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Synthesis and Fragmentation of New 2-Phosphabicyclo[2.2.2]octene 2-Oxides

György Keglevich,[1] Helga Szelke,[1] Annamária Tamás,[1] Veronika Harmat,[2] Krisztina Ludányi,[3] Ágnes Gyöngyvér Vaskó,[1] and László Tőke[4]

[1]*Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

[2]*Department of Theoretical Chemistry, Eötvös University, 1518 Budapest, Hungary*

[3]*Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary*

[4]*Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

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ABSTRACT: *The substitution pattern of the 2-phosphabicyclo[2.2.2]octene framework and the skeleton itself were varied to obtain new cycloadducts usable in phosphorylations and to study their ability to undergo fragmentation. Thus, an N-methyl and several P-trialkylphenyl derivatives (***7** *and* **9**, *respectively) were synthesized, together with two diaza species (***8***) whose stereostructure was evaluated by single crystal X-ray analysis. Mechanistic studies on the UV light-mediated photolysis of the P-aryl phosphabicyclooctenes (***9***) in the presence of methanol supports the suggestion of a novel addition–elimination reaction path.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:626–632, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10052

Dedicated to Professor Dr. Andras Messmer on the occasion of his eightieth birthday.

Correspondence to: György Keglevich; e-mail: keglevich@oct.bme.hu.

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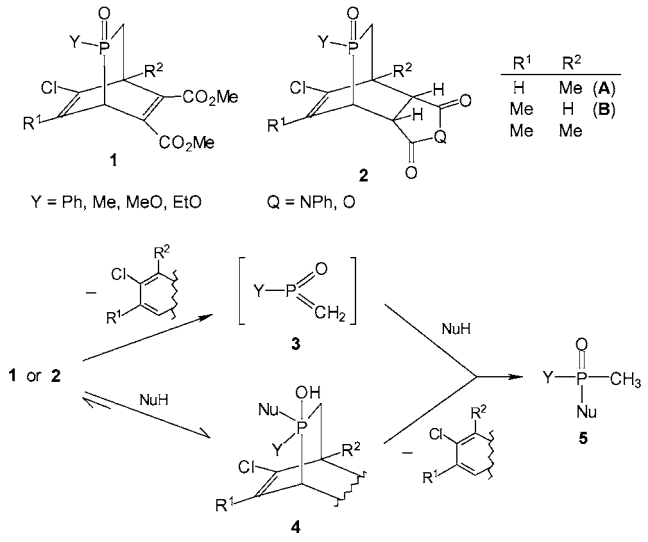
INTRODUCTION

In the past decade, the syntheses and fragmentation abilities of phosphabicyclooctadienes (**1**) and phosphabicyclooctenes (**2**) were intensively studied [1–8]. The bridged P-heterocycles (**1** or **2**) prepared by the Diels–Alder reaction of 1,2-dihydrophosphinine oxides with dienophiles [1–3] may undergo fragmentation to afford methylenephosphine oxide (**3**) that can be utilized in the phosphorylation of nucleophiles, such as hydroxy compounds and amines (Scheme 1) [2,4–6]. It was found that the phosphabicyclooctadienes (**1**), because of their more strained framework, are more suitable for use in thermo induced fragmentations than the corresponding bicyclooctene derivatives (**2**) [6–8]. Both precursors (**1** and **2**), however proved to be excellent in UV-light mediated phosphorylations [2,4,5]. For the photolyses, we have substantiated an alternative mechanism involving an intermediate with a pentavalent, pentacoordinate phosphorus atom (**4**) furnishing the phosphorylated product (**5**) by fragmentation (Scheme 1) [2,9].

In this article, we give an account of our results on the syntheses of novel precursors and on their fragmentation reactions.



