Rearrangements during Oxidations of the 9-Phosphabicyclo[6.1.0]nona-2,4,6-triene System: Formation of Phosphonin Oxides[1]

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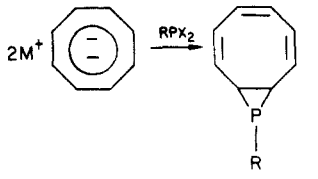
Abstract: *P*-Phenyl and *P*-*tert*-butyl derivatives of the title compound react with hydrogen peroxide or *tert*-butyl hydroperoxide at −15 °C; the C–C bond of the three-membered ring is opened, and the first observable product is the *cis,cis,cis,trans*-phosphonin oxide. When this oxide warms to room temperature, intramolecular cycloaddition occurs to form the *trans*-3a,7a-dihydrophosphindole oxide system. The products of both processes have the stereochemistry predicted from orbital symmetry rules; their structures were established by ^{31}P, ^{1}H, and ^{13}C NMR studies, as well as by conversion to known derivatives. When oxygen was used as the oxidizing agent, a different product (*anti*-9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene 9-oxide) was formed and was useful as a precursor, on ultraviolet irradiation, of *syn*-9-phenyl-9-phosphatricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene oxide. This compound was also obtained by isomerization of the anti 9-phenyl derivative with water. These oxides were reduced to the phosphines, which were characterized by NMR techniques; the syn phenyl product, however, was unstable in concentrated media and unlike the anti isomer could not be isolated. The X-ray crystallographic analysis of *syn*-9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene confirmed the stereochemical assignment and provided a structural basis for other derivatives.

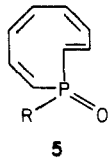
The synthesis of the 9-phosphabicyclo[6.1.0]nona-2,4,6-triene system can be accomplished by the reaction of phosphonous dihalides[2,3] or phosphorus trihalides[3] with metallic derivatives of cyclooctatetraene.[2-5]



1, R = *t*-C_4H_9
2, R = C_6H_5

This heterocyclic system is quite reactive and is prone to undergo rearrangements such as those of Scheme I found for the *P*-phenyl derivative.

We have studied the behavior of this system to oxidizing agents and have identified a new pathway for its skeletal rearrangement. While the major product of oxidation with oxygen proved to be the *P*-oxide of the bicyclic system **4**, the first detectable product from hydrogen peroxide or *tert*-butyl hydroperoxide was the relatively unstable *cis,cis,cis,trans*-phosphonin ring system **5**.[7]



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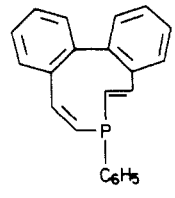

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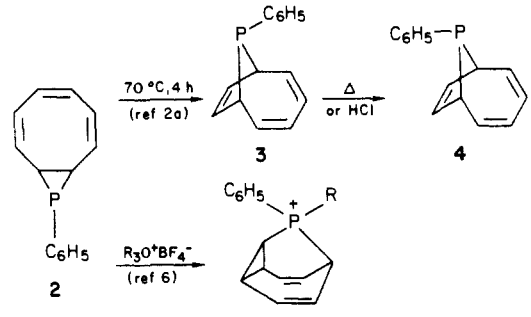
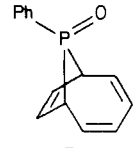
Little is known about the phosphonin system, but it is of great interest since, with phosphorus in the trivalent state, a 10-π-electron system is present. The only phosphonin derivative that has been studied as a potentially aromatic species is *P*-phenyldibenzo[*d,f*]phosphonin (**6**), which because of severe crowding and distortion of the ring from planarity is constrained from showing indications of electron delocalization.[8] Monocyclic phosphonins remain[9] as highly desired species that might deserve inclusion among the aromatic heteronins.[10] The main route to cyclononatetraene and the heteronins with N or O has, in fact, been the opening of the 1,8-bond in the bicyclo[6.1.0]nonatriene framework. This reaction has failed with the 9-thia derivative,[11] and in the present program we have been unsuccessful with phosphirane **2**.[12] It is for this reason that the new oxidation pathway is of synthetic significance in phosphonin chemistry. Oxygen oxidation also proved to be of value as a new route to **7** and products derived from it. Experiments on the extension of the oxidation technique to the formation of the thionin oxide system are presented elsewhere.[13]

Scheme I





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(1) Taken in part from: Rao, N. S. Ph.D. Dissertation, Duke University, 1983.

(2) (a) Katz, T. J.; Nicholson, C. R.; Reilly, C. A. *J. Am. Chem. Soc.* **1966**, *88*, 3832. (b) Turnblom, E. W.; Katz, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 4292. (c) Katz, T. J.; Carnahan, J. C., Jr.; Clarke, G. M.; Acton, N. *J. Am. Chem. Soc.* **1970**, *92*, 734.

(3) Märkl, G.; Abig, B. *Tetrahedron Lett.* **1982**, *23*, 4915.

(4) Evans, W. J.; Wink, D. J.; Wayda, A. L.; Little, D. A. *J. Org. Chem.* **1981**, *46*, 3925.

(5) Richter, W. J. *Chem. Ber.* **1985**, *118*, 97.

(6) Märkl, G.; Abig, B. *Tetrahedron Lett.* **1983**, *24*, 3981.

(7) Preliminary communication: Rao, N. S.; Quin, L. D. *J. Am. Chem. Soc.* **1983**, *105*, 5960.

(8) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905.

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(12) Refluxing **1** in toluene has been reported[5] to give a product mixture containing a dihydrophosphindole derivative, which may result from a phosphonin intermediate. This type of ring closure had first been observed for the phosphonin oxide.[7]

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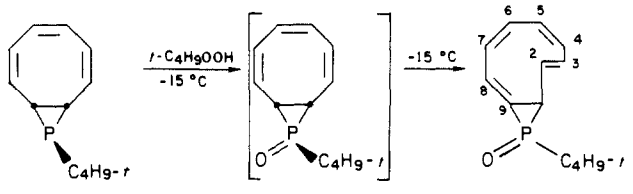
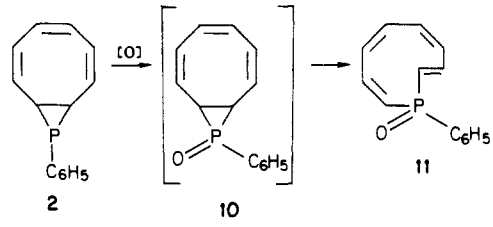
Phosphonin Oxides from Peroxide Oxidation. When a chloroform solution of 9-*tert*-butyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (**1**) was exposed to *tert*-butyl hydroperoxide at −15 ± 5 °C for 6 h, the characteristic upfield ^{31}P NMR signal of the phosphirane system (δ −141.6) was replaced with a new signal at δ +33.9. Since it was found that the substance giving this signal was not stable at room temperature, purification attempts and NMR measurements were performed at temperatures below −15 °C. Much of the *tert*-butyl alcohol formed from the hydroperoxide crystallized at −50 °C, and the remainder as well as the excess hydroperoxide was removed by treatment of the solution with calcium chloride at −15 °C. Evaporation of the solvent at −20 °C left a clear oil whose ^{13}C NMR spectrum was relatively free of extraneous peaks. The only signals in the sp^3 C region belonged to the *tert*-butyl group. Among the numerous signals in the sp^2 C region were two doublets with large coupling suggestive of one-bond connection to ^{31}P (δ 116.9, $^1J_{PC}$ = 95.6 Hz; δ 127.3, $^1J_{PC}$ = 95.6 Hz). Relatively downfield signals with small coupling were assigned to β-carbons of α,β-unsaturated units (δ 141.8, $^2J_{PC}$ = 5.5 Hz; δ 152.5, $^2J_{PC} \sim 0$ Hz). The data for the other four signals for the remaining sp^2 C are recorded in the Experimental Section. The data are only interpretable on the basis of a nine-membered, fully unsaturated cyclic phosphine oxide, and since none of the carbons are equivalent, the presence of one trans double bond (as in **9**) is indicated. The large difference in the chemical shifts of



the α-carbons, as well as the β-carbons, indicates the trans double bond to be attached to phosphorus. If the initial attack of the hydroperoxide is on P to form the phosphirane oxide **8**, then this substance is presumed to have no stability at −15 °C and undergoes retroelectrocyclization to the phosphonin oxide. Since the ring fusion in **1** is cis,[2a] orbital symmetry considerations predict[10,14] that the thermal ring opening will be conrotatory and will result in one trans double bond, just as observed from the ^{13}C NMR spectrum. The ^{31}P NMR signal (δ +33.2) was in the region expected for a phosphonin oxide.[8,9]

