of an 88:12 mixture of (*Z*)- and (*E*)-1,2-dimethylcyclododecenes (**9b** and **8b**).

Acknowledgments. We are indebted to the National Science Foundation for support of this work through a research grant (MPS 75-07777). We thank Professor R. E. Ireland for unpublished procedures and advice on the preparation of phosphoramidates.

Registry No.—**1a,** 96-01-5; **1b,** 3008-41-1; **4a,** 61349-14-2; **4b,** 61349-15-3; **5a,** 61376-40-7; **5b,** 61376-41-8; **6b** (R = 3-butenyl), 61349-16-4; **7a** (R = Me; Z = NMe_2), 61376-42-9; **7a** (R = Me; Z = OEt), 61349-17-5; **7b** (R = Me; Z = NMe_2), 61376-43-0; **7b** (R = Me; Z = OEt), 61349-18-6; **7b** (R = 3-butenyl; Z = NMe_2), 61349-19-7; **8a,** 61349-20-0; **9a,** 14113-67-8.

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The Structure in Solution of the Halogen Adducts of Phosphines and Arsines

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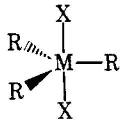
Received October 29, 1976

1-Methylphosphorinane (**4**) and 1-methylarsenane (**6**) form 1:1 and 1:2 adducts with Br_2 and I_2, but only 1:1 adducts with Cl_2, as determined by conductometric titrations and by isolation. The 1-phenyl compounds (**5, 7**) exhibit the same behavior. These materials can have either a trigonal bipyramidal structure with As or P between the two halogen atoms, or a simple molecular complex structure with As or P at the end of the halogens. We have been able to distinguish these structural types by the conductance of the adducts in solution and by the *R* value analysis (vicinal coupling constants) of deuterated derivatives. The 1:1 arsine adducts with Cl_2 and Br_2 are nonconducting trigonal bipyramids. All the 1:1 phosphine adducts, the 1:1 adducts of the arsines with I_2, and all the 1:2 adducts of both the phosphines and the arsines are highly conducting molecular complexes with presumably little distortion in the shape of the ring.

The halogen complexes of trivalent phosphines and arsines have been of interest not only because of their structural complexities but also because of their use in synthesis, as in the Wiley reaction for the preparation of alkyl halides[2a] and in the cleavage of the C–O bond of acids, acid anhydrides, esters, and lactones to form a C–Br bond under very mild conditions.[2b] A number of different structural methods have been applied to these compounds,[3] but hard structural data are particularly lacking in the solution phase. Previous work[3] has demonstrated that both 1:1 and 1:2 adducts are possible (eq 1). For the 1:1 adducts, there are at least two general

$$R_3M \xrightarrow{X_2} R_3MX_2 \xrightarrow{X_2} R_3MX_4 \tag{1}$$

structural classes possible. The central atom M can be located between the two halogen atoms X, so that M is pentacoordinate and the overall structure is a trigonal bipyramid (TB) (**1**). Alternatively, the atom M can be at the end of the two halogens, in a simple molecular complex (MC), which can exist in hydrogen-bond-like (**2**) or ionic (**3**) forms. The problem, therefore, is to determine which structure (**1–3**) exists in solution for each of the adducts of trivalent phosphorus or arsenic with chlorine, bromine, or iodine. We hope to extend the results to antimony and fluorine by induction.



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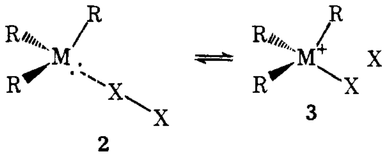
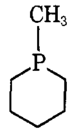


2 **3**

Although distinguishing the trigonal bipyramid and molecular complex would be fairly straightforward by x-ray crystallography, the problem is more difficult in solution.[3] A critical difference between the two structural types is the R–M–R valence angle, which in the molecular complex is little changed from the parent base but in the trigonal bipyramid is enlarged to about 120°. When the R groups on M take the form of a six-membered ring, the enlarged angle in the trigonal bipyramid brings about a significant flattening of the ring. On the other hand, the molecular complex would exhibit little ring deformation with respect to the shape of the parent base. Thus, to provide a general solution to the problem of the structure of these adducts in solution, we have chosen to study the conformations of the adducts of 1-methyl- and 1-phenylphosphorinane and -arsenane (**4–7**) with the halogens



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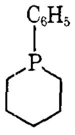

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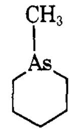

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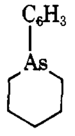
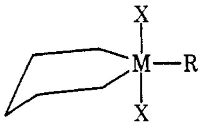


7

(Cl_2, Br_2, I_2). These rings should be considerably flattened in the trigonal bipyramid (**8**) and essentially undistorted in the molecular complex (**9**, **10**).



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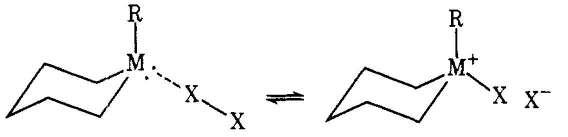
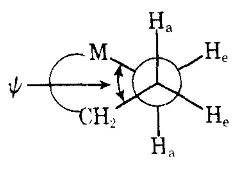
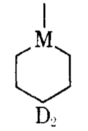


