Phospholes with Reduced Pyramidal Character from Steric Crowding. 1. Synthesis and NMR Characterization of 1-(2,4-Di-*tert*-butyl-6-methylphenyl)-3-methylphosphole†

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The sterically crowded 1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methylphosphole was synthesized by dehydrohalogenation of the corresponding 3,4-dibromophospholane, in order to probe the possibility that the steric congestion would cause some flattening of the phosphorus pyramid and an increase in electron delocalization. The phosphole was a recrystallizable solid with ^{31}P NMR δ 1.8. Semiempirical calculations indicated that the pyramidal shape was retained but was noticeably flatter than in 1-phenylphosphole. In the low energy conformation, the phosphole and phenyl ring planes are approximately orthogonal, with the 2-*tert*-butyl group in the less crowded position that is *syn* to the lone pair on phosphorus. The 6-methyl group is positioned under the phosphole ring. This conformational prediction was amply confirmed by several chemical shift and coupling effects in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum displayed an unusually large four-bond coupling (6 Hz) of ^{31}P to the *m*-phenyl proton *syn* to the lone pair (and none to the *anti*-*meta* proton), consistent with the orthogonal conformation. The oxide of the phosphole showed more stability than that of less crowded phospholes and gave a ^{31}P NMR signal that was detectable over a several hour period at room temperature. The oxide proceeded to give the usual Diels−Alder dimer and also formed a cycloadduct with *N*-phenylmaleimide. The phosphoryl group of the latter was reduced with trichlorosilane to give the phosphine. This new 7-phosphanorbornene derivative gave the most downfield ^{31}P NMR shift (δ 153.3) of any member of this family, all of which are characterized by remarkable deshielding in the *syn* isomer.

Theoretical calculations by Chesnut and Quin[1] have recently been published that bring attention to the importance of the geometry at phosphorus in controlling the extent of electron delocalization in the phosphole ring system and the relevance of this geometry in establishing the ^{31}P NMR shift of the system. These calculations, and those of others,[2] predict that delocalization would be extensive in a phosphole with planarity at phosphorus, but quite small in the natural form with pyramidal phosphorus. The planar form is 25.8 kcal/mol higher in energy.[1] The low level of delocalization in phospholes is clearly revealed by the chemical and physical properties of typical members of the family, as is discussed in recent reviews.[3,4] The Bird Index,[5] which is based on experimental bond parameters, is a convenient way of assessing the extent of delocalization in related cyclic systems, and when applied to a phosphole for which structural data are available (1-benzyl[6]), an Index of 35.5, below that of furan (43; cf. to 59 for pyrrole and 66 for thiophene) was obtained.[7]

In our theoretical studies,[1] as the phosphorus atom was gradually allowed to lose its pyramidal geometry and approach planarity, the extent of delocalization was observed to increase, and when full planarity was achieved delocalization was extensive, as indicated by pronounced shortening of the single bonds and lengthening of the double bonds. We have attempted to perform flattening of the phosphorus pyramid experimentally, by placing on it a substituent of such size as to cause serious congestion with the atoms of the phosphole ring. While it is unlikely that this approach can force complete planarity at phosphorus, it nevertheless could cause modification of the measurable properties of the phosphole in directions that would reveal an increase in electron delocalization. Particularly suggestive of this effect would be the bond parameters established by X-ray diffraction analysis, and the ionization energies provided by photoelectron spectroscopy.

In selecting the bulky substituent to be placed on phosphorus, we were guided by PM3 semiempirical calculations, using the Spartan program (version 3.1, Wavefunction, Inc.). We examined the bond angle at phosphorus for carbon of the exocyclic substituent (β), and the related parameter of the angle (α) by which the exocyclic carbon atom falls below the plane of the C_2−P−C_5 section of the ring. These angles are known for 1-benzylphosphole from X-ray analysis of the crystal[6] to be 106° and 66.9°, respectively, and the validity of our calculations was confirmed by closely reproducing these values for this model phosphole (106.3° and 66.5°, respectively) when in the same conformation (with the benzene ring lying under the phosphole ring) as found in the crystal. Results of the calculations for several groups on phosphorus are shown in Table 1 (the angles

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(4) Hughes, A. N. In *Handbook of Organophosphorus Chemistry*; Engel, R., Ed.; Marcel Dekker: New York, 1992; pp 512−514.

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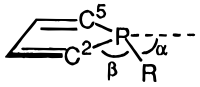
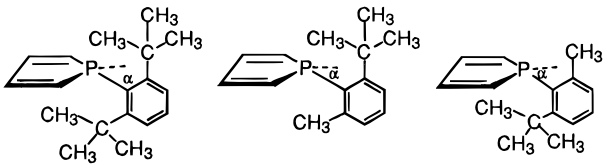
Table 1. Calculated Effects of P−Substituent on the Pyramidal Shape at Phosphorus in 1-*R*-phosphole