The 300-MHz ^1H NMR spectrum of **9** was also obtained and supports the assignment of a trans double bond at C-2,C-3. The spectrum is complex and required selective irradiation experiments to locate the source of some of the couplings. The results are summarized in the Experimental Section. The carbons α and β to phosphorus were easily recognized from the large couplings to ^{31}P. The significant differences between the chemical shifts of the protons on the two α-carbons ($\Delta\delta$ 0.7) as well as on the β-carbons ($\Delta\delta$ 0.68) support the proposal from the ^{13}C NMR spectrum that the two double bonds have different substitution; the vicinal H–H coupling constants [$^3J_{H\text{-}2,H\text{-}3}$ = 15.0 Hz (trans); $^3J_{H\text{-}8,H\text{-}9}$ = 10.7 Hz (cis)] also differ. The vicinal coupling constants for the other double bonds were determined to be 7.3 (H-4,H-5) and 14.0 Hz (H-6,H-7); the latter value may raise the question of the possible presence of a second trans double bond at C-6,C-7, but cis coupling constants of this magnitude are known for nine-membered, unsaturated rings (e.g., 14.0 Hz for a benzazonine[15a] and 14.5 Hz for a benzocyclononatetraenyl anion[15b]) and are unreliable for structural analysis when taken alone. Structure **9** for the phosphonin oxide is further supported by the stereochemistry of the ring fusion in the dihydrophosphindole oxide that forms at room temperature (vide infra); the trans fusion predicted from orbital symmetry considerations is indeed found experimentally. (Were a trans double bond also present at C-6,C-7 a cis-fused product would result.)

The same oxidation and isolation conditions applied to 9-phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (**2**) resulted in its complete transformation to the phosphonin oxide **10** with δ



(^{31}P) +16.2 (−20 °C). The ^{13}C NMR spectrum showed no sp^3 carbons, but signal overlap made assignment of the sp^2 C signals more difficult than in the *tert*-butyl case.

Both oxidations were also successfully accomplished with hydrogen peroxide (30%) in methanol (1:1) at −15 °C. Since the phosphiranes are not as soluble in this medium as they are in chloroform, and removal of water from the product prolongs the isolation procedure, the *tert*-butyl hydroperoxide method is preferred. Oxidation by *tert*-butyl hypochlorite, manganese dioxide, or bromine gave complex mixtures.

To confirm that the phosphirane oxide is an intermediate in the formation of the phosphonin ring, this structure was generated by a different method, the reaction of the dianion of cyclooctatetraene with phenylphosphonic dichloride at −78 °C. The product mixture was rather complex and was easier to analyze after the intramolecular cyclization, described later, of the phosphonin oxide has taken place (at 25 °C). The major product (**13**) was the same as that formed from phosphonin oxide **11**. This observation supports the proposal that in the peroxide oxidations the species undergoing valence tautomerism is indeed the phosphirane oxide and not an intermediate of the oxidation such as the dioxyphosphorane. The increase in bond angle accompanying the P(III) to P(IV) conversion must increase the strain in the three-membered ring, rendering it more easily cleaved.

The ^{31}P NMR signal of 1-phenylphosphonin oxide **11** (δ +16.2) is very nearly the same as that reported[8] for the dibenzo derivative **6** (δ +17.2). Replacement of phenyl by *tert*-butyl routinely causes deshielding,[16a] and this accounts for the more downfield value (δ +33.9) found for **9**. The only other known[9b] phosphonin oxide (*cis,cis,cis,cis*-1-phenyl-3,8-bis(trimethylsiloxy)) has δ +30.3.

Attempts to deoxygenate the phosphonin oxides have not yet been successful. These reactions must be conducted at −15 °C to prevent the internal ring closure, but the various methods available usually have a higher energy requirement. The reagents tried included trichlorosilane, trichlorosilane with triethylamine, hexachlorodisilane, phenylsilane, $LiHAl(OBu\text{-}t)_3$, and $LiAlH_4$. In no case was evidence obtained for the formation of the phosphonin. A single attempt to perform a Diels–Alder reaction on the phosphonin oxide **2** with phenyltriazolinedione, used successfully with oxonin and azonine derivatives,[10] led only to a complex mixture.

Electrocyclization of Phosphonin Oxides. When the phosphonin oxides were warmed to 25 °C, they were completely converted to isomers that were identified as the dihydrophosphindole derivatives. The dihydrophosphindoles were also formed in high yield when the phosphiranes **1** and **2** were oxidized with hydrogen peroxide in methanol at 0 °C. The presence of the five-membered ring was suggested by the downfield shifting of the ^{31}P NMR signal into the region characteristic of phospholene derivatives.[16a] Consistent with the structure was the presence of two sp^3 C signals in the ^{13}C NMR spectra, with one carbon having the large coupling (**12**, 79.1 Hz; **13**, 77.2 Hz) expected for direct attachment to P. Assignments of the sp^2 C are given in Table I; notable is the

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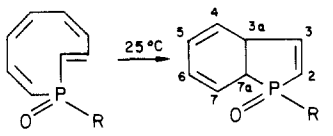
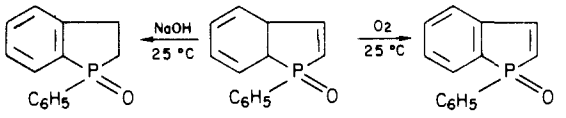
(16) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; Wiley-Interscience: New York, 1981; (a) Chapter 5, (b) Chapter 6, (c) pp 333–344.



12, R = C_4H_9-*t*
13, R = C_6H_5

presence of one carbon with the larger one-bond coupling from ^{31}P.

Chemical proof of the dihydrophosphindole structure was obtained with the *P*-phenyl compound by performing conversions to known substances. The double bond of the five-membered ring was rearranged to give the benzenoid structure **14**,[17] and the

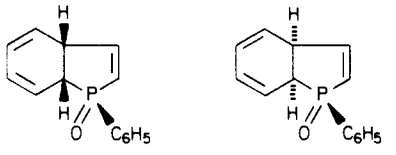


14 **13** **15**

phosphindole oxide **15**[17] was generated by air oxidation. Identifications were accomplished by comparisons of NMR spectra to published data.

By observing the rates of decay of the ^{31}P NMR signals of the phosphonin oxides and the appearance of the dihydrophosphindole oxide signals, it was possible to determine approximate values for the half-lives of the former species. For the 1-phenyl compound, the half-life at 24 °C was about 4 min; the *tert*-butyl compound was more stable (8 min). While no data for the carbocyclic analogue are available for a comparison, these half-lives are much shorter than that of *cis,cis,cis,cis*-cyclononatetraene (50 min at 23 °C[18]), which undergoes intramolecular cycloaddition to give the dihydroindene. The lower stability may be due to the difference in geometry or to a double bond activation effect by phosphoryl.