9 **10**

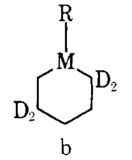
NMR coupling constants provide one means of determining the nature of ring deformations in solution.[4] We have previously used such an approach to study the structures of the complexes of sulfides and selenides with halogens in solution.[5] Any $-CH_2CH_2-$ fragment in a six-membered ring can yield two averaged vicinal coupling constants, $J_{\text{trans}}[\frac{1}{2}(J_{aa} + J_{ee})]$ and $J_{\text{cis}}[\frac{1}{2}(J_{ae} + J_{ea})]$, whose ratio R gives the internal torsional angle of the ring directly from eq 2.[4] Therefore, to determine the shape of the phosphorinane or arsenane ring, suitable bismethylene fragments must be isolated and their NMR spectra analyzed. Thus the two deuterated forms a and b suffice to provide a solution to the conformational problem,



$$\cos \psi = \left(\frac{3}{2 + 4R}\right)^{1/2} \qquad (2)$$



a



b

provided that the four-spin spectra can be analyzed. The torsional angles of a molecular complex (**9** or **10**) should be close to that of the parent, uncomplexed ring for both the α,β (a) and the β,γ (b) segments. There are considerable distortions, however, in the trigonal bipyramid (**8**), with the α,β segment considerably flattened (Ψ decreased).[5]

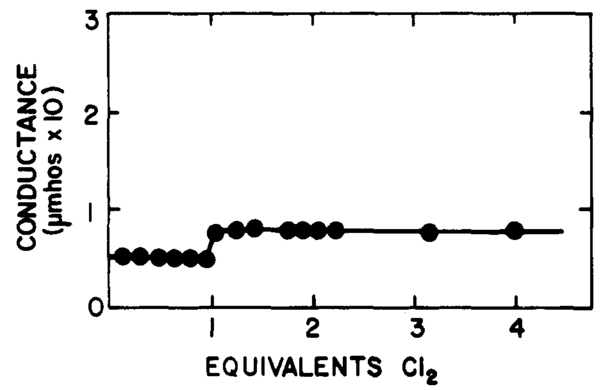


Figure 1. The conductance of 1-methylarsenane (**6**) in $ClCH_2CH_2Cl$ at 25 °C as a function of added equivalents of Cl_2 in $ClCH_2CH_2Cl$.

Following the method of Harris and co-workers,[6] we have also examined the conductance of solutions of these adducts in the same or a similar solvent as used for our NMR studies, in order to distinguish the ionized (**10**) and un-ionized (**9**) forms of the molecular complex. Addition of halogen in increments to a solution already containing the phosphine or arsine provides a titration curve that gives the stoichiometry and relative conductance of the various adducts. Thus by the combined NMR/conductance method, we can unambiguously distinguish the three structural types (**8**, **9**, **10**).

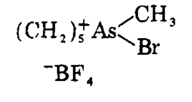
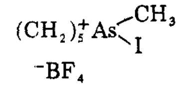
Results

Crystalline adducts could be isolated with both the 1:1 and the 1:2 stoichiometry for the Br_2 and I_2 complexes of all four substrates (**4–7**). Only a 1:1 adduct, however, was isolable for the Cl_2 complexes of the same materials. The conductance of the adducts was measured in two different fashions. First, the isolated, crystalline adducts were dissolved in 1,2-dichloroethane or methylene chloride and the molar conductivity measured. These values are given in Table I (designated by footnote *c*). Conductometric titrations were also performed by adding increments of the halogen, dissolved in 1,2-dichloroethane or methylene chloride, to a solution of the substrate (**4–7**) in the same solvent. The results of these titrations are illustrated in Figures 1–6 for the halogen adducts of 1-methylphosphorinane (**4**) and 1-methylarsenane (**6**).[7] Essentially identical results were obtained with the phenyl substrates (**5**, **7**). In our hands, triphenylphosphine and -arsine produced conductance titrations identical with those reported previously.[6] Molar conductivities were calculated at the 1:1 and 1:2 (substrate/halogen) points on the titration curves, and these values may also be found in Table I. All conductances in Table I were corrected for volume, although those in the figures represent raw data.

In order to have a fully ionic standard, we prepared the tetrafluoroborate derivatives of the 1-methylarsenane system ($R_3As^+X\ BF_4^-$) by reaction of the appropriate 1:1 halogen adduct (only Br_2 and I_2) with silver tetrafluoroborate. Attempts to prepare the tetrafluoroborate derivatives of 1-methylphosphorinane in this manner failed. The molar conductivities for the arsenane systems are given in Table I.

The NMR spectrum of both deuterated variants of the parent base 1-methylarsenane (**6a** and **6b**) are ABCD. The analyses have been given elsewhere.[8] In contrast, all the 1:1 and 1:2 halogen adducts of 1-methylarsenane gave AA′BB′ or AA′XX′ spectra for both variants, a and b. The spectral nonequivalence in the parent compound is caused by slow inversion about arsenic. The higher symmetry of the spectra of the adducts must be due to static higher symmetry or a

Table I. Molar Conductivities (mho cm^2 mol^{-1})[a]

Registry no.		Cl_2	Br_2	I_2	$2Br_2$	$2I_2$
39763-50-3	$(CH_2)_5PCH_3$ (4)	21.0[b] 18.7[b,c]	3.1 3.3[c]	12.8[b] 13.7[b,c]	9.6 8.8[c]	25.9[b] 25.4[b,c]
3302-83-8	$(CH_2)_5PC_6H_5$ (5)	5.9	5.9	8.5	12.9	18.5
30077-31-7	$(CH_2)_5AsCH_3$ (6)	0.07 0.06[c]	0.02 0.04[c]	2.1 3.2[c]	6.2 5.6[c]	13.8 14.1[c]
30077-30-6	$(CH_2)_5AsC_6H_5$ (7)	0.18	0.27	3.6	9.7	13.2
61394-98-7	 $(CH_2)_5^+As(CH_3)(Br)\ {}^-BF_4$		23.8			
61395-00-4	 $(CH_2)_5^+As(CH_3)(I)\ {}^-BF_4$			25.0		

[a] All measurements were performed in $ClCH_2CH_2Cl$ by the titration method at concentrations in the range 4–8 × 10^{-3} M, unless otherwise specified. [b] Measured in CH_2Cl_2 because of low solubility in $ClCH_2CH_2Cl$. [c] Measured by dissolving a known amount of the crystalline adduct in solution.

