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Synthesis of Phosphonane and Dibenzo[*d*,*f*]phosphonin Derivatives[1]

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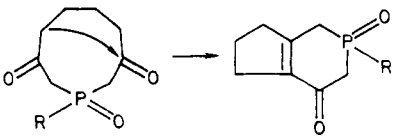
The 3,8-dioxo derivatives of phosphonanes, readily formed by ozonolysis of cyclohexano[*c*]phospholene oxides, are valuable precursors of other phosphonane derivatives. For the 1-methyl derivative, the bis(ethylene dithioketal) derivative can be reduced to the parent phosphonane ring, and the carbonyl groups can be reduced ($NaBH_4$ or H_2) to the diol (diastereomeric mixture). On dehydration of the diol, a 1,5 hydride shift occurred to give a conjugated diene. Intramolecular aldol condensation can occur easily with acidic or basic reagents to generate derivatives with the new cyclopentano[*c*]phosphorinane ring structure. 5,6-Dibromo-3,8-phosphonanediones when reacted with zinc form the 3,8-dioxo-2,4,7,9-tetrahydrophosphonin system; with base, the dibromo derivatives undergo intramolecular alkylation and dehydrobromination to form derivatives of cyclopentano[*b*]phosphorinane, also a new ring system. The dibenzo derivative of 1-phenyl-3,8-phosphonanedione 1-oxide provides on reduction a single diol with a rigid ring structure; dehydration gave the first phosphonin 1-oxide, with cis,trans double bonds. Deoxygenation was performed to yield 7-phenyldibenzo[*d*,*f*]phosphonin, whose ^1H NMR and UV spectra gave no indication of electron delocalization as found in some heteronins.

The recently synthesized[2] 3,8-dioxo derivatives of phosphonanes (from ozonolysis of cyclohexano[*c*]-phospholene oxides) suggest themselves to be excellent starting materials for the preparation of other types of compounds containing this little-known ring system. Of special interest, as we have noted elsewhere,[2,3] would be completely unsaturated forms with trivalent phosphorus, since these compounds (phosphonins) would belong to the 10-π-electron heteronin series[4] and could conceivably possess properties describable as "aromatic". For lack of synthetic methods to prepare suitable models, this point has never been treated in the literature. In this paper, we will show that the phosphonanediones do indeed have a rich chemistry and that phosphonin synthesis is possible from them, although the particular form that has been synthesized in the initial work is complicated by the presence of two benzo groups which add their own features of uniqueness to the ring structure.

Intramolecular Interactions. The discussion must commence with treatment of the propensity for the nine-membered ring to react internally and form a six–five bicyclic system, for this tendency is strong and frequently dictates the reaction conditions allowable for retention of the original monocyclic ring.

(a) Intramolecular Aldol Condensation. This reaction occurs readily under acidic or basic conditions and is a major complication in working with the diketones. However, the reaction has synthetic utility, since the bicyclic products represent a new ring system.[5] For preparative purposes, the reaction is performed in refluxing benzene containing a trace of *p*-toluenesulfonic acid, with continuous water removal (**3**, 87%). For the condensation



1, R = CH_3
2, R = OH

3, R = CH_3
4, R = OH

with phosphinic acid **2**, the reaction is self-catalyzed (93% on refluxing in benzene). Indeed, the tendency for **2** to cyclize is so great that it occurs even in the solid state; a sample standing at room temperature for 1 month was found to be nearly completely converted to **4**.

The structure of the aldol products was readily assigned from their spectral features. Thus, the α,β-unsaturated carbonyl system was revealed by their ^{13}C NMR spectra (Table I), which possessed signals for two sp^2 carbons, one of which had the distinct deshielding of the β-C (e.g., δ 154.9 for **3**). The single carbonyl carbon was also shifted

(1) Taken in part from the Doctoral Dissertation of E.D.M., Duke University, 1980. Supported by Grant CHE77-17876 from the National Science Foundation.

(2) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Am. Chem. Soc.*, in press.

(3) Middlemas, E. D.; Quin, L. D. *J. Am. Chem. Soc.* **1980**, *102*, 4838.

(4) Anastassiou, A. G.; Kasmai, H. S. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1978; Vol. 23, pp 55–102.

(5) For a preliminary communication, see: Quin, L. D.; Middlemas, E. D. *J. Am. Chem. Soc.* **1977**, *99*, 8370.

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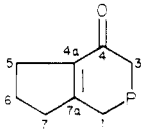
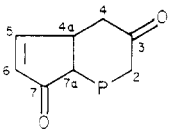
Table I. ^{13}C NMR Spectral[a] Data for Bicyclic Reaction Products



3, 4



7, 8

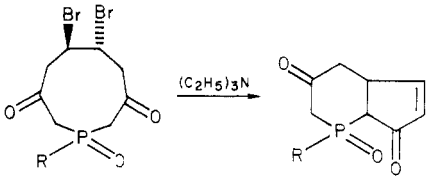
compd	shift, δ							
	C-1 or C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-7a
3[b]	31.1 (63.5)	42.8 (69.3)[c]	189.4 (1.9)	139.8 (30.5)	30.5	20.9	40.6 (25.4)[c]	154.9 (1.9)
4	30.0 (90.8)	42.0 (81.1)[c]	188.9	140.0	30.7	20.9	40.3 (12.7)[c]	154.7
7	42.7 (61.5)	200.7 (5.9)[c]	39.6	43.2 (4.9)	164.9 (1.9)	134.8	200.9[c]	48.1 (62.5)

[a] In $CDCl_3$. Values in parentheses are J_{PC} values (in hertz). [b] P-CH_3, δ 14.0 (J_{PC} = 70.3 Hz). [c] May be reversed.

to the higher field position (**3**, δ 188.9) expected for conjugation. Other signals on the ^{13}C NMR spectra were easily assigned on the basis of the bicyclic structure.

The aldol condensation occurs so easily that it frequently is a complication when some simple ketone reactions are attempted under acidic or basic conditions. Thus, attempts to perform the following reactions, using diketone **1** as the example, led only or primarily to the aldol product. (1) Grignard addition: With 2 mol of C_6H_5MgBr in ether, 1 mol of the diketone gave the aldol compound **3** as the only product after acidification to neutralize the initially formed enolate. No other Grignard additions have been attempted, but it seems likely that the aldol condensation will be a persistent problem. (2) Ketalization: With triethyl orthoformate and an acid catalyst, the only product was again that from the aldol reaction. (3) Catalyzed silylation: Trimethylchlorosilane in the presence of either pyridine or $TiCl_4$ as catalysts gave only the aldol product.

(b) Intramolecular Alkylation. The dibromophosphonanediones **5** and **6** were prepared in our earlier



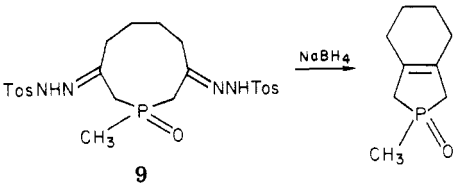
5, R = C_6H_5
6, R = CH_3

7, R = C_6H_5
8, R = CH_3

work[2] with the expectation that dehydrobromination would provide a practical way to introduce double bonds into the ring. When attempted with **5** by using triethylamine in acetone at room temperature, the only product (66%) proved to be bromine-free but had a bicyclic structure. The presence of only one double bond, clearly α,β to carbonyl from the usual ^1H and ^{13}C NMR (Table I) spectral features, suggested that a nucleophilic displacement must have accompanied a dehydrobromination. An anionic center at C-2, created with the triethylamine, could act as the nucleophile, and structure **7** would result. This structure is compatible with all of the spectral features of the reaction product, and the assignment seems firm. Dibromo compound **6** gave a product (**8**) with similar spectral properties, but it could not be adequately purified for analysis.

