Synthesis and Molecular Structures of Spirocyclic Arsoranes Containing Bulky Substituents[1]

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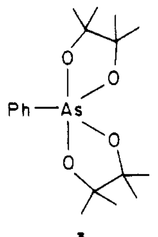
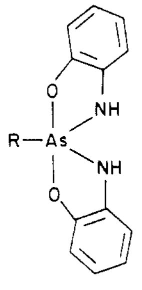
A variety of reactions are described leading to new spirocyclic arsoranes containing sterically encumbered five-membered rings. Prepared are the nonamethyl arsolane $(Me_4C_2O_2)_2AsMe$ (**9**), the tetra-*tert*-butyl arsoles $[(t\text{-}Bu)_2C_6H_2O_2]_2AsMe$ (**10**), $[(t\text{-}Bu)_2C_6H_2O_2]_2AsOH$ (**11**), and $[(t\text{-}Bu)_2C_6H_2O_2]_2AsPh$ (**13**), the octachloro arsole $(C_6Cl_4O_2)_2AsPh$ (**12**), and the mixed-ring arsorane $[(t\text{-}Bu)_2C_6H_2O_2](Me_4C_2O_2)AsMe$ (**14**), containing both an arsole and an arsolane ring. The X-ray structures revealed that **9** and **10** exhibited little steric interactions, the structures were close to trigonal bipyramidal. For **11**, a hydrogen-bonded dimer resulted which had a structure intermediate between a trigonal bipyramid and a rectangular pyramid. At most, the steric interaction in **11** is modest. Comparisons with related five coordinated germanium and silicon derivatives suggest that structural distortions on arsoranes so far are determined largely by substituent and ring preferences. Compound **9** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.306$ (3) Å, $b = 12.132$ (3) Å, $c = 13.784$ (2) Å, $\beta = 106.75$ (2)°, and $Z = 4$. Compound **10** crystallizes in the monoclinic space group $P2/c$ with $a = 13.716$ (4) Å, $b = 5.948$ (2) Å, $c = 18.430$ (3) Å, $\beta = 105.15$ (2)°, and $Z = 2$. Compound **11** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.780$ (1) Å, $b = 10.577$ (2) Å, $c = 14.671$ (3) Å, $\alpha = 71.72$ (1)°, $\beta = 78.90$ (1)°, $\gamma = 85.35$ (1)°, and $Z = 2$. The final conventional unweighted residuals were 0.059 (**9**), 0.056 (**10**), and 0.039 (**11**).

Introduction

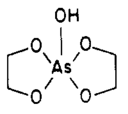
A number of spirocyclic arsoranes have been structurally characterized[3-7] which vary in the nature of the ring atoms attached to arsenic and in the type of ring system present. Most of these contain oxygen and nitrogen atoms directly bound to arsenic in five-membered saturated or unsaturated rings. Compared to phosphoranes,[8-10] the structural chemistry of this class of arsenic compounds has received only modest attention.



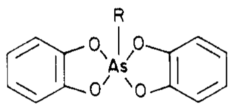
1[3]



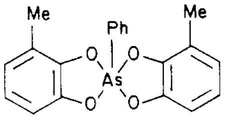
2[4] R = Ph
3[5] R = Me



4[3]



5[6] R = Me
6[4] R = Ph



7[7]

The X-ray structures of *1*–*3*[3-5] are close to trigonal bipyramidal. They show molecular structures which are displaced in the range of 18–23% from the trigonal bipyramid (TBP) toward the square or rectangular pyramid (RP) based on the dihedral angle method using unit bond distances.[8] In contrast, the X-ray structures of **4**–**7**[3,4,6,7] are more nearly rectangular pyramidal, falling in the range of 59–99% displacement from the TBP to the RP. Studies on phosphoranes revealed a continuous series of structures extending from the trigonal bipyramid to the square pyramid.[8-10] For pentacoordinated arsenic compounds, the absence of structures in the mid range most likely is associated with the limited number of studies conducted so far.

Relative to isoelectronic anionic five coordinate germanium derivatives, interesting comparisons also may arise. The recently studied hydroxyspirogermanate[1] containing *tert*-butyl groups, $[(t\text{-}Bu_2C_6H_2O_2)_2GeOH][Et_3NH]$ (**8**), has a highly rectangular-pyramidal geometry.

To ascertain how closely arsenic does model phosphorus in its pentacoordinated state and to extend the studies to include the effects of ring components containing bulky groups, the synthesis and crystal structural determination of the dioxarsolane $(Me_4C_2O_2)_2AsMe$ (**9**) and the benzodioxarsoles $[(t\text{-}Bu)_2C_6H_2O_2]_2AsMe$ (**10**) and $[(t\text{-}Bu)_2C_6H_2O_2]_2AsOH$ (**11**) are reported here. The preparations of the related phenyl analogues $(C_6Cl_4O_2)_2AsPh$ (**12**) and $[(t\text{-}Bu)_2C_6H_2O_2]_2AsPh$ (**13**) and the mixed-ligand species, $[(t\text{-}Bu)_2C_6H_2O_2](Me_4C_2O_2)AsMe$ (**14**) are included.