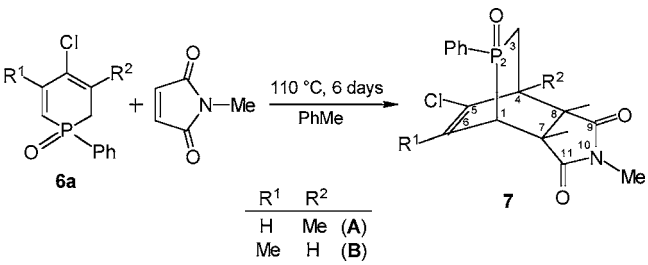
SCHEME 1

RESULTS AND DISCUSSION

The Diels–Alder reaction of a 3:1 mixture of the double-bond isomers (**A** and **B**) of dihydrophosphinine oxide (**6a**) with *N*-methylmaleimide gave a similar isomeric mixture of phosphabicyclooctenes **7A** and **7B** in 73% yield after column chromatography (Scheme 2). It is noteworthy that only one P-configurational isomer of each form (**A** and **B**) was found to have been formed. The structures of the cycloadducts (**7A** and **7B**) were identified by ^{31}P, ^{13}C NMR (Table 1), as well as ^{1}H NMR and mass spectroscopy.

Thermal examinations (TG and DTG) of product **7** revealed that the bridging $PhP(O)CH_2$ moiety was ejected in the range of 335–410°C. Since the *N*-phenyl analogue was fragmented in the range of 320–450°C [3], it is noted that the change of the phenyl group to a methyl substituent on the nitrogen atom does not have a significant impact on the thermostability.

It was interesting to explore the effect of the introduction of heteroatoms, such as nitrogen atoms, into the phosphabicyclooctene skeleton. The

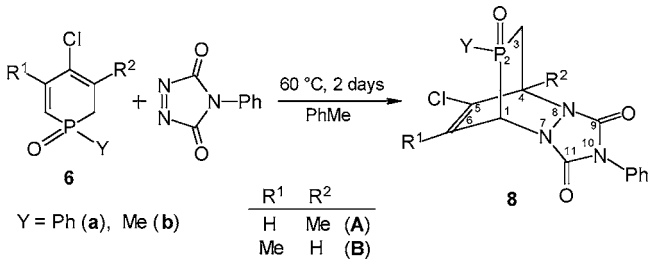


SCHEME 2

TABLE 1 ^{31}P and ^{13}C NMR Spectral Parameters of Phosphabicyclooctenes **7A** and **7B** in $CDCl_3$

	δP (%)	δ (J_{PC} in Hz)													
		C_1	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{11}	C–CH_3	N–CH_3	C_α	C_β	C_γ	C_δ
7A	37.8	38.9	36.8	44.2	140.1	122.2	49.6	40.1	174.9	176.5	23.6	25.2	130.7	128.9[a]	131.2[a]	132.6
	(75)	(62.9)	(76.1)	(6.5)	(11.0)	(6.1)	(10.6)	(2.6)		(14.9)	(10.8)		(99.0)	(12.0)	(8.6)	(2.2)
7B	37.5	44.3	27.8	39.1	128.5	130.1	45.4	42.3	176.0	176.7	18.8	25.2	130.4	128.9[a]	131.0[a]	132.6
	(25)	(62.5)	(77.4)	(2.1)	(11.8)	(6.1)	(12.0)	(7.0)		(15.3)	(2.6)		(99.7)	(11.8)	(9.4)	(2.2)

[a]May be reversed.



SCHEME 3

cycloadditions of dihydrophosphinine oxides **6a** and **6b** with 4-phenyl-1,2,4-triazoline-3,5-dione afforded the diazaphosphabicyclooctenes **8a** and **8b**, respectively (Scheme 3) [10]. Starting from the ca. 4:1 mixture of dihydrophosphinine oxides **6A** and **6B**, **8a** was obtained, after flash column chromatography, as four isomers [$\mathbf{A_1}$ (49%), $\mathbf{A_2}$ (31%), $\mathbf{B_1}$ (13%), and $\mathbf{B_2}$ (7%)], while **8b** was formed as only two isomers [**A** (60%) and **B** (40%)]. Repeated column chromatography gave isomer **8Ab** in a pure form. The products (**8a** and **8b**) were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopical data, as well as by mass spectrometry. The ^{31}P and ^{13}C NMR data of isomers **8Aa$_1$, 8Aa$_2$, 8Ab**, and **8Bb** are summarized in Table 2.