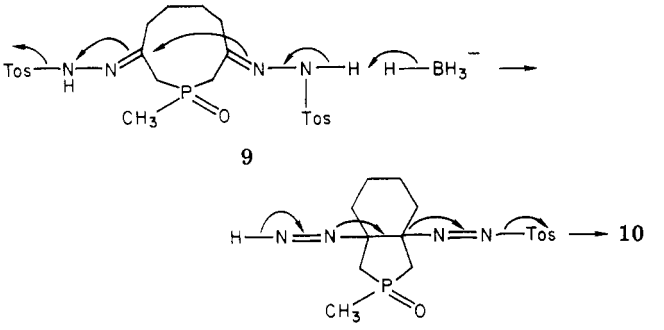
Just as in the case of the aldol condensation products, the bicyclic compounds such as **7** represent new heterocyclic systems which may well have synthetic utility of their own. These possibilities remain to be explored.

(c) Intramolecular Reduction. Reduction of tosylhydrazones with $NaBH_4$ to methylene groups is generally a reliable process and was applied to bis(tosylhydrazone) **9** (vide infra) in an attempt to prepare the parent phos-



9 10

phonane ring, presently unknown. However, the only product, isolated in 47.7% yield, was established to have bicyclic structure **10**. This compound is, in fact, the precursor of the phosphonanedione **1** (by ozonolysis[2]) and was easily identified by spectroscopic comparison. The intramolecular reduction can be accounted for on the basis of the initial formation of a hydrazone anion by the action of BH_4^-. Transannular attack on the other hydrazone to form a diimide[6] then occurs, followed by loss of nitrogen.



9

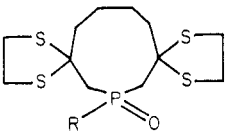
10

A similar transannular reaction has been reported to occur with the dihydrazone of 7*H*-1,2:3,4-dibenzocyclononadiene-5,9-dione under Wolf–Kishner conditions.[7]

Carbonyl Properties. A few reactions of the carbonyl group have been effected without the occurrence of transannular interactions. Both (2,4-dinitrophenyl)hydrazine and *p*-toluenesulfonylhydrazine formed dihydrazone derivatives in good yield (e.g., **9**, 74%). The bis(dithioketals) **11** and **12** were formed from ethanedithiol and BF_3 etherate as catalyst. The dithioketals will be shown to be useful precursors of the parent phosphonanes.

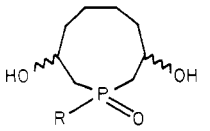
Sodium borohydride in ethanol, lithium tri-*tert*-butoxyaluminum hydride in tetrahydrofuran, or hydrogen over Raney nickel proved to be effective for the reduction of the two carbonyls to form the diols. For the monocyclic

(6) House, H. O. "Modern Synthetic Reactions", 3rd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 231–232.
(7) Rabinovitz, M.; Willner, I.; Gamliel, A.; Gazit, A. *Tetrahedron* 1979, *35*, 667.



11, R = CH_3; 56%
12, R = C_6H_5; 32%

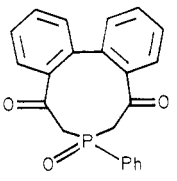
diketone 1, reduction gave a mixture of the three possible diastereomeric forms of **13a** (one *dl* and two meso). The



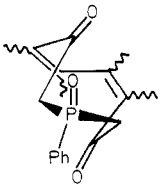
13a, R = CH_3
b, R = C_6H_5

isomers were detected by the presence of three ^{31}P NMR signals (δ 42.6, 47.5, 48.7) and by the numerous, poorly resolved ^{13}C NMR signals in the COH (δ 64–68) region. Similarly, the *P*-phenyl derivative **13b** was prepared by the reduction of the corresponding phosphonanedione[2] and gave ^{31}P NMR signals at δ 35.8, 39.1, and 40.2. Both diols were extremely hygroscopic and noncrystallizable; satisfactory elemental analyses could not be obtained.

From the previously reported[2] dibenzophosphonanedione **14** was formed a single crystalline diol [**15**, $\delta(^{31}P)$ 29.9] on $NaBH_4$ reduction. The dione is known[2] to exist in a single unsymmetrical conformation in solution due to the rigidity of this twisted molecule. Conformation **14a**, with anti C=O groups, is clearly the unsymmetrical

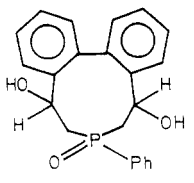


14

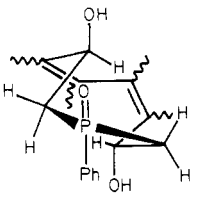


14a

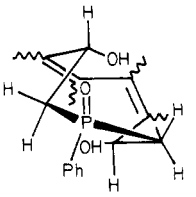
form of lowest energy. The rigidity and twisting of the nine-membered ring imposed by fusion of two benzo groups will be a property of all derivatives containing this structural feature. The diol formed from **14** retains the nonequivalence of comparable carbons characteristic of the ketone; thus, there are two signals (doublets, each with J = 2.0 Hz) for the carbinol carbons (δ 62.6 and 65.0). Conformation **15a** (or the more crowded invertomer **15b**)



15



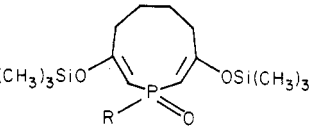
15a



15b

may therefore be proposed for the diol, where the anti arrangement is preserved and each carbinol is in a different environment due to their relations to the two substituents on phosphorus. That a *single* diol is formed suggests that the hydride transfer occurs at each carbonyl from the same direction (i.e., both from the "outside" or from the "inside" faces of **14a**). If attack on the carbonyls could occur with similar ease from either face, one might expect a mixture of the diastereomeric forms to result. Conformation **15a** results from hydride attack at both "inside" faces; attack at both "outside" faces could produce **15b**, or ring inversion could ensue to produce **15a**. Form **15a** seems to have some validity on the basis of the chemistry of the product (dehydration; vide infra) and is certainly less crowded than the conformer with both OH groups projecting inward. It is also indicated from a 250-MHz ^1H NMR study in Me_2SO-d_6, which clearly revealed that the protons on the carbinol carbons were experiencing different shielding effects ($\Delta\delta$ = 0.32 ppm). Structure **15a** would more readily account for the shielding difference than would **15b**, since in the former, one carbinol proton is close to the (deshielding) phosphoryl oxygen. In **15b**, neither carbinol proton is close to the phosphoryl oxygen. Another feature of the ^1H NMR spectrum is the pronounced deshielding of one of the four α-CH_2 protons. The signal (δ 3.10) stands out clearly from the three-hydrogen multiplet (δ 2.00–3.00) for the remainder. A model of **15a** shows that a conformation could easily be adopted where the four methylene protons are nonequivalent, with one significantly closer to phosphoryl oxygen than the others.

