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New 7-Phosphanorbornenes Derived from 2-Methyl-1-phenyl- and 1-Cyclohexyl-3-methyl-2,5-dihydro-1*H*-phosphole 1-Oxides

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ABSTRACT: *Novel 7-phosphanorbornene derivatives, such as* **4, 5, 10**, *and* **11** *were synthesized utilizing 1-phenyl-2-methyl-2,5-dihydro-1H-phosphole oxide (***1***) and 1-cyclohexyl-3-methyl-2,5-dihydro-1H-phosphole oxide (***7***) as the starting materials. Products* **4** *and* **10** *were prepared by trapping the corresponding phosphole oxide intermediates (***3** *and* **9**, *respectively) by N-phenylmaleimide, while* **5** *and* **11** *were obtained by the dimerization of* **3** *and* **9**, *respectively. The trapping reaction was studied in details; on one hand, bromo-2,3-dihydro-1H-phosphole oxides (***6-1** *and* **6-2***) were pointed out as the intermediates, on the other hand, the trapping reaction was optimized. Bridged P-heterocycles* **4, 5, 10**, *and* **11** *were tested in the fragmentation-related phosphorylation of methanol. Hydrogenation of phosphanorbornenes* **4** *and* **5** *led to the corresponding phosphanorbornanes (***12** *and* **14**, *respectively) and to a reductive type of retro cycloaddition.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:320–326, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20097

INTRODUCTION

P-heterocycles are of current interest due to their rich chemistry and the different applications. The 3-methyl-2,5-dihydro-1*H*-phosphole oxides including the *P*-phenyl derivative available via the McCormack cycloaddition of isoprene and phosphorus halogenides are versatile intermediates of other *P*-heterocycles, such as phospholes, phosphinine derivatives (phosphinines themselves and their dihydro-, tetrahydro-, and hexahydro-derivatives) [1–4]. The piperylene-based 2-methyl-2,5-dihydro-1*H*-phosphole derivatives are less studied [5–7]. Quin introduced the 1-phenyl-2-methyl-2,5-dihydrophosphole oxide and studied its double-bond rearrangement [5,6]. We examined the possibility of its ring enlargement by dichlorocarbene and prepared some of its derivatives including phosphine boranes [7].

In this paper, new 7-phosphanorbornenes with skeletal methyl group at the bridgehead carbon atom or with cyclohexyl group on the phosphorus atom are synthesized and their fragmentation properties are studied.

RESULT AND DISCUSSION

Dihydrophosphole oxide **1** was utilized in the preparation of 7-phosphanorbornene derivatives. The key

Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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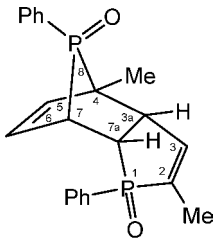
intermediate was dibromo-tetrahydrophosphole oxide **2** that was synthesized by the addition of bromine to the double-bond of **1**. The dibromo species **2** was, in fact, formed as four isomers of the possible eight. The diastereomers of **2** were characterized by ^{31}P and ^{13}C NMR, as well as mass spectrometry. Double dehydrobromination of **2** by triethylamine led to phosphole oxide **3** that was trapped by *N*-phenylmaleimide, or was allowed to undergo dimerization to furnish phosphanorbornene derivative **4** or phosphole oxide dimer **5**, respectively (Scheme 1).

Optimization of the **2** → **3** → **4** reaction sequence showed that performing the dehydrobromination and the subsequent trapping at 26°C, the dimerization can be avoided. Preparation of the dimer **5** can, however, be efficiently carried out in boiling toluene in a relatively fast reaction. After purification by column chromatography, products **4** and **5** were obtained in ca. 62% and were characterized by ^{31}P, ^{13}C, and ^{1}H NMR as well as mass spectral data.

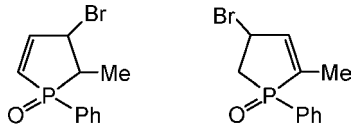
In a small portion (24%), another isomer of the phosphole oxide dimer, was also formed. According to ^{13}C NMR data, the minor product can be formulated as **5′**.



5'

This experience is unique, as the dimerization of phosphole oxides is known to be regio-and stereospecific [8].

It is noteworthy that interrupting the dehydrobromination and the trapping at a conversion of ~70%, it was possible to detect 3-bromo-2,3-dihydrophosphole oxide intermediates **6-1** and **6-2** by ^{31}P NMR (δ_P ($CDCl_3$) 52.6 and 51.1 in a ratio of 3:1), as well as by MS ($(M+H)^+ = 271$).

