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(8) This name is proposed to describe the symmetry of a shape which is chiral but asymmetric; cf. M. Nakazaki, K. Naemura, and H. Yoshihara, *Bull. Chem. Soc. Jpn.*, **48**, 3278 (1975).
(9) In this paper, ketones are conveniently classified according to their symmetry. C_s-ketones belong to the C_s point group and have the plane of symmetry coincident with the carbonyl plane; C_2-ketones belong to the C_2 point group and have the C_2 axis coincident with the carbonyl axis; and C_1-ketones have no symmetry element passing through the carbonyl axis.
(10) The axial and equatorial notations of hydroxyl groups in **10** and **11**, respectively, were given by Gschwend.[11]
(11) H. W. Gschwend, *J. Am. Chem. Soc.*, **94**, 8430 (1972).
(12) In order to minimize errors due to optical fractionation on repeated recrystallization, the optical purities and rotations cited in this paper are mostly for specimens purified by sublimation in vacuo.
(13) Based on their absolute values to be discussed in the subsequent section.
(14) K. Mislow, M. Brzechffa, H. W. Gschwend, and R. T. Puckett, *J. Am. Chem. Soc.*, **95**, 621 (1973).
(15) The reported facile racemization[11] ($t_{1/2}$ = 47.4 h at 25 °C) of the ketone **9** may be responsible for this rather low optical rotation.
(16) In meso diketone **12**, one of the enantiomeric ketone groups which leads to a *pR* compound when considered to be preferred to the other is termed *pro-pR* and the other termed *pro-pS*, as analogized to central prochiral compounds.[17,18]
(17) IUPAC tentative rules for the nomenclature of organic chemistry, Section E, *J. Org. Chem.*, **35**, 2849 (1970).
(18) K. R. Hanson, *J. Am. Chem. Soc.*, **88**, 2731 (1966).
(19) The axial-equatorial, axial-axial, and equatorial-equatorial notations of hydroxyl groups in **14**, **17**, and **19**, respectively, were given by Lehner et al.[20]
(20) C. Glotzmann, E. Haslinger, E. Langer, and H. Lehner, *Monatsh. Chem.*, **106**, 187 (1975).
(21) See Experimental Section.
(22) Calculated from the absolute rotation, $[\alpha]_D$ +25°, estimated by Schlögl et al.[23]
(23) B. Kainradl, E. Langer, H. Lehner, and K. Schlögl, *Justus Liebigs Ann. Chem.*, **766**, 16 (1972).
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(27) Eu(facam)$_3$ = tris(3-trifluoroacetyl-*d*-camphorato)europium(III).
(28) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 1038 (1974).
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Synthesis of the Phosphasteroid System and of Potential Tricyclic Precursors by the McCormack Cycloaddition Method[1]

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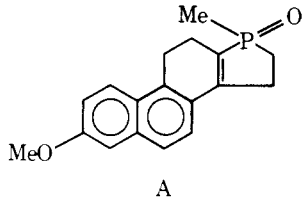
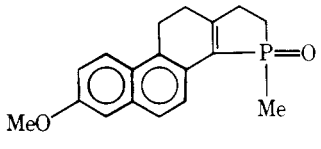
Received September 8, 1978

Cycloaddition of the diene 3,4-dihydro-7-methoxy-1-vinylphenanthrene and CH_3PCl_2 proceeded in good yield to give, after hydrolysis, a derivative with the tetracyclic steroid system containing phosphorus at the 17 position (A). The isomeric 2-vinyl compound also gave a tetracyclic derivative (a 15-phosphasteroid, B), but less readily. Hydrogenation of the remaining double bond in the 17-phosphasteroid was shown by ^{13}C and ^{31}P NMR spectral studies to proceed with high stereoselectivity, hydrogen entering cis with regard to the P-CH_3 group. Similar specificity was observed in the hydrogenation of the tricyclic phospholene oxides prepared in like manner from the 1- and 2-vinyl derivatives of 3,4-dihydro-6-methoxynaphthalene. These hydrogenated tricyclic compounds underwent smooth Birch reduction with lithium in a liquid NH_3–*tert*-butyl alcohol medium, giving enol ethers that were easily converted to ketones (nonconjugated) with an oxalic acid solution. The phosphoryl group was not attacked in the Birch reduction, although the same conditions applied to a related tricyclic phospholene sulfide cleanly removed sulfur to form a phosphine. The styrenoid double bond is also reduced when it is present in the tricyclic compounds.

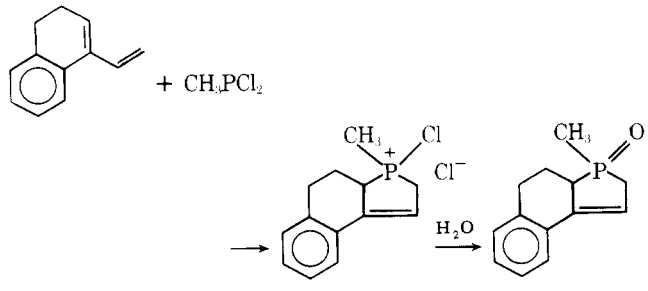


A



B

We recently showed[2] that 1-vinylcyclohexenes participate readily in the McCormack cycloaddition[3] with phosphorus(III) halides, making available a number of new bicyclic phosphorus compounds. An example of formation of a tricyclic phospholene oxide from a benzo derivative of the cyclohexene was included in this study. We recognized in this reaction the potential for producing compounds with the tetracyclic steroid system, of necessity having phosphorus in the D ring. Two approaches to such compounds were visualized: an ABC → ABCD route applying the cycloaddition to an appropriate naphthocyclohexene, and a BC → BCD → ABCD route, wherein a benzocyclohexene derivative (BC) would be used in the cycloaddition to form the tricyclic BCD structure, followed by annelation at ring B. These potential methods are illustrated in Scheme I for the synthesis of 17-phosphaster-



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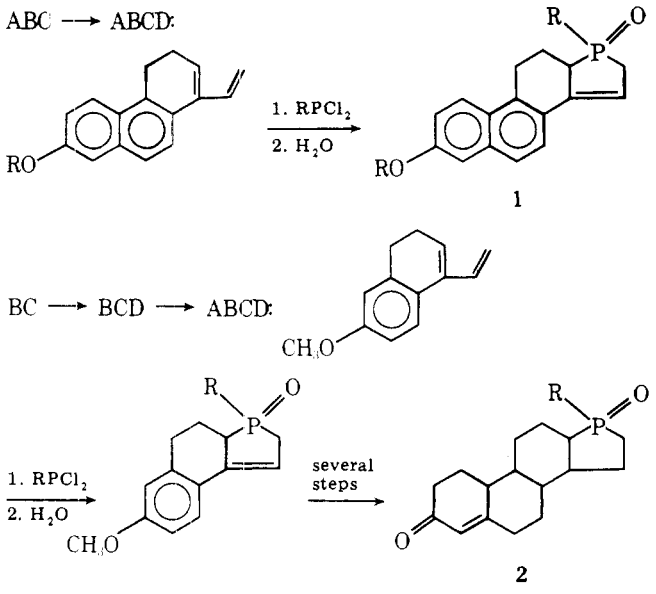
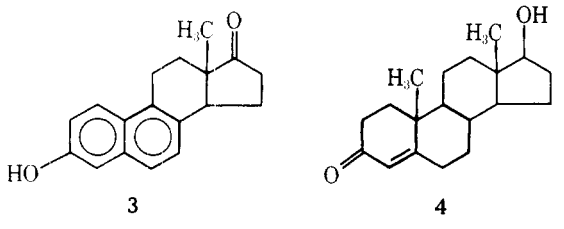
Scheme I



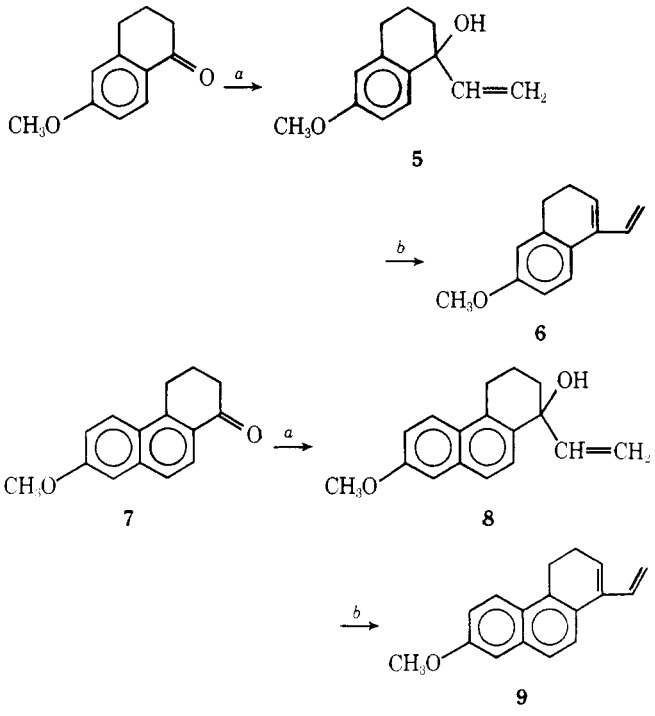
oids; the methods are also capable of forming the 15-phospha compounds as will be seen. The two methods would lead to quite different functionality in the A and B rings; the first method would give phosphasteroids (**1**) resembling the equilenin type (**3**), while the product (**2**) of the second method



would resemble the nonaromatic hormones, such as testosterone (**4**). Important differences would exist (e.g., the absence of angular methyl groups and uncertain stereochemistry of ring fusions), but the strong similarities to highly potent steroids provide ample motivation for the demonstration of these synthetic proposals, following which attention to structural detail could occur. Examples of phosphasteroids can be found in recent literature,[4] including cases where phosphorus is present in the D ring,[4b,c,e] but none are as close in resemblance to the natural steroids as those proposed here. No biological data have been reported for the members of this family.

In this paper, we report in detail[5] the accomplishment of the ABC → ABCD route. As a preliminary to this work, certain synthetic operations were perfected with the much more readily available tricyclic compounds. This has provided useful information relevant to the BC → BCD sequence, and is included in this paper. With these BCD substances in hand, it was possible to explore the feasibility of their conversion to forms potentially capable of undergoing conventional annelation reactions to develop phosphasteroids of type **2**. This work, which employs Birch reduction and formation of tricyclic ketones, is also reported here. The chirality of phosphorus increases the magnitude of the stereochemical problem, but relations developed in earlier[2] ^{13}C and ^{31}P NMR studies proved to be a great help in determining many of the stereochemical features of the various products.

