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Fragmentation-Related Phosphinylations Using 2-Aryl-2-phosphabicyclo[2.2.2]oct-5-ene- and -octa-5,7-diene 2-Oxides

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ABSTRACT: *A series of new P-methylphenyl P-heterocycles are introduced. The para and ortho substituted 2,5-dihydro-1H-phosphole oxides (***1a** *and* **1b***) were converted to the double-bond isomers (***A** *and* **B***) of 1,2-dihydrophosphinine oxides (***3a** *and* **3b***) via the corresponding phosphabicyclo[3.1.0]hexane oxides (***2a** *or* **2b***). Isomeric mixture (***A** *and* **B***) of the dihydrophosphinine oxides (***3a** *and* **3b***) gave, in turn, the isomers (***A** *and* **B***) of phosphabicyclo[2.2.2]oct-5-enes (***4a** *and* **4b***) or a phosphabicyclo[2.2.2]octa-5,7-diene (***5***) in Diels-Alder reaction with dienophiles. The bridged P-heterocycles (***4** *and* **5***) were useful in the photo- or thermoinduced fragmentation-related phosphinylation of hydroxy compounds and amines. The new precursors (***4a** *and* **4b***) were applied in mechanistic investigations.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:443–451, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10176

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INTRODUCTION

The phosphinylation of nucleophiles by low-coordinated P-fragments, like methylenephosphine oxides or sulfides, is a novel synthetic method [1]. An attractive approach is one wherein the methylenephosphine oxide is generated by the fragmentation of bridged P-heterocycles, such as 2-phosphabicyclo-[2.2.2]octa-5,7-diene- or phosphabicyclo[2.2.2]oct-5-ene derivatives [2–10]; the simplest way of achieving the fragmentation is thermolysis above 200°C [3–5]. Because of their more strained framework, the fragmentation of bicyclooctadienes is easier than that of bicyclooctenes [4,11].

To achieve phosphinylation, the low-coordinated P-fragment should be generated in the presence of a nucleophile [3–5]. Another way of utilizing the phosphabicyclooctene derivatives in phosphinylations is their UV light-mediated reaction with alcohols or amines [6–10]. Besides the elimination–addition (EA) mechanism via a methylenephosphine oxide, a novel addition–elimination (AE) route involving an intermediate with a pentavalent pentacoordinated phosphorus atom was also substantiated by us [9,10,12,13].

In this paper, new P-aryl phosphabicyclooctene derivatives are described as precursors in O- and N-phosphinylations, and as suitable model compounds in mechanistic studies.

RESULTS AND DISCUSSION

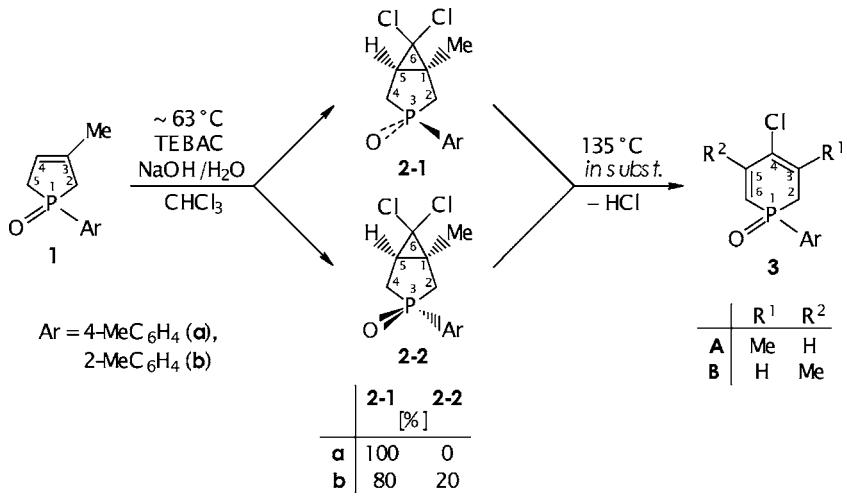
First we prepared the starting materials of the desired new precursors, the *para*- and *ortho*-methylphenyl-1,2-dihydrophosphinine 1-oxides **3a** and **3b**, respectively. The five-membered ring of the corresponding aryl-2,5-dihydro-1*H*-phosphole oxides (**1a** and **1b**) was expanded by making use of ring-enlargement method [14], according to which dichlorocarbene was added to the double-bond of the starting material (**1a** and **1b**) in the first step, followed by the thermal ring opening of the phosphabicyclo[3.1.0]hexane 3-oxides (**2a** and **2b**) so formed to give the desired P-aryl 1,2-dihydrophosphinine oxides (**3a** and **3b**) as a ca. 3:1 mixture of double-bond isomers (**A** and **B**).

The *para*-methylphenyl phosphabicyclohexane (**2a**) was formed as a single isomer **2-1**, while the *ortho*-methylphenyl counterpart (**2b**) was formed as an 80–20% mixture of isomers **2-1** and **2-2** (Scheme 1).

The assumption that **2-1** is the diastereomer containing the aryl group *cis* to the dichlorocyclopropane ring, while the other one (**2-2**) is the species with *anti* geometry is in full agreement with earlier cases, according to which during the dichlorocarbene addition reaction of the 1-phenyl-2,5-dihydro-1*H*-phosphole only the *cis* isomer was formed [14], while during the cyclopropanation of model compounds with sterically demanding substituents, such as the 2,4,6-trimethylphenyl- and the 2,4,6-triisopropylphenyl, the resulting phosphabicyclohexane consisted of two isomers with minor *cis* component [15,16].

The starting aryl-dihydro-1*H*-phosphole oxides (**1a** and **1b**), the phosphabicyclohexanes (**2a-1**, **2b-1**, and **2b-2**), and the double-bond isomers (**A** and **B**) of the dihydrophosphinine oxides (**3a** and **3b**) were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectroscopical data. The spectral parameters showed close resemblance to those of earlier described analogues [15–17].

