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Novel 2-Phosphabicyclo[2.2.2]oct-5-ene Derivatives and Their Use in Phosphinylations

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ABSTRACT: *The [4 + 2] cycloaddition of the double-bond isomers (***A** *and* **B***) of dihydrophosphinine oxide* **1** *afforded novel phosphabicyclo[2.2.2]oct-5-ene derivates (***2–4***), formation of which was justified by PM3 semiempirical calculations. The compounds of dimer type (***2–4***) were utilized in the UV light-mediated fragmentation-related phosphinylation of nucleophiles, especially in that of alcohols. To explore the role of structural modifications on the fragmentation ability, disulfide* **5***, phosphabicyclooctane* **7** *obtained by the hydrogenation of* **2***, and the adduct of dihydrophosphinine oxide* **1** *with benzoquinone (***7***) were also synthesized and tested in fragmentation.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:97–106, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10221

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INTRODUCTION

The phosphorylation of *O*- and *N*-nucleophiles by low-coordinated P-fragments, like methylenephosphine oxides, is a novel synthetic method [1]. Because of their strained framework, the phosphabicyclo[2.2.2]octenes and -octadienes are excellent precursors of methylenephosphine oxides, and hence they can be used in the fragmentation related phosphorylation of a variety of nucleophiles [2–7]. The photolysis of phosphabicyclo[2.2.2]octene derivatives in the presence of alcohols or amines led to phosphonic and phosphinic esters/amides [3–5]. The potential of this method is that the

phosphonic and the phosphinic derivatives are obtained selectively and under mild conditions. The phosphabicyclooctadienes were also efficient in the thermo-induced phosphorylation of phenol derivates [7].

As regards the mechanism of the fragmentation-related phosphorylations, the thermolyses involve methylenephosphine oxides as the intermediates [2,7], at the same time, the photolyses rather follow an addition–elimination route with a pentavalent-pentacoordinated P-intermediate [2–4,8,9]. Recently, new types of phosphabicyclooctenes with sterically demanding substituent on the phosphorus atom [9,10], as well as derivatives incorporating nitrogen atoms in the framework [9], have been described.

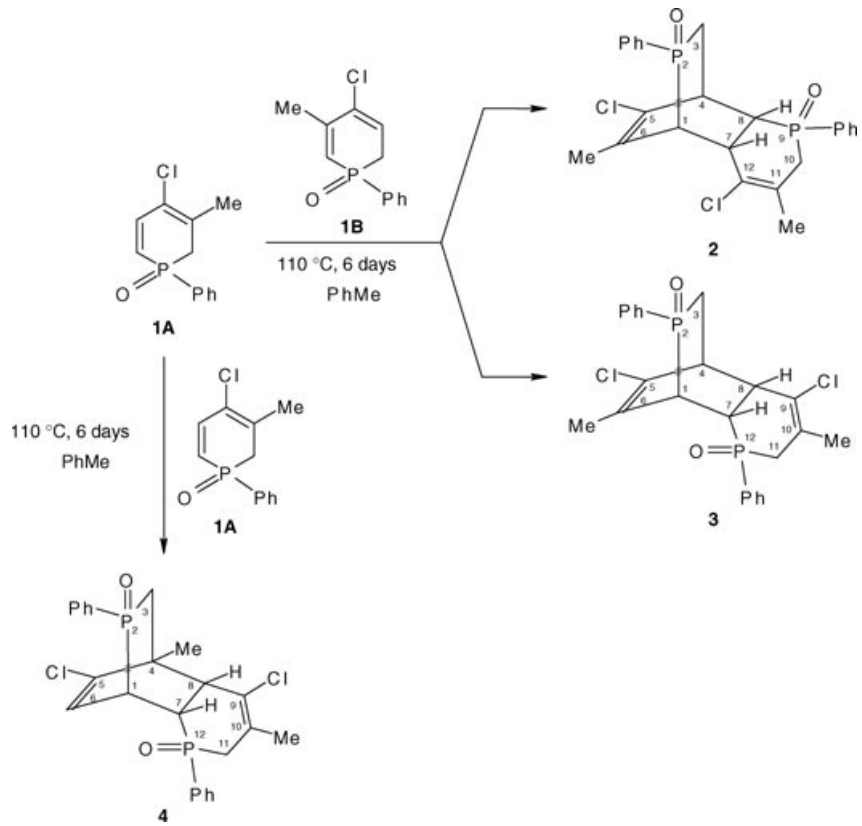
In this paper, a novel dimerization reaction affording phosphabicyclo[2.2.2]octenes with a six-membered ring fusion in positions 7 and 8 is presented and the fragmentation properties of the cycloadducts related are discussed.

RESULTS AND DISCUSSION

We have recently observed that the double-bond isomers of methyl-4-chloro-1,2-dihydrophosphinine oxides may enter into Diels-Alder cycloaddition with each other at 110°C [11]. As can be seen on the example of the P-phenyl substituted model compound, isomer **1B** served as the diene component, while **1A** acted as the dienophile to afford phosphabicyclooctene **2** which can be regarded to be a dimer of two units of dihydrophosphinine oxide **1** (Scheme 1).

Dimer **2** was isolated in 34% yield after chromatography and its stereostructure was confirmed by single crystal X-ray analysis showing that the two six-membered P-cycles are joined in the endo ring fusion (Fig. 1).

In the phosphabicyclo[2.2.2]oct-5-ene moiety of molecule **2**, all the three rings have a boat conformation with C(1) and C(4) on the same side of the plain, determined by the remaining four atoms. The annellating tetrahydrophosphinine ring has a screw boat conformation with P(9) above and C(10) below the plain laid through the C(7), C(8), C(11), and C(12) atoms. The phenyl group attached to P(9) is in axial position. At the same time, the P(2)-phenyl substituent is in an equatorial position toward the C(1), P(2), C(3), C(4), C(8), C(7) ring, while in an axial position toward the C(1), P(2), C(3), C(4), C(5), C(6) ring. Endocyclic torsion angles summarized in Fig. 1 define the conformation of the molecule (**2**). The