Enolic character is noticeable in the phosphonanediones, as evidenced by the complete exchange of the four protons of **1** on the α-carbons simply on dissolving the compound in excess neutral D_2O. Although the NMR spectra of the diketones do not possess signals arising from an enolic form, the UV spectrum of **1** may be indicative of a contribution of a small concentration of this form. Thus, were structure **1** fully correct for the diketone, the only UV absorption would occur from n $\rightarrow$ π^* excitation of the carbonyls, and indeed absorption at 292 nm ($\epsilon \sim 100$) can be attributed to this excitation. However, there is a stronger absorption at 250 nm (apparent ϵ 700); this could be associated with $\pi \rightarrow \pi^*$ excitation of an enol, since enols of cyclic β-diketones have UV maxima in this region [e.g., dimedon, λ_{max} 255 nm (ϵ 17 000[8])]. Other evidence for enolic character came from the ease of silylation; the bis enol form was trapped successfully with the silylating agent bis(trimethylsilyl)acetamide under neutral conditions at room temperature. Two products (**16** and **17**) of this type



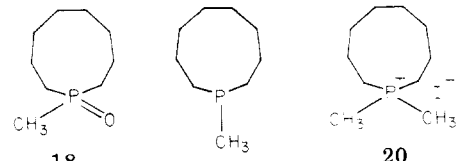
16, R = CH_3
17, R = C_6H_5

have been isolated and spectrally characterized. These compounds hydrolyze with great ease (exposure to water at room temperature) back to the diketones, and successful elemental analyses have not been obtained. However, spectral analysis leaves no doubt that the structures are correct, with both double bonds α,β to phosphoryl. Thus, the ^{13}C NMR spectrum for **16** contained only two signals for sp^2 carbons, in the positions expected for an enolic derivative. The upfield β-carbon of the enol ether is positioned next to phosphorus and thus has the expected large one-bond ^{31}P–^{13}C coupling (δ 100.2, $^1J_{PC}$ = 119.3 Hz). Other features of the spectrum were consistent with the structure, and the ^1H NMR spectrum provided further support by showing the expected upfield doublet for the proton on the enolic β-carbon (δ 4.68, $^3J_{PH}$ = 19 Hz).

Synthesis and Properties of a Phosphonane. The unsubstituted parent ring of the phosphonane system has never before been prepared. The bis(dithioketals), however, are useful precursors of this system. Thus, **11** was

(8) Bladon, P. In "Physical Methods in Organic Chemistry"; Schwarz, J. C. P., Ed.; Holden-Day: San Francisco, 1964; pp 142–143.

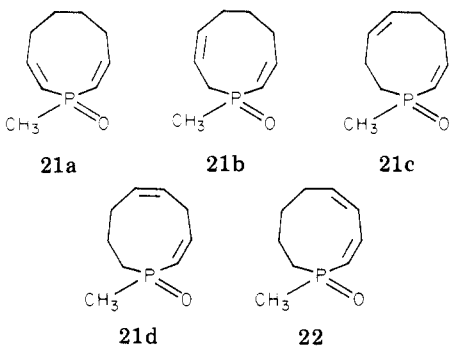
reductively desulfurized with Raney nickel in refluxing ethanol to afford phosphonane **18** in 51% yield. The oxygen was then removed with phenylsilane to give a crude sample of the phosphine **19**, which was readily quaternized with methyl iodide to the recrystallizable salt **20**. The ^{31}P shift for the phosphonane oxide **18** is distinctly downfield of the value for the diketo derivative **1** (δ 32.6). Conformational preferences no doubt are different for the two rings and may contribute to this difference. Also, the oxygens of the carbonyl groups are γ to phosphorus and could cause shielding from this well-known steric influence. It is also of interest to compare this value to those of the smaller rings, but data are available in the P–CH_3 series only for a six-membered model (1,4-dimethylphosphorinane 1-oxide:[9] cis, δ 40.9; trans, δ 38.7), where a distinct shielding in the smaller ring is detected. Similarly, the phosphine **19** is deshielded relative to the corresponding six-membered ring (1-methylphosphorinane,[10] δ −53.7). This ring size effect is probably caused by the conformational differences. Thus, in the phosphorinanes, the dihedral angle relating the γ-carbon to phosphorus is restricted to about 55–60° by the chair shape (e.g., 58° in 1-phenyl-4,4-dimethoxyphosphorinane[11]), while the greater flexibility of the larger rings can allow dihedral angles to exceed this range. As the angle increases, steric compression at P is lessened, and shielding is diminished.



18 $\delta(^{31}P)$ 48.9 **19** $\delta(^{31}P)$ −33.8 **20** $\delta(^{31}P)$ 31.9

The conformations adopted by the dioxo derivatives have been discussed in another paper,[2] where the twist chair–chair shape was seen by X-ray diffraction analysis to be common. The ^{13}C NMR spectrum of the parent phosphonane oxide **18** possesses a difference that is suggestive of a conformational modification. The three-bond coupling of ^{31}P to the γ-carbon is nil in the diketones, consistent with a dihedral angle relation of about 90°,[12] but coupling is present (though small, 3.7 Hz) in the parent **18**. This suggests that a different dihedral angle may prevail in the parent, and hence a modified conformation, possibly other than a twist chair–chair, may be present. Nine-membered rings, of course, have numerous conformational possibilities.[13] Another sterically related difference occurs at the carbons α to phosphorus; the one-bond ^{31}P–^{13}C coupling constants are distinctly smaller in the diketo compounds (about 55 Hz[2]) than in the parent **18** (65.3 Hz) and indeed in parents of the entire series from five to nine ring members (~60–65 Hz[3]). The importance of this observation is not clear; bond angles (and hence hybridization) will differ drastically over the five to nine ring size of the parents, yet $^1J_{PC}$ is hybridization sensitive and remains nearly constant. A bond angle difference in the diketone, therefore, does not seem to be a likely explanation for its diminished $^1J_{PC}$ value.

Unsaturated Phosphonane Derivatives from Diol Dehydrations. The mixture of diastereomeric diols (**13a**) prepared from reduction of diketone **1** was considered as a potential precursor of the unsaturated system **21**. Some common dehydrating conditions (e.g., heating with *p*-toluenesulfonic acid or with H_2SO_4) failed to give a recognizable product, but treatment with $POCl_3$–pyridine at room temperature supplied an oil that was comprised of a single compound (one ^{31}P NMR signal, δ 36.4; one PMe proton doublet, δ 1.58). The elemental analysis showed that a diene had been formed; the ring structure was maintained, since hydrogenation provided the phosphonane oxide **18**. However, the spectral data indicate that the expected diene **21a** was not formed. Thus, there were four different signals for sp^2 carbons in the ^{13}C NMR spectrum, only one of which had the very large coupling expected for direct attachment to P (δ 126.6, J = 90.3 Hz). The β-carbon in an α,β-unsaturated phosphine oxide is strongly deshielded;[14] in the spectrum of this diene, the only signal (δ 150.6) in the proper downfield region showed no coupling to ^{31}P. Unsaturated β-carbons generally show substantial coupling[14] (20–30 Hz). This would therefore eliminate alternative structures **21b–d** and leave **22** as the best representation. The downfield signal is then accounted for on the basis of vinylogous transmission of the deshielding effect of the phosphoryl group, causing the δ-carbon in this conjugated system to be deshielded. Since it is four-bonds removed from ^{31}P, coupling should be small or not observable, as is the case. The UV spectrum supports this assignment; absorption occurs at 212 nm (ϵ 2750), which is similar to that of a carbocyclic analogue [*cis,trans*-1,3-cyclononadiene,[15] λ_{max} 219 nm (ϵ 2500)]. Conjugation of double bonds with phosphoryl groups would cause little change in UV absorption.[16] It is not yet confirmed, however, that the double bonds in **22** are cis and trans. The UV maximum observed would not originate from any of structures **21a–d**; their isolated double bonds should be associated with absorption below 200 nm. Structure **22** is also reasonable from a mechanistic standpoint; it can be accounted for by an intramolecular 1,5 hydride shift, a common occurrence in the larger carbocyclic rings.[17]



