1- and 2-Phenyloctahydroindolizines 14f, 15f, and 16f. *N*-Oxide **5** (190 mg, 1.65 mmol) and styrene (**9f**) (189 mg, 1.82 mmol) are treated with LDA (5.78 mmol) for 3 h. Procedure B gives a crude mixture of three cycloaddition products **14f**, **15f**, and **16f** (246 mg, 1.22 mmol, 74%). GLC analysis (column A) shows the presence of three peaks in a 1/0.5/0.4 ratio. The MS of those three fractions analyzed on a spectrometer equipped with a GLC apparatus are identical (*m/e* 201, 196, 97). Chromatography on neutral alumina (hexane–CH_2Cl_2 50/50) gives two fractions. The first one (163 mg, 0.82 mmol, 50%) is a mixture of the two diasteroisomers of 1-phenylindolizidine, **14f** and **15f**, containing 10% of **16f**: picrate mp (EtOH) 174 °C (lit.[18] mp 172–173 °C) for the isomeric mixture **14f** + **15f**. The second one (93 mg, 0.46 mmol, 28%) contains **14f** contaminated by 14% of **16f**. **14f**: IR 2780, 2750, 2650 (shoulder), 1440, 860, 700 cm^{-1}; ^1H NMR (400 MHz) δ 1.2 (b m, 3 H), 1.5–1.9 (b m, 5 H), 2.1 (dt, 1 H, H_{5ax}), 2.4 (b m, 2 H, $H_{2\alpha}$, $H_{3\beta}$), 2.85 (dd, 1 H, $H_{1\alpha}$), 3.15 (b d, 1 H, H_{5eq}), 3.25 (m, 1 H, $H_{3\alpha}$), 7.3 (m, 5 H).

1-(4-Methoxyphenyl)octahydroindolizine (14g). *N*-Oxide **5** (390 mg, 3.39 mmol) and *p*-methoxystyrene (**9g**) (500 mg, 3.75 mmol) are treated with LDA (11.86 mmol) for 3 h. Procedure A gives a crude mixture (900 mg) containing unreactive olefin. GLC analysis (column A) shows the presence of three cycloadducts in 1/0.1/0.2 ratio. Chromatography on neutral alumina (hexane–CH_2Cl_2 50/50) gives two major fractions. The first one is constituted by a mixture of **14g** (272 mg, 1.17 mmol, 34%) containing 15% of its α isomer **15g**; the second one is constituted by the same compound **14g** (220 mg, 0.95 mmol, 28%) containing 30% of the 2β isomer **16g**. **14g**: IR 2750, 2700, 2650 (shoulder), 1600, 1500, 1440, 1250, 830, 740; MS, *m/e* 231, 97; ^1H NMR (400 MHz) δ 2.10 (dt, 1 H, H_{5ax}), 2.20 (m, 1 H, $H_{2\alpha}$), 2.40 (m, 1 H, $H_{3\beta}$), 2.80 (dd, $H_{1\alpha}$), 3.10 (b d, 1 H, H_{5eq}), 3.20 (dd, 1 H, $H_{3\alpha}$), 3.8 (s, 3 H, OMe), 7.1–7.4 (AB system, 4 H, J_{ortho} = 6 Hz); picrate mp (EtOH) 169–171 °C. Anal. Calcd for $C_{21}H_{24}N_4O_8$: C, 54.78; H, 5.21; N, 12.17; O, 27.82. Found: C, 54.21; H, 5.12; N, 11.97; O, 27.71.

Acknowledgment. We thank Dr. D. Guénard (I.C.S.N., C.N.R.S., Gif-sur-Yvette) for helpful discussions concerning the ^1H NMR results.

Registry No. **5**, 17206-00-7; **8** (isomer 1), 1771-52-4; **8** (isomer 2), 494-69-9; **9a**, 74-85-1; **9b**, 142-29-0; **9c**, 645-49-8; **9d**, 103-30-0; **9e**, 4747-15-3; **9f**, 100-42-5; **9g**, 637-69-4; **10a**, 13618-93-4; **10a**·picrate, 5210-66-2; **10b**, 96947-16-9; **10b**·picrate, 96996-79-1; **10c**, 96866-60-3; **10c**·picrate, 96947-19-2; **10d**, 96947-17-0; **10d**·picrate, 96996-80-4; **11d**, 96947-18-1; **11d**·picrate, 96996-81-5; **11e**, 96866-61-4; **11e**·picrate, 96947-21-6; **12**, 695-56-7; **13a**, 96866-67-0; **13a**·picrate, 96947-20-5; **13b**, 96866-68-1; **14f**, 96866-62-5; **14f**·picrate, 96866-69-2; **14g**, 96866-64-7; **14g**·picrate, 96866-71-6; **15f**, 96866-63-6; **15f**·picrate, 96866-70-5; **15g**, 96866-65-8; **16f**, 96896-97-8; **16g**, 96866-66-9; *N*-methylpiperidine, 626-67-5.