Experimental Section

Diethyl ether and benzene were distilled from lithium aluminum hydride. Triethylamine was distilled and stored under nitrogen. Acetonitrile was distilled off of phosphorus pentoxide. Tetrahydrofuran was dried over molecular sieves. Deuterated solvents were obtained from Norell, Inc. Reagents were from commercial sources and were used without further purification. Proton NMR spectra were recorded on a Varian A-60 spectrometer and referenced vs. tetramethylsilane.

Synthesis. 2,4,4,4′,4′,5,5,5′,5′-Nonamethyl-2,2′-spirobi(1,3,2-dioxarsolane), $(Me_4C_2O_2)_2AsMe$, 9. Different syntheses of this compound have been reported in the literature.[11,12] The

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(1) Pentacoordinated Molecules. 59. Previous paper in the series: Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 193.

(2) This work represents a portion of the Ph.D. Thesis of C. A. Poutasse, University of Massachusetts, Amherst, MA.

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(4) Day, R. O.; Holmes, J. M.; Sau, A. C.; Devillers, J. R.; Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2127.

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procedure adopted here represents a new method. Methylarsine pinacolate (0.5778 g, 2.803 mmol), prepared according to Wieber and Werther,[13] was stirred in 30 mL of dry benzene under nitrogen. Pinacol (0.3370 g, 2.852 mmol) and triethylamine (0.5674 g, 5.607 mmol) were added with no change to the colorless solution. Bromine (0.448 g, 2.803 mmol) in 20 mL of dry benzene was added dropwise. The bromine was immediately decolorized and a white precipitate formed. When the addition was completed, the solution was orange. The solid was filtered off and washed with ether. This was found by solubility and melting point behavior to be triethylamine hydrobromide. The volume of the solution was reduced to 10 mL and cooling produced a small quantity of white solid. The solvent was removed to yield an orange oil which subsequently crystallized (yield 0.8342 g, 92%); mp 65–68 °C; ^{1}H NMR (CD_3COCD_3) δ 1.15 (d, 24 H), 1.92 (s, 3 H). Anal. Calcd for $C_{13}H_{27}O_4As$: C, 48.45; H, 8.44. Found: C, 47.17; H, 8.62.

2-Methyl-4,4′,6,6′-tetra-*tert*-butyl-2,2′-spirobi(1,3,2-benzodioxarsole), $[(t\text{-}Bu)_2C_6H_2O_2]_2AsMe$, 10. *o*-Phenylene methylarsine (0.4272 g, 2.157 mmol), prepared according to Wieber and Werther,[11] was dissolved in 30 mL of dry ether with stirring. 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.4705 g, 2.136 mmol) was dissolved in 20 mL of dry ether in a dropping funnel. Dropwise addition under nitrogen caused initial decolorization of the benzoquinone, with a light green color remaining when the addition was completed. After the mixture was filtered, the volume was reduced to 10 mL and cooled to produce a crystalline white solid. This was filtered out, washed with heptane, and dried briefly under vacuum (yield 0.3061 g, 54%): mp 228–229 °C; ^{1}H NMR (C_6D_6) δ 1.27 (s, 18 H), 1.55 (d, 21 H), 7.1 (d, 4 H). Anal. Calcd for $C_{29}H_{43}O_4As$: C, 65.65; H, 8.17. Found: C, 64.88; H, 8.06. Crystals suitable for X-ray diffraction were grown out of benzene solution by slow evaporation of solvent.

2-Hydroxy-4,4′,6,6′-tetra-*tert*-butyl-2,2′-spirobi(1,3,2-benzodioxarsole), $[(t\text{-}Bu)_2C_6H_2O_2]_2AsOH$, 11. The spirocyclic compound 11 was prepared from pentamethoxy arsorane, which was made from arsenic trichloride.[14] Sodium (0.76 g, 33.00 mmol) was reacted in 25 mL of methanol to yield a clear, colorless solution of sodium methoxide in methanol. Arsenic trichloride (1.19 g, 6.56 mmol) was stirred in under nitrogen, producing a white solid. The mixture was cooled in an ice bath, and bromine (1.056 g, 6.608 mmol) was dissolved in 10 mL of methanol in a dropping funnel. Dropwise addition of the bromine to the arsenic solution was followed by immediate decolorization until the last drops when the solution turned yellow. This mixture was stirred briefly, and then the methanol was removed under vacuum. Ether (30 mL) was added and the new mixture stirred at room temperature under nitrogen while 3,5-di-*tert*-butylcatechol (2.9372 g, 13.211 mmol) was dissolved in 20 mL of ether in a dropping funnel. Dropwise addition caused the solution to turn dark green. When stirred overnight, it became much lighter and brownish in color. Filtration removed a white, water-soluble solid. The light filtrate was split into two parts. One part was treated with 40 mL of hexane and allowed to evaporate in the air. The other part was allowed to evaporate under argon.

Both produced similar looking products, fine green needles mixed with lumpy, light yellow crystals. Under a microscope, the crystals had very small red crystals adhering to them; yield of the yellow crystals, approximately 0.5 g (14%). The yellow crystals turn green at 132 °C and melt at 137–140 °C. Anal. Calcd for $C_{28}H_{41}O_5As$: C, 63.15; H, 7.76. Found: C, 62.37; H, 7.90. The yellow crystals could be cut to yield a crystal suitable for X-ray analysis. The green solid was not identified.

