A Study on the Ability of 2,5-Dihydro- and 2,3,4,5-Tetrahydro-1H-phosphole oxides, as well as 7-Phosphanorbornene 7-Oxide Derivatives to Undergo UV Light-mediated Fragmentation-related Phosphinylation of Methanol

György Keglevich,[1]* János Kovács,[1] Helga Szelke[2] and Tamás Körtvélyesi[3]

[1]Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary. E-mail: keglevich@oct.mail.bme.hu
[2]Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary
[3]Department of Physical Chemistry, University of Szeged, 6701 Szeged, Hungary

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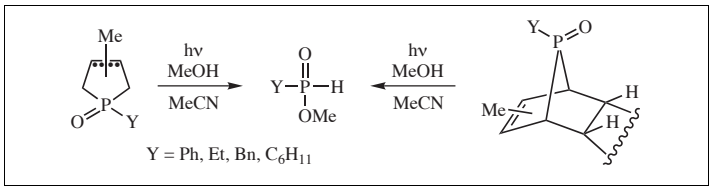

Reactivity of the title P-heterocycles (**1**-**14**) in the photoinduced fragmentation-related phosphinylation of methanol was found to be influenced by the extent of ring strain and the UV absorption at 254 nm. The 7-phosphanorbornene oxides (**7**-**14**) are universal precursors due to their ring strain, no matter if they are UV-active or not at 254 nm. The easily available 2,5-dihydro-1*H*-phosphole oxides can be applied only in case of 1-phenyl substitution that enhances the absorption at 254 nm. The ring strain of representative P-heterocycles (**5**-**8**) was evaluated by HF/6-31G* and B3LYP/6-31+G* calculations. UV spectra of compounds **5**-**8** were interpreted by ZINDO/S and MNDO-d calculations. The new precursors (**11**-**14**) made possible the extension of the phosphinylations.

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Introduction.

It has been known for long that the UV light-mediated reaction of 1-phenyl-2,5-dihydro-1*H*-phosphole oxides with methanol results in the formation of methyl phenyl-H-phosphinate [1,2]. Tomioka and co-workers proposed that irradiation of the dihydrophosphole oxide provides an oxophosphine (or phosphinidene oxide, PhP(O)) that reacts fast with the methanol present in the mixture [3,4]. It was Quin and Jankowski who pointed out later on that the real intermediate is rather a pentacoordinated adduct formed by the addition of methanol on the P=O group of the starting P-cycle [5]. A variety of 7-phosphanorbornene derivatives including P-sulfides were also utilized in the above type fragmentation-related phosphinylation of simple alcohols [6-10]. A study of 7-phosphanorbornene 7-oxides with sterically demanding 2,4,6-trialkylphenyl substituents on the phosphorus atom confirmed the addition–elimination reaction path [8,9]. Recently, the reaction was extended to the preparation of P-aryl, P-alkyl- and P-cycloalkyl H-phosphinates and it was evaluated in which cases the easily available 2,5-dihydrophosphole oxides can be used and in which instances the application of 7-phosphanorbornene 7-oxides is inevitable [11].

In the present paper, the factors governing the reactivity of P-heterocycles in fragmentation-related phosphinylation are explored to make possible to chose the appropriate precursor suitable for the preparation of the target H-phosphinates (HP(O)(OMe)Y, Y = aryl, alkyl, cycloalkyl). On the other hand, new precursors of phosphinylation are introduced.

Results and Discussion.

Figure 1 shows the variety of P-heterocycles (**1-14**) studied in fragmentation-related phosphinylations. As can be seen, the precursors include 2,5-dihydro-1*H*-phosphole oxides (**1-5**), a 2,3,4,5-tetrahydrophosphole oxide (**6**) and 7-phosphanorbornene oxides, such as the dimers of 1*H*-phosphole oxides (**7**, **9**, **11** and **13**), as well as the cycloadducts of 1*H*-phosphole oxides with *N*-phenylmaleimide (**8**, **10**, **12** and **14**). Bridged P-heterocycles **7-14** were prepared by well-established general methods [8]. A part of the 7-phosphanorbornene 7-oxides (**11-14**) are new whose synthesis is shown in Scheme I. It can be seen that the 2,5-dihydro-1*H*-phosphole oxides (**3** or **4**) were converted to dibromo-tetrahydrophosphole oxides **15** and **16** giving phosphole oxides **17** and **18** by double dehydrobromination. Intermediates **17** and **18** were dimerised spontaneously to afford phosphanorbornenes **11** and **13**, or trapped by NFMI to yield species **12** or **14**. The

dibromo-tetrahydrophosphole oxides (**15** and **16**) consisted of diastereomeric pairs (**A** and **B**).