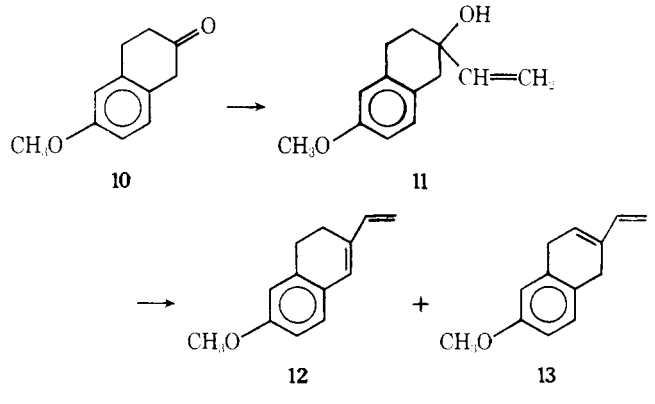
Synthesis of Dienes. One of the features of our earlier work on 1-vinylcycloalkenes[2] as participants in the McCormack reaction was their ease of preparation from the cycloalkanone by addition of vinylmagnesium bromide followed by dehydration of the alcohol. The method can be applied to α-tetralones as well,[2] and from 6-methoxy-α-tetralone, diene **6**[6] was prepared in 91% yield for service as the BC fragment in



[a] CH_2=CHMgBr in THF, then NH_4Cl. [b] I_2 and quinoline in benzene, Δ.

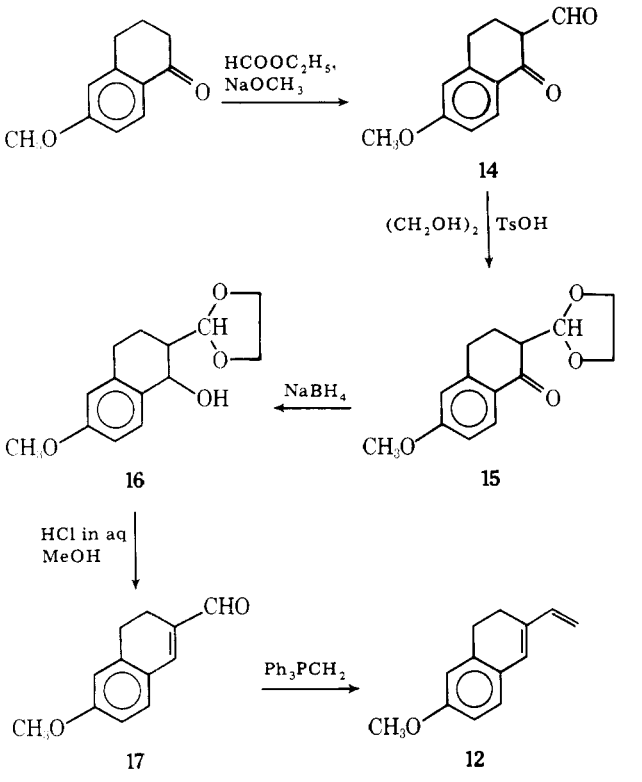
a synthesis of a 17-phosphasteroid **2**. The method was also applied to the corresponding tetrahydrophenanthrene derivative (**7**, commonly known as Butenandt's ketone and synthesized in four steps from 6-methoxy-α-tetralone[7]), giving diene (**9**) in 80% crude yield. Both alcohol dehydrations were conveniently accomplished by the iodine–quinoline method in benzene with azeotropic water removal.

For the construction of the dienes needed for 15-phosphasteroids, the above methods would have to be applied to the corresponding β-keto derivatives. However, β-tetralones are well-known to perform poorly in Grignard additions, giving considerable amounts of the enolate. We confirmed the existence of this difficulty for the combination of 6-methoxy-β-tetralone (**10**) and vinylmagnesium bromide; about a third of the ketone was converted to the enolate and was recovered unchanged after the hydrolysis. This necessitated a separation step based on the formation of the sodium bisulfite addition product of the ketone. While this method worked satisfactorily and provided the alcohol **11** in good purity, difficulties encountered in the dehydration step caused its abandonment. Dehydration by the iodine–quinoline method failed, and the $POCl_3$–pyridine method[8] gave a product (45%) consisting of the isomeric dienes **12** and **13**.



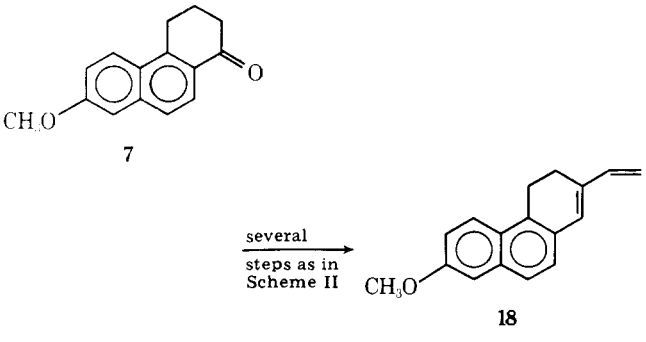
While the desired diene **12** constituted 65% of the mixture, it was not easily isolated in pure form. Since it was anticipated

Scheme II

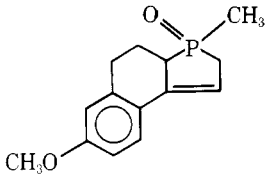


that the dihydrophenanthrene derivative would give similar poor results in a synthesis of 1, a new method (Scheme II) for the synthesis of diene **12** and its tricyclic counterpart was devised. Formylation of 6-methoxy-α-tetralone gave the previously reported[9] aldehyde **14** (largely enolic) which underwent specific reaction with ethylene glycol at the aldehyde carbonyl. Following procedures for related syntheses,[10] the keto carbonyl of **15** could then be reduced to the alcohol (**16**), which on heating in an acidic medium underwent dehydration and acetal hydrolysis simultaneously, forming the new aldehyde **17**. The aldehyde gave the desired diene **12** by the Wittig method. Except for this last step (65% yield), all yields exceeded 85%, and each product was obtainable in good purity. The crude product of each step could be used to carry on the synthesis, delaying purification (distillation) until the diene was reached. The synthesis is quite practical, starting as it does with a commercially available ketone.

The reactions of Scheme II were then applied to Butenandt's ketone **7**, with similar success and yields. The final product **18** was a crystalline solid, purified by chromatography on alumina.



Synthesis of Tricyclic Phospholene Oxides and Sulfides. McCormack cycloadditions are normally performed in a hydrocarbon solvent at room temperature and the precipitated cycloadduct is then collected for hydrolysis to the phospholene oxide. This procedure was applied successfully to diene **6**; the standing period was terminated after 1 week, and a 53% yield of oxide **19** was obtained when the hydrolysis was performed in a cold excess water–ice mixture. Without control of the heat of hydrolysis, the highly acidic medium caused rearrangement of the double bond, providing **20** in comparable yield. This rearrangement also occurred on per-



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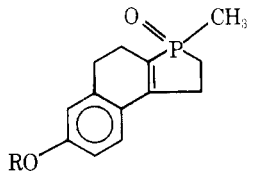
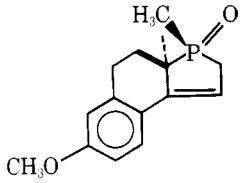
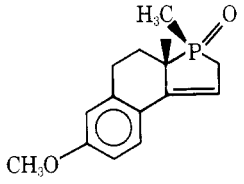


20, R = CH_3
21, R = H

forming cleavage of the methoxy group of **19** by refluxing 48% HBr; phenol **21** was so obtained (65%). The occurrence of the rearrangement is easily recognized by the loss of the olefinic proton of **19**, which appears clearly in the ^1H NMR spectrum at δ 6.07 as a doublet ($^3J_{PH}$ = 26 Hz). The unrearranged compound **19** is capable of existence in cis (**19a**) and trans (**19b**) forms, and these are indicated to be present by two



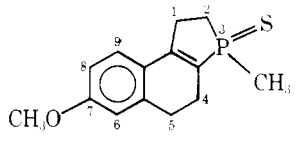
19a (cis)



19b (trans)

signals in the ^{31}P NMR spectrum [δ +62.5 (10%), +70.5 (90%)]. The stereochemical result from cycloadduct hydrolysis is variable and dependent on reaction conditions.[2,11] In this case, the cis isomer predominates since the relation has been established that the cis structure has the more downfield ^{31}P shift.[2]

When the cycloadduct from diene **6** was suspended in benzene and treated with hydrogen sulfide,[11] the phospholene sulfide with rearranged double bond (**22**) was obtained. The

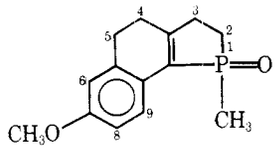


22

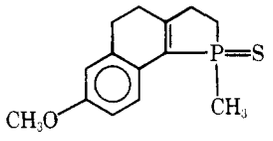
release of both heat and HCl in this process accounts for the ease of rearrangement. Along with other spectral data, the ^{13}C NMR spectrum was obtained for this compound and is discussed here to illustrate the basis for spectral assignments for other members of the tricyclic series. The proper numbering is shown on structure **22**. The aromatic carbons were easily assigned since the CH_3O group strongly deshields the carbon of attachment (δ 159.5) and shields the two ortho carbons (C-8, δ 110.2; C-6, δ 113.3, deshielded by C-5). Of the three remaining carbons, C-9 is recognized by its intensity, while the fusion carbons can be distinguished by the stronger three-bond coupling to ^{31}P at 9a (12 Hz; this is consistent with values for other phosphine sulfides where a dihedral angle approaching 180° is present[12]) than at 5a (four-bond, 3 Hz). The olefinic carbon signals are also readily assigned; both are coupled to ^{31}P, with the α carbon having the expected large value (δ 127.0, 80 Hz) while the β carbon is strongly deshielded relative to the α carbon (δ 145.8, 28 Hz). Large one-bond coupling to ^{31}P also allowed easy recognition of P-CH_3 (50 Hz) and of C-2 (50 Hz). In 1-methyl-2-phospholene sulfide,[11] the carbon corresponding to C-1 of **22** occurs at δ 31.6 (J = 13 Hz) and γ shielding by C-9 of **22** apparently accounts for a small upfield shift to δ 27.0 (or δ 27.2). In the central ring, C-4 is

shielded (δ 18.3, J = 18 Hz) by γ interactions with the phosphorus substituents, leaving a quite reasonable δ 27.2 (or δ 27.0) for C-5. The spectrum of the related oxide **20** (see Experimental Section) was interpreted along similar lines that are discussed more fully elsewhere,[13] where additional derivatives of this ring system are described.