2-Phenyl-4,4′,5,5′,6,6′,7,7′-octachloro-2,2′-spirobi(1,3,2-benzodioxarsole), $(C_6Cl_4O_2)_2AsC_6H_5$, 12. Phenylarsonic acid (0.7289 g, 3.6077 mmol) and tetrachlorocatechol (1.7936 g, 7.2359 mmol) were stirred in 60 mL of benzene and refluxed with a Dean–Stark trap attached for the azeotropic distillation of water. After 6 h the solution was a cloudy yellow color. This was mixed with 20 mL of acetonitrile and filtered, some solid being discarded. The yellow liquid was reduced to 10 mL and ether added to induce crystallization. A yellow solid was collected and air dried (yield 1.3278 g, 57%); mp >250 °C; ^{1}H NMR (CD_3CN–Me_2SO) δ 1.05 (t, 6 H), 3.4 (q, 4 H), 7.55 (br peak, 3 H), 7.7–7.9 (br band, 2 H). There appears to be a molecule of diethyl ether in the solid, as diethyl ether has a triplet centered at δ 1.13 and a quartet centered at δ 3.38. This is confirmed in the analysis. Anal. Calcd for $C_{22}H_{15}O_5Cl_8As$ (12 with one ether molecule): C, 36.81; H, 2.11; Cl, 39.51. Found: C, 37.14; H, 1.77; Cl, 40.13.

2-Phenyl-4,4′,6,6′-tetra-*tert*-butyl-2,2′-spirobi(1,3,2-benzodioxarsole), $[(t\text{-}Bu)_2C_6H_2O_2]_2AsPh$, 13. Phenylarsonic acid (0.6066 g, 3.002 mmol) was stirred with 3,5′-di-*tert*-butylcatechol (1.3350 g, 6.012 mmol) in 60 mL of benzene. The solution was refluxed with a Dean–Stark trap for the azeotropic removal of water. After 5 h, the arsonic acid had dissolved, so the now yellow solution was cooled and filtered. The benzene was removed by evaporation under vacuum to yield a yellow solid. The solid was recrystallized several times from benzene–heptane solutions (1:4) (yield 1.3664 g, 80%); mp 215–216 °C; ^{1}H NMR (C_6D_6–CD_3COCD_3) δ 1.25 (d, 18 H), 1.5 (d, 18 H), 7.0–7.3 (broad band, 7 H), 7.75–7.95 (broad band, 2 H). Anal. Calcd for $C_{34}H_{45}O_4As$: C, 68.90; H, 7.65. Found: C, 68.64; H, 8.05.

2,4′,4′,5′,5′-Pentamethyl-4,6-di-*tert*-butylspiro[1,3,2-benzodioxarsole-2,2′-(1′,3′,2′-dioxarsolane)], $[(t\text{-}Bu)_2C_6H_2O_2](Me_4C_2O_2)AsMe$, 14. Methylarsine pinacolate[13] (0.4687 g, 2.274 mmol) was dissolved in 25 mL of dry ether with stirring under nitrogen. 3,5-Di-*tert*-butyl-*o*-benzoquinone was dissolved in 25 mL of dry ether forming a dark green solution and placed in a dropping funnel (0.5018 g, 2.278 mmol). Dropwise addition was followed by immediate decolorization. When the addition was completed, a light green solution resulted, so small crystals of methylarsine pinacolate were added until a colorless solution occurred. The solvent was removed to yield a white solid. This solid was found to be soluble in all the solvents it was tested in heptane, ether, benzene, acetone, methylene chloride, tetrahydrofuran, and acetonitrile, so it was difficult to purify. It could only be isolated by complete evaporation of the solvent. It was dried briefly under vacuum (yield 0.9234 g, 95%): mp 103–105 °C; ^{1}H NMR (CD_3COCD_3) δ 1.25 (s, 21 H), 1.35 (s, 9 H), 2.1 (s, 3 H), 6.77 (s, 2 H). Anal. Calcd for $C_{21}H_{35}O_4As$: C, 59.15; H, 8.27. Found: C, 58.10; H, 8.23.

X-ray Studies. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[15] Crystals of all three compounds were mounted inside of sealed thin-walled glass capillaries as a precaution against moisture sensitivity. All data were collected by using the θ–2θ scan mode. No corrections were made for absorption. The structures were solved by using standard Patterson and differences Fourier techniques and were refined by full-matrix least squares.[16]

X-ray Crystallographic Study for $(Me_4C_2O_2)_2AsMe$, 9. A colorless crystal (approximately triangular prismatic, edge lengths 0.23, 0.45, 0.45 mm; height 0.28 mm) which was cut from a polycrystalline mass was used for the X-ray study.

Crystal data: $C_{13}H_{27}O_4As$, **9**, monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^5—No. 14],[17] a = 10.306 (3) Å, b = 12.132 (3) Å, c = 13.784 (2) Å, β = 106.75 (2)°, Z = 4, and $\mu_{\mathrm{MoK}\bar{\alpha}}$ = 2.179 mm^{-1}; 2892 independent reflections ($+h,+k,\pm l$) were measured for $2° \leq 2\theta_{\mathrm{MoK}\bar{\alpha}} \leq 50°$.

The 18 independent non-hydrogen atoms were refined anisotropically. The three independent hydrogen atoms bonded to CM were located on a difference Fourier synthesis and were included in the refinement as fixed isotropic scatters. The remaining hydrogen atoms could not be located and were omitted from the refinement. The final agreement factors[18] were R = 0.059 and R_w = 0.079 for the 2109 reflections having $I \geq 2\sigma_I$.

