Structure and Sterochemistry of Phospholene Sulfides from Reaction of Hydrogen Sulfide with Diene–Phosphonous Dihalide Cycloadducts[1]

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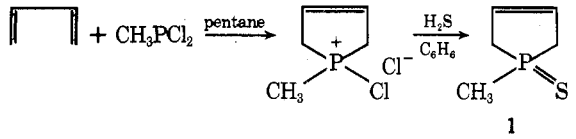
The cycloadduct (a 1-halophospholenium halide) from butadiene and methylphosphonous dichloride reacts smoothly with hydrogen sulfide to form 1-methyl-3-phospholene sulfide, rearrangeable with base (in part) or acid (complete) to the isomeric 2-phospholene sulfide. The chloroprene cycloadduct treated with H_2S gave exclusively the 2-phospholene sulfide; the chlorine was replaceable by methoxide ion to form the enol ether, which was easily hydrolyzed to 1-methyl-3-phospholanone sulfide. The piperylene cycloadduct gave exclusively *cis*-1,2-dimethyl-3-phospholene sulfide, and 1-vinylcyclohexene gave a single bicyclic phospholene sulfide shown spectroscopically also to have cis structure. Likewise, 1-(1-bromovinyl)cyclohexene gave a single sulfide stereoisomer, presumably cis. The hydrogen sulfide reaction therefore differs considerably from hydrolysis which gives variable mixtures of cis, trans isomers. ^{13}C NMR spectra of several sulfides were determined; notable is the strong deshielding of the 3 carbon of a 2-phospholene sulfide, possibly a result of delocalization of the π electrons into phosphorus d orbitals.

The McCormack cycloaddition[2] of dienes with trivalent phosphorus halides has provided the major pathway to derivatives of the phospholene ring system for many years. The cycloadducts are generally hydrolyzed to the more stable phosphine oxides as a preliminary step before performing other chemical transformations. McCormack mentioned in one of his patents[3] that phospholene sulfides were formed on addition of hydrogen sulfide to the cycloadducts, but only one example (from $C_6H_5PCl_2$ and isoprene) was given and the literature is devoid of any other mention of this reaction. We have previously examined the double bond[4] and cis, trans isomerism[5] in certain phospholene oxides formed from the McCormack adducts and now have applied our methods to the phospholene sulfides resulting from the hydrogen sulfide reaction. In working with the sulfides, we have found that they have much more desirable properties than the corresponding oxides. They are less polar, and accordingly have solubility in a more useful range of organic solvents. Furthermore, they are nonhygroscopic, and are quite easy to handle. The phospholene sulfides have also recently been approached by another route,[6] the reaction of McCormack-derived phospholene oxides with phosphorus pentasulfide.

The butadiene–methylphosphonous dichloride adduct, as a slurry in benzene, reacted smoothly with gaseous hydrogen sulfide. A clear solution resulted when the reaction was complete. The solid sulfide (**1**) was recovered in 66% yield after recrystallization. The ^1H NMR spectrum agreed with that



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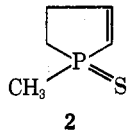
reported by Moedritzer;[6] it was very much like that of the oxide,[4] and left no doubt that the double bond was in the 3 position. Thus, the olefinic protons gave a 2 H doublet with the expected large coupling to ^{31}P (28 Hz). As for the hydrolysate of the same cycloadduct,[4] there was no indication of any 2-phospholene isomer in the reaction product.

The double bond of **1** could be rearranged by heating with potassium *tert*-butoxide. The product then consisted of a 1:1 mixture of **1** and 2-phospholene sulfide **2**. The oxide also is

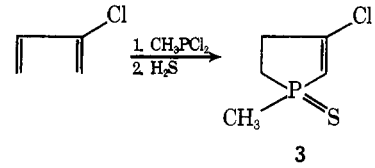


2

reported to give such a mixture with the same base.[6] However, heating **1** in 48% hydrogen bromide (in an unsuccessful attempt to add HBr to the double bond) gave virtually complete rearrangement to **2**.