The stereochemistry of the ring fusion in the dihydrophosphindole oxides should be trans from the interaction of the trans double bond in the phosphonin oxides with a diene unit, as predicted by orbital symmetry considerations[14] and observed in the reaction of *cis,cis,cis,trans*-cyclononatetraene.[19] This was immediately confirmed for the *P*-phenyl compound **13** since its ^{31}P NMR resonance was strongly shifted upfield (δ +46.9) relative to resonances for the known cis-fused forms **16** and **17**, prepared

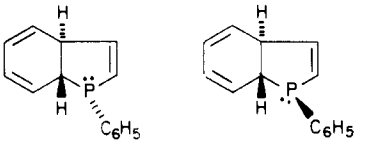


16, $\delta(^{31}P)$ +62.4 **17**, $\delta(^{31}P)$ +71.1

in earlier work.[9a] The phosphonin oxide rearrangement product **13** was found to be epimerized to the known cis isomer **16** under mild conditions (benzene–aqueous NaOH solution at 25 °C for 2 min), further confirming its trans-fused structure. If it is assumed that the configuration at P is not affected by these conditions, then the center undergoing epimerization appears to be C-3a rather than C-7a. ^1H NMR spectra are also useful in assigning cis or trans fusion in dihydroindene and heterocyclic derivatives; trans fusion is recognized by the very large $^3J_{H\text{-}3a,H\text{-}7a}$ value (20 Hz in 1,1-dimethyl-*trans*-3a,7a-dihydroindene;[20] 23.5 Hz in the 1-oxa derivatives[19]) compared to the values for cis-fused derivatives (12 Hz in *cis*-3a,7a-dihydroindene;[20] 7 Hz in the 1-oxa derivative[21]). In the cis-fused dihydrophosphindoles **16**, $^3J_{H\text{-}3a,H\text{-}7a}$ was 12.4 Hz. The NMR spectrum of the cyclization product **12** from phosphonin oxide **9** was adequately resolved to allow analysis of the coupling. H-3a gave a broad doublet at δ 3.75 with $^3J_{H\text{-}3a,H\text{-}7a}$ = 18 Hz, and H-7a gave a doublet of doublets (both broad) at δ 2.30 ($^3J_{H\text{-}3a,H\text{-}7a}$ = 18, $^2J_{P,H}$ = 9 Hz). The chemical shift separation of H-3a and H-7a was much less for **13**; the spectrum had ABX characteristics and was not readily analyzed. However, the five-line AB part at δ 3.0–3.3 was qualitatively similar to a calculated spectrum[22] where $\nu_A - \nu_B \sim 4$, $J_{AB} \sim 20$, $J_{AX} \sim 8$, and $J_{BX} \sim 0$ Hz. These approximate values are in good agreement with those found in the first-order spectrum of **13**. Another useful feature was the absence of three-bond coupling of H-3a to ^{31}P; this is consistent with the dihedral angle of about 90° relating these nuclei.[23] In the cis isomers, this coupling is quite large (e.g., 12 Hz in **16**), consistent with the large dihedral angles (~180°) seen on models of this isomer; the value for $^3J_{HH}$ is of similar size.[9a]

The ^{13}C NMR spectra of the isomer pair differing in configuration at C-3a also possessed a significant ^{31}P–^{13}C coupling difference that has been noticed for other isomeric dihydrophosphindoles;[24] for the trans-fused compounds **12** and **13**, the coupling to C-3 in the phospholene ring was quite small (6.8 and 10.3 Hz, respectively) in comparison to that in a cis-fused compound (**16**, 29.5 Hz). Such large values are common in monocyclic 2-phospholene oxides.[16b] The coupling to C-3 takes two pathways, through a two-bond path (P—C_2=C_3) and a three-bond path (P—C_5—C_4—C_3), and the observed value is the sum of the two coupling constants. The two-bond component is probably very similar in both of the dihydrophosphindole isomers; there is little difference in geometry in this section of the molecule, and in any case $^2J_{PC}$ is not dependent on the stereochemistry.[16b] However, the three-bond P–C coupling is strongly controlled by the dihedral angle θ relating the coupled nuclei and has the usual maximum at θ = 0° and 180° and minimum at θ = 90°. Examination of Dreiding models suggests that θ is nearly 0° in the cis-fused isomer, thus allowing a large $^3J_{PC}$ component in the observed coupling, but that it is around 60° in the trans-fused isomer, which leads to a much smaller $^3J_{PC}$ contribution. Regardless of the signs of the couplings, the net P–C coupling expected at C-3 will be smaller in the trans isomer, as is observed.

Since no features of the spectra of the *trans*-dihydrophosphindole oxides formed from the phosphonin oxides would allow the assignment of the configuration at phosphorus, it was necessary to reduce the oxide structure to the trivalent form where the stereodependency of two-bond ^1H–^{31}P coupling could be used. Thus, it would be expected that phosphine **18** would have a large



18 **19**

value of $^2J_{P,H\text{-}7a}$ (e.g., 22.7 Hz in *cis,cis*-1,2,5-trimethyl-3-phospholene[25]) because of the close proximity of ^1H and the lone pair, while **19** would have a small value (2 Hz in the 1,2,5-trimethyl-3-phospholene with trans *P*-methyl). The reduction was performed on the *P*-phenyl oxide **13** using trichlorosilane as the reducing agent. This reduction occurs with retention of configuration when applied to phospholenes.[26] The signals for H-3a and H-7a were not well resolved and gave a broad multiplet at δ 2.6–3.3. It was necessary to examine a proton-coupled ^{31}P NMR spectrum to obtain the $^2J_{P,H\text{-}7a}$ value. In fact, no coupling was detectable (and hence was <4 Hz); the only discernible coupling was the characteristic[16c] large value arising from H-2 in the 2-phospholene ring (41 ± 2 Hz). This suggests that the P-substituent is cis to the proton at C-7a (as in **19**) and therefore that the dihydrophosphindole oxides generated from the phosphonin

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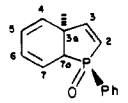
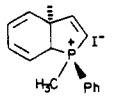
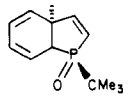
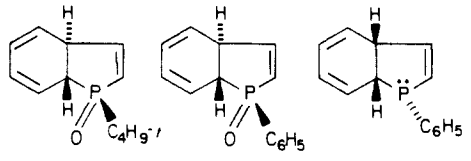
Table I. ^{13}C NMR Data[a] for *trans*-3a,7a-Dihydrophosphindole Derivatives

	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a
 13a[b]	c	151.4 (10.3)	42.6 (14.6)	128.7[d] (13.2)	128.0 (0)	128.5[d] (3.0)	125.0 (24.9)	46.6 (79.1)
 e	116.4 (77.8)	160.2 (5.4)	46.4 (10.8)	130.2[c] (8.1)	128.2 (0)	*f*	127.1[c] (17.5)	43.2 (64.4)
 12a[g]	125.1 (100.6)	151.9 (6.8)	44.6 (7.8)	129.7[c] (13.7)	123.4 (2.0)	*f*	126.7 (15.6)	37.5 (77.2)

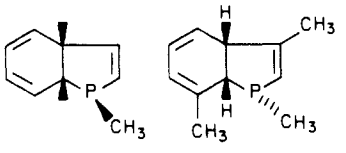
[a] Spectra were run in $CDCl_3$ solutions. Chemical shifts (ppm) are downfield of internal Me_4Si. Values in parentheses are J_{CP} coupling constants (Hz). [b] Phenyl carbons: ortho 130.2 (10.2), meta 128.5 (11.7), para 131.8 (2.9). [c] Downfield portion of doublet not visible. [d] Assignment uncertain. [e] CH_3 10.8 (53.7); phenyl carbons: ipso 116.0 (79.3), ortho 132.8 (10.7), meta 130.3 (13.5), para 135.0 (2.0). [f] Not observed. [g] CH_3C 32.0 (70.3), CH_3C 25.7 (21.5).

oxides have the stereochemistry depicted by structures **12a** and **13a**. In another study,[9a] we have described a dihydrophosphindole



12a **13a** **20**

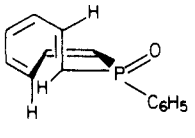
(**20**) with the P-substituent trans to this proton, and the expected large $^2J_{P,H}$ value (15 Hz) was observed on the ^1H-coupled ^{31}P NMR spectrum. Trans-fused phosphines similar to **19** have very recently been reported from the heating of certain phosphines (including *P-tert*-butyl) with the 9-phosphabicyclo[6.1.0]nona-2,4,6-triene structure. Our attempts to prepare this fused phosphine by deoxygenation of *P*-oxide **12** were thwarted by ring cleavage reactions. A comparison of properties would be desirable, since this phosphine was assigned[5] the opposite configuration at P even though $^2J_{P,H\text{-}7a}$ was only 6.6 Hz. Another NMR-based technique for assigning stereostructure, which is quite reliable, depends on the specificity of $^2J_{PC}$; the value is large (20 ± 5 Hz) when the coupled carbon is close to the lone pair and is small or negligible when remote.[16b] While we have not yet been able to interpret with confidence the complicated sp^2 C region of the ^{13}C NMR spectrum of the *P*-phenylphosphine **19**, it is noted that the $^2J_{P,C\text{-}7}$ value (16 Hz) reported for the phosphines of the other study[5] is of similar size to that of a compound (**21**) known to have



21 **22**

P-methyl trans to C-7. A cis-fused phosphine (**22**) with *P*-phenyl cis to C-7 was recently prepared here[24] and had the expected small value (2.0 Hz) for $^2J_{P,C\text{-}7}$.