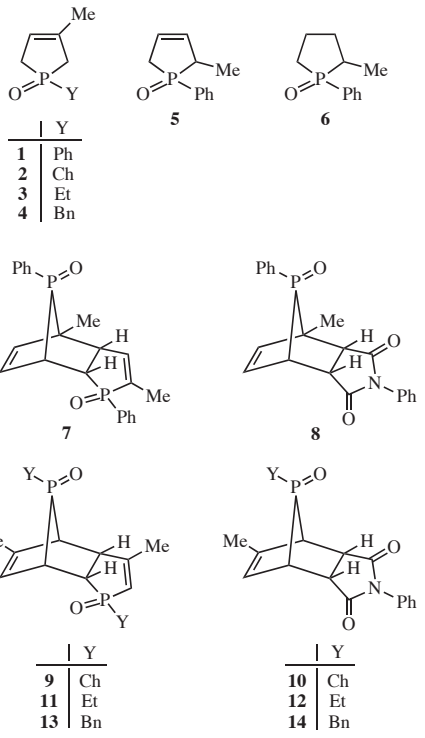
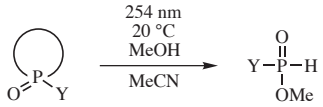


Figure 1

Table 1 summarises the results of the photoinduced fragmentation-related phosphinylations. As can be seen, from among the 2,5-dihydro-1*H*-phosphole oxides (**1-5**), only 1-phenyl derivatives **1** and **5** could be used well in the preparation of methyl phenyl-H-phosphinate (**19**, Y = Ph). Reaction of the 1-cyclohexyl-dihydrophosphole oxide (**2**) proceeded reluctantly (12% conversion after a 6 h's irradiation), while the 1-ethyl derivative (**3**) failed to enter into reaction under the conditions applied. The P-benzyl derivative (**4**) participated only in side-reactions. Phenyl-tetrahydrophosphole oxide **6** could be involved in the reaction discussed, that was, however, much slower (13% conversion after a 2 h's irradiation), as compared to that of dihydro derivative **1**. The results can be interpreted by considering the measure of the ring strain and the extent of the UV absorption of the individual P-heterocycles at 254 nm (Table 2). The 2,5-dihydrophosphole oxides that are only of medium ring strain (*cf.* with 3-cyclopentenone) are useful only in the case of a strong UV absorption at 254 nm. This is fulfilled only for P-heterocycles **1** and **5** due to the UV activity of the phenyl ring attached to the P=O group (Figure 2/curves **1** and **5**). The less strained 1-phenyl-tetrahydro derivative **6** with a high absorbance at 254 nm (Figure 2/curve **6**) displays only a lower reactivity with a reaction time of 14 h. The P-cyclohexyl, P-ethyl and P-benzyl dihydrophosphole oxides (**2**, **3** and **4**, respectively) can be regarded to be useless in the reaction under discussion due to the low absorbance at 254 nm (Figure 2/curves **2-4**).

Table 1

The use of P-heterocycles in fragmentation-related phosphorylations.



Starting P-cycle	Y	Time of irradiation [h]	Conversion [%]	Yield of **15** [%]	Ref.
1	Ph	1	100	95	[11]
2 [14]	Ch	6	12		[11]
3 [15]	Et	6	0	0	[11]
4	Bn	1	[a]	0	
5 [16]	Ph	1	100	95	[11]
6 [16]	Ph	14	100	[b]	[11]
7 [14]	Ph	1	100	~93	[14]
8 [14]	Ph	1	100	~93	[14]
9 [14]	Ch	1	100	~93	[14]
10 [14]	Ch	1	100	~93	[14]
11	Et	1	100	77	
12	Et	1	100	75	
13	Bn	1	100	80	
14	Bn	1	100	83	

In all experiments 0.10 g of the P-cycle was irradiated in the mixture of 40 ml of acetonitrile and 4 ml of methanol; [a] Only side-reactions could be observed; [b] No yield was provided.

Regarding the 7-phosphanorbornene oxides, all precursors (**7-14**) could be used well in the fragmentation-related phosphinylation of methanol, practically no matter what P-substituent the bridged P-heterocycle bears. The enhanced reactivity is obviously the consequence of the high ring strain of the 7-phosphanorbornene framework

Scheme I

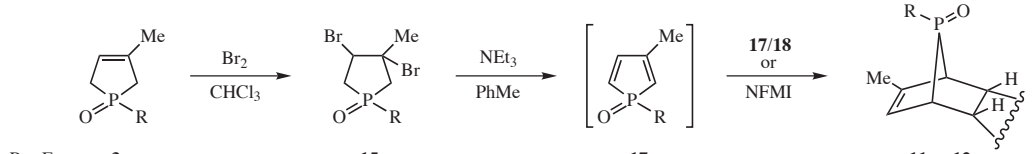


Table 2
The effect of parameters on the fragmentation properties of P-heterocycles **1-11.**

P-cycle	Ring strain				UV absorption at 254 nm	Overall ability of the P-cycle to undergo fragmentation-related phosphorylation		
	moderate	medium	high	low	strong	none	moderate	high
1		+			+			+
2		+		+			+	
3		+		+		+		
4		+		+		+		
5		+			+			+
6	+				+		+	
7			+		+			+
8			+		+			+
9			+	+				+
10			+		+			+
11			+	+				+
12			+		+			+
13			+	+				+
14			+		+			+

