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The ability of 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxides to undergo fragmentation of the bridging P-moiety

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Abstract

New 2-phosphabicyclo[2.2.2]octene 2-oxides (**2** and **3**) were synthesized by the Diels–Alder reaction of 1,2-dihydrophosphinine oxides (**1**) and dienophiles, such as *N*-phenyl maleimide and maleic anhydride. The X-ray structure of one of the products (**2Ab**) suggests that the phosphabicyclooctenes have a less strained framework than the phosphabicyclooctadienes described earlier. As a consequence of this, also confirmed by thermal examinations and semiempirical calculations, thermal fragmentation of the phosphabicyclooctenes requires more forcing conditions, than that of the bicyclooctadienes. The methylenephosphine oxide (**10**) ejected could be utilized in the phosphorylation of hydroquinone in moderate yield. Mass spectral fragmentation of cycloadducts **2** and **3** under electron-impact conditions seems to be in agreement with the preparative experiences.

Keywords: 2-Phosphabicyclo[2.2.2]octene 2-oxide; Thermostability; Energy profile; Phosphorylation

1. Introduction

It is known that the 2-phosphabicyclo[2.2.2]octa-5,7-diene 2-oxides and the 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxides are precursors of methylenephosphine oxides [1–3]. The unsaturated derivatives of phosphabicyclooctanes may lose the bridging moiety upon irradiation at 254 nm. The methylenephosphine oxide ejected may phosphorylate the alcohol added to the reaction mixture prior to the irradiation [1–3]. This method is a good choice for the phosphorylation of alcohols, especially primary alcohols, due to the easy implementation and the high yields. The phosphabicyclo-octadienes were also utilized in the thermo-induced phosphorylation of phenols, although the yields were poor in these instances [4]. Stereostructure of the phosphabicyclooctadienes was evaluated by X-ray crystallography [5]. Much less is known on phosphabicyclooctenes. For this reason, we wished to synthesize new members of the family of phosphabicyclooctenes and to evaluate their physical and chemical properties, especially their ability to undergo fragmentation.

2. Results and discussion

2.1. Synthesis and characterization of some 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxides

The new phosphabicyclooctenes were prepared by the Diels–Alder cycloaddition reaction of dihydrophos-

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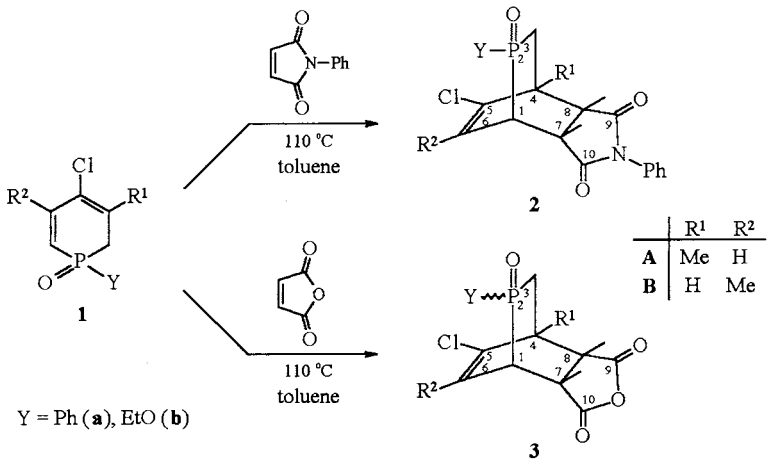


Scheme 1.