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[12] Dale, A. J.; Froeyen, P. *Acta. Chem. Scand., Ser. B* **1975**, *B29*, 741.

[13] Wieber, M.; Werther, H. U. *Monatsh. Chem.* **1968**, *99*, 1159.

[14] Dale, A. J.; Froeyen, P. *Acta. Chem. Scand., Ser. B* **1975**, *B29*, 362.

[15] Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

[16] The function minimized was $\sum w(|F_0| - |F_c|)^2$, where $w^{1/2} = 2F_0L_p/\sigma_I$. Mean atomic scattering factors were taken from ref 17, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Cl and P were taken from the same source, pp 149–150.

[17] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; *Vol.* I, p 99.

[18] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

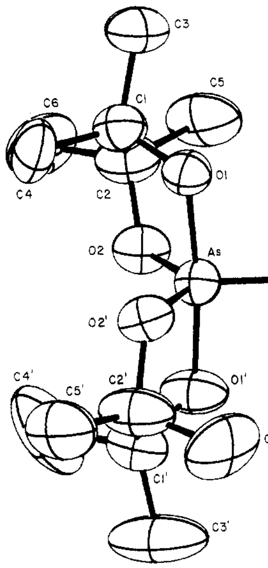

Figure 1. ORTEP plot of $(Me_4C_2O_2)_2AsMe$, **9**, with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are represented as spheres of arbitrary radius.

Table I. Atomic Coordinates in Crystalline $(Me_4C_2O_2)_2AsMe$, 9[a]

atom type[b]	coordinates 10⁴x	10⁴y	10⁴z
As	−472.5 (7)	−156.7 (6)	1765.1 (5)
O1	320 (5)	−1225 (4)	2672 (3)
O2	1104 (5)	523 (4)	2091 (4)
O1′	−1205 (5)	1023 (4)	989 (4)
O2′	−1667 (4)	36 (4)	2438 (4)
C1	1529 (8)	−843 (6)	3378 (6)
C2	2196 (8)	−107 (7)	2721 (7)
C3	2384 (10)	−1884 (7)	3843 (7)
C4	1181 (9)	−199 (7)	4237 (6)
C5	2816 (10)	−779 (9)	2026 (7)
C6	3243 (9)	743 (9)	3396 (8)
C1′	−2059 (8)	1669 (7)	1418 (6)
C2′	−2688 (9)	874 (8)	2004 (7)
C3′	−3016 (11)	2357 (11)	630 (9)
C4′	−1093 (13)	2469 (10)	2180 (14)
C5′	−3201 (11)	1297 (9)	2861 (7)
C6′	−3898 (9)	239 (10)	1201 (10)
CM	−922 (10)	−1149 (7)	641 (6)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

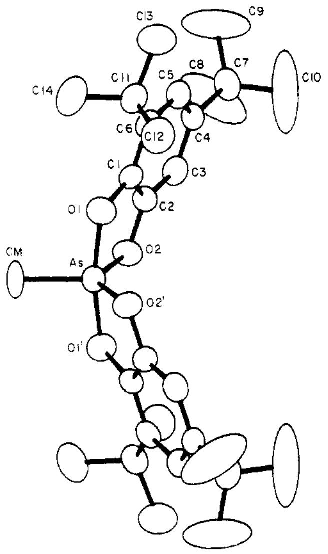

Figure 2. ORTEP plot of $[(t\text{-Bu})_2C_6H_2O_2]_2AsMe$, **10**, with thermal ellipsoids shown at the 50% probability level. For purposes of clarity, hydrogen atoms have been omitted. Primed atoms are related to unprimed ones by $-x, y, {}^1/_2 - z$.

Table II. Atomic Coordinates in Crystalline $[(t\text{-Bu})_2C_6H_2O_2]_2AsMe$, 10[a]

atom type[b]	coordinates 10⁴x	10⁴y	10⁴z
As	0[c]	3704 (2)	2500[c]
O1	1379 (3)	4020 (9)	2775 (2)
O2	−37 (3)	5106 (9)	3348 (3)
CM	0[c]	467 (17)	2500[c]
C1	1689 (5)	5257 (12)	3413 (4)
C2	923 (5)	5829 (11)	3740 (4)
C3	1085 (6)	7086 (12)	4389 (4)
C4	2067 (6)	7811 (12)	4743 (4)
C5	2841 (5)	7226 (12)	4404 (4)
C6	2674 (5)	5964 (12)	3737 (4)
C7	2279 (6)	9231 (13)	5457 (4)
C8	1577 (10)	8658 (29)	5950 (6)
C9	3309 (9)	8794 (30)	5956 (7)
C10	2231 (19)	11619 (20)	5284 (7)
C11	3530 (6)	5389 (13)	3384 (4)
C12	3282 (6)	6377 (16)	2572 (4)
C13	4558 (6)	6349 (17)	3838 (5)
C14	3624 (7)	2816 (16)	3342 (6)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Fixed.

X-ray Crystallographic Study for $[(t\text{-Bu})_2C_6H_2O_2)_2AsMe$, 10. A colorless crystal (0.13 mm × 0.13 mm × 0.37 mm) which was cut from a larger needle was used for the X-ray study.

