portions of pentane, and the combined pentane extracts were washed twice with 10 mL of 50% dimethyl sulfoxide/water and three times with 10 mL of water. The pentane extracts were dried ($MgSO_4$), and the pentane was removed. Plug filtration of the residue (silica gel, pentane) afforded 1.3 g of an amber oil which displayed methyl signals at 0.73 and 1.26 ppm in a ratio of ca. 4:1. Preparative GLC of the oil on a 5% SE-52 column at 150 °C yielded 1.03 g of (+)-β-selinene: $[\alpha]^{23}_D$ +49.2° (c 0.234, hexane) (lit. $[\alpha]_D$ +43°[13]; +48°[14]); IR (neat) 1639, 877 cm^{-1}; NMR (CCl_4) 0.71 (s, 3, CH_3), 1.70 (s, 3, $=CCH_3$), 4.41 (s, 1, vinyl H), 4.68 (s, 3, vinyl H).

Registry No. 1, 18172-67-3; **2**, 86954-28-1; **3**, 42913-51-9; **4**, 81600-98-8; **5**, 86954-29-2; **6**, 86954-30-5; **11**, 86954-31-6; **12**, 35338-72-8; **15**, 71616-19-8; **16**, 5003-59-8; **17**, 87036-86-0; **18**, 87036-87-1; **19**, 17066-67-0; **20**, 83434-35-9.

1-Phenyl-*cis*-3a,7a-dihydrophosphindole and Its Properties[1]

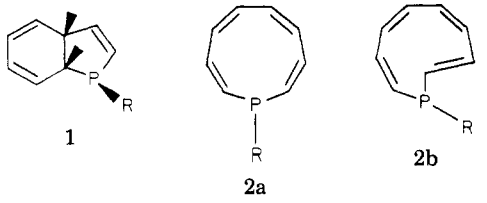
Louis D. Quin* and Nandakumar S. Rao

Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

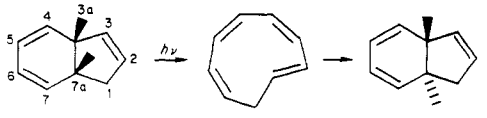
Received March 10, 1983

Deoxygenation of the dimer of 1-phenylphosphole oxide gives the diphosphine, whose thermal decomposition provides a useful route to *r*-1-phenyl-*c*-3a,*c*-7a-dihydrophosphindole. In the gas phase in the temperature range 345–370 °C the dihydrophosphindole undergoes partial epimerization about the phosphorus atom. However, in the higher temperature range of 460–490 °C ring cleavage occurs to give the isomeric phenyl-2-styrylphosphines in nearly quantitative yield. Peroxide oxidation of the dihydrophosphindole provides the corresponding oxide, which on thermolysis in the gas phase rearranges to the isomeric 2,3-dihydrophosphindole 1-oxide. Attempts at deoxygenation of the 3a,7a-dihydrophosphindole 1-oxides with trichlorosilane–triethylamine yielded phenyl-*cis*-2-styrylphosphine. Treatment of derivatives of the *cis*-3a,7a-dihydrophosphindoles with base (triethylamine or hydroxide) also effects ring cleavage to give styryl-substituted phosphines.

Although several derivatives of *cis*-3a,7a-dihydrophosphindole **1** have been reported,[2,3] the primary emphasis has been with regard to their usefulness in transformations to the phosphindole system. Other aspects of the chemistry of this class of phosphorus heterocycles have largely been left unexplored. Our attention was attracted to this system during a search[4] for synthetic methods that could provide simple derivatives of the 10-π-electron phosphonin molecule; retrocycloaddition could conceivably provide this ring system (**2a** or **2b**). Such conversions are

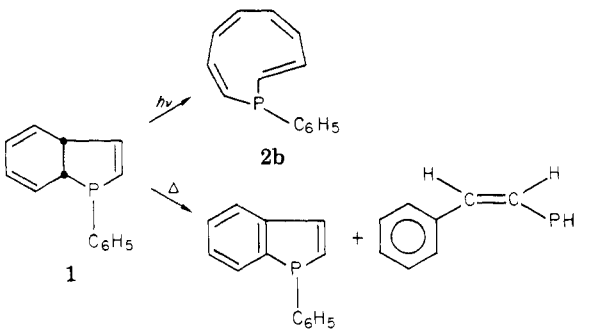


known for their carbocyclic counterpart (dihydroindenes); under photolytic conditions *cis*-3a,7a-dihydroindene was converted to *trans*-3a,7a-dihydroindene,[5] no doubt through the intermediacy of *cis,cis,trans*-cyclononatetraene.



However, under thermolytic conditions, *cis*-3a,7a-dihydroindene provided different products: indene, by a concerted 1,4-elimination of hydrogen followed by a 1,5 hydrogen shift, and allylbenzene, by transfer of a hydrogen atom from C(3a) to C(3) with the rupture of the C(1)–C(7a) bond.[6] Scheme I summarizes the products that could be obtained if similar events occurred for *cis*-3a,7a-dihydrophosphindoles. While photocleavage of the C(3a)–C(7a) bond could provide phosphonin derivatives, a thermal one-step elimination of hydrogen (in analogy to the transformation of cyclopentene to cyclopentadiene[7]) could give the fully unsaturated phosphindole system, and rupture of the P–C(7a) bond could occur to yield secondary phosphines. This paper presents the results of a study of these possibilities.

Scheme I



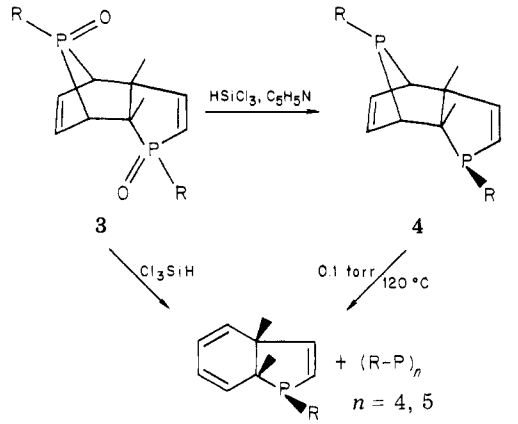
Synthesis of 3a,7a-Dihydrophosphindole Derivatives

Our route to the 3a,7a-dihydrophosphindole system makes use of the readily available dimers of phosphole oxides.[8,9] Thus dimer **3** (R = C_6H_5) was reduced to the

(1) Supported by Grant CHE-7717876 from the National Science Foundation.
(2) Holah, D. G.; Hughes, A. N.; Kleemola, D. *J. Heterocycl. Chem.* **1977**, *14*, 705.
(3) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.
(4) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905.
(5) Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1969**, 833.
(6) Frey, H. M.; Metcalfe, J. *J. Chem. Soc. A* **1970**, 2529.
(7) Baldwin, J. E. *Tetrahedron Lett.* **1966**, 2953.
(8) Mathey, F. *Tetrahedron* **1974**, *30*, 3127.

