4.85–5.35 (m, 2 H, $CCO_2CH(CH_3)_2$, $COCO_2CH(CH_3)_2$); IR (KBr) 3480 (OH), 1710 (C=O) $cm^{-1}$. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.14; H, 7.59.

Dibenzyl 4-hydroxy-4-methyl-2-oxopentanedioate: NMR ($CDCl_3$) $\delta$ 1.42 (s, 3 H, $CCH_3$), 3.31 (s, 2 H, $CH_2$), 5.11 (s, 2 H, $CCO_2CH_2Ph$), 5.17 (s, 2 H, $COCO_2CH_2Ph$), 7.24 (s, 5 H, $CCO_2CH_2C_6H_5$), 7.28 (s, 5 H, $COCO_2CH_2C_6H_5$); IR (neat) 3500 (OH), 1730 (C=O) $cm^{-1}$. Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.31; H, 5.81.

Di-*tert*-butyl 4-hydroxy-4-methyl-2-oxopentanedioate: NMR ($CDCl_3$) $\delta$ 1.40 (s, 3 H, $CCH_3$), 1.48 (s, 9 H, $CCO_2C(CH_3)_3$), 1.58 (s, 9 H, $COCO_2C(CH_3)_3$, 3.20 (s, 2 H, $CH_2$); IR (KBr) 3520 (OH), 1740 (C=O) $cm^{-1}$. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.52; H, 8.21.

**Photoinduced Dimerization of Ethyl Pyruvate Catalyzed by Hydridocobaloxime 3.** $Co(OAc)_2 \cdot 4H_2O$ (49.8 mg, 0.2 mmol) and dimethylglyoxime (46.4 mg, 0.4 mmol) were dissolved in MeOH (2 mL), and the solvent was evaporated after the addition of pyridine (0.016 mL, 0.2 mmol). Ethyl pyruvate (2.2 mL, 20 mmol) was added to the Co(II) complex, and the mixture was degassed by a freeze-thaw-pumping cycle and replaced with hydrogen. The reaction was carried out by irradiation with a tungsten lamp (200 W) at a distance of 10 cm from the reaction vessel at 15 °C for 72 h to give a mixture of dimer (14%), polymeric products (16%), and other products (69%).

**Detection of Ethyl 4-Phenyl-2-oxobutanoate (7).** Benzyl(pyridine)cobaloxime (1.378 g, 3 mmol), ethyl pyruvate (3.484 g, 30 mmol), and $CH_2Cl_2$ (30 mL) were added into a Schlenk tube, and the mixture was degassed by a freeze-thaw-pumping cycle and replaced with an argon gas. The reaction was carried out by irradiation with a tungsten lamp (400 W) for 6 days at 35 °C. After the reaction, the solvent was evaporated, and the organic compounds were separated from the reaction mixture by column chromatography (silica gel). The mixture was investigated by GC–MS. The molecular ion peak at $m/e$ 207 (M + 1) of the $\alpha$-keto ester 7 was found. There are main fragment peaks at $m/e$ 116 ($CH_3CH_2OCOCH_2^+$) and $m/e$ 91 ($PhCH_2^+$).

**Registry No.** 1, 27860-79-3; 6 (R′ = $CH_3$), 113548-35-9; 6 (R′ = $C_2H_5$), 113548-36-0; 6 (R′ = $i$-$C_3H_7$), 113548-37-1; 6 (R′ = $t$-$C_4H_9$), 113548-38-2; 6 (R′ = $CH_2C_6H_5$), 113548-39-3; 7 (R = $C_6H_5CH_2$, R′ = $Cx_2H_5$), 64920-29-2; $CH_3COCO_2H$, 127-17-3; $CH_3COCO_2CH_3$, 600-22-6; $CH_3COCO_2C_2H_5$, 617-35-6; $CH_3COCO_2C_3H_7$-$i$, 923-11-5; $CH_3COCO_2C_4H_9$-$t$, 76849-54-2; $CH_3COCO_2CH_2C_6H_5$, 18854-19-8.

# Synthesis and NMR Spectral Properties of Phosphines in the 2-Phosphabicyclo[2.2.2]oct-5-ene and 2-Phosphabicyclo[2.2.2]octa-5,7-diene Systems[1]

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1,6-Dihydrophosphorin 1-oxides were synthesized by dehydration of 3-hydroxy-1,2,3,6-tetrahydrophosphorin 1-oxides; Diels–Alder reactions with maleic acid derivatives gave the 2-phosphabicyclo[2.2.2]oct-5-ene ring system, while reaction with dimethyl acetylenedicarboxylate gave the corresponding octa-5,7-diene system. The latter system was also approached by lead tetraacetate oxidation of a dicarboxylic acid in the oct-5-ene system. Removal of the phosphoryl oxygen required very gentle conditions with the dienes to prevent fragmentation. This was accomplished with trichlorosilane at −8 to 0 °C. The dienic phosphines were stable at 0–25 °C but lost the P-containing bridge at 30–50 °C. The $^{31}P$ NMR shifts of all compounds were normal and resembled monocyclic phosphorin models. This ring structure, either with one or two double bonds, therefore does not cause the strong deshielding so characteristic of the related 7-phosphanorbornene system. To interpret the $^1H$ and $^{13}C$ NMR spectra of the dienic phosphines, 2-D techniques were used.

Phosphines with the 7-phosphanorbornene framework were first synthesized in 1980 and immediately became of interest because they displayed unusual spectral and chemical properties. To illustrate, such compounds give the most downfield $^{31}P$ NMR shifts ever recorded for a tertiary phosphine[2] and tend to form P(V) adducts with various reagents, leading to fragmentation by retrocycloaddition.[3] Even the synthesis of the phosphines is made complicated by the tendency to form P(V) adducts; the phosphines are synthesized by deoxygenation of the corresponding phosphine oxides with silanes, but for success a procedure is required that avoids the possibility of P(V) intermediates. The combination of a highly contracted bond angle at P and forced proximity of P to a double bond appears to be responsible for these and other effects.

It is not known if homologous phosphines, having the 2-phosphabicyclo[2.2.2]octene framework, possess any of these or other special properties; a *P*-(trifluoromethyl)-3,3-difluoro derivative ($^{31}P$ NMR $\delta$ +5.8) is the only known[4] phosphine with this ring system, but it is not a good model for NMR considerations. We have devised a procedure that provides less specialized derivatives, and we have synthesized the first phosphines in the 2-phosphabicyclo[2.2.2]octa-2,5-diene series as well. This work, as well as some properties of the new compounds, is reported in this paper.

Our synthetic approach makes use of the unsaturated 3-phosphorinone derivatives that were reported earlier[5] as being easily formed in a two-step sequence from readily

(1) Some of this work was conducted at Duke University. Taken in part from the doctoral dissertation for J.C.K., Duke University, Durham, NC, 1985.

(2) Quin, L. D.; Mesch, K. A. *J. Chem. Soc., Chem. Commun.* **1980**, 959.

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

(4) Grobe, J.; Le Van, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 467.

(5) Quin, L. D.; Kisalus, J. C. *Phosphorus Sulfur* **1985**, *22*, 35.