When diene **12** was subjected to the usual cycloaddition conditions, the reaction was quite slow; the adduct collected after 19 days at room temperature gave on hydrolysis in water–ice only a 37% yield of phospholene oxide (**23**). That the



23

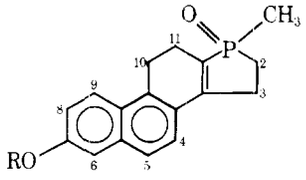


24

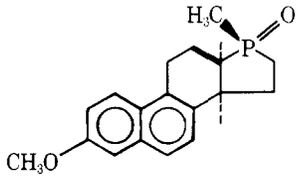
double bond had rearranged was evident from the absence of an olefinic proton signal; this was fully confirmed by the ^{13}C NMR spectrum, which clearly showed the double bond in conjugation with phosphoryl. The cycloaddition was then attempted at 60 °C, and after 6 days a yield of **23** of 60% was obtained. The same rate difference between the tricyclic dienes **9** and **18** was later observed and will receive comment in the following section. The phospholene sulfide was also prepared by H_2S treatment of the cycloadduct and similarly shown to have the rearranged structure (**24**).

Synthesis of Tetracyclic Phospholene Oxides. Tricyclic diene **9** responded very well to room temperature cyclization with CH_3PCl_2, and hydrolysis of the adduct formed after 1 week gave a 66% yield of phospholene oxide. The rearranged structure (**25**) was expected from the hydrolysis conditions (no base or temperature control), and ^1H and ^{13}C NMR confirmed this structure. Part of the aromatic region of the ^{13}C NMR spectrum was interpreted with the aid of assignments given[14] to 2-methyl-6-methoxynaphthalene as a model. The crowding of C-11 in ring C by the phosphorus substituents, as in the tricyclic compounds, led to its ready recognition at δ 19.3. Notable also is the effect of the second benzo ring on the sp^3 carbon attached to the aromatic system (C-10, δ 22.9); this signal is shifted upfield by several parts per million, presumably as a consequence of crowding with aromatic C-9.

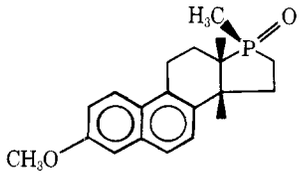
This phosphasteroid, unlike its tricyclic counterparts, proved to have very low water solubility and a quite high melting point (205 °C dec). The methoxy group was easily cleaved by refluxing HBr, forming naphthol **26** in 71% yield.



25, R = CH_3
26, R = H



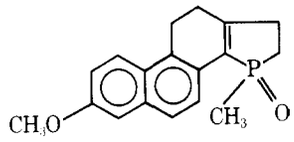
27a (CH_3 cis)



27b (CH_3 trans)

Catalytic hydrogenation also proceeded readily (atmospheric pressure with Pd–C), forming C/D-cis compound **27.** Two configurations are possible about phosphorus, with P-CH_3 cis (**27a**) or trans (**27b**) to the carbon of ring C. The isomers were present in a ratio of 84:16 based on ^{31}P NMR analysis (δ +67.7 and +71.8, respectively). The relation found[2] in monocyclic and bicyclic phospholene oxides would suggest that the more prominent upfield signal is caused by the trans isomer (**27b**). The ^{13}C signal of P-methyl is also a useful indicator of stereochemistry;[2] however, in the perhydrophosphindole 1-oxides, steric crowding in the isomer with P-CH_3 cis to ring C causes the signal to be substantially upfield of the trans (δ 13.7 vs. δ 17.3). The major isomer of **27** if truly trans should have its P-CH_3 signal matching the latter value, as it does (**27b**, δ 17.5). From this stereochemical assignment, it is seen that hydrogen was delivered to **25** primarily from the same face as methyl. This is consistent with the recent report[15] that a monocyclic 2-phospholene oxide (1-phenyl-3-methyl) is selectively hydrogenated from this face. However, such hydrogenations are not always selective; a roughly 1:1 mixture was formed on hydrogenation of a bicyclic 2-phospholene oxide.[2]

The 15-phosphasteroid system resulted when diene **18** was used in the McCormack cycloaddition with CH_3PCl_2. However, the reaction was quite slow; the adduct collected after 21 days at room temperature gave only a 21% yield of phospholene oxide **28.** An attempt to speed up the cycloaddition by running it in refluxing benzene gave mostly polymeric product, and did not improve the yield of **28.**

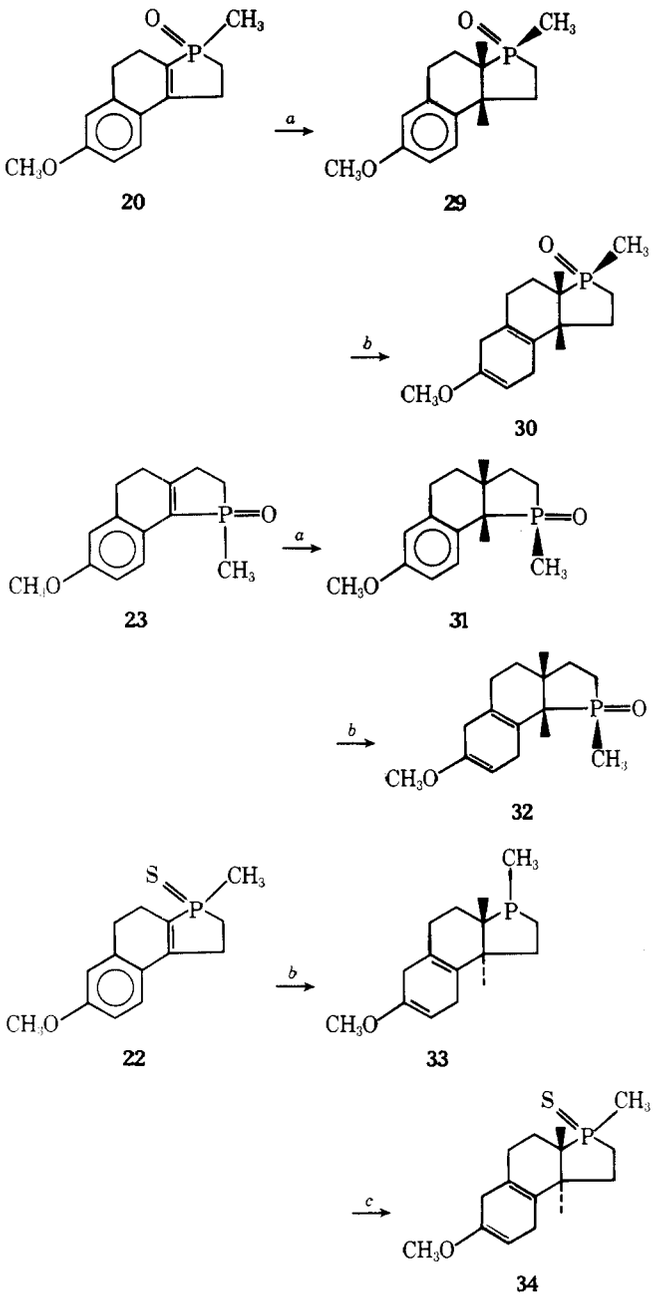


28

The relatively slow cycloaddition with dienes **12** and **18,** which have the diene unit linearly conjugated with the aromatic system, compared to cross-conjugated dienes **6** and **9** has a parallel in noncyclic systems; 1-phenylbutadiene is reported to cycloadd more slowly than the cross-conjugated 2-phenylbutadiene.[3] This difference in conjugation, and hence stability of the starting diene, may be the cause of the difference in rates. Alternative explanations do exist, however; an attractive one is the presence of a peri-like interaction between the ortho proton of the adjacent aromatic ring and the incoming phosphorus atom, which would be present for dienes **12** and **18** but not for the reactive **6** and **9.** In another view, the nature of the grouping around the internal double bond of the diene unit differs considerably in the two types of dienes, and steric effects may operate in **12** and **18** to raise the energy requirement for the bond rotation that accompanies this concerted process.

Birch Reductions of the Tricyclic Compounds. The Birch reduction conditions (adding lithium wire to the reactant dissolved in a liquid ammonia–alcohol medium[16]) are capable not only of accomplishing 1,4-hydrogen addition to an aromatic ether but also of reducing styrenoid double bonds. Before applying the process to the tricyclic phosphine oxides, we chose first to hyrogenate the styrenoid double bond, thus ensuring a definite geometry (cis) for the C/D fusion (the rings are lettered in steroid fashion to facilitate the discussion). For the 2-phospholene oxide **23,** the hydrogenation proceeded stereospecifically to give only one of the two possible dihydro derivatives, as was easily determined by ^1H, ^{13}C, and ^{31}P NMR determinations. For **20,** the ^{31}P NMR spectrum indicated one isomer to be formed in great predominance (95%). As has been noted for the similar reduction of tetracyclic phospholene oxide **25,** it is probable that hydrogen is delivered to the face

Scheme III



[a] H_2, Pd–C. [b] Li, NH_3–*t*-BuOH. [c] S_8.

bearing the *P*-CH_3 group, and the products from **23** and **20** seem tentatively representable by structures **31** and **29**, respectively (Scheme III). For **29**, this is supported by the observation that the ^{13}C NMR signal at δ 16.7 of the *P*-CH_3 group, which is a sensitive indicator of stereochemistry, appeared in the same region as seen for both the perhydrophosphindole 1-oxide isomer with trans *P*-CH_3 (δ 17.3) and the tetracyclic compound **27b** (δ 17.5). The ^{31}P NMR shift for **29** (δ +67.0) also agreed with the value of **27b** of δ +67.7. More complex results were obtained when 3-phospholene oxide **19** was used in this reaction; the starting material is a cis–trans mixture, and each isomer can be hydrogenated from either face. While an excellent yield was obtained from the hydrogenation, no attempt was made to analyze the mixture of diastereoisomers produced.

Birch reduction of the phospholane oxide derivatives **29** and **31** proceeded smoothly and gave the desired enol ethers **30** and **32**, respectively, in good purity. As expected,[16] the enol ethers had a nonconjugated diene unit from the 1,4-hydrogen addition. This was easily determined from their proton NMR spectra, which showed the presence of a single olefinic proton in the upfield region (δ 4.5–4.7) expected for a β hydrogen of an enol ether. Birch reduction of the mixture of diastereoisomeric phospholane oxides derived from the 3-phospholene oxide **19** also gave a high yield (81%) of a mixture of isomeric enol ethers. In none of the various reductions was any attack on the phosphoryl group noticed.