The stereostructure of phosphabicyclohexane **2b-1** was confirmed by single crystal X-ray analysis. It can be seen in Fig. 1 that the relative position of the dichlorocyclopropane ring and the aryl group is indeed *cis*. The C(1), C(2), P(3), C(4), C(5) ring of **2b-1** has an envelope conformation with P(3) atom below the plain of the other four atoms. This type of conformation is due to the C(1), C(5), C(6) cyclopropane ring attached to the five-membered ring. The phenyl group attached to P(3) atom is in the equatorial, while O(1) is in the axial position. The tetrahedron around P(3) is



	2-1	2-2
	[%]	
a	100	0
b	80	20

	R1	R2
A	Me	H
B	H	Me

SCHEME 1

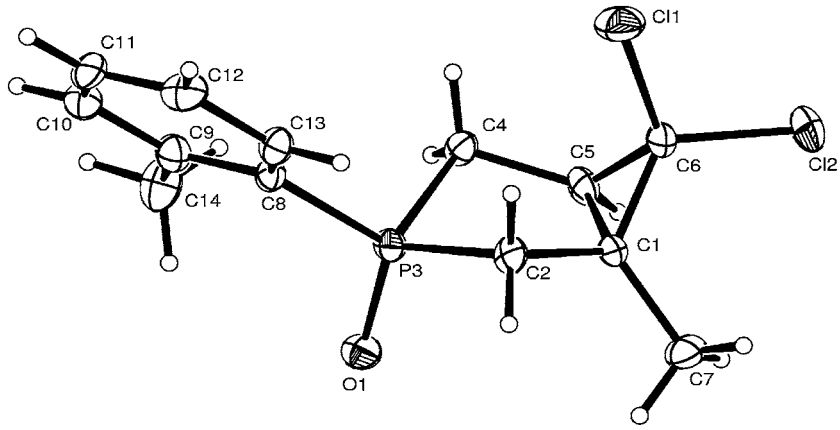


FIGURE 1 Perspective view of **2b-1** with the bond distances (Å), bond angles (°), and torsion angles (°) selected. [P_3—C_2 1.817(10), C_2—C_1 1.515(11), C_1—C_6 1.477(13), C_6—C_5 1.483(15), C_1—C_5 1.515(11), C_5—C_4 1.509(13), C_4—P_3 1.841(9); P_3—C_2—C_1 103.6(6), C_2—C_1—C_6 116.1(8), C_1—C_6—C_5 62.3(7), C_6—C_5—C_4 120.7(9), C_5—C_4—P_3 101.8(6), C_4—P_3—C_2 94.4(4), C_4—P_3—O_1 112.2(4), O_1—P_3—C_8 114.7(4), O_1—P_3—C_2 113.3(5), C_8—P_3—C_2 111.6(4), C_8—P_3—C_4 108.8(4), C_2—C_1—C_5 110.3(8), C_1—C_5—C_4 114.4(7), C_2—C_1—C_7 115.5(8); C_{14}—C_9—C_8—P_3 −0.8(14), C_6—C_1—C_2—P_3 92.3(9), C_6—C_5—C_4—P_3 −89.0(9), C_7—C_1—C_5—C_4 138.0(10), C_7—C_1—C_2—P_3 −116.6(9)].

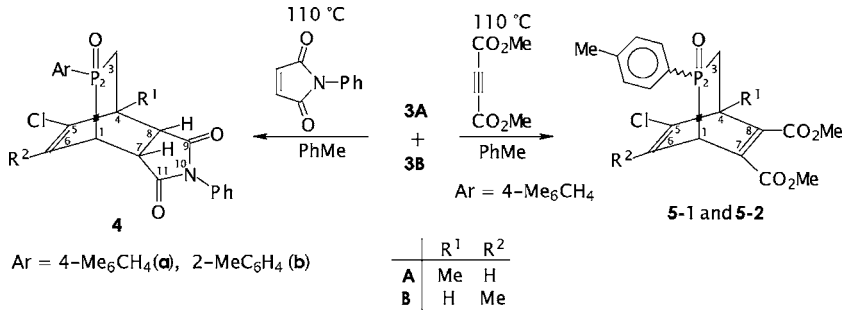
somewhat distorted. The two most extreme values are 94.4(4)° for C(4)—P(3)—C(2) and 114.7(4)° for O(1)—P(3)—C(8) as expected

In the next stage of our work, the aryl-1,2-dihydrophosphinine oxides (**3a** and **3b**) were utilized in the synthesis of bridged P-heterocycles. The Diels–Alder reaction of 1-tolyl-dihydrophosphinine oxides **3a** and **3b** with *N*-phenylmaleimide in boiling toluene furnished phosphabicyclooctenes **4a** and **4b**, respectively. Starting from the 3:1 isomeric mixture of the dihydrophosphinine oxides (**3**), the cycloadducts (**4**) were obtained as a ca. 3:2 isomeric mixture after column chromatography (Scheme 2). The isomers (**A** and **B**) of the products (**4a** and **4b**) were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectroscopical data.

The *para*-methylphenyl-dihydrophosphinine oxides (**3Aa** and **3Ba**) were also converted to the corresponding phosphabicyclooctadienes (**5A** and **5B**). In this case, the double-bond isomers (**5A** and **5B**) consisted of configurational isomers (**5A-1, 5A-2, 5B-1**, and **5B-2**) (Scheme 2). The isomers were characterized by ^{31}P and ^{13}C NMR, as well as mass spectroscopical data. NMR spectral features of the P-tolyl cycloadducts (**4a, 4b**, and **5**) were in agreement with those reported for the P-phenyl analogues [7,9].

The P-aryl precursors (**4a, 4b**, and **5**) were then utilized in fragmentation-related phosphinylations. The acetonitrile solutions of the tolyl-phosphabicyclooctenes (**4a** and **4b**) were irradiated (254 nm) at 26°C in the presence of simple alcohols or primary amines to give phosphinic esters (**7–11/a,b**) or amides **12,13/a,b**, respectively, in reasonable yields after flash column chromatography (Schemes 3 and 4) (Table 1).