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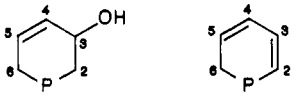
**Table I. $^{13}C$ NMR Spectral Data for Dihydro- and Tetrahydrophosphorin Derivatives[a]**

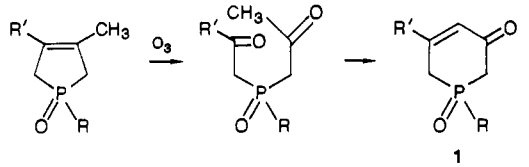


4, 7 5, 8

| | δ | | | | | |
|---|---|---|---|---|---|---|
| C | 4a[b] | 4b[b] | 7a | 7b | 5 | 8c |
| 2 | 34.7 (58.5) | 33.9 (62.4) | 34.4 (62.5) | 34.7 (62.5) | 120.0 (92.3) | 122.6 (93.8) |
| 3 | 64.7 (s) | 63.7 (3.9) | 65.8 (2.0) | 63.8 (2.0) | 139.5 (s) | 140.5 (s) |
| 4 | 133.6 (11.0) | 133.6 (11.0) | 133.9 (11.7) | 135.0 (9.8) | 124.1 (23.1) | 123.8 (23.5) |
| 5 | 120.4 (3.8) | 120.8 (5.8) | 121.2 (4.9) | 119.8 (5.9) | 126.3 (11.0) | 126.3 (10.7) |
| 6 | 26.8 (65.9)[d] | 26.9 (65.6)[d] | 26.7 (66.4) | 27.2 (66.4) | 28.3 (71.4) | 29.9 (71.3) |
| $PCH_3$ | 15.8 (68.2) | 13.1 (67.2) | | | 16.2 (73.6) | |

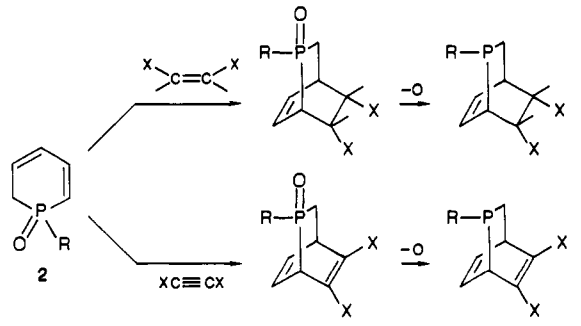
[a] $CDCl_3$ solutions. Values in parentheses are $^{31}P-^{13}C$ coupling constants, in hertz. [b] Mixture of isomers. A spectrum for pure 4a matched one set of signals. [c] Ortho C, 130.3 (9.8); meta C, 128.4 (12.7); para C, 131.7 (2.9). [d] May be reversed.

available 3-phospholene oxides. The sequence involves ozonolysis, followed by intramolecular aldol condensation.



1

We have succeeded in converting the unsaturated 1,2,3,6-tetrahydro-3-phosphorinones 1 into 1,6-dihydrophosphorins 2, which participate[6] as dienes in Diels–Alder reactions and thereby give the desired framework. Deoxygenation to the phosphines requires special conditions but, as will be discussed below, does indeed lead to the desired products.



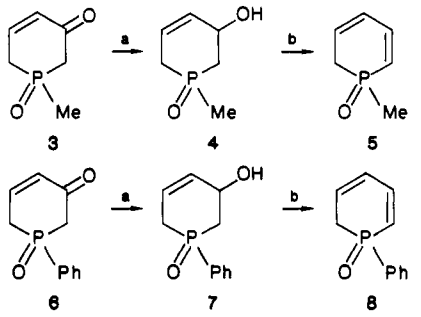
2

**Synthesis of 1,6-Dihydrophosphorins.** The two-step sequence of Scheme I was used for the synthesis of the two 1,6-dihydrophosphorins 5 and 8.

The reduction of the carbonyl of 3 and 6 was effected with the $NaBH_4$–$CeCl_3$ reagent[7] in methanol, which is reported to be specific for the reduction of the carbonyl group in α,β-unsaturated ketones. This proved to be the case for 3 and 6; the reductions proceeded in good yield (55% and 93%, respectively) and gave only the desired 3-hydroxy derivatives 4 (with occasional exceptions; see footnote 27) and 7, without evidence of any reduction of the double bond. Cerium salts were easily removed from 7 by silica gel chromatography, but 4 required an ion-exchange technique for complete removal.

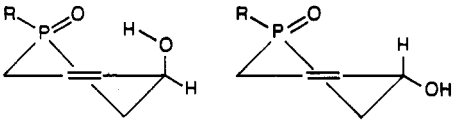
The alcohols 4 and 7 were obtained as mixtures of geometric isomers (with cis OH and PR or trans OH and PR). They are represented as having the twist-chair form

**Scheme I[a]**



[a] (a) $NaBH_4$, $CeCl_3$ in MeOH; (b) $KHSO_4$, chlorobenzene, Δ.

common for cyclohexene,[8] with the larger P substituent in the pseudoequatorial position (as is favored in saturated phosphorinane oxides[9]). The isomers, roughly in equal



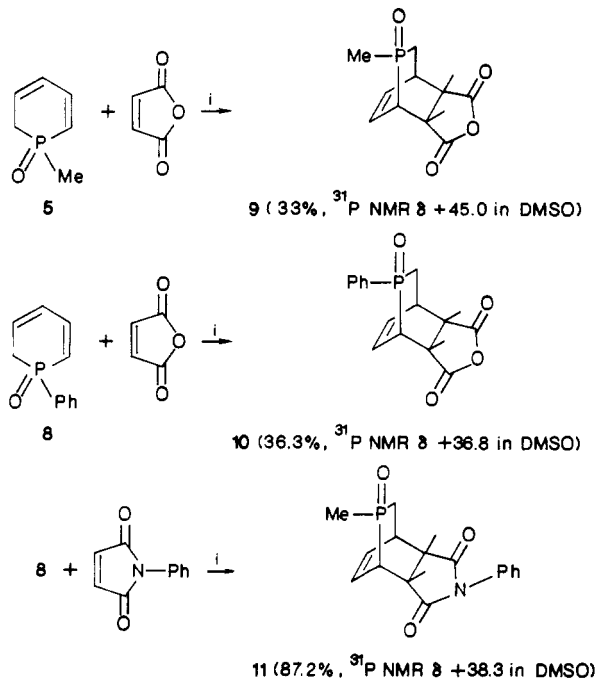
trans cis

4a, R = Me; 7a, R = Ph 4b, R = Me; 7b, R = Ph

amount, were easily detected by $^{31}P$ NMR analysis of the reduction products, which for 4 gave signals at δ +47.8 and +48.2 ($D_2O$) and for 7 at δ +31.3 and +32.1. The isomers of 7 were separated by fractional crystallization from acetone–hexane; that isomer with δ +31.3 was obtained as a crystalline solid, but the other isomer remained an oil. The $^{13}C$ NMR spectra (Table I) showed some differences but possessed no features allowing a structural assignment. The $^1H$ NMR spectra had more important differences. The carbinol proton of the crystalline isomer of 7 was significantly upfield (δ 4.4) relative to the other isomer (δ 4.9). This difference probably arises from the influence of the P=O group, which can contribute to the deshielding of syn-oriented protons more than to anti-oriented protons.[10] Thus we can assign the trans structure (7a) to the crystalline isomer and the cis structure (7b) to the other isomer. The *P*-methyl derivatives 4a and 4b could not be easily separated by crystallization, but it was observed that some separation occurred on the Dowex 50 ion-exchange column used to remove cerium. After an isomer mixture

(6) Deschamps, E.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1984**, 1214.
(7) Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2226. Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.
(8) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; p 239.
(9) Quin, L. D.; Lee, S. O. *J. Org. Chem.* **1978**, *43*, 1424.
(10) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; Wiley-Interscience: New York, 1981; pp 350–353.

Scheme II[a]




[a] (i) In refluxing benzene.

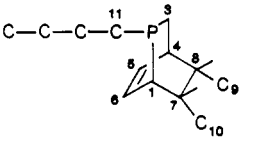
had been eluted, a single alcohol was obtained from the column and had $^{31}P$ NMR $\delta$ +47.5 ($CH_3OH$). It gave a carbinol proton signal at $\delta$ 4.4 and thus is assigned trans structure **4a**. The other gave a carbinol proton in the isomer mixture at lower field ($\delta$ 4.7) and must have cis structure **4b**.

Dehydration of the alcohols (as isomer mixtures) was accomplished with fused $KHSO_4$ in refluxing chlorobenzene. This solvent proved to be superior for the highly polar phosphine oxides to the more conventional toluene or xylene and gave much better yields (**5**, 67%; **8**, 86%).