(18) Reinecke, M. G.; Kray, L. *J. Org. Chem.* **1966**, *31*, 4215.

1,1,6,6-Tetramethyldibenzo[*b*,*e*]phosphajulolidine

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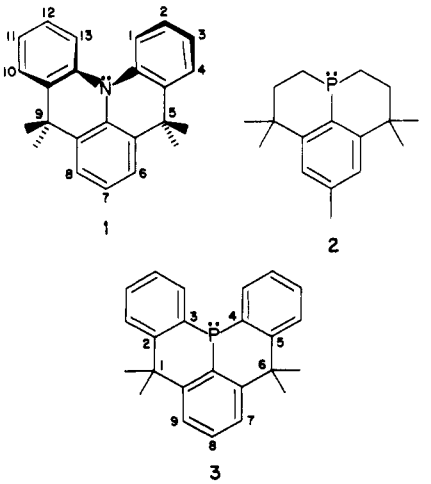
1,1,6,6-Tetramethyldibenzo[*b*,*e*]phosphajulolidine (**3**), the phosphorus analogue of 5,5,9,9-tetramethyl-5*H*,9*H*-quino[3,2,1-*d*,*e*]acridine, was synthesized. Single-crystal X-ray analysis of **3** showed that the molecule, because of the longer P–C bonds (1.820–1.836 Å) and the pyramidality of phosphorus, has approximately C_s symmetry, whereas the nitrogen analogue has C_2 symmetry. The geometry about phosphorus is pyramidal, with the phosphorus atom 0.81 Å out of the plane of the three bonded carbon atoms. The corresponding C–P–C angles are 99.0°, 98.3°, and 108.5°.

The bridged triphenylamine 5,5,9,9-tetramethyl-5*H*,9*H*-quino[3,2,1-*d*,*e*]acridine (**1**) has been shown by variable-temperature ^1H NMR and X-ray analyses to have appproximate C_2 symmetry along the axis connecting C7 and the nitrogen.[1] To minimize the steric interaction between H1 and H13, the nitrogen in this conformation is flattened, lying only slightly outside the plane (0.03 Å) formed by the three N–C bonds linking the phenyl groups, with C–N–C bond angles of 117–124°.[2]

As part of a study of the n–π interaction between the lone-pair electrons on the phosphorus and the adjacent aromatic π system in a rigidized bicyclic framework, we recently reported the synthesis of the first phosphajulolidine **2**.[3] Its cyclic voltammetric and UV spectroscopic (λ_{max} 255 nm) data suggest that **2** has no n–π interaction between the lone-pair electrons on the phosphorus and the adjacent π system.[4]



1 2 3

Examination of a Dreiding stereo model of **2** reveals also a strain-free and somewhat flexible bonding framework around the *pyramidal* phosphorus. To confirm these and other findings from our earlier work[3,5] single-crystal X-ray

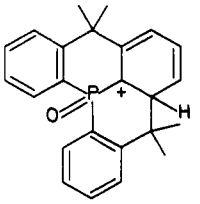
(1) Hellwinkel, D.; Melan, M. *Chem. Ber.* **1974**, *107*, 616.
(2) These preliminary crystallographic data were cited in ref 1, from H. Irngartinger of the University of Heidelberg. However, the complete structure of **1** has yet to appear in the literature.
(3) Chen, C. H.; Brighty, K. E.; Michaels, F. M. *J. Org. Chem.* **1981**, *46*, 361.
(4) Halpern, E. J.; Mislow, K. *J. Am. Chem. Soc.* **1967**, *89*, 5224.
(5) Chen, C. H.; Brighty, K. E. *Tetrahedron Lett.* **1980**, *21*, 4421.

0022-3263/85/1950-2914$01.50/0

analysis of the phosphajulolidyl system would be highly desirable. Since **2** is a liquid that oxidizes on exposure to air at room temperature, obtaining meaningful X-ray scattering data was difficult, if not impossible. We have now synthesized the stable, crystalline, dibenzo-fused phosphajulolidine **3**,[6] which is an analogue of the bridged triphenylamine **1**, and report herewith its characterization, spectroscopic properties, cyclic voltammograms, and crystal structure, particularly with respect to the bonding characterisitcs and the geometry about the phosphorus.