0022-3263/83/1948-3754$01.50/0

diphosphine **4** with retention of configuration by the procedure employing trichlorosilane and pyridine.[10] Distillation of **4** in a Kugelrohr apparatus at 120–125 °C and 0.1 torr then provided the dihydrophosphindole **1a** in 93% yield, free of the cyclopolyphosphine byproduct. The reduction of dimer **3** with trichlorosilane in refluxing benzene also gives the dihydrophosphindole[10] but in less satisfactory yield. The *P*-methyl derivative (**1b**) is also available[10] but was not included in this study.



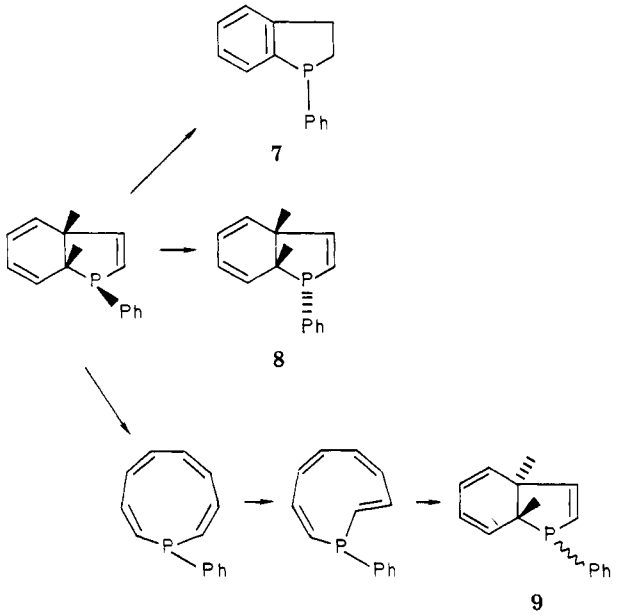
1a, R = C_6H_5
b, R = CH_3

The structure of the dihydrophosphindoles was readily confirmed by their ^{13}C NMR spectra. Signal congestion in the sp^2 carbon region required that the spectra be obtained at two frequencies (15.0 and 22.5 MHz) to insure that the lines were properly associated into doublets of constant *J*. To confirm that the two carbons in the sp^3 region were of the expected tertiary structure, the pulse sequences of the INEPT program[11] were used; with a delay of $2/4J_{CH}$ before FID, all signals arising from carbons bearing a single hydrogen were enhanced. Tentative assignments of the six sp^2 carbons of the ring system were based on a combination of shift and coupling characteristics. The spectrum of **1b** has been published;[12] data for **1a** are provided in the Experimental Section. The signals of the 2-phospholene unit were readily recognized from the characteristics[13] of strong deshielding for the β-carbon (δ 144.1, J = 7.3 Hz) and large C–P coupling for the α-carbon (δ 127.7, J = 15.9 Hz). The remaining sp^2 carbons of the diene unit are less readily assigned.

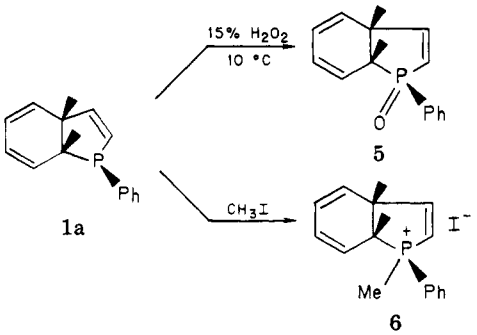
The ^{31}P shifts of the *cis*-dihydrophosphindoles (**1a**, +26.2; **1b**, +12.4) are at unusually low field and differ considerably from a value obtained in other work[14] for a trans-fused isomer (δ −16.4). The phosphorus atom is in quite different steric situations and exposed to different long-range interactions in these isomers. Variations in steric interactions in isomers can, in fact, cause even more dramatic differences in ^{31}P shifts than these, as has been revealed in derivatives of the *syn*- and *anti*-7-phosphanorbornene system where $\Delta\delta(^{31}P)$ can be 70–100 ppm.[10]

1-Phenyl-*cis*-3a,7a-dihydrophosphindole 1-oxide (**5**) was prepared by peroxide oxidation of **1a** in a biphasic (benzene–water) solvent system at 10 °C for 30 min.

Scheme II



Undesirable side reactions were avoided by these gentle conditions.



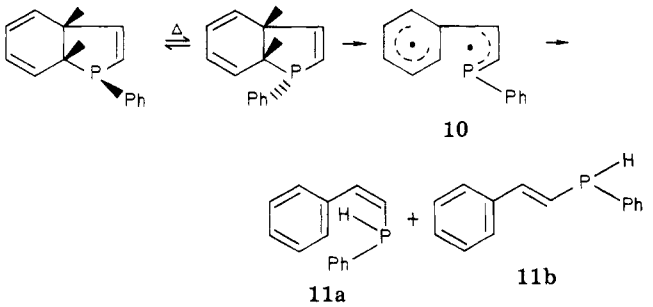
Phosphine **1a** was also readily quaternized with methyl iodide, giving the recrystallizable salt **6**. Spectral data for compounds **5** and **6** were consistent with the proposed structures.