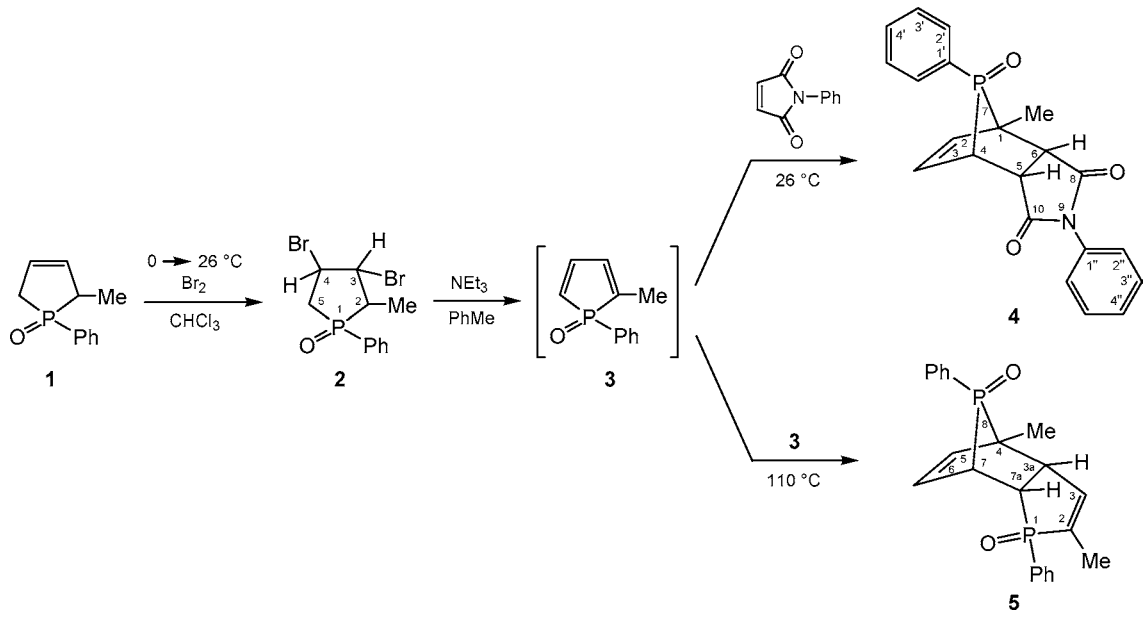


6-1 **6-2**

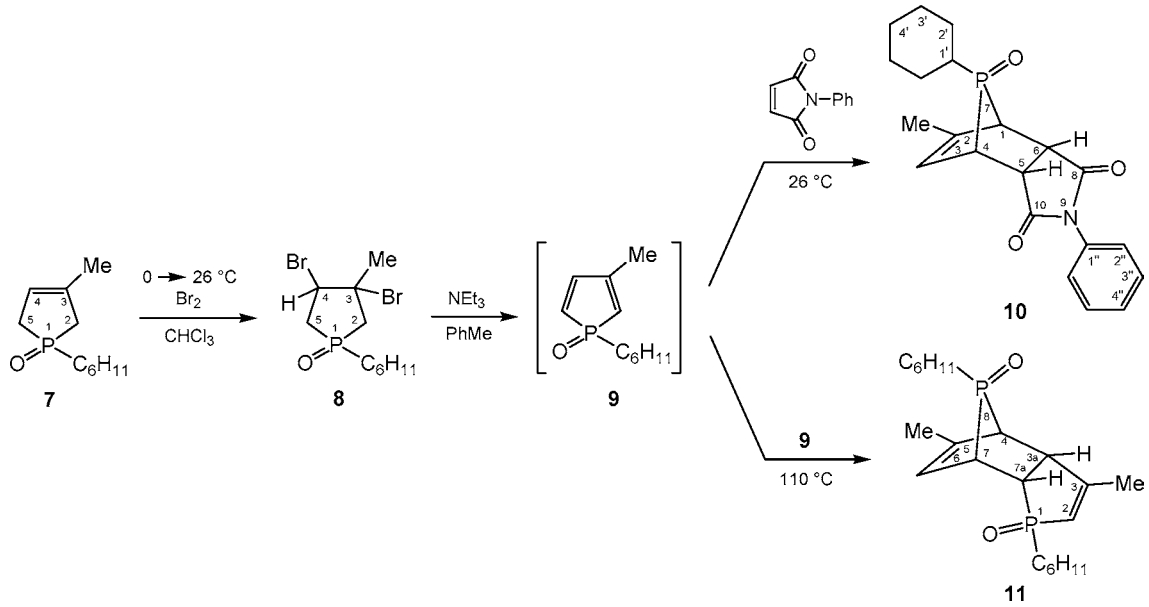
In the next stage of our work, novel 7-phosphanorbornenes (**10** and **11**) bearing a cyclohexyl group on the phosphorus atom were prepared from 1-cyclohexyl-2,5-dihydro-1*H*-phosphole oxide **7**, applying the protocols used for the synthesis of bridged compounds **4** and **5** starting from dihydrophosphole oxide **1** (Scheme 2).