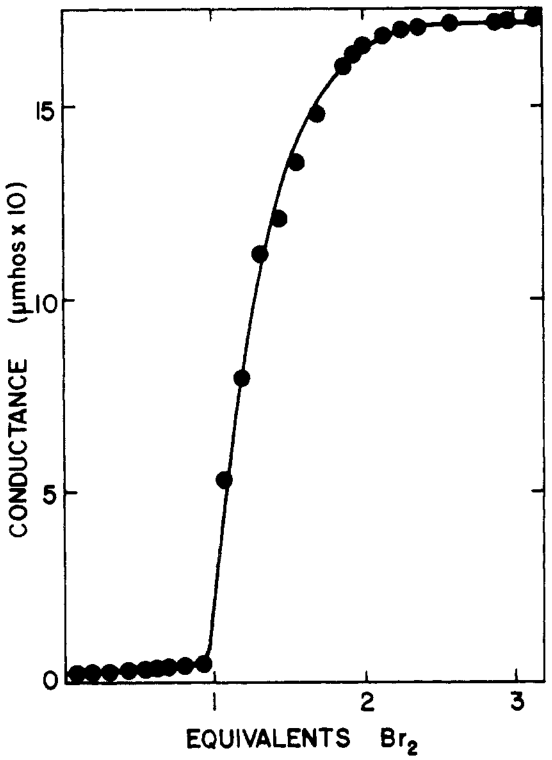


Figure 2. The conductance of 1-methylarsenane (6) in $ClCH_2CH_2Cl$ at 25 °C as a function of added equivalents of Br_2 in $ClCH_2CH_2Cl$.

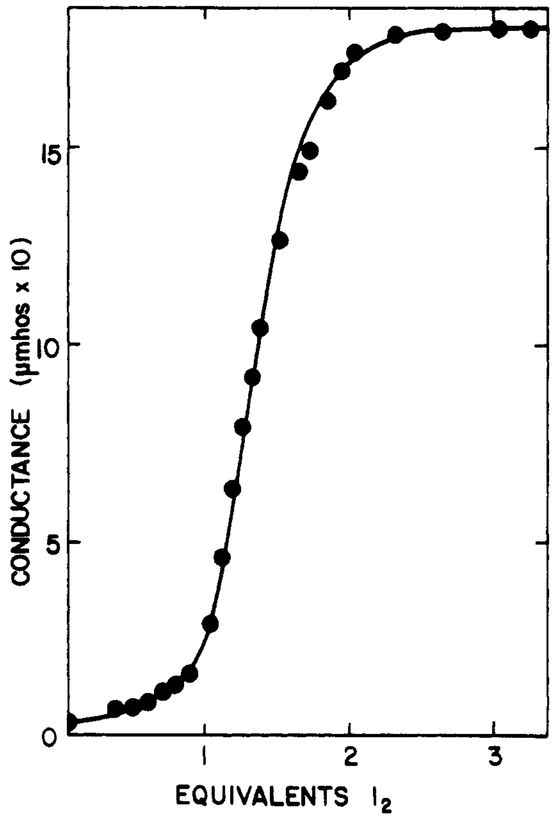


Figure 3. The conductance of 1-methylarsenane (6) in $ClCH_2CH_2Cl$ at 25 °C as a function of added equivalents of I_2 in $ClCH_2CH_2Cl$.

dynamic process that averages spectral lines. This point will be examined again in the Discussion. The observed spectra for **6a**-X_2 (Cl_2, Br_2) and **6b**-X_2 (Br_2) are given in Figures 7–9.[7] The spectrum of **6b**-Cl_2 has been presented elsewhere.[9] The spectra for **6a**-Br_4 and **6b**-Br_4 are given in Figures 10 and 11.[7] The iodine complexes were insufficiently soluble to give acceptable spectra. The 1-phenylarsenane adducts (**7**-X_2) were not examined by the NMR methods.

Initial values of coupling constants and chemical shifts for the complexes of 1-methylarsenane were estimated, and final values were obtained by standard iterative procedures.[10] The calculated spectra are given in the figures, along with the experimental spectra. In the case of the γ-deuterated compounds (**6a**), analyses were carried out on both 60- and 270-MHz spectra, but 60-MHz analyses were sufficient for the α,β′ compounds (**6b**), which were obtained with irradiation at the deuterium frequency. Deuterium irradiation was not available at 270 MHz. Analyses of 1-methylphosphorinane and all its halogen derivatives were also attempted, and approximate solutions have been obtained.[10] These data, however, could not be refined and will not be reported here, because of the added complications of coupling to phosphorus-31. Arsenic has a spin of 3/2, but coupling constants to As are not resolved because of rapid quadrupole relaxation. The coupling constants, R values, and torsional angles Ψ are listed in Table II. The details of the analysis of each individual case have been discussed elsewhere.[10] In certain cases, the geminal (AA′ and BB′) couplings could not be measured. This result is characteristic of bismethylene AA′BB′ spectra with very large or very