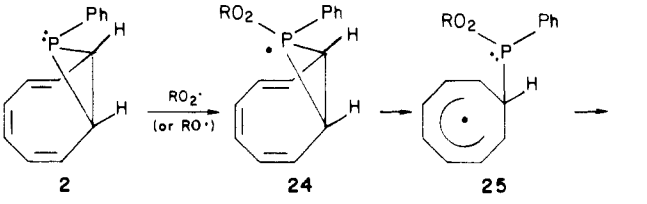
A possible conformation of the *cis,cis,cis,trans*-phosphonin oxide **11** that would give the observed stereochemical result is shown as **23**. In the disrotatory ring closure, the *P*-phenyl group and



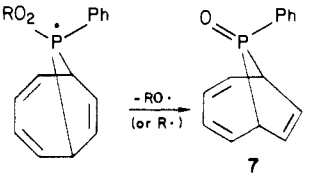
23

the α-proton of the trans double bond (which becomes H-7a) will assume the cis relation. A model suggests the interactions between the *P*-phenyl group and other atoms of the ring are minimized in such a conformation. The ring closure gives none of the isomer with oxygen cis to H-7a.

Oxidation with Oxygen: 7-Phosphanorbornene Derivatives. The oxidation of phosphirane **2** was also performed by agitating a benzene solution under an oxygen atmosphere for several days. The solution became dark, and some solids precipitated. No **2** remained, and none of the dihydrophosphindole oxide **13a** or its oxidation product **15** could be detected. From the solution, however, was isolated a crystalline solid in 38% yield that had the melting point and ^1H NMR spectrum of the known[2] *anti*-9-phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene 9-oxide (**7**). The oxidation of phosphines by oxygen has been shown to proceed by a radical mechanism,[27] initiated with attack of a species $RO_2\cdot$ on P, and this is quite different from the reaction with hydroperoxides where nucleophilic attack by phosphorus on oxygen is involved.[28] With dialkyl peroxides, a biphilic insertion mechanism is currently[28c] favored. It is implied that an unstable intermediate (e.g., **24**, on the basis of recent spectroscopic confirmation[5] of the anti structure for phosphine **2**) is formed in the oxidation that collapses



2 **24** **25**



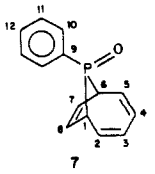
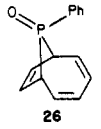
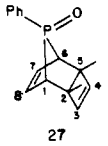
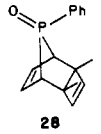
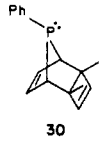
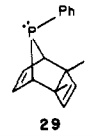
7

to the observed product *before* breakdown to the phosphirane oxide can occur, since the phosphirane oxide will lead to the phosphonin oxide (as seen in the $PhPOCl_2$–Li_2COT reaction). The radical intermediate **24** could achieve stabilization by cleavage of a C–P bond and re-formation of a more stable species. A possible representation would involve a delocalized radical intermediate such as **25** which would collapse to the observed product. Since this process gives a single isomer, it would be necessary to assume

(27) (a) Kirby, A. J.; Warren, S. G. *The Organic Chemistry of Phosphorus*; Elsevier: Amsterdam, 1967; pp 176–178. (b) Buckler, S. A. *J. Am. Chem. Soc.* **1962**, *84*, 3093.

(28) (a) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: London, 1976; pp 152–157. (b) Denney, D. B.; Goodyear, W. F.; Goldstein, B. *J. Am. Chem. Soc.* **1960**, *82*, 1393. (c) Hammond, P. J.; Scott, G.; Hall, C. D. *J. Chem. Soc., Perkin Trans. 2* **1982**, 205.

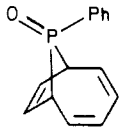
Table II. ^{13}C NMR Data[a] for Bridged Products

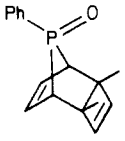
	C-1, C-6	C-2, C-5	C-3, C-4	C-7, C-8	C-9	C-10	C-11	C-12
 **7**	40.3 (62.5)	129.9 (3.5)	128.4 (3.4)	124.8 (12.2)	*b*	131.4 (8.3)	128:4 (11.7)	131.8 (3.0)
 **26**	42.3 (62.6)	128.9 (2.2)	126.2 (2.2)	122.8 (6.6)	*b*	130.1 (10.0)	127.6 (12.1)	131.3 (3.3)
 **27**	42.1 (61.6)	44.2 (18.7)	134.9 (9.9)	128.1 (10.9)	130.6 (83.5)	131.8 (7.7)	127.8 (11.5)	131.3 (2.7)
 **28**	41.8 (62.5)	41.0 (30.3)	135.0 (9.6)	128.2 (4.4)	133.1 (73.1)	129.0 (9.8)	128.8 (12.2)	131.4 (2.5)
 **30**	44.9 (9.7)	45.1 (41.5)	137.8 (12.2)	127.6 (3.9)	139.2 (28.2)	131.5 (13.7)	129.3 (4.9)	127.3 (~0)
 **29**	41.0 (10.7)	48.2 (2.5)	137.7 (~0)	128.4 (15.4)	141.7 (38.8)	130.3 (20.5)	128.2 (6.0)	126.4 (0.8)

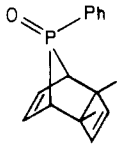
[a] In $CDCl_3$. Chemical shifts are referenced to Me_4Si as 0 ppm; ^{31}P–^{13}C coupling constants are in given in parentheses in hertz. [b] Not clearly observed.

that no rotation around the P–C bond occurs before formation of the new bond or else that the new bond is partially formed before cleavage of the old bond is complete. It is notable that the stereochemical result is the opposite of that in the thermolysis of phosphine **2**, which also is stereospecific.[2a]

The oxidation method offers a more direct approach to **7** than was previously possible[2] (12% yield in five steps from phosphirane **2**) and has provided adequate material to allow characterization by ^{31}P NMR (δ +28.6) and ^{13}C NMR spectroscopies (Table II). A set of proposed assignments for the ^{13}C signals (resembling those used for the all-carbon system[29]) is included in the table, and a comparison with the data for isomer **26** is also provided. The


26


27


28

spectra are quite similar but do possess one difference of stereochemical importance; the two-bond ^{31}P–^{13}C coupling to C-7,C-8 is controlled by the configuration at P, and as noted earlier for some 7-phosphanorbornene derivatives,[30] it is larger when the oxygen on P is oriented anti to these carbons (**7**, 12.2 Hz; **26**, 6.6 Hz). We also subjected **7** to the photochemical [2 + 2] cycloaddition[2c] to form the 7-phosphanorbornene derivative **27**. This compound exhibited the pronounced ^{31}P deshielding characteristic of the 7-phosphanorbornene series; its shift of δ +95.0 was close to that found earlier[31] for the anti isomer **28** (δ +98.8). The isomers also showed the influence of the configuration at P on the two-bond ^{31}P–^{13}C coupling to C-7,C-8; as for oxides **7** and **26**, the value was larger when oxygen was oriented anti to the coupled carbon (**27**, 10.9 Hz; **28**, 4.4 Hz). The effect was even more pronounced at the saturated carbons (C-2,C-5), where an anti oxygen (in **28**) was associated with the quite large value of 30.3 Hz (cf. 18.7 Hz in **27**). These values are similar to those found in other 7-PNB oxides.[30] Small differences in shift and coupling constant for the ipso phenyl orientation resemble those reported[30] for *P*-methyl carbons in dimers of phosphole oxides, where the syn carbon in the 7-PNB unit is at higher field and has a smaller coupling constant than the anti isomer.