Results and Discussion

Synthesis. We selected as our starting material the bicyclic phosphorane **8**,[7] which was prepared by an improved procedure in two steps (overall yield 29%) from 1-methyl-1-(2-bromophenyl)ethanol[8] (**4**) with an (isobutyloxy)methyl ether as the protective group before lithiation. The phosphorane **8** was chosen because it can be regarded as an internally protected phenylbis[2-[1-methyl-1-(benzyloxy)ethyl]phenyl]phosphine oxide (**7**).[7] Furthermore, **8** is remarkably stable, highly crystalline, and easy to isolate in pure form. Heating **8** briefly in 115% polyphosphoric acid (PPA)[9] produced the monoannulated phosphorin **9** in 83% yield.



A

The second cyclization from **9** to give the bicyclic phosphine oxide **10**, however, was difficult. After numerous attempts under various conditions, we found the optimum cyclodehydration condition was to heat **9** in 115% PPA at 185–187 °C for about 1.5 h. Nevertheless, we isolated **10** in only about 4% yield after purification by chromatography. The extent of this cyclization was closely monitored by ^{1}H NMR by observing the emergence of **10**, which has two new singlets at δ 1.93 and 2.0 and a new multiplet centered at δ 8.37. The temperature and the duration of the reaction were critical, because the starting material **9** decomposed simultaneously. We attributed the poor yield of the second annulation to the highly strained transition state involving the intermediate carbonium ion A, which was also destabilized by the adjacent phosphoryl electron-withdrawing group. Reduction of the phosphine oxide **10** with trichlorosilane[10] proceeded smoothly to give the desired phosphine **3** in high yield.

Reasoning that part of the strain in A was probably due to the presence of the phosphoryl group, we decided to reduce **9** first to give the more flexible phosphine derivative **12**. Treatment of **12** with the mild dehydrating agent 10% P_2O_5–methanesulfonic acid (MSA) produced only the olefinic phosphine **11**. Heating **12** in the presence of 115% PPA at about 120 °C for 10 h gave the desired cyclized product **3** in 45% yield.

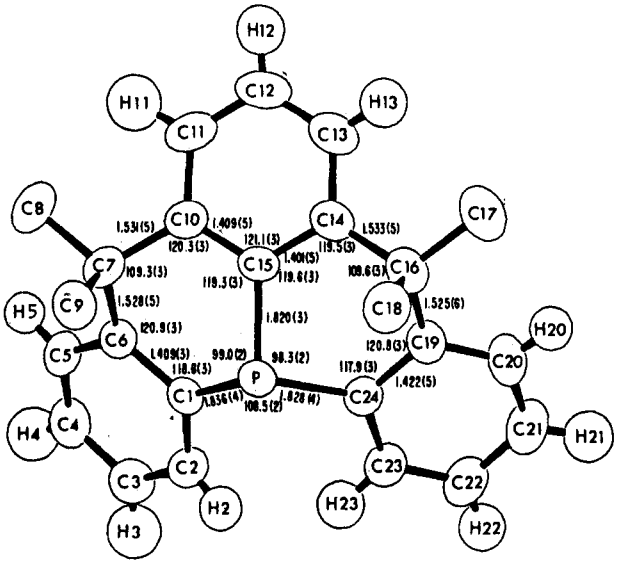
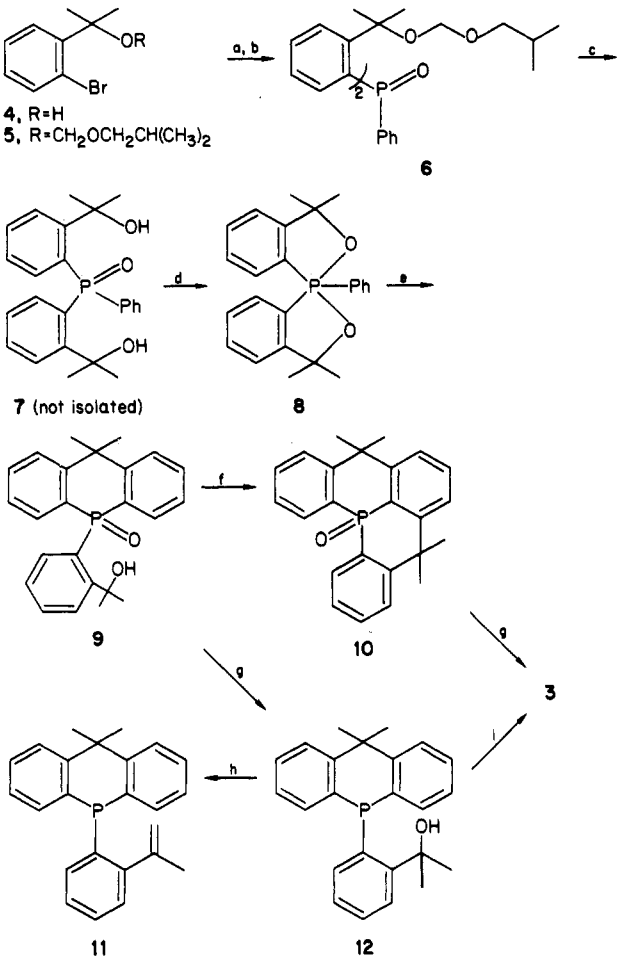