21a **21b** **21c** **21d** **22**

The single diol **15** in the dibenzo series, on the other hand, was smoothly dehydrated by the $POCl_3$–pyridine method (100 °C for 1 H) to give a crystalline solid (**23**) in 58% yield. Dehydration can only occur to install both double bonds α,β to phosphoryl, but in rings of this size both cis and trans geometries are possible and are known for heteronins[4] as well as for the related 1,2:7,8-dibenzocyclononatetraene.[18,19] The product was homogeneous

(9) Quin, L. D.; Lee, S. O. *J. Org. Chem.* **1978**, *43*, 1424.
(10) Featherman, S. I.; Quin, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 4349.
(11) McPhail, A. T.; Breen, J. J.; Somers, J. H.; Steele, J. C. H., Jr.; Quin, L. D. *Chem. Commun.* **1971**, 1020.
(12) Quin, L. D.; Gallagher, M. J.; Cunkle, G. T.; Chesnut, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 3136.
(13) Hendrickson, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 4854.
(14) Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981; p 297.
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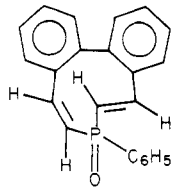

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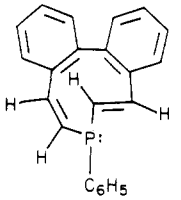
(one ^{31}P signal, δ 17.2), and ^{1}H NMR indicated that indeed a trans double bond, as well as a cis, was formed. The spectrum showed two sets of signals for the α-CH (the more downfield β-CH signals were entangled with the aromatic signals), which were interpreted as two doublets with an important difference in the vicinal H–H coupling constants. A large constant (14 Hz) was suggestive of trans coupling, while a small constant (4 Hz) suggested cis coupling. The two-bond P–H coupling constants also differed (24 and 14 Hz, respectively), but in phosphoryl compounds (unlike phosphines) there is no reliable stereodependence of $^{2}J_{PH}$. The dehydration product of diol **15** is therefore assigned cis,trans structure **23**.

Formation of a trans-double bond from diol **15** is perfectly in keeping with the conformation **15a** proposed for this compound, for there is present the antiperiplanar OH–H relation needed for an E2 elimination as involved in $POCl_3$–pyridine dehydration, an elimination that installs the trans double bond. The second double bond is required to have cis geometry since a second trans double bond is prohibited by a large strain energy barrier. It is this chemical property of the diol which supports the assignment of conformation **15a**; this structure does not allow dehydration to the cis,cis isomer.

Compound **23** is the first known phosphonin oxide. It is a stable solid, showing no tendency to polymerize, a property no doubt provided by the presence of the benzo groups. The molecule is badly distorted from planarity, as suggested by models. A consequence of the severe twisting is that π orbitals of the benzene rings do not significantly interact with each other or with the double bonds. This is revealed by the UV spectrum, which is totally unlike that expected for a conjugated system of eight π centers or even for isolated interactions of the biphenyl or styrene types. The spectrum consisted only of an intense band at 202 nm (ϵ 46 000) with a shoulder at 259 nm (ϵ 7600).

The ^{31}P shift of δ 17.2 is also of interest, since it is significantly upfield from the phosphonanes with sp^3 carbons at the α-positions. This same effect seems to prevail in five-membered counterparts, although the only unsaturated model to consider is 1,2,5-triphenylphosphole (other phosphole oxides dimerize on formation). Here the ^{31}P shift was found to be δ 41.5; the best saturated model for comparison is 3-methyl-1-phenylphospholane 1-oxide,[20] δ 56. Admittedly this is a poor model, since the substituents differ, but no better data are available. Occupancy of the phosphorus d orbitals by the π electrons of the adjacent double bonds could account for this shielding,[21] but conformational changes also are associated with the installation of the double bonds and cannot be ignored. In any event, double unsaturation about phosphoryl in cyclic systems now seems to be characterized by a substantial shielding and makes ^{31}P NMR a useful technique for confirming this structural feature.

With a stable phosphonin oxide in hand, an approach to the corresponding 10-π-electron phosphonin **24** then



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became possible. This was smoothly accomplished with $HSiCl_3$–pyridine in refluxing benzene, giving the phosphonin as a stable solid. Again, trans geometry is indicated by the ^{1}H NMR data for the α-CH, providing support to the assignment of this feature in the oxide. The chemical shifts of these protons are of special significance, for they could reveal the presence of a ring current through any unusual deshielding of the outer α-proton. In fact, the shifts of both protons are similar (δ 5.67 and 5.97) and do not indicate the presence of a ring current; in the phosphole system, shifts of δ 6.5–7.5 are common for α-CH.[22] Furthermore, the UV spectrum is virtually unchanged from that of the oxide, again showing that no special orbital interactions are allowed. The severe twisting from planarity imposed by the benzo groups is certainly a preventive factor in the attainment of electron delocalization, and it is quite obvious that the matter of phosphonin aromaticity will have to await synthesis of simpler structures before it can be evaluated. The same situation prevails in the thionin field; the parent monocyclic system has never been prepared, and *cis,cis*-dibenzo[*d,f*]thionin possesses no aromatic character.[23] The severe twisting in the phosphonin is detectable from an NMR coupling feature; two-bond ^{31}P–^{1}H coupling at sp^3 carbons in phosphines is only large (20–25 Hz) when the lone-pair orbital on P is close to the coupled proton and is at a maximum in the eclipsed structure. $^{2}J_{PH}$ diminishes rapidly as the dihedral angle holding the lone pair orbital and the coupled proton becomes large, and when this angle reaches about 90° or more, coupling of only a few hertz is common.[24] The phosphorus atom in **24** has two quite different coupling constants (35 and 11 Hz) to the α-CH bonds. A twisted conformation such as **24a** would account for this result; H is close to the lone pair orbital ($\phi \approx 30°$) and gives the large coupling quite common for 2-phospholenes (e.g., 42 Hz in 1,3-dimethyl-2-phospholene[25]) with this same ϕ, while H_b is more remote ($\phi \approx 120°$) and consequently weakly coupled.

The ^{31}P chemical shift (δ −24.7) also revealed no special conjugative interaction; phospholes are characterized by substantial downfield shifting relative to saturated counterparts, but the phosphonin value observed here is in the same range as that for the saturated phosphonane **19** (δ −33.8, recognizing that the replacement on P of methyl by phenyl generally causes downfield shifting of 10–15 ppm).

The phosphonin readily formed a crystalline methiodide (**25**). The positive character of the P more strongly de-

(19) Attempts[7] to prepare 1,2:3,4-dibenzocyclononatetraene by dehydration of the diol analogous to **15** gave only a transannular interaction, generating a phenanthrene. There was no indication of the occurrence of this reaction in the dehydration of **15**.

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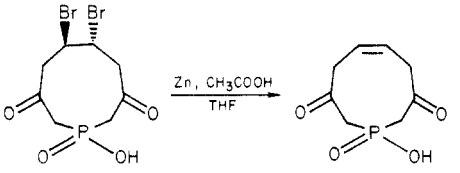
shields protons on the α,β double bond than does phosphoryl, and this effect shifts the β-CH signal of the trans double bond clear of the aromatic signals for the first time in this series of compounds. However, the α-CH signal then became obscured by the aromatic signals. The UV spectrum of **25** resembled that of the phosphine and the oxide; this remarkable similarity throughout the series of three quite different phosphonin derivatives attests again to the lack of any special conjugative effects for the important P(III) form that could be attributed to heteronin-type aromaticity.