Diene **5** was obtained only as an oil, and **8** as a low-melting solid; each gave single $^{31}P$ NMR signals, however, and the correct exact mass by mass spectrometry. Their $^{13}C$ NMR spectra (Table I) supported the assigned diene structure, since only one $sp^3$ ring carbon was present. The $^{31}P$ NMR shifts were significantly displaced upfield relative to the alcohol precursors. Thus, **5** had $\delta$ +23.0 and **8** had $\delta$ +16.2. Shifts in this range appear to be characteristic of 1,6-dihydrophosphorins (e.g., $\delta$ +29 for the 1-benzyl-2-hydroxy-4,5-dimethyl-2-phenyl 1-oxide derivative) as approached by a different method (ring expansion of a phosphole).[11]

**Synthesis of Some 2-Phosphabicyclo[2.2.2]oct-5-ene 2-Oxide Derivatives.** Two dienophiles, maleic anhydride and *N*-phenylmaleimide, were found to give crystalline adducts with dihydrophosphorins **5** and **8** (Scheme II). In every case, there was obtained only one product, as was easily determined by $^{31}P$ NMR analysis, in spite of the fact that the cycloadditions could have given exo or endo isomers. In addition, two configurations are possible at phosphorus. That the ring fusion occurred to give the endo product was easily established from the $^{13}C$ NMR spectra of adducts **9** and **10** (Table II). The stereospecificity of 3-bond $^{13}C$–$^{31}P$ coupling[12] was used for this purpose. This coupling is controlled by the dihedral angle relating these

Table II. $^{13}C$ NMR Spectral Data for 2-Phosphabicyclo[2.2.2]oct-5-ene Derivatives[a]




| C | δ 9[b,c] | 10[b,d] | 12[e,f] | 16[e,g] |
|---|---|---|---|---|
| 1 | 36.1 (58.6) | 36.2 (59.8) | 37.2 (63.5) | 31.6 (12.1) |
| 3 | 26.4 (75.7) | 26.0 (78.1) | 29.4 (77.2) | 26.7 (25.3) |
| 4 | 32.7 (8.5) | 32.9 (8.6) | 33.6 (7.3) | 32.0 (s) |
| 5 | 134.4 (13.4)[h] | 135.2 (12.2)[h] | 134.6 (12.2)[h] | 130.1 (3.9) |
| 6 | 128.5 (6.1)[h] | 128.1 (6.1)[h] | 127.3 (7.3)[h] | 129.1 (3.9) |
| 7 | *i* | 40.2 (3.7)[h] | 40.8 (2.4)[h] | 44.7 (25.3) |
| 8 | 45.2 (12.2) | 45.5 (12.2)[h] | 46.7 (11.0)[h] | 46.9 (s) |
| 9 | 172.9 (s) | 172.8 (s) | 172.1 (s) | 172.5 (s) |
| 10 | 173.7 (17.1) | 173.1 (17.1) | 171.7 (14.6) | 172.2 (18.7) |

[a] Chemical shifts in ppm downfield of $Me_4Si$; values in parentheses are $^{31}P$–$^{13}C$ coupling constants, in hertz. [b] In DMSO-$d_6$. [c] $PCH_3$, 14.8 (70.8). [d] Ipso C, 132.2 (98.9); ortho C, 131.2 (8.5); meta C, 128.5 (11.0); para C, 131.9 (3.7). [e] In $CDCl_3$. [f] $OCH_3$, 51.8 (s) and 51.6 (s); ipso C, 131.6 (98.9); 131.2 (8.5); 128.2 (11.0); 131.8 (2.4). [g] $OCH_3$, 51.5 (s) and 51.4 (s). [h] Distinguished by assuming $\gamma$-effects of P-function causes upfield shifts at C-6 and C-7. [i] Obscured by solvent.

nuclei; in phosphine oxides, values near 0 Hz are found for angles around 90° and 20 Hz or more for angles around 0° or 180°. The endo isomers would have a dihedral angle around 180° and exo around 90° and thus should be clearly assigned by the $^3J_{PC}$ value. These values were 17.1 Hz for **9** and **10** and 14.7 for **11**, and the endo structure may be assigned to all. The configuration at phosphorus was not revealed by any of the spectral data, but after conversion into the tertiary phosphines by a stereospecific (retention) reduction, as is described later, NMR features became available that allowed the assignment of the P-substitutent on the phosphoryl group to the syn position with respect to the double bond. Diels–Alder reactions among phosphole oxides are stereospecific in exactly the same respects.[13]

The three cycloadducts had $^{31}P$ NMR shifts in the range $\delta$ +38 to +45 and thus resembled closely the corresponding monocyclic phosphorinane oxides (e.g., *cis*-1,4-dimethylphosphorinane oxide,[9] $\delta$ +40.9; **9**, +45.0). There is, therefore, a marked difference in this ring system relative to the 7-phosphanorbornene oxide; in the latter, there is very pronounced additional deshielding (some 20–30 ppm[14]) relative to monocyclic models.

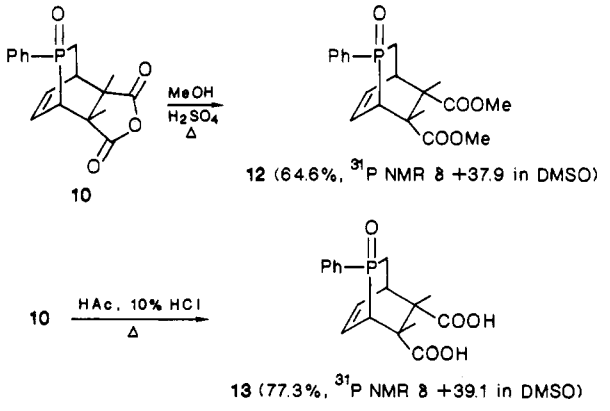
Some other dienophiles that were investigated were acrolein, dimethyl maleate, benzyne, tetracyanoethylene, tetrachlorobenzyne, and phenyl vinyl sulfoxide. The first three gave no indications of a reaction at 80–110 °C. The others gave complex mixtures (e.g., that from phenyl vinyl sulfoxide had 15 $^{31}P$ signals) and were not considered attractive for further examination.

The maleic anhydride adduct **10** could be converted into the corresponding diester and diacid by methanolysis and acid hydrolysis, respectively (Scheme III).

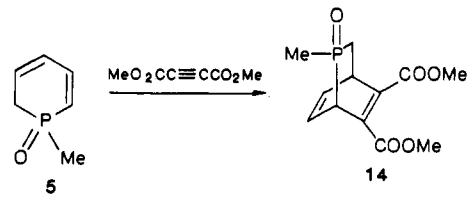
**Synthesis of Some 2-Phosphabicyclo[2.2.2]octa-5,7-diene 2-Oxide Derivatives.** Two approaches proved successful for the synthesis of the dienic ring system. The most direct was the use of an acetylenic dienophile in the Diels–Alder reaction with the 1,6-dihydrophosphorins,[15]

(11) Mathey, F. *Tetrahedron Lett.* **1979**, 1753.
(12) Quin, L. D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 12.
(13) Mathey, F. *Top. Phosphorus Chem.* **1980**, *10*, 1.
(14) Quin, L. D.; Mesch, K. A.; Bodalski, R.; Pietrusiewicz, K. M. *Org. Magn. Reson.* **1982**, *20*, 83.

**Scheme III**



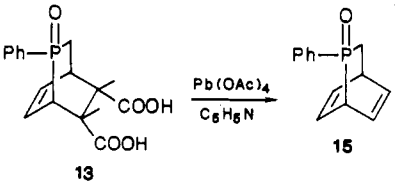

and indeed **5** when refluxed in methylene chloride for 2.5 h with dimethyl acetylenedicarboxylate, in the presence of 5 equiv of aluminum chloride, gave adduct **14** in 35% yield as a crystalline solid. The $^{31}$P NMR signal was




similar to that of the starting material, and again no special influence of the ring system on the shift is observed. A feature of interest was, however, noted in the $^{13}$C NMR spectrum; the methylene carbon in the bridging unit of the diene at δ 23.6 had a remarkably large one-bond coupling to $^{31}$P (96.7 Hz). This was also seen[6] in the adduct of dimethyl acetylenedicarboxylate with 1,6-dihydro-1,2-diphenyl-4,5-dimethylphosphorin 1-sulfide ($^1J_{PC}$ 85.5 Hz). The constant for **14** is some 20 Hz greater than the value found for the monoene **12** (77.2 Hz). At the bridgehead carbon attached to P (δ 44.0), the opposite effect is seen; a smaller value (49.4 Hz) was found in the diene than in the monoene **12** (63.5 Hz). The P-sulfide[6] also had a small constant, 36.6 Hz. These couplings suggest considerable differences may exist in the hybridization at P in forming bonds to the two attached carbons in **14**, with more s-character directed into the bridging carbon bond at the expense of the bridgehead carbon bond. The configuration at phosphorus is not indicated by any of the spectral data, and as will be noted differences even in the corresponding phosphine were not entirely adequate to make a firm assignment. The exact diastereoisomeric structure must remain uncertain at this time.