R	Spartan version 3.1 P_{oop}, deg[a]	α, deg[b]	β, deg[c]	$\angle C^2-P-C^5$, deg	POAV-2 method $\theta_{o\pi}-90$, deg
methyl	5.6	70.2	103.8	90.1	28.23
phenyl	6.4	68.5	105.0	90.2	27.55
1-adamantyl	6.17	68.1	105.3	90.1	27.42
benzyl	6.0	66.5[d]	106.3	90.3	26.80
mesityl	8.0	65.2	107.1	90.4	26.29
2,4,6-trimethoxyphenyl	9.6	61.7	109.5	90.6	24.89
2,4-di-*tert*-butyl-6-methylphenyl					
form **2A**	8.9	63.2[e]	108.5	90.5	25.55
form **2B**	9.1	58.0[e]		90.4	23.75
2,6-di-*tert*-butylphenyl	10.0	56	109.9[f]	90.8	22.74

[a] Angle by which P is out of plane (oop) (mean) of the phosphole ring carbon atoms. [b] Deflection from C_2-P-C_5 plane. [c] C_2-P-R bond angle. The C_5-P-R angle was essentially the same except as noted. [d] Cf. to experimental value of 66.9°.[6] [e] Confirmed by MOPAC (version 6.0) calculation. [f] C_5-P-R angle 116.2°. [g] Reference 8b.

should be considered as tentative and are to be refined in later work with higher level programs). The predicted value for α of 1-methylphosphole (70.2°) may be taken as a starting point for discussion. Replacement by phenyl or the more bulky 1-adamantyl reduced the value by only about 2°. Mesityl caused a further reduction of 3°. The flattening became quite pronounced for the 2,6-di-*tert*-butylphenyl substituent, where the angle was reduced to 56°. In these crowded aryl derivatives, it was found that in the low-energy conformation the planes of the phosphole and benzene rings are approximately perpendicular, which causes placement of one *ortho* substituent under the phosphole ring, the other above it. When the benzene ring is unsymmetrically substituted, as in 2-*tert*-butyl-6-methylphenyl, two conformations can be adopted, with the smaller (methyl) substituent located under the phosphole ring, as in **2A** or above as in **2B**. The energy difference (3.96 kcal/mol) indicates a very strong preference for **2A**. As might be expected, the reduction in angle α is larger (58°) with *tert*-butyl under the phosphole ring than when methyl is under the ring (63.2°). In all phospholes examined, the P atom was found to be forced out of the plane of the four ring carbons, reaching a maximum angle of deflection of 10.0° in 2,6-di-*tert*-butylphenyl. The reality of this effect was demonstrated years ago by the X-ray analysis of 1-benzylphosphole.[6]



1, α = 56° **2A**, α = 63.2° **2B**, α = 58°

The change in the pyramidal shape at phosphorus as the steric bulk of the exocyclic substituent is increased can also be expressed by the POAV (π-orbital axis vector) treatment, recently introduced to describe the pyramidal shape of a carbon center.[8] This treatment provides a single parameter ($\theta_{o\pi} - 90$, which for sp^3C is 19.47° and for sp^2C is 0.0°. We have applied a simplified version (POAV-2[8b]) to calculate the change in the pyramidal shape at the P center of the series of phospholes found in Table 1, using the calculated values for the bond angles presented therein. The results are also recorded in Table 1. The value decreases steadily as the steric bulk of the P-substituent increases.

We have proceeded to attempt the synthesis of phospholes with a *P*-aryl group bearing the *ortho* substitutents seen in **1** and **2**. We have been successful with the latter substitution pattern, and some of the properties for the compound prepared (1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methylphosphole, **9**, in Scheme 1) are described in this paper. In the following paper, the photoelectron spectrum and its use in assessing the degree of flattening of the phosphorus pyramid are presented. The more crowded 2,6-di-*tert*-butylphenyl substitution pattern of **1** has so far proved difficult to create in a phosphole. As will be seen, however, the properties of **9** are of considerable interest, prompting continued attempts to synthesize this and other crowded phospholes in future work.

Synthesis of 1-(2,4-Di-*tert*-butyl-6-methylphenyl)-3-methylphosphole (9). The preferred method of synthesis of phospholes is that described by Mathey in which the cycloadduct of a diene and a phosphorus(III) halide is subjected to dehydrohalogenation with an amine, usually a pyridine derivative.[9] However, the cycloaddition reaction is retarded by steric hindrance in the phosphorus halide,[10] and an alternative route to **9** had to be used in which the 3-phospholene ring is synthesized with a *P*-chloro substituent[11] that is then replaced by attack of an aryl Grignard reagent. To convert the phospholene to the phosphole, the phosphorus atom is first protected as the oxide, bromine is added to the double bond, and the oxide returned to the phosphine by reduction with trichlorosilane. Dehydrohalogenation with sodium methoxide then provides the phosphole. This method has been used in the synthesis of a number of phospholes,[10,12] and its application to the synthesis of phosphole **9** is outlined in Scheme 1.

Phosphole **9** was isolated by silica gel chromatography and obtained as an odorless solid that could be recrystal-

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(12) (a) Quin, L. D.; Borleske, S. G.; Engel, J. F. *J. Org. Chem.* **1973**, *38*, 1858. (b) Deschamps, E.; Mathey, F. *J. Org. Chem.* **1990**, *55*, 2494. (c) Deschamps, E.; Ricard, C.; Mathey, F. *Heteroatom Chem.* **1991**, *2*, 377.