SCHEME 1

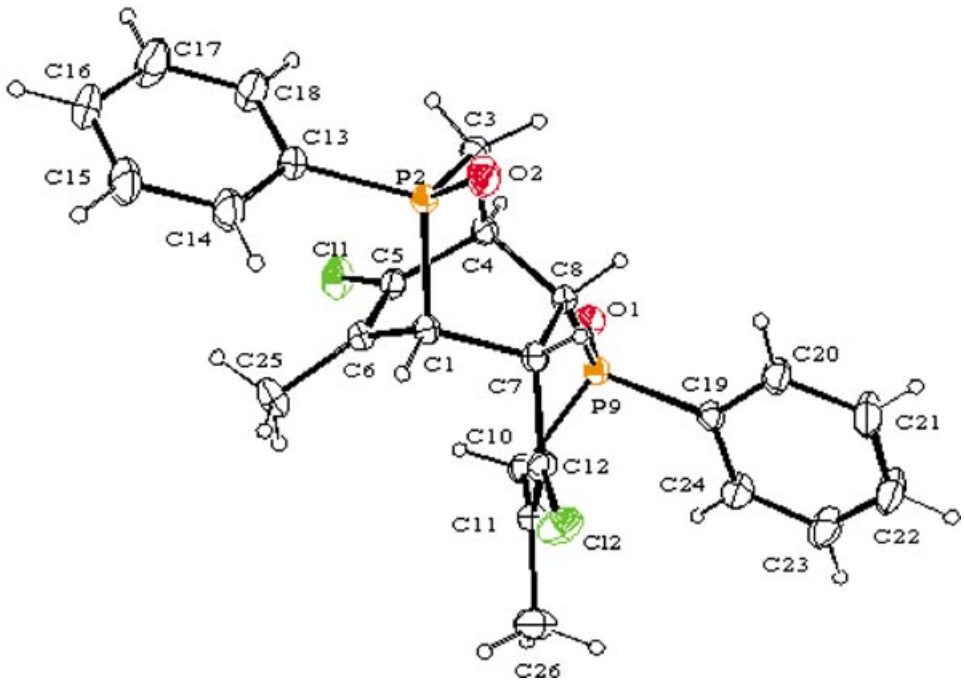


FIGURE 1 Perspective view of **2** with bond lengths (Å), bond angles (°), and torsion angles (°) obtained by X-ray. The geometrical data calculated by the PM3 method are shown in parentheses. C(1)—P(2) 1.822(3) [1.899], P(2)—C(3) 1.815(4) [1.854], C(3)—C(4) 1.555(5) [1.532], C(4)—C(5) 1.509(4) [1.505], C(5)—C(6) 1.328(4) [1.348], C(6)—C(1) 1.517(5) [1.487], C(1)—C(7) 1.566(4) [1.542], C(7)—C(8) 1.557(4) [1.539], C(8)—C(4) 1.547(4) [1.541], C(8)—P(9) 1.817(3) [1.888], P(9)—C(10) 1.797(3) [1.833], C(10)—C(11) 1.515(5) [1.480], C(11)—C(12) 1.329(5) [1.344], C(12)—C(7) 1.505(5) [1.502]. C(1)—P(2)—C(3) 98.20(16) [97.07], C(1)—P(2)—C(13) 106.67(16) [107.27], C(1)—P(2)—O(2) 113.20(16) [114.24], O(2)—P(2)—C(3) 115.80(18) [115.52], O(2)—P(2)—C(13) 112.81(17) [113.71], C(13)—P(2)—C(3) 108.84(18) [107.51], C(8)—P(9)—C(10) 102.90(16) [101.12], C(8)—P(9)—O(1) 113.20(15) [114.69], C(8)—P(9)—C(19) 106.94(16) [103.33], C(10)—P(9)—C(19) 103.96(17) [108.77], O(1)—P(9)—C(19) 113.95(16) [113.32], O(1)—P(9)—C(10) 114.80(16) [114.40]. C(6)—C(1)—P(2)—C(3) −62.2(2) [−51.4], C(7)—C(1)—P(2)—C(3) 57.6(2) [65.8], C(1)—P(2)—C(3)—C(4) 6.5(3) [−7.4], P(2)—C(3)—C(4)—C(5) 50.0(3) [62.9], P(2)—C(3)—C(4)—C(8) −68.5(3) [−57.4], C(8)—C(4)—C(5)—C(6) 52.9(4) [52.0], C(3)—C(4)—C(5)—C(6) −65.2(4) [−67.8], C(4)—C(5)—C(6)—C(1) 2.7(4) [−0.94], C(7)—C(1)—C(6)—C(5) −55.8(4) [−54.1], P(2)—C(1)—C(6)—C(5) 62.1(3) [61.0], C(6)—C(1)—C(7)—C(8) 50.2(3) [57.0], P(2)—C(1)—C(7)—C(8) −66.8(3) [−60.3], C(5)—C(4)—C(8)—C(7) −52.6(3) [−44.5], C(3)—C(4)—C(8)—C(7) 66.3(3) [74.0], C(5)—C(4)—C(8)—P(9) 75.6(3) [88.5], C(1)—C(7)—C(8)—C(4) 4.0(3) [−7.0].

tetrahedron around P(2) is somewhat distorted. The two most extreme values are C(1)—P(2)—C(3) 98.2(2)° and O(2)—P(2)—C(3) 115.8(2)°. A smaller distorsion can be seen around the P(9) atom. The two most extreme values are 104.0(2)° for C(10)—P(9)—C(19) and 114.8(2)° for C(10)—P(9)—O(1).

A careful refinement of the crude reaction mixture by chromatography led to two minor components that are new kinds of dimers (**3** and **4**) of dihydrophosphinine oxide **1** (Scheme 1).

Dimer **3** was derived by the Diels-Alder reaction of dihydrophosphinine oxides **1B** with **1A**, while product **4** by the [4 + 2] cycloaddition of two units of **1A**. Contrary to the case of dimer **2**, where the two phosphorus atoms are separated by four bonds, the two heteroatoms in phosphabicyclooctenes **3** and **4** are coupled ($^3J_{PP}$ = 38.3 and 41.7 Hz, respectively). The structure of all the products (**2–4**) was confirmed by ^{13}C NMR. The olefinic proton of compound **4** appeared at δ_H 6.4 in the ^{1}H NMR spectrum. The elemental composition of the dimers **2–4** was confirmed by HR-MS.