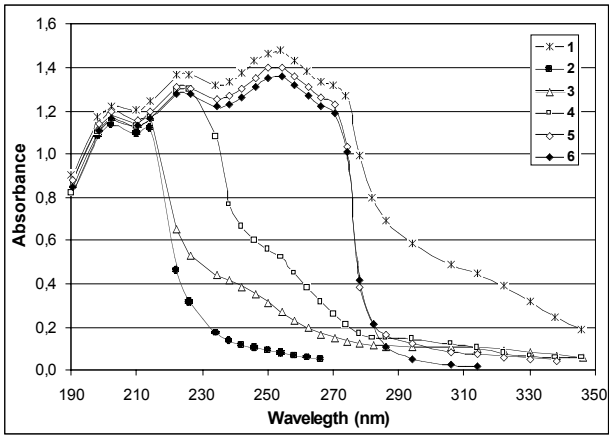


Figure 2. UV spectra of dihydro- and tetrahydro-1*H*-phosphole oxides obtained in acetonitrile.

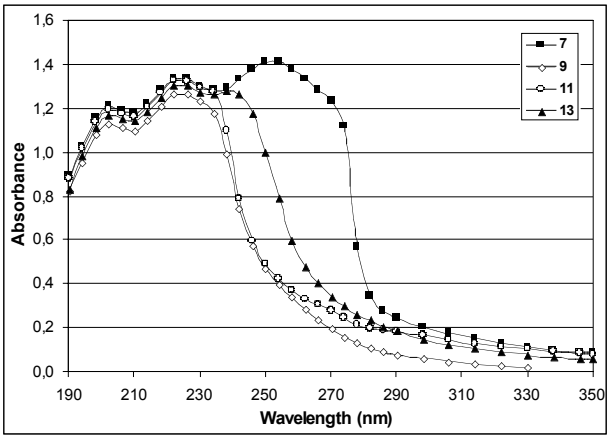


Figure 3. UV spectra of 7-phosphanorbornene derivatives (I) obtained in acetonitrile.

[8]. The P-phenyl derivatives (**7** and **8**) were found to be UV active at 254 nm (Figure 3/curve **7**, Figure 4/curve **8**). It was observed that the phenyl group attached to the imide moiety (as in **10**, **12** and **14**), may also enhance the UV absorption at 254 nm (Figure 4/curves **10**, **12** and **14**) and hence the reaction under discussion. Worth noting is that the cyclohexyl-, ethyl- and benzyl-1*H*-phosphole oxide dimers (**9**, **11** and **13**, respectively) can be used in phosphinylation, although they are practically UV inactive at 254 nm (Figure 3/**9**, **11** and **13**).

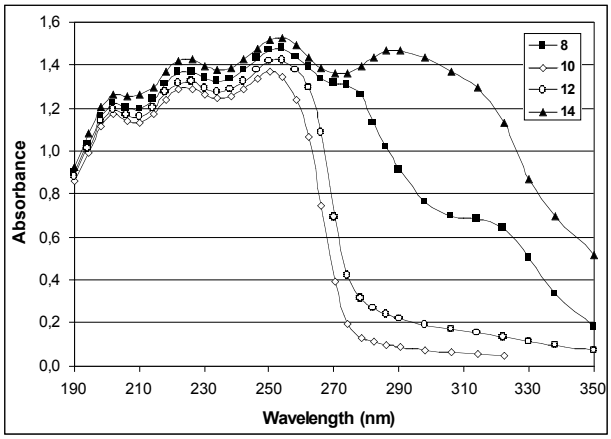


Figure 4. UV spectra of 7-Phosphanorbornene derivatives (II) obtained in acetonitrile.

The stereostructure and ring strain of P-heterocycles **5-8** was evaluated by HF/6-31G* and B3LYP/6-31+G* calculations. Stereostructures of 2,5-dihydro-1*H*-phosphole oxide **5** and 7-phosphanorbornene oxide **8** are shown in Figures 5 and 6, respectively. In the former case, the more stable diastereomer is represented.

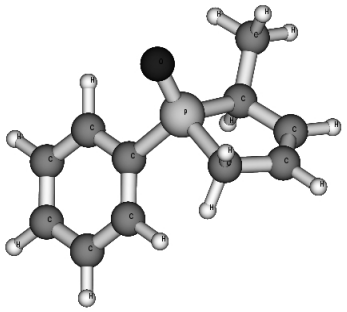


Figure 5. Perspective view of the more stable diastereomer of 2,5-dihydro-1H-phosphole oxide **5** obtained by HF/6-31G* calculation [P(1)-C(2): 1.840, C(2)-C(3): 1.510, C(3)-C(4): 1.322, C(4)-C(5): 1.519, C(5)-P(1): 1.852 (Å); C(5)-P(1)-C(1'): 107.17, C(2)-P(1)-O: 116.54, O-P(1)-C(1'): 112.19, O-P(1)-C(2)-CH_3: 7.22 (°)].