Figure 1. Plot of structure **3** with atomic labeling and selected bond distances and angles. The thermal ellipsoids are plotted at the 50% probability level. Methyl hydrogens were omitted for clarity.

Scheme I[a]



[a] Reagents and conditions: (a) *t*-BuLi/THF/−78 °C; (b) $PhP(O)Cl_2$; (c) 1 N HCl/EtOH/room temperature/1 h; (d) $-H_2O$; (e) 115% PPA/150–155 °C/30 min; (f) 115% PPA/185–187 °C/1.5 h; (g) $HSiCl_3$/PhH/Δ/5 h; (h) 10% P_2O_5/MSA/room temperature/1 h; (i) 115% PPA/120–125 °C/10 h.

Single-Crystal X-ray Results. Figure 1 shows a plot of structure **3** with selected bond distances and angles. The

(6) The systematic nomenclature for phosphajulolidine is phosphorinano[3,2,1-*ij*]tetrahydrophosphinoline. We believe that naming them as phosphorus analogues of julolidine (Mann, F. G.; Smith B. B. *J. Chem. Soc.* **1951**, 1898) is simpler and more descriptive.

(7) Granoth, I. *J. Chem. Soc., Perkin Trans. 1* **1982**, 735.

(8) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6205.

(9) Available from FMC Corporation.

(10) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

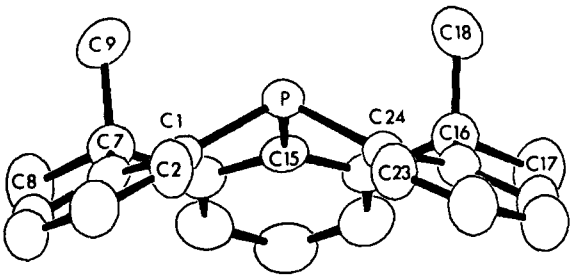


Figure 2. Plot of structure **3** showing the approximate C_s symmetry. The view is along the plane through the three carbons bonded to phosphorus.

molecule has approximately C_s symmetry, as shown in Figure 2. The geometry about the phosphorus is the pronounced *pyramidal* arrangement usually found for phosphines[11] (C–P–C angles of 99.0°, 98.3°, and 108.5°) with the phosphorus atom 0.81 Å out of the plane of the three bonded carbon atoms. This geometry is quite different from that of the N analogue **1** previously cited[1,2] and also from that found for trimesitylphosphine (C–P–C angles 108–111°),[11] where the flattening at phosphorus is due to steric crowding of the methyls attached ortho to carbons bonded to P. The steric crowding in **1** (Cl···C13, d = 3.15 Å), believed to be responsible for the flattening in this molecule, is relieved in **3** by the longer bonds to P (vs. N) and the opening of the exocyclic C–P–C angle.

The comparable nonbonded interaction distance in **3** (C2···C23) is 3.29 Å. This greater distance coupled with the pyramidality of phosphorus forces **3** to adopt C_s symmetry, whereas **1** is limited to C_2 symmetry. The ^{1}H NMR spectra for both **1** and **3** show two sharp signals with large differences in chemical shifts[12] (0.7[1] and 0.44 ppm, respectively), which can be attributed to the distinct axial and equatorial methyl groups (Figure 2). These peaks do not coalesce on heating the samples >160 °C, which for **1** was attributed to both the steric crowding of hydrogens at positions 1 and 13 during enantiomerization and the unfavorable endocyclic angle of ~120° required at the saturated carbons (positions 5 and 9) to achieve the planar transition state.[1] In **3**, a planar transition state would actually increase the distance between carbons (and hydrogens) at corresponding positions 1 and 13 (C2, C23 in Figure 1) but requires an unusually large exocyclic C–P–C angle (estimated by molecular models to be about 150°), which would lead to formidable ring strain.