Gas-Phase Reactions of 3a,7a-Dihydrophosphindole Derivatives

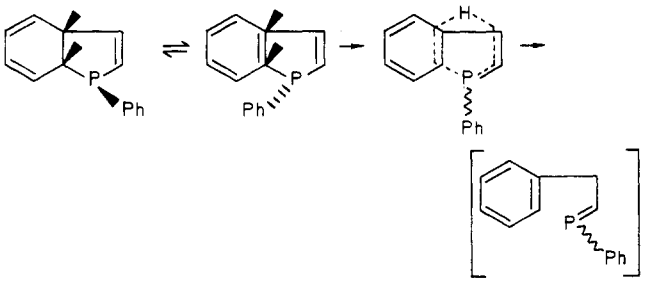
Frey and Metcalfe[6] have reported that in the gas phase at 358–399 °C, *cis*-3a,7a-dihydroindene undergoes both a dehydrogenation to indene and isomerization to allylbenzene. The dehydrogenation leading to indene follows a two-step mechanism; a concerted 1,4-elimination of hydrogen to yield isoindene is followed by a 1,5 hydrogen shift to yield the observed indene. Dihydrophosphindole **1a**, however, would not be expected to undergo the same dehydrogenation reaction as dihydroindene, since a phenyl substituent replaces a hydrogen atom in position 1. Furthermore, the one-step elimination of a molecule of hydrogen from the cyclohexa-1,3-diene unit is not allowed on the basis of conservation of orbital symmetry.[15] The reaction could, however, take the course of bond isomerization or bond cleavage to give isomers of the starting material. Indeed pyrolysis of phosphine **1a** at 345–370 °C at a pressure of 0.3–0.5 torr yielded a mixture comprised of two compounds in approximately equal amounts as evidenced by the intensities of the ^{31}P NMR peaks at δ +26.2 and +24.0. No significant change in the ratio was

(9) Quin, L. D.; Mesch, K. A.; Bodalski, R.; Pietrusiewicz, K. M. *Org. Magn. Reson.* **1982**, *20*, 83.
(10) Quin, L. D.; Mesch, K. A. *J. Chem. Soc., Chem. Commun.* **1980**, 959.
(11) Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6388.
(12) Spectrum No. 823, Supplementary Volume No. G-12, "Selected ^{13}C Nuclear Magnetic Resonance Spectral Data"; Thermodynamics Research Center, Texas A&M University, College Station, TX.
(13) Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley: New York, 1983; p 291.
(14) Rao, N. S.; Quin, L. D. *J. Am. Chem. Soc.* **1983**, *105*, 5960.
(15) Woodward, R. B.; Hoffmann, R. *Acc. Chem. Res.* **1968**, *1*, 17.

Scheme III



Scheme IV

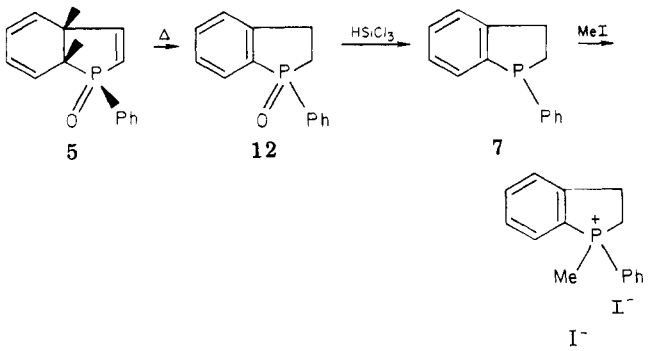


observed upon a second passage of the product mixture through the hot tube. The signal at +26.2 ppm was unambiguously assigned to the starting material (also δ +26.2) by comparison of its ^{13}C spectrum with that of an authentic sample. The other compound also possessed two sp^3 and six sp^2 carbons. The more probable structures (Scheme II) are **7** from double-bond migration or **8** from pyramidal inversion at phosphorus; less likely is **9**, from cleavage of the 3a,7a bond followed by cis–trans isomerization and ring closure. That the phosphorus atom occupied a position in a five-membered ring was readily proved by peroxide oxidation of the crude product to the corresponding phosphine oxide; two ^{31}P resonances were observed (δ +62.4, +71.1) both in the very characteristic downfield range of phospholene oxides. The upfield resonance was shown to be due to authentic dihydrophosphindole oxide **5** by comparison of ^{31}P and ^{13}C NMR spectra. Structure **7** may immediately be ruled out on the basis of the ^{13}C NMR spectrum run with the INEPT program, which revealed the sp^3 signals to arise from tertiary carbons. Structure **8** was confirmed when it was discovered that the same substance resulted from thermal epimerization performed on **1a** under conventional conditions;[16] a xylene solution of **1a** heated at 150 °C for 16.5 h provided a 70:30 mixture of **1a** and **8**, having the same ^{31}P shifts, gas chromatographic retention times, and ^{13}C NMR shifts as for the mixture formed from the gas-phase reaction. Furthermore, the two ^{31}P signals obtained with ^1H coupling were strikingly different, as would be expected[17] from the different orientation of the proton at C-7a to the lone-pair orbital on phosphorus. $^2J_{PH}$ for **8** was large (15 Hz), consistent with the proximity of the proton and the lone pair, and negligible for **1a**, where these features are remote.

At the higher temperature of 460–490 °C (0.3–0.5 torr), the crude product contained none of the dihydrophosphindoles **1a** or **8**. Instead, the ^{31}P NMR spectrum had signals at −51.8 and −64.4, both possessing the large P–H coupling constants (226.9 and 224.1 Hz, respectively) of secondary phosphines. That compound with δ −64.4 was identical with phenyl-*cis*-2-styrylphosphine (**11a**), prepared by an independent synthesis described in the next section. The other product is presumed to be the trans isomer **11b**, but this has not yet been confirmed. A possible pathway (Scheme III) for their formation involves an intermediate stabilized biradical (**10**), followed by a hydrogen abstraction. Phosphinyl radicals are generally considered to be fairly stable and are known to undergo radical abstraction reactions.[18]

An alternate pathway might also be considered that involves hydrogen atom transfer from C(3a) to C(3) with the simultaneous rupture of the P to C(7a) bond. This generates the unstable phosphaalkene shown in Scheme IV. The process is allowed on the basis of orbital symmetry arguments and was used previously to account for the formation of allylbenzene from *cis*-3a,7a-dihydroindene.[6] The phosphaalkene would then isomerize to the isomeric phenylstyrylphosphines.