The products **10** and **11** were characterized by ^{31}P and ^{13}C NMR, as well as mass spectrometry.

We wished to prepare the fully saturated derivatives of 7-phosphanorbornenes **4** and **5**. Catalytic hydrogenation of compounds **4** and **5** at 60°C and 22 bar led to phosphanorbornanes **12** and **14**, respectively. It is noteworthy that in the case of the reduction of **5**, the 2,3-dihydrophosphole moiety resisted the hydrogenation. The hydrogenation of **4** and **5** was, however, accompanied by a reductive type of



SCHEME 1



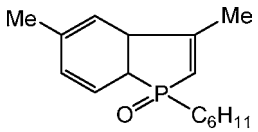
SCHEME 2

retro Diels Alder reaction resulting in the formation of tetrahydrophosphole oxide **13** as a single diastereomer (Schemes 3 and 4). This kind of fragmentation has only been observed in the mass spectra of some 7-phosphanorbornenes [9].

It is known that the bridging P(O)Y moiety (Y = Ph, alkyl) of the 7-phosphanorbornenes can be involved in some kind of reactions [2]. In earlier work, we applied 7-phosphanorbornenes in the UV light-mediated fragmentation-related phosphorylation of simple alcohols [10,11]. The new 7-phosphanorbornenes (**4** and **5**) were tested as precursors of the P(O)Ph moiety. Thermal examinations (TG, DTG, and DSC) revealed that for **4** and **5**, the P-fragment is ejected at 206 and 242°C, respectively, as the optimum temperatures.

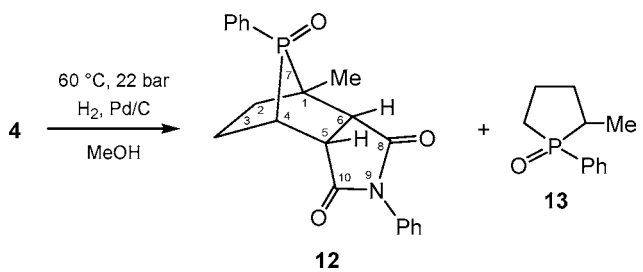
Photolysis of the bridged *P*-heterocycles **4** and **5** in acetonitrile in the presence of methanol led to methyl phenyl-*H*-phosphinate **15** in good yield that, on the basis of its δ_P shift of 27.8 and $^1J_{PH}$ coupling of 567 Hz, could be well identified [12] (Scheme 5).

The P-cyclohexyl 7-phosphanorbornenes **10** and **11** could also be photolyzed in the presence of methanol to afford methyl cyclohexyl-*H*-phosphinate **16** with δ_P 46.3 and $^1J_{PH} = 522$ Hz (Scheme 6). The presence of dihydrophosphindole **17** could also be detected in the crude reaction mixture (δ_P 81.5, $[M+H]^+ = 263$).

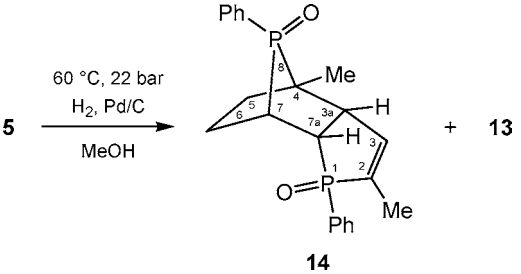


It is a novel observation that *P*-cyclohexyl-bridged heterocycles underwent UV light-mediated transformations.

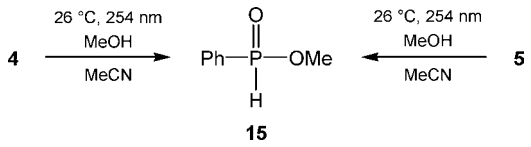
Based on our previous experiences [10,11], and in contrast to Tomioka's suggestion [13,14], we assumed the fragmentation-related phosphorylation to take place via an intermediate with a pentavalent



SCHEME 3



SCHEME 4



SCHEME 5

pentacoordinate phosphorus atom formed by the addition of methanol on the P=O group of the precursor **4** and **5** and not through an elimination-addition mechanism involving phosphinidine PhP(O) as an intermediate.

To summarize our results, new 7-phosphanorbornenes with skeletal methyl group(s) in unusual position(s) or with cyclohexyl group(s) on the phosphorus atom(s) were synthesized and tested in fragmentation–related phosphorylations. Hydrogenation of 7-phosphanorbornenes led to the corresponding phosphanorbornanes and to a reductive type of retro cycloaddition.

The 1-methyl-7-phosphanorbornene derivatives may be useful starting materials in Baeyer–Villiger oxidations. The presence of the methyl group in position 1 is expected to influence the course and the result of the reaction.