Unsaturated Phosphonane Derivatives from Debromination of *vic*-Dibromides. Treatment of the dibromophosphonanediones with zinc should lead to their debromination and installation of a 5,6 double bond. This reaction has been found to work extremely well with the dibromophosphinic acid **26** reported previously;[2] there was



26 27

obtained the unsaturated compound **27** as an easily crystallized, stable solid in 89% yield. The ^{13}C NMR spectrum provided conclusive proof of the structure. The conformation of the ring is symmetrical (as in the corresponding epoxide[2]), and only four signals were present, one being in the expected sp^2 region (δ 128.3). The multiple functionality of this type of compound should make it of value as a precursor to still other phosphonane or phosphonin derivatives, a possibility which is presently being investigated.

Experimental Section[26]

Aldol Condensation of 1 to 1,2,3,5,6,7-Hexahydro-2-methyl-4*H*-cyclopenta[*c*]phosphorin-4-one 2-Oxide (3). With Acid. A solution of dione 1 (2.0 g, 9.9 mmol) in benzene (100 mL) was refluxed overnight with a trace of *p*-toluenesulfonic acid. A Dean–Stark separator was used to collect the water formed during the reaction. The reaction mixture was concentrated to give a brown oily residue which, on trituration with pentane, solidified to give 1.6 g (87%) of **3** as a cream-colored solid, mp 92–95 °C. Recrystallization from benzene–ligroin (95–105 °C) gave white crystals: mp 97–98 °C; ^1H NMR ($CDCl_3$) δ 1.50 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 1.53–2.23 (m, CH_2), 2.23–3.27 (m, allylic CH_2 and $CH_2C{=}O$); ^{31}P NMR ($CDCl_3$) δ 42.3; IR ($CHCl_3$) 1650 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_9H_{13}O_2P$: C, 58.69; H, 7.11; P, 16.82. Found: C, 58.47; H, 7.18; P, 16.96.

With a Grignard Reagent. To a suspension of **3** (1.0 g, 5.0 mmol) in dry tetrahydrofuran (15 mL) was added a solution of phenylmagnesium bromide (11.0 mmol) in tetrahydrofuran (15 mL). The reaction mixture was allowed to stir overnight, after which a saturated NH_4Cl solution (30 mL) and ether (50 mL) were added. The layers were separated, and the aqueous layer was extracted with four 50-mL portions of $CHCl_3$. The organic solutions were combined, dried, and concentrated to give a yellow oil which had spectral properties identical with those of aldol product **3**.

With Pyridine–Chlorotrimethylsilane. To a mixture of chlorotrimethylsilane (10.9 g, 0.10 mol) and triethylamine (20.2 g, 0.20 mol) was added phosphonanedione 1 (1.0 g, 5.0 mmol). The resulting mixture was stirred at room temperature for 24 h and then poured slowly into an ice–cold, saturated $NaHCO_3$ solution (50 mL). The resulting mixture was extracted with chloroform (four 50-mL portions), and the chloroform extract was washed with 1% NaOH solution (20 mL), dried ($MgSO_4$), and concentrated to give a brown oil. The proton NMR of this residue was identical with that of aldol product **3**.

1,2,3,5,6,7-Hexahydro-2-hydroxy-4*H*-cyclopentano[*c*]phosphorin-4-one 2-Oxide (4). A suspension of phosphonanedione **2** (2.0 g, 9.8 mmol) in benzene (100 mL) was refluxed for 2.5 h, using a Dean–Stark trap to remove the water formed during the reaction. As the reaction progressed all solids dissolved. The reaction mixture was concentrated to give 1.7 g (93%) of **4** as a fine, white solid, mp 149–150 °C. Recrystallization from acetone gave white needles: mp 150–152 °C; ^1H NMR ($CDCl_3$) δ 1.86 (br q, $^3J_{HH}$ = 7 Hz, CH_2), 2.28–3.28 (m, allylic CH_2), 2.95 (d, $^2J_{PH}$ = 18 Hz, $PCH_2C{=}O$), 9.92 (br s, OH); ^{31}P NMR ($CDCl_3$) δ 46.8; ^{13}C NMR, Table I; IR ($CDCl_3$) 1610 ($\nu_{C=C}$), 1650 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_8H_{11}O_3P$: C, 51.62; H, 5.96; P, 16.64. Found: C, 51.79; H, 5.93; P, 16.76.

Intramolecular Alkylation of 1-Phenyl-5,6-dibromo-3,8-phosphonanedione 1-Oxide (5). To a suspension of **5** (2.0 g, 4.7 mmol) in acetone (50 mL) was added triethylamine (50 mL). All solids immediately dissolved, and then triethylamine hydrobromide precipitated from solution. The dark green reaction mixture was stirred for 1 h at room temperature, filtered, and concentrated to a volume of approximately 10 mL on a rotary evaporator. Column chromatography (silica gel, acetone) gave 800 mg (66%) of bicyclic compound **7** as a tan solid, mp 136–137 °C dec. Recrystallization from acetone–ligroin gave white needles: mp 151–153 °C dec; ^1H NMR ($CDCl_3$) δ 2.70–3.92 (complex m, CH_2), 6.35 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, $HC{=}CHC{=}O$), 7.37–8.12 (complex m, phenyl H and $HC{=}CHC{=}O$); ^{31}P NMR ($CDCl_3$) δ 51.1; ^{13}C NMR, Table I; IR(KBr) 1590 ($\nu_{C=C}$), 1690 cm^{-1} ($\nu_{C=C}$). Anal. Calcd for $C_{14}H_{13}O_3P$: C, 64.62; H, 5.03; P, 11.90. Found: C, 64.61; H, 5.15; P, 11.76.

1-Methyl-3,8-phosphonanedione 1-Oxide Bis(tosylhydrazone) (9). To a solution of dione 1 (1.0 g, 5.0 mmol) in methanol (15 mL) was added *p*-toluenesulfonylhydrazine (1.9 g, 10.0 mmol), and the mixture then refluxed for 15 min. During this time, copious quantities of a fine, white solid precipitated from the reaction mixture. The reaction mixture was cooled and the solid filtered off to give 2.0 g (74%) of **9** as a white solid, mp 153–154 °C dec. Recrystallization from a large volume of methanol gave white crystals, mp 158–159 °C. Compound **9** was poorly soluble in all common solvents, and NMR spectral data could not be obtained. The infrared spectrum (KBr) showed no carbonyl absorption. Anal. Calcd for $C_{23}H_{31}N_4O_5PS_2$: C, 51.29; H, 5.80. Found: C, 51.18; H, 5.86.

Attempted Reduction of 1-Methyl-3,8-phosphonanedione 1-Oxide Bis(tosylhydrazone) (9). To a suspension of **9** (2.0 g, 3.7 mmol) in methanol (100 mL) was added sodium borohydride (5.6 g, 0.15 mol) in small portions over a 1-h period. As the borohydride was added, the reaction mixture foamed extensively, and heat was evolved. The resulting solution was refluxed overnight. The reaction mixture was then concentrated to give a white solid. A 1% NaOH solution (25 mL) followed by water (75 mL) was added to dissolve the residue, and the solution which resulted was extracted continuously with chloroform for 24 h. The chloroform extract was dried ($MgSO_4$) and concentrated to give a brown oil. Kugelrohr distillation [120 °C (0.02 mm)] gave 300 mg of a yellow oil, which was identified as the bicyclic phospholene oxide **10** (47.7%) by comparison of its ^{13}C and ^1H NMR spectra to those previously obtained[2] for this compound.