Crystal data: $C_{29}H_{43}O_4As$, **10**, monoclinic space group $P2/c$ [C_{2h}^4—No. 13],[19] a = 13.716 (4) Å, b = 5.948 (2) Å, c = 18.430 (3) Å, β = 105.15 (2)°, Z = 2, and $\mu_{\text{Mo}K\bar{\alpha}}$ = 1.268 mm^{-1}; 1652 independent reflections ($+h,+k,\pm l$) were measured for $2° \leq 2\theta_{\text{Mo}K\bar{\alpha}} \leq 43°$.

The 18 independent non-hydrogen atoms were refined anisotropically. The two independent aromatic hydrogen atoms and the nine independent methyl hydrogen atoms bonded to C12, C13, and C14 were included in the refinement as fixed isotropic scatters. The 12 remaining independent methyl hydrogen atoms could not be located and were omitted from the refinement. The final agreement factors[18] were R = 0.056 and R_w = 0.075 for the 1340 reflections having $I \geq 2\sigma_I$.

X-ray Crystallographic Study for $[(t\text{-Bu})_2C_6H_2O_2)_2AsOH$, 11. A yellow crystal (0.23 mm × 0.25 mm × 0.35 mm), which was cut from a cluster of laths, was used for the X-ray study.

Crystal data: $C_{28}H_{41}O_5As$, **11**, triclinic space group $P\bar{1}$ [C_i^1—No. 2],[20] a = 9.780 (1) Å, b = 10.577 (2) Å, c = 14.671 (3) Å, α = 71.72 (1)°, β = 78.90 (1)°, γ = 85.35 (1)°, Z = 2, and $\mu_{\text{Mo}K\bar{\alpha}}$ = 1.305 mm^{-1}; 4991 independent reflections ($+h,\pm k,\pm l$) were measured for $2° \leq 2\theta_{\text{Mo}K\bar{\alpha}} \leq 50°$.

The 34 independent non-hydrogen atoms were refined anisotropically, while the hydroxyl hydrogen atom was refined isotropically. The four independent aromatic hydrogen atoms and 27 of the methyl hydrogen atoms were included in the refinement as fixed isotropic scatterers. The nine methyl hydrogen atoms bonded to C12′, C13′, and C14′ could not be located and were omitted from the refinement. The final agreement factors[18] were R = 0.039 and R_w = 0.058 for the 4304 reflections having $I \geq 2\sigma_I$.

Results

The atom labeling scheme for **9** is given in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I and selected bond lengths and angles are given in Table IV. The corresponding information for **10** is given in Figure 2 and Tables II and V and for **11** is given in Figure 3 and Tables III and VI. Thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and

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(19) Reference 17, p 97.

(20) Reference 17, p 75.

Table III. Atomic Coordinates in Crystalline $[(t\text{-Bu})_2C_6H_2O_2]_2AsOH$, 11[a]

atom type[b]	coordinates 10⁴x	10⁴y	10⁴z
As	3488.9 (3)	3123.6 (3)	751.2 (2)
O1	3077 (3)	1499 (2)	775 (2)
O2	2651 (2)	3844 (2)	−265 (2)
O1′	3510 (3)	4834 (2)	791 (2)
O2′	2968 (3)	2601 (2)	2033 (2)
O3	5241 (3)	2914 (2)	421 (2)
C1	2627 (3)	1573 (3)	−73 (2)
C2	2378 (3)	2859 (3)	−650 (2)
C3	1857 (3)	3109 (3)	−1507 (2)
C4	1620 (3)	1969 (3)	−1748 (2)
C5	1874 (3)	667 (3)	−1185 (2)
C6	2402 (3)	471 (3)	−330 (2)
C7	1501 (4)	4530 (3)	−2108 (3)
C8	334 (4)	5116 (4)	−1486 (3)
C9	964 (6)	4537 (4)	−3027 (3)
C10	2801 (5)	5402 (4)	−2421 (3)
C11	1653 (4)	−529 (3)	−1518 (3)
C12	2994 (5)	−749 (4)	−2207 (3)
C13	405 (5)	−289 (4)	−2055 (3)
C14	1365 (4)	−1805 (4)	−645 (3)
C1′	3346 (3)	4853 (3)	1745 (2)
C2′	3048 (3)	3626 (3)	2429 (2)
C3′	2822 (3)	3462 (3)	3422 (2)
C4′	2931 (4)	4626 (3)	3664 (2)
C5′	3230 (3)	5875 (3)	2984 (3)
C6′	3445 (3)	5989 (3)	1997 (2)
C7′	2500 (4)	2100 (4)	4180 (2)
C8′	2219 (6)	2192 (5)	5216 (3)
C9′	3766 (5)	1153 (5)	4080 (3)
C10′	1207 (5)	1520 (5)	4023 (3)
C11′	3307 (4)	7109 (4)	3327 (3)
C12′	4417 (9)	6889 (7)	3945 (7)
C13′	1891 (7)	7390 (7)	3861 (6)
C14′	3719 (11)	8371 (6)	2459 (5)
H3[c]	5616 (47)	3740 (45)	141 (33)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Refined isotropic thermal parameter, $B = 3\ (1)\ \text{Å}^2$.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $(Me_4C_2O_2)_2AsMe$, 9[a]