The stereostructure of the diaza product **8Ab** was also confirmed by single crystal X-ray analysis (Fig. 1). A selection of the geometrical parameters are listed in Table 3. The C_1—P_2—C_3 bond angle of 96°; confirms the considerable ring strain in the diazaphosphabicyclo skeleton. On the other hand, the P_2—C_1—N_7—C_{11} dihedral angle of 160° indicates the endo fusion of the triazolinedione ring.

Thermal examinations of cycloadduct **8a** showed that it underwent fragmentation in the range of 228–315°C, suggesting its lower thermostability as compared to that of the carbocyclic analogue (320–450°C) [3].

It was a challenge for us to synthesize phosphabicyclooctenes with bulky substituents on the phosphorus atom. These kinds of precursors seemed to be promising in mechanistic examinations. From among the two double bond isomers (**A** and **B**) of the triisopropylphenyl-dihydrophosphinine oxide (**6c**) [11], only the minor isomer (**6Bc**) was amenable to undergo a [4 + 2] cycloaddition with *N*-phenylmaleimide to give **9Bc**; the major isomer (**6Ac**), as a result of the increased steric hindrance due to the skeletal methyl substituent, resisted the reaction. Even the Diels–Alder reaction of isomer **6Bc** was significantly slower than that of the *P*-phenyl derivative [2] (Scheme 4).

It seemed to be more appropriate to synthesize the aryl-phosphabicyclooctene (**9c**) by another

TABLE 2 ^{31}P and ^{13}C NMR Spectral Parameters of Diazaphosphabicyclooctenes **8A** and **8B** in $CDCl_3$

	δ_P (%)	δ (J_{PC} in Hz)													
		C_1	C_3	C_4	C_5	C_6	C_9	C_{11}	CH_3	C_α	C_β	C_γ	C_δ	$C_{\alpha'}$	$C_{\beta'}$	$C_{\gamma'}$	$C_{\delta'}$
8Aa$_1$	28.40	51.9	39.4	64.1	138.8	122.4	152.7	151.8	22.7	126.7	128.9[a]	131.7[a]	133.3	131.0	125.5[b]	129.1[b]	128.5
	(49)	(78.1)	(62.5)	(7.0)	(7.8)	(2.2)	(11.9)		(9.7)	(100.4)	(12.5)	(9.4)	(2.5)				
8Aa$_2$	28.68	53.6	36.4	64.1	140.1	122.8	152.7	151.5	22.6	128.4	128.5[c]	131.4[c]	133.3	131.0	125.9[d]	129.1[d]	128.5
	(31)	(70.4)	(63.9)	(7.5)	(7.7)		(10.3)		(10.6)	(100.0)	(11.3)	(9.5)	(2.5)				
8Ab	38.65	51.2	39.8	63.4	138.1	121.4	152.7	151.2	22.3	12.4				125.7	125.4[e]	128.8[e]	128.3
	(60)	(76.9)	(60.9)	(6.7)	(7.7)	(2.7)	(11.5)		(9.2)	(69.5)							
8Bb	38.76	55.6	31.4	56.9	131.0	130.6	154.5	153.8	17.9	13.1				125.8	124.9[f]	128.9[f]	128.4
	(40)	(74.5)	(61.1)	(7.7)	(2.7)		(13.0)			(68.0)							

[a–f] May be reversed.