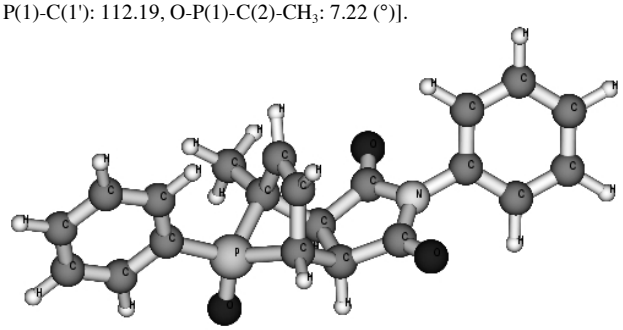


Figure 6. Perspective view of 7-phosphanorbornene **8** obtained by HF/6-31G* calculation [C(1)-C(2): 1.559, C(2)-C(3): 1.545, C(3)-C(4): 1.569, C(4)-C(5): 1.516, C(5)-C(6): 1.327, C(6)-C(1): 1.512, C(1)-P(7): 1.850, C(4)-P(7): 1.861 (Å); C(1)-P(7)-O: 116.42, C(4)-P(7)-O: 115.28, C(1)-P(7)-C(1'): 114.97, C(4)-P(7)-C(1'): 114.55, O-P(7)-C(1'): 110.51 (°).

The bond angles in the hetero rings of **5**-**8** are listed in Table 3. The sum of the absolute values of the deviations of the actual angles from the ideal ones (109.5° or 120°) may be regarded to be an indicator of the ring strain. This number ($\Sigma\Delta_1$) was found to be 28.94, 27.49 96.56 and 106.94 for P-cycles **5**, **6**, **7** and **8**, respectively, confirming that the 7-phosphanorbornene precursors are indeed of significant ring strain as compared to the 5-ring heterocycles (**5** and **6**). The C–P–C angle of the bridging unit in **7** and **8** was found to be 82.79 and 82.77°, respectively, that is in accord with the literature data of around 82° obtained for analogous derivatives [12,13]. The strain of phosphole rings **5** and **6** can be compared by the sum of the absolute values of the deviations of the actual angles from 105° that is the standard angle in 5-membered rings. This number ($\Sigma\Delta_2$) was found to be 37.50 and 17.19 for **5** and **6**, respectively, suggesting that the 2,3,4,5-tetrahydro-1*H*-phosphole ring is less strained than the 2,5-dihydro heterocycle. Comparing the results of HF/6-31G* and B3LYP/6-31+G* calculations, position of the plane of the P-phenyl ring was found to be slightly different in phosphanorbornenes **7** and **8**.

The possible mechanism for the fragmentation-related phosphinylations governed mainly by the ring strain discussed above is that on irradiation the P-heterocycle (**1-14**) gets to an excited state to afford species **20** that reacts fast with the nucleophile. The pentacoordinated intermediate (**21**) so formed is then stabilized to yield H-phosphinate **19** (Scheme II).

The UV spectra of P-heterocycles **5-8** that are of diagnostic value from the point of view photolysis were subjected to a detailed study. The results of ZINDO/S calculations for compounds **5**-**8** support the experimental spectra. The S0→S1 transition of molecules **5**-**7** was found at 262.6–262.7 nm, with a similar oscillator strength (0.0005–0.0006) that may be due to the O=P–Ph chromophore. For compound **8**, maximum of the S0→S1 transition is located at 320.7 nm with an oscillator strength of 0.0049 that is probably due to the presence of the $(–CO)_2N–Ph$ chromophore. In its tendency, similar results were obtained by MNDO-d C.I.=6 calculations (with 400 microstates) for the ground- and the first excited singlet electronic state. With the exception of compound **8**, there is no significant absorbance above 320 nm. The S0→S1 excitation energy for compounds **5**-**7** was found to be 3.928 eV, 3.930 eV and 3.928 eV, respectively, supporting similar spectra in the lower wave number range of the UV spectra. The torsion angle of the phenyl groups were changed in the different excited states. It is probable that in all cases (**5**-**8**), the π*← π transition of the phenyl group is involved that is affected by the presence of the P=O or the $N(CO–)_2$ moiety. For compound **8**, the band at 320 nm must be due to the π*← n transition of the C=O group. The S0→S2, and the S0→S3 transitions were found at lower wave lengths with greater oscillator strengths.

