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Stable Monocyclic Monoalkoxyhalophosphoranes: Possible Examples of Structures on the Borderline between Haloalkoxyphosphoranes and Alkoxyphosphonium Halides

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Abstract: The Grignard reagent made from 1-methyl-1-(2-bromophenyl)ethanol and phenylphosphonous dichloride give 1-phenyl-3,3-dimethyl-3*H*-2,1-benzoxaphosphole (**2**). Stable compounds **3** and **4**, thought to be borderline cases between halophosphoranes and phosphonium halide salts, are obtained from **2** and methyl iodide or benzyl bromide, respectively. Spectroscopic data are presented in support of the assigned structures. Stable, covalent monocyclic alkoxyphosphoranes **5** and **6** are obtained from **3** and carbanions. These phosphoranes are found to be moderately strong bases.

Seeking stable models for reactive intermediates,[2] we have recently prepared a stable *P*-hydroxyphosphorane,[3] a sodium phosphoranoxide,[4] a bromoalkoxyphosphorane,[5a] and a lithium phosphoranide (a tetracoordinated phosphorane).[4] These related species[5b] are of both practical and theoretical interest in the rapidly expanding area of organophosphorus chemistry. Studies of hypervalent organosulfur species[6] and of other hypervalent compounds[7] have yielded closely parallel mechanistic and structure–stability–reactivity correlations for species with like geometries.

Little is known of the chemistry of bromoalkoxyphosphoranes except that they are sometimes present in solutions during the Arbuzov rearrangement and related reactions.[5,8] The same is true for the monoalkoxyphosphoranes bearing four carbon ligands.[9] Most alkoxyphosphoranes are relatively unstable species which are easily hydrolyzed.[9] We now report simple and versatile syntheses of stable isolable examples of both classes of compounds. Evidence is presented that compounds **3** and **4** may have structures intermediate between halophosphoranes and phosphonium halides, with covalent phosphorus–halogen bonds which have a very large degree of ionic character.

Experimental Section

Infrared spectra were recorded for $CHCl_3$ solutions. NMR chemical shifts are reported in parts per million downfield from Me_4Si for ^{1}H and ^{13}C and in parts per million downfield from 85% H_3PO_4 for ^{31}P. Unless otherwise stated, NMR spectra were obtained for $CDCl_3$ solutions. Electron-impact mass spectra were obtained at 70 eV and 150–200 °C source temperature by using the direct insertion probe. Solution of products in organic solvents were dried ($MgSO_4$) and evaporated under reduced pressure. Elemental analyses (C, H, Br, I, P) are within 0.4% of calculated values, unless otherwise noted.

1-Phenyl-3,3-dimethyl-3*H*-2,1-benzoxaphosphole (2). 1-Methyl-1-(2-bromophenyl)ethanol[10] (10.8 g, 50 mmol) in dry tetrahydrofuran (THF) (70 mL) was treated with CH_3MgBr (16.5 mL of 3.1 M in ether, 51.2 mmol) with stirring. Magnesium shavings (1.22 g, 0.05 mol) were then added, and the mixture was refluxed until most of the magnesium was dissolved (1.5–3 h). The resulting dark brown solution was cooled in a nitrogen atmosphere, and a solution of phenylphosphonous dichloride (7.9 g, 44 mmol) in dry THF (10 mL) was added dropwise. This mixture was stirred for 18 h at room temperature and then added to cold aqueous NH_4Cl solution. The THF layer and one ether (70 mL) extract were either dried and used without further purification or fractionally distilled: bp 145–150 °C (1 mmHg) (7.1 g, 66%); ^{1}H NMR δ 1.41 (3 H, s, Me), 1.60 (3 H, s, Me), 7.00–7.85 (9 H, m, H-Ar); ^{31}P NMR δ 113.0. This compound was always contaminated with variable amounts of its *P*-oxide (1-phenyl-3,3-dimethyl-3*H*-2,1-benzoxaphosphole 1-oxide): ^{1}H NMR δ 1.70 (3 H, s, Me), 1.78 (3 H, s, Me), 7.05–7.85 (9 H, m, H-Ar); ^{31}P NMR δ 43.5.

1-Phenyl-1,3,3-trimethyl-3*H*-2,1-benzoxaphospholium Iodide (3). The crude product **2**, from the above reaction (ca. 7.1 g, 29 mmol), in dry ether (100 mL) was treated with CH_3I (12 g, 85 mmol) in the dark for 24 h. The crystalline precipitate, mp 188–189 °C dec (ethanol), was stored in a dark container (7.5 g, 67%): ^{1}H NMR δ 1.92 (3 H, s, Me), 1.95 (3 H, s, Me), 3.14 (3 H, d, $^{2}J_{\mathrm{HP}}$ = 14 Hz, MeP), 7.55–8.27 (8 H, m, H-Ar), 8.65–8.85 (1 H, m, H ortho to P); ^{31}P NMR δ 87.1; MS (no M^+), *m/e* (relative intensities) 256 (M − HI, 100%), 255 (M − HI − H, 63), 241 (M − HI − H − Me, 57), 179 (71), 165 (72), 91 (21), 77 (20).

Methylphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphine Oxide (7). Methiodide **3** (0.1 g, 0.26 mmol), in $CHCl_3$ (5 mL) was successively washed with aqueous $NaHCO_3$, sodium bisulfite solutions, and water. The crude oil obtained from the organic layer (0.6 g, 83%) could not be further purified: ^{1}H NMR δ 1.63 (3 H, s, Me), 1.69 (3 H, s, Me), 2.12 (3 H, d, $^{2}J_{\mathrm{HP}}$ = 13 Hz, MeP), 7.11–7.80 (9 H, m, H-Ar); field desorption MS, *m/e* (relative intensities) 275 (M + H, 6%), 257 (M − OH, 100).

1-Benzyl-1-phenyl-3,3-dimethyl-3*H*-2,1-benzoxaphospholium Bromide (4). Crude **2** (0.4 g, 1.65 mmol) in dry ether (5 mL) was treated with benzyl bromide (0.4 g, 2.34 mmol) for 1 day. The resulting precipitate was recrystallized from 1:1 ethanol ether: mp 216–218 °C (0.5 g, 71%); ^{1}H NMR δ 1.20 (3 H, s, Me), 1.78 (3 H, s, Me), 4.48 (1 H, dd, $^{2}J_{\mathrm{HH}}$ = 15 Hz, $^{2}J_{\mathrm{HP}}$ = 18 Hz, CHPh), 6.20 (1 H, dd, $^{2}J_{\mathrm{HH}}$ = 15, $^{2}J_{\mathrm{HP}}$ = 9 Hz, CHPh), 7.15–7.76 (11 H, m, H-Ar), 8.29–8.55 (2 H, m, phenyl H ortho to P), 9.21–9.48 (1 H, m, H ortho to P); ^{31}P NMR δ 86.6.

Benzylphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphine Oxide (8). A $CDCl_3$ (0.5 mL) solution of **4** (0.1 g, 0.24 mmol) was shaken with water (0.1 g, 5.6 mmol) ^{1}H NMR showed ca. 1:1 mixture of **4** and **8**, and the aqueous layer was acidic to litmus (HBr). Addition of excess sodium bicarbonate completed the hydrolysis. The organic layer and a $CHCl_3$ (2 mL) extract gave the phosphine oxide **8**: mp 121 °C (pentane–ether) (50 mg, 59%); ^{1}H NMR δ 1.50 (3 H, s, Me), 1.56 (3 H, s, Me), 1.90 (1 H, s, HO), 3.72 (1 H, dd, $^{2}J_{\mathrm{HH}}$ = 15 Hz, $^{2}J_{\mathrm{HP}}$ = 19.5 Hz, CHPh), 3.87 (1 H, dd, $^{2}J_{\mathrm{HH}}$ = 15 Hz, $^{2}J_{\mathrm{HP}}$ = 21 Hz, CHPh), 7.05–7.78 (14 H, m, H-Ar); ^{31}P NMR δ 40.8; field desorption MS, *m/e* (relative intensities)

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350 (M$^+$, 41%), 335 (M − Me, 100), 259 (M − PhCH$_2$, 98).

1-Benzyl-1-phenyl-3,3-dimethyl-3*H*-2,1-benzoxaphospholium Trifluoromethanesulfonate (9). A solution of phosphine oxide **8** (20 mg, 0.057 mmol) and trifluoromethanesulfonic acid (25 mg, 0.17 mmol) in CDCl$_3$ (0.5 mL) was added to dry ether (40 mL), which was then cooled to −20 °C. Crystalline **9** (22 mg, 81%) was collected by filtration: mp 148 °C; ^{1}H NMR δ 1.18 (3 H, s, Me), 1.74 (3 H, s, Me), 4.24 (1 H, dd, $^2J_{HH}$ = 15 Hz, $^2J_{HP}$ = 16.5 Hz, CHPh), 4.98 (1 H, dd, $^2J_{HH}$ = 15 Hz, $^2J_{HP}$ = 8 Hz, CHPh), 7.13–7.78 (11 H, m, H-Ar), 7.90–8.18 (2 H, m, H-Ar), 8.50–8.70 (1 H, m, H ortho to P); ^{31}P NMR δ 85.9. The ^{1}H NMR of **9** was not changed by twofold dilution of the CDCl$_3$ solution.

