# COMPOUNDS OF PENTACOORDINATED ARSENIC(V)

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## I. Introduction

Since about 1969 there has been increased interest in the pentacoordination of main-group elements and also in the role of pentacoordination in reaction mechanisms (*101–106, 112, 118, 124, 136, 151, 163, 186, 201*). Structural studies have shown that compounds that contain pentacoordinated elements form a continuous range of conformations extending from the ideal trigonal bipyramid to the square or rectangular pyramid. In this respect, the compounds of pentacoordinated phosphorus (*105, 106, 124*), arsenic, and antimony (*112*) are unique and interesting. During these years a considerable number of papers have been published dealing with the chemistry of compounds of pentacoordinated arsenic(V) (arsorane) and organoarsenic(V) (organoarsorane), but have been mentioned in a scattered fashion in some review articles, books, and treatises (*41, 49, 50, 111, 130, 153, 178*). Although since 1967, the work published on the chemistry of organoarsoranes has been abstracted in *Annual Surveys of Organometallic Chemistry*, there is as such no review article dealing exclusively with compounds of pentacoordinated arsenic(V). This account has been constructed mainly to focus attention on the dynamic stereochemistry, structure,

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and bonding aspects of these compounds. An attempt has been made to cover almost all of the pertinent literature through the end of 1982.

## II. As—C-Containing Compounds

Many compounds of pentacoordinated arsenic(V) containing only As—C bonds are reported in the literature and are summarized in Table I.

Although more than 100 years ago Cahours (*35*) claimed to have obtained pentamethylarsorane by the reaction of dimethylzinc with tetramethylarsonium iodide, subsequent attempts (*55, 195*) to synthesize pentaalkylarsoranes by the reaction of tetraalkylarsonium salts with organometallic compounds were unsuccessful. However, Mitschke and Schmidbaur (*137*) have obtained pentamethylarsorane in 80% yield by the following reaction:

$$Me_3AsCl_2 + 2MeLi \xrightarrow[-60°C]{Me_2O} Me_5As + 2LiCl$$

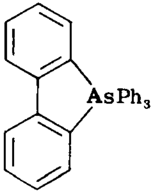
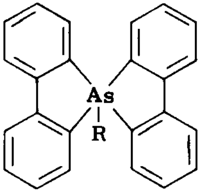
On the basis of spectral studies a trigonal–bipyramidal structure has been proposed for this compound. Low-temperature $^1$H-NMR spectra in toluene indicate that all methyl protons are magnetically equivalent down to −95°C and that the exchange of methyl groups at the equatorial and axial positions in $Me_5As$ is faster than the NMR scale (*137*).

As compared to pentaalkylarsorane, a considerable number of pentaarylarsoranes are known (Table I). Pentaphenylarsorane has been prepared in 65% yield by the reaction of phenyllithium and tetraphenylarsonium bromide (*194*). Reaction of triphenyldichloroarsorane and phenyllithium also gives the same compound, but in poor yield. Formation of this compound has also been reported by the reaction of phenyllithium with triphenylarsenic oxide or with the imine *p*-$CH_3C_6H_4N{=}AsPh_3$ (*198*). The reactions of pentaphenylarsorane have been investigated (*194, 198*). It reacts with excess halogens to give the corresponding tetraphenylarsonium halides and halobenzenes. It can also be cleaved by acids. It decomposes on heating to give mainly triphenylarsane with smaller amounts of biphenyl and benzene.

The unit cell of $Ph_5As$ has been reported by Wheatley and Wittig (*187*). From these data it has been concluded that the molecule adopts the expected trigonal–bipyramidal conformation, very similar to that found for pentaphenylphosphorane (*189*). It is interesting to mention here that the unsolvated $Ph_5Sb$ crystallizes with square–pyramidal geometry (*15, 188*) in a triclinic cell rather than in the monoclinic *Cc*

TABLE I

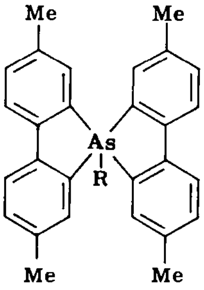
COMPOUNDS OF PENTACOORDINATED ARSENIC(V) CONTAINING As—C BONDS

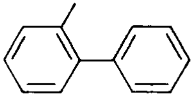
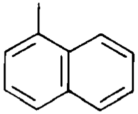
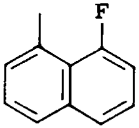
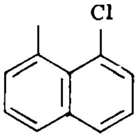
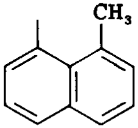
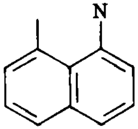
| Compound | Melting point (°C) | Physical measurements | Reference |
|---|---|---|---|
| $Me_5As$ | −6 to −7<br>(bp −10/0.1) | Vibrational spectra, $^1H$ NMR, DTA, mass spectra | *137, 195* |
| $Ph_5As$ | Colorless crystals<br>139.5 (decomp.) | Dipole moment, vibrational spectra, mass spectra, X-ray diffraction | *14, 31, 96, 126, 187, 194, 196, 198* |
| $Ph_5As \cdot 0.5C_6H_{12}$ | 149–150 | Lattice energy calculations, X ray | *30, 32* |
| $(p\text{-}MeC_6H_4)_5As$ | 139–140 | $^1H$ NMR, $^{13}C$ NMR | *84, 87, 121* |
| $(p\text{-}ClC_6H_4)_5As$ | 149 | $^1H$ NMR | *87* |
|  | 188–189 | Thermal decomposition | *87, 196, 198* |
|  | | | |
| R = Me | Colorless crystals<br>215–216 | IR, $^1H$ NMR, mass spectra, thermal decomposition | *87, 96* |

(*continued*)

TABLE I (*continued*)

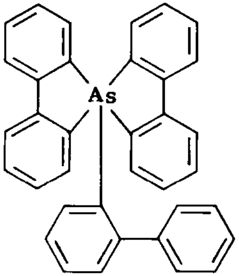
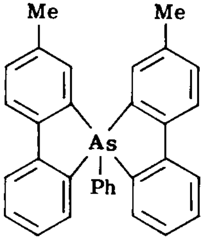
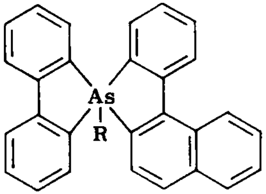
| Compound | Melting point (°C) | Physical measurements | Reference |
|---|---|---|---|
| R = Et | 173–174 (decomp.) | IR, mass spectra, thermal decomposition | *87* |
| R = *i*-Pr | 148–149 (decomp.) | IR, $^1$H NMR, mass spectra, thermal decomposition | *94* |
| R = Bu | 166–166.5 (decomp.) | IR, mass spectra, thermal decomposition | *87, 199* |
| R = *t*-Bu | 102–103 (decomp.) | IR, $^1$H NMR, mass spectra, thermal decomposition | *94* |
| R = Vinyl | 176–177 (decomp.) | IR, $^1$H NMR, mass spectra, thermal decomposition | *94* |
| R = Cyclopentyl | 114–115 (decomp.) | IR, $^1$H NMR, mass spectra, thermal decomposition | *94* |
| R = Ph | 233–235 | IR, mass spectra, thermal decomposition | *87, 96, 196, 198, 199* |
| R = *cis*-Styryl | 124–126 | IR, $^1$H NMR, thermal decomposition | *94* |
| R = *trans*-Styryl | 115–117 | IR, $^1$H NMR, thermal decomposition | *94* |
| R = *p*-$ClC_6H_4$ | 196–197 | | *87* |
| R = *p*-$CH_3C_6H_4$ | 211–212 | | *87* |
| R = *p*-$(CH_3)_2NC_6H_4$ | 234–236 | Thermal decomposition | *87, 198* |

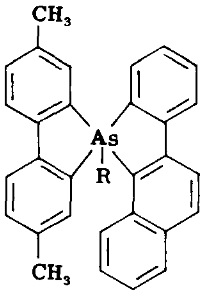
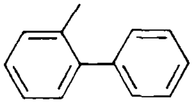
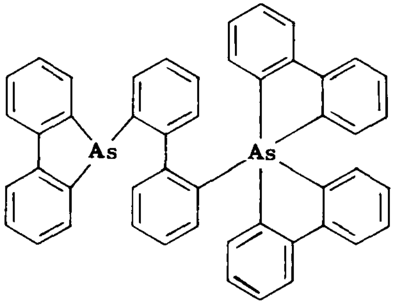


| | | | |
|---|---|---|---|
| R = $PhCH_2$ | 142–144 | IR, $^1H$ NMR, mass spectra | *88, 95, 97* |
| R =  | 141–143 | IR, $^1H$ NMR, mass spectra | *88, 95, 97* |
| R =  | 223–224 | IR | *97* |
| R =  | 211–213 | IR, $^1H$ NMR | *97* |
| R =  | 220–221 | IR, $^1H$ NMR | *97* |
| R =  | 215–217 | IR, $^1H$ NMR | *97* |
| R =  | 182–184 | IR, $^1H$ NMR | *97* |

(*continued*)

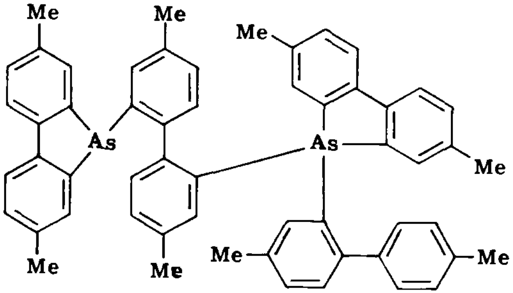
TABLE I (*continued*)

| Compound | Melting point (°C) | Physical measurements | Reference |
|---|---|---|---|
|  | 230–232 | Optical activity | *82, 126* |
|  | 191–193 | Optical activity | *198* |
|  <br>R = $p$-$(CH_3)_2NC_6H_4$ | 190 |  | *198* |

| | | | |
|---|---|---|---|
|  | | | |
| R = Ph | 198–200 | $^1$H NMR | *98* |
| R =  | 224–227 | $^1$H NMR | *98* |
|  | 221–224 | $^1$H NMR, mass spectra | *89, 93* |

(*continued*)

TABLE I (*continued*)

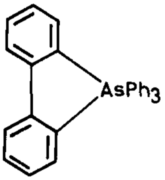
| Compound | Melting point (°C) | Physical measurements | Reference |
|---|---|---|---|
|  | 185–188 | $^1$H NMR | *93* |

cell observed for the arsenic and phosphorus molecules. It has been suggested that crystal-packing forces in the solid state cause $Ph_5Sb$ to exhibit square–pyramidal geometry (*15, 188*). Later, a detailed study has been reported of the low-frequency (below 400 $cm^{-1}$) solid state and $CH_2Cl_2$ or $CH_2Br_2$ solution vibrational spectra of both $Ph_5As$ and $Ph_5Sb$ (*14*). From this study, it has been suggested that both compounds retain their solid-state structures in solution and that the structure of $Ph_5Sb$ in the solid state might not be due to packing effects. The role of coulombic interactions in explaining the anomalous structure of $Ph_5Sb$ has been advanced (*31*).