Assuming an endo fusion of the rings, as suggested by analogies [3] and disregarding the configuration of the phosphorus atoms, the combination of the double-bond isomers (**A** and **B**) of dihydrophosphinine oxide **1** may lead to eight structures (Fig. 2), from which the formation of two species (**2** and **3**) seems to be more favourable due to the lack of steric compression caused by the skeletal methyl group(s). As a matter of fact, products **2** and **3** were among those isolated from the reaction mixture. To evaluate the relative stability of the products, the values of heat of formation (ΔH_f°) were calculated for the eight possible isomers (Fig. 2) by the PM3 method [12] that is well suited to computation of phosphorus-containing systems [13,14]. The quantum chemical calculations justified the preference

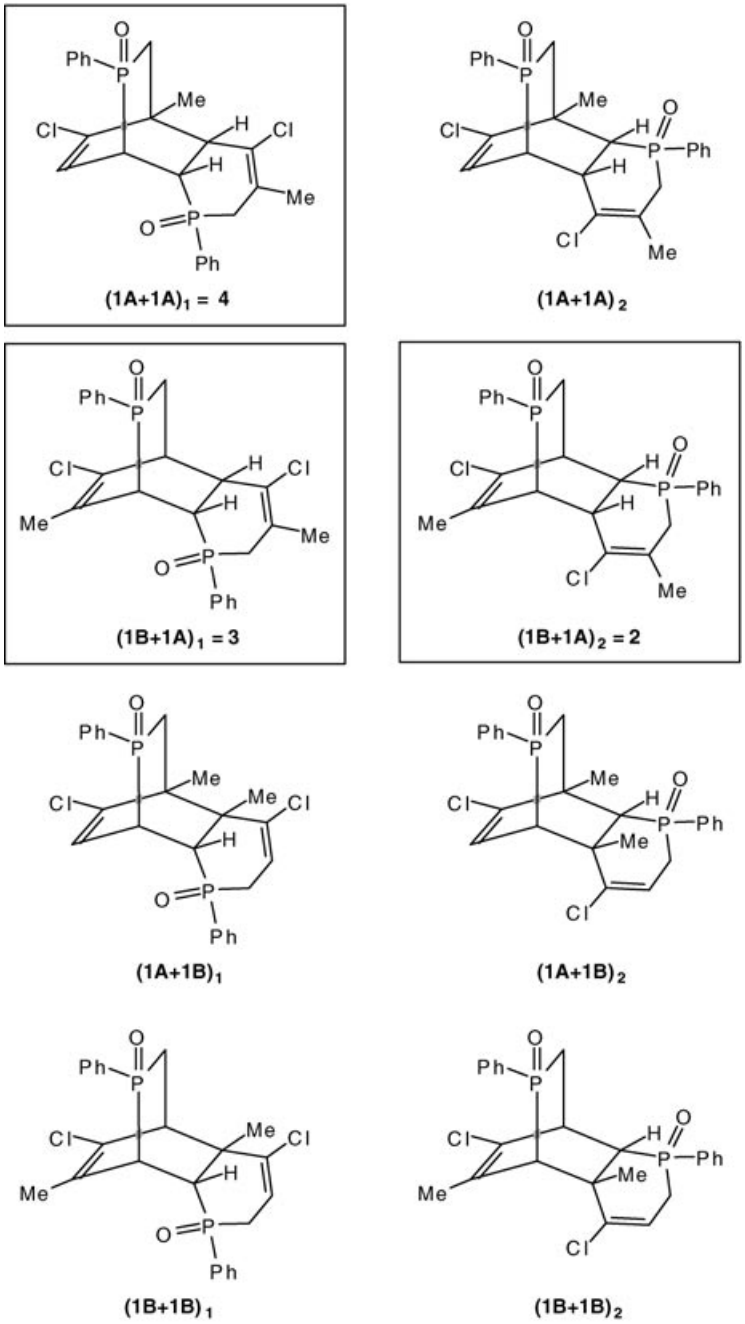


FIGURE 2 Possible products from the interaction of two units of dihydrophosphinine oxide **1A**/**1B**.

for the formation of isomers **2** and **3** with ΔH_f° values of −24.09 and −22.84 kcal/mol, respectively (column 5 of Table 1). For the third species isolated (**4**), an enthalpy of −13.73 kcal/mol was obtained which was comparable with the corresponding values of isomers **(1A + 1A)$_2$, (1B + 1B)$_1$**, and **(1B + 1B)$_2$** (−12.34, −17.44, and −14.53 kcal/mol, respectively). The perspective view of products **3** and **4** is shown in Figs. 3 and 4, respectively. **(1A + 1B)$_1$** and **(1A + 1B)$_2$** having methyl groups in and around the junction were the most unfavourable species in the series as suggested by the ΔH_f° values of −7.60 and −1.14 kcal/mol, respectively. It is noted that each of the eight ΔH_f° values is the average of those obtained for the corresponding four P-configurational isomers (columns 1–4 of Table 1). The difference between the extreme values of the members within the series fell in the range of 0.50–2.65 kcal/mol (column 6 of Table 1). The geometrical data obtained for product **2** by the PM3 method were in acceptable

TABLE 1 Heat of Formation (ΔH_f°) in kcal/mol for the Possible Cycloadducts Calculated by the PM3 Semiempirical Method

Products	*Diastereomers*				*Average for the Four Diastereomers*	*Difference of the Two Extreme Values*
	P=O–P=O	*P=O–O=P*	*O=P–P=O*	*O=P–O=P*		
(1A + 1A)$_1$ = 4	−13.03	−14.62	−13.70	−13.58	−13.73	1.59
(1B + 1A)$_1$ = 3	−22.19	−23.77	−22.64	−22.77	−22.84	1.58
(1A + 1B)$_1$	−5.79	−8.44	−7.60	−8.28	−7.53	2.65
(1B + 1B)$_1$	−15.85	−18.18	−17.66	−18.08	−17.44	2.33
(1A + 1A)$_2$	−10.83	−12.91	−12.18	−13.42	−12.34	2.59
(1B + 1A)$_2$ = 2[a]	−23.89	−23.68	−24.16	−24.62	−24.09	0.94
(1A + 1B)$_2$	−0.59	−1.77	−0.32	−1.87	−1.14	1.55
(1B + 1B)$_2$	−14.79	−14.42	−14.62	−14.29	−14.53	0.50

[a]The ΔH_f° values for the diastereomers obtained by the MNDO-d method are −94.60, −94.29, −94.94, and −94.68, respectively.

agreement with those calculated from the X-ray structure (Fig. 1). This means that the PM3 calculations indeed describe the pentavalent organophosphorus compounds adequately.

To see how the structural modification affects the fragmentation properties, bis(phosphine oxide) **2** was converted to the corresponding bis(phosphine sulfide) (**5**) by a standard procedure [15] in a yield of 68% after chromatography (Scheme 2).