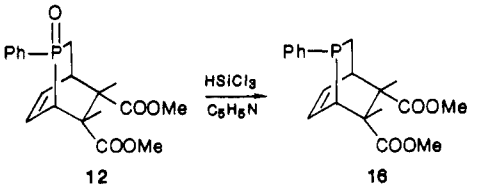
The second approach to the diene system involved the oxidative decarboxylation with lead tetraacetate[16] of the diacid **13**. This was accomplished in pyridine solution and gave diene **15** as an oil with $^{31}$P NMR δ +40.5 and appropriate $^1$H and $^{13}$C NMR spectra. Again the methylene carbon had a much larger $^1J_{PC}$ value than did the bridgehead carbon (108.0 vs 52.7 Hz), just as observed for the diester **14**.

The dienic compounds **14** and **15** were reasonably stable at room temperature. Heating **15** in toluene at 130 °C for 24 h caused some precipitation of a black solid, but no



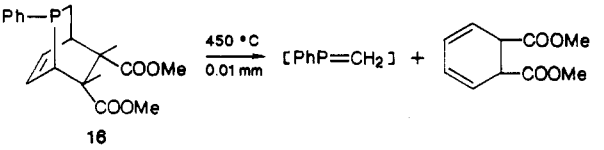

change in the $^{31}$P NMR spectrum of the solution was observed. Compound **14** was somewhat less stable, and about 50% decomposed after the same treatment. The product mixture, which contained a major $^{31}$P NMR signal at δ +55, has not yet been successfully separated for product identification.

**Conversion of Bridged Phosphine Oxides to Phosphines.** Phosphine oxide **12** was deoxygenated with the trichlorosilane–pyridine mixture used successfully for similar purposes in the 7-phosphanorbornene series. The usual conditions, refluxing in benzene for 1–2 h, were quite satisfactory and provided a clean product in 96% yield. The stereochemistry of the phosphine was revealed by the relative magnitude of the two $^2J_{PC}$ values (Table II). That for C-7 was 25.3 Hz, suggesting close proximity of the phosphorus lone pair,[12] while that for C-6 was 3.9 Hz, thus suggesting being remote from the lone pair. The structure is therefore proposed to have the syn orientation of phenyl and the double bond, as in **16**. Since reduction under




these conditions is known to proceed with retention of configuration,[17] this experiment also proves the structure of the starting oxide as **12**. This was confirmed by reoxidation with 30% hydrogen peroxide (also with retention[18]) to the original oxide. The same phosphine was produced by reduction with trichlorosilane in the absence of pyridine, with none of the difficulty (loss of the P fragment, inversion) observed in the 7-phosphanorbornene system.[3]

Compound **16** was quite stable thermally; a solution in toluene held at 130 °C for 4 days showed no fragmentation and no inversion to the anti isomer. Heating the phosphine in the vapor phase at 450 °C and 0.01 mm, however, did cause extensive, but still incomplete, decomposition. Some




20 $^{31}$P NMR signals were recorded for the condensate, which also contained dimethyl dihydrophthalate and dimethyl phthalate as detected by GC–MS. These products suggest a major pathway for the decomposition to be the loss of the phosphorus–carbon bridge, which in principle could appear as the highly reactive phosphaalkene $PhP{=}CH_2$. The complexity of the reaction product discouraged further study of this process; as will be described elsewhere,[19] the presence of a second double bond as in the 2-phosphabicyclo[2.2.2]octa-5,7-diene system permits a

(15) While this work was in progress, the reaction of 1,6-dihydro-1,2-diphenyl-4,5-dimethylphosphorin 1-oxide with dimethyl acetylenedicarboxylate was published.[6] The catalytic effect of aluminum chloride was first reported by these authors.

(16) Grob, C. A.; Ohta, M.; Weiss, A. *Angew. Chem.* **1958**, *70*, 343. Cimarusti, C. M.; Wolinsky, J. *J. Am. Chem. Soc.* **1968**, *90*, 113.

(17) Horner, L.; Balzer, W. D. *Tetrahedron Lett.* **1965**, 1157.

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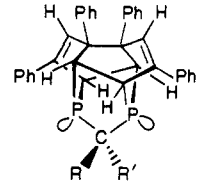
much more facile decomposition by this mechanism and is a process of considerable interest. The synthesis of such compounds is described later in this paper.

The $^{31}P$ NMR signal recorded for the phosphine **16** appeared at $\delta$ −31.6, a value similar to that for a simple monocyclic phosphorinane (1-phenyl,[20] $\delta$ −34.3). By contrast, the *P*-phenyl derivatives of 7-phosphanorbornene phosphines have values that are nearly 100 ppm downfield of monocyclic models. This enormous effect, which is also known for other nuclei in the 7-position of the norbornene framework (O-17,[21] Si-29,[22] N-15,[23] and even C-13[24]), has been attributed to a hyperconjugative interaction involving the $\sigma$ electrons and the $\pi^*$ orbital, which has the effect of withdrawing electron density from phosphorus and thus causing deshielding. The present study suggests that the effect weakens when the bridge is expanded by one carbon as in phosphine **16** (and in the oxides as well). There appears, therefore, to be a definite geometrical requirement for the proposed $\sigma$–$\pi^*$ interaction to be of significance, if indeed this is the real cause of the deshielding. On the other hand, the same molecular framework found in **16** can be discerned in the highly unusual diphosphachiropteradienes **17** recently reported by Märkl et al.,[25] and here the framework is associated with quite low-field shifts ($\delta$ +66.8 to +94) that approach those of the *syn*-7-phosphanorbornenes. Our results with the less highly substituted




17

2-phosphabicyclo[2.2.2]octadiene system suggest that if the NMR effect in **17** does arise from an orbital interaction with the double bond, it probably is of a different nature from that in the 7-phosphanorbornenes. Thus, compound **16** with syn orientation at phosphorus is seen to be far upfield of **17**, which may be described as having the anti orientation. This is the opposite of the syn,anti relation seen in the 7-phosphanorbornenes. However, other features of the structure of **17** may prove to be responsible for the deshielding observed. Detailed theoretical analysis of these still unfolding structural effects on $^{31}P$ shifts would be of great interest.

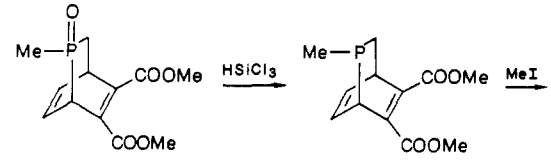
When phosphine oxides **14** and **15** were reduced with trichlorosilane in refluxing benzene, very little of the desired phosphines was obtained; degradation of the ring system occurred, as was implied by the appearance of signals in the secondary phosphine region that also showed characteristic one-bond $^1H$–$^{31}P$ coupling. However, conditions have been developed that do permit the synthesis of the desired tertiary phosphines without complication and in high yield. Thus, it was found that the deoxygenation could be conducted at temperatures well below those usually used (refluxing benzene) for this purpose. The *P*-methylphosphine oxide **14** was smoothly deoxygenated

**Table III. $^1H$ and $^{13}C$ NMR Data[a] for 2-Phenyl-2-phosphabicyclo[2.2.2]octa-5,7-diene (20) and Its Methiodide (21)**