^{13}C NMR spectra (Table I) of the isomers **1** and **2** reveal an important electronic effect of the thiophosphoryl group on the double bond; in the 2 isomer (**2**), the β-olefinic carbon is deshielded by 19.4 ppm relative to the α carbon. We believe that this is the first instance of the observation of this strong ^{13}C effect for a vinyl phosphine sulfide. The effect is only slightly weaker than that in the corresponding phospholene oxide (23.8 ppm, Table I), and, as pointed out elsewhere,[7] is consistent with diminished electron density on this carbon through delocalization of the π electrons into a phosphorus d orbital. The strong deshielding of all α carbons, as expected from the behavior of noncyclic phosphine sulfides,[8] was observed. The large ^{31}P–^{13}C coupling constants for the α carbons aided greatly in all assignments made in this study.

The chloroprene–methylphosphonous dichloride cycloadduct has given varying results on hydrolysis, but generally an isomer mixture rich in the 2-phospholene oxide is obtained.[9] The reaction of this cycloadduct with hydrogen sulfide has been found to be quite specific; *only* the 2 isomer (**3**)



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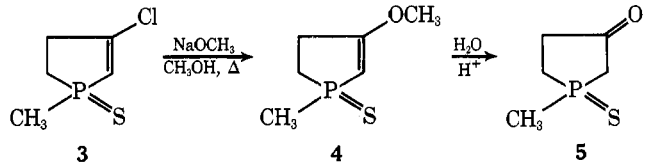
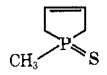
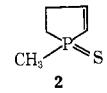
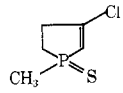
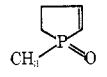
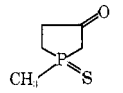
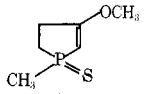
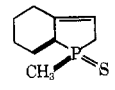
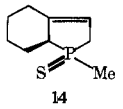
was formed. Again the ^1H NMR spectrum resembled that of the corresponding oxide; the methylene protons had well-separated chemical shifts, and the olefinic proton had weak allylic coupling to the methylenes at C-4, thus appearing as a doublet ($^2J_{PC}$ = 22 Hz) of triplets ($^4J_{HH}$ = 2 Hz).

A valuable property of the 3-chloro-2-phospholene oxide system has been the sensitivity of the chlorine to displacement by methoxide; this provides an enol ether readily hydrolyzed to the 3-keto phospholane oxide.[9] The low electron density of the 3 position of a 2-phospholene sulfide as revealed by the ^{13}C NMR spectrum of **2** suggested that chlorine at this position might be displaceable as it is in the oxide, and this proved to be the case. The enol ether **4** was so obtained and was readily hydrolyzed to the ketone **5**. Spectral examination of



3 **4** **5**

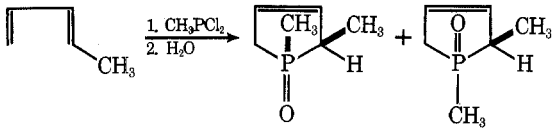
Table I. ^{13}C NMR Spectral Data of Some Phospholene Sulfides[a]

Compd	C-2	C-3	C-4	C-5	PCH_3
 1	38.9 (55)	127.6 (10)	127.6 (10)	38.9 (55)	20.6 (50)
 2	127.9 (75)	147.3 (20)	31.6 (13)	30.3 (45)	22.8 (50)
 3	123.4 (75)	150.0 (40)	36.8 (s)	31.9 (55)	23.7 (50)
	126.9 (92)	150.6 (25)	29.5 (10)	24.5 (68)	17.4 (68)
 5	45.4 (55)	207.4 (15)	37.7 (8)	30.6 (50)	20.4 (52)
 4	91.2 (92)	171.6 (40)[b]	30.4 (s)	29.9 (60)	25.0 (50)
 15	37.6 (55)	117.0 (5)	142.9 (10)	49.5 (55)	16.3 (50)
 14	38.6 (54)	115.2 (5)	143.5 (10)	45.0 (58)	20.9 (49)

[a] Chemical shifts in parts per million downfield from external Me_4Si. Values in parentheses are $^{31}P-^{13}C$ coupling constants in hertz. [b] OCH_3 signal at 57.8 (s).