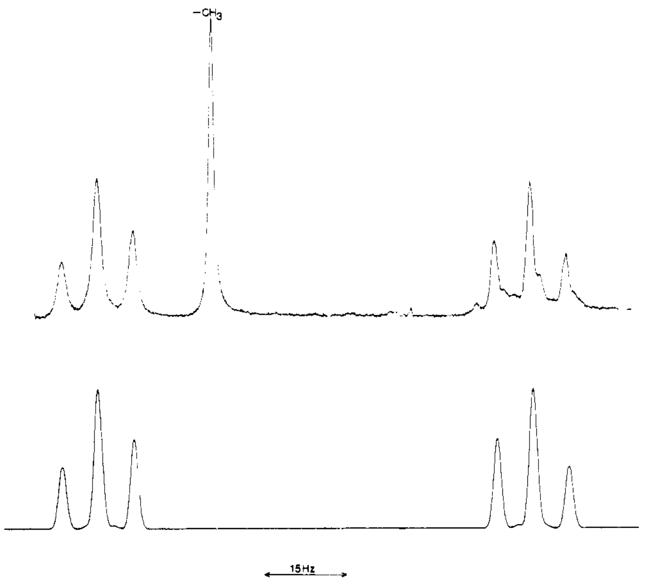


Figure 8. The observed and calculated 60-MHz proton spectra of 1-methylarsenane-*4,4-d*$_2$ 1,1-dibromide (**6a**-Br$_2$) with deuterium decoupling.

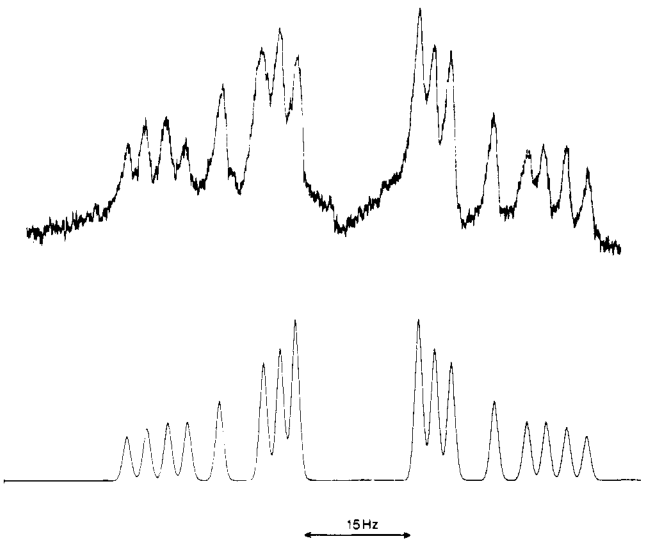


Figure 9. The observed and calculated 60-MHz proton spectra of 1-methylarsenane-*2,2,5,5-d*$_4$ 1,1-dibromide (**6b**-Br$_2$) with deuterium decoupling. The α-proton and methyl singlets are omitted.

small chemical shift differences ($\Delta\nu_{AB}$) and has been discussed in detail elsewhere.[9]

Although coupling constants provide the most important structural information from the NMR spectrum, we have also recorded the proton and carbon-13 chemical shifts for 1-methylarsenane and its halogen adducts (Table III).[11]

Discussion

Conductance. The conductance curves clearly show the existence of both 1:1 and 1:2 adducts of Br$_2$ and I$_2$ but only 1:1 adducts of Cl$_2$ (Figures 1–6)[7] for both the phosphine and the arsine systems. The respective adducts with appropriate stoichiometries subsequently were isolated. All of the 1:2 adducts have very high ionic character (Table I). This statement is true no matter what the halogen (Br, I), central atom (P, As), or substituent (CH$_3$, C$_6$H$_5$) is. Our UV studies showed the presence of Br$_3^-$ or I$_3^-$ in these solutions. Therefore, the best structure for the 1:2 adducts appears to be the ionized form **11**. Our results in this matter only serve to corroborate the observations of others in similar systems.[3,6]

Table II. Coupling Constants and Torsional Parameters for 1-Methylarsenane (6) and Its Halogen Adducts

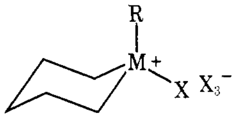
		J_{trans}, Hz	J_{cis}, Hz	ΔJ_{gem}, Hz	R	Ψ, deg
Parent[a]	$\alpha\beta$	10.0, 8.6	3.3, 3.5	0.7	2.7	61
	$\beta\gamma$	8.0, 7.6	3.1, 2.7	0.9	2.7	61
Cl$_2$[b]	$\alpha\beta$	7.0	7.0	2.5	1.0	45
	$\beta\gamma$	9.3	2.2	0.0	4.2	66.5
Br$_2$[c]	$\alpha\beta$	7.5	6.1	2.5	1.2	49
	$\beta\gamma$	9.2	2.1	0.0	4.3	67
Br$_4$[d]	$\alpha\beta$	8.6	4.0	3.0	2.2	58
	$\beta\gamma$	8.8	2.7	0.0	3.3	63

[a] Taken from ref 8; there are two J_{trans} and two J_{cis} couplings because the spectra are ABCD or AA′CD; all spectra of the adducts are AA′BB′ or AA′XX′. [b] Taken in CCl$_4$; all others were taken in CH$_2$Cl$_2$. Registry no., 60958-64-7. [c] Registry no., 60958-65-8. [d] Registry no., 61395-01-5.