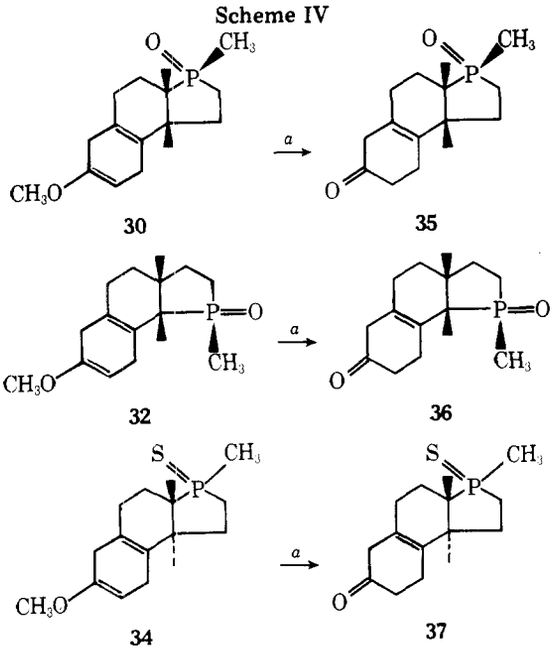
One attempt was made to reduce a phospholene oxide (**20**) directly, without prior hydrogenation. The results were much less satisfactory than when the corresponding phospholane oxide **29** was used; ^{31}P NMR analysis showed that a mixture consisting of three major components (δ +62.6, +63.5, and +69.2) and several minor components was obtained. The ^{13}C NMR spectrum showed unequivocally that reduction of the styrenoid double bond had accompanied the reduction of the benzene ring since the easily recognized doublets of the 2-phospholene oxide moiety were absent. The complexity of the mixture made its examination difficult, and its analysis remains incomplete. Two of the major components (probably diastereoisomers) appear to have the enol ether structure; prominent signals for both carbons of the enol ether double bond were present (α at δ 152.5 and 154.5, β at δ 90.1 and 91.4), and hydrolysis did give a largely ketonic product (discussed in the next section). Birch reduction of styrenoid double bonds usually results in trans geometry,[17] and none of the major ^{31}P NMR peaks matched that of the single isomer **30** with C/D cis (δ +66.6). However, this is not conclusive evidence for C/D trans since another (unavailable) diastereoisomer with C/D cis is also a structural possibility. The phospholene sulfide **22**, on the other hand, underwent smooth Birch reduction, and a single product was obtained in good yield. While this product had the expected enol ether structure, it was also clear from its spectral properties that not only had the styrenoid double bond been reduced, but also desulfurization had occurred, giving structure **33**. The product was easily restored to the sulfide form (**34**) by addition of sulfur. A single diastereoisomer was obtained from this series of reactions; while it is likely that C/D trans has resulted as is specified in structure **34**, no information is available at this time on the configuration at phsophorus and the complete stereochemical structure remains unknown.

The enol ethers showed some tendency to undergo rearomatization on standing. They were generally converted to the more stable ketones by acid hydrolysis soon after synthesis, as is discussed in the next section.

Tricyclic Ketones from Birch Reduction Products. Birch-type enol ethers can be hydrolyzed to ketones under conditions that will allow retention of the position of the double bond (oxalic acid in aqueous methanol) or that will give rearrangement to the α,β-unsaturated system (aqueous HCl).[18] We had uniform success with the former method when applied to the tricyclic phospholane derivatives; the new β,γ-unsaturated ketones **35**, **36**, and **37** were obtained in excellent purity by the oxalic acid hydrolysis of enol ethers **30**, **32**, and **34**, respectively (Scheme IV). The diastereoisomeric mixture of phospholane oxides derived from hydrogenation of 3-phospholene oxide **19** and then Birch reduction also gave the expected β,γ-unsaturated ketones as an analytically pure mixture of stereoisomers. That the keto group remained out of conjugation in all of these derivatives was apparent from the infrared absorption band at 1710–1715 cm^{-1}; the ^{13}C NMR spectra obtained for two structures were also conclusive in this regard (**35**, δ C=O = 206.8; **37**, δ C=O = 207.2).

It was noted in the preceding section that direct Birch reduction of phospholene oxide **20**, without the preliminary hydrogenation step, gave a complex mixture of products. The mixture was somewhat simplified when it was hydrolyzed by the oxalic acid technique, and a product was obtained that was comprised of 75% of a nearly 1:1 mixture of β,γ-unsaturated

Scheme IV



[a] $(COOH)_2$ in aqueous CH_3OH.

ketones. This structural feature was readily apparent from the ^{13}C NMR spectrum that contained two signals at δ 209.2 and 209.7. No signals for α,β-unsaturated carbonyl were present. ^{31}P NMR provided the analysis of the mixture; a spectrum with two major signals (δ +62.8 and +68.9) was obtained, neither of which matched the known C/D cis compound **37** (δ +65.0) on admixture. For reasons already mentioned, it is probable that these ketones have C/D trans, but the complexity of the mixture makes this an unattractive synthetic route to attain structures with this stereochemical feature. A superior approach to a C/D trans phospholane oxide product could simply involve oxidation of the phosphine **33**, obtained in single stereoisomeric (presumably C/D trans) form in good yield in the Birch reduction of phospholene sulfide **22**.

Experimental Section

General. All manipulations involving trivalent phosphorus compounds were conducted in a glovebag with a nitrogen atmosphere. Melting points are corrected. ^1H NMR spectra were obtained with a JEOL MH-100 spectrometer using Me_4Si as an internal standard. Proton-decoupled ^{31}P NMR were obtained with a Bruker HFX-10 system at 36.43 MHz; both the CW and FT modes were used. The standard was 85% H_3PO_4; positive and negative shifts refer to downfield and upfield, respectively. Proton-decoupled FT ^{13}C NMR spectra were obtained on the Bruker instrument at 22.62 MHz; chemical shifts are downfield from Me_4Si. Elemental analyses were performed by MHW Laboratories, Garden City, Mich.

6-Methoxy-1,2,3,4-tetrahydro-1-vinyl-1-naphthol (5). To a solution of vinylmagnesium bromide (prepared from 28.0 g (0.26 mol) of vinyl bromide and 8.0 g (0.25 g-atom) of magnesium in 250 mL of tetrahydrofuran) was added a solution of 31.0 g (0.18 mol) of 6-methoxy-α-tetralone in 150 mL of tetrahydrofuran over a 90-min period. The resulting mixture was then refluxed for 1 h. The flask was cooled in ice and 150 mL of saturated NH_4Cl solution added. The layers were separated, and the aqueous layer was extracted with ether (3 × 100 mL). The ethereal extracts were combined, dried ($MgSO_4$), and concentrated on a rotary evaporator to give 33.7 g (94%) of **5**[6a] as a light tan oil: NMR ($CDCl_3$) δ 1.6–2.0 (m, $ArCH_2CH_2$), 2.5–2.8 (m, $ArCH_2CH_2CH_2$), 3.0 (broad s, OH), 3.63 (s, OCH_3), 5.05 (d, $^3J_{HH}$ = 8 Hz, $-CH{=}CH_2$, cis), 5.18 (d, $^3J_{HH}$ = 13 Hz, $-CH{=}CH_2$, trans), 5.93 (d of d, $^3J_{HH}$ = 13 Hz, $^2J_{HH}$ = 8 Hz, $-CH{=}CH_2$), 6.41–7.21 (m, Ar–H); IR (neat) ν_{O-H} 3350, $\nu_{C=C}$ 1610 cm^{-1}.

3,4-Dihydro-6-methoxy-1-vinylnaphthalene (6). This known compound[6] was prepared in 97% yield (crude) by dehydrating alcohol **5** with I_2–quinoline:[6b] NMR ($CDCl_3$) δ 2.15 (m, 2 H, $ArCH_2CH_2$–), 2.58 (broad t, $ArCH_2CH_2$–), 2.55 (s, OCH_3), 5.09 (d of d, ^3J = 10 Hz, ^2J = 2 Hz, $-CH{=}CH_2$, cis), 5.46 (d of d, ^3J = 18 Hz, ^2J = 2 Hz, $-CH{=}CH_2$, trans), 5.90 (broad t, ring olefinic H), 6.38–6.72 (m, Ar–H and $-CH{=}CH_2$); IR (neat) $\nu_{C=C}$ 1600 cm^{-1}.

7-Methoxy-1-hydroxy-1,2,3,4-tetrahydro-1-vinylphenanthrene (8). To a solution of vinylmagnesium bromide (prepared from 14.0 g (0.13 mol) of vinyl bromide and 4.0 g (0.125 g-atom) of magnesium in 125 mL of tetrahydrofuran) was added a solution of 20.3 g (0.09 mol) of the phenanthrone **7**[7] in 100 mL of tetrahydrofuran over a 45-min period. The resulting mixture was stirred at room temperature for 1 h. The flask was cooled in ice and 100 mL of saturated NH_4Cl solution added. The layers were separated, and the aqueous layer was extracted with ether (3 × 100 mL). The ethereal extracts were combined, dried ($MgSO_4$), and concentrated to give 20.5 g (90%) of **8** as an oil which solidified on standing: NMR ($CDCl_3$) δ 1.73–2.10 (m, $-CH_2CH_2$–), 2.40 (s, OH, disappeared on addition of D_2O), 2.84–3.12 (m, $-CH_2$–), 3.80 (s, OCH_3), 5.04–5.28 (m, $-CH{=}CH_2$), 5.84–6.12 (m, $-CH{=}CH_2$), 6.92–7.80 (m, Ar–H); IR (neat) ν_{OH} 3350, $\nu_{C=C}$ 1610 cm^{-1}. The compound was used directly in the synthesis of **9** without further purification.

3,4-Dihydro-7-methoxy-1-vinylphenanthrene (9). To a solution of 20.0 g (0.08 mol) of alcohol **8** in 300 mL of dry benzene was added 5 mL of quinoline and a crystal of iodine. The flask was fitted with a Dean-Stark trap, and the mixture was refluxed under nitrogen until the theoretical amount of water had been removed (2 h). The solution was cooled, washed with saturated $NaHCO_3$ solution (3 × 100 mL), and dried ($MgSO_4$). The residual solution was concentrated to give 16.6 g (88%) of **9** as a yellow oil which solidified on standing: NMR ($CDCl_3$) δ 2.24–2.50 (m, $-CH_2$), 3.08 (t, $^3J_{HH}$ = 8 Hz, $-CH_2$–), 3.85 (s, OCH_3), 5.10–5.64 (m, $CH{=}CH_2$), 6.16 (t, $^3J_{HH}$ = 4 Hz, ring olefinic CH), 6.48–6.84 (m, $-CH{=}CH_2$), 7.00–7.96 (m, Ar–H); IR (neat) $\nu_{C=C}$ 1600 cm^{-1}. The compound was used without further purification in the synthesis of phospholene oxide **25**.