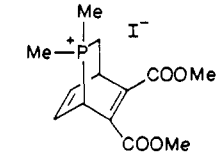
| | 20 | | 21 | |
|---|---|---|---|---|
| | $\delta$ | 2-D interactions[b] | $\delta$ | 2-D interactions[b] |
| H-1 | 4.35 (m) | 6.0, 6.38 | 5.6 (m) | 6.2, 6.65 |
| H-3a | 2.12 (ddd)[c] | 1.60, 4.10 | 2.7 (m) | 4.45 |
| H-3b | 1.60 (ddd)[d] | 2.12, 4.10 | 2.7 (m) | |
| H-4 | 4.10 (m) | 6.20, 6.38, 1.60, 2.12 | 4.45 (d[e] of m) | 2.7, 6.75 |
| H-5 | 6.38 (m)[f] | 4.10 | 6.85 (m)[g] | 6.65 |
| H-6 | 6.38 (m)[f] | 4.35 | 6.65 (m)[g] | 6.85, 5.6 |
| H-7 | 6.0 (m) | 4.35, 6.20 | 6.2 (m) | 5.6, 6.75 |
| H-8 | 6.20 (m) | 4.10, 6.0 | 6.75 (m)[g] | 4.45, 6.2 |
| C-1 | 38.0 [21.3] | 4.35 | 34.5 [22.5] | 5.6 |
| C-3 | 27.5 [24.0] | 1.6, 2.12 | 25.4 [96.0] | 2.7 |
| C-4 | 36.1 [6.4] | 4.10 | 35.8 [6.3] | 4.45 |
| C-5 | 130.7 [4.4] | 6.38 | 138.6 [4.4][h] | 6.85[h] |
| C-6 | 135.9 [11.0] | 6.38 | 127.5 [3.4] | 6.65 |
| C-7 | 131.0 [3.9] | 6.0 | 127.0 [3.9] | 6.2 |
| C-8 | 129.5 [10.3] | 6.20 | 139.8 [4.0][h] | 6.75[h] |

[a] $^{31}P$–$^{13}C$ coupling constants (Hz) are given in brackets; $CDCl_3$ solutions. [b] For $^1H$ NMR COSY technique; for $^{13}C$ NMR HETCOR technique. Spectra of **20** were obtained at −55 °C. All values are $^1H$ NMR $\delta$. [c] $^2J_{PH}$ = 31.2 Hz; $^2J_{HH\text{-}3b}$ = 12.5 Hz; $^3J_{HH\text{-}4}$ = 3.6 Hz. [d] $^2J_{PH}$ = 6.5 Hz; $^2J_{HH\text{-}3a}$ = 12.5; $^3J_{HH\text{-}4}$ = 2.9 Hz. [e] $^2J_{PH}$ = 25.5 Hz. [f] Overlapped. [g] Unresolved in $CDCl_3$; values obtained for a $CD_3CN$ solution. [h] Resolution inadequate for firm assignment.

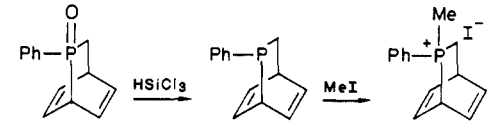
at 0 °C after 4.5 h to give a single phosphine **18** with $^{31}P$ NMR $\delta$ −36.0. The preferred solvent medium was benz-




14 18




19




15 20 21

ene–toluene (8:1). Similarly, the *P*-phenylphosphine oxide **15** gave the desired phosphine **20** at −6 to −8 °C in methylene chloride; it had its $^{31}P$ NMR signal at $\delta$ −29.0. These dienic phosphines, unlike the monene **16**, were relatively unstable and required preservation in the refrigerator. The nature of their decomposition will be the subject of another report.[19] They were successfully characterized by reoxidation to the original phosphine oxides and by conversion into their methiodides, **19** and **21**.

The $^1H$ and $^{13}C$ NMR spectra of the phosphines and their methiodides presented challenges in interpretation that required the aid of 2-D techniques for signal assignment. The data for phosphine **20** and its methiodide **21** are presented in Table III. Except for overlap of two of the olefinic protons, the nonaromatic $^1H$ NMR signals were well resolved at 300 MHz. The bridgehead protons appeared as multiplets at $\delta$ 4.10 and 4.35. Using the COSY technique, it was found that $\delta$ 4.10 had a strong interaction

(20) Featherman, S. I.; Quin, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 4349.
(21) Nguyen, T. T.; Delseth, C.; Kintzinger, J.-P.; Carrupt, P.-A.; Vogel, P. *Tetrahedron* **1980**, *36*, 2793.
(22) Sakurai, H.; Nakadaira, Y.; Koyama, T.; Sakaba, H. *Chem. Lett.* **1983**, 213.
(23) Quin, L. D.; Caster, K. C.; Marsi, B. G.; Miller, J. A. *J. Org. Chem.* **1986**, *51*, 3724.
(24) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972; Chapter 3.
(25) Märkl, G.; Beckh, H. J.; Mayer, K. K.; Ziegler, M. L.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 236.

with the two methylenic protons at δ 1.60 and 2.12 and thus can be assigned to H-4. The nonequivalence of the methylene protons arises from the proximity (approaching eclipsing) of one proton to phenyl and the other to the lone pair on P. That proton close to the lone pair should have a very large two-bond coupling to $^{31}P$,[26] while the remote proton should have a small value. The quite large coupling of 31.2 Hz was found for the signal at δ 2.12, and this may be confidently assigned to H-3a. The proton at δ 1.60 has two small couplings (2.9 and 6.5 Hz); the latter is assigned to $^2J_{PH_b}$. In the olefinic region, two one-proton signals were relatively shielded (δ 6.0 and 6.2, both as unresolved multiplets) and seen to be located on the same side of the ring from their strong, mutual interaction in the COSY spectrum. The other two protons had indistinguishable shifts, at lower field. The obvious explanation for two protons giving upfield signals is that they are influenced by the shielding effect of the *P*-phenyl group in the syn orientation. Since the signal at δ 6.20 interacted with H-4 in the COSY spectrum, it can be assigned to the adjacent proton, H-8. Similarly, the signal at δ 6.0 interacted with H-1 and must be due to H-7.

It then became possible to interpret the $^{13}C$ NMR spectrum by using the heteronuclear correlation technique (HETCOR), where the proton–carbon interactions can be identified. The carbon signal at δ 38.0 interacted with H-1, that at δ 36.1 with H-4, and that at δ 27.5 with the two methylenic protons, and thus all assignments of the $sp^3$ carbons are unequivocal. The magnitude of the P–C coupling fits the assignments; the one-bond values were 21.3 and 24.0 Hz, while the two-bond value, influenced by the lone pair orientation and here remote from it, had the expected small size of 6.4 Hz. In the olefinic region, C-7 is identified at δ 131.0 from its interaction, and the small coupling of 3.9 Hz is consistent with the remoteness of the lone pair. Then C-8 is identified at δ 129.5 from its interaction with the proton at δ 6.20. This leaves olefinic signals at δ 130.7 and 135.9 to be assigned to C-5 and C-6, and this was accomplished with chemical shift effects since the protons on these carbons gave unresolved signals that made HETCOR not useful. It can be expected that C-5 and C-8 should have similar shifts since they are in similar environments; hence, if C-8 has δ 129.5, then the signal at δ 130.7 may be assigned to C-5. This places C-6 at δ 135.9; this is several ppm downfield of C-7 on the opposite face of the system, but this is entirely reasonable, since the steric compression effect of the phenyl should cause upfield-shifting at this position. The assignment is supported by the magnitude of the two-bond coupling (11.0 Hz) to be associated with this carbon. This value is somewhat smaller than that seen in other systems (e.g., 25.3 Hz in phosphine **16**) but certainly is significantly larger than the value of 3.9 Hz seen at the carbon at the opposite face.

For the methiodide **21**, the assignments of the $sp^3$ carbons and the attached protons are unequivocal (Table III) from the 2-D experiments. Here, however, it was not possible to observe separate signals for the two methylenic protons. In the olefinic proton region, one signal was significantly upfield; this was assigned to H-7 and assumed to arise from the phenyl shielding effect. The carbon interacting with H-7 had δ 127.0; the carbon on the opposite face might have a similar shift, since the steric environment resulting from the tetrahedral phosphorus should not differ greatly on the two faces, unlike the situation in the pyramidal phosphine. The other $sp^2$ carbons

(26) Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 11.