Scheme 1

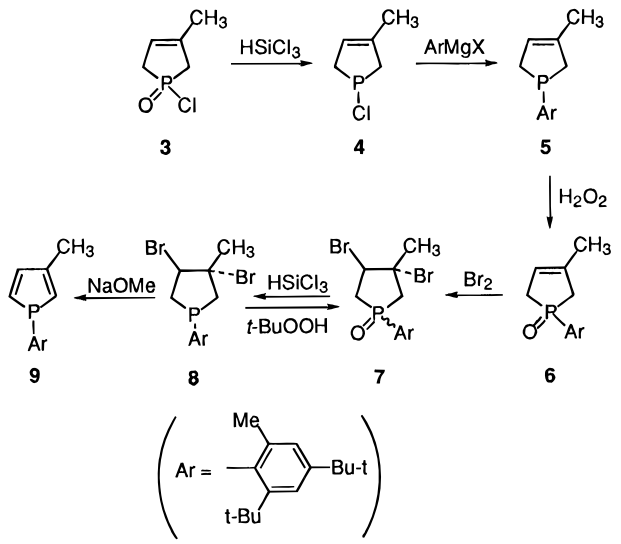
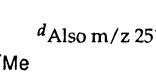
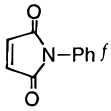


Table 2. Mass Spectral Data[a] for Phosphole 9, Dimer 11, and Cycloadduct 12

	9[b]	11	12[d]
M^+	300 (92)	632 (13)	489 (6)
M–$Me^{\cdot+}$	285 (46)	617 (21)	474 (1)
M-2, 4-di*t*Bu-6-$MeC_6H_2^{\cdot+}$	97 (5)	429 (14)	286 (5)
M-2, 4-di*t*Bu-6-$MeC_6H_2PO^{\cdot+}$	---	382 (40)	239 (15)
M-2, 4-di*t*Bu-6-MeC_6H_2PO-$Me^{\cdot+}$	---	367 (42)	---
	---	316 (13)[c]	316 (1)[e]
316-$Me^{\cdot+}$	---	301 (9)	301 (1)
2,4-di*t*Bu-6-$MeC_6H_2PO^{\cdot+}$	---	250 (29)	250 (58)
250-$Me^{\cdot+}$	---	235 (46)	235 (42)
			92 (100)[f]
$C_7H_7^+$	91 (5)	91 (22)	91 (46)
$C_4H_9^+$	57 (100)	57 (100)	57 (46)

[a] EI; m/z (relative intensity in %). [b] Also m/z 269 (18) and 189 (17).

[c] M^+ -  [d] Also m/z 251 (64). [e] M^+ -  [f] $PhNH^+$.

lized from acetone in analytically pure form. Unfortunately, crystals suitable for X-ray diffraction analysis have not yet been produced, and attempts at obtaining structural parameters have failed. Phosphole **9** was stable in the atmosphere, but was best preserved under nitrogen. These properties are unlike those for the corresponding 1-phenyl compound,[13] an oxidizable, malodorous liquid. The phosphole had the characteristic feature[14] of giving an intense peak (92% relative abundance) in its mass spectrum (Table 2) for the molecular ion. NMR spectral characterization is presented in the following section.

The reactions of Scheme 1 proceeded in normal fashion and showed no special influences from the large P-substituent. With one exception the intermediates had the expected properties. Dibromophospholane oxide **7**, which was obtained after chromatography as a 4:1 mixture of diasteroisomers from addition of bromine (presumed to be trans) to the phospholene oxide, had ^{31}P NMR shifts of δ 72.0 (major) and 71.5 (minor), but when **7** was prepared by oxidation of dibromo phospholane **8**, the major isomer had a shift of δ 50.5 ($CDCl_3$). A similar shift (δ 49.4) was obtained when a sample of the dibromide formed from **6** was exposed briefly to triethylamine at room temperature. When this oxide (designated **7A**) was mixed with an equal amount of the oxide (designated **7B**) from the halogen addition to **6**, a single peak was obtained (δ 54.2 in $CDCl_3$). The ^{13}C NMR spectra of samples **7A** and **7B** were nearly the same, establishing the authenticity of both as dibromo oxide **7**, and as will be seen both underwent dehydrobromination to give the same product. This peculiar NMR effect requires further study before an explanation can be developed.

NMR Spectral Characterization of Phosphole 9. Phosphorus-31. The ^{31}P NMR shift of phosphole **9** in $CDCl_3$ was δ 1.8, somewhat upfield of that of the 1-phenyl derivative (δ 7.5[9]). This is in accord with the presence of *ortho* substituents on the phenyl ring, which are γ-related to phosphorus. Shielding is a common occurrence of γ substituents in both aliphatic and aromatic compounds, as is seen from tabulated data[15] for some *o*-tolyl derivatives (cf. diphenyl-*o*-tolylphosphine, δ -13.0, to triphenylphosphine, δ −4.7; the effects are additive, and tri-*o*-tolylphosphine has δ −29.9). The effect on the ^{31}P NMR shift of increased delocalization through any flattening of the phosphorus pyramid is not expected to be significant. Thus the calculated value for planar 1-methylphosphole is only 10.9 ppm downfield of that for pyramidal 1-methylphosphole.[1] The deshielding from a moderate approach toward a flatter pyramid in **9** could be offset by the γ shielding effect.