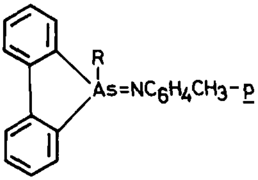
The structure of the cyclohexane solvate of pentaphenylarsorane, $Ph_5As \cdot \frac{1}{2}C_6H_{12}$, has been determined by X-ray crystallographic analysis (*30*). The substance crystallizes in space group $P\bar{1}$, cell dimensions $a$ = 10.448(9), $b$ = 10.566(21), $c$ = 14.905(25) Å, $\alpha$ = 121.09(5), $\beta$ = 106.38(4), $\gamma$ = 92.44(5)°, with one $Ph_5As$ and one-half $C_6H_{12}$ molecule in the asymmetric unit. This molecule is an undistorted trigonal bipyramid with average axial and equatorial As—C bond lengths of 2.105(7) and 1.964(11) Å, respectively. The molecular conformation, as measured by phenyl ring rotations, of $Ph_5As$ has been found to be very similar to that of the analogous phosphorus compound (*189*) and to that of $Ph_5Sb \cdot \frac{1}{2}C_6H_{12}$ (*27*). $^{13}C$-NMR solution spectral study indicates that $\alpha$-carbons of both pentaphenylarsorane and pentaphenylstiborane are magnetically equivalent down to 173 K. This suggests a rapid interconversion between axial and equatorial sites, presumably through an intermediate square–pyramidal geometry (*171*). Semiempirical calculations have been made for crystals of $Ph_5M \cdot \frac{1}{2}C_6H_{12}$ (M = P, As, or Sb) (*32*). From this study, it has been suggested that the molecular packing is not considerably affected by a change in the central group VA element.

The $^1H$-NMR spectrum of penta-*p*-tolylarsorane exhibits a single signal of the methyl protons (*84*). The magnetic equivalence of the five methyl groups is not consistent with either a trigonal–bipyramidal or a square–pyramidal structure. It has been assumed that rapid pseudorotation averages the environment of the five groups attached to the arsenic atom. $^1H$- and $^{13}C$-NMR investigations of this compound as well as of pentaaryl group VA compounds have also been reported (*87, 121*). The question of the stereochemistry of these compounds in solution is not readily answered. There is no static solution structure, except at low temperatures. The low-energy barrier indicates that ligand size is not a dominant factor in limiting the exchange process.

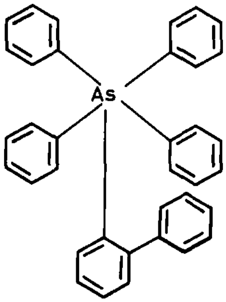
Reaction of the imine *p*-$CH_3C_6H_4N{=}AsPh_3$ with 2,2′-biphenylenedilithium yields the heterocyclic compound **I** (*198*). This compound can also be obtained by the reaction of a dilithium compound with an imine of type **II** or by the reaction of spirocyclic arsonium halides with either



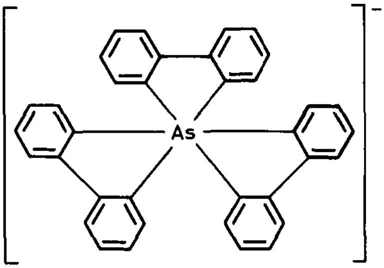
I



II (R = alkyl or aryl)

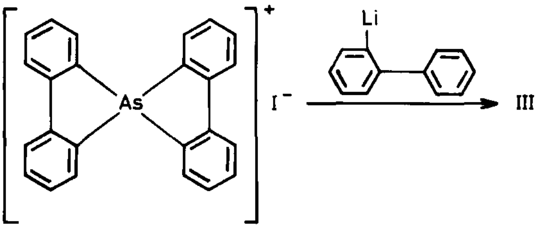


III



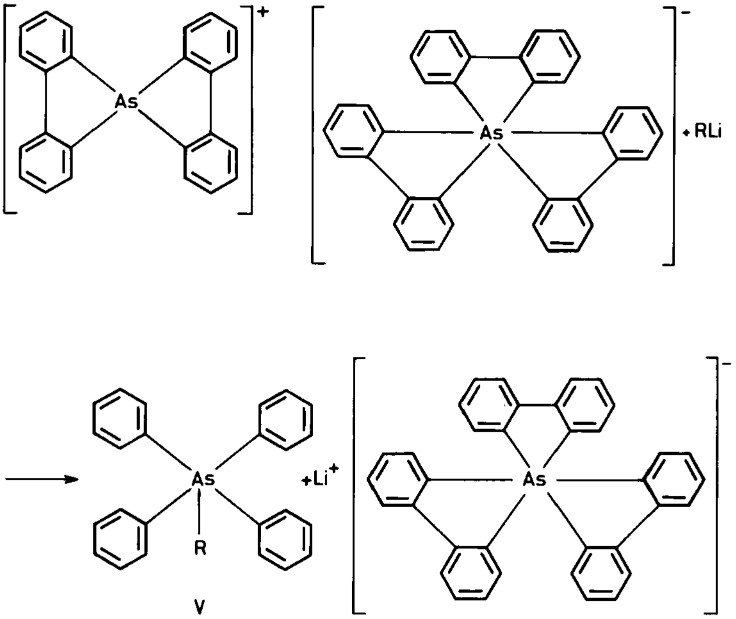
IV

lithium (*87*, *198*) or Grignard (*198*) reagents. Compound **III** may be obtained by the acid cleavage of the lithium salts of **IV** or by the following reaction (*86*):

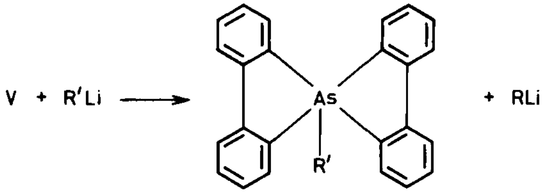


Compound **III** has been found to be optically inactive, suggesting pseudorotation between trigonal–bipyramidal and tetragonal conformations (*86*).

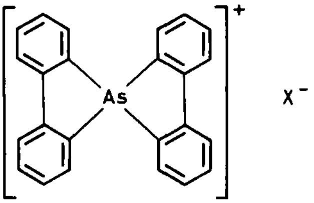
Compounds of type **V** have been prepared by the following reaction (*86*):



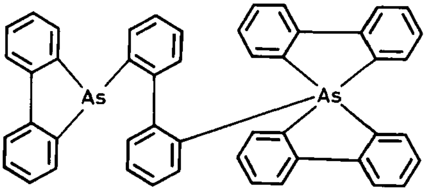
Alternatively, use may be made of exchange reactions of the following type:



The isopropyl compound **V**, (R = $Me_2CH$) has readily been obtained from **VI** and isopropylmagnesium chloride in ether solution (*94*); but when R = cyclopentyl, THF has been found to be necessary for effecting the reaction. When R = *tert*-butyl the Grignard reaction yielded the dimer **VII**, but the desired **V** (R = *tert*-butyl) has been obtained

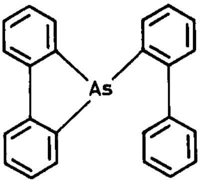


VI



VII

from *tert*-butyllithium and the arsonium salt **VI**. Compound **V** (R = *tert*-butyl) has been found to be unstable at room temperature. It decomposes to the tertiary arsane **VIII** and isobutylene. The reactions of the compounds of type **V** have been found to be quite similar to those of the pentaphenylarsorane (*87, 94*). For example, **V** (R = Ph) reacts with several electrophilic reagents with cleavage of one of the heterocyclic rings and the formation of an arsonium compound. The cleavage of the compounds **V** (R = Me, Et, or $PhCH_2$) with boiling alcohol has also been investigated. The tertiary arsane **VIII** has been obtained in each case. The reaction has been followed by means of deuterium-labeled ethanol.

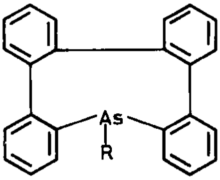


VIII

When compounds of type **V** are subjected to strong nucleophiles such as lithium organyls, the spiro skeleton remains unaffected and only the single ligand R is exchanged (*85, 87*). It has been shown that the exchangeability of R increases along the following sequence (*87*):

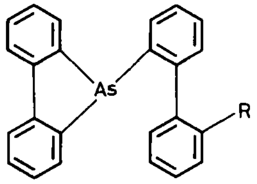
$$n\text{-}C_4H_9 \ll p\text{-}Me_2NC_6H_4 \sim CH_3 \sim p\text{-}MeC_6H_4 < p\text{-}ClC_6H_4 < C_6H_5$$

When compounds **V** (R = ethyl, isopropyl, cyclopentyl, *n*-butyl, or *tert*-butyl) have been heated 30–50°C above their melting points, **VIII** and the corresponding olefins have been obtained by $\beta$ elimination (*87, 94*). The course of the reaction has been controlled by the use of the deuterium-labeled compound **V** (R = $CD_2Me$). It has been shown that all of the deuterium occurred in the ethylene formed by thermolysis (*94*). When R is methyl or phenyl, the thermolysis of **V** results in formation of **IX**. The styryl derivatives of **V** (R = *cis*-CH═CHPh and *trans*-CH═CHPh) have also been synthesized from **VI** and the corresponding Grignard reagents (*94*). Interestingly, thermolysis of these deriva-



IX

tives did not produce phenylacetylene by β elimination as expected, but rather **X** (R = *cis*-styryl and *trans*-styryl, respectively). Thermolysis of the vinyl compound **V** (R = CH═$CH_2$) gives a mixture of acetylene, **VIII**, and the rearranged product **X**.



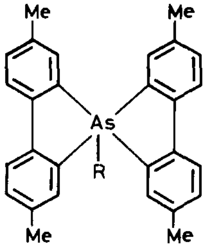
X

Reaction of **VI** with neopentylmagnesium bromide yields a product of molecular weight, as found by mass spectroscopy, corresponding to **V** (R = $CH_2CMe_3$). However, this compound exhibits all the properties of the tertiary arsane **X** (R = $CH_2CMe_3$) (*94*).

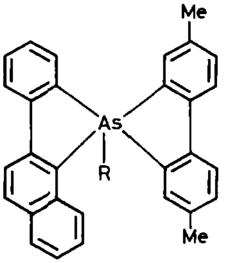
Mass spectra of pentaphenylarsorane and some compounds of type **V** have been reported and compared with the corresponding derivatives of group VA elements (*92, 94, 96*). The mass spectra of some of the phosphorus- and arsenic-substituted biphenyl systems show doubly charged parent ions of higher abundance than the singly charged molecular ions (*92*). Characteristic IR bands of compounds of type **V** have been summarized in Table II.

Dynamic NMR spectroscopy of compounds of types **V** and **XI** (R = organyl) indicates that these, like analogous phosphorus compounds, possess trigonal bipyramidal ground states that show intramolecular ligand equilibrations even at low temperatures (*95*). Activation energies of the order of 12–19 kcal/mol have been observed, depending on the bulkiness of the organyl group R (*84, 90, 94, 95, 97*).

Hellwinkel *et al.* (98) have also carried out an $^1$H-NMR investigation of some overcrowded asymmetric phosphoranes, arsoranes, and stiboranes. In **XII** (R = phenyl or biphenyl), the two different positions are reversibly equilibrated at elevated temperatures.