In contrast to phosphine **1a**, the corresponding oxide **5** provided a single product in 20% yield in the gas phase at 380–410 °C. The ^{31}P chemical shift (δ +54.2) along with ^{13}C INEPT data (which revealed two methylene groups in the structure) suggested the product to be the 2,3-dihydro isomer **12** of the starting material. The ^1H NMR spectrum

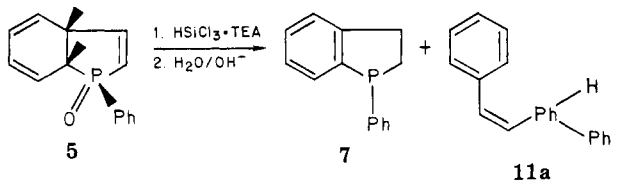


was identical with that reported for this structure in the literature.[19] For further characterization, the oxide was reduced with trichlorosilane to the corresponding phosphine **7** ($\delta(^{31}P)$ −3.9), which was then quaternized with methyl iodide. Analytical data were correct for the salt.

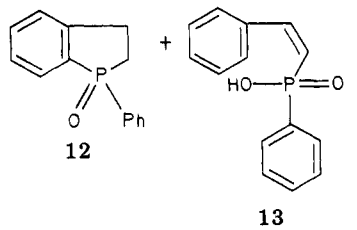
Reduction of 1-Phenyl-*cis*-3a,7a-dihydrophosphindole 1-Oxide with Trichlorosilane–Triethylamine Complex

Dihydrophosphindole oxide **5** can be reduced smoothly (90%) to the phosphine **1a** with $HSiCl_3$ in benzene, a reagent known to reduce phosphine oxides with retention of configuration.[20] In an effort to synthesize the anti epimer **8**, the oxide **5** was treated with the complex formed with $HSiCl_3$ and triethylamine, which is known to reduce phosphine oxides with inversion of configuration.[20] Two products with $\delta(^{31}P)$ −3.9 and −64.4 were obtained after workup. The low-field signal was shown to arise from 1-phenyl-2,3-dihydrophosphindole (**7**), previously obtained by reduction of the phosphine oxide **12** formed from thermal isomerization of **5**. The ^{31}P signal at −64.4 ppm had $^1J_{PH}$ = 224 Hz and was coincident in a mixed sample with the high-field resonance of the previously obtained product (**11a**, δ +64.4) from the high-temperature reaction (460–490 °C) of **1a**. Comparison of their GC retention

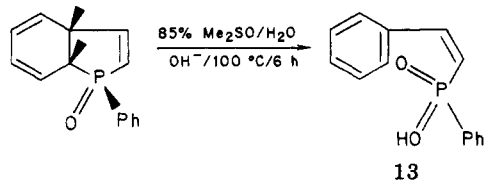
(16) Horner, L.; Winkler, H.; Rapp, A.; Mentrup, A.; Hoffman, H.; Beck, P. *Tetrahedron Lett.* **1961**, 161.
(17) Albrand, J. P.; Gagnaire, D.; Martin, J.; Robert, J. B. *Bull. Soc. Chim. Fr.* **1969**, *40*.
(18) Walker, B. J. "Organophosphorus Chemistry"; Penguin Books: Baltimore, MD, 1972; pp 211–216.
(19) Chan, T. H.; Wong, T. L. *Can. J. Chem.* **1971**, *49*, 530.
(20) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.



times confirmed that the two products were identical. The mixture of **7** and **11a** was oxidized with 12% aqueous peroxide to generate a mixture of phosphine oxide **12** and phosphinic acid **13**. Extraction of a basified solution of

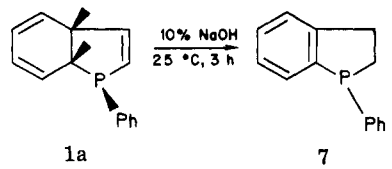


the mixture with chloroform provided pure **12**; acidification of the aqueous layer and reextraction yielded **13**. Unequivocal proof of structure **13** was obtained through its synthesis by an alternate approach shown below. The



stereochemistry about the double bond of **13** was assigned the cis structure shown on the basis of its ^1H NMR spectrum. Thus the observed doublet of doublets for the olefinic proton α to phosphorus exhibited similar coupling[21] to that for cis double bonds in styrylphosphine oxides ($^3J_{HH}$ = 13.2 Hz; $^2J_{PH}$ = 13.4 Hz).

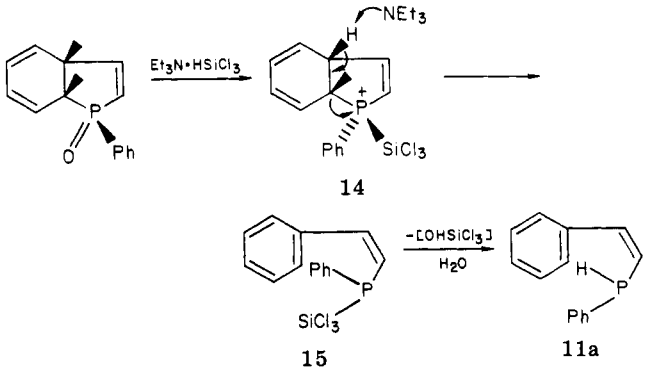
It seems reasonable to speculate that **7** arises in this basic reaction medium by migration of the Δ^2 bond to establish the benzene ring. The ease of base-promoted rearrangement was confirmed by observing the formation of **7** upon treatment of **1a** with 15% aqueous sodium hydroxide at room temperature.