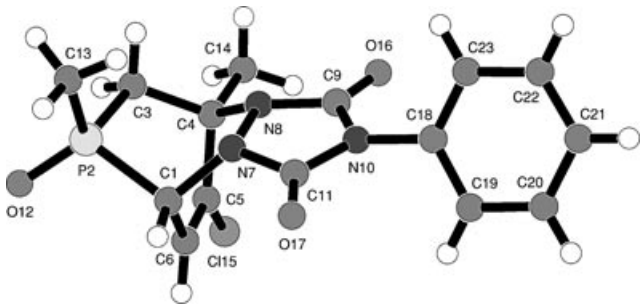


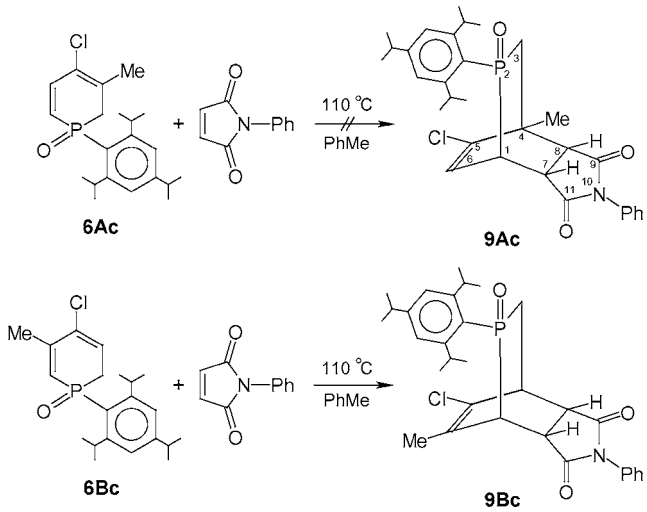
FIGURE 1 Perspective view of diazaphosphabicyclooctene **8Ab**.

approach, namely by substitution at the phosphorus atom. The isomers (**A** and **B**) of the easily available *P*-ethoxy cycloadduct (**2**, Y=EtO, Q=NPh) were converted to the corresponding phosphinic chlorides (**10A** and **10B**) by reaction with phosphorus pentachloride. Then, the oxygen atom of the P=O group in intermediates **10A** and **10B** was deoxygenated by trichlorosilane to furnish phosphinous chlorides **11A** and **11B**, these giving phosphines **12A** and **12B** by reaction with arylmagnesium bromide. Oxidation of the phosphines (**12A** and **12B**) led to the *P*-aryl phosphabicyclooctene oxides (**9Ac** and **9Bc**) (Scheme 5). The major isomer (**9Ac**) was obtained in a pure form after repeated column chromatography. The product (**9Ac**) was characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectroscopical data.

Then the precursors were examined with respect to fragmentation-related phosphorylations. Irradiation of the acetonitrile solution of the *N*-methyl

TABLE 3 Selected Bond Lengths, Bond Angles, and Torsion Angles for **8Ab** with the Estimated Standard Deviations

Bond lengths			
P2—C3	1.79(1)	N10—C11	1.35(2)
P2—C1	1.83(1)	N10—C9	1.37(1)
N7—C11	1.36(1)	C1—C6	1.47(2)
N7—N8	1.42(1)	C3—C4	1.54(2)
N7—C1	1.473(9)	C4—C5	1.52(1)
N8—C9	1.37(2)	C5—C6	1.29(1)
N8—C4	1.50(2)		
Bond angles			
C13—P2—C3	109.3(5)	C4—C3—P2	113.4(8)
O12—P2—C1	112.3(6)	N8—C4—C5	105.6(9)
C3—P2—C1	96.3(8)	C5—C4—C3	107.7(7)
N8—N7—C1	115(1)	C6—C5—C4	117.2(9)
N7—N8—C4	113.3(8)	C5—C6—C1	116.3(8)
N7—C1—C6	109(1)		
Torsion angles			
C11—N7—C1—P2	159.7(6)	P2—C3—C4—C5	50(1)
C9—N8—C4—C3	−160.9(8)	P2—C1—C6—C5	63.9(9)
P2—C3—C4—C14	177.7(6)		