Product **5** was characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectroscopical data. As a

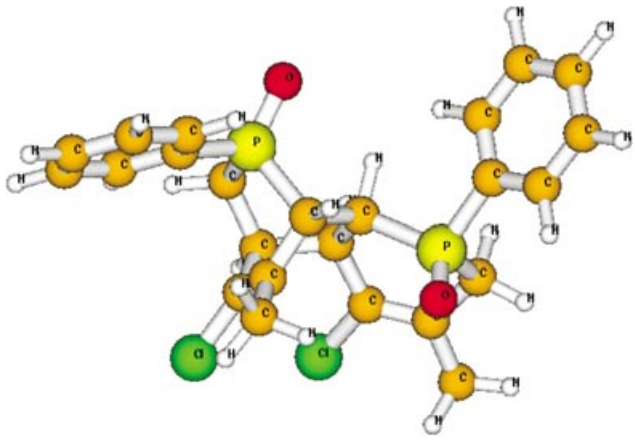


FIGURE 3 Perspective view of **3** with bond lengths (Å), bond angles (°), and torsion angles (°) calculated by the PM3 method. C(1)—P(2) 1.896, P(2)—C(3) 1.859, C(3)—C(4) 1.527, C(4)—C(5) 1.501, C(5)—C(6) 1.348, C(6)—C(1) 1.490, C(1)—C(7) 1.524, C(7)—C(8) 1.545, C(8)—C(4) 1.556, C(8)—C(9) 1.501, C(9)—C(10) 1.349, C(10)—C(11) 1.476, C(11)—P(12) 1.838, P(12)—C(7) 1.893. C(1)—P(2)—C(3) 96.13, C(1)—P(2)—C(13) 107.25, C(1)—P(2)—O(2) 114.81, O(2)—P(2)—C(3) 115.27, O(2)—P(2)—C(13) 113.93, C(13)—P(2)—C(3) 107.79, C(11)—P(12)—C(7) 99.95, C(11)—P(12)—O(1) 116.35, C(11)—P(12)—C(19) 102.56, C(7)—P(12)—C(19) 105.23, O(1)—P(12)—C(19) 113.68, O(1)—P(12)—C(7) 117.09. C(6)—C(1)—P(2)—C(3) −57.9, C(7)—C(1)—P(2)—C(3) 61.2, C(1)—P(2)—C(3)—C(4) 2.3, P(2)—C(3)—C(4)—C(5) 54.9, P(2)—C(3)—C(4)—C(8) −63.7, C(8)—C(4)—C(5)—C(6) 53.5, C(3)—C(4)—C(5)—C(6) −67.2, C(4)—C(5)—C(6)—C(1) 1.9, C(7)—C(1)—C(6)—C(5) −51.6, P(2)—C(1)—C(6)—C(5) 61.4, C(6)—C(1)—C(7)—C(8) 41.3, P(2)—C(1)—C(7)—C(8) −73.6, C(5)—C(4)—C(8)—C(7) −58.5, C(3)—C(4)—C(8)—C(7) 61.2, C(6)—C(1)—C(7)—P(9) −92.3, C(1)—C(7)—C(8)—C(4) 12.5.

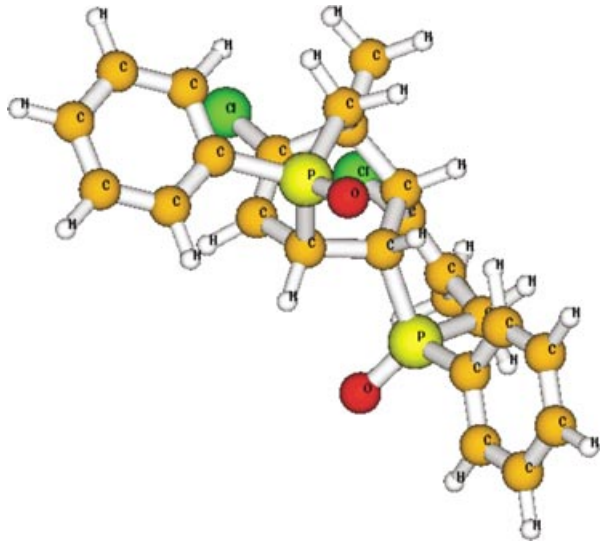
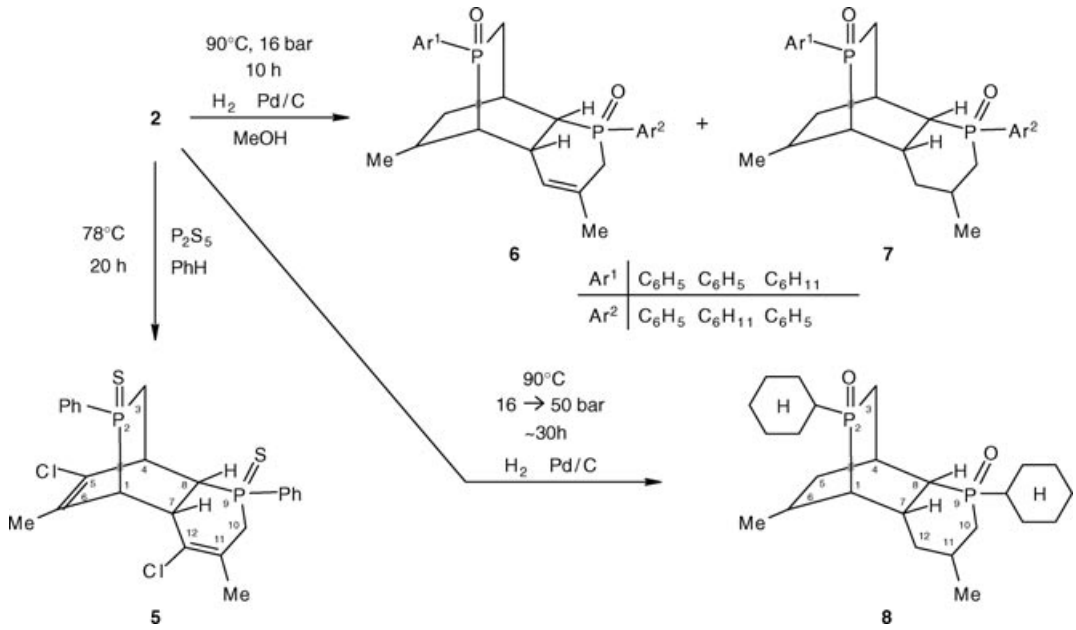