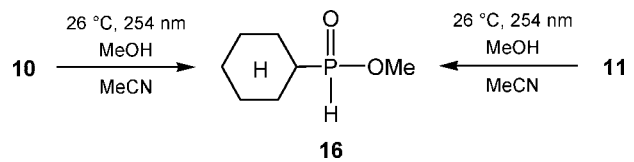
EXPERIMENTAL

The ^{31}P-, ^{13}C-, and ^{1}H-NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 160.4 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The couplings are given in Hz. FAB mass spectrometry was performed on a ZAB-2SEQ instrument.

The 2-methyl-1-phenyl-2,5-dihydro-1*H*-phosphole oxide (**1**) was prepared as described earlier [5].

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

1.5 mL (28.6 mmol) of bromine in 15 mL of chloroform was added to the 50 mL of chloroform solution of 5.0 g (26.0 mmol) of dihydrophosphole oxide **1** at 0°C. After 0.5 h of stirring, 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 7.6 g (83%) of **2** as a mixture of **2-1** (44%), **2-2** (22%), **2-3** (20%), and **2-4** (14%). HR-MS, $(M+H)^+_{found} = 350.9125$, $C_{11}H_{14}OPBr_2$ requires 350.9149.



SCHEME 6

2-1: ^{31}P NMR ($CDCl_3$) δ 52.0; ^{13}C NMR ($CDCl_3$) δ10.4 (J = 1.7, C(2)—Me), 37.1 (J = 66.9, C(2)), 37.7 (J = 61.4, C(5)), 49.8 (J = 5.0, C(4)),[a] 60.0 (J = 7.2, C(3)),[a] 128.8 (J = 12.1, C(3′)),[b] 130.4 (J = 10.8 C(2′)),[b] 132.0 (J = 2.6, C(4′)), 138.1 (J = 86.9, C(1′)).

2-2: ^{31}P NMR ($CDCl_3$) δ 47.2; ^{13}C NMR ($CDCl_3$) δ 11.8 (C(2)—Me), 37.9 (J = 64.2, C(5)), 45.9 (J = 59.1, C(2)), 49.7 (J = 9.1, C(4)),[c] 59.9 (J = 18.9, C(3)),[c] 128.5 (J = 12.2, C(3′)),[d] 130.3 (J = 9.8, C(2′)),[d] 130.4 (J = 96.0, C(1′)), 132.7 (J = 1.9, C(4′)).

2-3: ^{31}P NMR ($CDCl_3$) δ 42.6; ^{13}C NMR ($CDCl_3$) δ 10.5 (J = 3.0, C(2)—Me), 40.0 (J = 56.4, C(5)), 44.6 (J = 60.2, C(2)), 49.3 (J = 4.6, C(4)),[e] 60.8 (J = 15.8, C(3)),[e] 128.7 (J = 12.3, C(3′)),[f] 129.6 (J = 10.0, C(2′)),[f] 130.1 (J = 95.8, C(1′)), 132.1 (C(4′)).

2-4: ^{31}P NMR ($CDCl_3$) δ 53.1; ^{13}C NMR ($CDCl_3$) δ 13.0 (C(2)—Me), 35.4 (J = 62.8, C(5)), 38.9 (J = 64.8, C(2)), 49.4 (J = 9.2, C(4)),[g] 61.0 (J = 10.7, C(3)),[g] 128.3 (J = 12.3, C(3′)),[h] 131.3 (J = 9.9, C(2′)),[h] 132.5 (J = 2.2, C(4′)); [a–h] may be reversed.

*1-Methyl-10-oxo-4,10-diphenyl-4-aza-phosphabicyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (**4**) [15]*

2.7 mL (19.6 mmol) of triethylamine was added to the 50 mL of toluene solution of 3.2 g (8.9 mmol) of **2** and 1.9 g (11.1 mmol) of NFMI. After 6 days of stirring at room temperature, the mixture was heated 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 2.0 g (60%) of **4**. ^{31}P NMR ($CDCl_3$) δ 87.5; ^{13}C NMR ($CDCl_3$) δ 12.0 (C(1)—Me), 42.6 (J = 63.5, C(4)), 44.6 (J = 12.8, C(5)),[a] 48.2 (J = 14.3, C(6)),[a] 51.1 (J = 67.6, C(1)), 124.7 (J = 87.8, C(1′)), 126.3 (C(3″)),[b] 128.4 (J = 11.0, C(3′)),[c] 128.5 (C(4″)), 128.9 (C(2″)),[b] 130.5 (J = 10.5, C(3)), 131.4 (C(1″)), 132.3 (J = 1.9, C(4′)), 132.9 (J = 7.9, C(2′)),[c] 135.4 (J = 13.7, C(2)), 174.4 (J = 14.2 C(8)),[d] 174.6 (J = 13.4, C(10))[d]; [a–d] may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.81 (d, 3H, Me), 3.83 (s, 1H, CH), 3.85 (s, 1H, CH), 6.17 (m, 1H, =CH), 7.13–7.80 (10H, Ar—H); HR-MS, $(M+H)^+_{found} = 364.1103$, $C_{21}H_{19}NO_3P$ requires 364.1037.