Carbon-13. ^{13}C NMR spectra generally reveal little about cyclic electron delocalization but are quite sensitive to influences from steric interactions. The spectrum of phosphole **9** in fact abounds in both steric-derived coupling and shift effects which uniquely define an important feature of the geometry of the molecule, namely, the preferred near-perpendicular relation of the planes of the phosphole and phenyl rings as predicted by calculations and shown in two conformations in Figure 1.

The preferred conformations shown in Figure 1 were used in the interpretation of the spectrum (Table 3). Shifts and $^{31}P-^{13}C$ coupling constants for the 3-methylphosphole moiety of **9** resembled, in general, those reported[16] for this moiety in 3-methyl-1-phenylphosphole, also recorded in Table 3. However, there was a pronounced upfield shift of the two α-carbons in **9** (C-2 by 3.5 ppm, C-5 by 3.7 ppm) relative to those in 3-methyl-1-phenylphosphole. Upfield shifts frequently arise from steric interaction with γ-related carbons; here the γ carbons would be those at positions 8 or 12 of the phenyl ring, in which case the effect should be reciprocal. This is indeed present in a rather striking way for one of the phenyl carbons; C-8 was assigned a shift of δ 122.8, significantly upfield from the position found in a model

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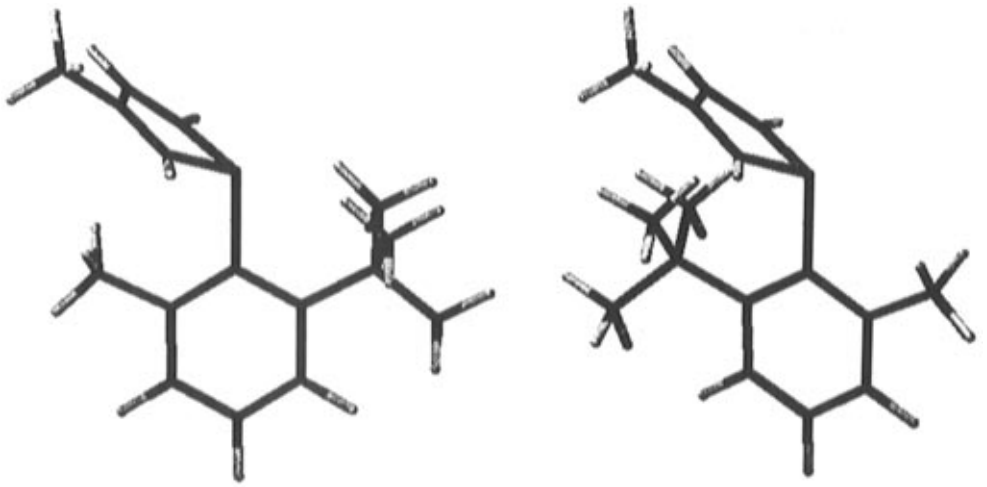
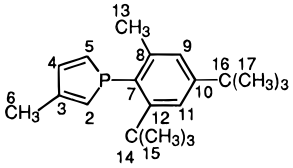


Figure 1. Computed minimum energy conformations of phosphole **9**.

Table 3. ^{13}C NMR Spectral Data for Phosphole 9[a]

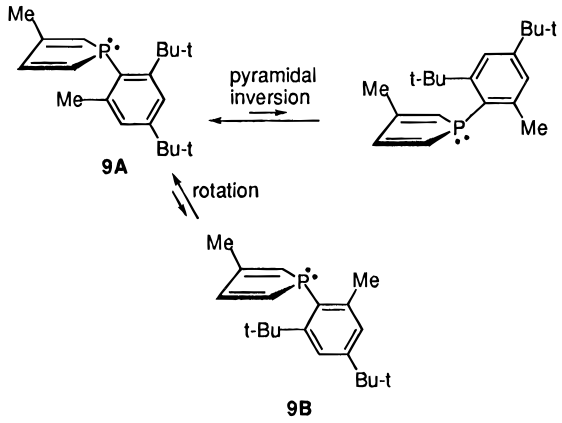


	9		3-methyl-1-phenylphosphole[15]	
carbon	δ	J_{PC}, Hz	δ	J_{PC}, Hz
2	125.1	3.0	128.56	1.2
3	148.7	5.7	147.38	8.8
4	135.8	15.4	140.07	7.6
5	132.3	0	136.0	5.3
6	18.9	m[b]	18.53	3.7
7	143.1	17.6	130.62	10.5
8	122.8	17.0	132.98	19.0
9	125.5	1.4	127.99	8.0
10	152.5	2.0	128.09	0
11	121.4	12.3	127.99	8.0
12	157.0	28.7	132.98	19.0
13	18.7	m[b]		
14	37.8	2.8		
15	33.1	11.5		
16	34.8	0.5		
17	31.2	0		

[a] At 75.1 MHz in $CDCl_3$ at 20 °C. ^{31}P−^{13}C couplings were confirmed at 20 MHz. [b] In deuterotoluene, C_6 was a doublet with $J_{PC} = 0.7$ Hz, and C_{13} was a doublet with $J_{PC} = 3.6$ Hz. No other significant differences were noted.