6-Methoxy-1,2,3,4-tetrahydro-2-vinyl-2-naphthol (11). To a solution of vinylmagnesium bromide (prepared from 3.4 g (0.14 g-atom) of magnesium and 10.8 mL (0.15 mol) of vinyl bromide in 150 mL of tetrahydrofuran) was added 17.6 g (0.10 mol) of 6-methoxy-2-tetralone (**10**, prepared by the method of Sims et al.[18]) in 100 mL of tetrahydrofuran over a period of 1 h. The mixture was then refluxed for 10 h and allowed to stand overnight. Saturated NH_4Cl (150 mL) was added to the chilled mixture, which was then stirred for 20 min. The layers were separated, and the aqueous layer was extracted with ether (6 × 100 mL). The ethereal extracts were combined, dried ($MgSO_4$), and concentrated on a rotary evaporator. The residue was then stirred with 100 mL of saturated $Na_2S_2O_5$ solution for 30 min to remove unreacted **10**. Ethanol (100 mL) was added, and the mixture was cooled in ice. The precipitated bisulfite addition product was filtered off, heated with 10 mL of 3 N HCl, and extracted with ether (3 × 50 mL). The ether was dried ($MgSO_4$) and concentrated to give 2.8 g of the starting **10**. The ethanolic filtrate was extracted with ether (5 × 100 mL), and the ethereal extracts were combined, dried ($MgSO_4$), and evaporated to give a green oil. Distillation of this oil gave 11.8 g (69% based on consumed ketone) of **11** as a colorless oil: bp 93–98 °C (0.04 mm); NMR ($CDCl_3$) δ 1.80 (broad t, $ArCH_2CH_2COH$), 2.53 (s, OH), 2.50–3.20 (m, 4 H, benzylic $-CH_2$–), 3.77 (s, OCH_3), 5.14 (d of d, $^3J_{HH}$ = 11 Hz, $^2J_{HH}$ = 2 Hz, $-CH{=}CH_2$, cis), 5.37 (d of d, $^3J_{HH}$ = 18 Hz, $^2J_{HH}$ = 2 Hz, $-CH{=}CH_2$, trans), 6.15 (d of d, $^3J_{HH}$ = 18 Hz, $^2J_{HH}$ = 11 Hz, $-CH{=}CH_2$), 6.72–6.96 (m, H-5, H-7), 7.07 (d, $^3J_{HH}$ = 8 Hz, H-8); IR (neat) ν_{OH} 3350, $\nu_{C=C}$ 1610 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.47; H, 7.84. Found: C, 76.33; H, 7.76.

3,4-Dihydro-6-methoxy-2-vinylnaphthalene (12) and 1,4-Dihydro-6-methoxy-2-vinylnaphthalene (13). To a cooled (0 °C) solution of 13.3 g (65.2 mmol) of **11** in 12 mL of pyridine was added a mixture of 4.3 mL of phosphorus oxychloride in 5.2 mL of pyridine. The rate of addition was regulated to maintain the temperature at 0–10 °C. After the addition was complete, the mixture was stirred at 0 °C for 2 h. The dark mixture was then poured into 100 mL of ice water. The water was extracted with ether (5 × 100 mL). The ethereal extracts were combined, washed with 3 N HCl (3 × 50 mL), dried ($MgSO_4$), and concentrated. Distillation of the crude oil gave 5.1 g (43%) of **12** and **13** as a colorless oil: bp 91–95 °C (0.02 mm); **12** (65%) NMR ($CDCl_3$) δ 2.58 (m, $ArCH_2CH_2$–), 3.67 (s, OCH_3), 4.90–5.35 (m, $-CH{=}CH_2$), 6.33 (s, $ArCH{=}C$–), 6.55–7.08 (m, Ar–H and $-CH{=}CH_2$); **13** (35%) NMR ($CDCl_3$) δ 3.39 (s, 4 H, benzylic $-CH_2$–), 3.67 (s, OCH_3), 4.90–5.35 (m, $-CH{=}CH_2$), 6.33–7.08 (m 5 H, ring olefinic H, $-CH{=}CH_2$, and ArH); IR (neat) $\nu_{C=C}$ 1600 cm^{-1}. Separation of the isomers was not performed.

2-Formyl-6-methoxy-1-tetralone (14). 6-Methoxy-1-tetralone and ethyl formate gave **14** (98%), mp 62–63 °C, as reported[9] (mp 65–68 °C): NMR (CCl_4) δ 2.33–2.91 (m, 4 H, $-CH_2$), 3.75 (s, OCH_3), 6.50–6.80 (m, H-5 and H-7), 7.81 (d, $^3J_{HH}$ = 8 Hz, H-8), 7.83 (s, CHO).

2-(Ethylenedioxymethyl)-6-methoxy-1-tetralone (15). A mixture of 20.4 g (0.1 mol) of **14**, 5.6 mL (0.1 mol) of ethylene glycol, and 500 mg of *p*-toluenesulfonic acid was dissolved in 200 mL of toluene and refluxed for 2.5 h. The mixture was then washed with saturated $NaHCO_3$ (3 × 100 mL) and water (2 × 100 mL) and dried ($MgSO_4$). The solvent was removed under vacuum, and the resulting oil solidified on standing to give 24.2 g of a tan solid. Recrystallization (ligroin–benzene) gave 22.8 g (93%) of **15**: mp 64–66 °C; NMR (CCl_4) δ 2.00–3.05 (m, 4 H, $-CH_2-$), 3.80 (s, OCH_3), 3.83 (m, $-OCH_2CH_2O-$), 5.4 (d, $^3J_{HH}$ = 3 Hz, OCHO), 6.55–7.88 (m, Ar–H); IR (Nujol) $\nu_{C=C}$ 1667 cm^{-1}. The compound was used directly in the next step.

2-(Ethylenedioxymethyl)-6-methoxy-1,2,3,4-tetrahydro-1-naphthol (16). To a solution of 20.0 g (0.081 mol) of **15** in 500 mL of methanol was added 9.2 g (0.243 mol) of sodium borohydride over a period of 20 min. The mixture was then refluxed for 1 h and cooled, and the methanol was removed under vacuum. The residue was taken up in 100 mL of water and extracted with methylene chloride (3 × 100 mL). The methylene chloride extracts were combined, dried ($MgSO_4$), and concentrated to give a light yellow solid. Recrystallization (ligroin–benzene) gave 19.5 g (96%) of **16**: mp 97–101 °C; NMR ($CDCl_3$) δ 1.71–2.90 (m, 4 H, $-CH_2-$), 3.68 (s, OCH_3), 3.87 (m, $-OCH_2CH_2O-$), 4.72–5.01 (m, CHOH and OCHO), 6.51–7.25 (m, Ar–H); IR (KBr) ν_{OH} 3390 cm^{-1}. The compound was used directly for the next reaction.

3,4-Dihydro-2-formyl-6-methoxynaphthalene (17). To a solution of 18.0 g (0.072 mol) of **16** in 350 mL of methanol and 350 mL of water was added 10 mL of concentrated HCl. The resulting mixture was heated on a steam bath for 1 h. The methanol was removed under vacuum, and the aqueous mixture was extracted with ether (3 × 100 mL). The ethereal extracts were combined, dried ($MgSO_4$), and concentrated to give 12.7 g (94%) of **17**: mp 39–40 °C; NMR (CCl_4) δ 2.25–2.88 (m, 4 H, CH_2-), 3.72 (s, OCH_3), 6.52–7.19 (m, Ar–H), 9.45 (s, CHO); IR (neat) $\nu_{C=C}$ 1670 cm^{-1}. This compound was used in the next reaction directly.

3,4-Dihydro-6-methoxy-2-vinylnaphthalene (12). To a solution of 79.2 mL (0.19 mol) of *n*-butyllithium (2.4 M in hexane) in 400 mL of ether was added 67.8 g (0.19 mol) of methyltriphenylphosphonium bromide over a period of 30 min. The mixture was stirred at room temperature for 4 h and then treated dropwise with 35.9 g (0.19 mol) of liquid **17**. The reaction mixture was then refluxed for 24 h, cooled, and filtered. The filtrate was washed with water until neutral, dried ($MgSO_4$), and concentrated to give 31.0 g of a yellow oil. Distillation gave 21 g (61%) of **12**: bp 80–85 °C (0.005 mm); NMR (CCl_4) δ 2.18–2.82 (m, 4 H, $-CH_2$), 3.57 (s, OCH_3), 4.91–5.22 (m, $C=CH_2$), 6.20–6.80 (Ar–H, ArCH=C, and $CH=CH_2$); IR (neat) $\nu_{C=C}$ 1600 cm^{-1}. Since the diene was somewhat unstable, it was immediately used to form phospholene oxide **23**.

2-Formyl-7-methoxy-1-phenanthrone. To a stirred mixture of sodium methoxide (1.3 g, 0.024 mol) in 50 mL of anhydrous benzene was added 2.6 g (0.0115 mol) of Butenandt's ketone (**7**) and a solution of 3.4 g (0.046 mol) of ethyl formate in 80 mL of anhydrous benzene. The mixture was stirred overnight and then poured into 1 L of ice water. The layers were separated, and the aqueous layer was extracted twice with 100-mL portions of ether. The combined organic layers were extracted twice with 300-mL portions of 5% NaOH. The aqueous layer was acidified with concentrated HCl, and the light yellow precipitate that formed was filtered and dried (2.6 g, 89%), mp 125–128 °C (lit.[19] mp 129–131 °C).

2-(Ethylenedioxymethyl)-7-methoxy-1-phenanthrone. The formyl ketone prepared by the preceding method (3.0 g, 0.0118 mol) was converted to the ketal by the procedure used for **15**: the yield was 3.0 g (85%); mp 155–159 °C; IR (Nujol) $\nu_{C=C}$ 1680 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.66; H, 6.16.

2-(Ethylenedioxymethyl)-7-methoxy-1-phenanthrol. The ketal prepared according to the preceding method (10.8 g, 0.0362 mol) was dissolved in 1.3 L of refluxing absolute methanol and reduced with $NaBH_4$ as in the preparation of **16**: the yield was 10.8 g (99.3%); mp 121–125 °C; IR (Nujol) ν_{O-H} 3700 cm^{-1}, $\nu_{C=O}$ absent. A sample was recrystallized from benzene–ligroin (mp 121–125 °C).

Anal. Calcd for $C_{18}H_{20}O_4$: C, 72.00; H, 6.67. Found: C, 72.16; H, 6.71.

3,4-Dihydro-2-formyl-7-methoxyphenanthrene. To 800 mL of methanol was added 9.8 g (0.0326 mol) of the alcohol prepared as in the preceding experiment and 18 mL of concentrated HCl in 600 mL of water. The mixture was refluxed under nitrogen for 1 h. On cooling, some of the product crystallized and was filtered off and dried. The solvent was stripped from the filtrate, and the residue was taken up in ether. The ether solution was washed with water, dried over $MgSO_4$, and evaporated to dryness. The residue was combined with the first crop of product, total yield 6.6 g (85%), mp 115–118 °C. A sample recrystallized from water–methanol had mp 115–118 °C; ^1H NMR ($CDCl_3$) δ 2.69 (t, 2 H), 3.36 (t, 2 H), 3.93 (s, OCH_3), 7.1–8.1 (m, aromatic H), 9.75 (s, aldehydic H); IR $\nu_{C=O}$ 1665 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 81.06; H, 5.82.