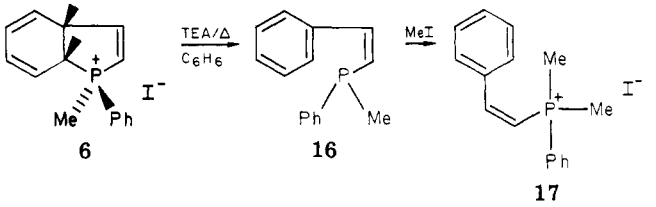
A mechanism for the formation of the secondary phosphine **11a** during $HSiCl_3$–TEA reduction of **5** is outlined in Scheme V. The formation of the styrylphosphine **11a** is also accompanied by aromatization, which must account for the ease of the process. The reaction can be interpreted (Scheme V) as an E2 elimination where the phosphorus moiety is the leaving group. It is likely that phosphorus is in the P(IV) state so as to depart as a stable P(III) group; possibly an intermediate such as **14**[20] that forms during the silane reduction is involved in the elimination. This provides a tertiary phosphine **15** bearing a phosphorus–silicon bond, which will be hydrolyzed during workup. Support for a mechanism such as that shown in Scheme V was obtained by reacting phosphonium salt **6** with triethylamine in refluxing benzene to give a 43% yield of

(21) Aguiar, A. M.; Daigle, D. *J. Org. Chem.* **1965**, *30*, 3527.

Scheme V



tertiary phosphine **16** (isolated as the phosphonium salt **17**).



The reactions described not only demonstrate the unusual reactivity of the 3a,7a-dihydrophosphindole system but also offer a new and useful approach to styryl-substituted phosphorus compounds. By varying the substitution on P in quaternary salt **6** for the reaction with triethylamine, a variety of substituted (tertiary) styrylphosphines may be realized. Similarly, phosphinic acids bearing a styryl moiety may be prepared by the cleavage of various 3a,7a-dihydrophosphindoles with hydroxide. Finally, secondary phosphines bearing a styryl group may be prepared by the gas-phase rearrangement of substituted dihydrophosphindoles.

Photolysis of 3a,7a-Dihydrophosphindole Derivatives

All attempts to prepare phosphonins by photolytic cleavage of the C(3a)–C(7a) bond of both the phosphine **1a** and the corresponding oxide **5** yielded very complex mixtures of substances, probably arising by cleavage of one or both of the endocyclic P–C bonds. Decomposition of all the starting material resulted on photolyzing a solution of **1a** in benzene for 2 h at 0 °C through Vycor (>230 nm). Photolysis of 2- and 3-phospholenes has been reported to effect the ejection of phosphinidene;[22] however, the reaction conditions were more vigorous (direct photolysis at ambient temperature), and the reaction times were much longer (8–12 h) in that work. The presence of the cyclohexadiene moiety in **1** no doubt presents other reaction alternatives and also weakens the P–C(7a) bond, thereby providing the complex mixture observed. No attempts were made to identify any of the products.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Proton NMR spectra were obtained on a JEOL FX-90Q spectrometer at 89.6 MHz or on a Bruker WM-250 spectrometer at 250 MHz. Carbon-13 FT NMR spectra (including the INEPT program) were taken on the JEOL FX-90Q spectrometer at 22.5 MHZ; spectra were also obtained at 15.0 MHz with a JEOL FX-60 spectrometer. Both utilized an internal deuterium lock and were

(22) Tomioka, H.; Takata, S.; Kato, Y.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1017. Tomioka, H.; Hirano, Y.; Izawa, Y. *Tetrahedron Lett.* **1974**, 1865. Tomioka, M.; Izawa, Y. *Ibid.* **1973**, 5059.

proton noise decoupled. Proton and ^{13}C NMR chemical shifts are expressed in ppm downfield from tetramethylsilane. Phosphorus-31 FT NMR spectra were obtained with the JEOL FX-90Q at 36.2 MHz; chemical shifts are expressed in ppm relative to external 85% H_3PO_4 with positive shifts downfield. Gas chromatographic analysis was performed with a 5 ft × $^1/_4$ in. column packed with 20% SE-30 on 60–80 mesh Chromosorb W. Mass spectra were run at the Research Triangle Mass Spectrometry Center on an AEI MS-903 spectrometer. Elemental analyses were performed by commercial laboratories.

1,*syn*-8-Diphenyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole 1,8-Dioxide (3, R = C_6H_5). A solution of 61.1 g (0.18 mol) of 3,4-dibromo-1-phenylphospholane 1-oxide, prepared by the procedure of Märkl and Potthast,[23] in 150 mL of acetone was cooled to 0 °C. Triethylamine (100 mL) was added dropwise to the stirred solution over a period of 1.5 h. Stirring was continued for 18 h while the temperature was maintained between 10 and 20 °C. The mixture was filtered and the white solid consisting of triethylamine hydrobromide and **3** was dissolved in 500 mL of water and extracted with chloroform (4 × 250 mL). The combined chloroform extracts were dried ($MgSO_4$), filtered, and concentrated to yield an off-white solid. Recrystallization from toluene gave 30.0 g (94%) of **3**: mp 236–238 °C (lit.[23] mp 234–237 °C); ^{31}P NMR ($CDCl_3$) δ +84.9 (d, $^3J_{PP}$ = 36.6 Hz, ^8P), +55.5 (d, $^3J_{PP}$ = 36.6 Hz, ^1P).

1,*syn*-8-Diphenyl-3a,4,7,7a-tetrahydro-4,7-phosphinidene-1(*H*)-phosphindole (4, R = C_6H_5). This compound was prepared in 90% yield by the procedure of Quin and Mesch.[10]

***r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole[24] (1a). Method A.** A mixture of 1.0 g (2.8 mmol) of **3** (R = C_6H_5) and 1.5 g (11.1 mmol) of trichlorosilane in 50 mL of benzene was refluxed for 2 h. Following slow hydrolysis with excess 30% NaOH, the organic layer was separated, dried ($MgSO_4$), and concentrated to give 0.6 g of a yellow oil that upon distillation (110 °C (0.01 torr)) provided 0.3 g (50%) of **1a** as a clear oil: ^1H NMR (benzene-d_6) δ 3.0–3.4 (m, CH, 1 H), 3.7–4.0 (m, CH, 1 H), 5.2–6.8 (m, CH=, 6 H), 7.3–8.2 (m, CH=, 5 H); ^{31}P NMR (benzene-d_6) δ +26.2; ^{13}C NMR (benzene-d_6) C-2 δ 127.7 (d, J = 15.9 Hz), C-3 144.1 (d, J = 7.3 Hz), C-3a 45.1 (d, J = 1 Hz), C-4, C-5, C-6, C-7 [unassigned, 121.0 (d, J = 11.0 Hz), 122.2 (d, J = 3.7 Hz), 124.3 (d, J = 4.9 Hz), 129.8], C-7a 44.4 (d, J = 8.5), phenyl ipso 137.7 (d, J = 29.3), phenyl ortho 131.9 (d, J = 19.5) phenyl meta 128.4 (d, J = 4.9), phenyl para 128.1.