o-tolylphosphine (*e.g.*, tri-*o*-tolylphosphine, δ 134.4[17]). The magnitude of the upfield shift of about 12 ppm suggests a γ effect of about 6 ppm associated with each of the phosphole ring carbons, which would be reasonable if conformation **9A** of Figure 1 dominated the conformational equilibrium. This conformation receives ample documentation from coupling phenomena. Thus, the magnitude of three-bond P−C coupling is empirically related to the orientation of the lone pair on P in rigid systems, being large when close to the coupled C, small or even absent when remote. It is for this reason that $^3J_{P-C}$ to C-11 (12.3 Hz) is much larger than that to C-9 (1.4 Hz), since as seen in Figure 1 the restricted rotation holds C-11 in closer proximity to the lone pair. The three-bond coupling to the methyl at C-8 should also be small in this conformation, and indeed this carbon shows no coupling to P. Two-bond coupling is also controlled in the same way by orientation of the lone pair, and this is reflected here in the larger $^2J_{P-C}$ value for C-12 (28.7 Hz) than for C-8 (17.0 Hz). Another consequence of the conformational biasing is seen in the four-bond coupling to C-15 of the *o-tert*-butyl group, which is remarkably large at 11.5 Hz. The size of this coupling supports a prediction[18] that $^4J_{P-C}$ will be large in the structural fragment P−C=C−C−C if the lone pair is close to the terminal C.

Scheme 2



The repositioning of the aryl Me and *tert*-butyl groups can be accomplished either by rotation around the C−P bond or by inversion of the phosphorus pyramid (Scheme 2). Pyramidal inversion in phospholes has been proposed to have a significantly lower energy barrier (about 16 kcal/mol) than that in phosphines (about 35 kcal/mol);[19] if sterically hindered phospholes have a similar barrier, inversion could take place at or near room temperature. However, in the present case of an unsymmetrically substituted *P*-phenyl substituent in a plane orthogonal to the phosphole ring plane, a larger energy difference would be present between the two participants in the

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(18) Quin, L. D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds., VCH Publishers: Deerfield Beach, FL, 1987; pp 417−420.

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Table 4. ^{1}H NMR Spectral Data for Phosphole 9[a]

	9		1,3-Dimethylphosphole[11]	
proton	δ	couplings, Hz	δ	couplings, Hz
H_2[b]	6.46	^{31}P, 37.4; H_4, 1.6; CH_3, ~1.5	6.52	^{31}P, 41; CH_3, 1.5; H_4, 1.33
H_4[c]	6.84	^{31}P, 16.7; H_5, 7.0; H_2, 1.6	6.93	^{31}P, 12.15; H_5, 7.5; H_2, 2.5
H_5	6.91	^{31}P, 37.4; H_4, 7.0; H_2, 2.4	7.01	^{31}P, 40; H_4, 7.0; H_2, 2.4
3-CH_3	2.24	^{31}P, 6; H_2, ~1.5	2.31	^{31}P, 3.3; H_2, 1.5
8-CH_3	1.72	^{31}P ~0.5		
H_9	6.94	H_{11}, 2.3		
10-C(CH_3)$_3$	1.28			
H_{11}[d]	7.41	^{31}P, 6; H_9, 2.3		
12-C(CH_3)$_3$	1.73	^{31}P, ~2		

[a] At 300 MHz, in $CDCl_3$ at 20 °C. For numbering, see Table 3. [b] Confirmed by NOE of 5−6% to 3-CH_3. [c] Confirmed by NOE of 4−5% to 3-CH_3. [d] Confirmed by NOE of 10−12% to both C(CH_3)$_3$ groups.

inversion process, leading to a biasing toward the lower energy form just as would be seen in a rotational equilibrium. The uncertainty about the nature of the mechanism for any interconversion that might take place has no impact on the conclusions of the present study.

The very strong preference for conformation **9A**, predicted by computation and consistent with the ^{13}C−^{31}P coupling effects, was confirmed by variable temperature ^{13}C NMR studies. The temperature was reduced to −50 °C, with no indication of line broadening or the development of a second set of signals that could be associated with conformation **9B** that might be in equilibrium with the major conformation (**9A**) as established by NMR spectroscopy. Similarly, the ^{13}C NMR spectrum was unchanged when recorded at 100 °C. Phosphole **9** therefore appears to be conformationally homogeneous over the range −50 to 100 °C and is properly represented by a single conformer, **9A**.

Proton NMR. The ^{1}H NMR spectrum (Table 4) for the 3-methylphosphole moiety of **9** was interpreted with reference to that reported for 1,3-dimethylphosphole,[12a] and with the aid of NOE measurements. There was strong resemblance in the shifts for the two phospholes and in their complex coupling patterns, and no special effects were present. In the phenyl ring of **9**, however, an unusually large four-bond coupling (6 Hz) to ^{31}P was noticed for the *meta* proton (H-11) that was *syn* to the lone pair orbital. No coupling was observed to the other *meta* proton (H-9). This conformational effect provides ^{1}H NMR spectral support to the conclusion that phosphole **9** has adopted conformation **9A**.