5 showed the absence of detectable amounts of the enol. This is a marked departure from the corresponding oxide, where substantial amounts of enol form are present.[9] It is probable that the greatly reduced hydrogen-bonding ability of sulfur vs. oxygen is largely responsible for this difference; this property has been proposed as an important stabilizing effect in the keto oxide.[9]

The cycloadduct from piperylene on hydrolysis is known to give the 3-phospholene system but as a mixture of cis (6) and trans (7) isomers.[5] When this cycloadduct was treated



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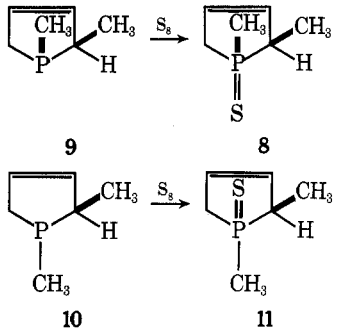
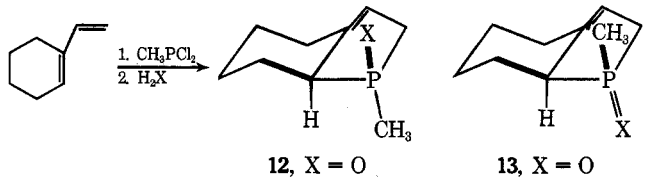
with hydrogen sulfide in the usual way, the product (8) consisted of *only one* stereoisomer; there was no detectable amount of the other isomer by either ^1H or ^{31}P NMR spectroscopy. That sulfide 8 was a 3-phospholene of cis structure was easily established by comparing it to the sulfides formed stereospecifically (retention[10]) on addition of sulfur to the corresponding isomeric phosphines 9 and 10. These had been separated and characterized in previous work.[5] The phosphine known to have the cis structure (9) gave a sulfide identical with 8, while the trans phosphine 10 gave a sulfide (11) of quite different properties.



9 8

10 11

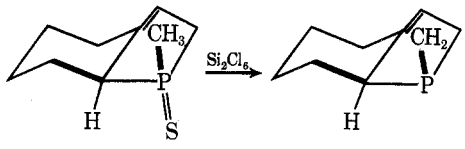
The remarkable stereospecificity of the hydrogen sulfide reaction was observed in another case, that of the cycloadduct from 1-vinylcyclohexene.[11] Again, trans (12) and cis (13) 3-phospholene isomers are possible from this reaction (and are observed in 2:3 ratio on hydrolysis), but only one sulfide isomer was obtained. The assignment of the position of the double bond was straightforward; there was only one olefinic proton in the NMR spectrum. It might be expected that the



12, X = O
14, X = S

13, X = O
15, X = S

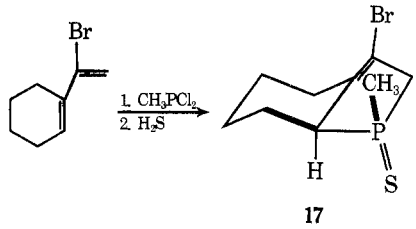
compound would have the cis structure **15**, by analogy to the steric result from the piperylene adduct. This was established by removing sulfur with hexachlorodisilane, a reaction known to occur with retention,[12] which produced a phosphine identical with that of cis structure (**16**). This structure has been



15 **16**

established in another study.[11] This proof was approached from the other direction as well; a trans-rich sample of the phosphine, also available from other work,[11] was treated with sulfur (retention) to form a mixture of sulfides **14** and **15**. The minor product (cis) of the reaction was identical with that obtained from the hydrogen sulfide reaction. Finally, the ^{13}C NMR spectrum (Table I) contained a feature indicative of the isomer structure; as for the oxides,[11] steric crowding in the cis isomer caused its PCH_3 signal to be displaced several parts per million upfield.