Products **11a** and **11b** consisted of two diastereomers. The purity of the phosphinic derivatives (**7–13**) characterized by ^{31}P and, in some cases, by ^{13}C NMR spectroscopical data was ca. 95% according to GC–MS. The EI mass spectra were obtained



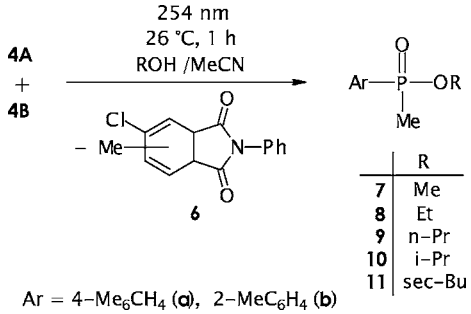
SCHEME 2

TABLE 1 Phosphinic Derivatives **7–12** Prepared by the Photolysis of Cycloadducts (**4** or **5**) in the Presence of Nucleophiles

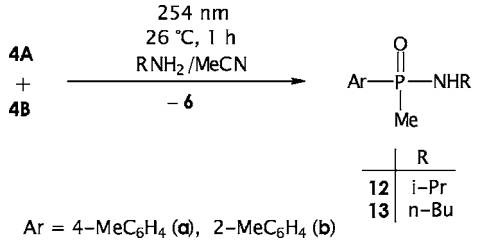
						HRFAB	
Precursor	*Nucleophile*	*Product*	*Yield (%)*	δ_P *($CDCl_3$)*	*MS, m/z (rel. int.)*	$(M+H)_{found}$	$(M+H)_{calc}$
4a	MeOH	**7a**[a]	91	45.3	184 (M^+, 30), 183 (37), 169 (100), 154 (18), 139 (23), 91 (52)	185.0709	185.0731
4a	EtOH	**8a**[b]	89	43.5	198 (M^+, 13), 197 (5), 170 (59), 155 (100), 153 (20) 139 (24), 91 (54)	199.0859	199.0888
4a	*n*-PrOH	**9a**	85	43.3	212 (M^+, 2), 171 (100), 170 (35), 155 (99), 153 (58) 139 (16), 91 (53)		
4a	*i*-PrOH	**10a**	88	41.8	212 (M^+, 4), 171 (90), 170 (29), 155 (100), 153 (56) 139 (14), 91 (50)		
4a	*sec*-BuOH	**11a**		42.3 (53%) 42.5 (47%)		227.1139	227.1201
4b	MeOH	**7b**	87	45.0	184 (M^+, 64), 183 (56), 169 (47), 154 (35), 139 (96), 91(100)	185.0705	185.0731
4b	EtOH	**8b**	92	43.0	198 (M^+, 15), 197 (8), 170 (50), 155 (100), 153 (19) 139 (31), 91 (95)	199.0855	199.0888
4b	*i*-PrOH	**10b**	89	41.3	212 (M^+, 14), 171 (14), 170 (100), 155 (36), 153 (18), 139 (3), 91 (40)		
4b	*sec*-BuOH	**11b**		41.3 (53%) 41.5 (47%)		227.1142	227.1201
4a	*i*-$PrNH_2$	**12a**	69	30.1	211 (M^+, 2), 196 (61), 153 (100), 91 (46)	212.1164	212.1204
4a	*n*-$BuNH_2$	**13a**	78	32.1	225 (M^+, 8), 153 (100), 91 (35)	226.1309	226.1361
4b	*i*-$PrNH_2$	**12b**	65	29.3	211 (M^+, 3), 196 (20), 153 (57), 91 (100)	212.1167	212.1204
4b	*n*-$BuNH_2$	**13b**	82	31.5	225 (M^+, 7), 153 (68), 91 (100)	226.1303	226.1361
5	MeOH	**7a**	86	45.2	$(M+H)^+ = 185$		

[a] δ_C ($CDCl_3$) 15.5 ($J = 103.2$, P-Me), 21.6 (Ar-Me), 51.0 ($J = 6.2$, MeO).
[b] δ_C ($CDCl_3$) 16.4 ($J = 106.7$, P-Me), 16.8 (CH_2CH_3), 22.0 (Ar-Me), 60.8 ($J = 6.2$, CH_2O).

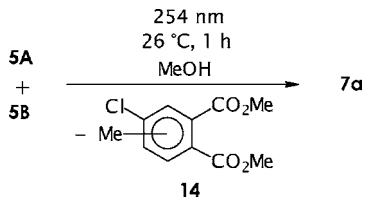
by GC–MS. Elemental compositions of the products (**7–13**) were confirmed by HRFAB measurements. The NMR and mass spectral parameters are listed in Table 1. The isomeric composition of the precursors (**4**) did not cause any problem, as the bridging unit of both isomers (**A** and **B**) was utilized in the fragmentation-related phosphinylation. Arylphosphabicyclooctadiene **5**, as the mixture of four isomers (**A-1, A-2, B-1**, and **B-2**), was used in both



SCHEME 3



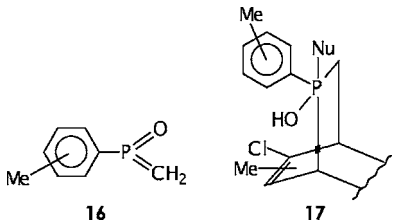
SCHEME 4



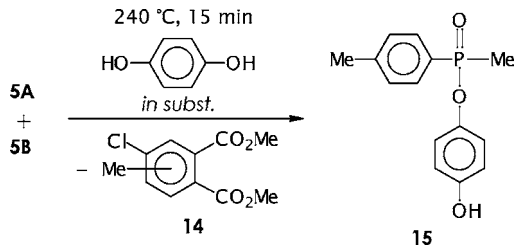
SCHEME 5

UV light-mediated and in thermo-induced phosphinylations (see Schemes 5 and 6, respectively). The phosphinylation of hydroquinone was not so efficient (the yield of phosphinate **15** was 35% after flash column chromatography), since a temperature of 240°C had to be applied. Product **15** was identified by ^{31}P NMR and MS. It is recalled that only the phosphabicyclooctadienes exhibiting a considerable ring strain are useful in thermally achieved phosphorylations [4,5].