Bond Lengths

As-O1[b]	1.822 (4)	O1-C1	1.419 (8)
As-O2	1.761 (5)	O2-C2	1.429 (9)
As-O1′	1.816 (4)	O1′-C1′	1.428 (9)
As-O2′	1.758 (4)	O2′-C2′	1.461 (9)
As-CM	1.910 (8)		

Bond Angles

O1-As-O2	87.7 (2)	O1′-As-O2′	88.3 (2)
O1-As-O1′	173.1 (2)	O1′-As-CM	93.2 (3)
O1-As-O2′	88.6 (2)	O2′-As-CM	117.9 (3)
O1-As-CM	93.7 (3)	As-O1-C1	111.7 (4)
O2-As-O1′	88.7 (2)	As-O2-C2	114.3 (4)
O2-As-O2′	122.6 (2)	As-O1′-C1′	112.9 (4)
O2-As-CM	119.5 (3)	As-O2′-C2′	114.1 (4)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

Table V. Selected Bond Lengths (Å) and Angles (deg) for $[(t\text{-Bu})_2C_6H_2O_2]_2AsMe$, 10[a]

Bond Lengths

As-O1[b]	1.835 (5)	O1-C1	1.357 (8)
As-O2	1.785 (5)	O2-C2	1.394 (8)
As-CM	1.93 (1)		

Bond Angles

CM-As-O1	95.9 (2)	As-O1-C1	111.2 (4)
CM-As-O2	117.9 (2)	As-O2-C2	111.0 (4)
O1-As-O2	88.5 (2)	O1-C1-C2	114.2 (6)
O1-As-O1′	168.3 (1)	O1-C1-C6	125.7 (6)
O1-As-O2′	86.0 (2)	O2-C2-C1	114.9 (6)
O2-As-O2′	124.3 (3)	O2-C2-C3	122.1 (6)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $[(t\text{-Bu})_2C_6H_2O_2]_2AsOH$, 11[a]

Bond Lengths

As-O1[b]	1.785 (2)	O3-H3	0.91 (5)
As-O2	1.770 (2)	O1-C1	1.375 (4)
As-O1′	1.830 (2)	O2-C2	1.396 (5)
As-O2′	1.768 (3)	O1′-C1′	1.384 (4)
As-O3	1.704 (2)	O2′-C2′	1.394 (4)
O3[c]···O1′	2.704 (3)	H3[c]···O1′	1.83 (5)

Bond Angles

O1-As-O2	90.5 (1)	As-O1′-C1′	110.6 (2)
O1-As-O1′	167.8 (1)	As-O2′-C2′	111.8 (2)
O1-As-O2′	87.4 (4)	As-O3-H3	107 (2)
O1-As-O3	94.7 (1)	O1-C1-C2	114.6 (3)
O2-As-O1′	84.6 (1)	O1-C1-C6	123.4 (3)
O2-As-O2′	135.8 (5)	O2-C2-C1	113.7 (3)
O2-As-O3	112.6 (1)	O2-C2-C3	124.3 (3)
O1′-As-O2′	88.5 (1)	O1′-C1′-C2′	113.7 (3)
O1′-As-O3	97.4 (1)	O1′-C1′-C6′	123.6 (3)
O2′-As-O3	111.6 (1)	O2′-C2′-C1′	114.3 (3)
As-O1-C1	109.6 (2)	O2′-C2′-C3′	124.0 (3)
As-O2-C2	109.8 (2)	O3[c]-H3[c]···O1′	159 (4)
		As-O1′···H3[c]	127 (1)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Related by $1 - x$, $1 - y$, $-z$.

deviations from selected least-squares mean planes for all three compounds are provided as supplementary material.

Discussion

Structural Analysis. Both **9** and **11** have a pseudo twofold axis which is coincident with the As–CM (for **9**) or As–O3 (for **11**) bond. To facilitate the examination of this pseudosymmetry, atoms for **9** and **11** have been labeled so that, except for terminal methyl groups, the primed ones are pseudo twofold related to the unprimed ones.

In the case of **10**, the twofold symmetry is crystallographic, with the As atom and CM lying on the twofold axis and the hydrogen atoms bonded to CM disordered about this axis.

All three of the compounds have a geometry about As that lies between a trigonal bipyramid (TBP) with O1 and O1′ in the axial positions and a rectangular pyramid (RP) with O1, O1′, O2, and O2′ occupying basal positions. In terms of the Berry pseudorotation coordinate, **9** is displaced 11.1% (12.9% using unit vectors) from the TBP to the RP. For **10** and **11** these values are 20.5% (22.2%) and 45.4% (44.4%), respectively. For **11**, there is a hydrogen bond between the hydroxyl hydrogen atom H3 and the axial oxygen atom O1′ of an inversion related molecule. This interaction results in the formation of hydrogen-bonded dimeric units (Figure 3).

As has been observed for Si compounds having hydrogen bonds to ring oxygen atoms,[21,22] the As–O_{ax} bond length involving the hydrogen bond acceptor [As–O1′ = 1.830 (2) Å] is significantly longer than the other As–O_{ax} bond [As–O1 = 1.785 (2) Å]. By way of comparison, the two As–O_{eq} bonds [As–O2 = 1.770 (2) Å and As–O2′ = 1.768

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(21) Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Organometallics* **1984**, *3*, 347.

(22) Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984**, *3*, 341.