phinine oxides and dienophiles, such as *N*-phenyl maleimide (NPMI) and maleic anhydride (MA). Reaction of the P-ethoxy dihydrophosphinine (**1b**) with NPMI gave cycloadduct **2b**, while the interaction of the P-phenyl and P-ethoxy dihydrophosphinines (**1a** and **1b**) with MA afforded products **2a** and **2b**, respectively (Scheme 1). Starting from the double-bond isomers (**A** and **B**) of the dihydrophosphinines (**1**), the cycloadducts (**2** and **3**) were also formed as the mixture of regioisomers (**A** and **B**). Similarly to the earlier described **2a** [3], cycloadduct **2b** was also obtained as single configurational isomers. Isomer **2Ab** could be obtained in a pure form by repeated column chromatography and fractional crystallization. The regioisomers (**A** and **B**) of products **3a** and **3b** consisted of configurational isomers ($\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{B_1}$ and $\mathbf{B_2}$) [6]. Column chromatography afforded a mixture of the major components ($\mathbf{A_1}$ and $\mathbf{B_1}$) in both cases. The cycloadducts (**2** and **3**) obtained in a yield of 63–77% were characterized by ^{31}P-, ^{13}C- and ^{1}H-NMR, as well as mass spectroscopic methods. The ^{31}P- and ^{13}C-NMR data are listed in Table 1. The ^{13}C-NMR assignments were confirmed in all cases by spectra obtained by the Attached Proton Test Technique. The spectral parameters were similar to those reported for similar derivatives [3,7].

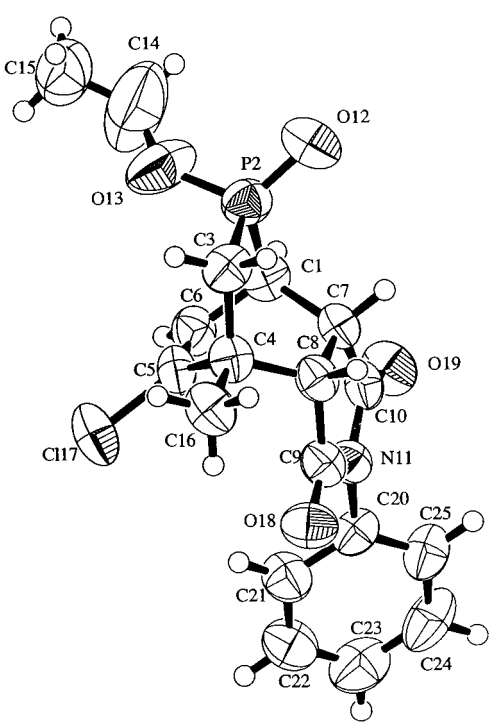


Fig. 1. X-ray structure of **2Ab**.

2.2. X-ray structure of a 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxide

The crystals of cycloadduct **2Ab** were suitable for single crystal X-ray analysis. The stereostructure of compound **2Ab** is shown in Fig. 1. One can see that in isomer **2Ab**, the position of the oxygen atom of the phosphoryl group is *anti* to the double-bond. The selected bond lengths and bond angles of **2Ab** are listed in Table 2. As a comparison, selected geometrical parameters of the earlier described phosphabicyclooctadiene **4** were also included [5]. It can be seen from the bond angles that, as expected, bicyclooctadiene **4** has a more strained framework than bicyclooctene **2Ab**. This can be expressed by an occasional indicator based upon the sum of the absolute values of the differences between the ideal (109.5 or 120°) and the measured bond angles for each skeletal atom. According to this, bicycles **4** and **2Ab** may be characterized by sums of 47.5 and 35.3, respectively. The bond angles around the phosphorus atom are practically the same in **4** and **2Ab**. As can be predicted on the basis of the relative measure of the ring strains, the phosphabicyclooctenes (**2** and **3**) must undergo thermal fragmentation under more forcing conditions, than the phosphabicyclooctadienes (e.g. **4**).

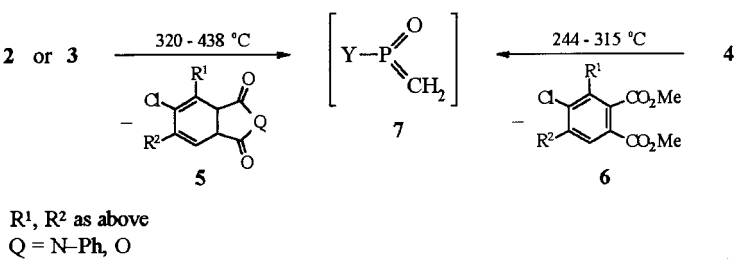
Table 1
^{31}P- and ^{13}C-NMR spectral parameters for the isomers (**A** and **B**) of phosphabicyclooctenes **2** and **3** in $CDCl_3$ solution