The P–C bonds (1.820–1.836 Å) are normal single-bond values[11,13] as expected, since the phosphorus lone pair of electrons is not in position to interact with the adjacent π systems. The bond distances in the three phenyl rings show that the aromatic character of these rings is not disturbed by bonding to P.

The pyramidal nature of the phosphorus atom in **3** is also reflected in its UV absorption (λ_{max} 266 nm)[4] and ^{31}P NMR (δ −55.66) spectra. The latter chemical shift for ^{31}P is normally found in the region that is typical for derivatives of triarylphosphine.[14] A cyclic voltammogram of **3** exhibits an irreversible oxidation wave at E_p = 1.18 V (Pt) vs. SCE in CH_2Cl_2, whereas the nitrogen analogue **1** exhibits a reversible $E^{\circ\prime}$ = 0.95 V. The lack of a reversible cyclic voltammogram in **3** coupled with the similarity in E_p's with that of phosphajulolidine **2**[3] (E_p = 0.99 V) further supports the absence of n–π interaction.[15]

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WH 270-MHz spectrometer, with Me_4Si as the internal standard. ^{31}P NMR spectra were recorded on a Nicolet 200 spectrometer at 80.96 MHz, with 85% H_3PO_4 as an external reference. Following the IUPAC convention, all ^{31}P chemical shifts are reported with a positive sign in the downfield direction and negative upfield from the standard. Field-desorption mass spectra were obtained on an MAT-731 mass spectrometer. Cyclic voltammograms were obtained on a Heath polarography system EUW-401. Melting points were determined with a Thomas-Hoover capillary melting point apparatus. Microanalyses were done by the Analytical Sciences Division, Kodak Research Laboratories.

Isobutyl 1-Methyl-1-(2-bromophenyl)ethyl Ether (5). To a 500-mL three-necked flask fitted with a condenser and a dropping funnel (100 mL) was added 16 g (1.1 equiv) of NaH (50% dispersion) under argon. Pentane (25 mL) was added to wash the NaH and removed with a syringe. Anhydrous THF (200 mL) was added to the fine powder (NaH), and 65 g (0.3 M) of **4** in 25 mL of anhydrous THF was added dropwise to maintain steady gas evolution (H_2) and reflux. The mixture was stirred overnight, 44.5 g (1.2 equiv) of isobutylchloromethyl ether (Kodak Laboratory Chemicals) (1.2 equiv) was added slowly via a dropping funnel, and the reaction mixture was stirred for 3 h. Water was added dropwise (exothermic) until all salts were dissolved. The reaction mixture was partitioned between 300 mL of water and 300 mL of Et_2O and extracted twice with 200 mL of Et_2O. Organic fractions were combined and dried over $MgSO_4$, and the solvents were removed under vacuum. The yellow liquid was distilled at 118–130 °C (1 mm Hg), yielding 70.6 g (74.6%) of pure **5**: field-desorption mass spectrum, m/e 300 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.87 (d, 6 H, J = 6 Hz), 1.74 (s, 6 H), ca. 1.7 (m, 1 H, methine), 3.3 (d, 2 H, J = 6 Hz), 4.6 (s, 2 H), 6.87–7.66 (m, 4 H, ArH). Anal. Calcd for $C_{14}H_{21}BrO_2$: C, 55.8; H, 7.0. Found: C, 56.3; H, 6.9.