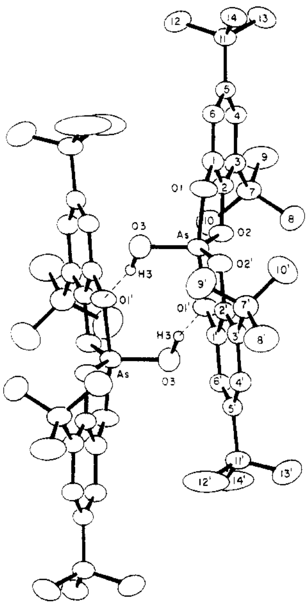
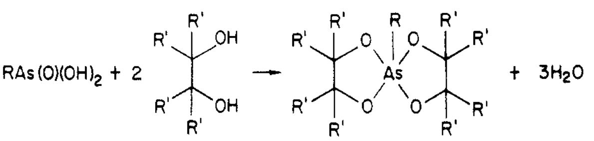


Figure 3. ORTEP plot of $[(t\text{-Bu})_2C_6H_2O_2]_2AsOH$, **11**, with thermal ellipsoids shown at the 50% probability level. To illustrate the hydrogen bonding, a symmetry related molecule $(1-x, 1-y, -z)$ is shown at the left in the figure. Hydrogen atoms, except for H3, which is represented as a sphere of arbitrary radius, have been omitted for purposes of clarity. Carbon atoms are identified by number only.

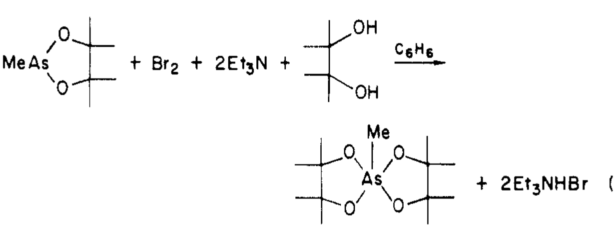
(3) Å] are equal within the limits of the error.

Synthetic Methods. In 1946, Salmi et al.[11] detailed the synthesis of 19 spirocyclic arsoranes by the method in eq 1. This is the method we employed to prepare the new



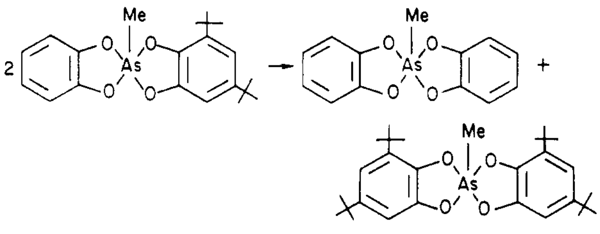
(1)

derivatives **12** and **13** using tetrachlorocatechol and 3,5-di-*tert*-butylcatechol, respectively. Although the bis(dioxarsolane) **9** has been prepared by the reaction in eq 1, a new method was employed here giving **9** in high yield. Methylarsine pinacolate was oxidized to arsenic(V) by bromine in the presence of ethylamine (eq 2). The bromines are immediately displaced by the pinacol as triethylamine hydrobromide settles out of solution.



(2)

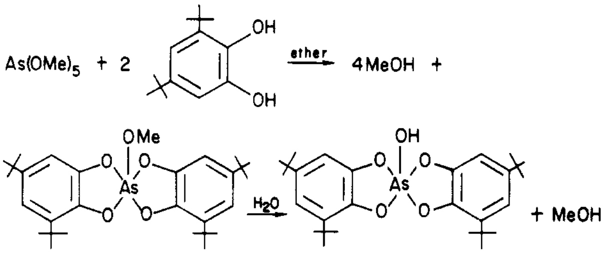
In an attempt to prepare a spirocyclic arsorane with two different bidentate ligands, *o*-phenylene methylarsine was reacted with 1 equiv of 3,5-di-*tert*-butyl-*o*-benzoquinone. However, on reducing the volume, a 54% yield of the symmetrical arsorane **10** containing two *tert*-butyl-substituted benzoquinone ligands settled out of the ether solution. It is surmised that the asymmetrical product formed and then disproportionated on heating according to eq 3. The bis(catechol) compound most likely has the greater solubility in ether and remained in solution.



(3)

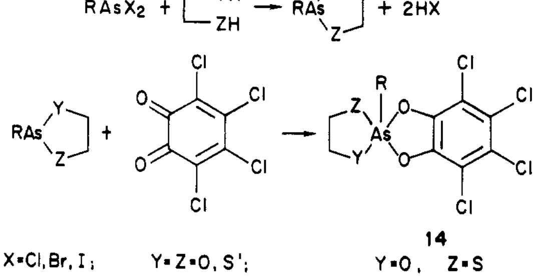
10

The reaction of pentamethoxyarsorane with 3,5-di-*tert*-butylcatechol in ether led to the isolation of the yellow crystalline arsorane **11** (14% yield) containing a hydroxyl group in the unique position. The formation of **11** is consistent with partial hydrolysis of the methoxy precursor which may have been the green solid (eq 4).



(4)

For the most part, spiroarsoranes containing unlike ring systems have been prepared by the procedure of Wieber and co-workers[13,23] (eq 5). Using this method, the previously unknown mixed-ring spirocyclic **14** was prepared in high yield from methylarsine pinacolate and 3,5-di-*tert*-butyl-*o*-benzoquinone.