	δ_P (proportion)	δ_C (J_{PC} in Hz)									
		C_1	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	CH_3
2Ab [a]	54.1 (62%)	37.1 (85.7)	35.5 (102.6)	45.0 (5.9)	138.4 (11.8)	122.6 (8.9)	41.6	49.3 (11.2)	173.9	175.4 (19.1)	23.7 (13.0)
2Bb	54.9 (38%)	42.0 (86.5)	27.5 (102.8)	43.4 (6.9)	[b]	[b]	40.6	45.0 (11.4)	175.2	175.6 (19.3)	18.8 (2.6)
3Aa [c]	42.3 (70%)	38.2 (65.4)	36.3 (76.3)	44.2 (5.6)	139.7 (12.5)	122.6 (6.8)	42.3	54.4 (7.8)	173.4	171.6 (15.9)	24.2 (12.1)
3Ba	42.7 (30%)	44.1 (65.0)	27.5 (77.1)	[b]	[b]	[b]	40.2	48.3 (9.0)	173.6	172.2 (15.6)	19.0
3Ab [d]	58.0 (52%)	36.2 (87.3)	35.1 (101.0)	44.5 (5.2)	137.5 (12.9)	122.6 (9.1)	41.4	52.2 (10.9)	173.5	171.3 (20.4)	24.2 (14.7)
3Bb	58.8 (48%)	43.8 (87.2)	27.6 (100.9)	43.7 (6.4)	126.7 [e] (13.4)	130.1 [e] (9.6)	41.9	47.5 (9.5)	173.6	171.9 (21.2)	18.8 (3.4)

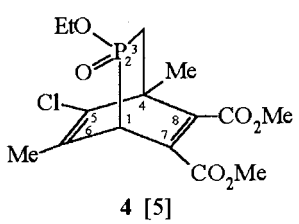
[a] 61.9 ($J = 6.0$, OCH_2), 16.6 ($J = 5.9$, CH_2CH_3), 131.5 ($C_{1'}$), 129.3, 126.6 ($C_{2'}$, $C_{3'}$), 129.1 ($C_{4'}$).
[b] Not resolved.
[c] 128.9 ($J = 11.9$), 131.5 ($J \sim 12$) ($C_{2'}$, $C_{3'}$), 132.7 ($C_{4'}$).
[d] 62.3 ($J = 6.7$, OCH_2), 16.5 ($J = 5.2$, CH_2CH_3).
[e] May be reversed.

Table 2
Selected bond angles and bond lengths for **2ab** as compared to those of **4** [5]

	α for **2Ab**	/109.5°−α/ or /120°−α/	α for **4**	/109.5°−α/ or /120°−α/
C_1–P_2–C_3	99.1(3)	10.4	99.5(2)	10.0
P_2–C_1–C_7	106.0(4)	3.5	105.3(3)	4.2
P_2–C_1–C_6	107.5(5)	2.0	102.3(4)	7.2
P_2–C_3–C_4	112.0(4)	2.5	109.5(4)	0
C_3–C_4–C_8	109.2(5)	0.3	105.4(4)	4.1
C_3–C_4–C_5	108.1(5)	1.4	106.9(4)	2.6
C_1–C_7–C_8	111.1(5)	1.6	116.0(5)	4.0
C_1–C_6–C_5	115.6(6)	4.4	113.4(5)	6.6
C_4–C_8–C_7	111.7(5)	2.2	116.1(4)	3.9
C_4–C_5–C_6	118.2(6)	1.8	119.5(5)	0.5
C_8–C_4–C_5	104.6(5)	4.9	106.2(5)	3.3
C_7–C_1–C_6	109.2(5)	0.3	110.6(4)	1.1
		Σ 35.3		Σ 47.5



Scheme 2.



4 [5]

2.3. Thermodynamic studies on the 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxides

To check the above prediction, the phosphabicyclooctenes (**2** and **3**) were subjected to thermal gravimetric (TG), differential thermal gravimetric (DTG) and differential scanning calorimetry (DSC) measurements. To be able to make a comparison, bicyclooctadiene **4** was also examined. According to the data, cycloadducts **2** and **3** were fragmented in the range of 320–450°C (Scheme 2, Table 3). As the similar range for compound **4** embraces 244–315°C, it can be seen that the phosphabicyclooctenes (**2** and **3**) are indeed more stable thermally, than the bicyclooctadienes (e.g. **4**). This must be due to the more flexible ring of the bicyclooctenes (**2** and **3**). All fragmentations examined were exothermic (Table 3).