1-Phenyl-1,1,3,3-tetramethyl-3*H*-2,1-benzoxaphosphole (5). (a) Methiodide **3** (0.56 g, 1.46 mmol) was suspended in dry THF (10 mL), and methylmagnesium bromide (5 mL of 3.1 M ether solution) was added. The exothermic reaction was completed by brief swirling of the flask. An hour later, aqueous ammonium chloride (5 mL of 4 M solution, 15.5 mmol) was added. The organic layer was separated as quickly as possible and the solvent removed under reduced pressure. The crude product mixture was extracted with ether (10 mL), giving phosphorane **5** (0.2 g, 50%): mp 52 °C (pentane); ^{1}H NMR δ 1.26 (6 H, s, Me), 1.74 (6 H, d, $^2J_{HP}$ = 10 Hz, MeP), 7.10–7.70 (9 H, m, H-Ar); ^{31}P NMR (THF) δ −78.7; ^{13}C NMR δ 27.16 (d, $^1J_{CP}$ = 73 Hz, MeP), 31.30 (s, Me), 70.08 (s, CMe$_2$), 122.10–154.56 (m, C-Ar); MS, *m/e* (relative intensities) 272 (M$^+$, 0.1%), 271 (M − H, 0.3), 257 (M − Me, 100), 195 (M − Ph, 12), 121 (10); field desorption MS *m/e* (relative intensities) 273 (M + H, 90%), 257 (M − Me, 100). (b) A suspension of methiodide **13** (0.5 g, 1.25 mmol) and sodium hydride (80 mg, 3.3 mmol) in dry ether (50 mL) was magnetically stirred at room temperature for 6 h, allowing evolved hydrogen to escape through a calcium chloride tube. Filtration and evaporation of the ether gave **5** (0.34 g, 100%), melting point and spectra the same as those above.

Reaction of Phosphorane 5 with Aqueous Ammonium Iodide. Phosphorane **5** (50 mg, 0.19 mmol) was dissolved in CDCl$_3$ (0.4 mL), and the ^{1}H NMR was recorded. Aqueous NH$_4$I (0.3 mL of 3 M solution, 0.9 mmol) was added. The tube was swirled well, and ammonia was detected by smell and pH measurement. The ^{1}H NMR was identical with that of methiodide **13**. (See below.)

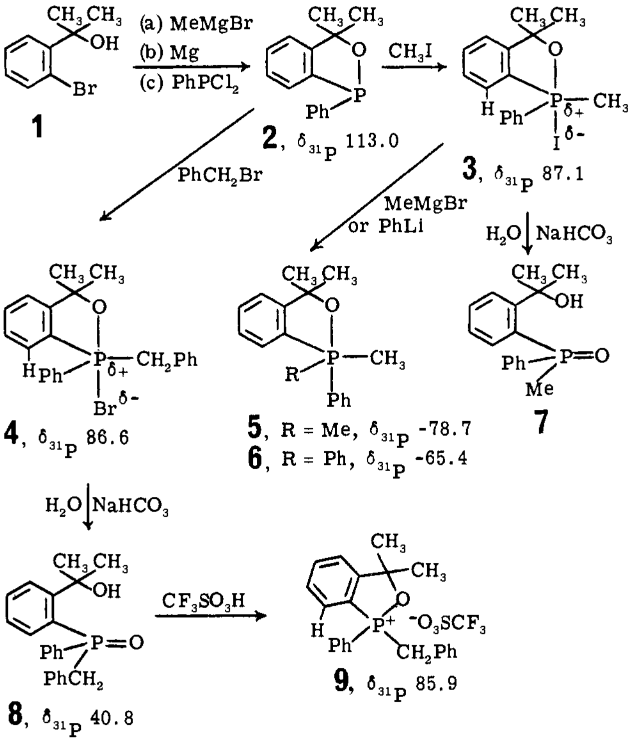
Dimethylphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphonium Iodide (13). Methiodide **3** (5.7 g, 14.8 mmol) was suspended in dry THF (40 mL) and methylmagnesium iodide (prepared from methyl iodide (7.3 g, 51.4 mmol) and magnesium shavings (1.2 g, 0.05 mol, in ether (30 mL)) was added dropwise with cooling and stirring. The resulting mixture was stirred at room temperature for 2 h, and then aqueous NH$_4$I (40 mL) of 3 M solution was added and the stirring continued for 20 min. The organic layer and a CHCl$_3$ (40 mL) extract gave light sensitive methiodide **13** (4.5 g, 76%) (ether trituration): mp 186 °C, ^{1}H NMR δ 1.52 (6 H, s, Me), 2.59 (6 H, d, $^2J_{HP}$ = 12.5 Hz, MeP), 4.75 (1 H, br s, HO), 7.28–7.83 (9 H, m, H-Ar); ^{31}P NMR δ 19.3; MS, *m/e* (relative intensities) 257 (M − HI − Me, 100%), 213 (10), 195 (16), 128 (16); field desorption MS, *m/e* (relative intensities) 257 (M − HI − Me, 100%), 213 (10), 195 (16), 128 (16); field desorption MS, *m/e* (relative intensities) 400 (M$^+$, 1%), 273 (M − I, 100).

Methyldiphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphonium Iodide (14). A suspension of methiodide **3** (1.8 g, 4.7 mmol) in dry THF (15 mL) and phenyllithium (15 mL of 3.18 M 47.7 mmol) was stirred at ambient temperature for 3 h and then quenched with ice water. The organic layer and a CHCl$_3$ (20 mL) extract were vigorously stirred with aqueous NH$_4$I (20 mL of 3 M solution, 60 mmol) for 20 min. The precipitated light sensitive product **14** (0.7 g, 32%) was filtered off and washed with ether: mp 201 °C, ^{1}H NMR δ 1.66 (6 H, s, Me), 3.14 (3 H, d, $^2J_{HP}$ = 13 Hz, MeP), 4.10 (1 H, br s, HO), 7.10–7.80 (14 H, m, H-Ar); ^{31}P NMR δ 26.4.

1,1-Diphenyl-1,3,3-trimethyl-3*H*-2,1-benzoxaphosphole (6). A suspension of methiodide **14** (0.4 g, 0.87 mmol) in dry ether (50 mL) with sodium hydride (0.1 g, 4.17 mmol) was stirred for 18 h at ambient temperature, allowing molecular hydrogen to escape through a calcium chloride tube. Filtration and removal of the solvent gave phosphorane **6** (0.23 g, 80%): mp 100 °C (pentane); ^{1}H NMR δ 1.40 (6 H, s, Me), 2.40 (3 H, d, $^2J_{HP}$ = 12 Hz, MeP), 6.49 (1 H, dd, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 8 Hz, H ortho to P), 7.06–7.45 (13 H, m, H-Ar); ^{31}P NMR (THF) δ −65.4; ^{13}C NMR δ 26.41 (d, $^1J_{CP}$ = 103 Hz, MeP), 31.23 (s, *Me*C), 73.50 (d, $^2J_{CP}$ = 3 Hz, CMe$_2$), 122.10–150.58 (m, C-Ar); MS *m/e* (relative intensities) 334 (M$^+$, 0.1%), 333 (M − H, 0.4), 319 (M − Me, 100), 275 (12), 257 (M − Ph, 95), 183 (14), 152 (14); field desorption MS *m/e* (relative intensities) 334 (M$^+$, 28%), 319 (M − Me, 72), 257 (M − Ph, 100).

Dimethylphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphonium Fluoride (15). Phosphorane **5** (40 mg, 0.15 mmol) was dissolved in CDCl$_3$ (0.5 mL), in a polyethylene vial, and anhydrous HF was carefully passed through the solution for 10 s. The resulting solution was dried over anhydrous K$_2$CO$_3$. The ^{1}H NMR spectrum showed a 3:2 mixture of salt **15** and olefin **20**: ^{1}H NMR δ 1.44 (6 H, s, Me), 2.35 (6 H, d, $^2J_{HP}$ = 12 Hz, MeP), 7.25–7.95 (9 H, m, H-Ar) and 1.68 (3 H, m, Me), 2.38 (6 H, d, $^2J_{HP}$ = 13.5 Hz, MeP), 4.60 (1 H, m, CH), 5.18 (1 H, m, CH), 7.25–7.95 (9 H, m, H-Ar); ^{31}P NMR δ 20.5 and 17.6, respectively. This mixture was not further purified.

Scheme I



Methyldiphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphonium Fluoride (16). Phosphorane **6** (26 mg, 0.078 mmol) was dissolved in dry ether (2 mL), in a polyethylene vial, and anhydrous HF was passed through the solution for 10 s. The resulting solution was evaporated, and the residue was extracted with CDCl$_3$ (0.5 mL); ^{1}H NMR δ 1.48 (6 H, s, Me), 2.98 (3 H, d, $^2J_{PH}$ = 12 Hz, MeP), 6.85–7.65 (14 H, m, H-Ar); ^{31}P NMR δ 25.8.

Dimethylphenyl-(2-(1-methyl-1-hydroxyethyl)phenyl)phosphonium Trifluoromethanesulfonate (17). Trifluoromethanesulfonic acid (30 mg, 0.2 mmol) was added to phosphorane **5** (40 mg, 0.15 mmol) in dry ether (10 mL), and the precipitated crystalline product was collected (50 mg, 81%): mp 126 °C; ^{1}H NMR δ 1.38 (6 H, s, Me), 2.44 (6 H, d, $^2J_{HP}$ = 12.5 Hz, MeP), 7.30–7.90 (9 H, m, H-Ar); ^{31}P NMR δ 21.2.