*3,10-Diphenyl-4,7-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dioxide (**5**) [15]*

3.4 mL (24.4 mmol) of triethylamine was added to the 35 mL of toluene solution of 3.9 g (11.1 mmol)

of **2**. The mixture was stirred at 110°C for a day, and for other 2 days at rt. After filtration, the filtrate was evaporated. The purification of the crude product by column chromatography (silica gel, 2% methanol in chloroform) led to 1.5 g of light yellow oil, containing dimers **5** (94%) and **5′** (6%). The fraction was further purified by column chromatography to furnish 1.3 g (62%) of dimer **5**. ^{31}P NMR ($CDCl_3$) δ 57.0 (P(1)), 83.1 (P(8)), $J = 35.1$; ^{13}C NMR ($CDCl_3$) δ 11.7 (C(2)—Me),[a] 12.8 ($J = 11.6$, C(4)–Me),[a] 41.2 ($J' = 76.3$, $J'' = 11.5$, C(7a)), 41.6 ($J'' = 60.2$, C(7)), 51.3 ($J'' = 70.0$, C(4)), 53.3 ($J' = 13.3$, $J'' = 13.4$, C(3a)), 126.3 ($J = 85.6$, C(1′)),[b] 128.1 ($J = 10.8$, C(3′)),[c] 128.4 ($J = 11.8$, C(3″)),[c] 130.2 ($J = 10.3$, C(2′)),[c] 131.7 (C(4′), C(4″)), 131.9 ($J = 95.3$, C(1″)),[b] 130.0 ($J = 8.5$, C(6)), 132.8 ($J = 7.7$, C(2″)),[c] 132.9 ($J'' = 7.2$, C(5)), 139.8 ($J' = 90.3$, C(2)), 140.8 ($J' = 30.3$, $J'' = 8.6$, C(3)); [a–c]may be reversed; J': coupled by P(1), J'': coupled by P(8); ^{1}H NMR ($CDCl_3$) δ 1.65 (d, $J_{PH} = 16.0$, 3H, Me), 1.82 (d, $J_{PH} = 11.5$, 3H, Me), 3.46 (d, 1H, $J_{HH} = 8$, C(7a)—H), 3.61 (s, 1H, C(7)—H), 3.95 (m, 1H, C(3a)—H), 5.79 (dd, 1H, $J_{HH} = 7.0$, $J_{PH} = 11.0$, C(5)—H), 6.47 (d, 1H, $J_{PH} = 41.0$, C(3)—H), 6.62 (m, 1H, C(6)—H), 7.40–7.72 (10H, Ar—H); HR-MS: $(M+H)^+_{found} = 381.1115$, $C_{22}H_{23}P_2O_2$ requires 381.1173.

The other fraction (0.20 g) consisted of 76% **5** and 24% **5′**.

5′: ^{31}P NMR ($CDCl_3$) δ 56.1 (P_1), 81.8 (P_8), $J = 35.8$; ^{13}C NMR ($CDCl_3$) δ 12.3 ($J = 11.7$, C(4)—Me),[a] 12.6 (C(2)—Me),[a] 44.6 ($J'' = 65.9$, C(7)), 46.1 ($J' = 75.9$, $J'' = 12.7$, C(7a)), 48.7 ($J' = 13.0$, $J'' = 13.0$, C(3a)), 50.9 ($J' = 2.5$, $J'' = 65.6$, C(4)), 125.8 ($J = 10.4$, C(6)), 128.4 ($J = 10.8$, C(3′)),[b] 128.7 ($J = 11.6$, C(2′)),[b] 128.8 ($J = 11.8$, C(3″)),[b] 130.3 ($J = 8.9$, C(2″)),[b] C(1′) overlapped at around 131,[c] 132.0 (C(4′), C(4″)), 133.2 ($J = 95.1$, C(1″)),[c] 137.5 ($J' = 5.3$, $J'' = 13.3$, C(5)), 139.3 ($J' = 90.1$, $J'' = 4.2$, C(2)), 143.0 ($J' = 30.2$, $J'' = 10.5$, C(3)); [a–c]may be reversed; J': coupled by P(1), J'': coupled by P(8); ^{1}H NMR ($CDCl_3$) δ 1.71 (d, $J_{PH} = 16.0$, 3H, Me), 1.80 (d, $J_{PH} = 9.0$, 3H, Me), 3.21 (d, 1H, $J_{HH} = 8.0$, CH, C(7a)—H), 3.43 (s, 1H, CH, C(7)—H), 4.28 (m, 1H, C(3a)—H), 6.07 (m, 1H, C(6)—H), 6.39 (d, 1H, $J_{PH} = 42.5$, C(3)—H), 6.48 (dd, 1H, $J_{HH} = 7.5$, $J_{PH} = 12.5$, C(5)—H), 7.35–7.73 (10H, Ar—H).