Table III. Chemical Shifts of 1-Methylarsenane and Its Halogen Adducts

		Parent[a]	Cl$_2$[b]	Br$_2$[c]	2Br$_2$[c]
^{1}H[d]	α	1.27, 1.64	3.30	3.60	3.43
	β	1.63, 1.78	2.30	2.25	2.10
	γ	1.45, 1.45	1.90	1.92	1.90
	CH$_3$	0.90	2.94	3.24	3.07
^{13}C[d,e]	α	22.4	51.1	47.2	51.9
	β	23.9	23.9	24.2	24.0
	γ	29.3	52.0	47.2	43.5
	CH$_3$	5.1	22.4	22.2	23.0

[a] ^{1}H spectrum in CCl$_4$; ^{13}C spectrum neat. [b] ^{1}H and ^{13}C spectra in CCl$_4$. [c] ^{1}H spectrum in CH$_2$Cl$_2$; ^{13}C spectrum in CDCl$_3$. [d] In parts per million downfield from Me$_4$Si. [e] Some of these ^{13}C data are reported in ref 11.



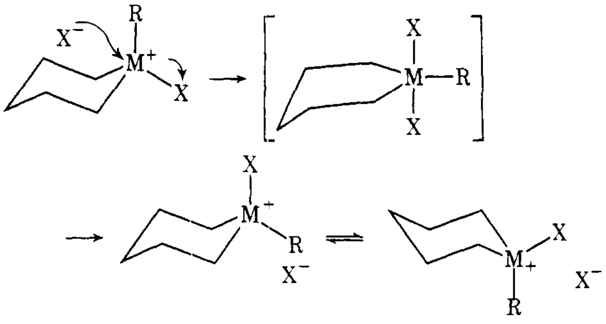
11

The 1:1 adducts give somewhat different results for the phosphines and arsines. All the phosphine adducts exhibit high conductance (Table I). We therefore consider that these materials most likely have the structure of the ionized molecular complex (**10**), although there may be some contribution from **9**. In contrast, the 1:1 arsine complexes with Cl$_2$ and Br$_2$ are essentially nonconducting. These results are consistent either with the nonionic molecular complex **9** or the trigonal bipyramid **8**. Past experience[5] has indicated that the nonconducting condition is usually a property only of the trigonal bipyramid. The arsine complex with I$_2$, however, is conducting and presumably of the form **10** (possibly with some **9**). The fully ionic tetrafluoroborates substantiate these conclusions. The bromoarsenanium tetrafluoroborate is two orders of magnitude more conducting than the simple 1:1 complex, whereas the iodoarsenanium tetrafluoroborate is only four times more conducting than the simple complex. It is unwise to attempt to calculate the ionic character of the iodine complex from these figures (% **9** vs. % **10**), because individual ionic conductances are not known and the anion is different in the two cases (I$^-$ and BF$_4^-$). That the 1:1 iodine complex must be nearly fully ionized (mostly **10**) is indicated by its yellow color, i.e., the I–I bond must be substantially broken. In contrast, the 1:1 molecular complex of I_2 with thiane (the analogous sulfur heterocycle) is deep violet at room temperature (significant contribution from **9**).[5]

The qualitative conclusions from the conductance data are that the 1:2 adducts possess the ionic, trihalide structure **11**, the 1:1 phosphine adducts possess the ionic molecular complex structure **10** (with possibly some contribution from **9**), the 1:1 I_2 adduct of the arsine also has the structure **10** (possibly with some **9**), and the 1:1 Cl_2 and Br_2 adducts of the arsine have the nonionic trigonal bipyramidal structure **8**.

Magnetic Resonance. The *R* value analysis of 1-methylarsenane (**6**) indicates that the entire molecule is slightly puckered with respect to the shape of cyclohexane (Table II, $\Psi = 61°$ for both α,β and β,γ segments).[8] This puckering is the distortion expected for the smaller C–As–C bond angle. Our preliminary analysis indicates that 1-methylphosphorinane is similarly puckered.[10] These conclusions refer to the average shape of the two conformations present.[8,12] The equatorial conformation actually may be puckered more and the axial conformation less (or even flattened).

Although ring reversal interconverts the axial and equatorial conformations of the arsenanes and phosphorinanes, it does not alter the cis/trans relationship of the ring protons with the 1 substituent, because atomic inversion is slow about phosphorus and arsine.[13] As a result, the spectrum of the α,β protons of **6a**, for example, is ABCD.[8] In contrast, all of the spectra of the halogen adducts are AA′BB or AA′XX′. Before examining the value of the coupling constants, we would like to comment briefly on this higher spectral symmetry, which can arise from a number of causes. (1) The trigonal bipyramid should give AA′BB′ spectra, provided that the rear end of the ring (**8**) is flipping rapidly above and below the plane of the C–As–C segments. (2) For the molecular complex **9**, rapid dissociation of halogen or methyl halide, atomic inversion, and association from the opposite side would render the spectrum AA′BB′. Normally, a halo substituent raises the barrier to inversion, so that this explanation seems unlikely in light of the known height of arsenic and phosphorus inversion barriers.[13] (3) Rapid nucleophilic attack by the anion X^- or X_3^- on the tetravalent central atom of the ionic molecular complex **10** (eq 3) would render the spectrum AA′BB′, since ring reversal is rapid at room temperature. Such a process requires no assumption as to whether the substituent R is axial or equatorial or a mixture. For the molecular complex, we favor the third rather than the second explanation for the AA′BB′ symmetry of the spectra, since it does not have to invoke rapid inversion about the central atom. The transition state for this process (eq 3) would in fact be the trigonal bipyramid (**8**). Alternatively, **8** could be an actual intermediate between the two molecular complexes of eq 3. The observed symmetry for the MC adducts therefore might only reflect the fact that they are in equilibrium with an unobservable TB. The main point to be emphasized, however, is that some dynamic process must be operating within the molecular complex, since the symmetry of the free base is such as to give an ABCD spectrum, and complexation alone does not alter this symmetry.