Bis[2-[1-(isobutoxymethoxy)-1-methylethyl]phenyl]-phenylphosphine Oxide (6). To a stirred solution of 50 g (0.16 M) of **5** in 250 mL of anhydrous THF under argon at −78 °C was added dropwise via syringe 175 mL (1.9 M/pentane) of *t*-BuLi (internal temperature kept <−60 °C). The yellow reaction mixture was stirred for 10 min, and 16 g (0.08 M) of phenylphosphonic dichloride in 10 mL of degassed anhydrous THF was added (internal temperature <−40 °C on addition). The acetone/CO_2 bath was removed, and the reaction was stirred for 1 h. The solvent was removed on a rotary evaporator, and the oily residue was flash chromatographed on silica gel eluted with EtOAc/hexanes (8.5:1.5 v/v) containing 1% Et_3N, to give 13 g (29%) of **6** as a clear oil that slowly solidified on keeping under vacuum: mass spectrum, m/e 566 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.75 (d, 6 H, J = 6 Hz), 1.3 (s, 6 H), 1.2 (m, 1 H, methine), 2.5 (br, 2 H), 4.5 (v br, 2 H), 6.8–7.6 (m, 13 H, ArH). Anal. Calcd for $C_{34}H_{47}O_5P$: C, 72.1; H, 8.4. Found: C, 72.3; H, 8.6.

3,3,3′,3′-Tetramethyl-1-phenyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (8). To 1 g (1.8 mmol) of **6** in 25 mL of EtOH was added 25 mL of 2 N HCl. The reaction mixture was stirred for 1 h, and the white precipitate was filtered, washed with water, and dried to give 0.58 g (86%) of **8**: mp 191–193 °C (lit.[7] mp 195 °C); field-desorption mass spectrum, m/e 361 (M^+ − Me); ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 6 H, Me), 1.53 (s, 6 H, Me), 7.1–7.6 (m, 11 H, ArH), 8.45 (2 sets of dd, 2 H, H ortho to P). Anal. Calcd for $C_{24}H_{25}O_2P$: C, 76.6; H, 6.7. Found: C, 76.3; H, 6.3.

1-[2-(1-Hydroxy-1-methylethyl)phenyl]-10,10-dimethyl-5,10-dihydrodibenzo[*b*,*e*]phosphorin 1-Oxide (9). To 100 mL of 115% PPA[9] (preheated to 150 °C in an oil bath) was added 7.5 g (19.9 mmol) of **8** under N_2, and the mixture was stirred mechanically for 30 min. The brown PPA solution was poured into 400 mL of ice and stirred for 1 h. The mixture was extracted

(11) Blount, J. F.; Maryanoff, C. A.; Mislow, K. *Tetrahedron Lett.* **1975**, 913.

(12) The higher-field doublet in **3** due to the long-range ^{31}P coupling was assigned to the axial methyl. See: Zurcher, R. F. *Helv. Chim. Acta* **1961**, *44*, 1755. Reich, H. J.; Jautelat, M.; Messe, M. T.; Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 7445.

(13) Cameron, T. S.; Howlett, K. D.; Miller, K. *Acta Crystallogr., Sect. B* **1978**, *34*, 1639.

(14) Crutchfield, M. M.; Dungen, C. H.; Letcher, L. H.; Mark, V.; VanWazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 1.

(15) Trimesitylphosphine, which was shown to have considerable n–π interaction,[11] is the only arylphosphine we studied that showed reversible CV ($E_1^{\circ\prime}$ = +0.69 V vs. SCE).[3]

with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated on a rotary evaporator, and the residue was washed with hexanes to give 6.2 g (86%) of **9**: mp 185–186 °C (white flakes from toluene/hexanes); field-desorption mass spectrum, *m/e* 377 (M^+) (8%), 375 (8%), 361 (100%); (trimethylsilylated sample) *m/e* 448 (M^+), 433 ($M^+ - CH_3$); ^1H NMR ($CDCl_3$) δ 1.8 (s, 3 H, Me), 1.88 (s, 6 H, Me), 1.96 (s, 3 H, Me), 6.79 (dd, 1 H), 6.91 (t, 1 H), 7.2–7.75 (m, 10 H, ArH), 8.0 (br s, 1 H, OH deuterium exchangeable). Anal. Calcd for $C_{24}H_{25}O_2P$: C, 76.6; H, 6.7; P, 8.2. Found: C, 76.6; H, 6.8; P, 8.3.