FIGURE 4 Perspective view of **4** with bond lengths (Å), bond angles (°) and torsion angles (°) calculated by the PM3 method. C(1)—P(2) 1.886, P(2)—C(3) 1.866, C(3)—C(4) 1.544, C(4)—C(5) 1.508, C(5)—C(6) 1.346, C(6)—C(1) 1.482, C(1)—C(7) 1.524, C(7)—C(8) 1.545, C(8)—C(4) 1.569, C(8)—C(9) 1.506, C(9)—C(10) 1.352, C(10)—C(11) 1.475, C(11)—P(12) 1.846, P(12)—C(7) 1.897. C(1)—P(2)—C(3) 94.49, C(1)—P(2)—C(13) 108.32, C(1)—P(2)—O(2) 115.84, O(2)—P(2)—C(3) 114.91, O(2)—P(2)—C(13) 113.69, C(13)—P(2)—C(3) 107.79, C(11)—P(12)—C(7) 99.11, C(11)—P(12)—O(1) 116.64, C(11)—P(12)—C(19) 102.50, C(7)—P(12)—C(19) 105.88, O(1)—P(12)—C(19) 113.88, O(1)—P(12)—C(7) 116.80. C(6)—C(1)—P(2)—C(3) −61.9, C(7)—C(1)—P(2)—C(3) 57.2, C(1)—P(2)—C(3)—C(4) 8.9, P(2)—C(3)—C(4)—C(5) 43.7, P(2)—C(3)—C(4)—C(8) −65.2, C(8)—C(4)—C(5)—C(6) 52.7, C(3)—C(4)—C(5)—C(6) −65.2, C(4)—C(5)—C(6)—C(1) 3.6, C(7)—C(1)—C(6)—C(5) −47.7, P(2)—C(1)—C(6)—C(5) 63.0, C(6)—C(1)—C(7)—C(8) 28.6, P(2)—C(1)—C(7)—C(8) −83.3, C(5)—C(4)—C(8)—C(7) −66.6, C(3)—C(4)—C(8)—C(7) 49.3, C(6)—C(1)—C(7)—P(9) −104.3, C(1)—C(7)—C(8)—C(4) 26.4.



SCHEME 2

further modification, we wished to prepare the fully saturated phosphabicyclooctane (**7**, $Ar^1 = Ar^2 = Ph$). The reduction could not be led to give the desired product (**7**, $Ar^1 = Ar^2 = Ph$) as the major component. At 90°C and 16 bar using a 10% palladium on carbon catalyst, a complex mixture containing species **6** and **7** with phenyl or cyclohexyl substituent(s) on the phosphorus atom(s) (**6**, $Ar^1 = Ar^2 = Ph$, $(M + H)^+ = 411$, 51%; **7**, $Ar^1 = Ar^2 = Ph$, $(M + H)^+ = 413$, 18%; **6**, $Ar^1 = Ph$ or C_6H_{11}, $Ar^2 = C_6H_{11}$ or Ph, $(M + H)^+ = 417$, 16%; **7**, $Ar^1 = Ph$ or C_6H_{11}, $Ar^2 = C_6H_{11}$ or Ph, $(M + H)^+ = 419$, 12%; **6**, $Ar^1 = Ar^2 = C_6H_{11}$, $(M + H)^+ = 423$, 3%) was obtained as suggested by the mass spectrum of the crude mixture (Scheme 2).

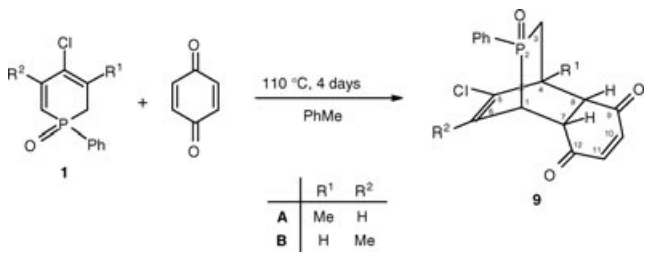
Forcing the hydrogenation at 90°C and 50 bar for 30 h, all unsaturations in **2** were completely saturated resulting in the formation of dicyclohexyl phosphabicyclooctane derivative **8** obtained as a single diastereomer in a yield of 27% after chromatography. It can be concluded that although the selective hydrogenation of compound **2** cannot be accomplished due to the presence of the six vulnerable moieties, a complete reduction is possible under appropriate conditions.

In the above examples (**2–8**), a tetrahydrophosphinine oxide ring was annellated to the usual phosphabicyclooctene (or -octane) skeleton in positions 7 and 8. To see a simpler case, we wished to synthesize a precursor annellated with cyclohexene ring. For this, a 3:1 mixture of dihydrophosphinine oxides **1A** and **1B** was reacted with benzoquinone in boiling toluene. The cycloaddition yielded phosphabicyclooctane **9** as the mixture of four isomers (the configurational isomers of double-bond isomers **9A** and **9B**) (Scheme 3).

Repeated column chromatography led to the mixture of the two isomers of **9B** that were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectroscopical data.

The investigation of cycloadducts **2, 5**, and **9** by TG and DTG suggested no significant difference between their thermostability. The minimum of the DTG curves was around 315°C in all cases. At the same time, the saturated derivative (**8**) revealed an increased thermostability with a 415°C minimum of the DTG curve. This clearly shows the impact of the unsaturation on the fragmentation ability of the precursor.

The bridged P-heterocycles (**2–5, 9**) synthesized were tested in fragmentation-related phosphinylations. The acetonitrile solution of dimer **2** was irradiated at 254 nm in the presence of simple



SCHEME 3

alcohols such as methanol, ethanol, propanol, and isopropanol for 1 h. The phosphinic esters (**11a–d**), which on the basis of δ_P shifts and HR-MS proved to be identical with authentic samples [3], were obtained in 71–89% yields after flash column chromatography (Scheme 4, Table 2).

Dimers **3** and **4** could be used in fragmentation-related phosphinylation similarly to analogue **2**. The phosphinylation of methanol took place in an efficiency of ca. 80% in both cases.

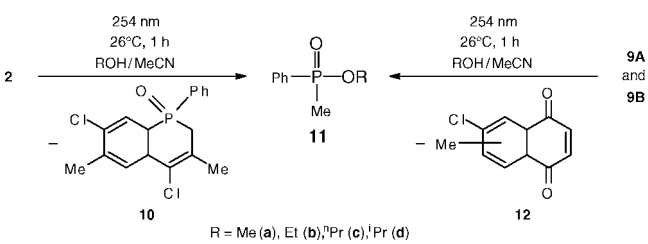
The isomeric mixture (**A** and **B**) of product **9** was also an efficient precursor in the phosphinylation of simple alcohols (Scheme 4, Table 1). Dimer **2** was not so efficient in the UV light-mediated phosphinylation of isopropylamine, as it was in that of alcohols. Isopropylamine was phosphinylated in 54% yield after the work-up (Scheme 5, Table 1).

The photolysis utilizing the P-sulfide precursor (**5**) in the presence of methanol led to thiophosphinate **15** (Scheme 6, Table 1).