(3)

Table IV. Structural Classification of 1:1 Halogen Complexes[a]

	Cl_2	Br_2	I_2
P	MC[b]	MC[b]	MC[b]
As	TB[c]	TB[c]	MC[b]
Sb	(TB)	(TB)	(TB)
S	(TB)(?)	MC[c]	MC[c]
Se	(TB)	TB[c]	MC[c]
Te	(TB)	TB[c]	(TB)

[a] Structures in parentheses are inferred. [b] Based on conductance only. [c] Based on conductance and NMR.

The spectra (Figures 7, 8)[7] of the α,β protons of the 1:1 Cl_2 and Br_2 complexes of **6** have the deceptively simple triplet structure that we have found to be characteristic of a low *R* value[5] and hence of an extremely flattened ring ($\Psi = 45–49°$) (Table II).[14] Furthermore, the *R* value of the β,γ portion of the ring (Figure 9)[9] indicates considerable puckering ($\Psi = 66–67°$), and this type of distortion is a common response to flattening at the opposite end of a six-membered ring.[5] These torsional angles are exactly what is expected of a trigonal bipyramid **8**, in agreement with the observation of extremely small conductance. Insolubility of the 1:1 I_2 complex prevented analysis of its NMR spectra. The conductance results indicate that the 1:1 I_2 complex should not be appreciably distorted in the molecular complex **10** from the shape of the parent arsenane.

The 1:2 Br_2 adduct (Figures 10 and 11)[7] gave *R* values and torsional angles ($\Psi = 58–63°$) (Table II) that are characteristic of the relatively undistorted (slightly puckered) ring expected for a molecular complex (**11**), in agreement with the conductance results.

Thus the NMR results prove conclusively that the 1:1 Cl_2 and Br_2 complexes of 1-methylarsenane are trigonal bipyramids (**8**), and confirm that the 1:2 Br_2 adduct has the molecular complex structure (**11**).

A few comments are in order on the magnetic resonance parameters listed in Table III. The α protons are shifted downfield by about 2 ppm, and the α carbons are shifted downfield about 30 ppm on complexation with halogen. Some of the shift must be due to the electron-withdrawing nature of the halogen substituent. The positive charge in the ionic molecular complex should also cause a downfield shift. Furthermore, in the trigonal bipyramid, the equatorial bonds from P or As to carbon are sp^2–sp^3. The sp^2 character of the orbitals from M to C would have a downfield effect. Electric field effects also might be important. The effect of halogen here is probably a complex function of several factors. One important feature of the ^{13}C spectrum of 1-phenylarsenane (**7**) is the extremely high-field resonance of the ipso carbon, 97 ppm (compared to 138 ppm for the ipso carbon of toluene). This upfield shift is another example of the heavy atom effect observed in bromo and iodo compounds. In fact, the chemical shift of the ipso carbon is almost the same in the arsenic compound **7** as it is in iodobenzene (95 ppm).

Comparison with the Group 6 Halogen Adducts. The results of these studies on the group 5 adducts are summarized in Table IV, together with our earlier results[5] on group 6 adducts, which did not include Cl_2. For the 1:1 Br_2 and I_2 adducts, the results for group 5 precisely parallel those for group 6. Our previous inference that all the group 6 Cl_2 adducts are trigonal bipyramids rather than molecular complexes may be in error, since we have now observed that the phosphine adduct is indeed a molecular complex. It would be worthwhile to examine the Cl_2 adducts of the group 6 compounds to determine whether any are simple molecular complexes, in particular the sulfide. To the extent that the experimental data go, however, at present there is complete structural parallelism between the two groups.

The group 5 bases form stable isolable 1:2 adducts with Br_2 and I_2. The conductance clearly levels off after 2 equiv of halogen has been added (Figures 2, 3, 5, 6).[7] There is no evidence for higher order adducts. In contrast, the group 6 bases show a sharp leveling off only at the 1:1 ratio, and the conductance then continues to increase slowly after many equivalents of halogen have been added. We interpreted these results in terms of the presence of higher order adducts (1:2, 1:3, 1:4, etc.) that are favored by the addition of excess halogen.[5] The group 5 results are cleaner, since only two adducts need to be considered.

Conclusions

The method of coupling constant ratios shows that the 1:1 Cl_2 and Br_2 adducts of 1-methylarsenane have the extremely flattened chair that is characteristic of the trigonal bipyramid **8**. In addition, these complexes are almost nonconducting. The conductance titrations indicate that the 1:1 I_2 adduct with 1-methyl- or 1-phenylarsenane and the 1:1 adducts of all three halogens with 1-methyl- or 1-phenylphosphorinane are ionic molecular complexes of the type **10**, although there may be an equilibrium with the nonionic form **9**. The R value, conductance, and ultraviolet experiments indicate that the 1:2 Br_2 and I_2 adducts with these substrates are all halo-onium trihalides of the type **11**, with a relatively undistorted ring. These results parallel most but not all of the characteristics of group 6 (sulfide, selenide, telluride) adducts with halogen.[5] The AA′BB′ nature of the proton spectra of all the group 5 complexes indicates in some cases that the trigonal bipyramid is favored and in others that the favored molecular complex must be in rapid equilibrium with an unobserved trigonal bipyramid through nucleophilic attack of the anion on the positively charged P or As. As is normally the case, strongly electronegative substituents (Cl) favor an apical position and hence the trigonal bipyramidal structure. Increased electropositive nature of the central atom (P to Sb) has the same effect. In reverse, the lower electronegativity substituents (I) and higher electronegativity central atoms (P) favor the molecular complex.[5]