Results and Discussion

Synthesis. The preparation of the monocyclic phosphorus compounds **2–6** and **9** is illustrated in Scheme I. The key intermediates in this synthesis are the Grignard reagent made from **1** and the cyclic phosphinate **2**. This Grignard reagent has been prepared earlier in this laboratory, using Rieke magnesium[11] or magnesium powder,[3] but it is now confirmed that ordinary magnesium turnings are quite satisfactory in this reaction.

Phosphinite **2** is easily oxidized by air and therefore is accompanied by the corresponding cyclic phosphinate. For the same reason, **2** is also difficult to purify. The products made from **2** in this work are, however, easily purified. (See Experimental Section.) The iodide **3** and bromide **4** are produced by an atypical "half-way" Arbuzov reaction. They are stable compounds which do not decompose at room temperature to give the normal Arbuzov reaction products (compounds with a P=O bond plus alkyl halides). All the iodides reported here are light sensitive and are best kept in dark containers.

Structure and Reactivity. We have recently reported[5a] the preparation of a thermally stable bromoalkoxyphosphorane (**10**). A relatively simple structure change, the introduction of a bulky

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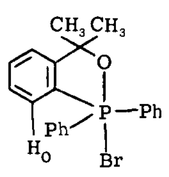
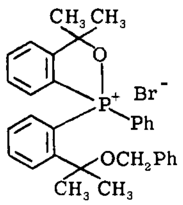
[11] J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, 99, 152 (1977).



10, $\delta_{^{31}P}$ -17.8
δ_{H_0} 8.33-8.53



11, $\delta_{^{31}P}$ 70.9
δ_{H_0} 6.75-8.10

ortho substituent in one of the phenyl rings, provides **11**, which we represent as an ionic phosphonium bromide salt. Evidence for these two structures came from both ^{31}P and ^{1}H NMR chemical shift measurements. Pentacoordinate phosphorus derivatives (phosphoranes) usually show ^{31}P chemical shifts at higher field than phosphoric acid, while phosphonium salts are found at lower field than phosphoric acid. Compounds **10** and **11** give ^{31}P chemical shifts consistent with the pictured structural assignments,[5a] −17.8 and +70.9 ppm, respectively. They also show ^{1}H chemical shifts for the aromatic ring proton ortho to phosphorus, at 8.33–8.53 ppm for **10** and 6.75–8.10 ppm for **11**, which provide evidence for these same structures. We have studied a wide variety of trigonal-bipyramidal hypervalent species, including compounds of sulfur,[12] iodine,[7a] and silicon,[7b] which share the feature of a five-membered ring linking an apical oxygen to an equatorial aromatic ring carbon. In all of these species the proton of this aromatic ring which is ortho to the hypervalent central atom is found at 1–3-ppm lower field than the other aromatic ring protons, generally in the range 8.1–9.7 ppm.[12] It is clear from the drawing of Figure 1 that the preferred geometry of these TBP systems, in which the three-center, four-electron bond joining the apical ligands to the central atom E is nearly linear, places the ortho proton in question, H_0, in close proximity to the polar E–X apical bond, where X is an electronegative apical substituent.

In all such cases which have been studied the conversion of the hypervalent species to the corresponding "onium" species by E–X bond heterolysis, despite the fact that such an ionization places a full positive charge on the central atom E, results in an *upfield* shift of adjacent protons such as the H_0 proton of Figure 1. This was first reported for hypervalent sulfur species by Johnson and Rigau[13] for an arylalkylalkoxyhalosulfurane. This observation can be understood if one considers the principal determinants of chemical shift for the ortho proton H_0 in **10**. The proximity of the C–H_0 bond to the E–X electric dipole results in a polarization of the C–H_0 bond electrons in such a way as to bring about marked magnetic deshielding of proton H_0.[14] The deshielding of such a proton can be treated quantitatively by eq 1,[15] where A is an

$$\Delta\delta_{el} = A\mu(3\cos\phi_l\cos\phi_R - \cos\phi_\mu)R^{-3} \qquad (1)$$

empirically determined factor which is given[14] values in the range (2–4.2) × 10^{-12} (esu), ϕ_l is the angle between the E–X bond and a line extending from the proton to the center of the E–X bond, ϕ_R is the angle between this line and the C–H bond, and ϕ_μ is the angle between the direction of μ_0 and the C–H bond.

It is clear from eq 1 that the downfield shift for such an ortho proton should increase as the E–X bond dipole (Figure 1) increases. This is expected[14] to be the most important factor in determining chemical shifts in systems, such as those being considered here, in which the E–X bond is very dipolar and the proton being observed is very near the E–X bond.