**Table IV. $^1H$ and $^{13}C$ NMR Data[a] for 2-Methyl-2-phosphabicyclo[2.2.2]octa-5,7-diene Derivative 18 and Its Methiodide 19**

| | 18 | | 19 | |
|---|---|---|---|---|
| | δ | 2-D interactions[b] | δ | 2-D interactions[b] |
| H-1 | 4.35 (m)[c] | 6.25 | 4.75 (m) | 6.20 |
| H-3a | 2.1 (ddd)[d] | 4.35, 1.0 | 1.9 (m)[c] | 4.25 |
| H-3b | 1.0 (ddd)[e] | 4.35, 2.1 | 1.9 (m)[c] | |
| H-4 | 4.35 (m)[c] | 1.0, 2.1, 6.25 | 4.25 (d of m)[f] | 6.43, 1.9 |
| H-7 | 6.25 (m)[c] | 4.35 | 6.20 (m) | 6.43, 4.75 |
| H-8 | 6.25 (m)[c] | | 6.43 (m) | 6.20, 4.25 |
| $CH_3P$ | 0.85 (d)[g] | | 1.6 (d)[h] | |
| $CH_3O$ | 3.75, 3.80 | | 3.40, 3.45 | |
| C-1 | 39.3 [22.0] | 4.35 | 36.0 [41] | 4.75 |
| C-3 | 30.4 [32.4] | 1.0, 2.1 | 25.5 [85.2] | 1.9 |
| C-4 | 39.3 [5.1] | 4.35 | 36.8 [10.2] | 4.25 |
| C-5 | 139.3 [3.7] | | 143.4 [19.6] | |
| C-6 | 141.7 [8.2] | | 137.9 [20.3] | |
| C-7 | 130.1 [2.3][i] | | 126.7 [10.7][i] | |
| C-8 | 128.6 [8.1][i] | | 135.3 [10.4][i] | |
| $CH_3P$ | 13.2 [25.9] | | 11.2 [52.3], 10.4 [49.5] | |
| $CH_3O$ | 52.3, 52.4 | | 53.0, 53.5 | |
| C=O | 165.5 [3.0], 166.0 [1.9] | | 163.9 [3.8], 164.0 [2.8] | |

[a] $^{31}P$–$^{13}C$ coupling constants (Hz) are given in brackets; $CDCl_3$ solution. [b] For $^1H$ NMR COSY technique; for $^{13}C$ NMR HETCOR technique. Spectra for **18** were obtained at −20 °C. All values are $^1H$ NMR δ. [c] Overlapped. [d] $^2J_{PH}$ = 30.6 Hz; $^3J_{HH\text{-}4}$ = 3.6 Hz; $^2J_{HH\text{-}3b}$ = 12.3 Hz. [e] $^2J_{PH}$ = 6.4 Hz; $^3J_{HH\text{-}4}$ = 2.8 Hz; $^2J_{HH\text{-}3a}$ = 12.3 Hz. [f] $^3J_{PH}$ = 26.2 Hz. [g] $^2J_{PH}$ = 7.0 Hz. [h] $^2J_{PH}$ = 15.3 Hz. [i] C–H coupling confirmed.

C-5 and C-8 should have similar shifts. HETCOR shows an interaction of one of the downfield carbons (δ 138.6) with H-8 at δ 6.75, and other relations seen in Table III allow a nearly complete interpretation of the carbon spectrum.

For the *P*-methylphosphine **18**, the overlap of some of the proton signals limited the use of 2-D techniques. The assignments in Table IV resemble those for the *P*-phenyl compound. The deshielding at the two carbons bearing the ester groups left the two carbons on the opposite face at relatively higher field. That with the smaller coupling of 2.3 Hz seems assignable to C-7, which is remote from the lone pair. The two-bond lone pair effect was also used to assign the two carbons bearing the ester groups; that with the larger coupling of 8.2 Hz is assigned to C-6. The $^{13}C$ NMR spectra therefore provide a tentative indication of the configuration at phosphorus (*P*-Me anti to C-5,6); however, the usually reliable[12] two-bond coupling constants are of reduced magnitude in this ring system, and designating the syn or anti structure without supporting data may be premature. The spectra of the methiodide of phosphine **18** were interpreted with the aid of 2-D techniques, following reasoning similar to that outlined in detail for the *P*-phenyl compounds. Data are recorded in Table IV.

From the data presented for the two methiodides **19** and **21**, it may clearly be seen that the unusual one-bond P–C coupling effects are present, where the coupling to the bridging methylene is abnormally large and that to the bridgehead carbon is abnormally small, as had been noted for the corresponding phosphine oxides **14** and **15**. The effect is much less pronounced in phosphine **18**, where the values of 32.4 and 22.0 Hz for the $CH_2$ and CH were found, and essentially is absent in phosphine **20** (24.0 and 21.3 Hz, respectively).

It was noted in connection with the monoenes in this ring system that perfectly normal $^{31}P$ NMR shifts, similar

to those of monocyclic models, were found. With the synthesis of the first two dienes in this ring system, where again normal values were observed, it can now be seen that the ring structure has relatively little influence on this parameter. This is a striking difference from the situation in the 7-phosphanorbornene system, and attests to the special nature of the interactions in that ring system. The only NMR anomaly worthy of special note is that of the distortion of the magnitudes of the one-bond coupling constants for $^{13}C$–$^{31}P$. The determination of structural parameters by X-ray analysis of the oxides or salts in the 2-phosphabicyclo[2.2.2]octa-5,7-diene system should be of value in the elucidation of this effect.

## Experimental Section

**General.** Phosphorus-31 NMR spectra (proton-decoupled, FT) are referenced to 85% phosphoric acid as an external standard, with an internal deuterium lock. Negative shifts are upfield and positive downfield of the reference. Carbon-13 NMR spectra (proton-decoupled, FT) employed tetramethylsilane as an internal standard. Mass spectra were obtained on an AEI MS 903 spectrometer at the Research Triangle Mass Spectrometry Center, Research Triangle Park, NC. Melting points were taken on a Mel-Temp apparatus and are corrected. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ, or by the University of Massachusetts Microanalytical Laboratory, Amherst, MA. All procedures involving trivalent phosphorus were performed under a nitrogen atmosphere.

**3-Hydroxy-1-methyl-1,2,3,6-tetrahydrophosphorin 1-Oxide (4).** To 3.0 g (0.0208 mol) of ketone **3**[5] in 60 mL of 0.4 M $CeCl_3$ in methanol was added 0.787 g (0.0208 mol) of $NaBH_4$ in small portions. The solution was stirred at 0 °C for 1 h and at room temperature for 1 h. Neutralization with 10% HCl, gravity filtration, and rotary evaporation gave a gelatinous material that was dissolved in water and passed through Dowex-50 (200–400 mesh) ion-exchange resin to remove ceric ion. Purification of the product was also accomplished by chromatography on a similar column and provided partial separation of the isomer mixture.[27] A mixture of diastereoisomers **4a** and **4b** (1.67 g, 55%) with $^{31}P$ NMR ($D_2O$) $\delta$ +47.8 and +48.2 in roughly equal amounts was first obtained; at the end of the elution, the fractions were found to contain a single isomer (**4a**, 0.1 g, mp 122–123 °C); $^{31}P$ NMR ($CH_3OH$) $\delta$ +47.5; $^1H$ NMR ($D_2O$) $\delta$ 1.53 (d, $^2J_{PH}$ = 14 Hz, $PCH_3$), 2.0–2.7 (m, 4 H, methylene H), 4.4 (br s, C*H*OH), 5.6–5.9 (m, 2 H, HC=CH). The spectrum of the mixture contained $^1H$ NMR signals for the other isomer **4b** at $\delta$ 1.68 (d, $^2J_{PH}$ = 14 Hz, $PCH_3$) and 4.73 (m, C*H*OH). The $^{13}C$ NMR spectra of isomers **4a** and **4b** are recorded in Table I. Elemental analysis was performed on the single isomer **4a**.

Anal. Calcd for $C_6H_{11}O_2P$: C, 49.32; H, 7.59. Found: C, 49.21; H, 7.51.

**3-Hydroxy-1-phenyl-1,2,3,6-tetrahydrophosphorin 1-Oxide (7).** To 6.0 g (0.0291 mol) of ketone **6**[5] in 75 mL of 0.4 M $CeCl_3$ in methanol was added 1.108 g (0.0291 mol) of sodium borohydride in small portions. The solution was stirred at 0 °C for 1 h and at room temperature for 1 h. Neutralization with 10% HCl, gravity filtration, and rotary evaporation gave a gelatinous material that was subsequently chromatographed on silica gel (8% MeOH–$CHCl_3$), yielding 5.6 g (93%) of **7** as a mixture of isomers. Fractional recrystallization (acetone–hexane) gave compound **7a** as a white crystalline solid: mp 156–158 °C; $^{31}P$ NMR ($CDCl_3$) $\delta$ +31.3; $^{13}C$ NMR, Table I; $^1H$ NMR ($CDCl_3$) $\delta$ 2.1–2.9 (m, 4 H, $CH_2$), 3.6 (d, $^3J_{HH}$ = 8.9 Hz, OH), 4.4 (m, 1 H, C*H*OH), 5.8–6.2 (m, 2 H, CH=CH), 7.4–7.8 (m, 5 H, $C_6H_5$).