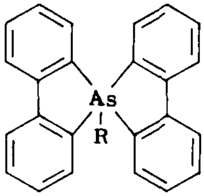
XI



XII

TABLE II

CHARACTERISTIC INFRARED BANDS OF



| R | Bands (cm$^{-1}$) | Reference |
|---|---|---|
| Methyl | 652, 667 | *87* |
| Ethyl | 652, 667 | *87* |
| Isopropyl | 643, 665 | *94* |
| Butyl | 650, 667 | *87* |
| *tert*-Butyl | 645, 664 | *94* |
| Cyclopentyl | 643, 665 | *94* |
| Vinyl | 650, 662 | *94* |
| *cis*-Styryl | 653, 669 | *94* |
| *trans*-Styryl | 655, 666 | *94* |
| Benzyl | 645, 665 | *94* |
| Phenyl | 653, 667 | *87* |
| *p*-Tolyl | 653, 670 | *87* |
| *p*-Chlorophenyl | 654, 670 | *87* |
| *p*-Dimethylaminophenyl | 653, 667 | *87* |
| 2-Biphenylyl | 655, 668 | *86* |
| 2′-(2,2′-Biphenylylenearsino)-2-biphenylyl | 653, 667 | *94* |

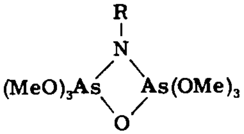
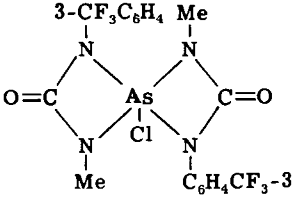
The free enthalpies of activation have been measured and an interpretation is offered starting with a trigonal–bipyramidal ground state conformation. The ligand exchange phenomenon is discussed in terms of a pseudorotation process and trigonal–bipyramidal transition states with diequatorial biarylylene groups.

## III. As—N-Containing Compounds

Compounds of pentacoordinated arsenic(V) containing at least one As—N bond are summarized in Table III. Only some of these need discussion. Cycloarsa(V)azanes, which are apparently five-coordinated, have been prepared by aminolysis of pentamethoxyarsorane (*75, 80*). Various products have been reported, depending on the nature

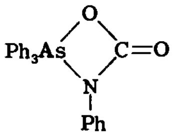
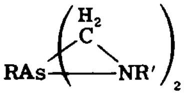
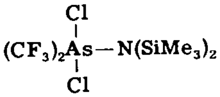
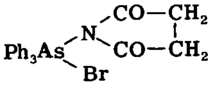
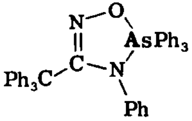
## TABLE III

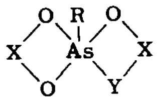
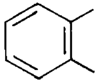
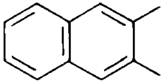
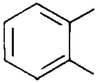
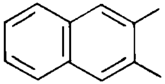
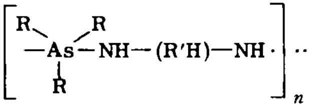
COMPOUNDS OF PENTACOORDINATED ARSENIC(V) CONTAINING As—N BONDS

| Compound | Melting point (°C) | Physical measurements | Reference |
|---|---|---|---|
| $[(MeO)_3AsNPh]_2$ | 120–121 | Molecular weight | *80* |
| $[(MeO)_2(n\text{-}PrNH)AsNPr]_2$ | 107–108 | Molecular weight | *80* |
| $[(MeO)_2(n\text{-}BuNH)AsNPr]_2$ | 54–55 | Molecular weight | *80* |
| $[(MeO)_2(PhCH_2NH)AsNCH_2Ph]_2$ | 80–81 | Molecular weight | *80* |
| $[(MeO)(PhCH_2NH)_2AsNCH_2Ph]_2$ | 72–74 | Molecular weight | *80* |
| $[(MeO)_2AsFNPr]_2$ | — | Molecular weight | *82* |
|  <br>R = $n$-Pr, $n$-Bu | — | $^1$H NMR, mass spectra | *81, 148* |
| $(MeO)_8As_4(NPh)_6$ | 180 (decomp.) | Molecular weight | *80* |
| $[(RNH)_2AsFNR]_2$ R = benzyl | 175 | Molecular weight | *82* |
| $(PrNH)_8As_4(NPh)_6$ | 155 (decomp.) | IR, $^1$H NMR, $^{19}$F NMR | *156* |
|  | 144–146 | IR, $^1$H NMR, $^{19}$F NMR | *156* |

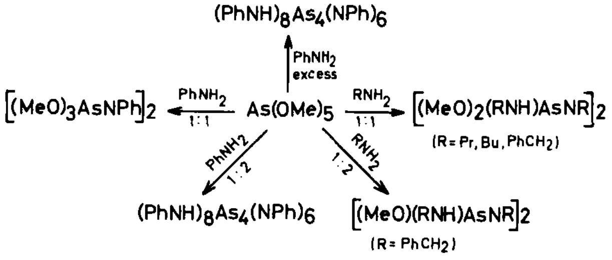
*(continued)*

TABLE III (*continued*)

| Compound | Melting point (°C) | Physical measurements | Reference |
|---|---|---|---|
|  | — | — | *29, 56, 57, 138* |
|  | — | — | *4* |
| $[(CF_3)_2AsClNSiMe_3]_2$ | 116 | IR, $^{19}F$ NMR, mass spectra, X ray | *23, 24, 157* |
|  $(CF_3)_2AsCl_2-N(SiMe_3)_2$ | 90 | IR, $^{1}H$ NMR, $^{19}F$ NMR, mass spectra, X ray | *23, 25* |
|  | 132–134 | IR, $^{1}H$ NMR | *43* |
| $Ph_3As(NCS)_2$ | 105; mp 104 | IR | *150, 21, 200* |
| ($p$-Tolyl)$_3$As(NCS)$_2$ | 158–160 | IR | *20, 21* |
|  | 182 | IR, mass spectra | *58* |

| | | | |
|---|---|---|---|
|  | | | |
| R = $CH_3$, X = $CH_2CH_2$, Y = $NCH_3$ | 40–42 | $^1H$ NMR, mass spectra | *128* |
| R = $CH_3$, X =  , Y = NH | 178–180 | $^1H$ NMR, mass spectra, X ray | *128, 204* |
| R = $CH_3$, X =  , Y = NH | 230–232 | $^1H$ NMR, mass spectra | *128* |
| R = $C_6H_5$, X = $CH_2CH_2$, Y = $NCH_3$ | 100 | $^1H$ NMR, mass spectra | *128* |
| R = $C_6H_5$, X =  , Y = NH | 178–180 (decomp.) | $^1H$ NMR, mass spectra | *128* |
| R = $C_6H_5$, X =  , Y = NH | 277–279 (decomp.) | $^1H$ NMR, mass spectra | *128* |
|  $\left[-\mathrm{As}(R)_3-NH-(R'H)-NH\cdot\right]_n\cdot\cdot$<br>$n$ = 4000; $10^5$ | — | Molecular weight | *36* |

of the amine and the molar ratio of the reagents, as shown below (**XIII**):



XIII

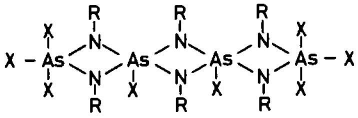
Aminolysis of other arsenic compounds also results in the formation of cyclodiars(V)azanes (*82*):

$$\mathrm{As(OMe)_4F + RNH_2 \longrightarrow As(OMe)_3(NHR)F + MeOH}$$

$$\mathrm{2As(OMe)_3(NHR)F \xrightarrow{vacuum} [As(OMe)_2(NR)F]_2 + 2MeOH}$$

$$\left.\begin{array}{r}\mathrm{As(OMe)_4F + RNH_2}\\ \mathrm{(excess)}\\ \mathrm{As(OMe)_3F_2 + RNH_2}\end{array}\right] \longrightarrow \begin{array}{c}\mathrm{[(RNH)_2AsFNR]_2}\\ \mathrm{(R = PhCH_2)}\end{array}$$

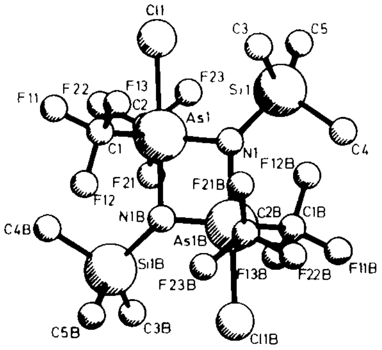
It has been suggested that dimers are probably four-membered As—N rings, with five-coordinated arsenic. However, no physical evidence is available except molecular weight measurements. Polymeric structures (**XIV**) may be suggested for $X_8As(NR)_6$; but again, any physical evidence is so far lacking:



XIV

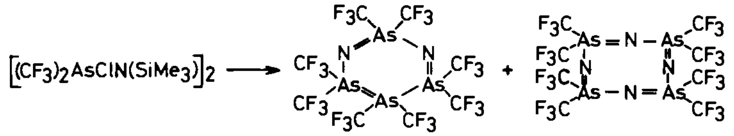
The synthesis, IR, $^{19}$F-NMR, and X-ray crystal and molecular structures of **XV** have been reported. It is the first well-characterized four-membered As—N ring compound with arsenic atoms of coordination number five. It has been prepared by the following reaction:

$$\mathrm{2(CF_3)_2AsN(SiMe_3)_2 + \underset{(5\text{–}10\%\ excess)}{2Cl_2} \longrightarrow [(CF_3)_2AsClN(SiMe_3)]_2 + 2Me_3SiCl}$$

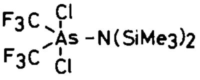


(XV) Molecular structure of $[(CF_3)_2AsClN(SiMe_3)]_2$

The $^{19}F$-NMR spectrum of **XV** indicates only one signal at −55.1 ppm at room temperature as well as at 153 K. Compound **XV** crystallizes in the orthorhombic space group *Pbca* with $a = 11.979(5)$, $b = 15.451(4)$, $c = 13.166(7)$ Å, $Z = 4$. The four-membered As—N ring is planar and the compound has a trigonal–bipyramidal geometry with axial and equatorial As—N bond distances of 1.933(7) and 1.768(7) Å. The difference of 0.165 Å between the two As—N bond lengths is somewhat greater than that in the corresponding cyclodiphos(V)azane (0.12–0.14 Å) (*170*). The axial As—Cl bond distance is 2.296(4) Å. Thermal decomposition of **XV** gives six- and eight-membered As—N rings (*23, 24*):



When the reaction of $(CF_3)_2AsN(SiMe_3)_2$ with $Cl_2$ is carried out in exactly 1 : 1 molar ratio, **XVI** is obtained (*25*). Compound **XVI** also possesses trigonal–bipyramidal geometry with chlorine atoms occupying axial positions. The crystals of **XVI** are monoclinic $P2_{1/m'}$ $a = 9.298(4)$, $b = 12.841(3)$, $c = 15.090(2)$ Å, $\beta = 95.96(5)°$, $Z = 4$. Both $^1H$- and $^{19}F$-NMR spectra of **XVI** in $CH_2Cl_2$ show one signal relatively unchanged from 193 K to room temperature.

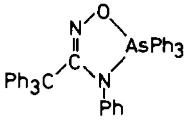


$(F_3C)_2AsCl_2{-}N(SiMe_3)_2$

XVI

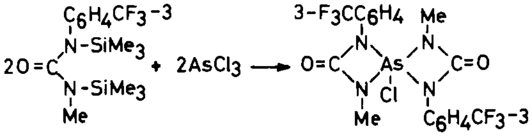
Although compounds of the type $As_2O(OMe)_6NR$ (R = $C_3H_7$, $C_4H_9$) have been characterized by $^1$H-NMR and mass spectra, they could not be obtained in a pure state (*81, 148*).