The compound assigned structure **4** differs from bromophosphorane **10** in that an equatorial phenyl ligand of **10** has been replaced by a benzyl substituent. While the ^{31}P NMR of **10** is in the range characteristic of phosphoranes, that of **4** is consistent with the molecule being an ionic phosphonium bromide. This is perhaps not surprising if one considers that the substitution of the sp^3 benzylic carbon of **4** for the more electronegative sp^2 phenyl carbon of **10** would be expected to promote P–Br ionization by σ-electron donation. In an apparent contradiction to this observation, the chemical shift of the ortho proton in **4**, at δ 9.21–9.48 (identified by its coupling to phosphorus, $^3J_{PH} \approx 10$ Hz) is in the range expected[12] for a covalent phosphorane rather than for the ionic phosphonium bromide structure postulated from a consideration of the ^{31}P chemical shift. The chemical shift of this ortho proton moves upfield by about 0.7 ppm on conversion of the bromide to the (probably ionic) triflate of **9**.

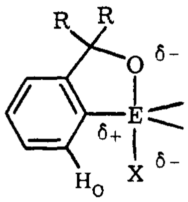


Figure 1. The geometrical relationship between an apical E–X bond and the adjacent ortho proton, H_0.

The importance of this dipolar effect on chemical shift is also reflected in the large difference in chemical shifts for the diastereotopic benzylic protons of **4** (δ 4.48 and 6.20) and the low-field shift of one of them. The lower field proton shifts from δ 6.20 *upfield* to δ 4.98 upon going from **4** to the ionic triflate **9**.

These observations are consistent with a structure for **4** which is borderline between the phosphorane and the phosphonium bromide, a structure with enough covalent character to maintain the position of the bromine atom expected for the structure drawn for **4** and a structure with the apical P–Br bond approximately colinear with the P–O bond. A change in structure which increases the ionic character of the P–Br bond (e.g., the change from **10** to **4**) will be expected to move the ^{31}P NMR absorption downfield toward the region characteristic of phosphonium ions. At the same time, since the electric dipole of the P–Br bond is increasing, its effect on the nearby ortho C–H bond will shift the ^{1}H peak to still lower field, exaggerating the evidence for the pentacoordination of phosphorus. When the directional character of the P–Br bond becomes weak enough, upon the introduction of suitable substituents, that the P–Br dipole is no longer oriented as in **4**, it is fair to say that heterolysis has occurred and the system exists as a phosphonium bromide ion pair as in **11**. Triflate **9** is very likely ionic.

The calculation of the effect of the P–Br dipole of **4** on the ortho proton using eq 1 can be carried out by using reasonable estimates[16] for the geometry and for the P–Br dipole of **4**.

The value calculated for the downfield shift is 1.5–3.1 ppm depending on the choice of reported best values for A in the range (2.0–4.2) × 10^{-12}. It is easy to see that as the bond becomes more ionic the increasingly downfield chemical shift of the ortho proton becomes a more reliable indicator of remaining covalent character in the P–Br bond than is the ^{31}P chemical shift, which is approaching that appropriate for the phosphonium salt. This is true even though the chemical shift difference between the covalent phosphorane and the ionic phosphonium halide is greater in ^{31}P NMR than in ^{1}H NMR (for the ortho proton). We therefore feel justified in suggesting that **4** has the borderline structure with the P–Br bond being largely ionic but with enough covalent character to preserve a geometry approximately that of a phosphorane.

The evidence for the covalent nature of iodophosphorane **3** is ambiguous since the downfield shift of the ortho proton (δ 8.65–8.85) is much less pronounced than for **4**.

Both this new type of structure and the relative sensitivity of ^{1}H and ^{31}P NMR chemical shifts to structural changes in orga-

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(15) Equations 10 and 11, p 217 of ref 14.

(16) We used values of 2.40 Å for the P–Br bond distance, 1.83 Å for C–P, 1.41 Å for aromatic C–C, and 1.00 Å for C–H and ϕ_R = 94.8°, ϕ_l = 64.8°, ϕ_μ = 30°, and μ = 9 D. The value of μ assumes the bond approaches 100% ionic character (which would predict 11.1 D for the P–Br dipole).

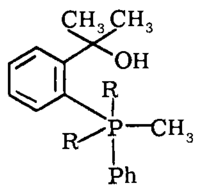
nophosphorus compounds have a recent precedent.[17,18] An X-ray diffraction study[17] on benzyl-(2-methoxyphenyl)diphenylphosphonium bromide has revealed that the P–O distance, in the crystal, is substantially shorter than the sum of the van der Vaals radii of phosphorus and oxygen. The oxygen is leaning toward the phosphorus. This weak bonding interaction is analogous to the P–Br bonding suggested in this work and very similar to the one discussed in our[5a] related paper. With the assumption that the weak P–O bonding obvious in the X-ray structure persists in solution, it has been shown[18] that such weak bonding is not reflected in the ^{31}P NMR chemical shift but is evidenced in the ^{1}H NMR chemical shift of the benzylic protons. These observations are quite analogous to our findings.