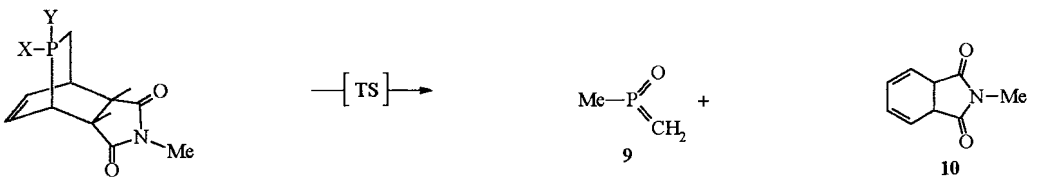
A similar conclusion can be reached by assuming product-like transition states. In this case, the value of activation energy must be less for the fragmentation of the phosphabicyclooctadienes (e.g. **4**), than for that of the bicyclooctenes (**2** and **3**), as the previous one goes with the formation of an aromatic phthalate (**6**), while the latter involves the formation of a dihydro species (**5**) (Scheme 2).

The above situation was evaluated by semiempirical calculations. Test molecules, phosphabicyclooctene **8** and phosphabicyclooctadiene **11** were chosen as the model compounds for the fragmentations resulting in methylenephosphine oxides. PM3 calculations [8] were carried out for both configurational isomers (**isomer$_1$** and **isomer$_2$**) of cycloadducts **8** and **11**. Assuming retrocycloaddition, activation enthalpies ($\Delta H^{\#}$) of 269.86 and 264.09 kJ mol^{-1} were calculated for bicyclooctenes $\mathbf{8_1}$ and $\mathbf{8_2}$, respectively (Table 4). The values of 213.14 and 199.22 kJ mol^{-1} obtained for $\mathbf{11_1}$ and $\mathbf{11_2}$ respectively, confirm that fragmentation of the phosphabicyclooctadienes (**11**) indeed requires less energy of activation than the fragmentation of the bicyclooctenes (**8**). It is worth mentioning that the value of $\Delta H^{\#}$ is somewhat higher for the fragmentation of isomers $\mathbf{8_1}$ and $\mathbf{11_1}$, where position of the P=*O* is *anti* to the double-bond, than that for isomers $\mathbf{8_2}$ and $\mathbf{11_2}$. The heat of formation (H_f) was also calculated for the products (**9**, **10** and **12**) of the fragmentation of cycloadducts **8**

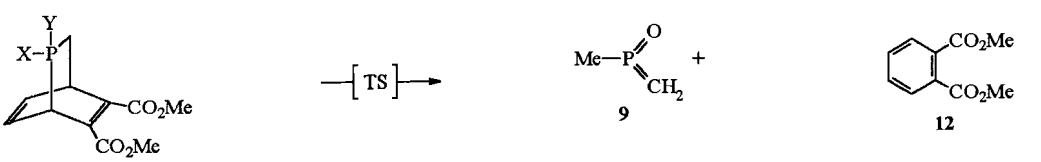
Table 3
Thermal examination of phosphabicyclooctenes **2** and **3**, as well as phosphabicyclooctadiene **4**

Cycloadduct	Range of fragmentation determined by DTG (°C)	The value for the minimum of the DTG curve (°C)	ΔH (kJ mol^{-1})
2a [3]	348–438	390	−299.12
2b	320–422	367	−253.51
3a	330–418	380	−82.68
3b	300–418	365	−71.10
4	244–315	295	

Table 4
Energy of activation ($\Delta H^{\#}$) for the fragmentation of cycloadducts **8** and **11**, as well as heat of formation (H_f) for the products (**9**, **10** and **12**) of the fragmentation calculated by the PM3 method



	X	Y	$\Delta H^{\#}$ (kJ mol^{-1})	H_f (**9**) (kJ mol^{-1})	H_f (**10**) (kJ mol^{-1})
8$_1$	Me	O	269.86	160.51	206.49
8$_2$	O	Me	264.09	160.51	206.49