We have considered the possibility of using the nuclear Overhauser effect (NOE) that might prevail between close-lying protons of the phosphole ring and the substituents (methyl as well as *tert*-butyl) on the phenyl ring, to provide further insight into the conformational preference of phosphole **9**. However, the semiempirical calculations on the preferred conformation **9A** (Figure 1) showed that the two ring planes were not exactly orthogonal, to relieve the congestion. In this conformation, one C−H of the *tert*-butyl group is 2.96 Å from H-5, and a C−H of the methyl group is 2.8 Å from H-2. Neither distance is fixed, however, since the conformation allows some oscillation around the P−C bond axis. One would therefore expect very similar NOE effects from both methyl and *tert*-butyl groups, and this was seen in the NOE experiments. However, the proximity of the 8-CH_3 and 12-(CH_3)$_3$C signals ($\Delta\delta$ 0.01 ppm) made selective irradiation difficult, and the observed NOE values (all in the range 1−3%) were not meaningful.

Characteristics of the Oxide of Phosphole 9. Phosphole oxides with the only ring substituent being a 3-methyl group are not directly observable due to the strong tendency to dimerize by a Diels−Alder mechanism immediately upon formation. However, effects from substituents can influence phosphole stability; with 3,4-dimethyl substitution, the lifetime of the 1-phenyl derivative is long enough that ^{31}P NMR signals (δ 42.3) can still be observed after several days of standing in the refrigerator.[20] We have proceeded to explore the effect of the steric demand of the large aryl substituent in 3-methyl phosphole **9** on the stability of its oxide.

The oxide **10** was synthesized by oxidation of the phosphole at room temperature with *tert*-butyl hydrogen peroxide in chloroform. There was immediate formation of a ^{31}P NMR signal at δ 53.4. The signal rapidly began to diminish with the appearance of the characteristic doublet of doublets for the Diels−Alder dimer **11** (δ 59.0 and 85, J = 39.5 Hz, also obtained by dehydrohalogenation of dibromophospholane oxide **7** with triethylamine in refluxing benzene), but was still observable after several hours. It is concluded that the large aryl substituent has indeed provided some stabilization of the phosphole oxide ring, but not enough to make compound **10** isolable.

The reactivity of the phosphole oxide toward the dienophile *N*-phenylmaleimide, commonly used as a trapping agent for phosphole oxides,[21] was also tested by including it in the reaction with triethylamine in refluxing benzene (Scheme 3). The Diels−Alder adduct **12** was obtained as a crystalline solid in 72% yield. Thus the steric congestion around P has exerted no influence on the cycloaddition reactions.

An incidental observation made in the dehydrohalogenation studies was that the same results were obtained when samples of the dibromide in form **7A** or form **7B** with different ^{31}P NMR shifts, as discussed earlier, were used, attesting further to the similarity of these forms.

Phosphines in the 7-phosphanorbornene system are characterized by extraordinary downfield shifting of the ^{31}P NMR signal when the 7-substituent is in the *syn* position, an effect which has recently received theoretical interpretation.[22] We have proceeded to remove the oxygen from phosphorus of Diels−Alder adduct **12** in the usual way[23] with trichlorosilane, thus synthesizing the 7-phosphanorbornene **13**, unique because of the presence of steric crowding at phosphorus. The ^{31}P NMR shift of δ 153.3 was found to be even further downfield than that

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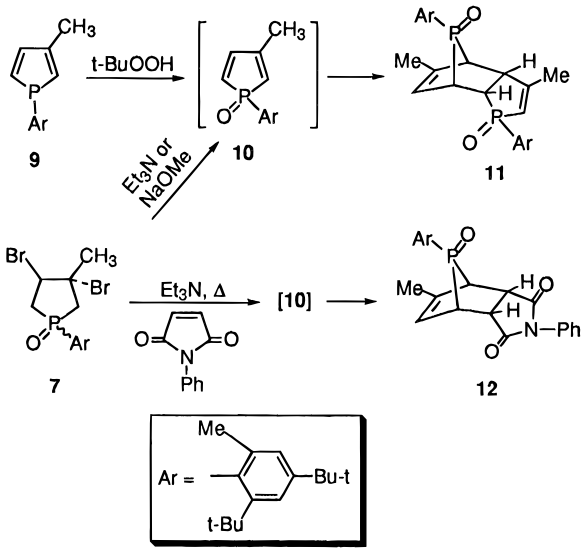
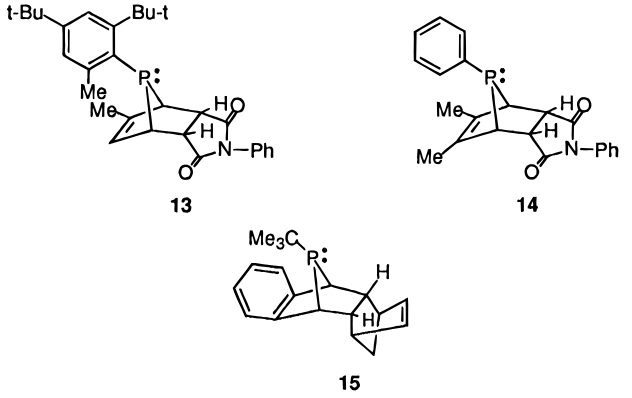
Scheme 3



of a related phosphine with a 7-phenyl substituent (**14**, δ 126.4[19]). Indeed, the value is the most downfield ever recorded for a 7-phosphanorbornene, just exceeding the previous extreme value (δ 152.5) found for the benzo derivative **15**.[24] It may be significant that this compound



also has a sterically demanding group (*tert*-butyl) at P, suggesting that in general steric congestion at the *syn*-7 position may be associated with substantial extra deshielding. This point has not yet been treated theoretically.