The chemical shift difference between the two benzylic geminal protons of **4** (1.72 ppm) is comparable to the differences between certain benzylic protons which have been reported as being extraordinarily large (1.75 ppm[19a] and 1.99 ppm[19b]). The nonequivalent benzylic protons in **4**, **8**, and **9** are also nonisogamous. In each compound, the two benzylic protons show different coupling constants $^2J_{\mathrm{HP}}$. (See Experimental Section.)

The analogy between **10** and **3** or **4** is extended to their hydrolysis.[5a] When a $CDCl_3$ solution of **4** is shaken with a drop of water, an equilibrium mixture containing comparable amounts of **4**, **8**, and HBr is established. Bromoalkoxyphosphorane **10** behaves similarly. In both cases the equilibrium is shifted toward hydrolysis products by quenching the HBr with bicarbonate. It is clear that the hydrolysis is a reversible process.

The high thermal stability of **3** and **4** is attributed to the five-membered ring effect,[20] a known source of stabilization of hypervalent derivatives of phosphorus[2] and sulfur[20] in which the heteroatom is included in a five-membered ring. Further stabilization is possibly due to the Thorpe-Ingold effect[21] provided by the *gem*-dimethyl group, a conformational effect favoring cyclic products. Steric crowding around the sp^3-hybridized ring carbon retards nucleophilic attack by halide at this site, thus suppressing completion of a normal Arbuzov reaction.

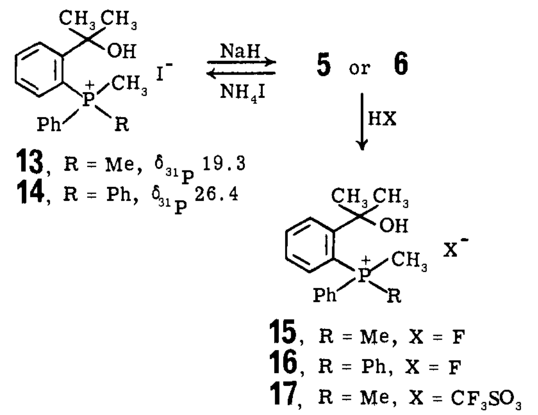
The reactions of **3** with methylmagnesium bromide or phenyllithium provides a route to monoalkoxy phosphoranes **5** and **6** bearing four carbon ligands. While yields are only modest, isolation by way of the hydroiodides **13** and **14** is very easy. Further reaction of **5** or **6** to give species of type **12** is not seen even when excess Grignard or organolithium reagent is employed. This may be yet another manifestation of the well-established above-mentioned five-membered ring effect.[20]



12

Phosphoranes **5** and **6** are fairly strong bases, stronger than ammonia. They react with acids[22] (Scheme II), to give phosphonium salts **15**–**17**, but not with water.

Scheme II



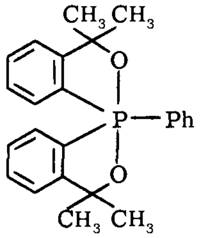
13, R = Me, $\delta_{^{31}\mathrm{P}}$ 19.3
14, R = Ph, $\delta_{^{31}\mathrm{P}}$ 26.4

15, R = Me, X = F
16, R = Ph, X = F
17, R = Me, X = CF_3SO_3

Many oxyphosphoranes are both water and heat sensitive,[9,22] even when the phosphorus is included in a five-membered ring. Phosphorane **5** was heated in air for 2 h at 120 °C without any noticeable decomposition. Shaking chloroform or ether solutions of **5** or **6** with aqueous ammonium halides produces ammonia and phosphonium salts such as **13** or **14**. The nucleophilicity of **5** or **6**, however, is small. Boiling a $CDCl_3$ solution of **6** with excess benzyl bromide for 1 day did not lead to any detectible change in these reagents by ^{1}H NMR. Nucleophilic attack of **5** or **6** on methyl fluorosulfonate in ether was observed at room temperature within 1 h.

Conversion of **13** and **14** to phosphoranes **5** and **6**, respectively, is quantitatively achieved by stirring an ether or THF suspension of the salts with excess sodium hydride until no more hydrogen is evolved. Ylides which could have been formed by deprotonation of a methyl directly bonded to phosphorus are not observed under these experimental conditions. Nor have we observed olefin formation from deprotonation of the *gem*-dimethyl group.