1-Methyl-3,8-phosphonanedione 1-Oxide Bis(2,4-dinitrophenylhydrazone). A solution of (2,4-dinitrophenyl)hydrazine (0.8 g, 4.0 mmol) and concentrated sulfuric acid (4 mL) in 6 mL

(26) Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Proton NMR spectra were obtained on a JEOL MH-100 spectrometer at 100 MHz or on either a Varian EM-360 or T-60 spectrometer at 60 MHz. The 250-MHz spectrum of **15** was recorded with a Bruker WM-250 spectrometer. Carbon-13 FT NMR spectra were taken on a JEOL FX-60 spectrometer at 15 MHz or on a Bruker HFX-10 spectrometer at 22.6 MHz, utilizing an internal deuterium lock, and are proton noise decoupled. Proton and ^{13}C NMR chemical shifts are expressed in parts per million (δ) downfield from internal tetramethylsilane. Phosphorus-31 FT NMR spectra (proton noise decoupled) were obtained with the Bruker HFX-10 at 36.43 MHz. ^{31}P chemical shifts are expressed in parts per million relative to external 85% H_3PO_4, with positive shifts downfield and negative shifts upfield. Infrared spectra were run on either a Perkin-Elmer 137 or 297 spectrophotometer. Ultraviolet spectra were obtained with a Perkin-Elmer 552 spectrophotometer, while mass spectra were run at the Research Triangle Mass Spectrometry Center on an AEI MS-903 spectrometer. Analyses were performed by commercial laboratories.

of water was added to a mixture of dione **1** (0.5 g, 2.5 mmol) in 25 mL of ethanol. After about 1 min a bright, insoluble orange precipitate (0.65 g, 60%) formed; mp 181–182 °C. Anal. Calcd for $C_{21}H_{23}N_8O_9P$: C, 44.85; H, 4.12; N, 19.92. Found: C, 44.89; H, 3.95; N, 20.17.

1-Methyl-3,8-phosphonanedione 1-Oxide Bis(ethylene thioketal) (11). To a suspension of phosphonanedione oxide **1** (0.5 g, 2.5 mmol) in ethanedithiol (0.5 mL) was added boron trifluoride etherate (0.5 mL), and the resulting mixture was warmed until all solids dissolved. After about 10 min, a solid began to precipitate. The reaction mixture was allowed to stand for 3 days at room temperature. Glacial acetic acid (5 mL) was added to break up the solid, which was filtered off and washed with two 10-mL portions of glacial acetic acid to give 0.5 g (56%) of thioketal **11** as a white solid, mp 213–217 °C dec. Recrystallization from acetone gave needles, mp 263–266 °C dec. The IR spectrum (Nujol) contained no C=O absorption: ^{13}C NMR ($CDCl_3$) δ 21.6 (J_{PC} = 69.0 Hz, P-CH_3), 25.13 (C-5,6), 38.8, 39.3, 40.0, 48.0 (J_{PC} = 58.6 Hz, C-2,9), 67.7 (J_{PC} = 8.79 Hz, C-3,8); ^{31}P NMR ($CDCl_3$) δ 63.8. Anal. Calcd for $C_{13}H_{23}OPS_4$: C, 44.04; H, 6.54; P, 8.74; S, 36.17. Found: C, 43.69; H, 6.71; P, 8.62; S, 35.89.

1-Phenyl-3,8-phosphonanedione 1-Oxide Bis(ethylene thioketal) (12). By use of a procedure similar to that described above, a reaction mixture containing dione **2** (1.0 g, 3.8 mmol), ethanedithiol (1.0 mL), and boron trifluoride etherate (1.0 mL) was warmed until all solids had dissolved. After 30 min at room temperature, no precipitate had formed, and glacial acetic acid (5.0 mL) was added to induce crystallization. Solids slowly began to precipitate, and after 9 days at room temperature the reaction mixture was diluted with 15 mL of acetic acid. The solid was filtered off and washed with two 10-mL portions of acetic acid to give 0.5 g (32%) of thioketal **12** as a white solid, mp 212–225 °C dec. Recrystallization from methanol gave needles, mp 285–286 °C dec. Because of low solubility of **12**, no spectral data were obtained. Anal. Calcd for $C_{18}H_{25}OPS_4$: C, 51.89; H, 6.05; P, 7.43; S, 30.79. Found: C, 51.90; H, 6.20; P, 7.50; S, 30.79.

3,8-Bis(trimethylsiloxy)-1-methyl-4,5,6,7-tetrahydro-1*H*-phosphonin 1-Oxide (16). A suspension of diketone **1** (1.0 g, 5.0 mmol) in bis(trimethylsilyl)acetamide (5.0 mL) was stirred for 24 h at room temperature. The reaction mixture was concentrated under vacuum to give a yellow oil which, by ^{13}C and ^1H NMR, appeared to be the bis enol ether **16** containing some monosilylated acetamide. Because of the extreme susceptibility of **16** to hydrolysis, no further purification could be accomplished: ^1H NMR ($CDCl_3$) δ 0.22 (s, $SiCH_3$), 1.42 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 1.77 (m, CH_2), 4.68 (d, J_{PH} = 19 Hz, PCH=C); ^{31}P NMR ($CDCl_3$) δ 20.3; ^{13}C NMR ($CDCl_3$) δ 0.9 ($SiCH_3$), 17.9 (J_{PC} = 69.0, PCH_3), 24.8 (C-5,6), 29.3 (C-4,7), 100.2 (J_{PC} = 111.8, C-2,9), 169.5 (J_{PC} = 12.7, C-3,8).

3,8-Bis(trimethylsiloxy)-1-phenyl-4,5,6,7-tetrahydro-1*H*-phosphonin 1-Oxide (17). To a suspension of phosphonanedione **2** (1.5 g, 5.7 mmol) in dry benzene (7.0 mL) was added bis(trimethylsilyl)trifluoroacetamide (2.9 g, 11.4 mmol). The resulting mixture was stirred overnight at room temperature, during which time all solids dissolved. The reaction mixture was concentrated under vacuum (0.5 mm) to give a pale yellow oil, which slowly solidified to the desired enol ether **17** (containing some monosilylated trifluoroacetamide) as a white water-sensitive solid: ^1H NMR ($CDCl_3$) δ 0.22 (s, $SiCH_3$), 1.54–2.50 (m, CH_2), 4.98 (d, $^2J_{PH}$ = 16 Hz, PCH=C), 7.22–8.22 (complex m, phenyl H); ^{31}P NMR ($CDCl_3$) δ 16.1; IR (melt) 1590 cm^{-1} ($\nu_{C=C}$); ^{13}C NMR δ 0.0 ($SiCH_3$), 25.3 (C-5,6), 30.6 (C-4,7), 100.8 (J_{PC} = 115.2 Hz, C-2,9), 170.3 (J_{PC} = 13.7, C-3,8). Since **17** could not be adequately purified, analysis was not performed.

1-Methylphosphonane 1-Oxide (18). A suspension of freshly prepared Raney nickel (20 g) and bis(thioketal) **11** (2.0 g, 5.6 mmol) in absolute ethanol (150 mL) was refluxed overnight. The Raney nickel was removed by filtration, and the filtrate was concentrated to give a wet solid. Kugelrohr distillation [108 °C (0.2 mm)] gave 500 mg (51%) of phosphonane oxide **18** as a hygroscopic white solid. Sublimation gave a compound melting at 117–120 °C: ^1H NMR ($CDCl_3$) δ 1.12–2.55 (m, containing a sharp singlet at 1.32, CH_2 and PCH_3); ^{31}P NMR ($CDCl_3$) δ 48.9; mass spectrum, *m/e* 174.1175 (calcd for $C_9H_{19}OP$, 174.1173); ^{13}C NMR ($CDCl_3$) δ 16.4 (J_{PC} = 67.1 Hz, PCH_3), 18.3 (J_{PC} = 3.7, C-3,8), 22.9 (C-5,6), 26.9 (J_{PC} = 65.3, C-2,9), 27.4 (J_{PC} = 3.7, C-4,7). Anal. Calcd for $C_9H_{19}OP$: C, 62.05; H, 10.99; P, 17.78. Found: C, 62.30; H, 10.88; P, 17.71.