3,4-Dihydro-7-methoxy-2-vinylphenanthrene (18). To a solution of 11.2 mL of 2.29 M *n*-butyllithium (0.0256 mol) in 100 mL of anhydrous ether was added 9.15 g (0.0256 mol) of freshly dried methyltriphenylphosphonium bromide over a 25-min period. The mixture was stirred under nitrogen for 5 h and then treated over a 1-h period with a solution of 6.1 g (0.0256 mol) of the aldehyde, prepared by the preceding method, dissolved in 150 mL each of benzene and ether. The mixture was brought to reflux, which was maintained for 17 h. The solid that precipitated was filtered off and washed with both ether and benzene. Organic fractions were combined, washed with water (five 100-mL portions), dried over $MgSO_4$, and evaporated to leave 5.4 g (90%) of diene **18**, mp 91–96 °C. The diene was purified by chromatography on alumina with benzene as eluant and used immediately in the synthesis of **28**: ^1H NMR ($CDCl_3$) δ 2.56 and 3.14 (both t, $-CH_2CH_2-$), 3.92 (s, OCH_3), 5.12 and 5.24 (both d, $^3J_{HH}$ = 17 and 24 Hz, $-CH=CH_2$), 6.5–6.7 (m, ArCH=C and $-CH=CH_2$), 7.1–8.1 (m, –ArH).

7-Methoxy-3-methyl-2,3a,4,5-tetrahydro-3*H*-benzo[*e*]phosphindole 3-Oxide (19). To a wide-mouth, screw-cap bottle was added 29.3 g (0.16 mol) of diene **6**, 17.8 mL (0.2 mol) of methylphosphonous dichloride, 1 g of copper stearate, and 200 mL of pentane. The bottle was sealed and allowed to stand for 1 week. The resulting cycloadduct was filtered off and washed with pentane (3 × 100 mL). The solid was slowly added to 100 mL of ice water, and the resulting solution was then made slightly basic with solid $NaHCO_3$. The aqueous mixture was then extracted continuously with chloroform for 24 h. The chloroform solution was dried (K_2CO_3) and concentrated to give a light brown solid. Recrystallization from acetone gave 21.0 g (53%) of **19**: mp 174–177 °C; ^1H NMR ($CDCl_3$) δ 1.45 and 1.70 (both d, $^2J_{HH}$ = 13 Hz, cis and trans P–CH_3), 2.0–3.2 (m, 6 H, $-CH_2-$), 3.75–3.40 (broad s, O–CH_3), 6.07 (d, $^3J_{PH}$ = 26 Hz, $-C=CH$), 6.50–7.48 (m, ArH); ^{31}P NMR (D_2O) δ +70.5 (90%), +62.5 (10%); IR (KBr) $\nu_{C=C}$ 1575, $\nu_{P=O}$ 1170 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}O_2P$: C, 67.76; H, 6.85; P, 12.49. Found: C, 67.71; H, 6.96; P, 12.51.

7-Methoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-benzo[*e*]phosphindole 3-Oxide (20). A portion of the cycloadduct prepared from the diene **6** and methylphosphonous dichloride was added to water. The exothermic reaction was not controlled. Neutralization of the solution followed by extraction gave the rearranged oxide **20** as a tan solid: ^1H NMR ($CDCl_3$) δ 1.76 (d, $^2J_{PH}$ = 13 Hz, P–CH_3), 2.12–3.25 (m, 8 H, $-CH_2-$), 4.02 (s, OCH_3), 6.82–7.55 (m, Ar–H); ^{13}C NMR ($CDCl_3$) δ 15.9 (d, $^1J_{PC}$ = 67.1 Hz, PCH_3), 19.5 (d, $^2J_{PC}$ = 9.8 Hz, C-4), 24.4 (d, $^1J_{PC}$ = 59.8 Hz, C-2), 26.9 (d, J = 1.8 Hz, C-1 or C-5), 28.3 (d, J = 6.1 Hz, C-1 or C-5), 55.2 (s, OCH_3), 111.5 (s, C-8), 114.0 (s, C-6), 124.9 (d, $^3J_{PC}$ = 13 Hz, C-9a; downfield half was obscured by C-9 signal), 125.3 (s, C-9), 129.1 (d, $^1J_{PC}$ = 58.4 Hz), 139.1 (d, $^4J_{PC}$ = 1.8 Hz, C-5a), 149.7 (d, $^2J_{PC}$ = 31.7 Hz, C-9b), 157.2 (s, C-7).

Anal. Calcd for $C_{14}H_{17}O_2P$: C, 67.76; H, 6.85; P, 12.49. Found: C, 67.60; H, 6.76; P, 12.35.

7-Hydroxy-3-methyl-1,2,4,5-tetrahydro-3*H*-benzo[*e*]phosphindole 3-Oxide (21). A mixture of 2.5 g (10 mmol) of **20** and 10 mL of 48% HBr was refluxed under N_2 for 3 h. The mixture was cooled to room temperature and made basic with 3 N NaOH solution. The basic solution was extracted with chloroform (3 × 50 mL). The solution was then made acidic by the addition of 10% HCl solution and extracted with chloroform (3 × 75 mL). The chloroform extracts were combined, dried (Na_2SO_4), and concentrated to give a tan solid. Recrystallization from aqueous methanol gave 1.5 g (64%) of phenol **21**: mp 225–226 °C; ^1H NMR (CF_3COOH) δ 2.08 (d, $^2J_{PH}$ = 13 Hz, P–CH_3), 2.40–3.50 (m, 4 H, $-CH_2-$), 6.75–7.40 (m, Ar–H); IR (Nujol) $\nu_{P=O}$ 1140 cm^{-1}; ^{31}P NMR (MeOH) δ +71.7.

Anal. Calcd for $C_{13}H_{15}O_2P$: C, 66.67; H, 6.41; P, 13.25. Found: C, 66.54; H, 6.65; P, 13.07.

7-Methoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-benzo[*e*]phosphindole 3-Sulfide (22). Through a suspension of the cycloadduct prepared from 22 g (0.12 mol) of diene **6** and a slight excess of methylphosphonous dichloride in 300 mL of benzene was bubbled a stream of H_2S until all solid had dissolved. The mixture was stirred for an additional 30 min at room temperature while a stream of nitrogen was bubbled through the solution to remove unreacted H_2S. The solution was washed with saturated $NaHCO_3$ solution (3 × 150 mL), dried ($MgSO_4$), and concentrated to give 15 g of a pale yellow solid. Recrystallization from ethanol–water gave 12 g (52%) of the sulfide **22**: mp 91–93 °C; ^1H NMR ($CDCl_3$) δ 1.75 (d, $^2J_{HH}$ = 12 Hz, P–CH_3), 2.16–3.20 (m, 8 H, $-CH_2-$), 3.83 (s, OCH_3), 6.72–6.84 (m, H-6,8), 7.18 (d, $^3J_{HH}$ = 8 Hz, H-9); ^{31}P NMR ($CDCl_3$) δ +62.1; ^{13}C NMR ($CDCl_3$)

δ 18.3 (d, $^2J_{PC}$ = 18 Hz, C-4), 20.8 (d, $^1J_{PC}$ = 50 Hz, PCH_3), 27.0 (s, C-1 or C-5), 27.2 (s, C-1 or C-5), 29.2 (d, $^1J_{PC}$ = 50 Hz, C-2), 54.2 (s, OCH_3), 110.2 (s, C-8), 113.3 (s, C-6), 123.9 (d, $^3J_{PC}$ = 12 Hz, C-9a), 124.3 (s, C-9), 127.0 (d, $^1J_{PC}$ = 80 Hz, C-3a), 137.6 (d, $^4J_{PC}$ = 3 Hz, C-5), 145.8 (d, $^2J_{PC}$ = 28 Hz, C-9b), 159.5 (s, C-7); IR (KBr) $\nu_{C=C}$ 1613 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}OPS$: C, 63.63; H, 6.43; P, 11.74. Found: C, 63.60; H, 6.55; P, 11.43.

7-Methoxy-1-methyl-2,3,4,5-tetrahydro-1*H*-benzo[*g*]phosphindole 1-Oxide (23). To a solution of 10 g (0.054 mol) of diene **12** and 0.5 g of copper stearate in 100 mL of cyclohexane was added 10 mL (0.011 mol) of freshly distilled CH_3PCl_2. The mixture was refluxed for 6 days; the solid was then filtered off, washed with pentane, and added to water without temperature control. The solution was neutralized with solid $NaHCO_3$ and then extracted with three 100-mL portions of chloroform. The extracts were dried ($MgSO_4$) and concentrated to leave 8.1 g (60%) of crude **23**. Recrystallization (ether–petroleum ether) gave 5.2 g (40%) of **23**: mp 121–123 °C; ^1H NMR ($CDCl_3$) δ 1.76 (d, $^2J_{PH}$ = 14 Hz, P–CH_3), 2.01–3.10 (m, 8 H, –CH_2–), 3.87 (s, –OCH_3), 6.85–7.01, 7.82 (Ar–H); ^{31}P NMR ($CDCl_3$) δ +63.6; ^{13}C NMR ($CDCl_3$) δ 17.0 (d, $^1J_{PC}$ = 70 Hz, P–CH_3), 25.2 (d, $^1J_{PC}$ = 58 Hz, C-2), 26.9 and 27.4 (C-4 and C-5, unassigned), 30.5 (d, $^2J_{PC}$ = 10 Hz, C-3), 55.2 (s, OCH_3), 111.1 (s, C-8), 114.2 (s, C-6), 123.4 (d, J = 8 Hz, C-5a or C-9a), 125.2 (s, C-9), 127.8 (d, half of signal was not clearly observable, C-9b), 136.0 (d, J = 8 Hz, C-5a or C-9a), 153.2 (d, $^2J_{PC}$ = 30 Hz, C-3a), 159.4 (s, C-7); IR (Nujol) $\nu_{P=O}$ 1155 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}O_2P$: C, 67.76; H, 6.85; P, 12.49. Found: C, 67.51; H, 6.91; P, 12.36.

7-Methoxy-1-methyl-2,3,4,5-tetrahydro-1*H*-benzo[*g*]phosphindole 1-Sulfide (24). A suspension of the cycloadduct prepared from 20 g (0.11 mol) of diene **12** and 15 mL (0.17 mol) of methylphosphonous dichloride in benzene was treated with a stream of H_2S over a 30-min period. The product was worked up as for **20** to give 12.5 g of a yellow solid. Recrystallization from ethanol–water gave 11.9 g (41%) of the sulfide **24** as white needles: mp 132–133 °C; ^1H NMR ($CDCl_3$) δ 2.00 (d, $^3J_{PH}$ = 14 Hz, P–CH_3), 2.20–3.05 (m, 8 H, –CH_2–), 3.85 (s, –OCH_3), 7.8 (m, H-6, H-8), 7.96 (d, $^3J_{HH}$ = 8 Hz, H-9); ^{31}P NMR ($CDCl_3$) δ +58.2; ^{13}C NMR ($CDCl_3$) δ 22.6 (d, $^1J_{PC}$ = 50.0 Hz), 26.3 (s, C-4 or C-5), 26.8 (s, C-4 or C-5), 29.0 (d, $^1J_{PC}$ = 50 Hz, C-2), 32.9 (d, $^2J_{PC}$ = 5 Hz, C-3), 54.7 (s, OCH_3), 110.6 (s, C-8), 113.9 (s, C-6), 125.0 (d, $^3J_{PC}$ = 3 Hz, C-9), 128.1 (d, $^1J_{PC}$ = 80 Hz, C-9b), 131.4 (d, J_{PC} = 10 Hz, C-5a or C-9a), 136.3 (d, J_{PC} = 8 Hz, C-5a or C-9a), 151.1 (d, $^2J_{PC}$ = 28 Hz, C-3a), 159.1 (s, C-7); IR (KBr) $\nu_{C=C}$ 1605 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}OPS$: C, 63.63; H, 6.43; P, 11.74. Found: C, 63.46; H, 6.55; P, 11.59.