	X	Y	$\Delta H^{\#}$ (kJ mol^{-1})	H_f (**9**) (kJ mol^{-1})	H_f (**12**) (kJ mol^{-1})
11$_1$	Me	O	213.14	160.51	536.71
11$_2$	O	Me	199.22	160.51	536.71

and **11** (Table 4). It can be seen that the energy gain is indeed higher for the fragmentation of bicyclooctadiene **11** (-697.22 kJ mol^{-1}), than for the fragmentation of bicyclooctene **8** (-367.0 kJ mol^{-1}). For aromatic **12** and nonaromatic **11**, the H_f is 536.71 and 206.49 kJ mol^{-1}, respectively. The energy profile calculated for the thermal fragmentation of cycloadducts **8** and **11** is shown in Fig. 2.

2.4. Utilization of the 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxides in thermo-induced phosphorylations

As mentioned in Section 1, the phosphabicyclooctadienes were useful in the phosphorylation of phenols [4]. These thermolyses were carried out in the range of 170–230°C. According to Table 3, similar reaction of the phosphabicyclooctenes (**2** and **3**) had to be carried out at somewhat elevated temperatures. Using 1.5 equivalents of hydroquinone as the trapping agent, cycloadduct **2a** was thermolyzed at 310–325°C for 10 min, while compound **2b** at 290–300°C for 15 min. These reaction conditions were in accord with the thermostability of the cycloadducts (**2**) (Table 3). The crude products obtained after flash column chromatography were analyzed by ^{31}P-NMR and GC-MS. In both cases, phosphinate **14** was the product, but the yield was better in the second case (16 vs. 9%) (Scheme 3). Presumably, polymerization of the methylenephosphine

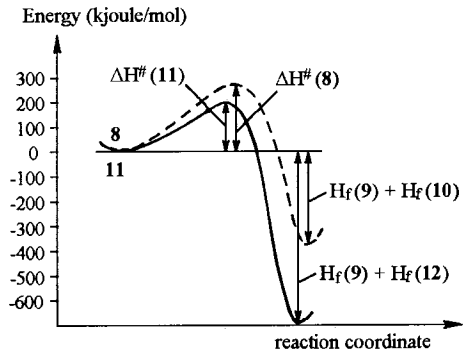


Fig. 2. Energy profile for the fragmentation of phosphabicyclooctene **8** (dotted line) and phosphabicyclooctadiene **11** (continuous line).

oxide (**13**) at the elevated temperatures is responsible for the low yields. The use of cycloadduct **2b** seems to be more appropriate in the phosphorylation of phenols, than that of **2a**. Due to their much better efficiency, the UV light-mediated phosphorylations seem to be more attractive [3]. A detailed study on the utilization of phosphabicyclooctenes in the photochemically induced phosphorylation of a variety of nucleophiles will be the subject of another paper.

2.5. Mass spectroscopic behavior of 2-phosphabicyclo[2.2.2]oct-5-ene 2-oxides

A comparative EI mass spectroscopic study on cycloadducts of type **2** and **3** was carried out at 300°C. The mass spectra of phosphabicyclooctenes **2** and **3** differed significantly. Compounds **2a** and **2b** revealed a molecular ion of 42 and 26%, respectively, and a rather weak $M-YP(O)CH_2-H^{\neg+}$ fragment ($m/z = 272$, with a relative intensity of 2% in both cases) with M-35$^{\neg+}$ as the base peak in both instances. In the case of cycloadducts **3a** and **3b**, the molecular ion was of lower intensity (1 and 4%, respectively), but the $M-YP(O)CH_2-CO_2-H^{\neg+}$ fragment ($m/z = 153$) was as intensive, as 100% in both instances. The presence of the $YP(O)CH_2^{\neg+}$ fragment in the mass spectrum of **3a** and **3b** was not significant. It can be seen that under EI conditions, cycloadducts **3** may lose the bridging moiety much easier than compounds **2**. Mass spectroscopic fragmentation of the two types of phosphabicyclooctenes (**2** and **3**) seems to be in agreement with their willingness to undergo thermal fragmentation: e.g. **3a** is fragmented easier than **2a** (Table 3) and gave better results also in the preparative phosphorylations (see above).