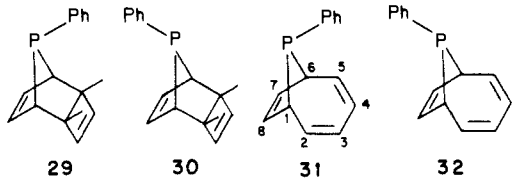
Another synthesis of the syn compound **27** was discovered during this work. The anti isomer **28** was found to undergo water-induced isomerization to **27**. The process was about 90% complete after 60 h at 50 °C; residual **26** was easily eliminated by column chromatography. The isomerization was effected in a carefully prepared benzene–water medium. The mechanism may be that of Scheme II. The fact that the isomerization is driven to the right in Scheme II confirms the greater stability of the syn isomer in this system.

The deoxygenation of 7-phosphanorbornene oxides requires special conditions to avoid loss of the bridging phosphorus by a retrocycloaddition from a P(V) intermediate. This is accomplished with the use of the pyridine complex of trichlorosilane, which has previously been applied successfully[31] to **26**. Relative to noncyclic or monocyclic tertiary phosphines, quite remarkable ^{31}P deshielding is seen in the 7-PNB series,[31] and the product **29** with a shift of δ +98.8 was no exception. However, studies of the 7-PNB system as incorporated in the phosphole dimer structure have consistently shown that the syn isomers experience much greater deshielding

(29) Gillissen, H. M. J.; Schipper, P.; van Ool, P. J. J. M.; Buck, H. M. *J. Org. Chem.* **1980**, *45*, 325.

(30) Quin, L. D.; Mesch, K. A.; Bodalski, R.; Pietrusiewicz, K. M. *Org. Magn. Reson.* **1982**, *20*, 83.

(31) Quin, L. D.; Caster, K. C.; Kisalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021.



29 30 31 32

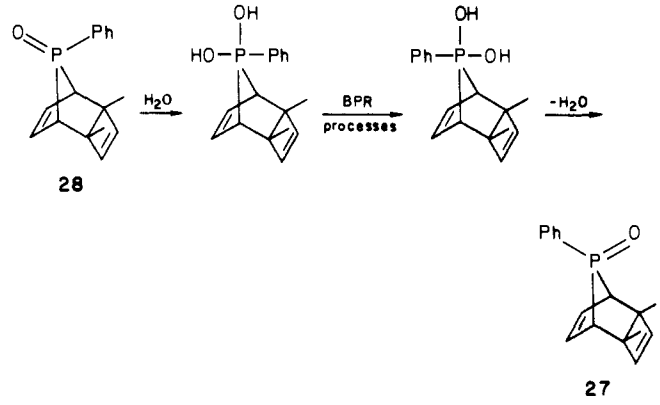
than do the anti isomers; they frequently have values in the δ +100 region whereas the anti isomers are more upfield by some 50–70 ppm, and this raised the question[32] of the correctness of the configuration assignments at phosphorus in the present series of compounds. This rested originally[2] on ^{1}H NMR spectral differences between phosphines **31** and **32**, but ^{13}C NMR properties support this assignment through the large difference in $^2J_{PC}$ to C-7,C-8 in the two isomers (these values agree with others recently published[5]), which correlate with the proximity of the lone pair.[16b] However, to remove any stereochemical ambiguity from our studies, X-ray diffraction analysis of phosphine **31** was performed. Atomic (non-hydrogen) fractional coordinates are provided in Table III; interatomic distances and angles are given in Table IV. The syn phenyl structure was indeed confirmed (Figure 1). The 9-phosphabicyclo[4.2.1]nona-2,4,7-triene system in **31** may be viewed as comprising three planes, viz., planes A (C-1–C-6), B (C-1,C-6–C-8), and C (C-1, P, C-6) (Table V) intersecting at the bridgehead carbons C-1 and C-6. Intramolecular repulsions between the *P*-phenyl substituent and the phosphacycloheptadiene ring are relieved by the bending of these moieties away from each other as reflected by the highly significant P atom displacement of 0.258 Å to the opposite side of the phenyl ring plane from the C-1–C-6 moiety in addition to its unequal displacements of 1.153 and 0.905 Å, respectively, from planes A and B. The bond angle involving P and the bridgehead carbons (88.9°) is considerably larger than that found in phosphines of the 7-phosphanorbornene system (79° for an anti 7-phenyl derivative[33]) but still contracted relative to that in acyclic tertiary phosphines (99.1° in Me_3P[34]). The bonding geometry at the P atom has the usual pyramidal shape, with the mean angle at P to the exocyclic phenyl carbon expanded to 107.4°.

Since all steps in the conversion of **31** to **29** involve retention of configuration, the anti configuration assigned to **29** is confirmed. It therefore became important to synthesize the unknown isomer **30** with syn phenyl since its ^{31}P shift might be expected to be well downfield of any so far observed with this structural feature. The synthesis of phosphine **30** from oxide **27** was accomplished with the $HSiCl_3$–C_5H_5N complex; as expected, its ^{31}P NMR shift (δ +147) was nearly 50 ppm downfield from that of the anti isomer. Phosphine **30** was stable in solution, but on concentration of the solution, or on vacuum sublimation of benzene from a frozen sample, extensive decomposition occurred, and it has not been possible to prepare a pure specimen. The instability is attributed to intermolecular reactions at phosphorus, which lead to P–P bond formation and fragmentation with the formation of $(C_6H_5P)_{4,5}$. Similar interactions have been encountered at the 7-phosphanorbornene moiety of phosphole dimers, which also decompose when concentrated solutions are heated.[24] Phosphine **30** was characterized by ^{13}C NMR spectral measurements (Table II) and by peroxide oxidation to regenerate the starting oxide. The phosphine also was unstable in methanol, presumably forming a P(V) adduct that underwent retrocycloaddition to give COT and methyl phenylphosphinite as noted[32] for the syn isomer.

The ^{13}C NMR spectra of the isomeric phosphines (Table II) showed the expected differences in $^2J_{PC}$ that arise from the relation of carbon to the phosphorus lone pair. Thus, unsaturated carbons 7 and 8 had the larger coupling (15.4 Hz) in phosphine **29**, where they are close to the lone pair; in isomer **30**, $^2J_{PC}$ was only 3.9 Hz. More striking were the values at saturated carbons 2 and 5, where proximity to the lone pair in **30** led to the very large coupling value of 41.5 Hz (cf. to 2.5 Hz in **29**[31]). Three-bond ^{31}P–^{13}C coupling is similarly affected by lone-pair orientation, and this is manifested in the differences at C-3,C-4 (**29**, $^3J_{PC} \sim 0$; **30**, $^3J_{PC}$ = 12.2 Hz). The one-bond coupling to the ipso phenyl carbon in the isomers follows the same relation as seen for P–CH_3 groups in phosphole dimers;[31] the syn position is associated with a more upfield shift and a smaller coupling constant. There is also a noticeable difference in $^2J_{PC}$ to the ortho phenyl carbons (**29**, 20.5 Hz; **30**, 13.7 Hz) which may arise from rotational preferences in the isomers that lead to preferred positioning relative to the lone pair.

(32) Mesch, K. A.; Quin, L. D. *Tetrahedron Lett.* **1980**, 4791.
(33) McPhail, A. T., unpublished results quoted in ref 30.
(34) Lide, D. R., Jr.; Man, D. E. *J. Chem. Phys.* **1958**, *29*, 914.

Scheme II



28 27

Table III. Non-Hydrogen Atom Fractional Coordinates (×10^4) for **31** with Standard Deviations in Parentheses

atom	*x*	*y*	*z*
C-1	2398 (5)	595 (2)	−56 (9)
C-2	3462 (4)	527 (2)	−1082 (13)
C-3	3701 (5)	676 (2)	−2716 (12)
C-4	3092 (6)	966 (3)	−4002 (10)
C-5	2046 (8)	1170 (2)	−3900 (10)
C-6	1215 (5)	1123 (2)	−2348 (10)
C-7	888 (4)	581 (2)	−2173 (10)
C-8	1483 (5)	313 (2)	−1035 (11)
P-9	1768 (1)	1233.3 (5)	0[a]
C-10	2879 (3)	1699 (2)	−243 (7)
C-11	3889 (4)	1645 (2)	707 (8)
C-12	4653 (4)	2039 (2)	723 (9)
C-13	4427 (4)	2485 (2)	−80 (11)
C-14	3430 (5)	2548 (2)	−1033 (9)
C-15	2658 (4)	2159 (2)	−1090 (8)

[a] The *z*-coordinate of P-9 was held constant throughout to define the origin in this direction.