Experimental Section[25]

1-(2,4-Di-*tert*-butyl-6-methylphenyl)-3-methyl-3-phospholene 1-Oxide (6). A solution of 0.059 mol of (2,4-di-*tert*-butyl-6-methylphenyl)magnesium bromide in THF (prepared from 1.42 g (0.059 mol) of magnesium and 16.7 g (0.059 mol) of 1-bromo-2,4-di-*tert*-butyl-6-methylbenzene (**1**) in 40 mL of dry THF) was added dropwise to 7.2 g (0.054 mol) of 1-chloro-3-methyl-3-phospholene (**4**, prepared from phosphinic acid **3** with $HSiCl_3$[11]) in 40 mL of THF at 0 °C with stirring under an argon atmosphere. After the addition, the cooling bath was removed and the contents of the flask were stirred for 2 h. Solvent was evaporated and the residue extracted four times with 50 mL portions of *n*-pentane. Solvent of the combined extracts was evaporated to give 16.0 g (98%) of phosphine **5** (^{31}P NMR ($CDCl_3$) δ −31.3; MS, *m*/*z* (rel int) 302 (M^+, 100), 287 (38), 234 (51), 219 (58), 178 (97), 57 (64)). A chloroform (60 mL) solution of phosphine **5** was slowly treated with 6.7 g (0.059 mol) of 30% hydrogen peroxide at 0 °C with vigorous stirring. After 1 h, the mixture was washed with 4 × 20 mL of water. The organic phase was dried ($MgSO_4$) and the solvent evaporated to give 16.7 g (97%) of oxide **6**: ^{31}P NMR ($CDCl_3$) δ 59.3; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9 H), 1.56 (s, 9 H), 1.63 (s, 3 H), 2.33 (s, 3 H), 2.55−2.98 (m, 4 H), 5.57 (d, $^3J_{PH}$ = 31.3 Hz, 1 H), 6.80−7.53 (m, 2 H); MS, *m*/*z* (rel int) 318 (M^+, 94), 303 (53), 250 (64), 235 (36), 204 (11), 189 (45), 57 (100); Anal. Calcd for $C_{20}H_{31}OP$: C, 75.43; H, 9.81. Found: C, 75.83; H, 9.85.

3,4-Dibromo-1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methylphospholane 1-Oxide (7). A solution of 2.5 mL (0.049 mol) of bromine in 50 mL of chloroform (or benzene) was added dropwise to 15.5 g (0.049 mol) of phospholene oxide **6** in 100 mL of chloroform (or benzene) at 0 °C. After the addition, the mixture was stirred at room temperature for 1.5 h. Evaporation of the solvent left a semisolid residue which was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 16.5 g (71%) of **7** as a mixture of diastereomers; ^{31}P NMR ($CDCl_3$) δ 72.0 (75%) and 71.5 (25%); ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 1.51 (s, 9 H), 2.13 (s, 3 H), 2.65 (s, 3 H), 2.78−3.66 (m, 4 H), 4.34−5.10 (m, 1 H), 6.97−7.50 (m, 2 H); ^{13}C NMR, partial, C_2 δ 49.3 (J = 62 Hz), C_3 66.3 (8.9), C_4 57.2 (7.1), C_5 43.9 (62.6); ^{13}C NMR, complete, Supporting Information Table 1): CI-MS: 477 (M^+ + H); EI-MS, *m*/*z* (rel int) 476 (M^+, <0.5), 397 (67), 317 (100), 250 (41), 235 (28), 57 (83).

Compound **7** was not stable on standing. New ^{31}P NMR signals developed at ca. δ 52 and 54 ($CDCl_3$) presumably due to loss of HBr.

Treatment of Dibromophospholane Oxide 7 with Triethylamine at Room Temperature. A solution of 2.58 g (0.0054 mol) of **7** [^{31}P δ 72.0 (75%) and 71.5 (25%)] in 14 mL of dry benzene was treated with 1.54 mL (0.0108 mol) of triethylamine at room temperature. After a 1 h period of stirring, the mixture was filtered and solvent of the filtrate evaporated. The recovered **7** so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 1.55 g (60%) of **7** as a mixture of diastereomers with ^{31}P NMR ($CDCl_3$) δ 49.4 (80%) and δ 50.6 (20%); ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 1.53 (s, 9 H), 2.15 (s, 3 H), 2.67 (d, ^4J(P,H) = 1.5, 3 H), 2.80−3.70 (m, 4 H), 4.37−4.83 (m, 1 H), 6.96−7.52 (m, 2 H); ^{13}C NMR, partial, C_2 δ 49.7 (63.1 Hz), C_3 66.5 (8.5), C_4 57.5 (7.5), C_5 43.9 (62.6); complete, Supporting Information, Table 1: CI-MS: 477 (M^+ + H); EI-MS, *m*/*z* (rel int): 476 (M^+, <0.5), 397 (35), 317 (100), 250 (20), 235 (11), 57 (57).