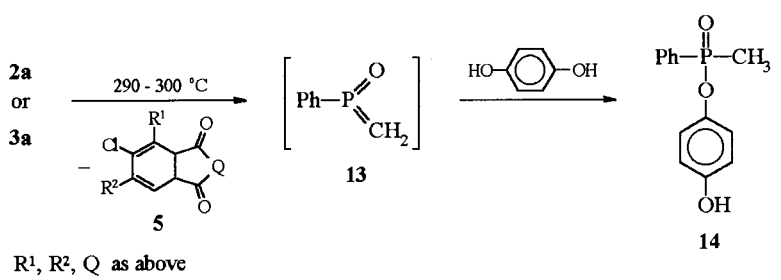
We note that the mass spectrum of phosphabicyclooctadiene **4** revealed $M-EtOP(O)CH_2-MeO^{\neg+}$ ($m/z = 225$) as the base peak with a molecular ion of 6% [5]. This seems to be in agreement with the phosphorylating ability of the phosphabicyclooctadienes under thermal conditions [4].

Table 5
Crystal data and structure refinement for **2Ab**

Empirical formula	$C_{18}H_{19}ClNO_4P$
Formula weight	379.76
Temperature (K)	293(2)
Wavelength (Å)	1.54178
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	24.661(7)
b (Å)	12.800(13)
c (Å)	11.515(6)
V	3635(4)
Z	8
$D_{calc.}$ (g cm^{-3})	1.388
Absorption coefficient (mm^{-1})	2.892
F(000)	1584
Crystal size (mm)	0.25 × 0.25 × 0.25
Theta range for data collection (°)	3.58–75.14
Reflections collected	3833
Independent reflections	3733 [$R_{int} = 0.0472$]
Absorption correction	Semi-empirical from ψ-scans
Max./min. transmission	1.000, 0.735
Data/restraints/parameters	3723/0/230
Goodness-of-fit on F^2	1.049
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0639$, $wR_2 = 0.1631$
R indices (all data)	$R_1 = 0.2054$, $wR_2 = 0.2560$
Largest difference peak and hole (e Å^{-3})	0.314 and −0.321

3. Experimental

The ^{31}P-, ^{1}H- and ^{13}C-NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 500



Scheme 3.

and 125.7 MHz, respectively. Mass spectra were obtained on an MS 25-RFA instrument at 70 eV. TG and DTG curves were determined with a Setaram Labsys thermoanalyzer using 25 mg samples in alumina crucibles in static air at a heating rate of 10°C min^{-1}. DSC measurements were performed on a Setaram DSC 92 thermoanalyzer at a heating rate of 10°C min^{-1} in static air with 10 mg samples in aluminum crucibles.

The dihydrophosphinine oxides (**1a,b**) were prepared as described earlier [9,10].

3.1. General procedure for the synthesis of the phosphabicyclooctenes (*2* and *3*)

The mixture of 0.022 mmol of the dihydrophosphinine oxide (**1**) and 0.028 mmol of the dienophile (NPMI, or MA) in 50 ml of toluene was stirred at boiling point for 5 days. Then the solvent was removed in vacuo and the residue so obtained purified by repeated column chromatography (3% methanol in chloroform, silica gel) to give the cycloadduct (**2** or **3**) as the mixture of two isomers (**A** and **B**). The following products were thus prepared.

3.2. N-Phenyl 4- and 6-methyl-5-chloro-2-ethoxy-2-oxo-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic imide (*2Ab* and *2Bb*)

Starting materials: **1b** and NPMI; Yield: 66% of **2b** as the mixture of 62% of isomer **A** and 38% of isomer **B**; MS, *m/z* (relative intensity): 379 (M^+, 26), 344 (M-35, 100), 272 (M–EtOP(O)CH_2–H, 2), 206 (M–NFMI, 29), 91 (67), 77 (42).

Repeated column chromatography and recrystallization (acetone) afforded **2Ab** (26%) in a pure form.