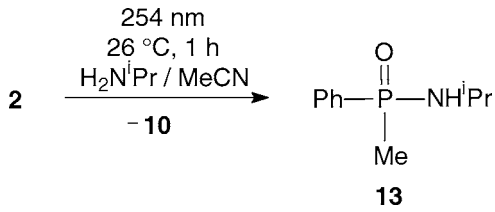
Phosphabicyclooctane **8** did not undergo a photo-induced reaction with methanol to furnish phosphinate **11a** indicating the dramatic effect of the lack of a significant ring strain. On the other hand, no stable molecule can be formed from **8** after the loss of the bridging P-moiety. Moreover, there is also a possibility that in the lack of an obvious chromophore, the UV light is not even absorbed by **8**.

Neither dimer **2**, nor cycloadduct **9** could be utilized in the thermo-induced phosphinylation of hydroquinone at 240°C. This seems to be in agreement with earlier experiences of ours [17] and with the thermostability of the cycloadducts (**2** and **9**) discussed above. The ring strain of the phosphabicyclooctenes is indeed not enough to stimulate a thermo-induced fragmentation [2].

In summary, phosphabicyclo[2.2.2]octenes of new type were introduced by the dimerization of 1-phenyl-dihydrophosphinine oxides. PM3 calculations justified the formation of the three isomers isolated from the reaction mixture. A study on the fine tuning of the structure and reactivity of phosphabicyclooctane derivatives annellated with a six-membered ring showed that the dimers as



SCHEME 4



SCHEME 5

well as a disulfide derivative and the [4 + 2] cycloadduct of the dihydrophosphinine oxide with benzoquinone were suitable precursors in UV light-mediated fragmentation-related phosphinylations. However, the fully saturated phosphabicyclooctane resisted the photoinduced transformation. None of the phosphabicyclooctenes underwent thermo-induced ejection of the bridging P-moiety suggesting that only the strained bicyclooctadienes may be useful in thermolyses.

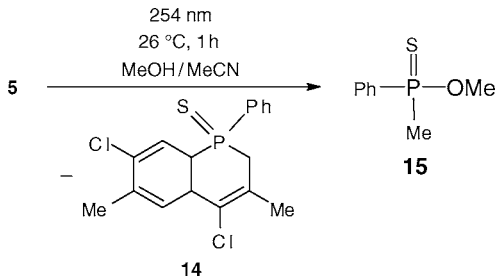
EXPERIMENTAL

General

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were performed 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. EI and/or FAB mass spectrometry was performed on a ZAB-2SEQ instrument. Photolyses were conducted in a photochemical reactor with a high pressure mercury lamp (125 W). The starting dihydrophosphinine oxide **1** was prepared as described earlier [18].

*6,11-Dichloro-5,12-dimethyl-3,5-diphenyl-3,9-diphosphatricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-3,9-dioxide (**2**) [19]*

A toluene solution (10 ml) containing 3.9 g (16.2 mmol) of dihydrophosphinine oxide (**1**) consisting



SCHEME 6

TABLE 2 Phosphinic Derivates (**11a–d, 13**, and **15**) Prepared by the Photolysis of Cycloadducts **2, 9**, and **5** in the Presence of Nucleophiles

	Nucleophile	*Product*	*Yield (%)*	δ_P *(CDCl$_3$)*	δ_P *[Ref.]*	$(M+H)^+$
2	MeOH	**11a**	89	45.2	44.8 [3], 45.0 [16]	171
2	EtOH	**11b**	84	43.2	42.7 [3]	185
2	*n*PrOH	**11c**[a]	79	42.9	42.8 [3]	199
2	*i*PrOH	**11d**[b]	71	41.2	41.3 [3]	199
9	MeOH	**11a**	78	45.1	44.8 [3], 45.0 [16]	171
9	EtOH	**11b**	73	43.7	42.7 [3]	185
9	*n*PrOH	**11c**	53	42.9	42.8 [3]	199
2	*i*PrNH$_2$	**13**[c]	54	31.4	29.8 [4]	198
5	MeOH	**15**	51	91.5		187

[a] *m/z* (rel. int.) 198 (M^+, 2), 183 (M–Me, 2), 139 (M–OPr, 100).
[b] *m/z* (rel. int.) 198 (M^+, 3.6), 183 (M–Me, 12.7), 139 (M–O^{i}Pr, 100).
[c] *m/z* (rel. int.) 197 (M^+, 1), 182 (M–Me, 83), 139 (M–NH^{i}Pr, 100).

of 70% of **A** and 30% of **B** isomer was stirred at boiling point for 7 days. The solvent was evaporated, and the residue purified by repeated column chromatography (silica gel, 3% methanol in chloroform) to give 0.66 g (34% based on **1B**) of dimer **2** as colorless crystals; mp 298–301°C (acetone); ^{31}P NMR ($CDCl_3$) δ 37.5 (P_2), 28.6 (P_9); ^{13}C NMR ($CDCl_3$) δ 19.6 (C_6–Me), 24.6 ($J''=7.4$, C_{11}–Me), 31.0 ($J''=63.4$, C_{10}), 32.0 ($J'=76.0$, $J''=10.9$, C_3), 39.7 ($J=5.9$, C_7[a]), 40.0 ($J'=67.2$, $J''=13.5$, C_1), 45.1 (C_4[a]), 47.7 ($J''=63.6$, C_8), 127.6 (C_6[b]), 127.7 (C_{11}[b]), 129.0, ($J=12.0$, $C_{2'}$[c]), 129.1 ($J=11.9$, $C_{2''}$[c]), 129.3 ($J=12.1$, C_{12}[d]), 130.1 ($J=9.6$, $C_{3'}$[e]), 130.2 ($J=10.0$, C_5[d]), 131.3 ($J=11.8$, $C_{3''}$[e]), 131.5 ($J=95.9$, $C_{1'}$[f]), 132.1 ($J=100.9$, $C_{1''}$[f]), 132.6 ($C_{4'}$, $C_{4''}$), J': coupled by P_2, J'': coupled by P_9, [a–f]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 3H, Me), 1.85 (s, 3H, Me), 7.46–7.76 (m, 5H, Ar); IR (KBr disc) 1168, 1196, 1436, 1650, 2935 cm^{-1}; MS, *m/z* (rel. int.) 476 (M^+, 20), 441 (M-35, 19), 337 (M–PhPO-15, 55), 125 (PhPO + H, 100), 77 (Ph, 72); $M^+_{found}=476.0527$, $C_{24}H_{24}Cl_2O_2P_2$ requires 476.0629 for the ^{35}Cl isotopes.