Compound **XVII** is formed by the reaction between $Ph_3As{=}NPh$ and triphenylacetonitrile *N*-oxide (*58*). The structure **XVII** has been assigned on the basis of that of the corresponding phosphorus compound (*109*):



XVII

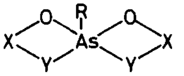
Compound **XVIII** has been synthesized by the following reaction (*156*):



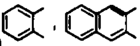
XVIII

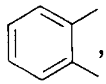
$^1$H- and $^{19}$F-NMR data indicate the presence of only one isomer in solution.

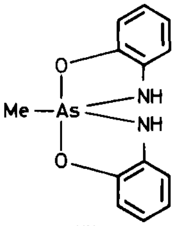
The compounds of type **XIX** have been prepared by the condensation reaction of phenylarsonic acid or by ester interchange of methyltetramethoxyarsorane with the corresponding amine (*128, 204*). The crystal



XIX

R = Me, Ph
X = $CH_2CH_2$, 
Y = $NCH_3$, NH

structure of one of the compounds **XIX** (R = Me, X = , Y = NH) has been reported (*204*). The crystals of $MeAs(C_6H_4ONH)_2$ (**XX**) are monoclinic $P2_{1/c}$, $a$ = 12.285(5), $b$ = 9.508(3), $c$ = 10.848(2) Å, $\beta$ = 104.66(2)°, $Z$ = 4. The geometry of the pentacoordinated arsenic atom is closer to that of a trigonal bipyramid (72%) than of a rectangular pyramid. The two O atoms occupy axial positions [As—O = 1.893(5) and 1.860(5) Å]. The axial O—As—O angle is 169.6° and the equatorial N—As—N and two N—As—C angles are 125.9, 118.9, and 115.2°, respectively (*204*). It has been pointed out that the structural distor-



XX

tions from the idealized geometries deviate significantly from the Berry exchange coordinate.

Single-crystal X-ray analysis of the phenyl derivative of (**XX**) [PhAs-$(C_6H_4ONH)_2$] reveals a trigonal–bipyramidal structure. The structure is displaced 22.9% from the trigonal bipyramid toward the rectangular pyramid (*46a*).

## IV. As—O- and As—S-Containing Compounds

Compounds of pentacoordinated arsenic(V) containing As—O and As—S bonds are summarized in Table IV. Acyclic compounds of type $As(OR)_5$ (R = Me, Et), $R_2As(OMe)_3$ (R = Me, Ph), and $R_3As(OMe)_2$ (R = Ph) have been prepared according to the following general reactions (*45, 59, 149*):

$$R_nAsX_{3-n} + Br_2 \longrightarrow R_nAsX_{3-n}Br_2$$

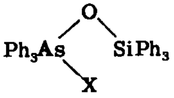
$$R_nAsX_{3-n}Br_2 + (5-n)NaOR' \longrightarrow R_nAs(OR')_{5-n} + (5-n)Na^+ + (3-n)X^- + 2Br^-$$

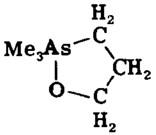
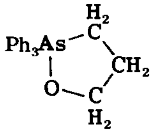
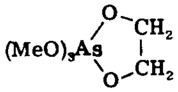
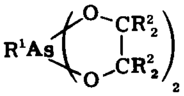
$$(X = \text{halide})$$

Mass spectra of these compounds have been examined, and their fragmentation behavior has been compared to that of the corresponding phosphorus compounds. The variable temperature $^1$H-NMR spectra of molecules $R_2As(OMe)_3$ and $Ph_3As(OMe)_2$ have been examined by Dale and Froyen (*45*) down to 173 K, and the results have been interpreted in terms of a pseudorotation process among structures with trigonal-bipyramidal geometry. According to these workers, only $Ph_2As(OMe)_3$ shows qualitative differences in the NMR spectrum at different temperatures. The low-temperature spectrum has been found to be in agreement with the predicted structure that the phenyl groups occupy equatorial positions. This geometry leads to greater shielding of the equatorial methoxy group. From the coalescence temperature and the chemical shift difference between the two types of methoxy

## TABLE IV

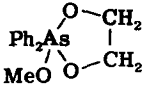
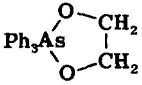
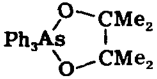
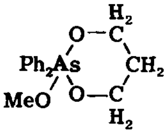
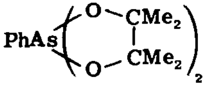
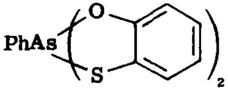
### COMPOUNDS OF PENTACOORDINATED ARSENIC(V) CONTAINING As—O AND As—S BONDS

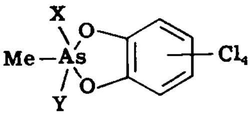
| Compound | Properties (°C) | Physical measurements | Reference |
|---|---|---|---|
| $As(OMe)_5$ | bp 39/2[a] | Mass spectra | *59, 149* |
| $As(OEt)_5$ | bp 47/0.3 | Mass spectra | *59, 149* |
| $As(OMe)_3(n\text{-}OBu)_2$ | | Mass spectra | *149* |
| $As(OMe)_4(n\text{-}OBu)$ | | Mass spectra | *149* |
| $MeAs(OMe)_4$ | bp 30/0.3 | $^1H$ NMR | *45* |
| $Me_2As(OMe)_3$ | bp 32/0.2 | $^1H$ NMR, $^{13}C$ NMR | *45, 47* |
| $Me_3As(OMe)_2$ | | IR, Raman spectra | *131, 147* |
| $Me_4As(OMe)$ | bp 38/17 | IR, Raman spectra, $^1H$ NMR, $^{13}C$ NMR | *137, 147, 164* |
| $Me_4As(OEt)$ | | IR, Raman spectra, $^1H$ NMR | *52* |
| $PhAs(OMe)_4$ | bp 70/0.1 | $^1H$ NMR | *45* |
| $Ph_2As(OMe)_3$ | bp 163/1 | $^1H$ NMR | *45* |
| $Ph_3As(OMe)_2$ | | $^1H$ NMR | *45* |
| $Me_4AsONH_2$ | bp 61–63/5 | IR, Raman spectra | *147* |
| $Me_4AsONHCH_3$ | bp 70–71/10 | IR, Raman spectra, $^1H$ NMR | *147* |
| $Me_4AsON(CH_3)_2$ | bp 60–62/10 | IR, Raman spectra, $^1H$ NMR | *147* |
| $Me_4AsON{=}CHCH_3$ | mp 86–90 | IR, Raman spectra, $^1H$ NMR | *147* |
| $Me_4AsON{=}C(CH_3)_2$ | mp 76–78 | IR, Raman spectra, $^1H$ NMR | *147* |
| $Me_3As[ON(CF_3)_2]_2$ | White crystalline solid | IR | *7* |
| $Me_2CF_3As[ON(CF_3)_2]_2$ | Colorless liquid, mp 10–20 | IR | *7* |
| $Me(CF_3)_2As[ON(CF_3)_2]_2$ | mp 22 and 33 (two isomers) | IR | *6, 7* |
| $Me_2As(OSiMe_3)_3$ | | | *100* |
| $Ph_3As(OAc)_2$ | mp 53–56 | IR, $^1H$ NMR | *34, 71* |
| | mp 210 | IR | *21* |
| $(p\text{-}Tolyl)_3As(OAc)_2$ | mp 248 | IR | *21* |
|  | | | |

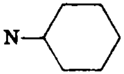
| | | | |
|---|---|---|---|
| X = Cl | mp 106–109 (decomp.) | $^{1}$H NMR | *42* |
| X = Br | mp 150 (decomp.) | $^{1}$H NMR | *42* |
| $(C_6F_5)_3AsCl(OR)$ | | | |
| R = Me | mp 215 | IR | *146* |
| R = Et | mp 210 | IR | *146* |
| R = Ph | mp 220 | IR | *146* |
|  | | $^{1}$H NMR, $^{13}$C NMR | *76, 165* |
|  | mp 116–117 | $^{1}$H NMR, thermal decomposition | *76* |
|  | mp 75/1 | $^{1}$H NMR | *44* |
|  | | | |
| $R^1$ = OH, $R^2$ = H | mp 120 | | *54* |
| | mp 118 | $^{1}$H NMR, $^{13}$C NMR, X ray | *69* |
| $R^1$ = OH, $R^2$ = Me | | $^{1}$H NMR | *54, 67, 161* |
| $R^1$ = OMe, $R^2$ = H | | $^{1}$H NMR | *54, 67, 161* |

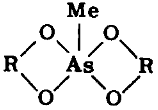
(*continued*)

TABLE IV (*continued*)

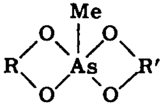
| Compound | Properties (°C) | Physical measurements | Reference |
|---|---|---|---|
| R$^1$ = OMe, R$^2$ = Me | | $^1$H NMR | *54, 67, 161* |
|  | | $^1$H NMR | *44* |
|  | mp 93–96 | $^1$H NMR | *44, 61* |
|  | mp 92–95<br>mp 107–108 | <br>$^1$H NMR, $^{13}$C NMR, mass spectra | *44, 61*<br>*13* |
|  | | $^1$H NMR | *44* |
|  | mp 103<br>mp 108 | <br>$^{13}$C NMR, X ray | *161*<br>*68, 69* |
|  | | | *5* |



| X | Y | | | |
|---|---|---|---|---|
| $OCH_3$ | $OCH_3$ | mp 190 (decomp.) | | *72* |
| $OC_2H_5$ | $OC_2H_5$ | mp 192–193 (decomp.) | | *72* |
|  | Cl | mp 158 (decomp.) | | *72* |
| $N(C_2H_5)_2$ | Cl | mp 167 (decomp.) | | *72* |
| $N(CH_3)C_6H_5$ | Cl | mp 147 (decomp.) | | *72* |
| $SC_2H_5$ | $SC_2H_5$ | | | *72* |

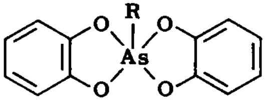
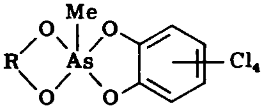
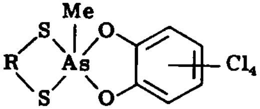


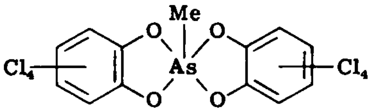
| | | | |
|---|---|---|---|
| R = $CMe_2CMe_2$ | mp 63–65<br>bp 131–132/3 | $^1$H NMR | *161, 192* |
| R = CHMeCHMe | bp 53–56/0.01 | $^1$H NMR | *192* |
| R = $CH_2CH_2$ | mp 52–54<br>bp 110–111/4 | $^1$H NMR | *161, 192* |

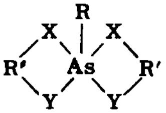


(*continued*)