Method B. Diphosphine **4** (R = C_6H_5; 0.9 g, 2.8 mmol) was heated in a Kugelrohr oven at 120–130 °C under vacuum (0.05–0.2 torr) until transfer of the volatiles to a bulb cooled to −78 °C was complete. The pale oil was distilled (bp 90–95 °C (0.1 torr)), yielding 0.5 (84%) of **1a** as a clear oil.

Phosphine **1a** was analyzed as the methyl iodide salt **6**, prepared by adding an excess of iodomethane to a benzene solution of **1a** and recrystallizing the resulting precipitate from methanol to give white plates: mp 120–130 °C dec; ^{31}P NMR (Me_2SO-d_6) δ +57.7; ^{13}C NMR (Me_2SO-d_6) δ 8.7 (d, J = 52.5 Hz, PCH_3), 37.9 (d, J = 50.0 Hz, C-7a), 47.6 (d, J = 8.5 Hz, C-3a), 118.5 (d, J = 129.4 Hz, C-2), 165.6 (d, J = 24.4 Hz, C-3), also 126.0 (d, J = 2 Hz), 128.4 (d, J = 12.2 Hz), 119.2 (d, J = 8.5 Hz), 124.0 (d, J = 6.1 Hz). Anal. Calcd for $C_{15}H_{16}IP$: C, 50.86; H, 4.56; P, 8.74. Found: C, 50.54; H, 4.87; P, 8.64.

***r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole 1-Oxide (5).** A solution of 1.0 g (4.7 mmol) of dihydrophosphindole **1a** in 25 mL of benzene was cooled to 10 °C in an ice bath. Two grams of 30% H_2O_2 (17.6 mmol) was added and the mixture stirred vigorously in the ice bath for 15 min and at room temperature for 15 min. The layers were separated, and the aqueous layer was extracted with benzene (3 × 15 mL). The combined benzene extracts were dried ($MgSO_4$), filtered, and concentrated, yielding 0.90 g (84%) of **5** as a clear oil: ^1H NMR (250 MHz in $CDCl_3$) δ 3.11 (H-3a, 1:2:1 pseudotriplet with $^3J_{PH} \sim {}^3J_{H\text{-}3a,H\text{-}7a} \sim 12.4$ Hz, split 4.1 Hz by H-4, further split with poor resolution by H-3 about 2–3 Hz), 3.90 (H-7a, 1:2:1 pseudotriplet with $^2J_{PH} \sim {}^3J_{H\text{-}3a,H\text{-}7a} \sim 13$ Hz, further splitting by H-7 and H-2 poorly resolved), 5.64 (tentatively H-4, d of d, $^3J_{H\text{-}4,H\text{-}5}$ = 9.6, $^3J_{J\text{-}4,H\text{-}3a}$ = 4.1 Hz), 5.76 (m, 1 H), 5.81–6.04 (m, 2 H), 6.48 (H-2, d of d of d, $^2J_{PH}$ = 25.9, $^3J_{H\text{-}2,H\text{-}3}$ = 8.4, $^4J_{H\text{-}2,H\text{-}7a}$ = 2.6 Hz), 7.05 (H-3, d of d of d, $^3J_{PH}$ = 43.5, $^3J_{H\text{-}3,H\text{-}3a}$ = 2.9 Hz), 7.4–7.7 (m, C_6H_5); ^{31}P NMR ($CDCl_3$) δ +62.4; ^{13}C NMR ($CDCl_3$) C-2 δ 125.2 (d, J = 80.6 Hz), C-3 153.4 (d, J = 29.5 Hz), C-3a 41.9 (d, J = 10.8 Hz), C-7a 38.3 (d, J = 67.1 Hz), C-4, C-5, C-6, C-7 (unassigned 118.8 (d, J = 9.4 Hz), 122.2 (d, J = 4.0 Hz), 122.9 (d, J = 2.7 Hz), 128.0).

Gas-Phase Reaction of *r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole (1a) at 345–370 °C. A 0.5-g sample of **1a** was volatilized at 120 °C and 0.3–0.5 torr and the vapor passed directly through a 0.5 × 13 in. column packed with 1.5-mm glass helices heated to 345–370 °C. The product (0.4 g), a mixture of epimers **1a** and **8** (51:49), was collected as a clear oil in a trap cooled to −78 °C: ^{31}P NMR (benzene-d_6) +26.2 (**1a**, $^2J_{PH\text{-}2}$ = 46.4 Hz), +24.0 (**8**, $^2J_{PH\text{-}2}$ = 44.0, $^2J_{PH\text{-}7a}$ = 15 Hz); ^{13}C NMR (benzene-d_6) C-3 δ 145.7 (d, J = 2.4 Hz), C-3a 38.3 (d, J = 13.4 Hz), C-7a 45.6 (d, J = 8.6 Hz), also 121.2 (d, J = 9.8 Hz), 134.0 (d, J = 20.8 Hz), 124.5 (d, J = 2.5 Hz), 124.7 in addition to signals seen for **1a**; ^1H NMR (benzene-d_6) δ 3.0–3.7 (m, CH), 5.3–6.9 (m, CH=), 7.3–8.1 (m, CH=).

Gas-Phase Reaction of *r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole (1a) at 460–490 °C. Compound **1a** (0.5 g) was passed through the hot tube in the temperature range 460–490 °C as above, yielding a 62:38 mixture of the two secondary phosphines: ^{31}P NMR (benzene-d_6) δ −64.4 (**11a**, $^1J_{PH}$ = 224.1, J_{PH} = 20 Hz), −51.8 (**11b**, tentatively, $^1J_{PH}$ = 226.9 Hz).