*Synthesis of 3-Methyl-1-cyclohexyl-2,5-dihydro-1H-phosphole Oxide (**7**)*

The Grignard reagent prepared from magnesium (8.4 g, 0.36 mol) and cyclohexylbromide (24.5 g, 0.15 mol) in THF (100 mL) was added dropwise with cooling to the THF solution (100 mL) of 1-chloro-2,5-dihydro-3-methyl-1*H*-phosphole 1-oxide (18.6 g, 0.12 mol) [16]. After 4 h of reflux, the mixture was stirred at rt overnight. The mixture was treated with concentrated hydrochloric acid (10 mL) in water (100 mL). The extraction with chloroform led to 15.2 g (64%) of 1*H*-phosphole oxide **7**. The crude product was purified by fractional distillation to give 5.9 g (25%) of **7**. bp 115–117°C (0.12 Hg mm); mp 63–64°C (10% chloroform in toluene), colorless, hygroscopic crystals.

7: ^{31}P NMR ($CDCl_3$) δ 73.1; ^{13}C NMR ($CDCl_3$) δ 20.2 ($J = 10.1$, C(3)—Me), 25.2 ($J = 2.8$, C(2′) and C(6′)), 25.9 ($J = 1.2$, C(4′)), 26.2 ($J = 13.1$, C(3′) and C(5′)), 30.2 ($J = 61.3$, C(5)),[a] 33.4 ($J = 64.1$, C(2)),[a] 38.5 ($J = 64.5$, C(1′)), 120.9 ($J = 6.9$, C(4)), 136.9 ($J = 11.7$, C(3)); [a]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.67 (s, 3H, Me), 5.38–5.55 (m, 1H, C(4)—H); HR-MS $(M+H)^+_{found} = 199.1237$, $C_{11}H_{20}PO$ requires 199.1252.

*3,4-Dibromo-1-cyclohexyl-3-methyl-2,3,4,5-tetrahydro-1H-phosphole 1-Oxide (**8**)*

0.5 mL (9.8 mmol) of bromine in 5 mL of chloroform was added to the 35 mL of chloroform solution of 1.6 g (8.1 mmol) of **7** at 0°C. After 0.5 h of stirring, 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 2.8 g (93%) of **8** as the mixture of two isomers (**A** and **B**). HR-MS $(M+H)^+_{found} = 356.9607$, $C_{11}H_{20}PO^{79}Br_2$ requires 356.9616.

8A: ^{31}P NMR ($CDCl_3$) δ 61.8; ^{13}C NMR ($CDCl_3$) δ 24.1 ($J = 7.9$, C(2′)), 25.0 (C(4′)), 25.4 ($J = 13.6$, C(3′)), 30.8 ($J = 5.7$, C(3)—Me), 35.4 ($J = 55.8$, C(5)), 39.7 ($J = 67.5$, C(1′)), 40.8 ($J = 56.2$, C(2)), 57.2 ($J = 5.6$, C(4)), 66.8 ($J = 6.7$, C(3)); ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H, Me), 2.42–2.51 (m), 2.59–2.71 (m), 2.88–2.95 (m), 4H, $2CH_2$, 4.60–4.68 (m, 1H, C(4)—H).

8B: ^{31}P NMR ($CDCl_3$) δ 66.0; ^{13}C NMR ($CDCl_3$) δ 24.2 ($J = 11.7$, C(2′)), 25.0 (C(4′)), 25.3 ($J = 13.6$, C(3′)), 32.4 ($J = 9.4$, C(3)—Me), 36.5 ($J = 57.2$, C(5)), 39.7 ($J = 60.7$, C(2)), 41.3 ($J = 68.1$, C(1′)), 50.9 ($J = 4.4$, C(4)), 67.1 ($J = 4.8$, C(3)).