7-Methoxy-1-methyl-2,3,10,11-tetrahydro-1*H*-naphtho[2,1-*e*]phosphindole 1-Oxide (25). Methoxy Cleavage and Hydrogenation. A mixture of 16.0 g (0.068 mol) of diene **9**, 7.6 mL (0.085 mol) of CH_3PCl_2, 500 mg of copper stearate, and 100 mL of dry benzene was allowed to precipitate cycloadduct for 1 week. The solid was added to water without temperature control, and the resulting slurry was extracted with chloroform (3 × 150 mL) to give 13.5 g (66%) of a light brown solid. Recrystallization of this solid from acetone gave 12.3 g (61%) of **25**: mp 205 °C dec; ^1H NMR ($CDCl_3$) δ 1.68 (d, $^3J_{PH}$ = 13 Hz, P–CH_3), 1.97–3.40 (m, 8 H, –CH_2–), 3.90 (s, OCH_3), 7.05–8.04 (m, Ar–H); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, $^1J_{PC}$ = 65 Hz, PCH_3), 19.2 (d, $^2J_{PC}$ = 10 Hz, C-11), 24.8 (d, $^1J_{PC}$ = 71 Hz, C-2), 22.9 (d, $^3J_{PC}$ = 5 Hz, C-10), 27.1 (d, $^2J_{PC}$ = 8 Hz, C-3), 55.0 (s, OCH_3), 105.8 (s, C-6), 118.5 (s, C-8), 121.0 (s), 124.8 (s), 125.0 (s), 125.8 (s), 128.3 (d, $^1J_{PC}$ = 80 Hz, C-11a), 132.6 (s), 134.7 (s, C-9b), 148.9 (d, $^2J_{PC}$ = 30 Hz, C-3a), 157.2 (s, C-7); ^{31}P NMR ($CHCl_3$) δ +65.1; IR (Nujol) $\nu_{C=C}$ 1508, $\nu_{P=O}$ 1180 cm^{-1}; mass spectrum, m/e 298.1119 (calcd for M^+, 298.1123).

Anal. Calcd for $C_{18}H_{19}O_2P$: C, 72.48; H, 6.38; P, 10.40. Found: C, 72.49; H, 6.36; P, 10.17.

Cleavage of the methoxy group of **25** (2.1 g, 0.0070 mol) was accomplished as for **21** yielding naphthol **26** (1.43 g, 71%): mp 289–290 °C dec; ^1H NMR (CF_3COOH) δ 2.02 (d, $^2J_{PH}$ = 13 Hz, PCH_3) 2.15–3.50 (aliphatic H), 7.15–8.21 (aromatic H); ^{31}P NMR (CF_3COOH) δ +68.3.

Hydrogenation of **25** in CH_3OH with 10% Pd on charcoal was quantitative at atmospheric pressure, forming a mixture of **27a** (16% from ^{31}P ($CDCl_3$) NMR, δ +71.8) and **27b** (84% from ^{31}P NMR, δ +67.7): partial ^{13}C NMR of **27b** ($CDCl_3$) δ 17.50 (d, $^1J_{PC}$ = 62.3 Hz, PCH_3), 18.0 (d, $^2J_{PC}$ = 4 Hz, C-11), 25.7 (s, C-10), 27.3 (d, $^1J_{PC}$ = 72.0 Hz, C-2), 30.8 (d, $^2J_{PC}$ = 4 Hz, C-3), 36.8 (d, $^1J_{PC}$ = 69.6 Hz, C-11a), 41.1 (d, $^2J_{PC}$ = 13.4 Hz, C-3a).

Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05; P, 10.31. Found: C, 72.12; H, 7.00; P, 10.47.

7-Methoxy-3-methyl-1,2,10,11-tetrahydro-3*H*-naphtho-[1,2-*g*]phosphindole 3-Oxide (28). A mixture of 1.9 g (0.008 mol) of diene **18**, 2.0 g (0.017 mol) of CH_3PCl_2, and 40 mg of copper stearate in 10 mL of anhydrous benzene was sealed in a bottle and allowed to stand for 21 days. The precipitated material was recovered by filtration under nitrogen and hydrolyzed by addition of 10 mL of water. After being neutralized with saturated $NaHCO_3$, the solution was extracted with CH_2Cl_2 (3 × 100 mL); the extract was dried ($MgSO_4$), and solvent was removed to leave 0.5 g (20.8%) of **28**. Sublimation gave a white solid: mp 194 °C dec; ^1H NMR ($CDCl_3$) δ 1.8 (d, $^2J_{PH}$ = 11 Hz, PCH_3), 2.0–3.5 (m, 8 H, –CH_2–), 3.93 (s, OCH_3), 7.1–8.0 (m, 5 H, aromatic H); ^{31}P NMR δ +63.5.

Anal. Calcd for $C_{18}H_{19}O_2P$: C, 72.48; H, 6.38; P, 10.40. Found: C, 72.55; H, 6.61; P. 10.50.

***r*-3-Methyl-7-methoxy-1,2,*c*-3a,4,5,*c*-9b-hexahydro-3*H*-benzo[*e*]phosphindole 3-Oxide (29).** A solution of 3.0 g (0.01 mol) of freshly recrystallized (toluene) phospholene oxide **20** in 100 mL of methanol was hydrogenated in the presence of 300 mg of 5% Pd on charcoal. Hydrogen consumption was complete after 24 h. Catalyst was filtered off, and the filtrate was freed of solvent to leave 2.8 g (93%) of **29** as an oil: partial ^1H NMR ($CDCl_3$) δ 1.62 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 3.64 (s, OCH_3); ^{31}P NMR ($CDCl_3$) δ +67.0 (95%), +71.4 (5%); partial ^{13}C NMR ($CDCl_3$) δ 16.7 (d, $^1J_{PC}$ = 61.6 Hz, PCH_3), 17.7 (d, $^2J_{PC}$ = 3.6 Hz, C-4), 26.6 (d, $^1J_{PC}$ = 57.4 Hz, C-2), 32.4 (d, $^1J_{PC}$ = 56 Hz, C-3a), 54.3 (s, OCH_3), 111.8 (s, C-6 or C-8), 112.8 (s, C-6 or C-8), 157.1 (s, C-7). The sample was used directly in the Birch reduction to form **30**.

***r*-3-Methyl-7-methoxy-1,2,*c*-3a,4,5,6,9,*c*-9b-octahydro-3*H*-benzo[*e*]phosphindole 3-Oxide (30).** A mixture of 2.8 g (0.01 mol) of phospholane oxide **29**, 150 mL of liquid ammonia, 75 mL of *tert*-butyl alcohol, and 75 mL of tetrahydrofuran in a flask fitted with a dry ice condenser was treated with 2.1 g (0.30 g-atom) of lithium wire over a 10-min period. The blue solution was stirred at −76 °C for 10 h; methanol (100 mL) was then added, and the ammonia was allowed to evaporate at room temperature. Other solvents were stripped off with a rotary evaporator, and the residue was taken up in 100 mL of water. The solution was extracted with three 150-mL portions of $CHCl_3$; the extracts were dried ($MgSO_4$) and concentrated to give 2.5 g (90%) of enol ether **30** as a low melting solid: partial ^1H NMR ($CDCl_3$) δ 1.54 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 3.38 (s, OCH_3), 4.46 (broad s, C=CH); partial ^{13}C NMR ($CDCl_3$) δ 17.5 (d, $^1J_{PC}$ = 61.7 Hz, PCH_3), 17.9 (d, $^2J_{PC}$ = 4.3 Hz, C-4), 30.1 (s, C-9), 33.7 (s, C-6), 37.4 ($^1J_{PC}$ = 70 Hz, C-3a), 41.0 (d, $^2J_{PC}$ = 13 Hz, C-9b), 53.8 (s, OCH_3), 90.1 (s, C-8), 125.8–126.0 (three lines, C-5a and 9a), 152.6 (s, C-7); ^{31}P NMR ($CDCl_3$) δ +66.6. The sample was used directly in the synthesis of ketone **37**.

7-Methoxy-*r*-1-methyl-2,3,*c*-3a,4,5,*c*-9b-hexahydro-1*H*-benzo[*g*]phosphindole 1-Oxide (31). A solution of 100 mg (0.040 mmol) of phospholine oxide **23** in 25 mL of 95% ethanol containing 10 mg of 10% Pd on charcoal was hydrogenated for 16 h to yield 80 mg (80%) of **31** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.15 (d, $^2J_{PH}$ = 12 Hz, P–CH_3), 1.6–3.65 (m, CH and CH_2), 3.73 (s, OCH_3), 6.58–6.90 (m, Ar–H); ^{31}P NMR ($CDCl_3$) δ +68.7; IR (neat) $\nu_{P=O}$ 1160 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}O_2P$: C, 67.20; H, 7.60; P, 12.40. Found: C, 67.53; H, 7.71; P, 12.32.

7-Methoxy-*r*-1-methyl-2,3*c*-3a,4,5,6,9,*c*-9b-octahydro-1*H*-benzo[*g*]phosphindole 1-Oxide (32). To a mixture of 3.0 g (12 mmol) of phospholane oxide **31** in 150 mL of liquid ammonia, 75 mL of tetrahydrofuran, and 75 mL of *tert*-butyl alcohol was added lithium wire (1.5 g, 0.21 g-atom) over a 15-min period. The resulting blue solution was stirred at −20 °C for 6 h. Methanol (30 mL) was then added, and the product was worked up as for **30** to give 2.8 g (93%) of **32**: mp 115–119 °C; ^1H NMR ($CDCl_3$) δ 1.43 (d, $^2J_{PH}$ = 12 Hz, P–CH_3), 1.00–2.95 (m, CH and CH_2), 3.50 (OCH_3), 4.59 (broad, C=CH–); IR (KBr) $\nu_{C=C}$ 1660, $\nu_{P=O}$ 1170 cm^{-1}.

Anal. Calcd for $C_{14}H_{21}O_2P$: C, 66.67; H, 8.33; P, 12.30. Found: C, 66.35; H, 8.01; P, 12.16.