Gas-Phase Reaction of *r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole 1-Oxide (5). Compound **5** (0.5 g) was passed through the hot tube in the temperature range 380–410 °C (0.3–0.5 torr) as above, yielding 0.12 g of a pale, viscous oil. Distillation (130 °C (0.01 torr)) provided 0.1 g (20%) of **12** as a clear, viscous oil: ^{31}P NMR ($CDCl_3$) δ +54.2; ^1H NMR[19] ($CDCl_3$) δ 2.2–2.6 (m, CH_2, 2 H), 2.9–3.4 (m, CH_2, 2 H), 7.2–7.7 (m, CH=, 9 H); ^{13}C NMR ($CDCl_3$) δ 28.1 (d, J = 70.8 Hz, C-2), 28.3 (d, J = 3.7 Hz, C-3), 132.8 (d, 2.4, C-5), 133.3 (d, J = 100.1 Hz, C-7a), 147.7 (d, J = 30.5 Hz, C-3a), also 126.5 (d, J = 11.0 Hz), 127.8 (d, J = 9.8 Hz), 129.1 (d, J = 8.6 Hz).

1-Phenyl-2,3-dihydrophosphindole (7). To a solution of 0.1 g (0.4 mmol) of **12** in 10 mL of benzene was added 0.5 g (3.7 mmol) of trichlorosilane. The reaction mixture was stirred at ambient temperature for 3.5 h. After hydrolysis with excess 30% NaOH, the organic layer was separated, and the aqueous layer was extracted with benzene (3 × 15 mL). The combined benzene extracts were dried ($MgSO_4$), filtered, and concentrated, yielding 0.09 g (95%) of **7** as a clear oil: ^{31}P NMR (benzene-d_6) δ −3.9; ^{13}C NMR (benzene-d_6) δ 26.6 (d, J = 9.8 Hz, C-2), 33.1 (d, J = 4.9 Hz, C-3), 148.2 (d, J = 2.5 Hz, C-3a), also 123.7 (d, J = 2.4 Hz), 129.8 (d, J = 3.7 Hz), 130.8 (d, J = 4.9 Hz), 139.7 (d, J = 23.2 Hz), 139.4 (d, J = 24.4 Hz).

Phosphine **7** was analyzed as the methyl iodide salt, prepared by adding an excess of iodomethane to a benzene solution of **7** and recrystallizing the resulting precipitate from methanol to give white plates, mp > 100 °C dec; ^{31}P NMR ($CDCl_3$) δ +43.2. Anal. Calcd for $C_{15}H_{16}IP$: C, 50.86; H, 4.56; P, 8.74. Found: C, 50.54; H, 4.41; P, 8.71.

Reduction of *r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole 1-Oxide (5). Phosphine oxide **5** (0.5 g, 2.2 mmol) was suspended in 15 mL of dry benzene; 0.6 mL (5.9 mmol) of trichlorosilane was added to the suspension in one portion, and the mixture was stirred at ambient temperature under nitrogen for 18 h. Twenty-five milliliters of 30% NaOH solution was carefully added to the cooled reaction mixture. The layers were separated, and the aqueous phase was extracted with benzene (3 × 25 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to give 0.30 g of phosphine **1a** as a clear oil: ^{31}P NMR ($CDCl_3$) δ +26.8.

Reduction of *r*-1-Phenyl-*c*-3a,*c*-7a-dihydrophosphindole (5) with Trichlorosilane–Triethylamine Complex. To a suspension of 0.5 g (2.2 mmol) of **5** in 15 mL of benzene was added the complex formed by reaction of 1.3 g (9.9 mmol) of trichlorosilane and 4.4 g (43.0 mmol) of triethylamine in 15 mL of benzene. The reaction mixture was stirred at ambient temperature for 5.5 h. After hydrolysis with excess 30% NaOH, the organic phase was separated and the aqueous layer extracted with benzene (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated, yielding 0.4 g of a 65:35 mixture of

(23) Märkl, G.; Potthast, R. *Tetrahedron Lett.* **1968**, 1755.

(24) Stereochemical notation: H at C(3a) and C(7a) are cis (c) to *P*-phenyl as reference (r).

11a and **7** as a clear oil: ^{31}P NMR (benzene-d_6) δ -64.4 ($^1J_{PH}$ = 224.0) and -3.9. To a solution of the mixture in 15 mL of benzene was added 5 mL of 12.5% H_2O_2 and the reaction mixture stirred at ambient temperature for 18 h. The benzene layer was separated and the aqueous layer diluted with 5 mL of water and extracted with $CHCl_3$ (3 × 15 mL). The combined organic extracts were concentrated, yielding a pale oil to which 15 mL of 1% NaOH was added, and the solution was then extracted with $CHCl_3$ (3 × 20 mL). The combined $CHCl_3$ extracts were dried ($MgSO_4$), filtered, and concentrated, yielding 0.2 g of **12** as a clear oil: ^{31}P NMR ($CDCl_3$) δ +54.1; ^{13}C and ^1H NMR were identical with those of **12** prepared by gas-phase reaction of **5**.

The basic aqueous layer was acidified to pH 2 with 2 N H_2SO_4 and reextracted with $CHCl_3$ (3 × 20 mL). The combined extracts were dried ($MgSO_4$) and concentrated to yield 0.25 g of **13** as an oil, which crystallized to an off-white solid upon drying under high vacuum: mp 105-110 °C; ^{31}P NMR ($CDCl_3$) δ +30.4; ^{13}C NMR ($CDCl_3$) δ 116.3-131.3 (complex, unassigned sp^2 carbons), δ 147.5 (C-3); ^1H NMR ($CDCl_3$) δ 5.9-6.3 (t, $^2J_{PH}$ 13.4, $^3J_{HH}$ = 13.2 Hz, PCH=), 7.0-7.4 (m, aromatic). Anal. Calcd for $C_{14}H_{13}O_2P \cdot {}^1/_2H_2O$: C, 66.39; H, 5.38; P, 12.33. Found: 66.39; H, 5.51; P, 12.31.