Anal. Calcd for $C_{11}H_{13}O_2P$: C, 63.46; H, 6.29; P, 14.88. Found: C, 63.66; H, 6.40; P, 14.79.

Rotary evaporation of the mother liquid gave compound **7b** as a clear oil that was not successfully crystallized: $^{31}P$ NMR ($CDCl_3$) $\delta$ +32.2; $^{13}C$ NMR ($CDCl_3$), Table I; $^1H$ NMR ($CDCl_3$) $\delta$ 4.9 (m, 1 H, C*H*OH).

**1,6-Dihydro-1-methylphosphorin 1-Oxide (5).** To 1.1 g (0.007 53 mol) of **4** in 50 mL of chlorobenzene was added 2.065 g (0.015 mol) of fused $KHSO_4$. The mixture was refluxed for 25 min, gravity filtered, and rotary evaporated to yield 0.81 g (86%) of **5**: $^{31}P$ NMR ($CDCl_3$) $\delta$ +22.3; $^{13}C$ NMR, Table I; MS, *m/e* 128.0390 ($M^+$, $C_6H_9OP$; calcd 128.0391).

**1,6-Dihydro-1-phenylphosphorin 1-Oxide (8).** To 6.4 g (0.0308 mol) of **7** in 200 mL of chlorobenzene was added 8.38 g (0.0615 mol) of fused $KHSO_4$. The mixture was refluxed for 30 min, gravity filtered, and rotary evaporated to yield 5.0 g (85.5%) of noncrystallizing **8**: $^{31}P$ NMR ($CDCl_3$) $\delta$ +16.2; $^{13}C$ NMR, Table I; $^1H$ NMR ($CDCl_3$) $\delta$ 2.7–3.3 (m, 2 H, $CH_2$), 5.9–6.9 (m, 4 H, =CH), 7.1–7.9 (m, 5 H, $C_6H_5$); MS, *m/e* 190.0546 ($M^+$, $C_{11}H_{11}OP$; calcd 190.0548).

***endo-syn*-2-Methyl-2-oxo-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic Acid Anhydride (9).** A mixture of 0.6 g (0.004 68 mol) of **5** and 0.505 g (0.005 15 mol) of maleic anhydride was refluxed in 100 mL of benzene for 12 h. The solvent was decanted while warm and rotary evaporated to give a yellow solid. The solid was washed with cold acetone and recrystallized (acetone/hexane) to give 0.35 g (33%) of **9**: mp 267–268 °C; $^{31}P$ NMR (DMSO-$d_6$) $\delta$ +45.0; $^{13}C$ NMR, Table II.

***endo-syn*-2-Phenyl-2-oxo-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic Acid Anhydride (10).** A mixture of 4.0 g (0.021 mol) of **8** and 2.06 g (0.021 mol) of maleic anhydride was refluxed in 500 mL of benzene for 24 h. The solvent was rotary evaporated to yield a yellow solid that was washed with cold acetone and recrystallized from acetone, giving 2.8 g (44%) of **10**: mp 261–262 °C; $^{31}P$ NMR (DMSO-$d_6$) $\delta$ +36.8; $^{13}C$ NMR, Table II.

Anal. Calcd for $C_{15}H_{13}O_4P$: C, 62.51; H, 4.55; P, 10.75. Found: C, 62.69; H, 4.72; P, 10.89.

**Reaction of 8 with *N*-Phenylmaleimide.** A mixture of 0.3 g (0.001 58 mol) of **8** and 0.3 g (0.001 74 mol) of *N*-phenylmaleimide was refluxed in 5 mL of benzene for 3 h. White crystals formed on the walls of the flask during the reflux. After cooling to room temperature the benzene was decanted, leaving 0.5 g (87.2%) of **11**: mp 271 °C; $^{31}P$ NMR (DMSO-$d_6$) $\delta$ +39.3 (not further characterized).

**Dimethyl 2-*syn*-Phenyl-2-oxo-2-phosphabicyclo[2.2.2]-oct-5-ene-7,8-dicarboxylate (12).** A mixture of 0.4 g (0.001 39 mol) of **10**, 25 mL of methanol, and 0.5 mL of $H_2SO_4$ was refluxed for 21 h. The solution was concentrated by rotary evaporation, and 10 mL of $H_2O$ was added. The aqueous layer was washed with $CHCl_3$ (3 × 10 mL), and the layers were separated. The organic layer was dried ($Na_2SO_4$) and evaporated (rotary and high vacuum) to yield 0.3 g (64.6%) of **12**, mp 146–147 °C (ethyl acetate/hexane): $^{31}P$ NMR ($CDCl_3$) $\delta$ +37.9; $^{13}C$ NMR, Table II; $^1H$ NMR ($CDCl_3$) $\delta$ 1.7–2.4 (m, 2 H, $CH_2P$), 3.2–4.4 (m, 4 H, CH), 3.6 (s, 6 H, $OCH_3$), 5.9–6.4 (m, 2 H, CH=CH), 7.3–7.9 (m, 5 H, $C_6H_5$).

Anal. Calcd for $C_{17}H_{19}O_5P$: C, 61.08; H, 5.73; P, 9.26. Found: C, 61.15; H, 5.70; P, 9.08.

**2-*syn*-Phenyl-2-oxo-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic Acid (13).** To 2.8 g (0.009 72 mol) of **10** were added 50 mL of glacial acetic acid and 50 mL of 10% HCl. The solution was refluxed for 36 h. The solvent was rotary evaporated to give a yellow solid that was recrystallized from $H_2O$, yielding 2.3 g (77.3%) of **13**: mp 200 °C dec (solidifies and remelts, 260 °C); $^{31}P$ NMR (DMSO-$d_6$) $\delta$ +39.1.

Anal. Calcd for $C_{15}H_{15}O_5P \cdot {}^1/_2H_2O$: C, 57.15; H, 5.12; P, 9.82. Found: C, 57.48; H, 5.09; P, 9.74.

**Dimethyl 2-Methyl-2-oxo-2-phosphabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (14).** To 0.65 g (0.005 07 mol) of **5** in 25 mL of $CH_2Cl_2$ at 0 °C were added 1.08 g (0.007 61 mol) of dimethyl acetylenedicarboxylate and 3.38 g (0.0254 mol) of aluminum chloride. The mixture was refluxed for 2.5 h, cooled to 0 °C, and hydrolyzed with 30 mL of saturated ammonium chloride. The organic layer was separated, dried ($Na_2SO_4$), and rotary evaporated to yield a clear oil. Chromatography on silica gel (5% MeOH/$CHCl_3$) and recrystallization from benzene gave 0.48 g (35%) of **14**: mp 148–149 °C; $^{31}P$ NMR ($CDCl_3$) $\delta$ +50.0; $^{13}C$ NMR ($CDCl_3$) $\delta$ 15.3 ($J$ = 96.7 Hz, $PCH_3$), 23.6 ($J$ = 96.7 Hz, C-3), 37.1 ($J$ = 9.9 Hz, C-4), 44.0 ($J$ = 49.4 Hz), 51.7 and 52.0 (both

(27) This synthesis has been performed successfully on many occasions. However, in two instances the desired product was formed in very low yield and was accompanied by a large amount of unidentified material.

s, $OCH_3$), 128.7 ($J$ = 7.7 Hz, C-7), 132.8 ($J$ = 18.7 Hz, C-6 or C-8), 135.2 ($J$ = 11.0 Hz, C-6 or C-8), 140.2 ($J$ = 20.0 Hz, C-5), 164.0 ($J$ = 2.2 Hz, C=O), 165.2 ($J$ = 3.3 Hz, C=O); $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.65 (d, $^2J_{PH}$ = 15.2 Hz, $PCH_3$), 1.55–1.85 (m, 2 H, $CH_2$), 3.79 and 3.82 (both s, $OCH_3$), 4.22 (d of m, $^3J_{PH}$ = 38 Hz, H-1), 4.43 (m, H-4), 6.33 (m, 2 H, olefinic H).