The stereospecificity of the hydrogen sulfide reaction was observed in another bicyclic synthesis, that of a 3-bromo derivative (**17**). The reaction product again consisted of a single



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isomer, to which we feel safe in assigning the cis structure from the previous results.

That only the cis isomer is formed in the hydrogen sulfide reaction is a point of significance with regard to the mechanism of nucleophilic displacement of halogen from the 1-halophospholenium ion. The result does not derive from any instability of the trans isomer in the acidic medium; this point was checked by bubbling H_2S and HCl through a benzene solution of **11** (trans) for 30 min, without effecting any conversion to cis isomer **8**. The only other nucleophilic displacement reaction for which data are available is that of hydrolysis, which can give mixtures dominated by either the cis[5,13] or trans[11] isomers. Even for the same cycloadduct, the experimental conditions play an important role in determining the cis:trans ratio.[5,13] From a recent observation[14] that the cis form of 1-phenyl-2,5-dimethyl-3-phospholene oxide rearranges to trans on standing, possibly through hydration to a pentacovalent dihydroxy form,[15] we suggest that the initially formed oxide on hydrolysis in general may be cis, and that rearrangement to the less crowded trans form occurs to whatever extent is allowed by the reaction conditions. Thus, we propose that the hydrogen sulfide and hydrolysis reactions may proceed by the same kinetically controlled steric pathway, but the product of the former is more indicative of this pathway since it is not prone to rearrange in the medium used.

The 1-halophospholenium ions can exist as cis or trans forms, but NMR spectral data have shown that these rapidly equilibrate through a pentacovalent dihalide.[5,13] The cis preference in sulfide formation would simply imply that one of the equilibrating isomeric halophospholenium ions reacts faster than the other. Whether it is the cis form, involving retention of configuration, or the trans, giving inversion, cannot be ascertained with the data so far at hand. Regardless of the exact steric course, the cis-product preference in this nucleophilic displacement of the cycloadducts now seems established, and the reaction joins two others of the cycloadducts for which a definite steric result can be expected: (1) dehalogenation to the phosphine with magnesium, which gives mostly the trans isomer,[5] and (2) conversion to the oxide with liquid sulfur dioxide, which gives only the cis product.[16]

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. All manipulations of phosphines were conducted under nitrogen in a glove bag. ^1H NMR spectra were taken with a JEOL MH-100 spectrometer; chemical shifts are relative to internal tetramethylsilane. ^{31}P NMR spectra were obtained on a Bruker HFX-10 system at 36.43 MHz with proton noise decoupling; chemical shifts are referenced to 85% H_3PO_4, with positive shifts upfield, negative downfield. Proton noise-decoupled Fourier transform ^{13}C NMR spectra (Table I) were also obtained on the Bruker spectrometer, at 22.62 MHz, utilizing C_6F_6 in a 3-mm coaxial capillary as an external heteronuclear lock. Chemical shifts are given in parts per million downfield from Me_4Si as zero. Methylphosphonous dichloride was obtained from the Ethyl Corp. Elemental analyses were performed by commercial laboratories.

1-Methyl-3-phospholene 1-Sulfide (1). The cycloadduct (50 g, 0.29 mol) prepared from 1,3-butadiene and methylphosphonous dichloride[4] was washed thoroughly with petroleum ether and suspended in 200 ml of dry benzene. Hydrogen sulfide gas was then bubbled through the stirred suspension until a clear solution resulted (about 45 min). The solution was washed with 200 ml of saturated $NaHCO_3$ solution and then 200 ml of water. The benzene solution was dried ($MgSO_4$) and concentrated on the rotary evaporator. The residual gummy solid was recrystallized from cyclohexane to give 25.1 g of **1** (66%) as colorless plates: mp 45–47 °C (lit.[6] mp 46 °C); ^1H NMR ($CDCl_3$) δ 1.82 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 2.76 (d, $^2J_{PH}$ = 10 Hz, $-CH_2-$), 5.87 (d, $^3J_{PH}$ = 28 Hz, $=CH-$); ir (Nujol) 1620 cm^{-1} (C=C); ^{31}P NMR (25% in $CDCl_3$) δ −54.8 (lit.[6] for the same concentration run proton coupled, −52.3).