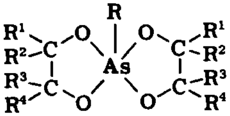
TABLE IV (*continued*)

| Compound | Properties (°C) | Physical measurements | Reference |
|---|---|---|---|
| R = $o$-$C_6H_4$, R′ = $CMe_2CMe_2$ | mp 73–75<br>bp 119–122/0.1 | $^1$H NMR | *192* |
| R = $CMe_2CMe_2$, R′ = $CH_2CH_2$ | bp 53–56/0.1 | $^1$H NMR | *192* |
|  | | | |
| R = Me | Canary yellow crystals<br>mp 150–152 | $^1$H NMR, X ray | *161, 192, 203* |
| R = Bu | Canary yellow crystals<br>mp 83 | | *161* |
| R = $PhCH_2$ | Canary yellow crystals<br>mp 147 | | *161* |
|  | | | |
| R = $CMe_2CMe_2$ | mp 176–178 | $^1$H NMR | *192* |
| R = $o$-$C_6H_4$ | mp 203–205 | $^1$H NMR | *192* |
|  | | | |
| R = $CH_2CH_2$ | | $^1$H NMR, mass spectra | *73* |

| | | | |
|---|---|---|---|
| R = $o$-$C_6H_4$ | | $^1$H NMR, mass spectra | *73* |
|  | Yellow crystals<br>mp 251 | $^1$H NMR | *73* |



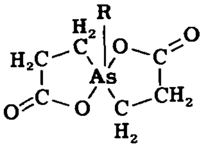
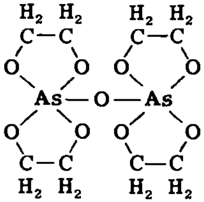
| R | R′ | X | Y | | | |
|---|---|---|---|---|---|---|
| Me | $H_2CCH_2$ | O | S | mp 65–67 | $^1$H NMR, mass spectra | *128* |
| Me | $H_2CCH_2$ | O | $NCH_3$ | mp 40–42 | $^1$H NMR, mass spectra | *128* |
| Me | $C_6H_4$ | O | NH | mp 178–180 | $^1$H NMR, mass spectra | *128* |
| Me | $C_{10}H_6$ | O | NH | mp 230–232 | $^1$H NMR, mass spectra | *128* |
| Ph | $H_2CCH_2$ | O | S | mp 99 | $^1$H NMR, mass spectra | *128* |
| Ph | $H_2CCH_2$ | O | $NCH_3$ | mp 100 | $^1$H NMR, mass spectra | *128* |
| Ph | $C_6H_4$ | O | NH | mp 178–180 | $^1$H NMR, mass spectra | *128* |
| Ph | $C_{10}H_6$ | O | NH | mp 277–279 | $^1$H NMR, mass spectra | *128* |

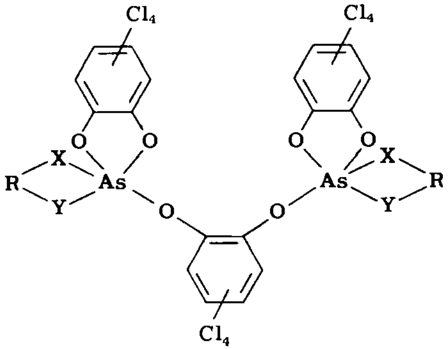
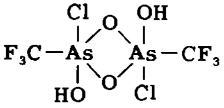
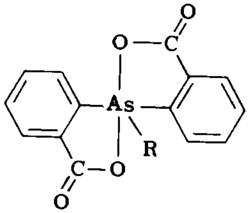


| | | | |
|---|---|---|---|
| R = Me; $R^1$, $R^2$, $R^3$, $R^4$ = H | bp 110–111 | $^1$H NMR | *37, 44, 60, 161, 162* |
| R, $R^1$ = Me; $R^2$, $R^3$, $R^4$ = H | bp 115.5–116 | | *161* |
| R, $R^1$, $R^2$, $R^3$, $R^4$ = Me | bp 131–132 | | *161* |

(*continued*)

TABLE IV (*continued*)

| Compound | Properties (°C) | Physical measurements | Reference |
|---|---|---|---|
| R = Bu; $R^1$, $R^2$, $R^3$, $R^4$ = H | mp 20<br>bp 140.5–141.5 | | *161* |
| R = Bu; $R^1$ = Me; $R^2$, $R^3$, $R^4$ = H | bp 142.6–143.4 | | *161* |
| R = Bu; $R^1$, $R^2$, $R^3$, $R^4$ = Me | bp 169–170 | | *161* |
| R = Ph; $R^1$, $R^2$, $R^3$, $R^4$ = H | mp 105.5 | $^1H$ NMR | *37, 44, 161* |
| R = Ph; $R^1$, $R^2$, $R^3$, $R^4$ = Me | mp 176 | $^1H$ NMR | *54, 67, 161* |
| R = $PhCH_2$; $R^1$, $R^2$, $R^3$, $R^4$ = H | | $^1H$ NMR | *37* |
| R = *p*-$MeOC_6H_4$; $R^1$, $R^2$, $R^3$, $R^4$ = H | | $^1H$ NMR | *37* |
| R = OMe; $R^1$, $R^2$, $R^3$, $R^4$ = H | | | *44* |
|  | | | |
| R = Ph | mp 235 | IR, $^1H$ NMR | *9, 28, 37* |
| R = *p*-$ClC_6H_4$ | mp 223 | IR | *28* |
|  | | | *192* |

| | | | | | |
|---|---|---|---|---|---|
|  | | | | | |
| R | X | Y | | | |
| $H_2CCH_2$ | S | S | mp 175–180 | | *193* |
| $H_2CCH_2$ | O | S | mp 232 | | *193* |
| $Me_2CCMe_2$ | O | O | mp 158 | | *193* |
|  | | | Colorless crystals | IR, X ray | *26* |
|  | | | | | *64* |

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[a] Divided values indicate °C/mm.

signals (58 Hz), the energy of activation has been estimated as 14.4 kcal/mol.

The variable-temperature $^1$H- and $^{13}$C-NMR spectra of $Me_2As(OMe)_3$ have been reinvestigated by Denney *et al.* (*47*). These findings suggest that it exists as a trigonal bipyramidal structure with one equatorial and two axial methoxy groups. The coalescence temperature for the process that renders the methoxy protons equivalent has been found to be 273 K, and the activation energy, 13.6 kcal/mol. The coalescence temperature for the process that renders the carbon atoms of the methoxy groups equivalent has been found to be 294 K, and the activation energy, 14.1 kcal/mol. It has been suggested that a slow intermolecular process cannot be entirely ruled out.

Reactions of bis(trifluoromethyl)nitroxyl with a number of methyl- and trifluoromethyl-substituted arsanes at room temperature give compounds of type $Me_{3-n}(CF_3)_nM[ON(CF_3)_2]_2$ ($n = 0, 1, 2$) (*6, 7*). A free radical mechanism has been proposed for these oxidative addition reactions.

Trialkyl- and triarylperoxyarsoranes have been obtained by the reaction of triorganyl dihaloarsoranes with either an alkylhydroperoxide in the presence of a tertiary amine or with the sodium salt of alkylhydroperoxides. These can also be prepared by the reaction between amino halides $R_3As(NH_2)X$ and an alkylhydroperoxide or by the following exchange reactions:

$$R_3As(OOR'')_2 + 2R'OOH \longrightarrow R_3As(OOR')_2 + 2R''OOH$$

These moisture-sensitive diperoxides are stable at room temperature, but explode when heated in a flame. No further investigations have been made on these compounds.

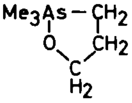
Reaction of triphenylarsane with lead tetraacetate lead to the formation of $Ph_3As(OAc)_2$ (*21, 34, 71*). This compound reacts with amines to give $Ph_3As{=}NR$:

$$Ph_3As + Pb(OAc)_4 \longrightarrow Ph_3As(OAc)_2 \xrightarrow{+RNH_2} Ph_3As{=}NR$$

A number of crystalline arsenic compounds of the type $R_3As(X)OSiPh_3$ have been obtained by the reaction of triphenylarsane with silyl hypohalites, $Ph_3SiOX$ (X = Cl, Br) (*42*).

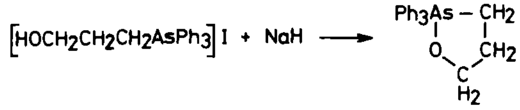
Monomeric covalent compounds of type $Me_4AsX$ ($X = OR, ONH_2, ONR_2$, or $ON{=}CR_2$) have been prepared by the reaction of pentamethylarsorane with equimolar amounts of alcohols, hydroxylamines, or oximes (*52, 147, 164*). According to vibrational spectra and low-temperature $^1$H-NMR spectra, these compounds possess trigonal–bipyramidal structures.

Cyclization of $Me_3As{=}CH_2$ with ethylene oxide gives **XXI**:

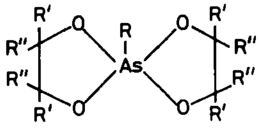


XXI

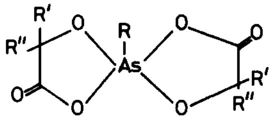
Variable-temperature $^1$H- and $^{13}$C-NMR data suggest a trigonal–bipyramidal structure for **XXI**, with a methyl group and an oxygen atom in axial positions. The phenyl derivative has been obtained by the following reaction (*76*):



The very stable spirocyclic compounds of types **XXII** and **XXIII** have been known for a long time (*10, 54, 60, 161*). These have been prepared by allowing 1 mol of the appropriate arsonic acid to react with 2 mol of the 1,2-dihydroxy compound, the water formed being removed either by performing the reaction in acetic anhydride or by azeotropic distillation from a suitable solvent, e.g., benzene (*161*).

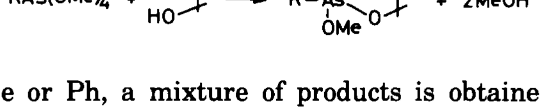


XXII

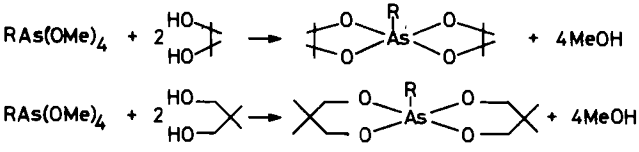


XXIII

Mixing of the arsorane $RAs(OMe)_4$ ($R = OMe$, Me, or Ph) with the diol compound in a 1 : 1 molar ratio leads to the formation of monocyclic arsoranes quantitatively only in the case where the diol is pinacol and R = OMe:

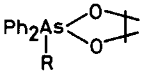


When R = Me or Ph, a mixture of products is obtained (*44*). The reaction of $RAs(OMe)_4$ with pinacol or neopentyl glycol in a 1 : 2 molar ratio leads to the formation of five- and six-membered cyclic spiroarsoranes, respectively:



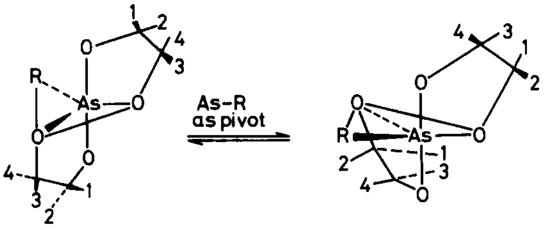
XXIV

Compounds of type **XXV** have been obtained by the reaction of $Ph_nAs(OMe)_{5-n}$ ($n$ = 2 or 3) with a diol. It has been observed that compounds containing two rings are thermodynamically more stable than compounds with one ring. This is independent of ring size.