Further chromatography of the additional fractions combined led to 0.12 g (7%) of dimer **3** and to 0.07 g (2%) of product **4**, both as thick oils, listed and characterized below.

*6,12-Dichloro-5,11-dimethyl-3,10-diphenyl-3,10-diphosphatricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-3,10-dioxide (**3**) [19]*

^{31}P NMR ($CDCl_3$) δ 31.1 and 40.0 $^3J_{PP}=38.3$; ^{13}C NMR ($CDCl_3$) δ 18.7 (C_6–Me), 24.6 ($J''=7.4$, C_{11}–Me), 28.1 ($J=75.4$, C_{11}[a]), 32.4 ($J=62.7$, C_3[a]), 32.6 ($J''=62.7$, C_7), 42.2 ($J'=61.5$, C_1), 45.6 ($J=6.8$, C_4), 51.4 ($J=7.7$, C_8), 127.0 (C_6),[b] 127.1 (C_{10}),[b] 128.7 ($J=11.6$, $C_{2'}$[c]), 128.8 ($J=11.2$, $C_{2''}$[c]), 130.0 ($J=8.6$, $C_{3'}$[e]), 130.4 ($J=14.9$, C_5[d]), 130.5 ($J=17.9$, C_9[d]), 131.0 ($J=11.0$, $C_{3''}$[e]), 132.3 ($J=100.5$, $C_{1'}$), $C_{1''}$ overlapped, 132.4 ($C_{4'}$, $C_{4''}$), J': coupled by P_2, J'': coupled by P_{12}, [a–e]may be reversed; IR (film) 1170, 1198, 1436, 1650, 2937 cm^{-1}; $M^+_{found}=476.0537$, $C_{24}H_{24}Cl_2O_2P_2$ requires 476.0629 for the ^{35}Cl isotopes.

*6,12-Dichloro-5,8-dimethyl-3,10-diphenyl-3,10-diphosphatricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-3,10-dioxide (**4**) [19]*

^{31}P NMR ($CDCl_3$) δ 36.0 and 38.7 $^3J_{PP}=41.7$; ^{13}C NMR ($CDCl_3$) δ 20.5 ($J'=11.3$, C_4–Me), 24.8 ($J''=9.9$, C_{10}–Me), 34.7 ($J''=59.3$, C_{11}[a]), 40.9 ($J'=73.8$, C_3[a]), 34.6 ($J=67.3$, C_7[b]), 38.6 ($J=61.0$, C_1[b]), 46.9 ($J=5.6$, C_4), 56.4 ($J'=13.1$, $J''=4.7$, C_8), 126.7 (C_{10}), 126.8 ($J=3.9$, C_6), 128.6 ($J=11.0$, $C_{2'}$[c]), 128.8 ($J=11.0$, $C_{2''}$[c]), 130.5 ($J=8.1$, $C_{3'}$[d]), 130.9 ($J=8.7$, $C_{3''}$[d]), 132.1 ($C_{4'}$)[e], 132.4 ($C_{4''}$)[e], 141.9 ($J'=10.2$, C_5), J': coupled by P_2, J'': coupled by P_{12}, [a–e]may be reversed; ^{1}H NMR ($CDCl_3$) δ1.66 (s, 3H, Me), 1.85 (s, 3H, Me), 6.44 (d, 1H, CH=); IR (film) 1171, 1200, 1437, 1649, 2937 cm^{-1}; $M^+_{found}=476.0530$, $C_{24}H_{24}Cl_2O_2P_2$ requires 476.0629 for the ^{35}Cl isotopes.

*6,11-Dichloro-5,12-dimethyl-3,5-diphenyl-3,9-diphosphatricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-3,9-disulfide (**5**) [19]*

To a degassed solution of 0.17 g (0.36 mmol) of dimer **2** in 8 ml of benzene was added 0.2 g (0.90 mmol) of phosphorus pentasulfide and the mixture was stirred at the boiling point, under nitrogen for 20 h. Solvent was evaporated and the residue so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford 0.12 g (68%) of disulfide **5** as a thick oil. ^{31}P NMR ($CDCl_3$) δ 41.9 (P_2) and 38.8 $^3J_{PP}=2.9$; ^{13}C NMR ($CDCl_3$) δ 19.7 ($J'=$

2.2, C_6–Me), 24.2 ($J'' = 7.5$, C_{11}–Me), 35.4 ($J'' = 48.7$, C_{10}), 38.3 ($J' = 60.7$, $J'' = 12.4$, C_3), 40.5 ($J' = 49.7$, $J'' = 11.3$, C_1), 41.4 ($J = 7.5$, C_7[a]), 45.7 ($J = 4.6$, C_4[a]), 50.1 ($J'' = 46.4$, C_8), 128.9 (C_6),[b] 129.0 (C_{11}),[b] 128.5 ($J = 12.1$, $C_{2'}$[c]), 128.8 ($J = 12.1$, $C_{2''}$[c]), 133.1 ($J = 8.1$, C_{12}[d]), 125.4 ($J = 9.7$, $C_{3'}$[e]), 127.7 ($J = 8.4$, C_5[d]), 131.2 ($J = 9.7$, $C_{3''}$[e]), 130.2 ($J = 78.0$, $C_{1'}$[f]), 132.1 ($J = 83.6$, $C_{1''}$[f]), 131.6 ($C_{4'}$), 131.9 ($C_{4''}$), J': coupled by P_2, J'': coupled by P_9, [a–f]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 3H, Me), 1.81 (s, 3H, Me) 7.43–7.84 (m, 5H, Ar); $(M+H)^+ = 509$; $M^+_{found} = 508.0111$ $C_{24}H_{24}Cl_2S_2P_2$ requires 508.0172 for the ^{35}Cl isotopes.