Anal. Calcd for C_5H_9PS: C, 45.45; H, 6.82; P, 23.48. Found: C, 45.50; H, 6.98; P, 23.34.

1-Methyl-2-phospholene 1-Sulfide (2). A mixture of 1 g (75 mmol) of **1** and 25 ml of 48% HBr was refluxed under N_2 for 8 h. The mixture was neutralized and extracted with chloroform (5 × 75 ml). The organic extracts were combined, dried ($MgSO_4$), and concentrated. Analysis by ^{31}P NMR spectroscopy showed the phospholene oxide composition to be 95% **2**, 5% **1**. Thick layer chromatography on silica gel with ether–petroleum ether (1:1) as eluent gave 0.49 g of pure **2** (49%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.93 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 2.10–2.65 (m, PCH_2CH_2), 2.75–3.15 (m, PCH_2), 6.08–7.28 (complex m, olefinic H); ir (neat) 1600 cm^{-1} (C=C); ^{31}P NMR (25% in $CDCl_3$) δ −65.5 (lit.[6] for the same concentration run proton coupled, −62.5).

Compound **2** also resulted from base-catalyzed rearrangement. To a mixture of 1 g (75 mmol) of **1** in 50 ml of benzene was added 1 g of potassium *tert*-butoxide. The resulting mixture was refluxed for 24 h. The benzene was washed with water (2 × 50 ml), dried ($MgSO_4$), and concentrated to give 0.7 g of a 50:50 mixture of **1** and **2** as determined from the two PCH_3 doublets (δ 1.85 and 1.95, respectively).

3-Chloro-1-methyl-2-phospholene 1-Sulfide (3). The cycloadduct (67 g, 0.33 mol) prepared from methylphosphonous dichloride and chloroprene[9] was washed with petroleum ether and suspended in 250 ml of dry benzene. Hydrogen sulfide was then bubbled through the suspension until all solid had dissolved (2 h). The benzene was washed with 200 ml of saturated $NaHCO_3$ solution and then 200 ml of water. The benzene solution was dried ($MgSO_4$) and concentrated. The resulting solid was recrystallized from ethanol to give 27.1 g of **3** (49%) as white needles: mp 68–69 °C; ^1H NMR ($CDCl_3$) δ 1.91 (d, $^2J_{PH}$ = 14 Hz, PCH_3), 2.22–2.63 (m, PCH_2CH_2), 2.83–3.20 (m, PCH_2), 6.15 (d of t, $^2J_{PH}$ = 22, $^4J_{HH}$ = 1.5 Hz, >C=CH–); ir (Nujol) 1610 cm^{-1} (C=C); ^{31}P NMR ($CDCl_3$) δ −58.5.

Anal. Calcd for C_5H_8ClPS: C, 36.04; H, 4.80; P, 18.57. Found: C, 36.03; H, 4.89; P, 18.57.

1-Methyl-3-methoxy-2-phospholene 1-Sulfide (4). To a stirred solution of sodium methoxide prepared from 1.27 g (0.055 g-atom) of sodium and 75 ml of methanol was added 8.6 g (0.05 mol) of chloride **3** in 75 ml of methanol. The resulting solution was refluxed for 15 h. The solution was cooled and neutralized with concentrated hydrochloric acid. The NaCl was filtered off and the solution was concentrated on the rotary evaporator. The residual oil was distilled to give 3.8 g of **4** (47%): bp 118–120 °C (0.3 mm); ^1H NMR ($CDCl_3$) δ 1.85 (d,

$^2J_{PH}$ = 12 Hz, PCH_3), 2.00–3.35 (m, 4, methylenes), 3.65 (s, OCH_3), 4.88 (d, $^2J_{PH}$ = 25 Hz, =CH); ir (neat) 1601 cm^{-1} (C=C); ^{31}P NMR ($CDCl_3$) δ −58.7.