It can be concluded that the reactivity of the five-ring P-heterocycles and 7-phosphanorbornenes in fragmentation-related phosphinylations is governed by the UV activity and the ring strain of the precursor. An intensive UV absorption at 254 nm or a highly strained ring is the *sine qua non* of the reaction under discussion. This means that simple 2,5-dihydro-1*H*-phosphole oxides can be used only

Scheme II

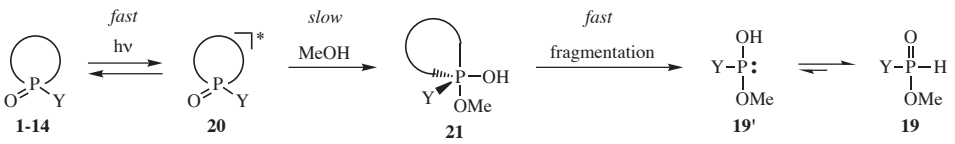
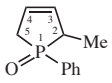
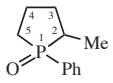
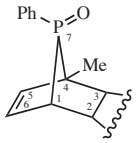


Table 3

Bond angles (α) in typical precursors obtained by HF/6-31G* calculation
($\Sigma\Delta_1$ is the sum of the absolute values of the differences from the ideal angle (109.5° or 120°),
while $\Sigma\Delta_2$ is the sum of the absolute values of the differences from the standard angle (105°) for 5-ring compounds).







	5	**6**		**7**	**8**
P_1–C_2–C_3	103.40	103.41	C_1–C_2–C_3	106.55	106.25
C_2–C_3–C_4	118.38	107.29	C_2–C_3–C_4	107.24	106.40
C_3–C_4–C_5	117.65	107.48	C_3–C_4–C_5	106.68	107.05
C_4–C_5–P_1	104.21	106.33	C_4–C_5–C_6	102.19	112.11
C_5–P_1–C_2	95.92	95.50	C_5–C_6–C_1	111.50	111.42
	$\Sigma\Delta_1$ = 28.94	$\Sigma\Delta_1$ = 27.49	C_6–C_1–C_2	107.86	108.39
	$\Sigma\Delta_2$ = 37.50	$\Sigma\Delta_2$ = 17.19	C_3–C_4–P_7	96.47	97.12
			C_2–C_1–P_7	96.94	97.17
			C_1–P_7–C_4	82.79	82.77
			C_5–C_4–P_7	99.82	99.80
			C_6–C_1–P_7	100.52	100.46
				$\Sigma\Delta_1$ = 96.56	$\Sigma\Delta_1$ = 106.94

in case of phenyl- (and obviously aryl) substitution. If the target molecule is an alkyl- or cycloalkyl H-phosphinate, the corresponding 7-phosphanorbornene should be the starting material of choice. Results of the theoretical calculations are in accord with the experimental data.

EXPERIMENTAL

The ^{31}P, ^{13}C and ^{1}H NMR spectra were obtained 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. Mass spectrometry was performed on a ZAB-2SEQ instrument. As the new compounds were dense oils, their purity (that was ca. 98%) was established by ^{1}H NMR and mass spectroscopy, as well as thin layer chomatography. UV spectra were obtained using ca. 10^{-5} mol·l^{-1} acetonitrile solutions.

The 3-methyl-2,5-dihydro- and 2,3,4,5-tetrahydro-1*H*-phosphole oxides (**2** [14], **3** [15], **5** [16] and **6** [16]), as well as the 7-phosphanorbornene 7-oxides (**7-10**) [14] were prepared as described earlier. P-cycles **5** and **6** were used as ca. 1:1 mixtures of diasteromers.

1-Benzyl-2,5-dihydro-1*H*-phosphole oxide **4** was synthesized by the method applied for the preparation of **2** [14]. The ^{13}C NMR spectral data of **4** were identical with those described in the literature [17]. ^{13}C NMR ($CDCl_3$) δ 20.4 (J = 10.5, C_3–Me), 31.6 (J = 63.8, C_5),[a] 34.6 (J = 66.8, C_2),[a] 37.5 (J = 57.4, CH_2Ph),[a] 120.7 (J = 8.3, C_4), 127.1 (J = 3.0, $C_{4'}$), 128.9 (J = 2.6, $C_{3'}$),[b] 129.6 (J = 5.1, $C_{2'}$),[b] 132.2 (J = 7.8, $C_{1'}$), 137.0 (J = 13.0, C_3); MS, $(M+H)^+$ = 207; [a,b]may be reversed; δ (lit [17]) 20.2 (J = 11.3, C_3–Me), 31.4 (J = 64.1, C_5), 34.4 (J = 67.1, C_2), 37.3 (J = 56.9, CH_2Ph), 120.6 (J = 8.0, C_4), 126.9 ($C_{4'}$), 128.8 ($C_{3'}$), 129.4 (J = 4.0, $C_{2'}$), 132.0 (J = 8.8, $C_{1'}$), 136.7 (J = 12.2, C_3).

Synthesis of the new 7-phosphanorbornene 7-oxides (**11-14**) and that of their intermediates (**15** and **16**) is described below.

General Procedure for the Preparation of Dibromo-tetrahydrophosphole oxides **16** and **15**.

Bromine (1.5 ml, 28.6 mmol) of in 15 ml of chloroform was added to the 50 ml chloroform solution of 26.0 mmol of dihydrophosphole oxide **4** and **3** at 0 °C. After 0.5 h, the mixture was allowed to warm up to room temperature and the stirring was continued for 4 h. Volatile components were then removed. Purification of the crude product by column chromatography (silica gel, 3% methanol in chloroform) afforded the corresponding dibromo-tetrahydrophosphole oxides (**16** and **17**, respectively) as a mixture of two isomers (**A** and **B**).