(5)

A significant difference between phosphorus and arsenic in the preparative chemistry designed to yield pentacoordinated compounds lies in the difficulty of oxidizing arsenic(III) to arsenic(V). The latter is illustrated relative to the pathway in eq 5. Some diketones that have been used extensively with phosphorus, such as benzil[24] and phenanthrenequinone,[25] were unable to oxidize arsenic(III). The only diketones that were found to work in this reaction were the *o*-benzoquinones[23] (eq 5).

Structural Comparisons. The structural placement of the hydroxyl derivative **11** approximately midway between the TBP and RP provides evidence that, like phosphoranes,[8-10] arsoranes will form a continuous series of structures between these two end configurations rather than a bunching at either end, as previously observed.[3-7] The methyl-substituted arsolane **9** has a structure not too different from the analogous phenyl derivative **1**[3] (18% TBP → RP for **1** vs. 12.9% for **9**). Similarly, the structures of the methyl and phenylbenzoxazarsoles **3**[5] and **2**[4] have closely related structures, displaced 23.3% and 22.9% from the TBP toward the RP, respectively. These observations suggest that packing influences are not highly significant for arsoranes when groups of modest size are present. On a more extensive basis set, it was concluded that inter-

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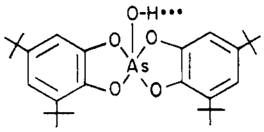
[23] Wieber, M.; Eichhorn, B.; Gotz, J. *Chem. Ber.* **1973**, *106*, 2738.

[24] Ogata, Y.; Yamashita, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 493.

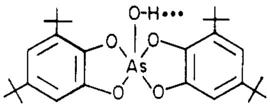
[25] Day, R. O.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3790.

molecular effects for phosphoranes were minor except for those cases where intermolecular hydrogen bonding[26] or steric interactions caused by bulky substituents[27] were present. These conclusions contrast with work on pentacoordinated antimony compounds[28,29] where lattice interactions take on more significance.

It is interesting to compare structural distortions for the *tert*-butyl-substituted arsoranes **10** and **11** with the related five coordinated germanate [(t-$Bu_2C_6H_2O_2)_2GeOH$][Et_3NH] (**8**).[1] The latter is very close to a rectangular-pyramidal geometry, 95.7%, whereas **10** and **11** are closer to trigonal bipyramidal, 22.2% and 44.4% TPB → RP, respectively, based on unit bond distances. Hydrogen bonding complicates the structural interpretation for **8** and **11**. In the germanates **8**, hydrogen bonding exists between the Et_3NH cation and the hydroxyl oxygen atom (N–H···O = 2.708 (10) Å). It has been reasoned[1] that this effect makes the unique ligand act as a much larger group resulting in a repulsion interaction with the ring substituted *tert*-butyl groups causing the structure to be stabilized near the rectangular pyramid. For the arsorane **11**, the hydrogen bonding is intermolecular between the hydroxyl OH and the "axial" oxygen atoms of the spirocyclic ring system, O3–H3···O1′. Here, it is noted that the *tert*-butyl groups are located on ring carbon atoms C5, C5′, C3, and C3′ and thus provide the least steric interaction with the dimer formation, i.e., the pattern



is obtained, rather than



(see Figure 3). A related five coordinated silicon analogue, recently prepared in our laboratory, [(t-$Bu_2C_6H_2O_2)_2SiPh$][Et_3NH] (**15**), shows an X-ray structure[30] displaced toward the rectangular pyramid, 29.0%, comparable to that of the arsorane **10**. Electron-releasing ring substituents, like *tert*-butyl groups, are expected to enhance the formation of the normally lower energy trigonal-bipyramidal geometry as a result of increased central atom bond electron pair repulsions.[31] This apparently is the case for **10** and **15**. It is concluded that in the absence of appreciable steric effects, e.g., in **10** and **15**, or intermolecular hydrogen-bonding interactions, the present data on arsoranes parallel structural interpretations on phosphoranes[8-10] in suggesting that structural distortions are determined largely by substituent and ring preferences rather than packing effects.

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Registry No. **9**, 32025-18-6; **10**, 94904-61-7; **11**, 94904-62-8; **12**, 94928-98-0; **13**, 94904-63-9; **14**, 94928-99-1; methylarsine pinacolate, 18882-64-9; pinacol, 76-09-5; *o*-phenylenemethylarsine, 18882-63-8; 3,5-di-*tert*-butyl-*o*-benzoquinone, 3383-21-9; arsenic trichloride, 7784-34-1; 3,5-di-*tert*-butylcatechol, 1020-31-1; phenylarsonic acid, 98-05-5; tetrachlorocatechol, 1198-55-6.

Supplementary Material Available: Table A, thermal parameters for **9**, Table B, hydrogen atom parameters for **9**, Table C, thermal parameters for **10**, Table D, hydrogen atom parameters for **10**, Table E, thermal parameters for **11**, Table F, fixed hydrogen atom parameters for **11**, Table G, additional bond lengths and angles for **9**, Table H, additional bond lengths and angles for **10**, Table J, additional bond lengths and angles for **11**, Table K, selected least-squares mean planes for **9**, **10**, and **11**, and a listing of observed and calculated structure factor amplitudes for **9–11** (41 pages). Ordering information is given on any current masthead page.

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