1-Methyl-3-phospholanone 1-Sulfide (5). To a mixture of 2 g (12 mmol) of enol ether **4** in 5 ml of water was added 6 drops of 3 N HCl. The stirred mixture was heated at 115 °C for 3.5 h under N_2. The solution was then cooled in ice and the resulting precipitate was filtered off. Sublimation of this solid at 50 °C (0.01 mm) gave 1 g of **5** (57%) as a white powder: mp 80–81 °C; ^1H NMR ($CDCl_3$) δ 1.89 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 2.20–2.98 (m, 4, methylenes); ir (CCl_4) 1720 cm^{-1} (C=O); ^{31}P NMR ($CDCl_3$) −42.4.

Anal. Calcd for C_5H_9OPS: C, 40.54; H, 6.08; P, 20.95. Found: C, 40.74; H, 6.15; P, 20.87.

***cis*-1,2-Dimethyl-3-phospholene 1-Sulfide (8).** The cycloadduct (40 g, 0.22 mol) prepared from methylphosphonous dichloride and *trans*-piperylene was washed with petroleum ether and suspended in 200 ml of dry benzene. Hydrogen sulfide was bubbled through the stirred mixture until all solid dissolved (about 1 h). The benzene was then washed with 200 ml of saturated $NaHCO_3$ solution followed by 200 ml of water. The benzene was dried ($MgSO_4$) and concentrated. The residual solid was recrystallized from ethanol to give 12.5 g of **8** (39%) as white needles: mp 50–51 °C; ^1H NMR ($CDCl_3$) 1.24 (d of d, $^3J_{PH}$ = 18, $^3J_{HH}$ = 7 Hz, C–CH_3), 1.61 (d, $^2J_{PH}$ = 12 Hz), 2.65–3.20 (m, CH_2 and CH), 5.80 (d, $^3J_{PH}$ = 26 Hz, =CH); ir (Nujol) 1615 cm^{-1} (C=C); ^{31}P NMR ($CDCl_3$) δ −63.4.

Anal. Calcd for $C_6H_{11}PS$: C, 49.32; H, 7.53; P, 21.23. Found: C, 49.51; H, 7.70; P, 21.20.

Reaction of the 1,2-Dimethyl-3-phospholenes 9 and 10 with Sulfur. To a solution of 500 mg (4.4 mmol) of the cis isomer (**9**) in 50 ml of dry benzene was added 500 mg of sulfur. The mixture was refluxed for 8 h. The excess sulfur was filtered off and the benzene removed on the rotary evaporator. The residue was recrystallized from ethanol to give 450 mg of **8** (70%), mp 49–50 °C; the ^1H and ^{31}P NMR and the ir spectra were identical with those reported above for compound **8**.

The trans phosphine **10** was treated with sulfur in the same way and gave a different sulfide **11**, mp 42–43 °C, ^{31}P NMR ($CDCl_3$) δ −60.8.

***cis*-1-Methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1*H*-phosphindole 1-Sulfide (15).** The cycloadduct (20 g, 0.08 mol) prepared from 1-vinylcyclohexene[11] and methylphosphonous dichloride was washed with petroleum ether and suspended in 150 ml of benzene. Hydrogen sulfide was bubbled through the stirred suspension for 1 h. The clear benzene solution was washed with saturated $NaHCO_3$ solution (200 ml) and water (200 ml). The benzene was dried ($MgSO_4$) and concentrated to an oil that solidified on cooling. Recrystallization from cyclohexane gave 7.8 g of **15** (46%) as white needles: mp 78–80 °C; ^1H NMR ($CDCl_3$) δ 1.65 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 1.2–2.9 (m, CH_2 and CH), 5.42 (d, $^3J_{PH}$ = 29 Hz, =CH); ir (Nujol) 1630 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ −59.9.

Anal. Calcd for $C_9H_{15}PS$: C, 58.06; H, 8.06; P, 16.67. Found: C, 57.87; H, 8.04; P, 16.86.