1-Methylphosphonane (19). A mixture of phosphonane oxide **18** (300 mg, 1.7 mmol) and phenylsilane (1.8 g, 1.7 mmol) was heated at 85 °C for 6 h. Kugelrohr distillation [113 °C (0.03 mm)] of the reaction mixture gave 250 mg (94%) of impure phosphine **19** as a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.99 (d, $^2J_{PH}$ = 4 Hz, PCH_3), 2.58 (m, CH_2); ^{31}P NMR ($CDCl_3$) δ −33.8. The phosphine was converted to its methiodide for analysis.

Phosphine **19** (250 mg, 1.4 mmol) was treated with excess methyl iodide (220 mg, 1.5 mmol) in benzene (2 mL) overnight at room temperature. The precipitate which formed was filtered off to give 190 mg (45%) of the phosphonanium salt **20** as a white solid, mp 206–220 °C dec. Recrystallization from absolute ethanol gave white needles: mp 265–267 °C dec; ^1H NMR ($CDCl_3$) δ 1.16–2.98 (complex m, including a br s at 1.58, CH_2), 2.18 (d, $^2J_{PH}$ = 14 Hz, PCH_3); ^{31}P NMR ($CDCl_3$) δ 31.9; ^{13}C NMR ($CDCl_3$) δ 8.8 (J_{PC} = 54.3 Hz, CH_3), 18.2 (J_{PC} = 4.9, C-3,8), 20.3 (J_{PC} = 48.8, C-2,9), 22.5 (C-5,6), 26.9 (J_{PC} = 4.3, C-4,7). Anal. Calcd for $C_{10}H_{22}IP$: C, 40.01; H, 7.39; P, 10.32. Found: C, 39.95; H, 7.66; P, 10.26.

Reduction of Carbonyl Groups of 3,8-Phosphonanedione 1-Oxides. To a solution of 1-methyl dione **1** (1.0 g, 5.0 mmol) in 25 mL of absolute ethanol was added 150 mg (4.0 mmol) of sodium borohydride. The reaction mixture was refluxed for 1.5 h and then concentrated to give a white solid residue. A 2 N H_2SO_4 solution (10 mL) was added, and the resulting solution was extracted continuously with chloroform for 48 h. The chloroform extract was dried ($MgSO_4$) and concentrated to give 1.0 g (96%) of diol **13a** (isomer mixture) as a viscous, hygroscopic, colorless oil. A sample dried azeotropically with benzene gave an extremely hygroscopic, amorphous solid, mp 65–93 °C. Attempts to crystallize or purify this solid for analysis were unsuccessful: ^1H NMR ($CDCl_3$) δ 0.67–3.07 (br m, CH_2 and PCH_3), 3.40–3.96 (br m, CH), 4.83 (br s, OH); ^{31}P NMR ($CDCl_3$) δ 47.6, 46.8, 42.4; IR (neat) 3300 cm^{-1} (ν_{OH}).

Diol **13a** was also obtained (quantitatively) from dione **1** by hydrogenation over a Raney nickel catalyst. A mixture of **1** (1.0 g, 5.0 mmol) and freshly prepared Raney nickel (1.0 g) in absolute ethanol (50 mL) was placed in a Parr hydrogenation bottle and shaken under hydrogen (50 psi) for 48 h. The catalyst was removed by filtration and the filtrate then concentrated to give a viscous, light yellow oil. The NMR and IR spectral properties of this material were identical with those reported above.

The same procedures were used to prepare the 1-phenyl diol **13b**: ^1H NMR ($CDCl_3$) 1.2–2.8 (br m, CH_2), 3.8–4.4 (br m, CH), 4.7 (br s, OH); ^{31}P NMR δ 35.8, 39.1, 40.2; IR (neat) 3300 cm^{-1} (ν_{OH}).

Dehydration of 1-Methyl-3,8-phosphonanediol 1-Oxide (13a). To a solution of **13a** (1.8 g, 9.0 mmol) in pyridine (37 mL) at 0 °C was slowly added phosphorus oxychloride (15.3 g, 0.10 mol) over a 20-min period. The resulting dark, red-brown mixture was stirred overnight at room temperature and then poured cautiously into an ice-cold 10% HCl solution. The resulting solution was extracted continuously overnight with $CHCl_3$. The $CHCl_3$ extract was dried ($MgSO_4$) and concentrated to give a dark oil (1 g). Kugelrohr distillation [98 °C (0.03 mm)] gave 540 mg (36%) of a white solid, which was tentatively identified as having the 1,3-diene structure of **22**: ^1H NMR ($CDCl_3$) δ 1.06–3.02 (complex m, CH_2), 1.58 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 5.32–6.70 (complex m, C=CH); ^{31}P NMR ($CDCl_3$) δ 36.4; ^{13}C NMR δ 18.2 (J_{PC} = 70.8 Hz, CH_3), 24.7 (J_{PC} = 3.0 Hz, C-7), 28.4 (C-6), 28.7 (J_{PC} = 6.7, C-8), 32.6 (J_{PC} = 64.7, C-9), 120.7 (J_{PC} = 11.6, C-3), 126.6 (J_{PC} = 90.3, C-2), 133.2 (J_{PC} = 9.8, C-4), 150.6 (C-5); UV (CH_3OH) λ_{max} 212 nm (ϵ 2750). Hydrogenation with Pd/C in methanol provided 1-methylphosphonane 1-oxide having the same ^1H, ^{31}P, and ^{13}C NMR spectra as **18**. Anal. Calcd for $C_9H_{15}OP$: C, 63.50; H, 8.90; P, 18.20. Found: C, 63.41; H, 8.62; P, 18.50.

5,9-Dihydroxy-7-phenyl-5,6,8,9-tetrahydro-7*H*-dibenzo[*d*,*f*]phosphonin 7-Oxide (15). To a solution of the diketone **14** (3.7 g, 10.3 mmol) in absolute ethanol (75 mL) was added sodium borohydride (420 mg, 11.0 mmol). The resulting solution was refluxed for 2 h. The reaction mixture was concentrated to approximately 20 mL and a 2 N H_2SO_4 solution (30 mL) was added. The solid which crystallized was filtered off and dried to give 2.9 g (78%) of diol **15** as a fine white solid, mp 217–225

°C. Recrystallization from absolute ethanol gave fine, white needles (mp 262–263 °C) which were found by elemental analysis and ^{1}H NMR to contain 1 equiv of ethanol: ^{1}H NMR (250 MHz, Me_2SO-d_6) δ 2.00–3.00 (m, 3 H) and 2.9 (m, 1 H) both P–CH_2, 4.49 and 4.78 (both m, 1 H, CHOH), 7.1–7.8 (m, 8 H, Ar H); ^{13}C NMR (Me_2SO-d_6) δ 62.6 ($^2J_{PC}$ = 2.0 Hz, CHOH), 65.0 ($^2J_{PC}$ = 2.0 Hz, CHOH), 126.1–142.7 (complex, aromatic C); ^{31}P NMR (Me_2SO-d_6) δ 29.9; IR (KBr) 3150 (ν_{OH}), 3375 cm^{-1} (ν_{OH}). Anal. Calcd for $C_{22}H_{21}O_3P \cdot C_2H_5OH$: C, 70.23; H, 6.63; P, 7.55. Found: C, 70.40; H, 6.73; P, 7.54.