1-Benzyl-3,4-dibromo-3-methyl-2,3,4,5-tetrahydro-1*H*-phosphole 1-oxide (**16**).

16: Yield, 68%, dense oil as a 66:34 mixture of diastereomers (**A** and **B**). HR-MS, $(M+H)^+_{found}$ = 364.9279, $C_{12}H_{16}POBr_2$ requires 364.9305.

16A (66%): ^{31}P NMR ($CDCl_3$) δ 60.1; ^{13}C NMR ($CDCl_3$) δ 31.9 (J = 8.3, C_3–Me), 37.1 (J = 60.7, CH_2–Ph),[a] 39.6 (J = 60.9, C_2),[a] 41.3 (J = 61.0, C_5),[a] 57.1 (J = 4.6, C_4), 68.0 (J = 7.7, C_3), 127.0 (J = 3.3, $C_{4'}$), 128.6 (J = 2.8, $C_{3'}$),[b] 129.2 (J = 5.6, $C_{2'}$),[b] 130.7 (J = 8.5, $C_{1'}$); [a,b] may be reversed; ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3H, C_3–CH_3), 4.61–4.68 (m, 1H, C_4–H), 7.24–7.38 (m, Ar–H).

16B (34%): ^{31}P NMR ($CDCl_3$) δ 61.8; ^{13}C NMR ($CDCl_3$) δ 32.5 (J = 10.4, C_3–Me), 37.7 (J = 60.9, CH_2–Ph),[a] 40.6 (J = 61.0, C_2),[a] 40.8 (J = 64.1, C_5),[a] 58.3 (J = 5.0, C_4), 67.4 (J = 5.7, C_3), 126.9 (J = 3.2, $C_{4'}$), 128.5 (J = 3.7, $C_{3'}$),[b] 129.3 (J = 5.5, $C_{2'}$),[b] 130.8 (J = 8.1, $C_{1'}$); [a,b]may be reversed; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3H, C_3–CH_3), 4.89–5.03 (m, 1H, C_4–H), 7.24–7.38 (m, Ar–H).

3,4-Dibromo-1-ethyl-3-methyl-2,3,4,5-tetrahydro-1H-phosphole 1-oxide (**15**).

15: Yield, 80%, dense oil as a 56:44 mixture of diastereomers (**A** and **B**). MS, $(M+H)^+_{found}$ = 302.9132, $C_7H_{14}OPBr_2$ requires 302.9149.

15A (56%): ^{31}P NMR ($CDCl_3$) δ 71.3; ^{13}C NMR ($CDCl_3$) δ 6.2 (J = 5.9, CH_2CH_3), 25.8 (J = 66.6, CH_2CH_3), 32.8 (J = 9.4, C_3–Me), 38.0 (J = 61.4, C_5),* 42.2 (J = 61.9, C_2),* 57.5 (J = 2.8, C_4), 68.7 (J = 7.3, C_3); *may be reversed.

15B (44%): ^{31}P NMR ($CDCl_3$) δ 72.3; ^{13}C NMR ($CDCl_3$) δ 6.3 (J = 4.8, CH_2CH_3), 26.8 (J = 66.6, CH_2CH_3), 33.2 (J = 10.8, C_3–Me), 38.9 (J = 61.2, C_5),* 41.2 (J = 64.6, C_2),* 58.5 (J = 4.5, C_4), 67.7 (J = 4.9, C_3); *may be reversed.

General Procedure for the Preparation of 7-Phosphanorbornene 7-oxides **14**, **12**, **13** and **11**.

A) Trapping of 3-Methyl-1*H*-phosphole oxides with NPMI.

Triethylamine (2.7 ml, 19.6 mmol) was added to the 50 ml toluene solution of 8.9 mmol of dibromo-tetrahydrophosphole oxide (**16** and **15**) and 1.9 g (11.1 mmol) of NFMI. After 6 days of stirring at room temperature, the mixture was stirred at the boiling point for 4 h. After filtration, the filtrate was evaporated and the crude product so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford the corresponding trapped products (**14** and **12**, respectively).

10-Benzyl-8-methyl-4-phenyl-4-aza-10-phosphatricyclo[5.2.1.0^{2,6}]-dec-8-ene-3,5-dione 10-oxide **14**.