1,1,6,6-Tetramethyldibenzo[*b*,*e*]phosphajulolidine Oxide (10). To 50 mL of 115% PPA preheated to 185 °C (oil bath) under N_2 and with vigorous mechanical stirring was added 0.5 g (1.3 mmol) of **9**. The viscous mixture was stirred at 185–187 °C for 1.5 h and poured into 400 mL of ice. The brown aqueous solution was extracted with CH_2Cl_2 (2 × 200 mL) and 200 mL of ether. The combined organic extracts were dried ($MgSO_4$–Na_2SO_4, 1:1), and the solvent was removed on a rotary evaporator. The residue was chromatographed over silica gel and eluted first with EtOAc/hexanes (1:1) to recover the starting material, giving 50 mg of **9**. The cyclized product was collected by eluting with EtOAc to give 20 mg (4.3%) of **10**: mp 185–186 °C (needles from toluene/hexanes); field-desorption mass spectrum, *m/e* 358 (M^+); ^1H NMR ($CDCl_3$) δ 1.93 (s, 6 H, Me), 2.0 (s, 6 H, Me), 7.35–7.55 (m, 5 H, ArH), 7.63 (dd, 2 H, ArH), 8.37 (ddd, 2 H, $J_{H_6}H$ = 7 Hz, J_{PH} = 11 Hz, J_{H_m} = <2 Hz, H ortho to P); ^{31}P NMR (CD_2Cl_2) 21.01 ppm. Anal. Calcd for $C_{24}H_{23}OP$: C, 80.4; H, 6.5. Found: C, 80.5; H, 6.7.

1-[(2-Isopropenyl)phenyl]-10,10-dimethyl-5,10-dihydrodibenzo[*b*,*e*]phosphorin (11). To 10 mL of a solution of 10% P_2O_5 in methanesulfonic acid was added 50 mg (0.14 mmol) of **12** at room temperature. The mixture was stirred for 1 h and poured into 100 mL of ice water. The white precipitate was collected, washed with water, and dried to give 43 mg (89%) of **11**: mp 154.5–155.5 °C (MeOH); mass spectrum, *m/e* 342 (M^+); ^1H NMR ($CDCl_3$) δ 1.42 (d, 3 H, J_{PH} = 2.75 Hz, axial Me), 2.02 (s, 3 H, equatorial Me), 2.31 (s, 3 H, vinyl Me), 5.1 (br s, 1 H, vinylic H), 5.32 (br s, 1 H, vinylic H), 6.77 (dd, 1 H , ArH), 6.96 (dt, 2 H, ArH), 7.02 (m, 3 H, ArH), 7.21–7.4 (m, 4 H, ArH), 7.6 (dd, 2 H, ArH). Anal. Calcd for $C_{24}H_{23}P$: C, 84.2; H, 6.8. Found: C, 83.8; H, 6.7.

1-[2-(1-Hydroxy-1-methylethyl)phenyl]-10,10-dimethyl-5,10-dihydrodibenzo[*b*,*e*]phosphorin (12). In one portion, 2 mL of $HSiCl_3$ was added to a solution of 180 mg (0.4 mmol) of **9** in 7 mL of benzene under N_2. The reaction mixture, from which a white solid immediately precipiated, was refluxed for 5 h and cooled to 0 °C, and 10 mL of 25% NaOH was added dropwise in 10 min. The aqueous phase was extracted with ether, the organic phase was washed with brine until neutal and dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The solid residue (180 mg) was recrystallized from 10 mL of toluene/heptane (1:2) to give 120 mg (83%) of **12**: mp 178–180 °C; field-desorption mass spectrum, *m/e* 361 ($M^+ + 1$), 360 (M^+); ^1H NMR ($CDCl_3$) δ 1.46 (d, 3 H, J_{PH} = 2.75 Hz, axial Me), 1.93 (s, 6 H, Me), 2.07 (s, 3 H, equatorial Me), 4.4 (br s, 1 H, OH, deuterium exchangeable), 6.8–7.8 (m, 12 H, ArH). Anal. Calcd for $C_{24}H_{25}OP$: C, 80.0; H, 7.0. Found: C, 79.7; H, 6.9.

1,1,6,6-Tetramethyldibenzo[*b*,*e*]phosphajulolidine (3) from 12. To 10 mL of 115% PPA preheated to 125 °C in an oil bath under N_2 was added 260 mg (0.72 mmol) of **12**. The solid slowly dissolved on stirring to form a brown, viscous solution, which was kept at 125 °C for 10 h and poured onto ice. The aqueous solution was extracted with ether, and the ether extracts were dried ($MgSO_4$). The solvent was removed on a rotary evaporator, and the residue (30 mg) was recrystallized from 10 mL of MeOH to give 10 mg (4%) of pure **3**: mp 178–179 °C; field-desorption mass spectrum, *m/e* 342 (M^+); ^1H NMR ($CDCl_3$) (assignments based on the numbering shown in Figure 1) δ 1.61 (d, 6 H, J_{PH} = 2.75 Hz, axial Me),[13] 2.05 (s, 6 H, equatorial Me), 7.29–7.39 (m, 5 H, ArH), 7.49 (dd, 2 H, $J_{H_{11}H_{12}}$ = 8 Hz, $J_{PH_{11}}$ = 2.3 Hz, H_{11} and H_{13}), 7.62 (ddd, $J_{H_4H_5}$ = 6.5 Hz, $J_{H_3H_5}$ = J_{PH_5} = 2 Hz, 2 H, H_5 and H_{20}), 8.18 (ddd, 2 H, $J_{H_2H_3}$ = 7 Hz, J_{PH_2} = 7 Hz, $J_{H_2H_4}$ = 2.3 Hz, H_2 and H_{23}); ^{31}P NMR (CD_2Cl_2) −55.66 ppm; λ_{max} (CH_2Cl_2) 266 (ε 13 200) nm. Anal. Calcd for $C_{24}H_{23}P$: C, 84.2; H, 6.8. Found: C, 84.1; H, 6.9.

