of dihydrophosphinine oxides 6a and 6b with NPMI

A similar reaction of 1.0 g (3.57 mmol) of the isomeric dihydrophosphinine oxides **6a** and **6b** and 0.71 g (4.10 mmol) of NPMI in 10 ml of toluene furnished 0.37 g (23%) of phosphabicyclooctene **10** as a 22–78% mixture of isomers **10a** and **10b** after repeated column chromatography carried out as above. MS, *m/z* (rel. int.) 453 ($M^+$, 73%), 438 (M − 15, 35), 418 (M − 35, 100), 91 (55); HR-FAB, $(M + H)^+_{found}$ = 454.1271. $C_{25}H_{26}ClNO_3P$ requires *m/z*, 454.1339 for the $^{35}Cl$ isotope.

**10a**: $^{31}P$ NMR ($CDCl_3$) $\delta$ 41.7; $^{13}C$ NMR ($CDCl_3$)† $\delta$ 21.1 ($C^{4'}$-Me), 23.5 ($J = 4.2$, $C^4$-Me), 24.5 ($J = 3.6$, $C^{2'}$-Me), 33.6 ($J = 77.1$, $C^3$), 39.1 ($J = 3.2$, $C^7$), 40.8 ($J = 60.9$, $C^1$), 44.6 ($J = 7.4$, $C^4$), 49.4 ($J = 10.9$, $C^8$), 121.1 ($J = 5.0$, $C^6$), 126.5 ($C^{3''}$),[a] 129.1 ($C^{4''}$), 129.4 ($C^{2''}$),[a] 131.1 ($J = 11.3$, $C^{3'}$), 140.5 ($J = 10.1$, $C^5$), 141.2 ($J = 11.3$, $C^{2'}$), 141.8 ($J = 1.9$, $C^{4'}$), 174.4 ($C^9$), 176.3 ($J = 15.1$, $C^{11}$),[a] may be reversed; $^1H$ NMR ($CDCl_3$) $\delta$ 1.74 (d, $J = 3.0$, $C^4$-Me), 5.96 (dd, $^3J_{PH} = {}^3J_{HH} = 6.0$, $C^6$-H).

**10b**: $^{31}P$ NMR ($CDCl_3$) $\delta$ 42.3; $^{13}C$ NMR ($CDCl_3$)† $\delta$ 18.4 ($J = 2.3$, $C^6$-Me), 21.1 ($C^{4'}$-Me), 24.5 ($J = 3.6$, $C^{2'}$-Me), 33.2 ($J = 75.9$, $C^3$), 39.7 ($J = 1.9$, $C^7$), 42.9 ($J = 7.4$, $C^4$), 44.9 ($J = 60.4$, $C^1$), 45.5 ($J = 11.1$, $C^8$), 128.6 ($J = 12.2$, $C^6$), 126.5 ($C^{3''}$),[b] 129.1 ($C^{4''}$), 129.4 ($C^{2''}$),[b] 131.4 ($J = 11.4$, $C^{3'}$), 140.6 ($J = 10.4$, $C^5$), 141.4 ($J = 10.0$, $C^{2'}$), 142.2 ($J = 1.9$, $C^{4'}$), 175.6 ($C^9$), 176.5 ($J = 15.3$, $C^{11}$),[b] may be reversed; $^1H$ NMR ($CDCl_3$) $\delta$ 1.47 (d, $J = 2.0$, $C^6$-Me), 1.62 (s, $C^{4'}$-Me), 2.30 (s, *o*-Me), 2.66 (s, *o*-Me).

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