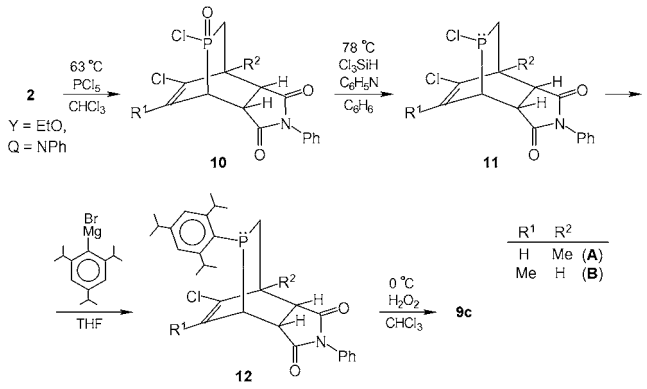


SCHEME 4

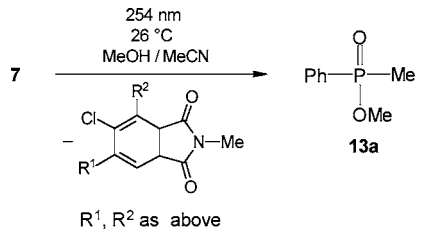
precursor (**7**) in the presence of methanol led to phosphinate **13a** in a clean reaction and with an excellent efficiency (93% yield after flash column chromatography) (Scheme 6).

Despite the significant ring strain, the diazaphosphabicyclooctenes (**8**) could not be used in UV light mediated phosphorylations at 254 nm. The diaza derivatives (**8**) proved to be UV-inactive around 254 nm.

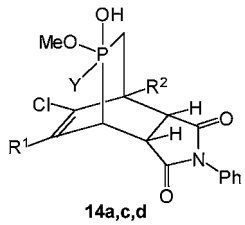
We evaluated how the trialkyl substitution at the *P*-phenyl ring affects the fragmentation ability of the cycloadduct (**9**) (Scheme 7). It was found that the rate, as measured by the decrease of the relative quantity of the precursor, decreased dramatically in the order of phenyl (**9a**), 2,4,6-trimethylphenyl (**9d**) 2,4,6-triisopropylphenyl (**9c**), which is well demonstrated by the $t_{1/2}$ values of 40 min, 3.5 h, and ~7 h, respectively. By use of cycloadducts **9a** and **9d**, the



SCHEME 5



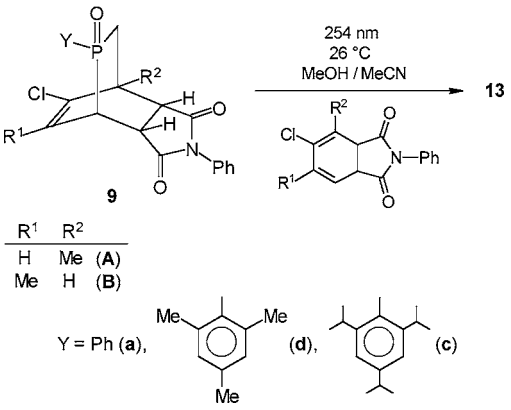
SCHEME 6



phosphorylation of methanol was quite efficient to afford phosphinates **13a** or **13d**, respectively. The similar reaction of the *P*-triisopropylphenyl precursor (**9c**) was complicated, however, by side-reactions. All these results attest to the increased role of steric hindrance in the fragmentation-related phosphorylations, phosphabicyclooctenes (**9**) being employed. According to this, the addition–elimination (AE) route involving an intermediate (**14**) with a pentavalent pentacoordinated phosphorus atom is most likely to be the predominating mechanism in the above reactions, as was suggested earlier [2,5,9]. In the other route, that is the elimination–addition (EA) mechanism involving methylenephosphine oxide (**3**) as the intermediate, the effect of the steric hindrance cannot be so remarkable.