***cis,trans*-7-Phenyl-7*H*-dibenzo[*d,f*]phosphonin 7-Oxide (23).** To a cooled (0 °C) suspension of diol **15** (27 g, 7.4 mmol) in dry pyridine (28 mL) was added phosphorus oxychloride (11.3 g, 0.074 mol), and the resulting mixture then heated at 95–100 °C for 1 h. The clear, dark solution which formed was allowed to cool and was cautiously poured onto ice. The hydrolysis mixture was extracted with methylene chloride (five 50-mL portions), and the CH_2Cl_2 extracts were combined and washed with two 25-mL portions of 10% HCl solution, water (25 mL), and finally a saturated NaCl solution (25 mL). The organic solution was then dried ($MgSO_4$) and concentrated to give a brown gummy solid; this was triturated with petroleum ether and filtered off to give 1.4 g (58%) of phosphonin oxide **23** as a brown, amorphous solid, mp 151–160 °C. A small sample of **23** crystallized out of the petroleum ether filtrate as a white, crystalline solid, mp 166–167 °C. This solid was indicated by elemental analysis to be the hemihydrate of **23**: ^{1}H NMR ($CDCl_3$) δ 6.04 (dd, $^2J_{PH}$ = 24 Hz, $^3J_{HH}$ = 14 Hz, H-2, trans), 6.08 (dd, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz, H-9, cis), 6.64–7.88 (m); UV (C_2H_5OH) λ_{max} 202 nm (ε 46 000), 259 (sh, ε 7600); ^{31}P NMR ($CDCl_3$) δ 17.2. Anal. Calcd for $C_{22}H_{17}OP \cdot 0.5H_2O$: C, 78.33; H, 5.38; P, 9.18. Found: C, 78.53; H, 5.36; P, 9.19.

***cis,trans*-7-Phenyl-7*H*-dibenzo[*d,f*]phosphonin (24) and Its Methiodide (25).** To a mixture of trichlorosilane (1.42 g, 10.5 mmol) and pyridine (1.7 g, 21.0 mmol) in dry benzene (15 mL) was added a suspension of phosphonin oxide **23** (700 mg, 2.1 mmol) in benzene (10 mL). The resulting slurry was refluxed for 1 h and cooled in an ice-bath, and an additional portion of benzene was added (25 mL). The reaction mixture was then hydrolyzed by the cautious addition of a 30% NaOH solution (35 mL), the resulting layers were separated, and the aqueous layer was extracted with three 25-mL portions of benzene. The benzene solutions were combined, washed with water (four 25-mL portions), saturated with NaCl solution (25 mL), dried ($MgSO_4$), and concentrated to give 636 mg (95%) of phosphonin **24** as a crystalline solid: mp 68–73 °C; ^{1}H NMR ($CDCl_3$) δ 5.67 (dd, $^2J_{PH}$ = 35 Hz, $^3J_{HH}$ = 15 Hz, H-2, trans), 5.97 (dd, $^2J_{PH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, H-9, cis), 6.77–7.82 (m); UV (C_2H_5OH) λ_{max} 202 nm (ε 43 500), 255 (sh, ε 6600); ^{31}P NMR ($CDCl_3$) δ −24.7. The phosphine was converted to its methiodide for analysis.

Treatment of **24** (266 mg, 0.85 mmol) with excess methyl iodide (280 mg, 2.0 mmol) in benzene (3 mL) immediately gave a viscous yellow oil. The reaction mixture was allowed to stand overnight at room temperature; the benzene solution was decanted, and absolute ethanol (2 mL) then added to the residue to cause crystallization of a yellow solid. Recrystallization from absolute ethanol gave 135 mg (35%) of methiodide **25** as a yellow crystalline solid, mp 208–210 °C. Recrystallization with charcoal treatment gave white crystals: mp 208–209 °C; ^{1}H NMR ($CDCl_3$) δ 2.37 (d, $^2J_{PH}$ = 14 Hz, PCH_3), 6.23–7.92 (m), 8.15 (dd, $^3J_{PH}$ = 25 Hz, $^3J_{HH}$ = 13 Hz, H-2, trans); UV (C_2H_5OH) λ_{max} 202 nm (ε 48 000), 259 (sh, ε 10 400); ^{31}P NMR ($CDCl_3$) δ 1.18. Anal. Calcd for $C_{23}H_{20}IP$: C, 60.81; H, 4.44; P, 6.82. Found: C, 60.65; H, 4.66; P, 6.77.

1-Hydroxy-3,8-dioxo-2,3,4,7,8,9-hexahydro-1*H*-phosphonin 1-Oxide (27). To a suspension of 0.65 g (1.8 mmol) of 1-hydroxy-5,6-dibromo-3,8-phosphonanedione 1-oxide[2] (**26**) in 10 mL of THF was added 0.60 g (9.2 mmol) of zinc dust (activated with 5% HCl for 15 min; washed with water, methanol, ethanol (absolute), and ether, and dried at 110 °C for 10 h). Glacial acetic acid (0.6 mL) was dropped in, and the mixture was heated to 40 °C. The suspended **26** dissolved completely in 10 min at this temperature; the reaction was continued for 15 min at room temperature. Excess zinc and zinc salts were removed by filtration and washed with THF. The filtrate was diluted with 5 mL of water and concentrated to a semisolid residue. The organic material was extracted with 20 mL of hot anhydrous methanol, and the insolubles removed by filtration. The fine white solid that formed on cooling of the filtrate was collected by filtration, washed with THF, and recrystallized from methanol: 0.32 g (89%); mp dec 110 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.8–3.1 (br, partially resolved doublet, H-2,9), 3.2 (s, H-4,7), 5.6 (br s, H-5,6); ^{13}C NMR (Me_2SO-d_6) δ 44.2 (C-4,7), 45.6 (J_{PC} = 76.8 Hz, C-2,9), 128.3 (C-5,6), 200.0 (J_{PC} = 6.0, C-3,8); ^{31}P NMR (Me_2SO-d_6) δ 30.0. Anal. Calcd for $C_8H_{11}O_4P$: C, 47.53; H, 5.50; P, 15.32. Found: C, 47.01; H, 5.20; P, 14.90.

^{31}P NMR Spectra of 1,2,5-Triphenylphosphole and Its 1-Oxide. 1,2,5-Triphenylphosphole was prepared (K. C. Caster) by a published method:[27] ^{31}P NMR ($CDCl_3$) δ 3.8. Oxidation with H_2O_2 provided the 1-oxide, ^{31}P NMR ($CDCl_3$) δ 41.5.

Registry No. **1**, 65114-88-7; **2**, 65114-89-8; **3**, 65489-16-9; **4**, 65489-15-8; **5**, 75531-99-6; **7**, 75401-39-7; **9**, 75401-32-0; **10**, 65482-10-2; **11**, 75401-30-8; **12**, 80461-79-6; **13a** (isomer 1), 80461-80-9; **13a** (isomer 2), 80513-17-3; **13a** (isomer 3), 80513-18-4; **13b** (isomer 1), 80461-81-0; **13b** (isomer 2), 80513-19-5; **13b** (isomer 3), 80513-20-8; **14**, 74078-08-3; **15**, 75443-54-8; **16**, 80461-82-1; **17**, 80461-83-2; **18**, 75401-31-9; **19**, 80461-84-3; **20**, 75401-44-4; **22**, 80461-85-4; **23**, 74078-10-7; **24**, 74078-11-8; **25**, 74078-12-9; **26**, 80461-86-5; **27**, 80461-87-6; 1-methyl-3,8-phosphonanedione 1-oxide bis(2,4-dinitrophenylhydrazone), 80461-88-7; 1,2,5-triphenylphosphole, 1162-70-5; 1,2,5-triphenylphosphole 1-oxide, 1794-96-3.

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