The basicity of **5** or **6** is considerably larger than that of symmetrical dioxyphosphoranes. Phosphorane **18**[5] and related dioxyphosphoranes[3,23] are inert toward strong acids. In fact, they may be prepared[3,23] by acid-catalyzed dehydration of the appropriate precursor hydroxyalkyl- or carboxyphenylphosphine oxides. This marked difference is adequately explained by consideration of the expected polarization of the unsymmetrical hypervalent C–P–O bond. Such a polarization would imply an important contribution of **19** to the resonance structures of **5** and **6**. This is consistent with the observed basicity of **5** and **6**, greater than ammonia but less than that expected from a tertiary alkoxide lacking the kind of phosphorus–oxygen interaction implied by the P–O bond in the structure drawn for these species. The basicity of the alkoxy oxygen in structure **19** is markedly lowered by intramolecular "solvation" by the electrophilic phosphorus making the compound less basic than hydroxide.



18, $\delta_{^{31}\mathrm{P}}$ -44.5

Considerable polarization of the hypervalent bond in unsymmetrical sulfuranes has been clearly demonstrated.[24] The

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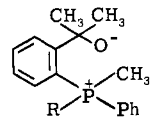
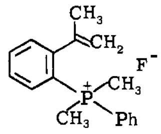
chemical shift values observed for **5** and **6** (δ −78.7 and −65.4) are, however, typical[9] of pentacoordinate phosphorus compounds (phosphoranes) rather than tetracoordinate phosphonium salts such as structure **19**. Consequently, we conclude that structures **5** and **6**, rather than **19**, are dominant for these compounds but with considerable polarization of the hypervalent C–P–O bond. The large P–O dipole is, however, not near to the rigidly oriented ortho proton in **5** or **6** so we do not find the downfield shift seen for the related proton in **4**.



19



20, $\delta_{^{31}P}$ 17.6

One example of an acid-catalyzed dehydration was observed. Treatment of **5** with anhydrous HF in $CDCl_3$ gave a 3:2 mixture of the salts **15** and **20**. It may well be that **15** undergoes acid-catalyzed dehydration, giving **20**.

Acknowledgment. This work was supported in part by a grant to J.C.M. from the National Cancer Institute (No. HEW PHS CA 13963) and by instrumentation for mass spectrometry provided by NIH Grants CA 11388 and GM 16864. We wish to thank Professor M. R. Wilcott, III, for helpful discussion and the Alexander von Humboldt Stiftung for an award to J.C.M.

Synthesis of 2,5-Dihydrotellurophene—A New Heterocyclic Compound[24]

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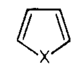
Contribution from the Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden.

Received August 28, 1980

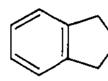
Abstract: 2,5-Dihydrotellurophene 1,1-dichloride was isolated in 62% yield when $TeCl_4$ was heated in acetonitrile with an excess of butadiene. Isoprene and 2,3-dimethylbutadiene reacted similarly affording the 3-methyl- and the 3,4-dimethyl-substituted 2,5-dihydrotellurophene 1,1-dichlorides which were easily reduced with aqueous Na_2S to the corresponding 2,5-dihydrotellurophenes. 2,5-Dihydrotellurophene could be converted to its 1,1-dibromide and 1,1-diiodide, respectively, by treatment with Br_2 and I_2. Treatment with XeF_2 afforded the 1,1-difluoride and oxidation with H_2O_2 similarly afforded 2,5-dihydrotellurophene 1-oxide, which was not isolated. The double bond of 2,5-dihydrotellurophene 1,1-dichloride was inert to treatment with Br_2 or Cl_2, probably due to an interaction, either steric or electronic, with the $TeCl_2$ group.

The unsaturated five-membered heterocycles 3-pyrroline (**1a**) and 2,5-dihydrofuran (**1b**) have long been known. The former[1] was obtained by reduction of pyrrole (**2a**), and the latter was formed by dehydrohalogenation of 3-bromotetrahydrofuran.[2] 2,5-Dihydrothiophene (**1c**) was one of the reduction products from thiophene (**2b**) when treated with sodium in liquid ammonia.[3]

1a, X = NH
1b, X = O
1c, X = S
1d, X = PCl_3
1e, X = GeI_2
1f, X = $SiCl_2$
1g, X = Te
1h, X = Se

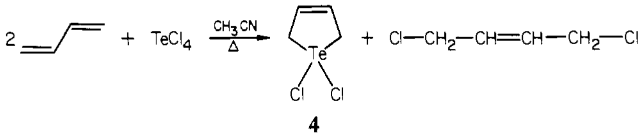


2a, X = NH
2b, X = S
2c, X = Te
2d, X = Se



3

Scheme I



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