EXPERIMENTAL SECTION

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.



SCHEME 7

General Procedure for the Preparation of Different Cycloadducts

To 4.0 mmol of the dihydrophosphinine oxide (**6a** or **6b**), consisting of ~75% of the **A** and ~25% of the **B** double-bond isomer, was added 4.61 mmol of *N*-methylmaleimide (NMMI) or 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in 40 ml of toluene, and the mixture was stirred at T°C for t days. Solvent was evaporated and the residue so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give the product as a mixture of isomers.

2-Phosphabicyclo[2.2.2]octene 2-Oxides **7A** *and* **7B**. Starting materials: **6a** and NMMI; $T = 110$°C; $t = 6$ days; Isomeric composition: 75% (**A**) and 25% (**B**); Yield: 73%; MS, *m/z* 349 (M^+); $M^+_{found} = 349.0629$, $C_{17}H_{17}NO_3PCl$ requires 349.0635.

7A: ^{31}P and ^{13}C NMR, Table 1; ^{1}H NMR ($CDCl_3$) δ 1.79 (s, C—CH_3), 2.99 (s, N—CH_3), 5.96 (dd, $^3J_{PH} = {}^3J_{HH} = 7.9$, C_6—H).

7B: ^{31}P and ^{13}C NMR, Table 1.

7,8,2-Diazaphosphabicyclo[2.2.2]octene 2-Oxides **8Aa$_1$, 8Aa$_2$, 8Ba$_1$**, *and* **8Ba$_2$**. Starting materials: **6a** and PTAD; $T = 60$°C; $t = 2$ days; Isomeric composition: 49% (**A$_1$**), 31% (**A$_2$**), 13% (**B$_1$**), and 7% (**B$_2$**); Yield: 56%; MS, *m/z* (relative intensity) 413 (M^+, 13), 378 (4), 275 (10), 239 (54), 77 (100); $(M + H)^+_{found} = 414.0750$, $C_{20}H_{18}N_3O_3PCl$ requires 414.0774.

8Aa$_1$: ^{31}P and ^{13}C NMR, Table 2; ^{1}H NMR ($CDCl_3$) δ 2.23 (s, CH_3), 6.78 (dd, $^3J_{PH} = {}^3J_{HH} = 7.1$, C_6—H).

8Aa$_2$: ^{31}P and ^{13}C NMR, Table 2; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, CH_3), 6.40 (dd, $^3J_{PH} = {}^3J_{HH} = 8.0$, C_6—H).

8Ba$_1$: ^{31}P NMR ($CDCl_3$) δ 28.46 (13%), ^{13}C NMR ($CDCl_3$) δ 18.3 ($J = 1.8$, CH_3), 31.3($J = 64.9$, C_3), 56.6 ($J = 75.6$, C_1), 57.7 ($J = 7.7$, C_4), 130.7 (C_6), 154.9 ($J = 13.2$, C_9), 154.5 (C_{11}).

8Ba$_2$: ^{31}P NMR ($CDCl_3$) δ 28.53 (7%).

7,8,2-Diazaphosphabicyclo[2.2.2]octene 2-Oxides **8Ab** *and* **8Bb**. Starting materials: **6b** and PTAD; $T = 60$°C; $t = 2$ days; Isomeric composition: 60% (**A**) and 40% (**B**); Yield: 56%; MS, *m/z* 351 (M^+); $M^+_{found} = 351.0480$, $C_{15}H_{15}N_3O_3PCl$ requires 351.0540.

8Ab: Repeated column chromatography afforded **8Ab** in a pure form; mp 185–187°C (acetone); ^{31}P and ^{13}C NMR, Table 2; ^{1}H NMR ($CDCl_3$) δ 1.94 (d, $^{2}J_{PH} = 13.6$, P—CH_3), 2.12 (s, C—CH_3), 6.65 (dd, $^{3}J_{PH} = {}^{3}J_{HH} = 6.9$, C_6—H).