*3,10-Dicyclohexyl-5,8-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dioxide (**11**) [15]*

1.4 mL (10.1 mmol) of triethylamine was added to the 25 mL of toluene solution of 1.51 g (4.24 mmol) of **8**. The mixture was stirred at 110°C for 3 days. After filtration, the filtrate was evaporated and the

crude product so obtained was purified by column chromatography (silica gel, 2% methanol in chloroform) to furnish 0.60 g (72%) of dimer **11**. ^{31}P NMR ($CDCl_3$) δ 68.7 (P(2)), 94.0 (P(8)), $J = 32.0$; ^{13}C NMR ($CDCl_3$) δ 18.5 ($J' = 15.8$, C(3)—Me), 18.7 ($J'' = 3.6$, C(5)—Me), 28.5 ($J' = 63.0$, C(1′)),[a] 39.0 ($J = 71.6$, C(1″)),[a] 34.9 ($J' = 70.9$, $J'' = 9.5$, C(7a)), 39.8 ($J = 2.5$, $J = 53.1$, C(7)),[b] 46.0 ($J = 59.0$, C(4)),[b] 51.7 ($J' = 10.8$, $J'' = 10.8$, C(3a)), 121.8 ($J' = 92.4$, C(2)), 123.4 ($J' = 8.6$, $J'' = 4.9$, C(6)), 134.8 ($J'' = 11.4$, C(5)), 158.5 ($J' = 21.1$, $J'' = 8.4$, C(3)); [a,b]may be reversed; J': coupled by P(1), J'': coupled by P(8); ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 3H, Me), 1.93 (s, 3H, Me), 2.96 (s, 1H, C(7)—H), 3.09 (s, 1H, C(4)—H), 3.10 (d, $J' = 6.0$, 1H, C(7a)—H), 3.77 (m, 1H, C(3a)—H), 5.80 (d, $J' = 23.9$, 1H, C(2)—H), 6.10 (d, $J'' = 12.8$, 1H, C(6)—H); HR-MS $(M+H)^+_{found} = 393.2083$, $C_{22}H_{35}P_2O_2$ requires 393.2112.

*9-Methyl-10-oxo-10-cyclohexyl-4-aza-phosphabicyclo[5.2.1.0^{2,6}] dec-8-ene-3,5-dione (**10**) [15]*

The mixture of 1.05 g (2.9 mmol) of **8**, 0.59 g (3.4 mmol) of NFMI, and 0.9 mL (6.5 mmol) of triethylamine in 25 mL of toluene was stirred at 26°C. After 6 days of stirring, the mixture was heated at the boiling point for 2 h. After filtration, the filtrate was evaporated and the crude product so obtained was purified by column chromatography (silica gel, 2% methanol in chloroform) to afford 0.88 g (81%) of phosphanorbornene **10**. mp 165–166°C (10% chloroform in toluene), colorless crystals; ^{31}P NMR ($CDCl_3$) δ 98.4; ^{13}C NMR ($CDCl_3$) δ 19.5 ($J = 3.3$, C(2)—Me), 25.4 ($J = 1.0$, C(4′)), 26.1 ($J = 6.2$) and 26.3 ($J = 6.2$, C(3′)),[a] 26.8 ($J = 7.0$) and 26.9 ($J = 6.8$, C(2′)),[a] 29.6 ($J = 59.9$, C(1′)), 42.7 ($J = 56.6$, C(4)),[b] 43.8 ($J = 10.0$, C(5)),[c] 45.1 ($J = 11.6$, C(6)),[c] 45.9 ($J = 56.1$, C(1)),[b] 121.8 ($J = 8.8$, C(3)), 126.6 (C(2″)),[a] 129.0 (C(4″)), 129.4 (C(3″)),[a] 131.8 (C(1″)), 140.9 ($J = 10.7$, C(2)), 175.5 ($J = 12.2$, C(8)),[d] 175.8 ($J = 12.8$, C(10))[d]; [a–d]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H, Me), 3.30–3.34 (m, 1H, C(6)—H), 3.43–3.49 (m, 1H, C(5)—H), 3.95–4.03 (m, 2H, C(1)—H, C(4)—H), 5.86–5.93 (m, 1H, C(3)—H), 7.09–7.14 (m, 2H, Ar—H), 7.35–7.49 (m, 3H, Ar—H); HR-MS $(M+H)^+_{found} = 370.1542$, $C_{21}H_{25}PO_3N$ requires 370.1572.

*Catalytic Hydrogenation of 7-Phosphanorbornene Derivative (**5**)*

0.39 g (1.02 mmol) of **5** in 40 mL of methanol was hydrogenated in the presence of 0.30 g of (10%) Pd/C at 60°C and at 22 bar for 14 h. The mixture was filtered, and the volatile components were removed. The crude product so obtained was purified by column chromatography (silica gel, 2% methanol in chloroform) to provide 0.24 g (61%) of phosphanorbornane **14** and 0.10 g (25%) of tetrahydrophosphole oxide **13** as a single diastereomer.

13: ^{31}P NMR ($CDCl_3$) δ 58.8, ^{13}C NMR ($CDCl_3$) δ 11.7 ($J = 3.1$, C(2)—Me), 23.2 ($J = 6.3$, C(3)),[a] 29.7 ($J = 66.0$, C(5)), 33.6 ($J = 10.6$, C(4)),[a] 35.0 ($J = 69.1$, C(2)), [a]may be reversed; MS, $(M+H)^+ = 195.1$ [7].