It is also recalled that while the thermoinduced phosphinylation obviously take place through an EA mechanism involving methylenephosphine oxide (e.g. **16**) as the intermediate [3–5], the photochemically initiated phosphinylations may also involve a novel AE route via an intermediate with a pentavalent pentacoordinated phosphorus atom (e.g. **17**) [9,10,12,13].



We utilized the newly synthesized precursors **4a** and **4b** to obtain new data on the mechanism of the photoinduced phosphinylations. We wondered if both *para*-methylphenyl- and *ortho*-metylphenyl-substituted phosphabicyclooctenes (**4a** and **4b**) show a similar or a somewhat different reactivity during the phosphinylation. Some information was anticipated to be able to substantiate the involvement of the EA or the AE mechanism. Because of these reasons, the equimolar mixture of **4a** and **4b** was irradiated in the presence of methanol, isopropanol, and *sec*-butanol and the reaction was monitored by ^{31}P NMR spectroscopy. With methanol and isopropanol, no discrimination between the two aryl derivatives (**4a** and **4b**) could be observed; the precursors (**4a** and **4b**) were consumed and the products (**7a/7b** or **10a/10b**) appeared in the same rate. At the same time, by using *sec*-butanol, the *ortho*-methylphenyl cycloadduct (**4b**) was consumed somewhat slower than the *para*-methylphenyl counterpart (**4a**) and the appearance of phosphinate **11b** was delayed as compared to that of **11a**. Esters **11a** and **11b** were formed as the mixture of diastereomers (Scheme 7 showing the molar percentages obtained on the basis of relative ^{31}P NMR intensities).



SCHEME 6

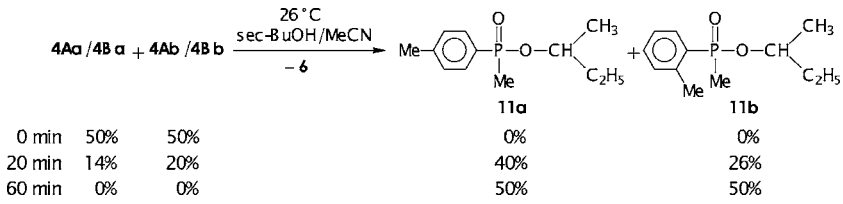
In an another kind of competitive experiment, the aryl-phosphabicyclooctenes (**4a** and **4b**) were irradiated in the presence of an equimolar mixture of methanol and *sec*-butanol. It was found that as a consequence of the more relevant steric hindrance due to the *ortho*-methyl substituent, significantly less of the butylphosphonate (**11**) was formed in the reaction of precursor **4b**, than in that of **4a** (12 and 19%, respectively) (Schemes 8 and 9). This also refers to the involvement of intermediate **17**, whose formation is probably more sensitive toward steric effects.

Indicating the role of steric hindrance, the above experiments seem to support the involvement of the AE mechanism with the intermediate of type **17** present. At the same time, the EA route may be a concurrent possibility in the UV light-mediated fragmentation-related posphinylation of alcohols.

In summary, new aryl-phosphabicyclo[2.2.2]oct-5-enes and an aryl-phosphabicyclo[2.2.2]octa-5,7-diene were synthesized and utilized in photo- and thermoinduced phosphinylation of alcohols, hydroquinone, and primary amines. Mechanistic studies with the aryl-substituted model compounds suggested the involvement of the novel AE mechanism for the photochemically induced fragmentation-related phosphinylations.

EXPERIMENTAL

The ^{31}P{^{1}H}-, ^{13}C{^{1}H}-, and ^{1}H-NMR spectra were recorded 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 Hz. The atoms of the aryl rings are numbered by 1′, 2′, 3′, etc. Mass spectrometry was performed on a PE SCIEX API



SCHEME 7

2000 type triple quadrupol and on a ZAB-2SEQ instrument.

*1-(4-Methylphenyl-)3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***1a***)*

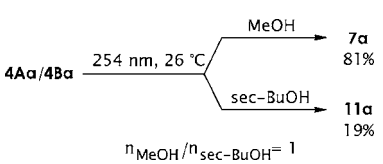
To 28.9 g (0.19 mol) of 1-chloro-3-methyl-2,5-dihydro-1*H*-phosphole oxide (obtained from the reaction of 24.8 g (0.19 mol) of 1-hydroxy-3-methyl-2,5-dihydro-1*H*-phosphole oxide and 17.0 ml (0.22 mol) of thionyl chloride in 80 ml of dry chloroform at 26°C for 20 h after concentration in vacuo) in 70 ml of tetrahydrofuran was added dropwise 0.21 mol of 4-methylphenylmagnesium bromide in 70 ml of tetrahydrofuran (prepared from 35.5 g (0.21 mol) of 4-methylbromobenzene and 5.0 g (0.21 mol) magnesium in 70 ml of tetrahydrofuran) at 0°C with stirring. After addition was complete, contents of the flask were stirred at 26°C for 4 h. Solvent was evaporated and the residue taken up in the mixture of 100 ml of chloroform, 5 ml of conc. hydrochloric acid, and 50 ml of water. The organic phase was dried (Na_2SO_4) and concentrated. The crude mixture was purified by repeated column chromatography (silica gel, 3% methanol in chloroform) to afford 30.2 g (78%) of the aryl-dihydrophosphole oxide (**1a**) as an oil. ^{31}P NMR ($CDCl_3$) δ 61.7; ^{13}C NMR ($CDCl_3$) δ 20.4 ($^3J = 11.0$, C_3–Me), 21.8 ($C_{4'}$–Me), 35.1 ($^1J = 64.9$, C_5), 38.0 ($^1J = 68.4$, C_2), 121.1 ($^2J = 7.3$, C_4), 129.4 ($^3J = 12.1$, $C_{3'}$),* 129.6 ($^2J = 10.2$, $C_{2'}$),* 137.1 ($^2J = 12.7$, C_3), 142.6 ($C_{4'}$),* may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.89 (s, C_3–Me), 2.42 (s, Ar–Me), 5.66 (d, $^3J_{PH} = 31.9$, C_4–H); ES–MS, 207 (M + H); $(M + H)^+_{found} = 207.0907$, $C_{12}H_{15}OP$ requires 207.0939.