***cis*-1-Methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1*H*-phosphindole (16).** To a solution of 600 mg (3.2 mmol) of **15** in 50 ml of dry benzene was added 3 ml (56 mmol) of hexachlorodisilane over a 30-min period. The solution was then refluxed for 4 h. The flask was cooled and 15 ml of 30% NaOH solution was added. The layers were separated and the aqueous layer was extracted with benzene (3 × 25 ml). The benzene was dried ($MgSO_4$) and distilled at atmospheric pressure. The residue was distilled at reduced pressure to give 250 mg of **16** (50%) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.65 (d, $^2J_{PH}$ = 4 Hz, PCH_3), 0.90–2.65 (m, CH_2 and CH), 5.22 (broad s, =CH); ^{31}P NMR ($CDCl_3$) δ +26.1.

The methiodide was prepared from a small portion of the phosphine by reaction with excess methyl iodide. Recrystallization from ether–methanol gave white crystals, mp 273 °C dec.

Anal. Calcd for $C_{10}H_{18}IP$: C, 40.54; H, 6.08; P, 10.47. Found: C, 40.65; H, 6.13; P, 10.32.

***cis,trans*-1-Methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1*H*-phosphindole 1-Sulfide.** To 1 g (6.5 mmol) of a mixture of *cis*- (40%) and *trans*- (60%) 1-methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1*H*-phosphindoles (prepared by the trichlorosilane reduction of the corresponding oxides)[11] dissolved in 25 ml of benzene was added 1 g of sulfur. The resulting solution was refluxed for 12 h. The excess sulfur was filtered off and the benzene was evaporated. The remaining oil solidified and was recrystallized from ethanol to give 680 mg of a mixture of **14** and **15** (56%) as white needles: mp 74–77 °C; ^1H NMR ($CDCl_3$) δ 1.65 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 1.73 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.2–2.9 (m, CH_2 and CH), 5.38 (d, $^2J_{PH}$ = 29 Hz, =CH–); ir (Nujol) 1625 cm^{-1} (C=C); ^{31}P NMR ($CDCl_3$) δ −58.0 (**14**, 65%) and −59.8 (**15**, 35%).

Anal. Calcd for $C_9H_{15}PS$: C, 58.06; H, 8.06; P, 16.67. Found: C, 58.03; H, 8.24; P, 16.40.

3-Bromo-1-methyl-$\Delta^{3(3a)}$-2,4,5,6,7,7a-hexahydro-1*H*-phosphindole 1-Sulfide (17). The cycloadduct (25 g, 81.9 mmol) prepared from 1-(1-bromovinyl)-1-cyclohexene[17] and methylphosphonous dichloride was washed with petroleum ether and suspended in 100 ml of dry benzene. Hydrogen sulfide was bubbled through the stirred suspension for 30 min. The resulting clear solution was then washed with saturated $NaHCO_3$ solution and water (200 ml). The benzene was dried ($MgSO_4$) and concentrated. The gummy residue was recrystallized from ethanol to give 8.3 g of **17** (38%) as white crystals: mp 126–128 °C; ^1H NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.1–3.15 (m, CH_2 and CH); ir (KBr) 1620 cm^{-1} (C=C); ^{31}P NMR ($CDCl_3$) δ −51.4.

Anal. Calcd for $C_9H_{14}BrPS$: C, 40.91; H, 4.92; P, 11.74. Found: C, 40.79; H, 5.15; P, 11.83.

Registry No.—**1**, 52988-60-0; **2**, 52988-61-1; **3**, 58311-81-2; **4**, 58311-82-3; **5**, 58311-83-4; **8**, 58311-84-5; **9**, 2329-12-6; **10**, 2329-00-2; **11**, 58311-85-6; **14**, 58311-86-7; **15**, 58311-87-8; *cis*-**16**, 57065-71-1; **16** methiodide, 57065-73-3; *trans*-**16**, 57065-72-2; **17**, 58311-88-9; 1,3-butadiene, 106-99-0; methylphosphonous dichloride, 676-83-5; chloroprene, 126-99-8; *trans*-piperylene, 2004-70-8; 1-vinylcyclohexene, 2622-21-1; methyl iodide, 74-88-4; 1-(1-bromovinyl)-1-cyclohexene, 57065-75-5.

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