Table IV. Interatomic Distances (Å) and Angles (deg) in **31**, with Standard Deviations in Parentheses

	Bond Lengths		
C-1–C-2	1.484 (9)	C-7–C-8	1.300 (9)
C-1–C-8	1.502 (8)	P-9–C-10	1.817 (4)
C-1–P-9	1.846 (5)	C-10–C-11	1.397 (6)
C-2–C-3	1.283 (12)	C-10–C-15	1.387 (7)
C-3–C-4	1.410 (10)	C-11–C-12	1.384 (7)
C-4–C-5	1.362 (11)	C-12–C-13	1.342 (8)
C-5–C-6	1.508 (10)	C-13–C-14	1.387 (8)
C-6–C-7	1.489 (7)	C-14–C-15	1.381 (7)
C-6–P-9	1.853 (7)		
	Bond Angles		
C-2–C-1–C-8	109.0 (5)	C-1–P-9–C-6	88.9 (3)
C-2–C-1–P-9	118.1 (4)	C-1–P-9–C-10	108.6 (2)
C-8–C-1–P-9	99.6 (4)	C-6–P-9–C-10	106.1 (2)
C-1–C-2–C-3	128.2 (6)	P-9–C-10–C-11	120.9 (4)
C-2–C-3–C-4	131.7 (6)	P-9–C-10–C-15	119.8 (3)
C-3–C-4–C-5	130.6 (7)	C-11–C-10–C-15	118.2 (4)
C-4–C-5–C-6	127.7 (6)	C-10–C-11–C-12	119.8 (5)
C-5–C-6–C-7	108.4 (5)	C-11–C-12–C-13	121.6 (5)
C-5–C-6–P-9	116.2 (5)	C-12–C-13–C-14	119.7 (5)
C-7–C-6–P-9	99.5 (5)	C-13–C-14–C-15	119.9 (5)
C-6–C-7–C-8	115.7 (5)	C-10–C-15–C-14	120.7 (5)
C-1–C-8–C-7	115.4 (5)		

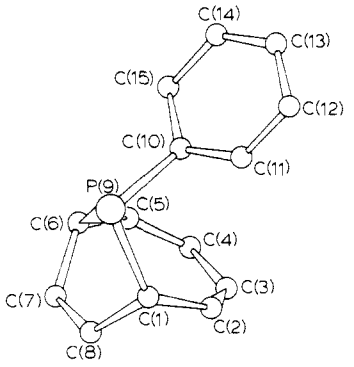


Figure 1. Molecular structure of *syn*-9-phenyl-9-phosphabicyclo-[4.2.1]nona-2,4,6-triene (**31**) from X-ray analysis.

Table V. Equations of Least-Squares Planes in **31** in the Form $PX + QY + RZ - S = 0$,[a] with Displacements (Å, in Square Brackets) of Selected Atoms from These Planes

Plane A: C-1–C-6

$-0.3684X - 0.8419Y - 0.3943Z + 2.3666 = 0$

[C-1, 0.005; C-2, −0.018; C-3, 0.014; C-4, 0.006; C-5, −0.017; C-6, 0.009; C-7, 1.307; C-8, 1.315; P-9, −1.153]

Plane B: C-1, C-6–C-8

$0.6344X - 0.2346Y - 0.7365Z - 1.4800 = 0$

[C-1, −0.002; C-2, 1.396; C-5, 1.433; C-6, 0.002; C-7, −0.004; C-8, 0.004; P-9, −0.905

Plane C: C-1, C-6, P-9

$0.8375X + 0.3832Y - 0.3895Z - 3.0162 = 0$

[C-1, 0.000; C-2, 1.286; C-5, 1.318; C-6, 0.000; C-7, −0.925; C-8, −0.923; P-9, 0.000]

Plane D: C-10–C-15

$0.4260X - 0.3398Y - 0.8385Z - 0.0826 = 0$

[C-1, 0.638; C-6, 0.959; P-9, −0.290; C-10, 0.006; C-11, −0.011; C-12, 0.014; C-13; −0.011; C-14, 0.006; C-15, −0.003]

[a] Cartesian coordinates (X, Y, Z) are related to the fractional atomic coordinates (x, y, z) in Table III by the following transformations: $X = xa$, $Y = yb$, $Z = zc$. Dihedral angles (deg) between planes: A/B, 75.3; A/C, 118.5; A/D, 62.6; B/C, 136.7; B/D, 14.6; C/D, 123.6.

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Proton NMR spectra were obtained on a JEOL FX-90Q spectrometer at 89.6 MHz or on a Bruker WM-250 spectrometer at 250 MHz. Carbon-13 FT NMR spectra were taken on the JEOL FX-90Q at 22.5 MHz using an internal deuterium lock and were proton noise decoupled. Proton and carbon chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane. Phosphorus-31 FT NMR spectra were obtained with the JEOL FX-90Q at 36.2 MHz; chemical shifts are given in ppm relative to external 85% H_3PO_4 with downfield shifts given positive signs. Mass spectra were run at the Research Triangle Mass Spectrometry Center on an AEI MS-903 spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

1-Phenyl-1*H*-phosphonin 1-Oxide (11). (a) To a suspension of phosphirane **2** (0.50 g, 2.4 mmol, prepared by a published procedure[2]) in methanol (30 mL) at −15 °C was added a 1:1 mixture of methanol and 30% H_2O_2 (6 mL, 11 mmol). The mixture was stirred at −15 °C for 8–10 h or until all starting material had been consumed as monitored by ^{31}P NMR. The methanol was removed at −15 to −20 °C under high vacuum. The remaining suspension of **11** was extracted with chloroform (3 × 10 mL) at −30 °C, and the combined $CHCl_3$ extracts were dried with $CaCl_2$. The $CHCl_3$ solution was then concentrated at −15 to −20 °C under high vacuum to give phosphonin oxide **11** (containing a few percent of the dihydrophosphindole oxide **13**) as a viscous, pale oil: ^1H NMR ($CDCl_3$, −20 °C) δ 4.9–6.7 (complex m, =C*H*), 7.4–7.9 (m, phenyl *H*); ^{31}P NMR ($CDCl_3$, −20 °C) δ +16.2; ^{13}C NMR ($CDCl_3$, −20 °C) δ 154.0 (s, C-3 or C-8), 141.6 (d, J = 2 Hz, C-3 or C-8), unassigned signals at 137.2, 134.8, 133.0, 131.7, 130.9, 129.9, 128.5, 128.2, 124.4.

(b) To a solution of phosphirane **2** (0.50 g, 2.4 mmol) in $CDCl_3$ (5 mL) at −15 °C was added *tert*-butyl hydroperoxide (0.22 g, 2.4 mmol), and the mixture was stirred at −10 to −15 °C for 8–10 h or until all starting phosphirane had been consumed. The reaction mixture was then dried ($CaCl_2$) at −15 °C and concentrated at −20 °C under high vacuum to give phosphonin oxide **11** as a viscous, pale oil: ^{31}P NMR ($CDCl_3$, −20 °C) δ +16.2.