7-Methoxy-3-methyl-1,2,3a,4,5,6,9,9b-octahydro-3*H*-benzo-[*e*]phosphindole 3-Sulfide (34). A mixture of 10 g (0.038 mol) of phospholene sulfide **22** in 150 mL of liquid ammonia, 75 mL of tetrahydrofuran, and 75 mL of *tert*-butyl alcohol was reacted with 4.6 g (0.66 g-atom) of lithium as in the preparation of **30** to yield 7.7 g of a colorless oil which was determined to be the phosphine **33**: ^1H NMR ($CDCl_3$) δ 0.99 (d, $^2J_{PH}$ = 3 Hz, P–CH_3), 1.46–3.21 (broad m, 14 H, CH and CH_2), 3.56 (s, OCH_3), 4.66 (broad t, C=CH–); IR (neat) $\nu_{C=C}$ 1662 cm^{-1}.

The phosphine was taken up in benzene (30 mL), and elemental sulfur (1.3 g) was added. The mixture was stirred overnight at room temperature. Excess sulfur was then filtered off, and the benzene was removed on a rotary evaporator to give 8.5 g of a yellow solid. Recrystallization from ethanol–water gave 7.3 g (72%) of the sulfide **34**: mp 75–76 °C; ^1H NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 13 Hz, P–CH_3), 1.40–3.01 (broad m, 14 H, CH and CH_2), 3.58 (s, OCH_3), 4.68 (broad t, –C=CH–); IR (KBr) $\nu_{C=C}$ 1650 cm^{-1}.

Anal. Calcd for $C_{14}H_{21}OPS$: C, 62.69; H, 7.84; P, 11.57. Found: C, 62.54; H, 7.73; P, 11.51.

***r*-3-Methyl-7-oxo-1,2,*c*-3a,4,5,6,7,8,9,*c*-9b-decahydro-3*H*-benzo[*e*]phosphindole 3-Oxide (35).** A solution of 4.3 g (0.017 mol) of enol ether **30** and 2.3 g of oxalic acid monohydrate in 50 mL of methanol and 20 mL of water was stirred for 1.5 h at room temperature and then neutralized with solid Na_2CO_3. The solution was extracted with $CHCl_3$, and the extract was dried ($MgSO_4$) and concentrated to leave 2.8 g (65%) of ketone **35:** mp 131–137 °C; the ^1H NMR ($CDCl_3$) spectrum was featureless, except for δ 1.58 (d, $^2J_{PH}$ = 12 Hz, P–CH_3), but contained no olefinic or –OCH_3 signals; partial ^{13}C NMR ($CDCl_3$) δ 17.5 (d, $^1J_{PC}$ = 61.5 Hz, PCH_3), 17.8 (d, $^2J_{PC}$ = 3.9 Hz, C-4), 27.1 (d, $^1J_{PC}$ = 59.6 Hz, C-2), 28.7 (s, C-9), 36.8 (d, $^1J_{PC}$ = 62.5 Hz, C-3a), 38.9 (s, C-8), 41.4 (d, $^2J_{PC}$ = 11.8 Hz, C-9b), 44.3 (s, C-6), 126.9–129.6 (four lines, C-5a and 9-a), 206.8 (s, C=O); ^{31}P NMR ($CDCl_3$) δ +65.0.

Anal. Calcd for $C_{13}H_{19}O_2P$: P, 13.03. Found: P, 12.66.

***r*-1-Methyl-7-oxo-2,3,*c*-3a,4,5,6,7,8,9,*c*-9b-decahydro-1*H*-benzo[*g*]phosphindole 1-Oxide (36).** A solution of 2.0 g (0.008 mol) of enol ether **32** and 1 g of oxalic acid monohydrate in 100 mL of methanol and 25 mL of water, worked up as for **35,** gave 1.1 g (58%) of the ketone **36** as an oily solid: ^1H NMR ($CDCl_3$) δ 1.5 (d, $^2J_{PH}$ = 13 Hz, P–CH_3), 1.21–3.13 (broad m, 16 H, CH and CH_2); IR (neat) $\nu_{C=O}$ 1714, $\nu_{P=O}$ 1160 cm^{-1}.

Anal. Calcd for $C_{13}H_{19}O_2P$: C, 65.55; H, 7.98; P, 13.03. Found: C, 65.21; H, 8.15; P, 12.74.

3-Methyl-7-oxo-1,2,3a,4,5,6,8,9,9b-nonahydro-3*H*-benzo-[*e*]phosphindole 3-Sulfide (37). A solution of 5.0 g (0.022 mol) of enol ether **34** and 5.0 g of oxalic acid monohydrate in 200 mL of methanol and 50 mL of water, worked up as for **35,** gave a viscous yellow oil which was filtered through 50 g of neutral alumina with CH_2Cl_2. Concentration of the filtrate gave 3.2 g (57%) of the keto sulfide **37:** mp 120–121 °C; ^1H NMR ($CDCl_3$) δ 1.82 (d, $^2J_{PH}$ = 12 Hz, P–CH_3), 1.40–2.95 (broad m, CH and CH_2); partial ^{13}C NMR ($CDCl_3$) δ 125.4 (s, C-5a), 127.6 (d, $^3J_{PC}$ = 10 Hz, C-9a), 207.2 (s, C=O); IR (KBr) $\nu_{C=O}$ 1709 cm^{-1}.

Anal. Calcd for $C_{13}H_{19}OPS$: C, 61.42; H, 7.48; P, 12.60. Found: C, 61.46; H, 7.56; P, 12.71.

Conversion of Phospholene Oxide 19 to a Mixture of Diastereoisomeric 3-Methyl-7-oxo-1,2,3a,4,5,6,7,8,9,9b-decahydro-3*H*-benzo[*e*]phosphindole 3-Oxides. The cis–trans mixture of phospholene oxide **19** (5.1 g, 0.020 mol) in 100 mL of methanol was hydrogenated over 500 mg of 10% Pd for 12 h. Sublimation of the solid product at 150 °C (0.01 mm) gave 4.8 g (93%) of a mixture of isomers with mp 98–104 °C; ^1H NMR ($CDCl_3$) δ 1.57–1.77 (overlapping PCH_3 signals), 1.60–3.20 (–CH_2), 3.78–3.82 (OCH_3), 6.58–7.25 (m, Ar–H).

Anal. Calcd for $C_{14}H_{19}O_2P$: C, 67.20; H, 7.60; P. 12.40. Found: C, 66.93; H, 7.49; P, 12.18.

To 5 g (0.020 mol) of the isomer mixture in 150 mL of liquid ammonia, 75 mL of tetrahydrofuran, and 75 mL of *tert*-butyl alcohol was added 2.3 g (0.34 g-atom) of lithium wire over a period of 10 min, and the mixture was worked up as for **30** to give oily residue. Upon addition of ether, 4.1 g (81%) of product precipitated as a white hygroscopic solid: ^1H NMR ($CDCl_3$) δ 1.56 and 1.74 (both d, $^2J_{PH}$ = 13 Hz, P–CH_3), 1.20–3.16 (broad m, 14 H, CH and CH_2), 3.59 (s, OCH_3), 4.70 (C=CH); IR (neat) $\delta_{C=C}$ 1667 cm^{-1}.

Anal. Calcd for $C_{14}H_{21}O_2P$: C, 66.67; H, 8.33; P, 12.30. Found: C, 66.53; H, 8.29; P, 12.21.

Hydrolysis of 6.0 g (0.024 mol) of the enol ether product with a solution of 2.3 g of oxalic acid monohydrate in 150 mL of methanol and 30 mL of water at room temperature for 1.5 h gave, after neutralization and extraction, 5.0 g (87%) of a white solid (mp 36–37 °C) mixture of the diastereoisomeric ketones: ^1H NMR ($CDCl_3$) δ 1.67 and 1.73 (both d, $^2J_{PH}$ = 13 Hz, P–CH_3), 1.00–3.10 (m, –CH_2–); IR (neat) $\nu_{C=O}$ 1711 cm^{-1}.

Anal. Calcd for $C_{13}H_{19}O_2P$: C, 65.55; H, 7.98; P, 13.03. Found: C, 65.28; H, 7.73; P, 12.81.

Direct Birch Reduction of Phospholene Oxide 20 and Hydrolysis of the Enol Ether. A sample of 5.0 g (0.02 mol) of phospholene oxide **20** was subjected to Birch reduction as for the preparation of **30.** The product (4.6 g, 92%) was a complex mixture [^{31}P NMR δ +62.6, +63.5, +69.3, and several minor signals; ^{13}C NMR δ 12.7, 13.2, and 13.4 (all d, $^1J_{PC}$ = 60 Hz, PCH_3), 53.8 (s, OCH_3), 90.1 and 90.4 (both s, β-C of enol ether), 152.5 and 154.5 (both s, α-C of enol ether)] that was hydrolyzed directly by the oxalic acid technique as in the synthesis of **35.** The product (3.1 g, 71.5%) had two nearly equal major ^{31}P NMR signals (δ +62.8 and +68.9), accounting for about 75% of the mixture, and several minor signals. The ^{13}C NMR spectrum has saturated C=O signals at δ 209.2 and 209.7; the enol ether signals were absent. The mixture was not further analyzed.

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Registry No.—**5,** 3125-36-8; **6,** 2811-50-9; **7,** 31184-49-3; **8,** 63347-68-2; **9,** 63347-70-6; **10,** 1078-19-9; **11,** 68950-64-1; **12;** 68950-65-2; **13,** 68950-66-3; **14,** 68950-67-4; **15,** 68950-68-5; **16,** 68950-69-6; **17,** 52714,10-0; **18,** 63347-67-1; *cis*-**19,** 68950-70-9; *trans*-**19,** 68950-71-0; **20,** 68950-72-1; **21,** 68950-73-2; **22,** 68950-74-3; **23,** 68975-01-9; **24,** 68950-75-4; **25,** 63347-72-8; **26,** 63347-73-9; **27a,** 68974-66-3; **27b,** 68974-67-4; **28,** 63347-76-2; **29,** 68950-75-4; **30,** 68950-77-6; **31,** 68950-78-7; **32,** 68950-79-8; **33,** 68950-80-1; **34,** 68950-81-2; **35,** 68950-82-3; **36,** 68950-83-4; **37,** 68950-84-5; 2-formyl-7-methoxy-1-phenanthrone, 63347-77-3; 2-(ethylenedioxymethyl)-7-methoxy-1-phenanthrone, 63347-78-4; 2-(ethylenedioxymethyl)-7-methoxy-1-phenanthrol, 68950-85-6; 3,4-dihydro-2-formyl-7-methoxyphenanthrone, 63347-79-5; vinyl bromide, 593-60-2; 6-methoxy-α-tetralone, 2472-22-2; ethyl formate, 109-94-4; methyltriphenylphosphonium bromide, 1779-49-3; methylphosphonous dichloride, 676-83-5.

References and Notes

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