14: ^{31}P NMR ($CDCl_3$) δ 57.7 (P(1)), 62.1 (P(8)), $J = 40.0$; ^{13}C NMR ($CDCl_3$) δ, 12.7 ($J = 11.0$, C(4)—Me),[a] 14.0 (C(2)—Me),[a] 18.4 ($J = 6.5$, C(6)), 24.6 ($J'' = 14.9$, C(5)), 34.6 ($J = 62.7$, $J = 3.0$, C(7a)),[b] 37.7 ($J'' = 72.2$, C(7)), 43.2 ($J'' = 71.1$, C(4)), 49.9 ($J = 4.9$, $J = 12.7$, C(3a)),[b] 128.5 ($J = 85.1$, C(1′)),[c] 128.6 ($J = 11.9$, C(3″)),[d] 129.0 ($J = 11.2$, C(3′)),[d] 130.1 ($J = 10.2$, C(2″)),[d] 130.4 ($J = 9.1$, C(2′)),[d] 131.8 ($J = 2.7$, C(4′)),[e] 132.1 ($J = 95.9$, C(1″)),[c] 132.2 ($J = 2.5$, C(4″)),[e] 139.4 ($J' = 89.2$, C(2)), 142.3 ($J' = 30.0$, $J'' = 9.5$, C(3)); [a–e]may be reversed; J': coupled by P(1), J'': coupled by P(8); HR-MS: $(M+H)^+_{found} = 383.1303$, $C_{22}H_{25}P_2O_2$ requires 383.1330.

Phosphanorbornene **4** was hydrogenated under similar conditions to afford 0.10 g (26%) of phosphanorbornane **12** and 0.16 g (76%) of tetrahydrophosphole **13** after the work-up.

12: ^{31}P NMR ($CDCl_3$) δ 62.8; ^{13}C NMR ($CDCl_3$) δ 14.4 (C(1)—Me), 18.6 ($J = 8.1$, C(3)),[a] 25.5 ($J = 13.7$, C(2)),[a] 34.6 ($J = 65.3$, C(4)), 43.4 ($J = 68.7$, C(1)), 43.7 ($J = 3.0$, C(5)),[b] 48.1 ($J = 5.0$, C(6)),[b] 126.5 (C(3″)),[c] 127.5 ($J = 88.1$, C(1′)), 128.9 (C(4″)), 129.2 (C(2″)),[c] 129.3 ($J = 11.5$, C(3′)),[d] 130.6 ($J = 9.3$, C(2′)),[d] 131.7 (C(1′)), 132.9 ($J = 2.7$, C(4′)), 175.7 ($J = 15.2$, C(8)),[e] 176.1 ($J = 14.8$, C(10))[e]; [a–e]may be reversed; HR-MS: $(M+H)^+_{found} = 366.1235$, $C_{21}H_{21}NO_3P$ requires 366.1259.

*Photoinduced Fragmentation-Related Phosphorylation Using 7-Phosphanorbornenes (**4, 5, 10**, and **11**)*

The solution of 0.3 mmol of cycloadduct **4, 5, 10,** or **11** in the mixture of 40 mL of acetonitrile and 4 mL of methanol was irradiated with a 125 W mercury lamp in a photochemical quartz reactor for 1 h at 26°C. Volatile components were removed, and the residue so obtained was purified by flash column chromatography (silica gel, 2% methanol in chloroform) to give *H*-phosphinate **15** or **16,** respectively, in a yield of 89–95%.

15: ^{31}P NMR ($CDCl_3$) δ 27.8, $J_{PH} = 567$ Hz (δ [11] 26.8, $J_{PH} = 568$ Hz); MS, $(M+H)^+ = 157.1$.

16: ^{31}P NMR ($CDCl_3$) δ 46.3, $J_{PH} = 522$ Hz (δ [17] 46.7, $J_{PH} = 521$ Hz).

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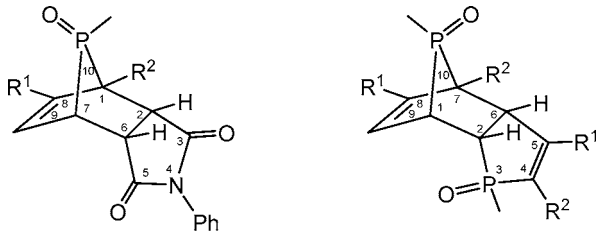
[15] According to the IUPAC nomenclature, the following numbering was used for naming products **4, 5, 10**, and **11**:



4, **10** **5**, **11**

R^1, R^2 = Me or H

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