1-*tert*-Butyl-1*H*-phosphonin 1-Oxide (9). By the procedures used to prepare the *P*-phenyl derivative **11**, phosphirane **1** (0.50 g, 2.6 mmol) was oxidized with either H_2O_2 (6 mL, 11 mmol) or *tert*-butyl hydroperoxide (0.23 g, 2.6 mmol) to give phosphonin oxide **9** as a clear, viscous oil: ^1H NMR ($CDCl_3$, −20 °C) δ 1.4 (d, $^2J_{PH}$ = 15 Hz, C*H*$_3$), 5.5–7.4 (complex m, =C*H*); ^{31}P NMR ($CDCl_3$, −20 °C) δ +33.2; ^{13}C NMR ($CDCl_3$, −20 °C) δ 25.3 (d, J = 28.6 Hz, *C*CH$_3$), 31.5 (d, J = 78.0 Hz, *C*CH$_3$), 116.9 (d, J = 95.6 Hz, C-2 or C-9), 127.3 (d, J = 95.6 Hz, C-2 or C-9), 130.2 (d, J = 8.8 Hz, C-4 or C-7), 129.3 (d, J = 5.5 Hz, C-4 or C-7), 135.9 (s, C-5 or C-6), 139.2 (s, C-5 or C-6), 141.8 (d, J = 5.5 Hz, C-3 or C-8), 152.5 (s, C-3 or C-8); ^1H NMR (300 MHz, $CDCl_3$, −30 °C) δ 5.64 (d of d, $^2J_{P,H-2}$ = 26.4, $^3J_{H-2,H-3}$ = 15.0 Hz, H-2), 5.86 (d, $^3H_{H-6,H-7}$ = 14.0 Hz, H-6), 6.2 (partly obscured by some **1**, d of d, $^3J_{H-4,H-5}$ = 7.3, $^3J_{H-4,H-3}$ = 5.5 Hz, H-4), 6.34 (d of d, $^3J_{PH-9}$ = 28.8, $^3J_{H-8,H-9}$ = 10.7 Hz, H-9), 6.59 (d of d, $^3J_{H-6,H-7}$ = 14.0, $^3J_{H-7,H-8}$ = 2.1 Hz, H-7), 6.76 (d of d of d, $^3J_{PH-3}$ = 40.5, $^3J_{H-2,H-3}$ = 15.0, $^3J_{H-4,H-3}$ = 5.5 Hz, H-3), 6.80 (d, $^3J_{H-4,H-5}$ = 7.3 Hz, H-5), 7.44 (d of d of d, $^3J_{PH-8}$ = 30.2, $^3J_{H-8,H-9}$ = 10.7, $^3J_{H-7,H-8}$ = 2.1 Hz, H-8); selective irradiations and affected signals were δ 5.64 (δ 6.76), 5.86 (6.59), 6.34 (7.44), 6.59 (5.86 and 7.44), 6.76 (5.64 and 6.2), 6.80 (6.2), 7.44 (6.34).

***r*-1-Phenyl-*t*-3a,*c*-7a-dihydrophosphindole 1-Oxide (13a).** (a) To a suspension of phosphirane **2** (0.5 g, 2.4 mmol) in methanol (30 mL) at 0 °C under nitrogen was added a 1:1 mixture of methanol and 30% H_2O_2 (6 mL, 11 mmol). The mixture was stirred at 0 °C for 2 h and then at room temperature overnight. Methanol was then removed under aspirator pressure, and the aqueous mixture was extracted with chloroform (3 × 10 mL). The combined chloroform extracts were dried ($MgSO_4$) and concentrated to give **13a** as a pale, viscous oil. Chromatography on alumina (10% methanol in benzene) provided **13a** as a colorless oil. During oxidation and workup, care must be taken to avoid prolonged exposure of **13a** to air: ^1H NMR ($CDCl_3$) δ 3.06–4.04 (2 H, five-line AB part of ABX, H-3a and H-7a), 5.9–6.4 (4 H, m, H-4, H-5, H-6, and H-7), 6.43 (1 H, d of d, $^2J_{PH}$ = 25.9, $^2J_{H-2,H-3}$ = 8.5 Hz, H-2), 7.22 (1 H, d of d, $^3J_{PH}$ = 39.2, $^3J_{H-2,H-3}$ = 8.5 Hz, H-3), 7.33–7.84 (5 H, m, phenyl *H*); ^{31}P NMR ($CDCl_3$) δ +46.9; ^{13}C NMR ($CDCl_3$), Table I; mass spectrum, m/z calcd for $C_{14}H_{13}OP$ [M^+ − 1] 227.0625, found 227.0625.

(b) **13a** was also prepared by quenching dilithium cyclooctatetraenide (9.6 mmol) with $C_6H_5POCl_2$ (1.9 g, 9.6 mmol) at −78 °C. The solution was warmed to room temperature; a strong ^{31}P NMR ($CDCl_3$) signal at δ +47.0 confirmed the presence of **13a**.

***r*-1-*tert*-Butyl-*t*-3a,*c*-7a-dihydrophosphindole 1-Oxide (12a).** By the procedure described above, phosphirane **1** was treated with H_2O_2 (6 mL, 11 mmol) to give the *tert*-butyldihydrophosphindole oxide **12a**: ^1H NMR ($CDCl_3$) δ 1.15 (d, $^3J_{PH}$ = 7 Hz, C*H*$_3$), 2.30 (d of d, $^2J_{PH}$ = 9, $^3J_{H-3a,H-7a}$ = 18 Hz, H-7a), 3.75 (br d, $^3J_{H-3a,H-7a}$ = 18 Hz, H-3a), 5.90–6.50 (complex, H-2, H-4, H-5, H-6, and H-7), 7.05 (d of d, $^3J_{PH}$ = 34, $^3J_{H-2,H-3}$ = 9 Hz, H-3); ^{31}P NMR ($CDCl_3$) δ +65.3; ^{13}C NMR, Table I; mass spectrum, m/z calcd for $C_{12}H_{17}OP$ [M^+] 208.1017, found 208.1014.

Measurement of Half-Life Times of Phosphonin Oxides 9 and 11. Solutions (0.75 M) of the phosphonin oxides **9** and **11** in $CDCl_3$ were placed in the NMR probe at operating temperature (measured to be 24 ± 2 °C). The ^{31}P NMR spectra of the samples were recorded every 30 s (10 transients each with pulse delay of 0.2 s) until conversion to the dihydrophosphindole oxides was complete. The approximate ratios of phosphonin oxide to dihydrophosphindole were determined by the intensity of the ^{31}P NMR signals. Then first-order plots of concentration vs. time provided the approximate half-lives of 4 min for the 1-phenylphosphonin oxide **11** and 8 min for the *tert*-butylphosphonin oxide **9**.

Partial Epimerization of *trans*-3a,7a-Dihydrophosphindole 1-Oxide (13a) to Its Cis Isomer 16. A solution of **13a** (0.20 g, 0.9 mmol) in benzene (30 mL) was shaken vigorously with 30% NaOH solution (30 mL) for 4 min. The benzene layer was separated, dried ($MgSO_4$), and concentrated to give a viscous oil which was examined by ^{31}P NMR spectroscopy. It contained some unchanged **13a** (δ +47.0), the cis isomer **16** (δ +61.1), and the product **14** of double bond rearrangement (δ +54.2).

Double Bond Rearrangement of 13a. A solution of dihydrophosphindole oxide **13a** (0.50 g, 2.2 mmol) and 15% NaOH solution (25 mL) was stirred at room temperature for 10 h. The reaction mixture was then extracted with chloroform (3 × 25 mL); the chloroform extract was dried ($MgSO_4$) and concentrated to give 0.40 g (80%) of the known[17] 2,3-dihydro isomer **14** (^{31}P NMR ($CDCl_3$) δ +54.2[9a]) whose ^1H NMR spectrum matched that reported.

1-Phenylphosphindole 1-Oxide (15). A solution of *trans*-dihydrophosphindole oxide **13a** (0.50 g, 2.2 mmol) in methanol (75 mL) was stirred vigorously under an atmosphere of oxygen for 5 days at room temperature. The reaction mixture was then concentrated and **15** isolated

from the resulting oil by chromatography on silica with benzene; the yield of clear oil was 0.30 g (60%): ^{31}P NMR ($CDCl_3$) δ +41.4; ^{1}H NMR spectral properties were identical with literature[17] values.