8Bb: ^{31}P and ^{13}C NMR, Table 2.

X-ray Structure Determination for Compound **8Ab**

Single crystals of **8Ab** were obtained by slow evaporation of an acetone solution of the compound. The crystals are monoclinic, space group $P2_1/n$, $a = 15.01(2)$, $b = 6.56(1)$, $c = 36.32(4)$ Å, $\beta = 94(2)^\circ$, $V = 3569(8)$ Å^3, $Z = 4$, $D_c = 1.430$ g cm^{-3}. The asymmetric unit contains two molecules of **8Ab**, an acetone molecule, and a partially occupied water (occupancy refined to 0.378) molecule $C_{33}H_{36.76}Cl_2N_6O_{7.38}P_2$, $M_w = 768.36$. X-ray data were collected from a crystal, having dimensions of $0.3 \times 0.05 \times 0.05$ mm^3 by a Rigaku RAXIS-II imaging plate detector using graphite monochromated Mo Kα radiation. A total of 3175 unique reflections were collected, $2\theta_{max} = 42.86^\circ$. The structure was solved by direct methods using the teXsan package [12]. Refinements were carried out using the SHELXL-97 program [13] for 469 variables. All non-hydrogen atoms were refined by the anisotropic mode, the hydrogen atoms being generated based upon geometric evidence and refined using the riding model. Two hundred eighty nine restraints were applied. The extinction coefficient was refined to 0.025. At the end of the refinement $R = 0.0841$, $R_w = 0.2229(I > 2\sigma I)$, and $R = 0.1241$, $R_w = 0.2589$ (all reflections). The highest residual peak of the final difference electron density map was 0.38(8) eÅ^{-3}.

Preparation of the P-(2,4,6-Triisopropylphenyl) 2-Phosphabicyclo[2.2.2]octene 2-Oxides **9Ac** *and* **9Bc**

To 2.4 g (6.2 mmol) of phosphinic ester **2** (Y=EtO, Q=NPh) in 50 ml of dry chloroform was added 1.9 g (9.0 mmol) of phosphorus pentachloride, and the mixture was stirred at the boiling point for 5 days. The solvent and the volatile components were removed in vacuo to leave a mixture of phosphinic chlorides **10A** and **10B** in quantitative yields suitable for further transformation [^{31}P NMR ($CDCl_3$) δ 57.2 (72%) for **10A** and δ 57.1 (28%) for **10B**; MS, m/z 369 (M^+)].

To ~2.3 g (~6.2 mmol) of phosphinic chloride **10** in 40 ml of degassed benzene was added 2.3 ml (28 mmol) of pyridine and 1.2 ml (11.9 mmol) of trichlorosilane. The contents of the flask were stirred at the boiling point in a nitrogen atmosphere for 8 h. After filtration, the filtrate was concentrated in vacuo to give a mixture of phosphinous chlorides **11A** and **11B** almost quantitatively.

Because of the sensitivity of the intermediate (**11**) toward air and moisture, it was immediately used in the next step. To ~2.2 g (~6.2 mmol) of phosphinous chloride **11** in 60 ml of dry tetrahydrofuran was added 7.8 mmol of arylmagnesium bromide [prepared from 0.19 g (7.9 mmol) of magnesium and 2.2 g (7.8 mmol) of 2,4,6-triisopropyl-1-bromobenzene in 20 ml of tetrahydrofuran] and the mixture was stirred at the boiling point for 14 h. The solvent was evaporated and the residue containing arylphosphine **12** was taken up in the mixture of 60 ml of chloroform and 10 ml of water. The chloroform phase was treated with 1.4 ml (~12.4 mmol) of 30% hydrogen peroxide at 0°C, the cooling bath was removed and the mixture stirred further at 26°C for 1.5 h. Excess of the peroxide was removed by extraction with 3×25 ml of water. The chloroform phase was dried (Na_2SO_4) and the solvent evaporated to afford a 4:1 mixture of phosphine oxides **9Ac** (δ_P 43.4) and **9Bc** (δ_P 42.3). Repeated column chromatography (3% methanol in chloroform, silica gel) furnished 0.83 g (25%) **9Ac** in a pure form.