Anal. Calcd for $C_{12}H_{15}O_5P$: C, 53.34; H, 5.60; P, 11.46. Found: C, 53.44; H, 5.77; P, 11.61.

**2-Phenyl-2-phosphabicyclo[2.2.2]octa-5,7-diene 2-Oxide (15).** To 0.229 g (0.747 mmol) of **13** in 8 mL of dry pyridine was added 1.33 g (2.99 mmol) of lead tetraacetate. The mixture was placed in an oil bath at 75 °C until carbon dioxide evolution ceased. The solution was rotary evaporated and chromatographed on alumina with o% MeOH in $CHCl_3$ and then on silica gel with 3% MeOH in $CHCl_3$, yielding 0.0645 g (40%) of **15**: $^{31}$P NMR ($CDCl_3$) $\delta$ +40.5; $^{13}$C NMR ($CDCl_3$) $\delta$ 25.8 ($J$ = 108.8 Hz, C-3), 35.7 ($J$ = 9.9 Hz, C-4), 43.0 ($J$ = 52.7 Hz, C-1), 128.2 ($J$ = 11.0 Hz, C-meta), 129.1 ($J$ = 8.8 Hz, C-6 or C-7), 129.2 ($J$ = 4.4, C-6 or C-7), 131.6 ($J$ = 3.3 Hz, C-para), 131.7 ($J$ = 8.8 Hz, C-ortho), 132.5 ($J$ = 94.5 Hz, C-ipso), 134.8 ($J$ = 22.0 Hz, C-5 or C-8), 135.9 ($J$ = 19.8 Hz, C-5 or C-8); $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.70 (m, 1 H, unresolved d of t, C*H*H), 2.0 (m, 1 H, unresolved d of d, CH*H*), 4.10 (m, 2 H, H-1 and H-4), 6.18 (m, 1 H, olefinic H), 6.45 (m, 1 H, olefinic H), 6.65 (m, 2 H, olefinic H), 7.3–7.9 (Ar H); MS, $m/z$ 216.0702 ($M^+$, $C_{13}H_{13}OP$; calcd 216.0704).

**Dimethyl 2-*syn*-Phenyl-2-phosphabicyclo[2.2.2]oct-5-ene-7,8-dicarboxylate (16).** To a solution of 0.559 g (0.0041 mol) of trichlorosilane in 50 mL of dry benzene was added 0.9775 g (0.0123 mol) of dry pyridine in 10 mL of dry benzene. A solution of 0.25 g (0.00 75 mol) of **12** in 5 mL of dry benzene was added. The mixture was refluxed for 1.5 h and then chilled in an ice bath for addition of 15 mL of 30% NaOH. The mixture was stirred for 15 min, and the layers were separated. The $H_2O$ layer was washed with benzene (2 × 10 mL). The combined benzene layers were dried ($MgSO_4$) and rotary evaporated to yield 0.23 g (96.4%) of **16** as a clear oil: $^1$H NMR ($CDCl_3$) $\delta$ 1.5–3.7 (m, 12 H, $sp^3$ CH), 5.9–6.5 (m, 2 H, =CH), 7.1–7.5 (m, $C_6H_5$); $^{13}$C NMR, Table III; $^{31}$P NMR ($CDCl_3$) $\delta$ −40.0.

To a sample of **16** in benzene was added excess methyl iodide. The mixture was stirred in the absence of light for 24 h at room temperature. Rotary evaporation gave a white solid that was recrystallized from methanol/ethyl acetate: mp 208–209 °C dec; $^{31}$P NMR (DMSO-$d_6$) $\delta$ +24.9; $^{13}$C NMR (partial, DMSO-$d_6$) $\delta$ 7.04 ($J$ = 46.4 Hz, $PCH_3$), 29.0 ($J$ = 48.8 Hz, C-1 or C-5), 32.1 ($J$ = 8.6 Hz, C-4), 45.8 ($J$ = 8.6 Hz, C-5 or C-6), 52.1 and 52.3 (both s, $OCH_3$), 170.2 (s, C-9), 171.3 ($J$ = 10.8 Hz, C-10).

Anal. Calcd for $C_{18}H_{22}IO_4P$: C, 46.97; H, 4.82; P, 6.73. Found: C, 46.68; H, 5.19; P, 6.83.

**Dimethyl 2-Methyl-2-phosphabicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (18).** A solution of 0.400 g (0.001 48 mol) of **14** in 16 mL of benzene and 2 mL of toluene was stirred with 2.15 g (0.0158 mol) of trichlorosilane at 0 °C for 4.5 h. The solution was evaporated to give a clear oil, which was dissolved in 80 mL of dichloromethane and then neutralized with 1 mL of 30% KOH. The organic layer was dried over molecular sieves and after solvent removal left **18** as a pale yellow oil (0.34 g, 90%): $^{31}$P NMR ($CDCl_3$) $\delta$ −36.0; $^1$H and $^{13}$C NMR, Table IV.

The phosphine was quaternized with methyl iodide to give the methiodide **19**: mp 163–164 °C; $^{31}$P NMR ($CDCl_3$) $\delta$ +31.6; $^1$H and $^{13}$C NMR, Table IV.

Anal. Calcd for $C_{13}H_{18}IO_4P$: C, 39.41; H, 4.58. Found: C, 39.00; H, 4.25.

**2-Phenyl-2-phosphabicyclo[2.2.2]octa-5,7-diene (20).** To 0.22 g (0.001 02 mol) of **15** in 15 mL of dichloromethane was added 2.0 g (0.0147 mol) of trichlorosilane. The mixture was stirred at −6 to −8 °C for 4.5 h and then worked up as for **18**. The major product in the residual oil was phosphine **20** [$^{31}$P NMR ($CDCl_3$) $\delta$ −29.0] with 8% unreacted **15** and 5% of a secondary phosphine [$^{31}$P NMR ($CDCl_3$) $\delta$ −71 ($^1J_{PH}$ = 200 Hz) (possibly PhMePH, $\delta$ −72.3 ($^1J$ = 222 Hz[28]))]. The phosphine was used in this condition for $^1$H and $^{13}$C NMR (Table III).

Phosphine **20** was converted to the crystalline methiodide **21** by stirring with methyl iodide in benzene; **21** was recrystallized from acetone and had mp 160–163 °C: $^{31}$P NMR ($CDCl_3$) $\delta$ +23.4; $^1$H and $^{13}$C NMR, Table III.

Anal. Calcd for $C_{14}H_{16}IP$: C, 49.14; H, 4.71. Found: C, 48.69; H, 4.51.

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# Steric Effects on Rates and Equilibria of a Cation–Anion Combination Reaction: The Methoxide Attachment to 4-Substituted 2,6-Di-*tert*-butylpyrylium Cations

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The kinetic and equilibrium constants for the reaction of 2,6-di-*tert*-butyl-4-R-pyrylium cations (R = H, Me, *t*-Bu, $Et_3C$, Ph) with methoxide ion, to yield the corresponding 2*H* and 4*H* adducts, have been determined in MeOH at 25 °C. The reaction involves the kinetically controlled formation of the 4*H* adduct only when R = H or Me, whereas in the other cases a mixture of both the 2*H* and 4*H* adducts is formed. The 2*H* adducts are the thermodynamically favored products, though in the case of the methyl-substituted cation a comparable amount of the anhydro base is also formed. The rate constants for the formation of the 4*H* adducts follow a regular trend showing a low sensitivity to steric effects, whereas the corresponding equilibrium constants are not affected by steric interactions until a certain value of the steric hindrance of the γ-substituent is reached. Above this value steric effects are greater on equilibria than on rates. These observations are interpreted in terms of an ion pair-like transition state in which the nucleophile specifically interacts with the electrophilic center.

Nucleophile–cation combination reactions play a central role in physical organic chemistry, due in part to the extensive work carried out by Ritchie,[1] which established a new empirical nucleophilicity scale to correlate the re-

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