1-(2,4-Di-*tert*-butyl-6-methylphenyl)-3-methylphosphole (9). A solution of 4.1 g (0.00858 mol) of dibromo compound **7** (from **6**, with major isomer ^{31}P δ 76.7) in 30 mL of dry benzene was added to a mixture of 2.29 mL (0.0283 mol) of pyridine, 0.95 mL (0.00941 mol) of trichlorosilane and 30 mL of benzene under a nitrogen atmosphere. After a reflux period of 4 h, the precipitated amine salt was filtered off. Concentration of the filtrate in vacuum gave 3.96 g (100%) of dibromophospholane **8**: ^{31}P NMR ($CDCl_3$) δ −39.2. Oxidation of a small sample

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(25) ^{31}P NMR spectra (FT, ^{1}H-decoupled) were recorded at 32.44 MHz; chemical shifts are referenced to 85% phosphoric acid and are positive if downfield. ^{13}C NMR spectra (FT, ^{1}H-decoupled) were taken at 75.1 MHz, and ^{1}H NMR spectra at 80 or 300 MHz. EI and CI (with isobutylene) mass spectra were obtained at 70 eV. Elemental analyses were performed by the University of Massachusetts Analytical Laboratory. Manipulations involving phosphines were performed under nitrogen or argon.

of **8** in $CDCl_3$ with 30% H_2O_2 gave **7** with ^{31}P NMR δ 50.5 for the major isomer and 51.6 for the minor isomer.

A solution of 0.93 g (0.0172 mol) of sodium methylate in 1.5 mL of methanol was added to a solution of 3.96 g (0.00858 mol) of dibromophospholane **8** in 40 mL of dry benzene. After 4 days of reflux in a nitrogen atmosphere, the mixture was filtered and solvent was evaporated. The residue so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 1.33 g (61%) of phosphole **9**: mp 97−99 °C (from acetone); ^{31}P NMR ($CDCl_3$) δ 1.8; MS, Table 1; ^{13}C NMR, Table 2; ^{1}H NMR, Table 3. Anal. Calcd for $C_{20}H_{29}P$: C, 79.94; H, 9.75. Found: C, 79.63; H, 9.32.

Phosphole **9** was formed in similar yield when the above procedure was applied to a sample of dibromo oxide **7** with ^{31}P δ 49.4 following the triethylamine treatment.

Oxidation of Phosphole 9. Oxidation of a small sample of **9** in $CDCl_3$ with one drop of 70% *tert*-butyl hydroperoxide resulted in the appearance of an intermediate signal at δ 53.4, attributed to phosphole oxide **10**. Simultaneously with the reduction of this signal, the shifts of the dimer (**11**, see below) appeared.

Dimer 11 of Phosphole Oxide 10. Triethylamine (0.88 mL, 0.00628 mol) was added to a solution of 1.5 g (0.00314 mol) of dibromo compound **7** in 15 mL of refluxing dry benzene. During the reaction, transient ^{31}P NMR signals at δ 52 and 54 were noted, presumably for monobromo intermediates. After 22 h of stirring at reflux, the mixture was filtered and the filtrate evaporated. The crude product so obtained was purified by column chromatography (silica gel, 4% methanol in chloroform, then benzene−acetone 2:3) to give 0.77 g (78%) of **11**: mp 168−170 °C (from petroleum ether−ethyl acetate 8:2); ^{31}P NMR ($CDCl_3$) δ 59.0 and 85.1 ($^{3}J_{PP}$ = 39.5 Hz); ^{1}H NMR, Supporting Information, Table 2; ^{13}C NMR, Supporting Information, Table 3; MS, Table 2. Anal. Calcd for $C_{40}H_{58}O_2P_2$: C, 75.92; H, 9.24. Found: C, 76.32; H, 9.01. The reaction was faster in refluxing toluene (16 h); when the reaction was conducted with 2 equiv of NaOMe in benzene at room temperature, dimer **11** formed within a few minutes (75%).

Diels−Alder Reaction of Phosphole Oxide 10 with *N*-Phenylmaleimide. Triethylamine (0.88 mL, 0.00628 mol) was added to a mixture of 1.5 g (0.00314 mol) of dibromophospholane **7**, 0.6 g (0.00346 mol) of *N*-phenylmaleimide, and 15 mL of benzene at reflux. After 22 h of refluxing, the precipitated salt was filtered off and the solvent evaporated. The crude product was purified by column chromatography (silica gel, benzene−acetone 2:3 and then 6% methanol in chloroform) to afford 1.1 g (72%) of **12**: mp 182−183 °C (from diethyl ether−ethyl acetate 9:1); ^{31}P NMR ($CDCl_3$) δ 88.9; ^{1}H NMR, Supporting Information, Table 2; ^{13}C NMR, Supporting Information, Table 4; MS, Table 2. Anal. Calcd for $C_{30}H_{36}NO_3P$: C, 73.60; H, 7.41. Found: C, 73.25; H, 7.12.

A portion of oxide **12** (100 mg) was reacted with trichlorosilane/pyridine in benzene in the usual way.[23] The product **13** was a solid that was recrystallized from chloroform and had mp 189−190 °C; ^{31}P NMR δ 153.3 ($CDCl_3$); high-resolution FAB-MS 474.2554 (Calcd for $M^+ + 1$ ($C_{30}H_{37}NO_2P$) 474.2562).

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