*1-(2-Methylphenyl-)3-methyl-2,5-dihydro-1H-phosphole 1-Oxide (***1b***)*

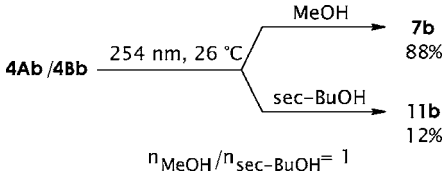
Compound **1b** was prepared similarly using 2-methylbromobenzene instead of 4-methylbromobenzene. Yield: 22.3 g (57%) oil; ^{31}P NMR ($CDCl_3$) δ 59.2; ^{13}C NMR ($CDCl_3$) δ 19.1 ($^3J = 10.9$, C_3–Me), 19.9 ($^3J = 3.4$, $C_{2'}$–Me), 33.6 ($^1J = 65.7$, C_5), 36.7 ($^1J = 68.8$, C_2), 120.0 ($^2J = 7.4$, C_4), 124.7 ($^3J = 11.4$, $C_{5'}$),* 130.1 ($^1J = 89.66$, $C_{1'}$) 130.6 ($^3J = 10.0$, $C_{3'}$),* 130.6 ($^2J = 10.3$, $C_{6'}$),* 130.9 ($C_{4'}$), 135.8 ($^2J = 12.4$, C_3), 139.7 ($^2J = 9.3$, $C_{2'}$), *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.81 (s, C_3–Me), 2.45 (s, Ar–Me), 5.57 (d, $^3J_{PH} = 31.0$, C_4–H); ES–MS, 207 (M + H); $(M + H)^+_{found} = 207.0908$, $C_{12}H_{15}OP$ requires 207.0939.

6,6-Dichloro-1-methyl-3-(4-methylphenyl-)3-phosphabicyclo[3.1.0]hexane 3-Oxide **2a**

To the solution of 15 g (37.2 mmol) of dihydrophosphole **1a** and 3.5 g (15.4 mmol) of trietylbenzylammonium chloride (TEBAC) in 180 ml of chloroform was added dropwise 90 g (2.25 mol) of sodium hydroxide, whereupon the temperature gradually rose to reflux. The contents of the flask were stirred for 4 h. After filtration and separation, the organic phase was made up to its original volume and 1.2 g (5.3 mmol) of TEBAC was added. The reaction mixture was treated with a second portion of aqueous sodium hydroxide as above and the procedure was completed with a third such treatment—this time without the addition of more catalyst. The solution obtained after filtration and separation was concentrated. The crude product so obtained was purified by column chromatography (silica gel, 3% methanol



SCHEME 8



SCHEME 9

in chloroform) to give 14.3 g (68%) of dichlorocarbene adduct **2a-1** as an oil. ^{31}P NMR ($CDCl_3$) δ 76.3; ^{13}C NMR ($CDCl_3$) δ 21.1 ($C_{4'}$–Me), 21.3 ($^3J = 3.0$, C_1–Me), 30.7 ($^1J = 68.1$, C_4), 35.9 ($^2J = 7.3$, C_1), 36.4 ($^2J = 5.5$, C_5), 36.8 ($^1J = 67.9$, C_2), 73.2 ($^3J = 14.3$, C_6), 126.4 ($^1J = 90.0$, $C_{1'}$), 129.1 ($^2J = 11.7$, $C_{2'}$),* 130.0 ($^3J = 9.7$, $C_{3'}$),* 142.6 ($C_{4'}$), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, C_1–Me), 2.41 (s, Ar–Me); ES–MS, 289 (M + H); $(M + H)^+_{found} = 289.0279$, $C_{13}H_{15}Cl_2OP$ requires 289.0316 for the ^{35}Cl isotopomer.

*6,6-Dichloro-1-methyl-3-(2-methylphenyl-)3-phosphabicyclo[3.1.0]hexane 3-Oxide (***2b***)*

Compound **2b** was prepared similarly using dihydrophosphole oxide **1b** instead of **1a** to furnish a 8:2 mixture of isomers **2b-1** and **2b-2**. Yield: 13.1 g (66%); **2b-1** could be separated as a crystalline compound by a simple filtration, mp 125–127°C (acetone); ES–MS, 289 (M + H); $(M + H)^+_{found} = 289.0276$, $C_{13}H_{15}Cl_2OP$ requires 289.0316 for the ^{35}Cl isotopomer.

2b-1: ^{31}P NMR ($CDCl_3$) δ 80.3; ^{13}C NMR ($CDCl_3$) δ 21.2 ($^3J = 3.5$, $C_{2'}$–Me), 21.4 ($^3J = 5.2$, C_1–Me), 30.1 ($^1J = 68.3$, C_4), 35.6 ($^2J = 7.5$, C_1), 36.1 ($^2J = 6.0$, C_5), 36.2 ($^1J = 68.3$, C_2), 72.1 ($^3J = 11.5$, C_6), 125.1 ($^3J = 11.7$, $C_{5'}$),* 129.8 ($^3J = 11.7$, $C_{3'}$),* 130.2 ($^1J = 93.3$, $C_{1'}$) 131.0 ($^2J = 9.9$, $C_{6'}$),* 131.6 ($C_{4'}$), 140.5 ($^2J = 7.4$, $C_{2'}$), *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.76 (s, C_1–Me), 2.67 (s, Ar–Me).