Experimental Section

^1H NMR spectra were recorded at 60 MHz on Varian T-60 and Perkin-Elmer R-20B spectrometers, at 90 MHz on a Bruker HFX-90 spectrometer, and at 270 MHz on a Bruker HX-270 spectrometer (at the University of Chicago). The HFX-90, HX-270, and R-20B spectrometers were equipped with variable temperature units. The HFX-90 and R-20B spectrometers were also equipped with heteronuclear broad-band noise decouplers for deuterium decoupling. Carbon-13 chemical shifts were obtained on the HFX-90 spectrometer, operating at 22.628 MHz as described elsewhere.[11]

Conductance measurements were obtained on an Industrial Instrument Inc. conductance bridge, Model 16B2. Conductance titrations were carried out by placing a solution (1,2-dichloroethane or dichloromethane) of the phosphine or arsine in the conductance cell at room temperature under N_2. Volumetrically calibrated amounts of halogen in the same solvent were then added in a stepwise fashion, and the conductance was measured after each addition. The conductance of the solutions did not vary with time. Conductances were corrected for volume. The cell constant was found to be 0.246 cm^{-1} from measurements on a 0.010 M aqueous solution of KCl at 25 °C. UV spectra were recorded on a Cary Model 14 spectrometer. IR spectra were obtained on Beckman IR-5, IR-9, and IR-10 spectrometers. A Control Data Corp. Model 6400 digital computer equipped with a Calcomp plotting accessory Model 1136 was used for NMR spectral analysis and plotting. Programs ENIT and NMRPLOT were used for the analyses. Melting points (uncorrected) were determined in a Thiele tube apparatus. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., and by H. Beck of the Analytical Services Laboratory, Department of Chemistry, Northwestern University. All reactions were carried out under dry N_2. Solvents were distilled from appropriate drying agents and stored over molecular sieves. Ethyl ether was distilled from $LiAlH_4$ prior to use. All other commercially available reagents were used without further purification.

1-Methylphosphorinane (4) was prepared by the method of Featherman and Quin.[12] Details may also be found elsewhere.[10] From 0.18 mol of methyldichlorophosphine (a gift from Ethyl Corp.) and 0.2 mol of the di-Grignard reagent from 1,5-dibromopentane was obtained 8.0 g (35%) of the product, bp 146–148 °C (lit.[12] 144–147 °C). Deuteration followed the procedures of our earlier work.[5]

1-Phenylphosphorinane (5) was prepared by a procedure analogous to that for 1-methylphosphorinane above.[10] Phenyldichlorophosphine (Eastman, 18.0 g, 0.1 mol) and 0.12 mol of the di-Grignard reagent from 1,5-dibromopentane were used to give 6.6 g (37%) of the desired product, bp 104–110 °C (12 mm) [lit.[15] 143–144 °C (16–18 mm)].

1-Methylarsenane (6) and its deuterated derivatives (**6a, 6b**) were prepared as described before.[8]

1-Phenylarsenane (7) was prepared by the same procedure as used for 1-methylarsenane (**6**). Phenyldichloroarsine (15.6 g, 0.07 mol) and 0.1 mol of the di-Grignard reagent from 1,5-dibromopentane were used to give a 31% yield of the desired product, bp 155–158 °C (20 mm) [lit.[16] 84 °C (0.5 mm)].

1-Methylarsenane 1,1-Dichloride (1:1 Adduct). Dry Cl_2 was bubbled through a 25-mL CCl_4 solution containing 0.176 g (1.1 mmol) of 1-methylarsenane (**6**) until the solution became slightly yellow. Solvent and excess Cl_2 were removed immediately at reduced pressure to leave a white solid. The yield was quantitative (>95%), mp 163 °C dec (sealed tube) (lit.[17] 166 °C). Anal. Calcd for $C_6H_{13}AsCl_2$: C, 31.20; H, 5.67. Found: C, 31.31; H, 5.67.

1-Methylarsenane 1,1-Dibromide (1:1 Adduct). 1-Methylarsenane (**6**, 0.16 g, 0.001 mol) was dissolved in 25 mL of CH_2Cl_2, and Br_2 (0.001 mol) in 15 mL of CH_2Cl_2 was added dropwise with ice cooling. After all the Br_2 had been added, the solvent was removed at reduced pressure to give white, hygroscopic, flaky crystals. The yield was quantitative (>97%), mp 62 °C dec (sealed tube) (lit.[18] 60 °C). Anal. Calcd for $C_6H_{13}AsBr_2$: C, 22.53; H, 4.10. Found: C, 22.55; H, 4.35.

1-Methylarsenane 2Br$_2$ (1:2 adduct) was prepared by dissolving 0.16 g (0.001 mol) of 1-methylarsenane (**6**) in 50 mL of $ClCH_2CH_2Cl$. To this solution was added quickly an excess of Br_2 (0.0025 mol) in 25 mL of the same solvent. After all the Br_2 had been added, the solution was stirred at room temperature for 1 h. The solvent and excess Br_2 were removed at reduced pressure to leave bright orange-red crystals. The yield was quantitative (>97%), mp 91–92 °C dec (sealed tube). The UV spectrum in $ClCH_2CH_2Cl$ gave two characteristic Br_3^- bands at λ_{max} 275 (ϵ 13 300) and 390 nm (1700). This compound is thermochromic. When cooled to −78 °C, the color becomes much lighter. Anal. Calcd for $C_6H_{13}AsBr_4$: C, 15.02; H, 2.73. Found: C, 15.15; H, 2.79.

1-Methylarsenane I$_2$ (1:1 Adduct). To a solution containing 0.16 g (0.001 mol) of 1-methylarsenane (**6**) and 50 mL of dry CCl_4 was added dropwise 0.25 g (0.001 mol) of I_2 in 50 mL of CCl_4 with ice cooling and vigorous stirring. A yellow solid precipitated out immediately. After all the I_2 had been added, the solvent was removed at reduced pressure. The yield was quantitative (>97%), mp 120 °C dec (sealed tube). This compound is slightly soluble in 1,2-dichloroethane (5.8×10^{-3} mol/L), 1,1,2,2-tetrabromoethane, and CH_2Cl_2. The 1,1,2,2-tetrabromoethane solution, however, gave a brown color that was different from the crystal color.