XXV (R = OMe, Ph)

The role of the pseudorotation process in compounds of types **XXII**, **XXIII**, **XXIV** (*37, 44, 67, 164*), and analogous phosphorus compounds (*108, 124*) has been studied by variable-temperature NMR spectroscopy. Goldwhite (*67*) reported the NMR spectral studies of a series of spirocyclic compounds of type **XXII** ($R' = R'' =$ H, Me; R = OH, OMe, Me, Ph) and concluded that these compounds exist as trigonal bipyramids with the two rings spanning axial–equatorial positions. The NMR results suggested rapid pseudorotation involving the two rings, even at temperatures as low as 173 K (**XXVI**). It has been suggested that the compounds of pentacoordinated arsenic(V) undergo pseudorotation more rapidly than the corresponding phosphorus compounds.



XXVI (Pseudorotation process)

This latter conclusion has been challenged by Casey and Mislow (*37*). These workers studied the barriers of pseudorotation in spiroarsoranes **XXII** (R = Me, $PhCH_2$, $p$-$MeOC_6H_4$, $p$-$NO_2C_6H_4$, Ph; $R' = R'' =$ Me). The $^1H$-NMR spectra of each compound showed that two methyl signals, associated with the ring-methyl protons, coalesced to a single

TABLE V

CRYSTAL DATA FOR $PhAs[O_2C_2(CH_3)_4]_2$ AND $HOAs(O_2C_2H_4)_4$

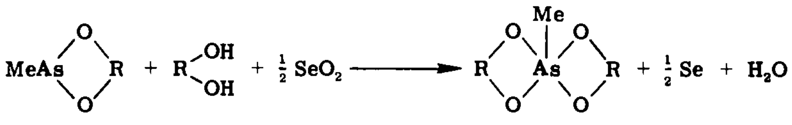
| Cell constants | $PhAs[O_2C_2(CH_3)_4]_2$ | $HOAs(O_2C_2H_4)_4$ |
|---|---|---|
| *a* | 9.150(5) Å | 9.415(4) Å |
| *b* | 12.699(8) Å | 6.791(2) Å |
| *c* | 17.386(7) Å | 12.426(5) Å |
| $\beta$ | 103.73(5)° | 119.11(6)° |
| Space group | $P2_{1/c}$, $Z = 4$ | $P2_{1/c}$, $Z = 4$ |

signal at elevated temperatures. They suggested that this process can only be explained by a Berry pseudorotation in which one of the rings spans two equatorial positions. A process of this type requries a high energy of activation. For the various compounds studied, the $\Delta G^\ddagger$ values lie in the range 20–23 kcal/mol. These values are slightly higher than values obtained for somewhat analogous compounds of phosphorus (*108*). These results suggest that the barriers of pseudorotation in arsenic and phosphorus compounds are comparable.

The dynamic stereochemistry of spiroarsoranes containing five- and six-membered ring systems has also been studied by Dale and Froyen (*44*). The variable-temperature NMR results have been interpreted in terms of pseudorotation processes. It has been concluded that the observed spectra do not allow deduction as to whether trigonal–bipyramidal, rectangular–pyramidal, or any other intermediate structure is the most stable configuration in solution (*44, 45*).

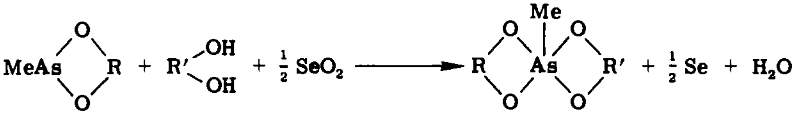
The crystal and molecular structures of two spiroarsoranes of type **XXI** ($R = Ph$, $R' = R'' = CH_3$ and $R = OH$, $R' = R'' = H$) have been determined by single-crystal X-ray diffraction analyses (*68, 69*). The crystal data for these compounds are summarized in Table V. Both compounds have a geometry at the arsenic atom that lies on the Berry coordinate between rectangular–pyramidal and trigonal–pyramidal. These structures show close parallels between the structures of related arsenic and phosphorus systems. It has been concluded that, since the solid-state structures of these compounds lie close to the Berry coordinate, the dynamic process in solution is distortion along that coordinate (*68, 69*).

Although the oxidation of $RAs(OR)_2$ with selenium dioxide leads to the esters of the corresponding arsenic(V) acids, Wieber *et al.* (*192*) have shown that oxidation of the cyclic esters with $SeO_2$ in the presence of a diol results in compounds of type **XXVII**:

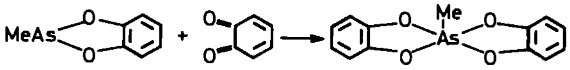


XXVII

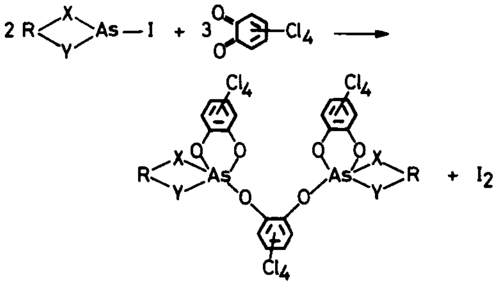
Unsymmetrical spirocyclic compounds have also been prepared:



The reaction of cyclic esters with quinones give either symmetrical or unsymmetrical spirocyclic compounds. For example, symmetrical spirocyclic compounds have been synthesized as follows (*192*):

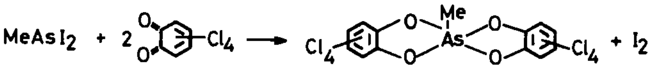


The oxidation of 2-iodo-1,3,2-diheteroarsolanes by tetrachloro-*o*-benzoquinone has been studied by Wieber and Götz (*193*). In this reaction the cleavage of the As—I bond occurred with the formation of spirocyclic arsoranes:



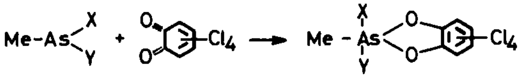
(X, Y = O or S; and R = $CH_2CH_2$ or $Me_2CCMe_2$)

It has additionally been observed that the same oxidizing agent can also cleave both As—I bonds in methyl diiodoarsane as depicted below:



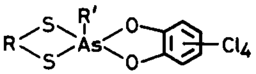
XXVIII

The same authors (*72*) have also reported that several substituents other than iodine do not undergo oxidative cleavage. Instead, these substituents are retained, and the oxidation by tetrachloro-*o*-benzoquinone proceeds in the following manner:



(X, Y = methoxy, ethoxy, chlorine, piperdine, diethylamine, etc.)

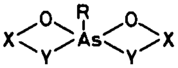
Thioesters of methylarsenic(III) acid and an equimolar amount of tetrachloro-*o*-benzoquinone give unsymmetrical compounds (**XXIX**) (*73*):



XXIX

Compounds of type **XXIX** are stable at room temperature but on heating rearrange to symmetrical compounds of type **XXIX**. When a second equivalent of tetrachloro-*o*-benzoquinone is added, the As—S bonds are oxidized, yielding symmetrical compounds of type **XXVIII** and disulfides.

Mallon and Weiber (*128*) have prepared spirocyclic arsoranes **XXX** by the reaction between $PhAs(O)(OH)_2$ or $MeAs(OMe)_4$ with HOXYH (where R = Me, Ph; X = $CH_2CH_2$, *o*-$C_6H_4$, 2,3-$C_{10}H_6$; Y = S, NH, NMe). Wunderlich (*203*) determined the crystal structure of

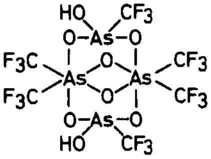


XXX

$MeAs(O_2C_6H_4)_2$. The compound crystallizes in the orthorhombic space group $Pca2_1$, with cell constants $a$ = 18.086(2), $b$ = 8.294(1), $c$ = 8.229(1) Å, $Z$ = 4. The geometry of the pentacoordinated arsenic atom is described as a 74% rectangular pyramid with the methyl group in the apical position. The molecule contains trans basal angles O—As—O of 158.6 and 143.1° and apical basal angles C—As—O of 108.6, 108.3, 100.2, and 100.1°.

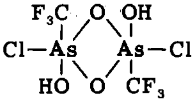
The crystal structure of $PhAs(O_2C_6H_4)_2$ reveals the first truly rectangular–pyramidal structure (*46a*). The compound crystallizes in the monoclinic space group, $P2_{1/c}$, with $a$ = 16.787(5), $b$ = 6.767(3), $c$ = 27.374(6) Å, $\beta$ = 90.37(2)°, and $Z$ = 8. The structure was refined to $R$ = 0.041, $Rw$ = 0.060, and showed two independent molecules per asymmetric unit. The displacement along the Berry coordinate for two molecules, based on unit bond distances, is 99.2 and 94.8% from the trigonal bipyramid toward the rectangular pyramid. These studies suggest that structural principles found for phosphoranes apply thus far to arsenic(V) [and apparently to antimony(V)] derivatives. Molecular mechanics calculations on related spirocyclic phosphoranes and arsoranes support this conclusion (*46a*).

When a mixture of $(CF_3)_2AsI$ and $CF_3AsI_2$ in a 1:1 molar ratio is oxidized by $H_2O_2$, compound **XXXI** is obtained (*26*):



XXXI

Compound **XXXI** reacts with $Me_3SiCl$ to give **XXXII**:



XXXII

The crystal and molecular structures of **XXXI** and **XXXII** have been determined by single-crystal X-ray diffraction analysis (*26*). Crystals of **XXXII** are monoclinic, space group $P2_{1n}$, $a = 5.543(1)$, $b = 9.345(2)$, $c = 11.496(2)$ Å, $\beta = 92.70(1)°$, $Z = 2$. It has a distorted trigonal–bipyramidal geometry with OH and $CF_3$ groups occupying axial positions.

## V. As—Halogen-Containing Compounds

Compounds of pentacoordinated arsenic(V) containing As—halogen bonds are summarized in Table VI. Compounds containing As—Br and As—I bonds are generally ionic and hence are not included in the table. For the same reason, compounds of type $R_4AsX$ have been excluded.