2b-2: ^{31}P NMR ($CDCl_3$) δ 78.2; ^{13}C NMR ($CDCl_3$) δ 21.0 ($^3J = 6.2$, C_1–Me), 21.6 ($^3J = 3.7$, $C_{2'}$–Me), 27.8 ($^1J = 68.5$, C_4), 32.7 ($^2J = 11.7$, C_1), 34.1 ($^1J = 67.0$, C_2), 34.3 ($^2J = 9.7$, C_5), 72.4 ($^3J = 14.3$, C_6), 125.5 ($^3J = 11.4$, $C_{5'}$),* 130.2 ($^1J = 86.2$, $C_{1'}$), 131.3 ($^3J = 10.9$, $C_{3'}$),* 131.9 ($C_{4'}$), 132.0 ($^3J = 9.5$, $C_{6'}$),* 141.3 ($^2J = 7.9$, $C_{2'}$), *tentative assignment.

3- and 5-Methyl-4-chloro-1-(4-methylphenyl-)-1,2-dihydrophosphinine 1-Oxide **3Aa** *and* **3Ba**

A 2.0 g (6.92 mmol) sample of **2a** was heated at 138°C in a vial until the evolution of hydrochloric acid ceased (ca. 7 min). The crude product was purified by column chromatography (as above) to provide 1.2 g (67%) of oily **3a** as a 3:1 mixture of isomers **A** and **B**; ES–MS, 253 (M + H); $(M + H)^+_{found} = 253.0507$, $C_{13}H_{14}ClOP$ requires 253.0549 for the ^{35}Cl isotopomer.

3Aa: ^{31}P NMR ($CDCl_3$) δ 16.4; ^{13}C NMR ($CDCl_3$) δ 21.6 ($C_{4'}$–Me), 23.4 ($^3J = 8.5$, C_3–Me), 36.6 ($^1J = 71.4$, C_2), 119.5 ($^1J = 93.8$, C_6), 123.8 ($^2J = 19.8$, C_3), 129.5 ($^2J = 12.4$, $C_{2'}$),* 130.6 ($^3J = 10.6$, $C_{3'}$),* 142.8 ($^4J = 2.8$, $C_{4'}$), 144.1 (C_5), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 2.07 (s, C_3–Me), 2.42 (s, Ar–Me), 6.18 (dd, $^2J_{PH} = {}^3J_{HH} = 12.8$, C_6–H), 6.89 (dd, $^3J_{PH} = 34.6$, $^3J_{HH} = 12.8$, C_5–H).

3Ba: ^{31}P NMR ($CDCl_3$) δ 15.3; ^{13}C NMR ($CDCl_3$) δ 21.6 ($C_{4'}$–Me), 25.0 ($^3J = 12.7$, C_5–Me), 30.7 ($^1J = 71.5$, C_2), 119.1 ($^1J = 97.2$, C_6), 122.9 ($^2J = 10.8$, C_3), 129.4 ($^2J = 13.1$, $C_{2'}$),* 130.9 ($^3J = 9.5$, $C_{3'}$),* 142.7 ($C_{4'}$), 149.8 (C_5), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, C_5–Me), 2.42 (Ar–Me), 6.29 (dt, C_3–H).

3- and 5-Methyl-4-chloro-1-(2-methylphenyl-)-1,2-dihydrophosphinine 1-Oxide **3Ab** *and* **3Bb**

Compounds **3Ab** and **3Bb** were prepared similarly by heating 0.50 g (1.73 mmol) of the isomeric mixture of dichlorocarbene adduct **2b** at 135°C for ca. 6 min. Yield: 0.31 g (70%) oil; ES–MS, 253 (M + H); $M^+_{found} = 253.0505$, $C_{13}H_{14}ClOP$ requires 253.0549 for the ^{35}Cl isotopomer.

3Ab: ^{31}P NMR ($CDCl_3$) δ 16.2; ^{13}C NMR ($CDCl_3$) δ 20.5 ($^3J = 3.3$, $C_{2'}$–Me), 22.3 ($^3J = 8.7$, C_3–Me), 34.6 ($^1J = 70.5$, C_2), 118.4 ($^1J = 93.3$, C_6), 122.6 ($^2J = 19.7$, C_3), 124.8 ($^3J = 12.0$, $C_{3'}$),* 129.3 ($^1J = 105.1$, $C_{1'}$), 130.5 ($^3J = 9.4$, C_4), 130.8 ($^3J = 11.0$, $C_{5'}$),* 131.1 ($^2J = 10.6$, $C_{6'}$),* 131.3 ($C_{4'}$), 139.8 ($^2J = 10.0$, $C_{2'}$), 142.4 (C_5) *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, C_3–Me), 2.50 (s, Ar–Me), 6.28 (dd, $^2J_{PH} = {}^3J_{HH} = 12.3$, C_6–H), 6.91 (dd, $^3J_{PH} = 34.9$, $^3J_{HH} = 12.8$, C_5–H).

3Bb: ^{31}P NMR ($CDCl_3$) δ 15.7; ^{13}C NMR ($CDCl_3$) δ 20.5 ($^3J = 3.3$, $C_{2'}$–Me), 24.0 ($^3J = 13.0$, C_5–Me), 28.8 ($^1J = 70.7$, C_2), 117.8 ($^1J = 96.8$, C_6), 122.6 ($^2J = 11.1$, C_3), 124.7 ($^3J = 12.0$, $C_{3'}$),* 129.3 ($^1J = 105.1$, $C_{1'}$), 130.8 ($^3J = 11.0$, $C_{5'}$),* 131.1 ($^2J = 10.6$, $C_{6'}$), *131.2 ($C_{4'}$), 139.9 ($^2J = 11.2$, $C_{2'}$), 148.0 (C_5) *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, C_5–Me), 2.52 (Ar–Me), 6.32 (dt, C_3–H).

General Procedure for the Synthesis of Cycloadducts **4a, 4b,** *and* **5**

A solution of 1.0 g (3.96 mmol) of tolyldihydrophosphinine oxide **3a** or **3b** consisting of ~75% of the **A** isomer and ~25% of the **B** isomer and 4.8 mmol of *N*-phenylmaleimide (0.84 g) or dimethylacetylene dicarboxylate (0.59 ml) in 25 ml of toluene was stirred at the boiling point for 5 days. Solvent was evaporated and the residue so obtained purified by column chromatography (silica gel, 3% methanol in chloroform) to furnish cycloadducts **4a, 4b**, and **5** as the mixture of isomers. The data are listed below.