2Ab: m.p. 222–223°C; ^{31}P- and ^{13}C-NMR, Table 1; ^{1}H-NMR ($CDCl_3$): δ 1.32 (t, $J = 6.8$, 3H, CH_2CH_3), 1.67 (s, 3H, C_4–Me), 1.80 (m, 2H, P–CH_2), 3.17 (d, $J = 7.8$, 1H, C_8–H), 3.52 (dd, $J_1 = 16.8$, $J_2 = 7.7$, 1H, C_7–H), 3.81 (dd, $J_1 = J_2 = 7.7$, 1H, C_1–H), 4.10 (m, 2H, OCH_2), 6.20 (dd, $J_1 = J_2 = 7.6$, 1H, CH=), 7.14–7.45 (m, 5H, Ph); Anal. Calc. for $C_{18}H_{19}ClNO_4P$: C, 56.92; H, 5.04. Found: C, 56.61; H, 4.83.

2Bb: ^{31}P- and ^{13}C-NMR, Table 1.

3.3. 4- and 6-Methyl-5-chloro-2-oxo-2-phenyl-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic acid anhydride (*3Aa* and *3Ba*)

Starting materials: **1a** and MA; Yield: 77% of **3a** as the mixture of 70% of isomer **A** and 30% of isomer **B**; m.p.: 142–143°C (acetone); MS, *m/z* (relative intensity): 336 (M^+, 1), 293 (M-43, 13), 280 (M-56, 9), 245 (280–35, 20), 153 (M–CO_2–PhP(O)CH_2–H, 100), 138 (PhP(O)CH_2, 14), 91 (80), 77 (23).

3Aa: ^{31}P-NMR and ^{13}C-NMR, Table 1; ^{1}H-NMR ($CDCl_3$): δ 1.44 (s, 3H, Me), 6.13 (dd, $J_1 = J_2 = 7.5$, 1H, CH=).

3Ba: ^{31}P-NMR and ^{13}C-NMR, Table 1.

3.4. 4- and 6-Methyl-5-chloro-2-ethoxy-2-oxo-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic acid anhydride (*3Ab* and *3Bb*)

Starting materials: **1b** and MA; Yield: 63% of **3b** as the mixture of 52% of isomer **A** and 48% of isomer **B**; MS, *m/z* (relative intensity) 304 (M^+, 4), 261 (M-43, 5), 248 (M-56, 3), 213 (248–35, 7), 153 (M–CO_2–EtOP(O)CH_2–H, 100), 105 (EtOP(O)CH_2–H, 26).

3A$_1$b: ^{31}P- and ^{13}C-NMR, Table 1; ^{1}H-NMR ($CDCl_3$): δ 1.32 (t, $J = 7.0$, 3H, CH_2CH_3), 1.97 (d, $J = 2.3$, 3H, C_4–Me), 6.35 (dd, $J_1 = J_2 = 8.4$, 1H, CH=).

3B$_1$b: ^{31}P- and ^{13}C-NMR, Table 1.

3.5. Preparation of 4-hydroxyphenyl methylphenylphosphinate (*14*) by the phosphorylation of hydroquinone

A mixture of 0.15 g (1.36 mmol) of hydroquinone and 0.3 g (0.893 mmol) of cycloadduct **3a** consisting of isomer **A** (70%) and isomer **B** (30%) was heated in a vial at 290–300°C for 15 min. Flash column chromatography (3% methanol in chloroform, silica gel) of the reaction mixture afforded 0.04 g of **14** in a purity of 91% (yield: 16%). ^{31}P-NMR ($CDCl_3$): δ 37.9; GC-MS: *m/z* 248 (M^+); HRMS: $M^+_{found} = 248.0553$, $C_{13}H_{13}O_3P$ requires 248.0602.

A similar reaction with **2a** as the precursor gave **14** in a yield of 9%.

3.6. X-ray structure determination for phosphabicyclooctene *2Ab*

X-ray data were collected by a Rigaku AFC6S diffractometer using graphite monochromated Cu–K_α radiation. The structure was solved by direct methods and nonhydrogen atoms were refined anisotropically. Initial calculations have been done with the help of the program system texsan [11], the hydrogen positions were generated and the final structure refinement calculations carried out with the program SHELXL-93 [12]. Crystal data and other details of the structure refinement are listed in Table 5. Full lists of atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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