***r*-1-Phenyl-*t*-3a,*c*-7a-dihydrophosphindole (19).** To a solution of phosphine oxide **13a** (0.70 g, 3.1 mmol) in benzene (50 mL) was added $SiHCl_3$ (1.5 g, 11.1 mmol), and the mixture was stirred under nitrogen overnight at room temperature. Excess 30% NaOH (30 mL) was added cautiously to the cooled (10 °C) reaction mixture. After addition the layers were separated. The aqueous layer was extracted with benzene (2 × 50 mL). The combined benzene extract was dried, filtered, and concentrated to give 0.40 g (66%) of **19** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 2.6–3.3 (2 H, br m, H-3a, H-7a), 5.75–6.90 (6 H, complex m, =C*H*), 7.3–7.9 (5 H, phenyl *H*); ^{31}P NMR ($CDCl_3$) δ −16.4, $^2J_{P,H-2}$ = 41.5, $^2J_{P,H-7a}$ < 4 Hz. The phosphine **19** was converted to the phosphonium salt by treating a benzene solution with excess methyl iodide. The resulting precipitate was filtered and washed with benzene, and a portion was recrystallized from methanol for analysis: ^{1}H NMR ($CDCl_3$) δ 2.95 (d, $^2J_{PH}$ = 15 Hz, PC*H*$_3$), 3.55–3.8 (m, C*H*), 6.05–7.05 (complex, = C*H*), 7.48–8.30 (phenyl *H*); ^{31}P NMR ($CDCl_3$) δ +34.9; ^{13}C NMR, Table I. Anal. Calcd for $C_{15}H_{16}IP$: C, 50.86; H, 4.56; P, 8.74. Found: C, 51.11; H, 4.61; P, 8.71.

***syn*-9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene 9-Oxide (27) by Isomerization of 28.** A dry sample of *anti*-9-phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene 9-oxide (**28**) (1.50 g, 6.5 mmol) was dissolved in 50 mL of dry benzene (distilled from CaH_2 before use). Water (1.0 mL) was added, producing a two-phase solution. This was stirred under N_2 at 50 °C for 60 h. The solution was then concentrated to dryness, leaving a colorless oil which by ^{31}P NMR analysis consisted of 90% **27** and 16% **28**. The crude product was flash chromatographed on a silica (230–400-mesh) column (2 × 15 cm) by elution with methanol in toluene (1:4). Unchanged **28** was eluted first, followed by **27**, which was concentrated to give a colorless oil (0.107 g, 71%), crystallizing upon standing: mp 106–109 °C [lit.[2c] mp 107.5–109 °C]; ^{1}H NMR ($CDCl_3$) δ 3.07 (d of t, $^3J_{HH}$ = 3.5, $^3J_{HH}$ = $^4J_{HH}$ = 3.4 Hz, H-1, H-6), 3.50 (d, $^3J_{HH}$ = 3.5 Hz, H-2, H-5), 5.79 (s, H-3, H-4), 6.00 (d of t, $^3J_{PH}$ = 12.4, $^3J_{HH}$ = $^4J_{HH}$ = 3.4 Hz, H-7, H-8), 7.3–7.8 (m, aryl H); ^{13}C NMR, Table II; ^{31}P NMR ($CDCl_3$) δ +95.0. Anal. Calcd for $C_{14}H_{13}OP$: C, 73.68; H, 5.70; P, 13.60. Found: C, 73.85; H, 5.66; P, 13.42.

***anti*-9-Phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene 9-Oxide (7).** A solution of phosphirane **2** (2.0 g, 0.4 mmol) in benzene (150 mL) was stirred vigorously under an atmosphere of oxygen at room temperature for 5 days. The reaction mixture was then heated to boiling and the insoluble material filtered off. The filtrate was concentrated to dryness and the red-brown residue triturated with ether (25 mL). The brown solid which resulted was filtered and recrystallized from acetone to give 0.80 g (38%) of the phosphine oxide **7** as white needles: mp 175–179 °C [lit.[2a] mp 177.5–177.7 °C]; the ^{1}H NMR spectrum matched the published spectrum;[2a] ^{13}C NMR, Table II.

***syn*-9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene 9-Oxide (27) from 7.** A solution of the bicyclic phosphine oxide **7** (0.50 g, 2.2 mmol) in deoxygenated benzene (340 mL) was irradiated through Pyrex by using a 450-W Hanovia mercury lamp at room temperature for 2.75 h. The reaction mixture was then concentrated and the yellow solid residue purified by chromatography on silica (5% methanol in benzene) to give 300 mg (60%) of **27** with the same spectral properties as for the product formed from isomerization of **28**.

***syn*-9-Phenyl-9-phosphatricyclo[4.2.1.0^{2,5}]nona-3,7-diene (30).** A solution of pyridine (1.0 mL, 13 mmol) of $HSiCl_3$ (0.5 mL, 4 mmol) in 50 mL of dry, distilled benzene was prepared at room temperature under an N_2 atmosphere. Solid phosphine oxide **27** (0.20 g, 0.88 mmol) was added directly, and the solution was heated at 70 °C for 1 h. The solution was cooled to 0 °C, and 10 mL of 30% NaOH was added slowly with stirring over a 20-min period. The layers were separated, and the benzene layer was dried over anhydrous $MgSO_4$ and filtered. By ^{31}P NMR analysis, the filtered solution contained only one phosphorus species (**30**, δ +146.6), but the oil obtained by evaporation of solvent and pyridine under vacuum contained about 15% of the decomposition products $(C_6H_5P)_{4,5}$. The ^{13}C NMR spectrum of **30** (Table II) was obtained from this crude sample.

***syn*-9-Phenyl-9-phosphabicyclo[4.2.1]nona-2,4,7-triene (31). Crystal Data.** $C_{14}H_{13}P$ **31**, M_r 212.23, orthorhombic, a = 11.941 (1) Å, b = 26.406 (3) Å, c = 7.269 (1) Å, V = 2292.0 Å^3, Z = 8, d_{calcd} = 1.230 g cm^{-3}, μ(Cu Kα radiation, λ = 1.5418 Å) = 18.0 cm^{-1}; space group *Iba*2(C_{2v}^{21}) or *Ibam*(D_{2h}^{26}) from systematic absences, hkl when $h + k + l \neq 2n$, $0kl$ when $k \neq 2n$, $h0l$ when $h \neq 2n$, shown to be the former by structure solution and refinement.

Crystallographic Measurements. A crystal of dimensions 0.20 × 0.40 × 0.60 mm was sealed inside a thin-walled glass capillary. Preliminary unit-cell parameters and space group information were obtained from oscillation, Weissenberg, and precession photographs. Intensity data for one octant of reciprocal space were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, incident-beam graphite monochromator; ω–2θ scans, θ_{max} = 67°). From a total of 1120 independent measurements, those 864 reflections with $I > 3.0\sigma(I)$ were retained for the structure analysis and corrected for the usual Lorentz and polarization effects. Empirical absorption corrections were also applied to these data. Refined unit-cell parameters were derived by least-squares treatment of the diffractometer setting angles for 25 high-order reflections widely separated in reciprocal space.

Structure Analysis. The crystal structure was solved by the heavy-atom approach. Approximate coordinates for the phosphorus atom were derived from a Patterson map. Weighted F_o Fourier syntheses yielded carbon atom positions which indicated that the potential molecular mirror plane of symmetry was not coincident with a crystallographic mirror plane of space group *Ibam*, thereby eliminating this centrosymmetric space group from further consideration, and all further calculations were performed using equivalent positions appropriate to space group *Iba*2. Full-matrix least-squares adjustment of the carbon and phosphorus atom positional and isotropic thermal parameters reduced R[35] to 0.129, at which point hydrogen atoms were located in a difference Fourier synthesis. Several further cycles of least-squares refinement of non-hydrogen atom positional and anisotropic thermal parameters, with hydrogen atoms included at their calculated positions, converged to R = 0.052 (R_w = 0.067).[35]

Non-hydrogen atom fractional coordinates are given in Table III; structural data are provided in Tables IV and V.

Neutral atom scattering factors and their anomalous scattering corrections were taken from ref 36. In the least-squares iterations, $\sum w\Delta^2$ ($w = 1/\sigma^2|F_o|$; $\Delta = |F_o| - |F_c|$) was minimized.

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Supplementary Material Available: Tables of torsion angles, anisotropic temperature factor parameters, calculated hydrogen atom fractional coordinates, and observed and calculated structure amplitudes (9 pages). Ordering information is given on any current masthead page.

(35) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.
(36) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.