1- and 11-Methyl-10-chloro-4-phenyl-8-p-tolyl-4-aza-8λ^5*-phosphatricyclo[5.2.2.0*^{2,6}*]undec-10-ene-3,5-dione 8-Oxide (***4Aa** *and* **4Ba***)* [18]. Yield: 1.0 g (61%) of **4a** as a 6:4 mixture of isomers **A** and **B**; mp 132–134°C (acetone); ES–MS, 426

(M + H); $(M+H)^+_{found}$ = 426.0967, $C_{23}H_{22}ClNO_3P$ requires 426.1026 for the ^{35}Cl isotopomer.

4Aa: ^{31}P NMR ($CDCl_3$) δ 37.8; ^{13}C NMR ($CDCl_3$) δ 21.6 ($C_{4'}$–Me), 23.7 ($^3J = 10.8$, C_4–Me), 37.1 ($^1J = 75.7$, C_3), 39.4 ($^1J = 62.9$, C_1), 40.5 (C_7), 44.5 ($^2J = 6.3$, C_4), 49.6 ($^2J = 10.7$, C_8), 122.7 ($^2J = 5.9$, C_6), 126.5 ($C_{3''}$),[a] 127.2 ($^1J = 103.2$, $C_{1'}$), 128.9 ($C_{4''}$), 129.2 ($C_{2''}$),[a] 129.7 ($^2J = 12.4$, $C_{2'}$),[b] 131.2 ($^3J = 9.6$, $C_{3'}$),[b] 131.6 ($C_{1''}$), 140.2 ($^3J = 11.0$, C_5), 143.5 ($C_{4'}$), 174.2 (C_9), 175.9 ($^3J = 15.1$, C_{11}), [a,b]may be reversed; ^1H NMR ($CDCl_3$) δ 1.84 (s, C_4–Me), 2.45 (s, Ar–Me), 6.09 (dd, $^3J_{PH} = {}^3J_{HH}$ 7.9, C_6–H);

4Ba: ^{31}P NMR ($CDCl_3$) δ 37.5; ^{13}C NMR ($CDCl_3$) δ 21.6 ($C_{4'}$–Me), 19.0 (C_6–Me), 28.1 ($^1J = 77.2$, C_3), 39.6 (C_7), 42.9 ($^2J = 6.9$, C_4), 44.8 ($^1J = 67.1$, C_1), 45.5 ($^2J = 12.2$, C_8), 126.4 ($C_{3''}$),[a] 129.0 ($C_{4''}$), 129.3 ($C_{2''}$),[a] 129.8 ($^2J = 12.2$, $C_{2'}$),[b] 130.7 ($^2J = 5.9$, C_6), 131.1 ($^3J = 11.2$, $C_{3'}$),[b] 143.5 ($C_{4'}$), 175.4 (C_9), 176.2 ($^3J_{PC} = 14.7$, C_{11}), [a,b]may be reversed; ^1H NMR ($CDCl_3$) δ 1.55 (s, C_6–Me), 2.45 (s, Ar–Me).

*1- and 11-Methyl-10-chloro-4-phenyl-8-o-tolyl-4-aza-8λ^5-phosphatricyclo[5.2.2.0^{2,6}]undec-10-ene-3,5-dione 8-Oxide (**4Ab** and **4Bb**)* [18]. Yield: 0.88 g (52%) of **4b** as a 58:42 mixture of isomers **A** and **B**; mp 105–107°C (acetone); ES–MS, 426 (M + H); $(M+H)^+_{found}$ = 426.0952, $C_{23}H_{22}ClNO_3P$ requires 426.1026 for the ^{35}Cl isotopomer.

4Ab: ^{31}P NMR ($CDCl_3$) δ 42.5; ^{13}C NMR ($CDCl_3$) δ 21.6 ($^3J = 4.2$, $C_{2'}$–Me), 23.7 ($^3J = 10.7$, C_4–Me), 37.7 ($^1J = 62.8$, C_1), 37.9 ($^1J = 74.9$, C_3), 40.4 (C_7), 44.4 ($^2J = 6.4$, C_4), 49.7 ($^3J = 10.5$, C_8), 122.2 ($^2J = 6.0$, C_6), 125.6 ($^3J = 12.2$, $C_{3'}$),[a] 126.3 ($C_{3''}$),[b] 128.7 ($C_{4''}$), 128.9 ($^1J = 100.5$, $C_{1'}$), 129.0 ($C_{2''}$),[b] 129.9 ($^3J = 10.6$, $C_{5'}$),[a] 131.4 ($C_{1''}$), 131.9 ($^2J = 10.8$, $C_{6'}$),[a] 132.3 ($C_{4'}$), 139.0 ($^3J = 11.0$, C_5), 142.1 ($^2J = 7.8$, $C_{2'}$), 173.8 (C_9), 175.8 ($^3J = 14.8$, C_{11}), [a]tentative assignment, [b]may be reversed; ^1H NMR ($CDCl_3$) δ 1.81 (s, C_4–Me), 2.74 (s, Ar–Me), 6.12 (dd, $^3J_{PH} = {}^3J_{HH}$ 8.0, C_6–H);

4Bb: ^{31}P NMR ($CDCl_3$) δ 42.4; ^{13}C NMR ($CDCl_3$) δ 18.5 ($^3J = 2.1$, C_6–Me), 21.9 ($^3J = 3.8$, $C_{2'}$–Me), 28.0 ($^1J = 78.5$, C_3), 39.3 ($^2J = 2.2$, C_7), 42.7 ($^2J = 7.1$, C_4), 43.8 ($^1J = 61.1$, C_1), 45.7 ($^3J = 11.1$, C_8), 125.5 ($^3J = 11.5$, $C_{3'}$),[a] 126.2 ($C_{3''}$),[b] 128.1 ($^1J = 99.3$, $C_{1'}$), 128.8 ($C_{4''}$), 129.1 ($C_{2''}$),[b] 130.1 ($^2J = 5.8$, C_6), 130.9 ($^3J = 10.7$, $C_{5'}$),[a] 132.2 ($^2J = 11.1$, $C_{6'}$),[a] 142.8 ($^2J = 8.4$, $C_{2'}$), 175.0 (C_9), 176.0 ($^3J = 15.1$, C_{11}), [a]tentative assignment, [b]may be reversed; ^1H NMR ($CDCl_3$) δ 1.43 (s, C_6–Me), 2.82 (s, Ar–Me).