Phenyl-*cis*-2-styrylphosphinic Acid (13). A solution of 0.6 g (2.6 mmol) of phosphine oxide **5** and 0.5 g (25 mmol) of NaOH in 50 mL of 85% Me_2SO-H_2O was heated at 100 °C for 6 h. Me_2SO and H_2O were removed by distillation at reduced pressure. The residue, dissolved in 40 mL of water, was extracted with $CHCl_3$ (3 × 50 mL) to remove nonacidic organics in the mixture. The aqueous layer was then acidified to pH 3 by addition of 2 N H_2SO_4 and reextracted with $CHCl_3$ (3 × 50 mL). This $CHCl_3$ extract was dried ($MgSO_4$) and concentrated to give 0.35 g (55%) of **13** as a clear oil, which crystallized slowly to a hygroscopic white solid: mp 106-110 °C; ^{31}P NMR ($CDCl_3$) δ +29.5; ^1H and ^{13}C NMR were identical with those of **13** prepared by the reduction method above.

Methylphenyl-*cis*-2-styrylphosphine (16). To a suspension of 1.1 g (3.1 mmol) of phosphonium salt **6** in 25 mL of benzene was added 10 mL of triethylamine. The mixture was refluxed under nitrogen for 2 days. The benzene solution was then decanted and the reaction flask rinsed with several portions of benzene. The solution was concentrated to give 0.30 g (43%) of **16** as a clear oil: ^{31}P NMR (benzene-d_6) δ -45.4; ^1H NMR (benzene-d_6) δ 1.3 (d, J = 6.1 Hz, PCH_3), 6.1-6.4 (d of d, $^2J_{PH}$ = 14.9, $^3J_{HH}$ = 4.1 Hz, PCH=), 7.0-7.9 (m, aromatic H); ^{13}C NMR (benzene-d_6) δ 14.6 (d, J = 12.2 Hz, PCH_3), 143.1 (d, J = 17.1 Hz, C-3), 141.9 (d, J = 13.4 Hz, C-4), 127.2-137.9 (complex, sp^2 C).

Phosphine **16** was analyzed as its methyl iodide salt, prepared by adding excess methyl iodide to a benzene solution of **16**. The resulting precipitate was filtered and washed with benzene, and a small amount was then recrystallized from methanol: mp 155-157 °C; ^{31}P NMR ($CDCl_3$) δ +12.5; ^{13}C NMR ($CDCl_3$) δ 11.7 (d, 57.4, PCH_3), 111.7 (d, 80.5, =CP), 127.6, 128.3, and 129.9 (styryl ring carbons), 129.7 (d, J = 12.2 Hz, phenyl ortho C), 131.2 (d, J = 11.0 Hz, phenyl meta C), 133.5 (d, J = 8.5 Hz, phenyl ipso C), 133.9 (d, J = 2.5 Hz, para C), 155.9 (C=CP). Anal. Calcd for $C_{16}H_{18}IP$: C, 52.19; H, 4.94; P, 8.41. Found: C, 52.06; H, 5.02; P, 7.95.

Epimerization of 1a to 8. A solution of 250 mg of dihydrophosphindole **1a** in 10 mL of xylene was heated at 150 °C for 16.5 h under nitrogen. The ^{31}P spectrum of an aliquot showed a 70:30 mixture of **1a** (δ -26.2) and **8** (δ -24.0); the gas chromatogram was identical with that for the mixture formed from **1a** at 345-370 °C.

Isomerization of 1a to 7. A solution of 0.5 g of **1a** in 15 mL of 15% NaOH was stirred at 25 °C for 3 h. The basic solution was neutralized with 2 N H_2SO_4 and extracted with $CHCl_3$ (3 × 25 mL). The organic extract was dried ($MgSO_4$) and concentrated to give 0.45 g of **7** as a clear oil: ^{31}P NMR (benzene-d_6) δ -3.9; ^{13}C and ^1H NMR were identical with those of **7** prepared by alternate methods.

Registry No. **1a**, 86901-20-4; **3** (R = C_6H_5), 76549-54-7; **4** (R = C_6H_5), 86941-21-1; **5**, 86940-55-8; **6**, 86901-21-5; **7**, 86901-22-6; **7** methyl iodide salt, 86901-28-2; **8**, 86941-22-2; **11a**, 86901-23-7; **11b**, 86901-24-8; **12**, 31236-96-1; **13**, 86901-25-9; **16**, 86901-26-0; **17**, 86901-27-1; $HSiCl_3$, 10025-78-2; 3,4-dibromo-1-phenylphospholane 1-oxide, 72620-95-2.

Crystal Structure of Orthosphenic Acid

Antonio G. González,* Braulio M. Fraga, Pedro González, Carmen M. González, Angel G. Ravelo, and Esteban Ferro

Instituto de Productos Naturales Orgánicos, CSIC, La Laguna, and Instituto de Quimica Orgánica, Universidad de La Laguna, Tenerife, Canary Islands, Spain

Xorge A. Dominguez and Martha A. Martinez

Instituto Tecnológico, Monterrey, Mexico

Aurea Perales and José Fayos

Departamento de Rayos-X, Instituto Rocasolano, CSIC, Serrano 119, Madrid, Spain

Received December 15, 1982

A new triterpenic compound, orthosphenic acid, has been isolated from *Orthosphenia mexicana* and its structure determined by X-ray analysis.

The study of Celastraceae has attracted considerable attention as this family contains physiologically active quinones.[1] From a member of this group of plants, *Orthosphenia mexicana* Standley,[2] we have isolated two triterpenic compounds, celastrol (**8**) and, to the best of our knowledge, a new compound, which we named orthosphenic acid (**1**).

The structure (**1**) given to this compound was based on the following data. The acid **1** ($C_{30}H_{48}O_5$) reacted with diazomethane to yield a methyl ester (**2**). Examination of the ^1H NMR spectrum of the latter showed absence of unsaturation and the presence of a secondary alcohol and of six methyl groups. Acetylation of **1**, with acetic anhydride in pyridine, gave the monoacetate **3** and the diacetate **5** in a 1:1 ratio. The proton geminal to the secondary alcohol group was shifted from δ 4.35 in **1** to δ 5.04 in the monoacetate **3** and to δ 5.85 in the diacetate **5**. When the

(1) Brüning, R.; Wagner, H. *Phytochemistry* **1978**, *17*, 1821.
(2) Rzedowsky, J. *Ciencia (Mexico City)* **1957**, *16*, 139.

0022-3263/83/1948-3759$01.50/0