9Ac: ^{31}P NMR ($CDCl_3$) δ 40.4; ^{13}C NMR ($CDCl_3$) δ 23.7 ($C_{4'}$—$CH(CH_3)_2$), 23.9 ($J = 10.3$, C_4—CH_3), 25.1 ($C_{2'}$—$CH(CH_3)_2$), 25.2 ($C_{6'}$—$CH(CH_3)_2$), 32.4 ($C_{2'}$—$CHMe_2$), 34.3 ($C_{4'}$—$CHMe_2$), 41.5 (C_7), 42.4 ($J = 63.6$, C_1), 43.5 ($J = 71.0$, C_3), 44.6 ($J = 5.8$, C_4), 49.8 ($J = 9.8$, C_8), 121.8 (C_6), 123.3 ($J = 11.3$, $C_{3'}$), 126.7 ($C_{3''}$), 129.1 ($C_{4''}$), 129.4 ($C_{2''}$), 140.2 ($J = 10.3$, C_5), 152.4 ($J = 10.8$, $C_{2'}$), 153.1 ($C_{4'}$), 174.5 (C_9), 176.5 ($J = 14.8$, C_{11}); ^{1}H NMR ($CDCl_3$) δ 1.26 (d, $J = 6.9$, $C_{4'}$—$CH(CH_3)_2$), 1.31 (d, $J = 6.2$, ortho—$CH(CH_3)_2$), 1.72 (s, C_4—CH_3), 6.12 (dd, $^{3}J_{PH} = {}^{3}J_{HH} = 7.7$, C_6—H); FAB–MS: $(M + H)^+ = 538$; $(M + H)^+_{found} = 538.2169$, $C_{31}H_{38}ClNO_3P$ requires 538.2278.

General Procedure for the Phosphorylation of Methanol Using Precursors **7, 9a, 9d**, *and* **9c**

The solution of 0.240 mmol of the phosphabicyclooctene (**7, 9a, 9d**, or **9c,**) consisting of isomers, in 45 ml of acetonitrile and 4 ml of methanol was irradiated in a photochemical reactor with a mercury lamp (125 W) for the appropriate time (see below). Volatile components were removed, and the residue so obtained was purified by flash column chromatography (silica gel, 3% methanol in chloroform) to afford the respective phosphinates (**13a, 13d**, and **13c**) alone or along with unreacted starting material.

Photolysis Using Cycloadduct **7**. Reaction time 70 min; yield of **13a**: 93%; ^{31}P NMR ($CDCl_3$) δ 45.1, δ [lit. 2] 44.8.

Photolysis Using Cycloadduct **9a**. $t_{1/2}$: 40 min, reaction time 1.5 h; yield of **13a**: 57%; ^{31}P NMR ($CDCl_3$) δ 44.8, δ [lit. 2] 44.8; FAB: $(M + H)^+ = 171$.

Photolysis Using Cycloadduct **9d**. $t_{1/2}$: 3.5 h; **13d**: ^{31}P NMR ($CDCl_3$) δ 51.6; FAB: $(M + H)^+ = 213$; HRMS, $(M + H)^+_{found} = 213.1003$; $C_{11}H_{18}O_2P$ requires 213.1044.

Photolysis Using Cycloadduct **9c**. $t_{1/2}$: ~7 h; This reaction led also to unidentified by-products. **13c**: ^{31}P NMR ($CDCl_3$) δ 51.9; FAB: $(M + H)^+ = 297$; HRMS: $(M + H)^+_{found} = 297.1913$, $C_{17}H_{30}O_2P$ requires 297.1983.

The above values for $t_{1/2}$ were determined by ^{31}P NMR spectroscopy on the basis of relative intensities.

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