*5,12-Dimethyl-3,5-dicyclohexyl-3,9-diphosphatricyclo[6.2.2.0^{2,7}]dodeca-3,9-dioxide (**8**) [19]*

Dimer **2** (0.30 g; 0.63 mmol) was hydrogenated in 30 ml of methanol in the presence of 0.3 g Pd/C at 90°C and 16 bar for 5 h in an autoclave, the pressure was then gradually increased to 50 bar, and the reduction was continued at 90°C for 30 h. The mixture was filtered and the filtrate evaporated to leave a crude product that was purified by column chromatography as above to give 0.07 g (27%) of product **8** as an oil and as a single isomer. ^{31}P NMR ($CDCl_3$) δ 52.5 (P_2) and 46.1; ^{13}C NMR ($CDCl_3$) δ 22.8 ($J = 15.7$, C_4)[a], 24.5 (C_6–Me)[b], 25.3 ($J = 6.1$, C_{11}–Me)[b], 25.9 (C_{12})[c], 28.3 (C_6)[d], 28.9 ($J = 1.5$, C_{11})[d], 30.0 (C_5)[c], 30.1 ($J'' = 59.0$, C_{10}), 31.7 (C_7)[a], 32.5 ($J'' = 12.0$, $J' = 52.7$, C_3), 34.1 ($J' = 66.7$, C_1), 40.0 ($J'' = 66.5$, C_8); [a–d]may be reversed, J': coupled by P_2, J'': coupled by P_9; ^{1}H NMR ($CDCl_3$) δ1.14($J = 6.1$, Me), 1.25 ($J = 7.1$, Me); IR (film) 1152, 1449, 2928 cm^{-1}; $(M+H)^+_{found} = 424.2595$, $C_{24}H_{42}O_2P_2$ requires 424.2660.

*1- and 12-Methyl 11-chloro-9-phenyl-9λ^5-phosphatricyclo[6.2.2.0^{2,7}]dodeca-4,11-diene-3,6-dione 9-oxide (**9**) [19]*

A 15 ml toluene solution containing 0.80 g (3.35 mmol) of dihydrophosphinine oxide **1** [16] consisting of 75% of the **A** and 25 % of the **B** isomer and 0.50 g (4.63 mmol) of benzoquinone was stirred at boiling point for 4 days. The solvent was evaporated, and the residual material purified by flash chromatography as above to furnish 0.42 g (36%) of product **8** consisting of four isomers (δ_P 32.0 (34%), 38.1 (17%), 38.2 (15%), and 40.5 (34%)). Repeated chromatography led to 0.20 g (67%) of cycloadduct **9** as a thick oil and as the 52–48% mixture of isomers **9B-1** and **9B-2**; $(M + H)^+ = 347$; $(M + H)^+_{found} = 347.0542$ $C_{18}H_{17}ClO_3P$ requires 347.0604 for the ^{35}Cl isotope. IR (film) 1198, 1438, 1610, 1654, 2935 cm^{-1}.

9B-1: ^{31}P NMR ($CDCl_3$) δ 40.9; ^{13}C NMR ($CDCl_3$) δ 20.1 ($J = 13.0$, C_6–Me), 31.7 ($J = 75.7$, C_3), 39.4 ($J = 67.2$, C_1), 39.9 ($J = 6.4$, C_8), 45.2 (C_7), 47.3 (C_4), 115.5 (C_{10})[a], 116.6 (C_{11})[a], 127.8 ($J = 5.5$, C_6), 129.6 ($J = 11.9$, $C_{2'}$)[b], 130.2 ($J = 9.0$, $C_{3'}$)[b], 133.3 ($C_{4'}$), 146.0 (C_9)[c], 150.9 (C_{12})[c], [a–c]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 3H, C_6–Me), 6.67–6.89 (m, 2H, CH=), 7.45–7.74 (m, 5H, Ar).

9B-2: ^{31}P NMR ($CDCl_3$) δ 32.4; ^{13}C NMR ($CDCl_3$) δ 20.1 ($J = 13.0$, C_6–Me), 31.6 ($J = 76.2$, C_3) 39.3 ($J = 67.6$, C_1), 39.9 ($J = 6.4$, C_8), 45.2 (C_7), 47.8 (C_4), 117.0 (C_{10}),[a] 117.6 (C_{11}),[a] 129.5 ($J = 11.5$, $C_{2'}$),[b] 131.4 ($J = 8.9$, $C_{3'}$),[b] 133.1 ($C_{4'}$), 150.3 (C_9),[c] 150.9 (C_{12}),[c]; [a–c]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3H, C_6–Me), 6.67–6.89 (m, 2H, CH=), 7.45–7.74 (m, 5H, Ar).

General Procedure for the Synthesis of Methyl-Phenylphosphinates **11a–d**

The solution of 0.10 g (0.21 mmol) of dimer **2** or 0.10 g (0.29 mmol) of cycloadduct **9** in 40 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. Volatile components were removed and the residue so obtained was purified by flash column chromatography (silica gel, 3% methanol in chloroform) to give the corresponding phosphinates (**11a–d**) as oils. The experimental details are listed in Table 2. The use of 4 ml of isopropylamine instead of an alcohol led to phosphinic amide **13**.

Disulfide **5** (0.10 g; 0.20 mmol) could replace dioxide **2**, but the air had to be removed by nitrogen prior to the irradiation.

Crystal Data for Phosphabicyclooctene **2**

X-ray diffraction data of single crystal of **2** were collected at 293 K; Crystal data for **2**: $C_{24}H_{24}O_2P_2Cl_2$, $M = 477.31$, colorless, needle shape crystal, approximate dimensions $0.20 \times 0.10 \times 0.50$ mm, triclinic, space group $P\bar{1}$, $a = 10.960(5)$ Å, $b = 12.766(6)$ Å, $c = 9.070(4)$ Å, $\alpha = 108.01(3)°$, $\beta = 96.88(4)°$, $\gamma = 103.33(4)°$, $V = 1149(1)$ Å^3, $Z = 2$, $D_c = 1.379$ gcm^{-1}, μ(Cu Kα) = 4.007 mm^{-1}; Structure solution with direct method was carried out with the teXsan package [20]. Refinement was carried out with SHELXL-97 [21]. Final R indices for **2** are $R = 0.0988$, $R_W = 0.1479$ (for all 9818 reflections) and $R = 0.0522$, $R_W = 0.1258$ ($I > 2\sigma(I)$).

The crystallographic data (CCDC 205727) have been deposited at the Cambridge Crystallographic Data Centre.

PM3 Semiempirical Calculations

The calculations of the heat of enthalpies and geometries of the substances were performed by PM3 [13,14] implemented in MOPAC93 [12]. The gradient norms were always less than 0.01 kcal/mol/RA in the end of the calculations. The force matrices of the molecules were found to be positive definite supporting that we localized the minima on the energy surface. In some cases the structures were calculated by MNDO-d included by HYPERCHEM [22] with the same options as before. Figures 3 and 4 were created by MOLDEN [23].

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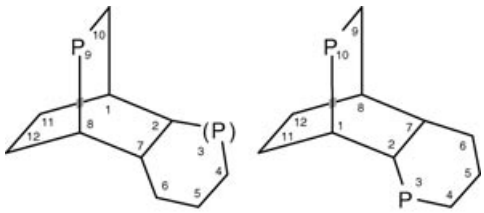

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