*4- and 7-Methyl-8-chloro-2-oxo-2-p-tolyl-2-phosphabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylic Acid Dimethyl Ester (**5**)* [18]. Yield: 0.67 g (43%) oily product after an additional chromatography (silica gel, benzene-acetone 2:3) as a 38, 36, and 26% mixture of three isomers; ES–MS, 395 (M + H); $(M+H)^+_{found}$ = 395.0741, $C_{19}H_{21}ClO_5P$ requires 395.0815 for the ^{35}Cl isotopomer.

5A-1: ^{31}P NMR ($CDCl_3$) δ 44.5 (38%); ^{13}C NMR ($CDCl_3$) δ 20.3 ($J = 10.3$, C_4–Me), 21.7 (Ar–Me), 32.1 ($J = 96.9$, C_3), 44.4 ($J = 50.9$, C_1), 47.4 ($J = 8.5$, C_4), 52.4, 52.5 (MeO), 116.8 ($J = 8.4$, C_6), 162.6, 166.0 (C=O).

5A-2: ^{31}P NMR ($CDCl_3$) δ 33.5 (36%); ^{13}C NMR ($CDCl_3$) δ 20.2 ($J = 11.2$, C_4–Me), 21.7 (Ar–Me), 32.3 ($J = 96.8$, C_3), 45.1 ($J = 50.1$, C_1), 48.0 ($J = 8.7$, C_4), 52.4, 52.7 (MeO), 116.8 ($J = 8.4$, C_6), 162.5, 166.1 (C=O).

5B: ^{31}P NMR ($CDCl_3$) δ 44.9 (26%); ^{13}C NMR ($CDCl_3$) δ 18.9 (C_6–Me), 21.7 (Ar–Me), 46.9 ($J = 9.2$, C_4), 50.8 ($J = 50.5$, C_1), 52.8, 52.9 (MeO), 161.8, 166.5 (C=O).

General Procedure for the Photostimulated Fragmentation-Related Phosphorylations

The solution of 0.10 g (0.24 mmol) of phosphabicyclooctene **4a** or **4b** consisting of ~60% of the **A** and ~40% of the **B** isomer in 45 ml of acetonitrile and 4 ml of the corresponding alcohol was irradiated in a photochemical quartz reactor with a 125 W mercury lamp for 1 h. The mixture was concentrated in vacuo and the residue so obtained was purified by flash column chromatography (silica gel, 3% methanol in chloroform) to give the corresponding phosphinate (**7a, 8a, 9a, 10a, 11a, 7b, 8b, 9b, 10b, 11b**) as an oil (Table 1).

Using primary amines (4 ml of each) as the nuchleophile, the result of the photolysis was the corresponding phosphinic amide (**12** or **13**) (Table 1). Phosphabicyclooctadiene **5** was used in the phosphorylation of methanol as described for the reaction of precursor **4a** (Table 1). The competitive photolysis was performed as above using a mixture of 0.05 g (0.12 mmol) of **4a** and 0.05 g (0.12 mmol) of **4b** and *sec*-butanol. The reaction was monitored by ^{31}P NMR till completion.

Thermoinduced Phosphorylation of Hydroquinone, Using Phosphabicyclooctadiene **5**

0.30 g (0.76 mmol) of cycloadduct **5** as the mixture of three isomers and 0.10 g (2.73 mmol) of hydroquinone was heated at 240°C in a vial for 15 min. Flash column chromatography (silica gel, 3% methanol in chloroform) afforded 0.11 g (35%) of phosphinate **15** in a purity of ca. 90%. ^{31}P NMR ($CDCl_3$) δ 44.5; ES–MS,

263 (M + H); $(M + H)^+_{found} = 263.0821$, $C_{14}H_{16}O_3P$ requires 263.0837 for the ^{35}Cl isotopomer. GC–MS, *m/z* (rel. int.) 262 (M^+, 27), 261 (27), 169 (2), 154 (9), 153 (100), 91 (37).

Crystal Data for Phosphabicyclohexane **2b-1**

X-ray diffraction data of product **2b-1** were collected at 293 K. Crystal data for **2b-1**: $C_{13}H_{15}Cl_2OP$, M = 298.12, transparent, needle shape crystal, approximate dimensions 0.32 × 0.12 × 0.1 mm, monoclinic, space group $P2_1/n$, $a = 8.947(4)$ Å, $b = 7.894(4)$ Å, $c = 19.347(3)$ Å, $\beta = 91.75(2)^\circ$, $V = 1366(1)$ Å^3, $Z = 4$, $D_c = 1.406$ gcm^{-1}, μ (Cu Kα) = 5.226 mm^{-1}. Structure solution with direct method was carried out with the teXsan package [19]. Refinement was carried out with SHELXL-97 [20]. Final R indices for **2b-1** are $R = 0.2122$, $R_W = 0.3305$ (for all 5778 reflections) $R = 0.1063$, $R_W = 0.2716$ ($I > 2\sigma(I)$).

CCDC 206074 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk).

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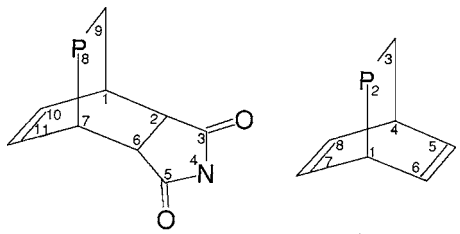
[18] According to the IUPAC nomenclature, the following numbering was used for naming the products:



4 **5**

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