Arsenic pentafluoride is made by the reaction between $AsF_3$ or the oxide and elemental fluorine (*166*). The greater volatility of $AsF_5$ compared with the trihalide is associated with the zero dipole moment of $AsF_5$. Vibrational spectra of $AsF_5$ have been interpreted in terms of $D_{3h}$ symmetry (*12*). $^{19}F$-NMR studies indicate that all five nuclei are equivalent even at the lowest temperature observable. This suggests

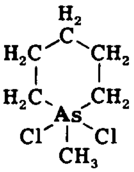
TABLE VI

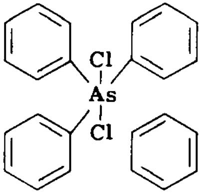
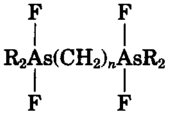
COMPOUNDS OF PENTACOORDINATED ARSENIC(V) CONTAINING ARSENIC–HALOGEN BONDS

| Compound | Properties (°C) | Physical measurements | Reference |
|---|---|---|---|
| $AsX_5$ | | | |
| X = F | mp −79.8<br>bp −52.8 | Vibrational spectra, $^{19}$F NMR, $^{75}$As NMR, mass spectra | *39, 107, 114, 117, 158, 166, 181* |
| X = Cl | | Vibrational spectra, mass spectra | *142, 167, 168* |
| $RAsX_4$ | | | |
| R = Ph, X = F | bp 52–53/2[a] | IR, NMR | *173* |
| R = Ph, X = Cl | | IR, $^{35}$Cl NQR | *22, 38, 48, 154* |
| $R_2AsX_3$ | | | |
| R = Me, X = F | mp 85 | $^{19}$F NMR | *140* |
| R = Me, X = Cl | | IR | *11, 154* |
| R = $CF_3$, X = Cl | bp 93–95/722 | IR | *53* |
| R = Ph, X = F | mp 94–96 | IR, $^{19}$F NMR | *123, 140, 159, 160, 177* |
| R = Ph, X = Cl | | Vibrational spectra, $^{35}$Cl NQR | *46, 63, 115, 154, 190* |
| R = $PhCH_2$, X = Cl | | | *133, 134* |
| R = Cyclohexyl, X = Cl | | | *175* |
| R = *o*-Biphenylyl, X = Cl | | Thermal decomposition | *197, 198* |
| $Ph_2As(CN)Cl_2$ | | | *132* |
| $R_3AsX_2$ | | | |
| R = Me, X = F | mp 69–70<br>bp 54/12 | Vibrational spectra, $^{1}$H NMR, $^{19}$F NMR, mass spectra | *144, 183, 202* |
| R = Me, X = Cl | mp 156–157 | Vibrational spectra, $^{1}$H NMR, $^{35}$Cl NQR, mass spectra, X ray | *48, 110, 144, 180, 183, 202* |
| R = $CF_3$, X = Cl | bp 98.5 | IR | *53* |

(*continued*)

TABLE VI (*continued*)

| Compound | Properties (°C) | Physical measurements | Reference |
|---|---|---|---|
| R = Et, X = F | | Vibrational spectra, $^{1}H$ NMR, $^{19}F$ NMR, mass spectra | *183* |
| R = Et, X = Cl | | Vibrational spectra, $^{1}H$ NMR, mass spectra | *180, 183* |
| R = *n*-Pr, X = Cl | | Thermal decomposition | *180* |
| R = *i*-Pr, X = F | | Vibrational spectra, $^{1}H$ NMR, mass spectra | *184* |
| R = *i*-Pr, X = Cl | | Vibrational spectra, $^{1}H$ NMR, mass spectra | *184* |
| R = Bu, X = Cl | | Thermal decomposition | *180* |
| R = Ph, X = F | mp 135–137 | Vibrational spectra, $^{1}H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR, X ray | *12, 48, 110, 144, 180, 183, 202* |
| | mp 139–140 | | *144* |
| R = Ph, X = Cl | mp 205 | Vibrational spectra, $^{35}Cl$ NQR | *19, 48, 79, 120, 126, 127, 179, 180* |
| | mp 214–215 | | *113* |
| R = $PhCH_2$, X = F | | Vibrational spectra, $^{1}H$ NMR, $^{19}F$ NMR, mass spectra | *139, 182, 184* |
| R = $PhCH_2$, X = Cl | | Vibrational spectra, $^{1}H$ NMR, mass spectra | *182, 184* |
| R = $C_6F_5$, X = Cl | mp 190 | IR | *146* |
| | mp 214–216 | | *78* |
| R = 2-Thienyl, X = F | | | *145* |
| R = *p*-$Me_2NC_6H_4$, X = Cl | | $^{1}H$ NMR | *116* |
|  | | Thermal decomposition | *70* |

| | | | |
|---|---|---|---|
|  | | Thermal decomposition | *197, 198* |
|  $R_2As(F_2)(CH_2)_nAs(F_2)R_2$ | | | |
| $n = 1$, R = Me | mp 166 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| $n = 1$, R = Et | bp 106/0.001 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| $n = 1$, R = *i*-Pr | bp 118/0.001 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| $n = 1$, R = Ph | mp 134 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| $n = 2$, R = Ph | mp 144 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| $n = 3$, R = Ph | mp 153 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| $RR'_2AsX_2$ | | | |
| R = Me, R′ = Ph, X = F | mp 96 | $^1H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR | *159* |
| R = Me, R′ = Ph, X = Cl | | | *33* |
| R = Et, R′ = Ph, X = Cl | | Thermal decomposition | *1, 3* |
| R = *n*-Pr, R′ = Ph, X = Cl | | Thermal decomposition | *1, 3* |
| R = Ph, R′ = Me, X = Cl | | Thermal decomposition | *1, 3* |
| R = Ph, R′ = Et, X = Cl | | $^1H$ NMR | *2* |
| R = Styryl, R′ = Me, X = Cl | | Thermal decomposition | *46* |
| $R(p\text{-}MeC_6H_4)_2AsCl_2$ (R = Et, Pr, $Me_2CH$, Bu, $Me_2CHCH_2$, pentyl) | | Thermal decomposition | *65* |
| $RR'R''AsX_2$ | | | |
| R = Me, R′ = Et, R″ = Ph, X = Cl | | | *33* |
| R = Me, R′ = α-naphthyl, R″ = Ph, X = Cl | | | *119* |

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[a] Divided values indicate °C/mm.

that the barrier to pseudorotation, which interchanges axial and equatorial halogens, is small. $^{75}$As-NMR spectra also support this observation (*114*). The molecular structure of $AsF_5$ has been determined by electron diffraction studies (*39*). The molecule has been found to be a trigonal bipyramid with axial bonds 0.055 ± 0.010 Å longer than equatorial bonds and an average arsenic fluorine bond length of 1.678 ± 0.002 Å.

Arsenic pentachloride has been prepared by irradiating a solution of $AsCl_3$ in chlorine with UV light at 168 K. It has been characterized by chemical analysis and by comparison of its Raman spectrum with those of $PCl_5$ and $SbCl_5$ (*167, 168*). Arsenic pentachloride is a soft yellow solid. It melts with partial decomposition at ~223 K. The Raman spectrum also suggests that it has a trigonal–bipyramidal structure in both the liquid and solid states. The difference in stability of $PCl_5$ and $AsCl_5$ has been attributed not to the As—Cl and P—Cl bond strengths but to the difference in the ionization energies in the first step of the chlorination reaction, which suffices to make the $AsCl_3$ reaction endothermic. It is interesting to mention here that the ionization energy of $AsCl_3$ is about 28 kcal/mol higher than that of $PCl_3$. Thus the large ionization energy in an excited state will be correspondingly increased. It has been suggested that this unexpected order follows the transition metal contraction. The small screening of the large nuclear charge of arsenic by the 3*d* electrons causes a lowering of the energy of the 4*s* orbitals, giving the nonbonding electron pair in $AsCl_3$ higher *s* character. Nonempirical valence shell SCFMO calculations suggest that the dissociation energy for the process $AsCl_5 \rightarrow AsCl_3 + 2Cl$ is negative.

Compounds of the type $RAsX_4$ are rare. Baeyer (*11*) reported that methyl tetrachloroarsorane is an unstable crystalline compound formed by the action of chlorine on methyldichloroarsane. Attempts to prepare $MeAsCl_4$ by this method led to explosions at low temperatures. It has been concluded that this compound is extremely unstable, if it exists at all (*48*). Phenyltetrachloroarsorane and the tolyl compounds have been synthesized by the reaction of chlorine with dichloroarsanes (*33*). However, the para-substituted isomer could not be obtained by this method. Many organyl tetrafluoroarsoranes have been prepared by the following route (*172–174*):

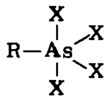
$$RAsO_3H_2 + 3SF_4 \xrightarrow{70^\circ C} RAsF_4 + 3SOF_2 + 2HF$$

If this reaction is run at low temperatures with less sulfur tetrafluoride, $RAsOF_2$ is formed (*174*).

All of the organyl tetrahaloarsoranes are readily hydrolyzed by water to the arsenic(V) acids. When heated in air, phenyltetrachloroarsorane produces the dichloroarsane and chlorine, but when heated to 150°C in a sealed tube, it gives chlorobenzene and trichloroarsane.

A trigonal–bipyramidal structure has generally been assumed for compounds of the type $RAsX_4$ ($X = F, Cl$). Smith (*173*) reported the IR and NMR spectra of $PhAsF_4$ but was unable to draw any conclusions regarding its structure. Muetterties *et al.* (*140*) observed only one single peak in the $^{19}F$-NMR spectrum for this compound and suggested that a fast intramolecular fluorine exchange might be occurring.

Vibrational spectra of $PhAsCl_4$ indicate that it has a trigonal–bipyramidal structure with an equatorial phenyl group (*154*). This conclusion gets support from a $^{35}Cl$-NQR study of $PhAsCl_4$ (*48*). In trigonal–bipyramidal molecules of type $RAsX_4$, an atom in an axial position has a much lower NQR frequency than that of a similar atom in an equatorial site. This is reasonable since the axial bonds are longer and therefore more ionic in character. The $^{35}Cl$-NQR spectrum of $RAsCl_4$ is very similar to that of the analogous phosphorane (*48, 125, 176*). It indicates four independent chlorine sites, two of which appear from the frequencies to be considerably more ionic than the others. This observation is entirely consistent with a trigonal–bipyramidal structure for the molecule, with the phenyl group occupying an equatorial site **XXXIII**:



XXXIII

Compounds of type $R_2AsX_3$ are also rare, but are relatively more stable than $RAsX_4$. They are generally prepared by the reaction of dry halogens on dialkyl- or diarylhaloarsanes. For example, dimethyltrichloroarsorane has been synthesized by the reaction of chlorine with dimethylchloroarsane in carbon disulfide solution or by the reaction of $PCl_5$ on $[(CH_3)_2As]_2O$ (*11*). Diphenyltrichloroarsorane has been prepared by the reaction of diphenylchloroarsane and chlorine. It can also be prepared by the action of thionyl chloride on diphenylarsenic(V) acid (*63*).

Bis(trifluoromethyl)trichloroarsorane has been obtained by allowing tris(trifluoromethyl)arsane to react with chlorine in a sealed tube for 1 month (*53*). Dibenzyltrichloroarsorane has been synthesized by heating tribenzylarsane with an excess of benzyl chloride at 200°C

(*134*). It can also be obtained when benzyl chloride and trichloroarsane are condensed with sodium (*133*).

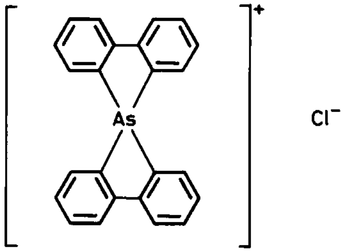
$Ph_2AsF_3$ has been prepared by the following reactions (*177*):

$$Ph_2AsO_2H + 2SF_4 \longrightarrow Ph_2AsF_3 + 2SOF_2 + HF$$

$$2AsF_5 + 2C_6H_6 \longrightarrow Ph_2AsF_2^+AsF_6^- + 2HF$$

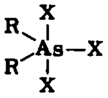
$$Ph_2AsF_2^+AsF^- + CsF \longrightarrow Ph_2AsF_3 + CsAsF_6$$

The diorganyl trihaloarsoranes are also moisture-sensitive compounds and are readily hydrolyzed to arsenic(V) acid. They are decomposed at relatively low temperatures. Dicyclohexyltrichloroarsorane, when warmed to 80–90°C, loses chlorocyclohexane to produce cyclohexyldichloroarsane (*175*). Diphenyltrichloroarsorane, when heated in a sealed tube to 200°C, gives chlorobenzene and phenyldichloroarsane (*122*). Di-*o*-biphenyltrichloroarsorane (*198*) loses hydrogen chloride at 265°C to yield **XXXIV**:



XXXIV

Vibrational spectral studies have suggested that $Me_2AsCl_3$ and $Ph_2AsCl_3$ have a trigonal–bipyramidal structure with methyl or phenyl groups in equatorial positions (**XXXV**) (*154*). These results are in complete agreement with the results of $^{35}$Cl-NQR studies (*48*).