The aqueous phase was neutralized with 25% NaOH and extracted with ether. The ether extracts were dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The residue was vacuum sublimed (in a Bantam-ware microsublimator in an oil bath at ~200 °C/1 mm) to give 100 mg more of **3**, which was contaminated with a trace of the corresponding phosphine oxide **10** (assay by TLC); total yield ~45%.

1,1,6,6-Tetramethyldibenzo[*b*,*e*]phosphajulolidine (3) from 10. To a solution of 77 mg (0.21 mmol) of **10** in 3 mL of benzene under N_2 was added 1 mL of $HSiCl_3$. The reaction mixture was refluxed for 4 h and cooled to 0 °C; 4 mL of 1 N NaOH was added dropwise, followed by 10 mL of ether. The ether phase was separated, and the aqueous phase was extracted with 20 mL of ether. The combined ether extracts were washed with brine (2 × 10 mL) and dried ($MgSO_4$), and the solvent was removed on a rotary evaporator. The residue was washed with hexanes to give 67 mg (93%) of **3**, which was characterized by comparison with an authentic sample.

X-ray Analysis. Single crystals of **3** were obtained by slow recrystallization from methanol. A crystal 0.15 × 0.36 × 0.36 mm was cut from a large, translucent, white flaky crystal and glued to a thin glass fiber for use in data collection. Procedures used for data collection and structure refinement were as described.[16] The setting angles for 25 reflections with 13° < 2θ < 24° were refined to give unit cell data: a = 10.778 (3) Å, b = 7.693 (7) Å, c = 11.422 (2) Å; β = 105.42 (2)°, V = 913 (1) Å^3, d_c = 1.246 g cm^{-3}, and Z = 2.

Systematic absence for 0*k*0, *k* odd, gave a space group ambiguity between $P2_1$ and $P2_1/m$; however, the latter was eliminated by packing considerations. Intensities were collected out to 2Θ = 56° at a scan rate of 1.2–20° 2Θ min^{-1}. The intensities of three standard reflections, remeasured periodically, were used to correct the data for a 6% change in intensity over the data collection period. Absorption correction was not necessary (μ = 1.5 cm^{-1} for Mo Kα).

The structure was solved by direct methods by using MULTAN 11/82.[17] The phase set having the second best ABSFOM and COMFOM but lowest residual gave an E map (220 E's >1.46) that contained a 13-atom molecular fragment. Subsequent difference electron-density maps gave all remaining atoms, including hydrogens.

Refinement by full-matrix least-squares converged to R = 0.042, R_w = 0.049, K = 2.207 (6), and EOUW = 1.028. Of the 2357 unique reflections, 1803 had $I > \sigma(I)$ and were included in the calculations. Residual density in the final difference map was insignificant (−0.19 to +0.25 e/Å^3).

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Registry No. **3**, 96897-82-4; **4**, 7073-69-0; **5**, 96897-83-5; **6**, 96897-84-6; **8**, 71433-47-1; **9**, 96928-55-1; **10**, 96897-85-7; **11**, 96913-33-6; **12**, 96897-86-8; isobutyl chloromethyl ether, 34180-11-5; phenylphosphonic dichloride, 824-72-6.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, and bond distances and angles (4 pages). Ordering information is given on any current masthead page.

(16) Chen, C. H.; Kelts, L. W.; Luss, H. R.; Fox, J. L. *J. Org. Chem.* **1984**, *49*, 5143.

(17) Programs used for this study were from the Structure Determination Package (SDP-PLUS), Enraf-Nonius Corp., Delft, Holland, V1.0 (1982).