14: Yield, 71%, dense oil; ^{31}P NMR ($CDCl_3$) δ 92.4; ^{13}C NMR ($CDCl_3$) δ 19.3 (J = 3.5, C_2–Me), 29.0 (J = 57.9, CH_2–Ph), 43.5 (J = 11.6, C_5),[a] 43.6 (J = 59.6, C_4),[b] 44.7 (J = 12.2, C_6),[a] 46.6 (J = 59.5, C_1),[b] 122.2 (J = 9.1, C_3), 126.5 ($C_{2''}$),[c] 127.5 (J = 3.0, $C_{4'}$), 129.0 ($C_{4''}$), 129.1 (J = 3.2, $C_{2'}$), 129.2 ($C_{3''}$),[c] 129.3 ($C_{3'}$),[c] 131.7 ($C_{1''}$), 132.0 (J = 8.6, $C_{1'}$), 141.2 (J = 11.1, C_2), 175.1 (J = 13.0, C_{10}),[d] 175.5 (J = 13.4, C_8)[d]; [a-d]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.89 (s, 3H, C_2–CH_3), 3.22–3.27 (m, 1H, CH), 3.32–3.38 (m, 2H, CH_2–Ph), 3.40-3.45 (m, 1H, CH), 3.96–4.01 (m, 2H, 2×CH), 5.93–5.98 (m, 1H, =CH), 7.24–7.54 (m, 10H, ArH); HR-MS, $(M+H)^+_{found}$ = 378.1228, $C_{22}H_{21}PO_3N$ requires 378.1259.

10-Ethyl-8-methyl-4-phenyl-4-aza-10-phosphatricyclo[5.2.1.0^{2,6}]-dec-8-ene-3,5-dione 10-oxide (**12**).

12: Yield, 62%, light yellow crystals, mp.: 176–177 °C (10% dichloromethane in hexane); ^{31}P NMR ($CDCl_3$) δ 96.7; ^{13}C NMR ($CDCl_3$) δ 7.7 (J = 5.1, CH_2CH_3), 13.6 (J = 63.7, CH_2CH_3), 19.3 (J = 3.3, C_2–CH_3), 43.2 (J = 50.1, C_4),[a] 43.7 (J = 1.3, C_5),[b] 44.8 (J = 12.3, C_6),[b] 46.6 (J = 58.6, C_1),[a] 121.8 (J = 9.0, C_3), 126.5 ($C_{2'}$),[c] 128.9 ($C_{4'}$),[c] 129.2 ($C_{3'}$),[c] 131.6 ($C_{1'}$), 141.1 (J = 10.9, C_2), 175.3 (J = 12.7, C_{10}),[d] 175.6 (J = 13.1, C_8)[d]; [a-d]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.27 (dt, $^3J_{PH}$ = 18.0, $^3J_{HH}$ = 7.8, 3H, CH_2CH_3), 1.92 (s, 3H, C_2–CH_3), 1.88–1.96 (m, 2H, CH_2CH_3), 3.30–3.40 (m, 1H, CH), 3.45–3.55 (m, 1H, CH), 3.96–4.05 (m, 2H, 2×CH), 5.86–5.95 (m, 1H, =CH), 7.11–7.14 and 7.37–7.48 (m, 5H, ArH); MS, $(M+H)^+_{found}$ = 316.1115, $C_{17}H_{19}O_3PN$ requires 316.1103.

B) Dimerisation of 3-Methyl-1*H*-phosphole oxides.

Triethylamine (3.4 ml, 24.4 mmol) was added to the 35 ml of toluene solution of 11.1 mmol of dibromo-tetrahydrophosphole oxide **16** and **15**. The mixture was stirred at 110 °C for a day and at 26 °C for 2 other days. After filtration, the filtrate was evaporated. Purification of the crude product by column chromatography (silica gel, 2% methanol in chloroform) led to a light yellow oil, containing the corresponding dimers (**13** and **11**, respectively).

3,10-Dibenzyl-5,8-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-4,8-diene 3,10-dioxide (**13**).

13: Yield, 65%, light yellow oil. ^{31}P NMR ($CDCl_3$) δ 63.0 (P_1), 88.6 (P_8), J = 34.3; ^{13}C NMR ($CDCl_3$) δ 19.0 (J^1 = 16.5, C_3–Me), 19.3 (J^2 = 3.9, C_5–Me), 28.6 (J^2 = 56.2, P_8–CH_2Ph), 36.7 (J^1 = 74.5, J^2 = 11.0, C_{7a}), 39.8 (J^1 = 63.8, P_1–CH_2Ph), 41.4 (J^1 = 2.5, J^2 = 57.6, C_7), 47.7 (J^2 = 61.8, C_4), 52.0 (J^1 = J^2 = 11.8, C_{3a}), 123.3 (J^1 = 95.5, J^2 = 2.3, C_2), 124.3 (J^1 = 5.0, J^2 = 8.9, C_6), 126.5 (J^1 = 3.0, $C_{4'}$),[a] 126.8 (J^2 = 2.6, $C_{4''}$),[a] 128.4 (J^1 = 2.5, $C_{3'}$),[b] 128.6 (J^2 = 2.0, $C_{3''}$),[b] 128.9 (J^1 = 5.4, $C_{2'}$),[c] 129.5 (J^2 = 5.2, $C_{2''}$),[c] 131.6 (J^1 = 7.2, $C_{1'}$),[d] 132.3 (J^2 = 8.6, $C_{1''}$),[d] 136.2 (J^2 = 11.8, C_5), 159.3 (J^1 = 22.4, J^2 = 8.7, C_3); [a-d]may be reversed; J^1: coupled by P_1, J^2: coupled by P_8; ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 2.77-2.81 (m, 1H, CH), 2.97–3.04 (m, 1H, CH), 3.06–3.09 (m, 1H, CH), 3.17–3.27 (m, 4H, 2×PCH_2), 3.47–3.53 (m, 1H, CH), 5.71–5.78 (m, 1H, =CH), 6.10–6.16 (m, 1H, =CH), 7.14–7.33 (m, 10H, ArH); HR-MS, $(M+H)^+_{found}$ = 409.1456, $C_{24}H_{27}P_2O_2$ requires 409.1486.