1-Methylarsenane 2I$_2$ (1:2 Adduct). To a solution containing 0.16 g (0.001 mol) of 1-methylarsenane (**6**) and 150 mL of $ClCH_2CH_2Cl$ was added slowly 0.51 g (0.002 mol) of I_2 in 100 mL of the same solvent with vigorous stirring. A deep violet solution was formed. The solvent was removed to give a quantitative yield of a deep red-violet powder of the desired product in quantitative yield (>97%), mp 110–114 °C dec (sealed tube). The UV spectrum in 1,2-dichloroethane revealed two absorption maxima characteristic of I_3^- ions: λ_{max} 295 (ϵ 30 000) and 365 nm (17 000).

1-Bromo-1-methylarsenanium Tetrafluoroborate. To an oven-dried 150 × 16 mm test tube was added 0.0371 g (0.192 mmol) of $AgBF_4$. The tube was sealed with a rubber septum. These operations were carried out in a drybox. A solution of 1-methylarsenane 1,1-dibromide was prepared by treating a $ClCH_2CH_2Cl$ solution containing 0.18 mmol of the arsine with 0.18 mmol of Br_2 in the same solvent. The resulting solution was transferred to the previously prepared tube of $AgBF_4$. The tube was shaken vigorously to ensure complete mixing. The tube then was centrifuged to compact the AgBr, and the sample was stored at −11 °C for 72 h. The supernatant was then removed via syringe to the conductance cell. The reaction tube was washed with 3×10 mL of $ClCH_2CH_2Cl$, followed each time by centrifugation, with the supernatant added to the conductance cell.

1-Iodo-1-methylarsenanium Tetrafluoroborate. The procedure paralleled the method given above for the bromine compound.

1-Methylphosphorinane Cl_2 (1:1 adduct), 1-methylphosphorinane Br_2 (1:1 adduct), 1-methylphosphorinane $2Br_2$ (1:2 adduct), 1-methylphosphorinane I_2 (1:1 adduct), and 1-methylphosphorinane $2I_2$ (1:2 adduct) were prepared from 1-methylphosphorinane (**5**) in the same fashion as the corresponding arsenic adducts described above.

Registry No.—Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; 1-methylarsenane I_2, 61395-02-6; 1-methylarsenane $2I_2$, 61395-03-7; 1-methylphosphorinane Cl_2, 61395-04-8; 1-methylphosphorinane Br_2, 61395-05-9; 1-methylphosphorinane I_2, 61395-06-0.

Supplementary Material Available. Figures 4–7, 10, and 11 (6 pages). Ordering information is given on any current masthead page.

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Photochemical 1,3-Addition of Anisole to Olefins. Synthetic Aspects

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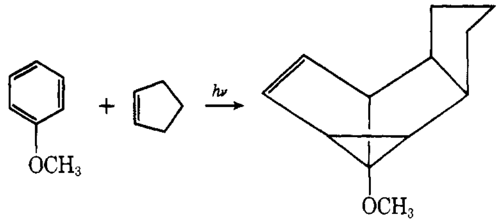
Received June 14, 1976

Anisole undergoes photochemical 1,3-addition to a variety of olefins with about the quantum efficiency of benzene but in considerably greater chemical yield. The latter feature may result from the stability of the adducts to continued irradiation. A 1,3 photoadduct of an aromatic compound (anisole) to cyclohexene has been isolated for the first time. All of the 1,3 adducts rearrange readily on treatment with acid to derivatives of bicyclo[3.2.1]oct-2-en-8-one.

The photochemical 1,3-addition of benzene to olefins has been the subject of numerous investigations over the past 10 years.[1] Although both 1,2- and 1,4-additions occur concurrently to various extents, 1,3-addition is usually the dominant process when olefins lacking powerful substituent groups are used. The synthetic potential of this reaction has been limited by the difficulty in the isolation of the products and the susceptibility of the photoadducts to secondary photolysis.

It has been shown[2] that the 1,3-addition of anisole to cyclopentene under the influence of light proceeds in high chemical yield and that the reaction shows a great degree of locospecificity. Since the product **1** underwent rearrangement readily with acid (often even without a preliminary separation) to a bicyclo[3.2.1]octen-8-one, the synthetic potential of this reaction merited further investigation. These results are reported here. A few data on the mechanistic aspects of this reaction are also included but the bulk of the studies on the mechanism are published elsewhere.[3]



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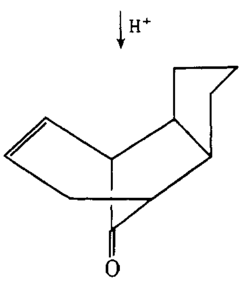

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(2)

Results

Exactly the same procedure was followed in all of the photoaddition reactions. A solution of the olefin (2 M) and anisole (2 M) in cyclohexane was irradiated at 254 nm without degassing the solution until product formation (as monitored by GLC) slowed down to a negligible rate. The isolated yields of the products, product composition, and the quantum yields in the initial stages of the reaction are given in Table IA and IB. The former lists the addition of anisole to various olefins and the latter the addition of alkyl-substituted anisoles to cyclopentene. *o*-Methylanisole did not undergo addition under these conditions. The structures of the 1,3 adducts have been established by (1) elemental analyses and/or high-resolution mass spectrometry which showed that they were 1:1