XXXV

Muetterties *et al.* (*140*) examined the $^{19}$F-NMR spectra of diphenyltrifluoroarsorane and dimethyltrifluoroarsorane. The spectrum of $Ph_2AsF_3$ was found to consist of a doublet and triplet of relative intensity 2 : 1 with a common coupling constant of 67 Hz. It was suggested that this compound has a slightly distorted trigonal–bipyramidal structure in which two fluorine atoms occupy axial positions and the other fluorine atom occupies an equatorial position (**XXXV**). Littlefield and Doak (*123*) questioned the published $^{19}$F-NMR spectrum. These workers fluorinated $Ph_2AsH$ or PhAsCl with $SF_4$ to obtain a crystalline solid, $Ph_2AsF_3$. The $^{19}$F-NMR spectrum of this compound consisted of a singlet relatively unchanged from 183 K to room temperature. These findings have been attributed to pseudorotation.

In order to settle this controversy, Tanzella and Bartlett (*177*) studied the $^{19}$F-NMR spectrum of $Ph_2AsF_3$ again. These workers found the same $^{19}$F-NMR spectrum as that reported by Muetterties *et al.* (*140*) and concluded that $Ph_2AsF_3$ is a rigid trigonal bipyramid, with phenyl groups in equatorial positions.

The structure of dimethyltrifluoroarsorane appears to be markedly different from that of the analogous alkyl and aryl derivatives of Group VA elements (*140*). Thus unlike $Ph_2AsF_3$, the dimethyl compound indicates evidence of association and is not very soluble in aromatic solvents. $^{19}$F-NMR spectra in acetone or acetonitrile show a singlet at 25°C and doublet–triplet resonances at low temperatures. It has been suggested that it is probably behaving as a Lewis acid and forming an octahedral species in solution. However, more studies are required to establish the structures of these compounds with certainty.

As compared to $RAsX_4$ and $R_2AsX_3$, compounds of the type $R_3AsX_2$ have been studied in much greater detail. The usual procedure for the synthesis of $R_3AsX_2$ is the treatment of a trialkyl- or triarylarsane in a nonpolar solvent with the halogens in the same solvent (*19, 33, 38, 45, 51, 119, 135, 169, 191*). $TlCl_3$, $PbCl_4$, $AsCl_3$, $TeCl_4$, $CuCl_2$, or $HgCl_2$ have been used instead of $Cl_2$ as chlorinating agents (*18, 21, 33, 62, 127, 146*). The reaction of triphenylarsane oxide with 2 mol of acetyl chloride gives $Ph_3AsCl_2$ (*179*):

$$Ph_3AsO + 2MeC(O)Cl \longrightarrow Ph_3AsCl_2 + (MeCO)_2O$$

Fluorination of $Ph_3AsO$ by aqueous HF (1–40%) gives $Ph_3AsF_2$ (*66*). Reaction of thionyl chloride or sulfur dichloride with triphenylarsane results in $Ph_3AsCl_2$ (*120*):

$$Ph_3As + SOCl_2 \longrightarrow Ph_3AsCl_2 + \tfrac{1}{2}S + \tfrac{1}{2}SO_2$$

A number of mixed aliphatic–aromatic dihaloarsoranes ($RR'_2AsX_2$ or $RR'R''AsX_2$) have been prepared from the arsanes and the appropriate halogens (*33, 49, 119*). The reaction of $RR'_2AsS$ with $PCl_3$ or acetyl-chloride yields $RR'_2AsCl_2$ (*1, 180*). Similarily, reaction of $RR'_2AsO$ with excess of HX gives $RR'_2AsX_2$ (*3, 40, 53, 134*).

Trialkyl- or triaryldifluoroarsoranes have been obtained by the metathetical reaction between trialkyl- or triaryldichloroarsorane and silver fluoride (*53, 144, 145*).

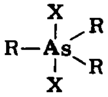
Fluorination of $Ph_2AsR$ with fluorine in $CHCl_3$ yields $Ph_2AsF_2R$ (R = Me, Ph). Similarly, $R_2As(CH_2)_nAsR_2$ produces $R_2AsF_2(CH_2)_nAsF_2R_2$ (R = Me, Et, $Me_2CH$, Ph). $Ph_2AsH$ and fluorine results in the formation of $Ph_2AsAsPh_2$, further fluorination of which gives $Ph_2AsF_3$ (*159*).

Compounds of type $R_3AsX_2$ are generally low-melting, crystalline solids, soluble in alcohol but only slightly soluble or insoluble in nonpolar solvents. These can readily be reduced to tertiary arsanes. They are hydrolyzed by water or alkali. Compounds containing at least one alkyl group yield on pyrolysis an alkyl halide and a haloarsane (*49*):

$$R_3AsX_2 \longrightarrow R_2AsX + RX$$

Initially, three possible structures have been suggested for $R_3AsX_2$ (X = halogen), namely, $(R_3As)^{2+}2X^-$, $(R_3AsX)^+X^-$, and $R_3AsX_2$, in which the arsenic atom is surrounded by six, eight, or ten valence electrons, respectively. The structure $(R_3As)^{2+}2X^-$ was discarded on the basis that even in dilute solution these compounds do not ionize completely (*143*). For the remaining two structural possibilities, conflicting results are reported in the literature (*129, 155*). It is interesting to point out here that vibrational studies indicated that $R_3PX_2$ has the $(R_3PX)^+X^-$ ionic structure (*74*), while X-ray data show that $R_3SbX_2$ exists as a trigonal bipyramid with the two halogens at the axial positions (*185*). The Sb—X distances, however, are longer than the sum of the covalent radii and suggest that the Sb—X bond is partially ionic. Conductivity and IR data (*19, 77, 126, 144, 145*) indicate that compounds of type $R_3AsX_2$ (R = Me, Et, $PhCH_2$, 2-thienyl, Ph; X = F, Cl) also have a trigonal–bipyramidal structure. The conductivities of $R_3AsBr_2$ (R = Me, Et, Ph) in acetonitrile are larger than those of the corresponding $R_3AsCl_2$ compounds but are low compared to the values observed for strong 1 : 1 electrolytes. Infrared spectra indicate that $Et_3AsBr_2$ has a covalent, but $Me_3AsBr_2$ has an ionic structure in the solid state (*144, 145*). $R_3AsI_2$ forms highly conducting solutions in acetonitrile.

A $^{35}$Cl-NQR study (*48*) indicates that $R_3AsCl_2$ (R = Me or Ph), unlike the phosphorus analogs, possesses a trigonal–bipyramidal structure in which all R groups occupy equatorial sites and the two chlorine atoms are situated on the axial positions (**XXXVI**):



XXXVI

A preliminary communication on the X-ray analysis (*110*) of $Me_3AsCl_2$ and $Me_3AsBr_2$ is in complete agreement with the earlier studies.

Muetterties *et al.* (*140*) observed that $Ph_3AsF_2$ is monomeric in benzene solution, and the $^{19}F$-NMR spectrum is consistent with a trigonal–bipyramidal structure, with the fluorine atoms in axial positions. Augustine *et al.* (*8*) determined the crystal structure of $Ph_3AsF_2$ from three-dimensional X-ray diffractometer data. Crystals of $Ph_3AsF_2$ are orthorhombic, space group *Pbcn*, with $a = 6.270(1)$, $b = 16.593(3)$, $c = 14.519(2)$ Å, and $X = 4$; molecular symmetry $C_2$. The crystals contain well-separated discrete molecules. The arsenic atom has nearly regular trigonal–bipyramidal geometry with axial fluorine atoms (**XXXVI**).

Moreland and co-workers (*139*) reported $^1H$- and $^{19}F$-NMR spectra of $(PhCH_2)_3AsF_2$ as a function of temperature. At 0°C the methylene protons occurred as a triplet, which coalesced to a broad singlet and finally to a sharp singlet as the temperature was raised to 45°C. This result suggests that an intermolecular exchange of fluorines occurs with increase in temperature. This exchange has been shown to be of first order and suggests that the lifetime is independent of concentration. Since the compound is monomeric, the mechanism of exchange is believed to involve a dissociative step. The energy of activation has been found to be 12.3 ± 2.0 kcal/mol.

Verdonck *et al.* (*182*) reported both vibrational and $^1H$- and $^{19}F$-NMR spectra for the compounds $(PhCH_2)_3MX_2$ (M = As or Sb and X = F or Cl). The vibrational spectra (in the solid state and in solution) have been interpreted in terms of a slightly distorted trigonal bipyramid. The methylene NMR signal has been found to split into a triplet by coupling with two fluorine atoms in $(PhCH_2)_3MF_2$ (M = As or Sb). However, in the case of the antimony compound, some collapse was observed and interpreted as due to intermolecular exchange of the fluorine atoms.

## VI. Conclusion

From this account, some general features have emerged, which can be summarized as follows. Although many compounds of pentacoordinated arsenic(V) have been synthesized, the fundamental hydrogenated skeleton, $AsH_5$, and the pentaalkylarsoranes are still unknown. An exception is $Me_5As$. The overall stabilities and reactivities of pentaorganyl arsoranes appear to be governed mainly by stereochemical factors, namely, bulkiness of the groups and angle strain when bidentate substituents are present.

Both the geometries and dynamics of compounds of pentacoordinated arsenic(V) and other Group VA elements have been studied. The stereochemistries of spirocyclic phosphoranes reveal a continuous series of angular geometries at phosphorus between the idealized trigonal–bipyramidal (symmetry $D_{3h}$) and square–pyramidal (symmetry $C_{4v}$) forms, the latter of which is reduced by chelation of the phosphorus to a rectangular pyramid (symmetry $C_{2v}$). Compounds of arsenic are expected to show similar stereochemical properties, but only a few experimental results exist. The stereochemistry of arsoranes and organoarsoranes can be described in terms of distorted trigonal bipyramidal ground states, which are subject to rapid intramolecular exchange processes of the Berry type, running through tetragonal–pyramidal transition states. Because of the large size of the arsenic atom, the influence of the steric hindrance in determining the geometry of pentacoordination is reduced.

In contrast to phosphorus, tetracoordinated arsenic appears to be less stable and rearranges to yield more stable pentacoordinated arsenic compounds. Thus compounds with As=N or As=O bonds dimerize or oligomerize to give compounds with pentacoordinated arsenic.

It is well known that pentacovalent cyclic phosphorus compounds play an important role as intermediates in reactions involving nucleophilic attack on tetracoordinated phosphorus in biological systems. According to this background it appears to us that it is important to prepare the arsenic derivatives, which are more stable than the corresponding phosphorus compounds and allow the study of their conformation.

## ACKNOWLEDGMENTS

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