3,10-Diethyl-5,8-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]-deca-4,8-diene 3,10-dioxide (**11**).

11: Yield, 50%, colourless oil. ^{31}P NMR ($CDCl_3$) δ 67.6 (P_1), 93.0 (P_8), J = 33.5; ^{13}C NMR ($CDCl_3$) δ 7.6 (P_1–CH_2CH_3), 7.4 (P_8–CH_2CH_3), 13.1 (J^2 = 63.1, P_8–CH_2), 19.1 (C_5–Me), 19.0 (J^1 = 4.8, C_3–Me), 24.4 (J^2 = 70.9, P_8–CH_2), 36.6 (J^1 = 73.5, J^2 = 9.2, C_{7a}), 40.3 (J^2 = 57.7, C_7), 47.3 (J^2 = 61.1, C_4), 51.9 (J^1 = J^2 = 11.5, C_{3a}), 122.9 (J^1 = 94.7, C_2), 123.8 (broad signal, C_6), 135.9 (J^1 = 11.6, C_5), 158.9 (J^1 = 21.8, J^2 = 8.7, C_3); J^1: coupled by P_1, J^2: coupled by P_8; ^{1}H NMR ($CDCl_3$) δ 0.96–1.19 (m, 6H, 2×CH_2–CH_3), 1.67 (s, 3H, skeletal–CH_3), 1.84 (s, 3H, skeletal–CH_3), 2.88–2.92 (m, 1H, CH), 2.96–3.03 (m, 1H, CH), 3.05–3.11 (m, 1H, CH), 3.70–3.79 (m, CH), 5.65–5.78 (m, 1H, =CH), 6.00–6.08 (m, 1H, =CH); HR–MS, $(M+H)^+_{found}$ = 285.1148, $C_{14}H_{23}O_2P_2$ requires 285.1173.

General Procedure for the Preparation of H-Phosphinates **19** using 7-Phosphanorbornene 7-oxides **11-14**.

A solution of 0.52 mmol of phosphanorbornene oxide **11**-**14** in 45 ml of acetonitrile and 4.0 ml of methanol was irradiated by a mercury lamp (125 W) in a quartz reactor for 1 hour. Solvent was evaporated and the crude product so obtained purified by flash column chromatography (silica gel, 3% methanol in chloroform) to afford the corresponding H-phosphinate (**19**) as shown in Table 1.

The use of precursors **13** or **14** led to product **19**, Y = Bn in a yield of 80 and 83%, respectively. ^{31}P NMR ($CDCl_3$) δ 39.2, J_{PH} = 546.5; ^{13}C NMR ($CDCl_3$) δ 37.0 (J = 88.4, CH_2Ph), 53.2 (J = 7.1, CH_3O), 127.5 (J = 3.6, $C_{4'}$), 129.2 (J = 3.3, $C_{3'}$),* 129.9 (J = 6.3, $C_{2'}$)*; *may be reversed; MS, $(M+H)^+_{found}$ = 171.0569, $C_8H_{12}O_2P$ requires 171.0575.

Applying phosphanorbornenes **11** and **12**, H-phosphinate **19**, Y = Et was obtained in 77 and 75% yield, respectively. ^{31}P NMR ($CDCl_3$) δ 43.8, δ (lit [11]) 44.3.

The other P-heterocycles (**1**, **5-10**) were used similarly.

Theoretical Calculations.

Structures **5-8** were calculated by *ab initio* and DFT quantum chemical methods with a basis set of HF/6-31G* and B3LYP/6-31+G*, respectively, implemented in Gaussian '03 [18]. The

force matrix of the fully optimized structures were found to be positive definite supporting that a minimum was found.

In order to support the change in the spectra at molecules **5**-**8**, the ground and the first excited singlet electronic states were calculated by MNDO-d with C.I.=6 method implemented in CS Chem3d Ultra Version 9.0.1 [19]. The structures were fully optimized in gas phase with a tolerance in gradient norm of 0.1. The energies of the S0→S1 transition for molecules **5-8** were compared with the experimental spectra. The energies of the excited states of **5**-**8** were also calculated by ZINDO/S implemented in Arguslab [20]. 10 Electronic states were considered in the C.I. method. The dielectric constant was 37.4 (acetonitrile) in the SCRF. The geometry, we applied was the HF/6-31G* *ab initio* optimized structure. The results are only informative, because the phosphorus d-orbital is not parameterized.

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